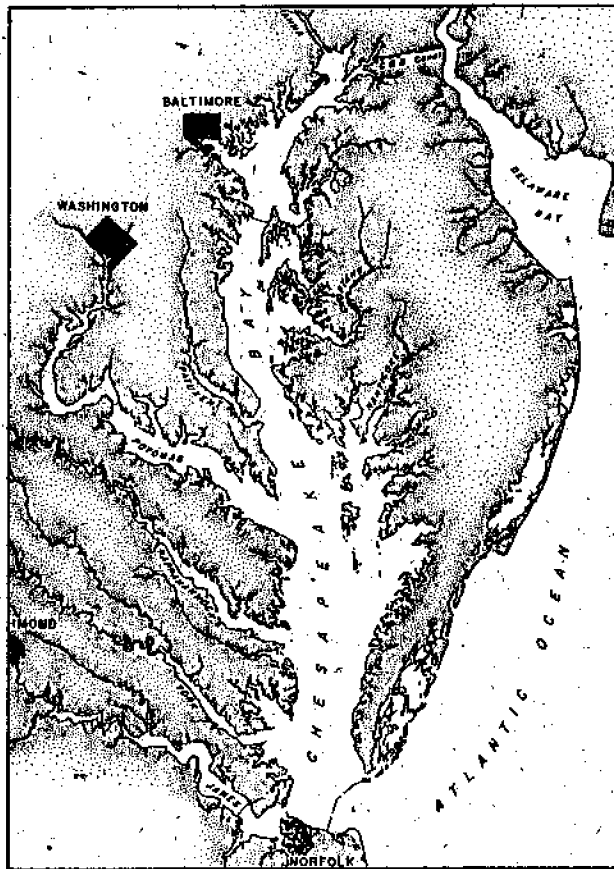


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# Chesapeake Bay Environmental Effects Studies

TOXICS  
RESEARCH  
PROGRAM

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## Workshop Report



VSG-92-03

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*Chesapeake Bay*  
*Environmental Effects Studies*  
TOXICS RESEARCH PROGRAM  
*Workshop Report*

*Edited by*

EUGENE J. OLMI, III

AND BETH HENS

*Virginia Sea Grant*

*College Program*



VSG-92-03



**Maryland  
Sea Grant**

PREPARED BY THE VIRGINIA SEA GRANT  
COLLEGE PROGRAM IN COOPERATION WITH  
THE MARYLAND SEA GRANT COLLEGE  
PROGRAM. 1992.

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*Virginia Sea Grant College Program Publication Number VSG-92-03*  
*Maryland Sea Grant College Program Publication Number UM-SG-TS-92-05*

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## SUMMARY

While there is considerable knowledge about the direct or acute effects that toxic compounds have on a range of organisms in Chesapeake Bay, our understanding of the fate and chronic effects of toxics at the ecosystem level is, at best, limited. Chronic effects are often so indirect that it is difficult to determine their cause, yet any attempt to establish realistic water quality standards depends on a sophisticated understanding of such subtle but important relationships.

A clear example is the need to understand the relationship between disease resistance in oysters and their chronic exposure to low level pollutants in the Bay. Another is the need to understand the dynamics of toxic sediments, which can be resuspended and transported far from their source, changed in chemical composition, and made available to organisms, both in the water column and at the site of redeposition. Just what happens when toxic chemicals enter Chesapeake Bay is complicated by the biological, chemical, and physical conditions which vary with environmental factors. The issues are extremely complex, and we are still learning to pose the best questions.

The Toxics Research Program (TRP) enlists investigators from throughout the Chesapeake Bay area in a coordinated effort to address these complex issues. In February 1992, a workshop was held to allow investigators to present preliminary findings and to facilitate dialogue between the research community and the management agencies (as the ultimate users of the research). This report summarizes the proceedings of the workshop.

While the approach of the TRP is to understand the transport, fate and effect of toxics in the Bay at the ecosystem level, the research is necessarily an integration of projects that range from the molecular level to the population level and includes studies of particulate sedimentation and suspension. Progress reports by the investigators in this workshop report highlight the approach, rationale and findings to date. While the Toxics Research Program is only in its second year, researchers have made progress in a number of areas. Among their findings:

- Periods of high suspended sediment concentrations in the mid-bay are short-lived because contaminated particles are often agglomerated into much larger aggregates which settle quite rapidly out of suspension.
- Studies of the distribution of hydrophobic organic contaminants (HOC) in suspended and settling solids indicate that the distribution varies highly and is dependent on particle size. Partitioning of HOC into the estuarine food web is strongly linked to the total lipid concentration of the particles.

- Wind and storm-generated resuspension of sediments occurs less frequently than tidal resuspension but is much more pronounced than tidal suspension. Stronger current speeds associated with wind events may suspend sediments that are unaffected by tidal currents.
- Oysters exposed to contaminated sediments are likely to survive exposure, but responses of their hemocytes are modified, resulting in decreased resistance to the pathogen Perkinsus (dermo).
- In studies of particle-reactive pollutants, high concentrations of lead, more than can be accounted for by atmospheric deposition, have been found in particular embayments. Such areas may be traps for particle-reactive toxic elements that enter the Bay.
- Fecal pellet production by zooplankton may be an important mechanism for increasing the flux of HOC to bottom sediments; rates of pellet production vary seasonally and with food quality and quantity.
- Anoxia is a significant factor in the movement of trace elements between contaminated sediments and water, causing a flux of arsenic and manganese out of the sediments and copper into the sediments. Under oxic conditions, however, these flux rates are low, except when facilitated by infaunal organisms.
- Isolated cell culture appears to be an accurate and cost-effective approach to risk assessment of the toxic effects of sediments contaminated by PAH's (polynuclear aromatic hydrocarbons).

Studies initiated in January 1992 include: 1) the role of benthic infauna on the flux and fate of organic contaminants, 2) how partitioning of PCBs (polychlorinated biphenyls) among dissolved and particulate phases affects the rates and extent of bioaccumulation by the eastern oyster, 3) characterization of stress-response proteins in oyster larvae and spat, 4) the role of phytoplankton in the cycling of hydrophobic organic contaminants, and 5) development of a simulation model to test the hypothesis that planktonic and benthic trophic dynamics and benthic-pelagic coupling control the speciation, transport, bioavailability, bioaccumulation, and toxic effects of synthetic organic contaminants in Chesapeake Bay.

A major concern of the Chesapeake Bay Program is to identify critical policy issues and to ensure effective communication between researchers and policy makers. Toward these ends, representatives of federal and state agencies involved in management or research of toxics in the Bay were invited to discuss the role of the Toxics Research Program relative to their agencies' missions and to make recommendations.



Clearly, there are differences of opinion whether or not toxic substances are a significant problem in the Bay and what role the Toxics Research Program should have in addressing the problem. Defining the scope of the problem is, in fact, a great challenge for the research community. For example, chronic exposure to arsenic causes a shift in species composition of the phytoplankton assemblage, but how or if this shift is transferred up the food web to more visible species is not known. Current water quality standards have been effective in reducing toxic discharges into the Bay, but these criteria are based on single species-single substance toxicity tests which do not address potential indirect or chronic effects.

The water quality agencies of Maryland and Virginia have a need for support services in the areas of criteria development and validation, monitoring, and technology development. A goal of the Toxics Research Program should be to supply useful information to the regulatory agencies, but meeting the immediate needs of the agencies should not be the sole purpose of the program. Process-oriented studies are necessary to understand how effects of toxic compounds in the Bay are influenced by a wide range of physical, chemical and biological conditions. Current research projects were viewed as complementary to ongoing criteria assessments by EPA and monitoring programs by EPA and NOAA.

Two strong recommendations emerged during the panel session and the discussion. First, there is a need for greater communication among the regulatory agencies, the research community and the groups involved in monitoring toxics in the Bay. The monitoring programs are in position to demonstrate changes in levels of contaminants over time. These data can be used to measure success of regulatory programs and to direct researchers to persistent substances or those on the increase. Also, needs of the regulatory agencies should be factored into the goals of the research and monitoring programs.

Second, the Toxics Research Program should be more focused. The modeling project will be very useful in this regard, but focusing the program on selected substances or species of concern would facilitate integration of the findings. The development of a risk assessment protocol could also be used as a framework for focusing the research program.

The Toxics Research Program is but one component of the Chesapeake Bay Program's effort to restore the health of the Chesapeake Bay. Coordinated process-oriented research on the transport, fate and effects of toxic substances in the Bay will improve our understanding of the complex linkages between the discharge of a substance and its eventual effect on the system. Increased communication among research and management groups will help to focus the research program and provide needed information to the regulatory agencies.

## BACKGROUND

In order to restore the productivity and ecological health of the Chesapeake Bay, the federal/state Chesapeake Bay restoration program set as a goal the reduction of nutrients and toxic substances entering the estuary. While the desire to reduce anthropogenic influence on the Bay was recognized, there was also a recognized need to establish how these inputs affect the ecological processes in the Chesapeake Bay.

Since 1985, Congress has appropriated funds to the National Oceanographic and Atmospheric Administration (NOAA) in support of environmental effects research in the Chesapeake Bay. The Chesapeake Bay Environmental Effects Committee (CBEEC) was established in 1987 by NOAA to oversee this program. CBEEC includes representation from Virginia, Maryland, and Pennsylvania. Research funds are awarded via a competitive peer-review process, and the funds are administered jointly by the Maryland and Virginia Sea Grant College Programs.

Beginning September 1985, a major effort was initiated to address the effects of low dissolved oxygen in Chesapeake Bay. The hypoxia program was conceived as an ecologically oriented study focusing on system-level effects. This research has greatly refined our understanding of the complex relationships between nutrients, production of organic material, carbon cycling, and the development of hypoxia. In addition, the impact of low dissolved oxygen on functioning and productivity of key species and communities was found to be significant.

Results of these studies have been widely disseminated via conferences, workshop reports, and publication in peer-reviewed journals. A recently completed book, Oxygen Dynamics in the Chesapeake Bay (1992), summarizes the current level of understanding of the interaction of physical, chemical and biological processes that create hypoxic conditions and the resulting effects upon the Bay's resources.

In 1990 the Environmental Protection Agency's (EPA) Chesapeake Bay Liaison Office joined the Environmental Effects Research Program (with fiscal support). In addition, members of the Chesapeake Bay Toxics Subcommittee were added to the CBEEC, and the focus of the research program was redirected from hypoxia to studies of toxic contaminants in Chesapeake Bay, an area where considerable information is needed to support management actions.

In conceiving the Toxics Research Program (TRP), CBEEC felt that it was important to maintain an ecological focus on system-level environmental effects, similar to the hypoxia program. Thus, the general goals of the TRP are:

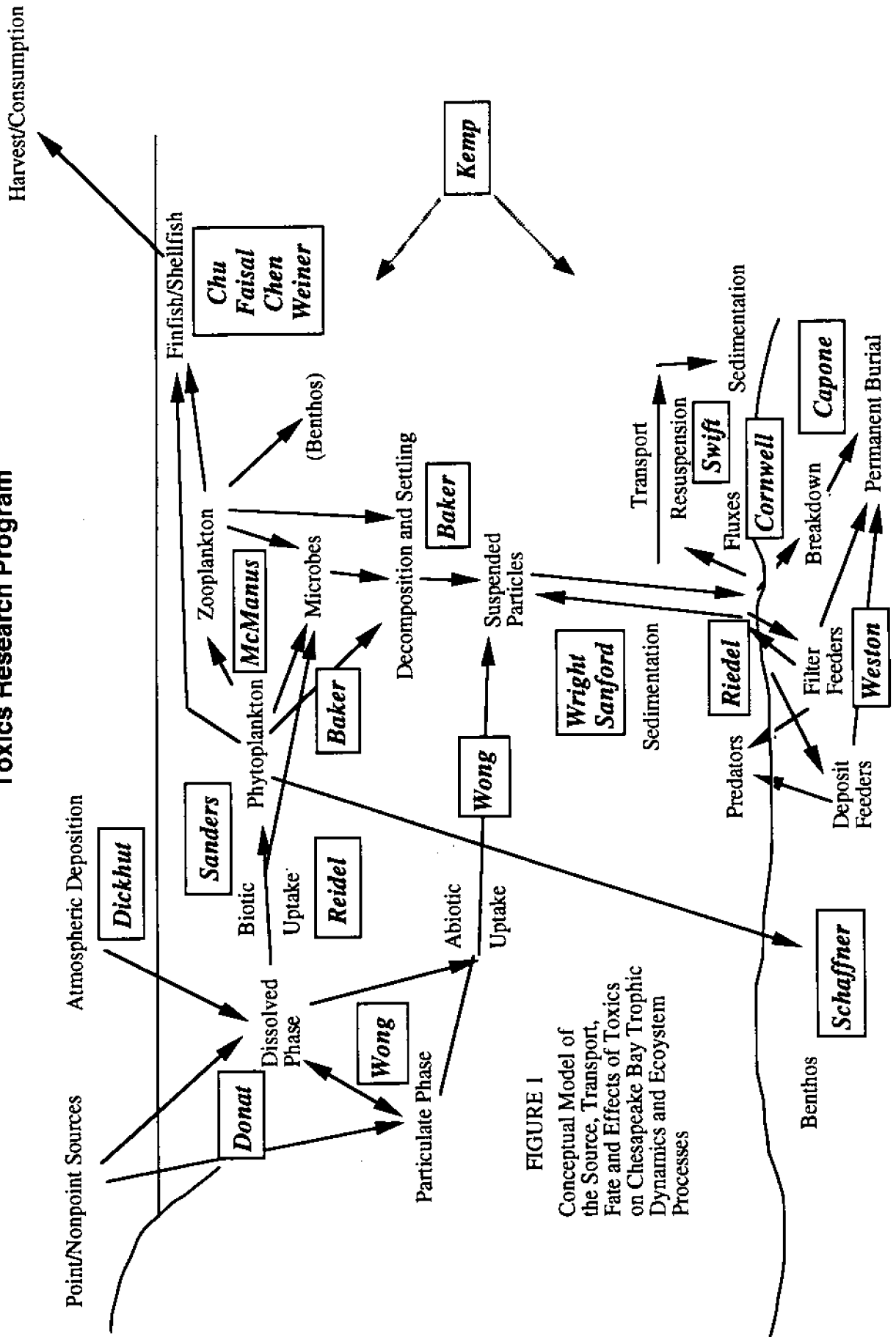
- \* to understand how Chesapeake Bay ecosystem processes influence the transport, fate and effect of toxicants; and

\* to understand the effects that representative toxicants have upon ecological processes, including trophic dynamics, in the Bay.

Long-term objectives of the TRP were based on the Chesapeake Bay Program Research Planning Committee's "Toxics Research Prioritizations" document, and focus on increasing the understanding of the source, transport, fate, and effects of toxicants in support of development of ecological risk assessments for the Chesapeake Bay. The CBEEC prepared a Request For Proposals based on these needs, emphasizing an ecosystem approach to the issue of toxics in Chesapeake Bay.

Ten projects funded under the Toxics Research Program were initiated in September 1990, and an additional seven projects were initiated in January 1992. A conceptual diagram of how these projects relate to the ecosystem processes that affect the transport, fate and effects of toxicants is given in Figure 1. In addition to the research projects, CBEEC has initiated a modeling effort to integrate findings of TRP projects into an ecosystem model of Chesapeake Bay.

# Chesapeake Bay Environmental Effects Toxics Research Program



**FIGURE 1**  
Conceptual Model of the Source, Transport, Fate and Effects of Toxics on Chesapeake Bay Trophic Dynamics and Ecosystem Processes

## INTRODUCTION

This document is the summary of a workshop, sponsored by the CBEEC, held at the Virginia Institute of Marine Science in Gloucester Point, Virginia on 19-20 February 1992. The purpose of the workshop was to provide a forum for:

- 1) presentation of progress reports by the investigators;
- 2) interaction among current and potential investigators to foster collaborative research;
- 3) evaluation of the Toxics Research Program in regard to duplication or overrepresentation of certain subject areas, possibly leading to new areas of emphasis; and
- 4) dialogue among researchers, managers, and the CBEEC regarding information needs and research directions for toxic studies in Chesapeake Bay.

The first day of the workshop was dedicated to presentation and discussion of interim results from research projects, brief summaries of which were provided by the investigators and are included in this document (p. 13). Investigators of projects that commenced in January 1992 were asked to provide only a synopsis of their objectives, approach and rationale. Projects were grouped into four subject areas and presented in the following order: Flux and Speciation (p. 13), Water-column Bioprocessing (p. 27), Benthic Processes (p. 44), and Effects (p. 61).

The second day of the workshop was devoted to integration of research activities and a discussion of management needs as related to the Toxics Research Program. First, a synopsis of the modeling effort (Kemp et al.) was presented (p. 70). The goal of this effort is integration of research results into an ecosystem model. Discussion of the modeling work was followed by an overview of toxic studies in the Chesapeake Bay watershed by R. Batiuk of the Environmental Protection Agency (p. 77).

The workshop closed with a panel discussion by members of state and federal regulatory agencies, who described the roles of their agencies in research and management of toxics in the Bay and engaged in discussion with investigators. Statements by panel members and the ensuing discussion have been summarized from tape recordings of the workshop (p. 72).

Included in the appendices are a list of funded projects (Appendix 1), list of investigators (Appendix 2), workshop agenda (Appendix 3), list of workshop registrants (Appendix 4), and panel members (Appendix 5).

This workshop report is intended to provide preliminary information on the progress of the Toxics Research Program, and address the relationship of this program to management needs in the Chesapeake Bay. For more information about the Toxics Research Program contact either the Maryland or Virginia Sea Grant College Program.

# AIR/WATER PARTITIONING AND MASS TRANSFER PROPERTIES OF TOXIC ORGANIC CHEMICALS

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## INTRODUCTION

Chemical transfer across the air/water interface is one of the dominant processes that controls concentrations and residence times of toxic organic chemicals in aquatic ecosystems. Air/water exchange mechanisms include: wet and dry particle deposition, vapor washout, volatilization/absorption at the water surface (vapor transfer), bubble stripping and bubble bursting.

Semivolatile hydrophobic organic chemical (HOC) pollutants exist in both the vapor and particle-associated phases in the atmosphere, and thus, are subject to both particulate (dry and wet particle deposition) and gaseous (volatilization/absorption and vapor washout) transport pathways. Consequently, to determine the net atmospheric input of HOCs into a water body such as Chesapeake Bay, both depositional and volatile/absorptive exchange processes need to be considered.

In the Chesapeake Bay watershed, researchers conducting the Chesapeake Bay Atmospheric Deposition (CBAD) study are determining the wet and dry depositional fluxes of selected HOCs and trace elements to Chesapeake Bay (Baker et al. 1991). Through our CBEEC research (Dickhut, 1990), we are determining the air/water partitioning and kinetic mass transfer properties of HOCs necessary for modeling the vapor transfer (volatilization/absorption) of organic contaminants to Chesapeake Bay.

## RATIONALE/APPROACH

The generally accepted method of calculating volatilization/absorption is the two resistance model (Whitman, 1923; Liss and Slater, 1974; Andren, 1983; Mackay and Yeun, 1983; Mackay et al., 1986; Baker and Eisenreich, 1990). The rate of gas transfer between the well-mixed air and water reservoirs, across the stagnant films at the interface, is assumed to be governed by molecular diffusion and is driven by the concentration (or fugacity) gradient between the equilibrium concentrations at the interface and bulk reservoirs. The volatile flux ( $F_{vol}$ ) is:

$$F_{vol} = k_{ol} (C_{f,w} - C_{v,atm} RT/H) \quad [1]$$

where

$$1/k_{ol} = 1/k_w + RT/Hk_a \quad [2]$$

and  $k_{ol}$ ,  $k_w$ ,  $k_a$  are the overall, water, and air mass transfer coefficients, respectively,  $C_{f,w}$  is the freely dissolved concentration of a HOC in surface water,  $C_{v,atm}$  is the vapor phase concentration of a chemical in the atmosphere,  $R$  is the gas constant,  $T$  is temperature (K), and  $H$  is the compound specific Henry's law constant.

Determinations of the air/water partitioning ( $H$ ) and kinetic mass transfer coefficients ( $k_w$  and  $k_a$ ) for organic chemicals under various environmental conditions are required to evaluate the passive-diffusive flux of HOCs to Chesapeake Bay. These coefficients can be determined from the basic physical-chemical properties: saturation vapor pressure ( $p_{sat}$ ), aqueous solubility ( $x$ ), air and water molecular diffusivities ( $D_a$ , and  $D_w$ ); of the HOCs.

#### OBJECTIVE

To develop and calibrate accurate techniques for measuring and estimating the physical-chemical properties  $p_{sat}$ ,  $x$ ,  $D_a$ ,  $D_w$  for predicting the air/water partitioning properties ( $H$ ) and kinetic mass transfer coefficients ( $k$ ) for "toxic" organic contaminants.

#### PROGRESS TO DATE

Our work to date, has concentrated on the measurement and prediction of three physical-chemical properties: saturation vapor pressure, aqueous solubility, and molecular diffusivity in water. Following is a description of our progress in each of these areas.

Systems for measurement of  $p_{sat}$  of both liquid and solid organic chemicals have been developed and evaluated. Vapor pressures have been measured for the following organic chemical pollutants: tetrachloroethylene (10, 25, 40°C), benzene (10, 25, 40°C), chlorobenzene (10, 25, 40°C), o-dichlorobenzene (10, 25, 40°C), p-dichlorobenzene (-14.5, -5.5, 10, 25, 40°C), phenanthrene (0, 25, 40°C, f(humidity)). The vapor pressure measurements on benzene and phenanthrene were utilized to evaluate our methods and we find that our experimental techniques compare well (within 10-20%) to those of others. In addition, we observed no effects of humidity on the vapor pressure of phenanthrene, and consequently, will not continue to examine this variable in our measurements of  $p_{sat}$ .

The technique we have found to be best for estimating vapor pressure is a relationship of the critical and boiling point temperatures to the enthalpy of vaporization ( $\Delta H_{vap}$ ):

$$\ln p_{sat} = (\Delta H_{vap,b}/\Delta Z_b RT_b) * [1 - (3-2T_r)^m/T_r - 2m(3-2T_r)^{m-1} \ln T_r] \quad [3]$$



where,  $\Delta H_{\text{vap},b}$  is the enthalpy of vaporization at  $T_b$ ,  $T_b$  is the boiling point temperature,  $\Delta Z_b$  is a compressibility factor,  $R$  is the gas constant,  $T_r$  is the reduced temperature ( $T/T_b$ ), and  $m$  is a regression coefficient dependent on the physical state of the organic chemical.

Results for both experimentally measured and predicted vapor pressures indicate that  $p_{\text{sat}}$  of HOCs is strongly dependent on temperature, increasing as temperature increases. Predicted vapor pressures using eq 3 tend to diverge from the measured values at higher temperatures although the estimated vapor pressures are still within 10-15% of the experimental values. Furthermore, the vapor pressure predictive technique appears to work well for solid as well as liquid aromatic hydrocarbons and eq 3 also works well over a wide range of temperatures (i.e. -15°C to 40°C).

Our solubility research has primarily included studies of the effects of dissolved organic substances on the solubility of HOCs. Organic substances in water are of potential importance in air/water transfer research as they can influence solubility of HOCs in the surface microlayer of an aquatic ecosystem. To date, solubility in organic solvent/water mixtures (25°C) has been measured for the following organic contaminants: naphthalene (methanol/water, ethanol/water, 1-propanol/water), phenanthrene (methanol/water, ethanol/water, 1-propanol/water), acenaphthene (methanol/water, ethanol/water, 1-propanol/water).

Finally, a system for measuring aqueous molecular diffusivities has been developed and calibrated in our laboratory. So far, we have measured molecular diffusion coefficients in water for several organic chemicals as a function of temperature including: benzene (10, 18, 25, 32, 40°C), toluene (10, 35, 40°C), naphthalene (10, 25, 40°C), and phenanthrene (4, 40°). We have also initiated a study to evaluate the effects of salinity on aqueous molecular diffusivity of HOCs.

Property estimation techniques for diffusivity in water are based on the Stokes-Einstein equation for fluid flow around spherical particles. One correlation based on the Stokes-Einstein equation is the Hayduk-Laudie (1974) equation:

$$D_w = 13.26(10)^{-5} / \eta_w^{1.4} V_s^{0.589} \quad [4]$$

where  $V_s$  is the molar volume of the solute and  $\eta_w$  is the viscosity of water. We have observed that predicted values of  $D_w$  for HOCs using eq 4 tend to consistently underpredict or overpredict the experimental data, but that the increase in diffusivity with temperature is adequately estimated. Because of these consistent differences in estimated values, we suspect that the discrepancies can be corrected by evaluating the size parameters (i.e. group contribution technique) used in the correlation.

## SUMMARY

Measurement of the physical-chemical properties ( $p_{\text{sat}}$ ,  $x$ ,  $D_w$ ,  $D_a$ ) of organic chemicals at specified environmental conditions can be used to determine the air/water partitioning and mass transfer properties necessary for modeling air/water exchange fluxes of organic contaminants. We have developed and calibrated methods for measurement of the physical-chemical properties ( $p_{\text{sat}}$ ,  $x$ ,  $D_w$ ) in our lab. Physical-chemical property data at selected environmental conditions (temperature, salinity, humidity) are currently being collected. Furthermore, property estimation techniques for  $p_{\text{sat}}$ ,  $x$ , and  $D_w$  have been evaluated for data collected to date. Property estimation methods for vapor pressure, aqueous solubility, and molecular diffusivity are reliable to within the expected accuracy of the data.

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# DETERMINATION OF THE CHEMICAL SPECIATION OF DISSOLVED COPPER AND CADMIUM IN CHESAPEAKE BAY

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## OBJECTIVES

My overall objective is to obtain a broad-scale picture for the Chesapeake Bay of the speciation and organic complexation of dissolved Cu and Cd, and to perform an initial investigation of the variability of surface water Cu and Cd speciation with salinity and season. My specific objectives are to determine:

- (1) the concentrations of the free ionic, organically complexed and inorganically-complexed fractions of dissolved Cu and Cd;
- (2) the concentrations of Cu- and Cd-complexing organic ligands;
- (3) the conditional stability constants of organic Cu and Cd complexes;
- (4) the concentrations of total dissolved Cu and Cd; and
- (5) the variability of the parameters listed in objectives (1) through (4) as functions of salinity and season. These data are essential to the formulation of hypotheses regarding biogeochemical processes involving Cu and Cd in the Bay.

## RATIONALE

Cu and Cd have been designated as "Baywide Toxics of Concern" (EPA, 1990). The identification and quantification of harmful effects of metals such as Cu and Cd in estuaries receiving anthropogenic inputs is difficult because of the multitude of pollutants potentially present and the uncertain relationship between metal concentrations and metal toxicity. Uncertainty also exists regarding the fate and transport of metals in estuaries. These uncertainties result from lack of definitive knowledge of the actual chemical forms (i.e., free ions, inorganic and organic complexes) of these metals and the concentrations of their forms (i.e., speciation) in estuarine waters.

Knowledge of metal speciation is critically important because different metal species can have different biological effects and geochemical reactivities. Laboratory studies have shown that the toxicity and availability of certain trace metals, including Cu and Cd, are controlled by the concentrations of the free ionic form of the metal rather than by the metal's total concentration (see Morel and Morel-Laurens, 1983; and Sunda, 1991 for reviews). Complexation of metals by organic ligands can control the availability of the metal to biota by regulating its dissolved free ion activities. Organic complexation has recently been demonstrated to control the speciation of dissolved Cu in various estuarine, coastal, and open ocean waters (see Donat and Bruland, submitted, for review); organic complexation has also been found to dominate the speciation of dissolved Cd in open

ocean waters (Bruland, 1992). The 1990 Chesapeake toxicological workshops recognized the importance of obtaining metal speciation data for the Chesapeake Bay and emphasized the need to "develop methods to investigate temporal and spatial variability of chemical speciation [of dissolved contaminants]", and to "investigate the geochemical controls (e.g., salinity, pH, redox state) of this speciation" (STAC, 1991). While initial studies by Newell and Sanders (1986) and Sunda et al. (1990) provide useful information on different, limited aspects of Cu speciation for the Patuxent River and the Elizabeth River estuary, respectively, we still have no comprehensive knowledge of the speciation of dissolved Cu and Cd in the Chesapeake Bay.

## APPROACH

I will collect water samples from five stations along a long-axis transect of the Bay at salinity values of approximately 0, 10, 15, 20 and 30, during summer and winter. The analyses of these samples will yield data for both the major freshwater (the Susquehanna River) and seawater endmembers and for a representative spread of salinities and geographical regions of the Bay, and will allow comparisons of dissolved Cu and Cd speciation between periods of relatively low (summer) and relatively high (winter) fresh water inputs, and between periods of relatively low primary productivity (winter) and relatively high productivity (summer). I will coordinate my exact station locations as much as possible with those of other CBEES PI's performing relevant work (e.g., Drs. J. Sanders and K. Sellner, Drs. Burdige, Cornwell, and Boynton).

Samples for total dissolved Cu and Cd and Cu and Cd speciation analyses will be collected and processed using appropriate techniques, and appropriately cleaned equipment, to prevent or minimize trace metal contamination (see Martin et al., 1976; Bruland et al., 1979, 1985). The salinity and pH of the water samples will also be determined.

I will determine total dissolved Cu and Cd concentrations by Differential Pulse Anodic Stripping Voltammetry (DPASV) using a thin mercury film, rotating, glassy carbon disk electrode (TMFRGCDE) (Bruland et al., 1985) after ultra-violet photooxidation at pH 2 to free Cu and Cd from organic complexes which would otherwise mask the concentrations. The method of standard additions will be used to correct for any matrix effects.

I will fully characterize the speciation and organic complexation of dissolved Cu and Cd in each sample by DPASV and Competitive Ligand Equilibration/Differential Pulse Cathodic Stripping Voltammetry (CLE/DPCSV). DPASV, using a TMFRGCDE, detects the inorganic Cu and Cd (i.e. free ions + inorganic complexes) originally present in the sample (Coale and Bruland, 1988; Bruland, 1989, 1992; Donat and Bruland, 1990). The concentrations of the individual fractions (free ions, inorganically complexed, and organically-complexed forms), are

calculated from these measurements via thermodynamic equilibria and mass balances (e.g., see Coale and Bruland, 1988; Bruland, 1989, 1992; Donat and Bruland, 1990).

CLE/DPCSV involves establishment of a competitive equilibrium between the metal-of-interest (i.e., Cu or Cd), the metal-complexing organic ligands present naturally in the sample, and a competing organic ligand (e.g., tropolone, 8-hydroxyquinoline, or catechol) added to aliquots of the sample (van den Berg, 1984; Donat and Bruland, 1988, 1990; Donat and van den Berg, 1992; van den Berg and Donat, 1992). The aliquots are spiked with incrementally increasing concentrations of the metal and allowed to establish a new equilibrium. The reduction current from the metal bound to the added competing organic ligand under the newly established equilibrium conditions is then measured, as the potential on a hanging mercury drop electrode is varied. This measurement is used to calculate the original speciation of the dissolved metal in the sample.

#### UTILITY OF RESULTS

Information on dissolved Cu and Cd speciation will help us to understand aspects of biological interactions and fate and transport of Cu and Cd (and other metals having similar biogeochemistry) in the Chesapeake Bay and other estuaries in the U.S. and internationally. Such aspects include: (a) bio-availability and toxicity of dissolved Cu and Cd, and potential deleterious effects of high concentrations and/or inputs of Cu and Cd to biota (e.g., CBEES work of Drs. J. Sanders and K. Sellner on uptake of Cu during dinoflagellate blooms); (b) the potential role of phytoplankton-derived organic compounds in complexation of Cu and Cd (e.g., CBEES work by Drs. J. Sanders, K. Sellner, J. Baker, R. Harvey, and R. Dawson). This information could also be used by water quality control agencies as a partial basis for establishing site-specific criteria for free  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  concentrations in the Chesapeake Bay.

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# **PARTICLE-REACTIVE RADIONUCLIDES AS ANALOGUES OF PARTICLE-REACTIVE POLLUTANTS IN CHESAPEAKE BAY**

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## **OBJECTIVES**

Many of the toxic pollutants that make their way into the Chesapeake Bay, for example, metals such as zinc, copper and lead, and organic compounds such as DDT, Kepone, hydrocarbons and PCBs, undergo extensive interactions between the dissolved and particulate phases in the aquatic environment and associate preferentially with the particulate phase. They are classified as the "particle-reactive" pollutants. The overall objective of this study is to understand and quantify the geochemical dynamics that govern the fate of these pollutants in the Bay. Specifically, this study attempts to determine:

1. in the sediments, the relative effectiveness of the various sedimentary sub-environments of the Bay as sinks for particle-reactive pollutants.

2. in the water column, the partition of particle-reactive pollutants between the dissolved and the particulate phases, the residence times of these pollutants in the water column and the effects of environmental conditions on the geochemical behavior of these pollutants.

## **APPROACH**

Studying the geochemical behavior of all particle-reactive pollutants individually is often prohibitively time-consuming, costly and thus impractical. Furthermore, it is also often difficult, if not impossible, to extract information involving time, such as reaction rates and residence times, by studying the distributions of these pollutants directly. Several naturally occurring radionuclides, namely, Be-7, Th-228, Pb-210 and Po-210, are known to be particle-reactive. The source terms of these particle-reactive radionuclides are well defined and can be determined exactly. Their half-lives, which range from weeks to decades, allow them to act as unique geochemical clocks for studying the geochemical dynamics of the particle-reactive pollutants since many of the processes that may govern the geochemical fate of these pollutants also occur within this range of time scales. Thus, in this study, an "ANALOGUE" approach, utilizing Be-7, Pb-210, Po-210 and Th-228 as the analogues, is used to study the geochemical dynamics which govern the phase association and fate of particle-reactive pollutants in the Chesapeake Bay.

## PROGRESS TO DATE

Large volume water samples were collected from the southern Lower Bay at 9 stations in the Summer (July 10 to 13, 1991), Fall (October 8 to 10) and in the Winter (January 8 to 10, 1992) and at 9 stations in the northern Lower Bay in the Summer (August 14 to 15, 1991) and Winter (January 29 to February 4, 1992). (A cruise to the northern Lower Bay was scheduled during the Fall of 1991. However, the cruise was canceled because of adverse weather conditions during the scheduled time slot and several backup time slots in late October and the early part of November. Subsequently, the R/V Holton was drydocked for major repairs and maintenance work from the middle of November through December.) Box cores were collected at 8 stations from the northern and southern Lower Bay in the Winter (January to February, 1992) and at 5 stations from the southern Lower Bay in the Fall (October, 1990). A precipitation station has been set up at Old Dominion University and monthly precipitation samples have been collected since August, 1991.

## PRELIMINARY FINDINGS

There is a significant focusing effect of particle-reactive radionuclides in the various sedimentary sub-environments in the Bay. The inventory of Pb-210 in sediment cores varies from undetectable to  $>60$  dpm/cm<sup>2</sup>. At the higher end of this range, the inventory is more than twice of what can be supported by the atmospheric depositional flux. Some of the highest inventories can be found in embayments such as Mobjack Bay and Pocomoke Sound. Such embayments may be significant traps of particle-reactive toxic elements that are added to the Bay. A more extensive sampling program will be needed if a more detailed evaluation of the various sedimentary sub-environments as potential sinks for particle-reactive elements is desired.

Based on our preliminary data on the distribution of Be-7 in the southern Lower Bay and the depositional flux of Be-7 in the Summer of 1991, the residence time of particle-reactive elements in this part of the Bay in Summer may be on the order of several weeks.

We have tested the possibility of using radionuclides as an analogue to study the changes in the speciation of particle-reactive pollutants in the Chesapeake Bay. Although this specific objective was not stated in the proposal, it fits under the overall objective of this study. We started the study with uranium since its concentration is higher, its inorganic speciation in seawater and its source term to the Bay is relatively well known. We have developed an analytical scheme for the determination of inorganic and organic uranium in marine waters and measured the concentration of these two forms of uranium in Atlantic Ocean water and Chesapeake Bay water. Our preliminary data suggest that the Chesapeake Bay may act as a geochemical reactor that can change the speciation of uranium significantly. The source of uranium to the Bay is primarily



through the intrusion of seawater from the Atlantic Ocean. Uranium exists exclusively as inorganic uranium in this incoming water. However, within the residence time of the water in the Bay, a significant fraction, up to 45% of total dissolved uranium, may be converted to the organic form. Since uranium is geochemically relatively unreactive, the speciation of the more reactive elements, such as stable Pb and its radioactive analogue  $Pb^{210}$ , may be even more extensively affected.

Two manuscripts, in which the support of this grant was acknowledged, have been prepared for publication. "The determination of leachable uranium in marine and lacustrine sediments by steam digestion" has been accepted for publication in Talanta. "A re-evaluation of two methods for the preconcentration of uranium from marine waters: A scheme for the determination of "strongly bound" uranium" has been submitted for publication in Marine Chemistry.

**PARTICLE REACTIVE POLLUTANTS IN SOUTHERN CHESAPEAKE BAY:  
ACCUMULATION, RESUSPENSION AND FLUX INTO THE BOTTOM**

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**OBJECTIVE**

We are developing methods to determine 1) the rate of accumulation of particle reactive pollutants (as proxied by radioisotopes), 2) residence times of pollutants in the seabed, and 3) the rates and mechanisms of pollutant release through storm resuspension and biological mixing.

**APPROACH**

Radionuclides as proxies.-- Toxic pollutants entering Chesapeake Bay are known to preferentially associate with the particulate phases, and their dispersal is therefore controlled by the natural cycle of fine sediment transport. The list of "particle-reactive pollutants" includes metals (zinc, copper, and lead), and organic compounds ranging from pesticides and herbicides such as DDT and Kepone to hydrocarbons and PCB's. The incorporation of particle-reactive pollutants into the particulate phase is essentially a unidirectional process so that redissolution is minimal. It is generally impractical in marine pollution analysis to study the behavior of each particle-reactive pollutant individually. Instead, an "analog" approach may be used, in which radionuclides act as proxies for particle reactive pollutants.

Seabed dynamics.--The shallow marine seabed plays a complex role in the transport and fate of particles and particle reactive pollutants. Accumulation of sediments and their adsorbed pollutants on the bay floor is a net accumulation; while it occurs, sediment and pollutants cycle between the bay floor and the turbid water column, at frequencies determined by tidal harmonics, and by the recurrence intervals of storm currents and river floods. At the same time, and for some time after, sediment and contaminants undergo mixing and advection in response to the activity of burrowing organisms. Eventually, a contaminated horizon passes downward into a zone of burial which can no longer be accessed by resuspension or benthic infauna. In the meantime, if seabed processes have been sufficiently active, the pollutant may have been largely returned to the water column. Our goal is to develop methods to assess the rates of seabed processes, so that we can predict the rates and patterns of pollutant dispersal.

Our program of seabed analysis is threefold. It is necessary to develop a probabilistic description of the hydraulic climate, so that resuspension depth can be presented as a function of frequency. Secondly, it is necessary to undertake a quantitative analysis of the benthic infauna and its space and time distribution, in order to establish diffusion and advection coefficients. Finally, it is necessary to undertake radiogeochemical analysis; to measure concentration profiles of radioisotopes with both short and medium half-lives, in order to calibrate diffusion and advection coefficients, and to determine accumulation rates. We have chosen as our study area the Wolf Trap ecological site on the Baystem plain of southern Chesapeake Bay, so that we may collaborate with the ongoing program at the Virginia Institute of Marine Science.

## RESULTS

Radiogeochemical analysis.--We have collected 10 vibracores and 10 piston cores from the Wolf Trap sector. The cores have been split, subsampled and X-radiographed. Grain size profiles have been measured and our colleague George Wong and students have measured  $^{210}\text{Pb}$  profiles on 5 cores. At present, radiogeochemical analysis is a problem area; Toxics Research Program samples are putting a heavy load on George Wong's laboratory; and ways of helping George expand output should be investigated.

Diffusion-advection modeling from faunal analysis.-- During the past year, we have developed computational methods for determining the biodiffusion coefficient from quantitative vertical distribution studies of the benthic infauna. Such a biology-based approach is much more sensitive to the shape of the depth-dependent  $D_b$  curve than are chemistry-based approaches utilizing concentration gradients. However, our radioisotope concentration curves will be an important means of calibrating the biodiffusion estimates.

At present, we are awaiting the results of vertical distribution studies planned by Linda Schaffner of VIMS. We plan to work with Linda to develop a parallel approach to the advection coefficient; in the benthic community of the Baystem plain, the advective term is a significant one.

Analysis of the hydraulic climate.-- High-quality time series of wave data from the Thimble shoals and Wolf Trap wave gage stations have been provided by John Boon and colleagues at VIMS. By choosing appropriate threshold criteria, we have been able to ascertain that both wind wave and swell events are common at Thimble shoals. However, the Wolf Trap gage is further up the Bay; swells reaching it are attenuated, and only wind wave events exceed the criteria. We have undertaken a wave hindcast study of the Wolf Trap ecological site, using the Army Corps of Engineers. ACES program, which is suitable for such a fetch-limited and

fetch-restricted setting, in order to develop a wave-height frequency distribution.

Studies by Don Wright and colleagues at VIMS have demonstrated that resuspension of bottom sediments at the Wolf Trap site does not normally occur unless wind waves are accompanied by peak tidal currents. We are presently working to establish the detail with which we need to investigate the frequency distributions of tidal current and residual (meteorological) current speeds.

Resuspension model.-- We now have available to us a numerical model to transform frequency distributions of current intensity into frequency distributions of resuspension depth. The model has been assembled over the past year by one of us (Alan Niedoroda), working with Chris Reed and Asish Mehta of the University of Florida. The model synthesizes developments in boundary layer theory that have taken place over the past decade, and can simulate flow-substrate interactions not accounted for by most other models, notably the capacity and competence limitations of sediment entrainment, and the limitation of entrainment due to cohesive forces in the substrate.

Modeling pollutant dispersal.-- Preliminary manipulation of our present data set, though incomplete, suggests that we can assemble our advection-diffusion model of sediment mixing, and our wave-current resuspension model into a more general numerical model of pollutant accumulation, seabed storage, and release. During the coming year, we will continue our data analysis, and will gather a supplementary data set at Old Plantation Flats, in collaboration with the VIMS group.

## THE IMPORTANCE OF DINOFLAGELLATE BLOOMS IN THE TRANSPORT OF CARBON AND TOXIC TRACE ELEMENTS IN CHESAPEAKE BAY

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Phytoplankton blooms are increasing throughout the world's coastal zones, perhaps as a function of man's activities. Many blooms are formed by nuisance species, such as dinoflagellates, and may not be subjected to high levels of planktonic herbivory. Thus, these blooms can be active accumulation sites for large pools of elemental contaminants and may act as reservoirs for subsequent transfer to consumer populations. Unfortunately, we know little about how the dynamics of phytoplankton blooms of unusual species affect or facilitate pollutant transport through the coastal zone and the potential for ecosystem impact.

Under normal conditions, toxic substances can be transported through an aquatic ecosystem via a number of pathways. The formation and senescence of algal blooms may comprise an alternate method of carbon and toxic trace element transport. If the plant cells remain uneaten by conventional grazers, carbon and trace elements accumulated by the bloom can sink directly to the sediments or cycle rapidly through the "microbial loop".

The concentration and repartitioning of toxic trace elements by phytoplankton blooms makes them an important pathway to examine in the movement of contaminants through coastal zones. This study is designed to examine this pathway, paying particular attention to the role of ungrazed phytoplankton blooms. In this study, we will investigate the role of phytoplankton blooms, particularly nuisance blooms of dinoflagellates, as concentrators and vectors for several toxic trace elements in Chesapeake Bay. We hypothesize that dinoflagellate blooms will effectively increase particulate trace element levels in bloom regions and facilitate the transfer of these elements to either microbial heterotrophs in the water column or sediments.

We will test our hypothesis by addressing the following objectives over a two-year period. Year One will focus on Objectives 1 and 3, Year Two will examine Objectives 1, 2, and 3.

1. Estimate the incorporation and transformation of several toxic trace elements in dinoflagellate and other algal blooms relative to non-bloom assemblages;

2. Determine the rates of transfer of bloom carbon and incorporated trace elements to other trophic levels; and

3. Determine the importance of bloom carbon and trace element concentrations in delivery of energy and contaminants to sediments and/or water column heterotrophs.

During Year One, we will be actively sampling natural blooms in Chesapeake Bay, examining bloom and non-bloom phytoplankton assemblages and associated trace element concentrations and the potential for transfer to either sediments or grazers within the water column. During Year Two, bloom and non-bloom assemblages will be returned to the laboratory and maintained in microcosms under natural conditions to examine trace element uptake rates and the rates of transfer to a variety of consumers as well as underlying sediments.

Results generated in the study will enable partitioning of metal concentrations between water column particulate and dissolved phases, sediments and their impact on the planktonic community in a eutrophic estuary. In addition, bloom-induced changes in trace element speciation could also dramatically influence toxicity during recurring coastal blooms. These results, in turn, can be used to estimate the effects of the partitioning of natural and anthropogenic trace elements by increasingly frequent phytoplankton blooms on coastal food webs and the productivity of commercially valuable living resources.

## ROLE OF PLANKTON IN CONTROLLING THE PARTITIONING AND TRANSPORT OF HYDROPHOBIC ORGANIC CONTAMINANTS IN CHESAPEAKE BAY.

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H. Rodger Harvey  
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The University of Maryland System

### RESULTS OF 1990-91 STUDIES

Beginning in October 1990, we conducted six cruises to characterize HOC partitioning to a variety of suspended and settling solids and to quantify the importance of sediment resuspension in supplying HOCs to the Bay's water column. Particle interceptor traps (*i.e.*, sediment traps) were deployed in near surface (3 m below surface) and near bottom (3 meters above bottom) for 3 to 5 day periods during each cruise to quantify the net flux of material. During each cruise suspended particles were also collected at similar depths by high volume filtration and split into four size fractions (<10  $\mu\text{m}$ , 10-64  $\mu\text{m}$ , 64-202  $\mu\text{m}$  and >202 $\mu\text{m}$ ). These samples were analyzed for total mass, organic carbon and nitrogen, total lipid and lipid classes, hydrophobic organic contaminants and pigments. In addition, dissolved organic contaminants and selected lipid biomarkers were also quantified.

Organic carbon and mass settling fluxes varied seasonally with a strong resuspension signal apparent in traps deployed near the bottom. The magnitude of the sediment resuspension flux into the bottom waters demonstrates the dynamic nature of the Chesapeake Bay estuary, and also illustrates the variation of sediment resuspension over time. Net mass flux near the sediment-water interface averaged over ten fold higher than the surface water mass flux, (190 versus 18.5  $\text{g}/\text{m}^2\text{-day}$ , respectively) while carbon flux averaged only 6 fold higher (7.3 versus 1.2  $\text{g}/\text{m}^2\text{-day}$ ). Strong wind events were present during the first October cruise, resulting in the resuspension of large amounts of material from bottom sediments, as evidenced by the mass and carbon fluxes during that time. Organic carbon and lipid values of the sediment trap material suggest that this material consists largely of resuspended bottom sediments. The magnitude of sediment resuspension was also estimated by comparing the chlorophyll-a and carbon settling fluxes. For surface traps in March 1991, chlorophyll-a and organic carbon fluxes averaged 1.54 and 250  $\text{mg}/\text{m}^2\text{-day}$ , respectively. Assuming a conservative carbon:chlorophyll-a ratio of 50 for the Chesapeake Bay, approximately 30% of the carbon flux can be accounted for by settling phytoplankton. Approximately 23% of carbon collected in the bottom traps are derived from fresh phytoplankton, using these assumptions.

Compared to trap material, the organic carbon content of suspended particles was much more consistent over the six cruises. Organic carbon showed a strong seasonality, with values increasing in surface waters during early March and continuing through the summer. Higher values in bottom waters were also observed, and the presence of significant concentrations of peridinin (a dinoflagellate carotenoid) together with diatom fucoxanthin suggest the early appearance of these taxa in Bay bottom waters in early March, 1991. Analysis of total lipid and lipid classes of both suspended and settling particles sampled over the past year show significant differences in the amount and composition of particles present in the water column. In the analyses thus far, trap material is dominated by more polar lipids, with significantly less of the intact neutral lipid hypothesized to be the important component for HOC partitioning usually present. In suspended particles, however, changes in lipid class composition are apparent and most notable for the  $>202 \mu\text{m}$  fraction, which shows a high triacylglycerol content. Visual analysis confirmed that this fraction was dominated by copepods and other microzooplankton and may be an important HOC reservoir. In addition to the  $>202 \mu\text{m}$  fraction, enhanced triacylglycerol content was also observed for the 64-202  $\mu\text{m}$  fraction in bottom waters which contained a significant number of copepod eggs when examined microscopically.

Specific compound analysis of surface and bottom water particulates during the early spring (*i.e.* March) cruise also suggests that the surface and bottom waters have substantially different particle populations. Summed concentrations of total extractable fatty acids, total sterols and all alcohols in the four size fractions suggest that while the lipid distribution in bulk surface and bottom water appear similar, lipids associated with each size fraction are distinct. Unfractionated surface waters, for example, most closely resemble the smallest ( $<10 \mu\text{m}$ ) particles in surface waters, while the lipid distribution in bottom waters more closely resembles larger particles. The bulk of chloropigments and carotenoids are in the  $<10 \mu\text{m}$  and 10-64  $\mu\text{m}$  fractions. However, pigments were relatively enriched in the 64-202  $\mu\text{m}$  fraction in bottom waters, presumably due to detrital or fecal matter. The complex picture that results suggests that even though overall distributions of lipids may appear similar throughout the water column, different sizes of particles may be responsible, thus underlining the need for further information concerning particle dynamics in estuarine systems.

To date, we have analyzed HOC concentrations in settling solids collected by surface and bottom water sediment traps deployed during the six cruises and in the various sized particles collected in October 1990 and March 1991. Total polychlorinated biphenyl ( $\Sigma$ -PCB) concentrations in suspended particles range from 37 to 530 ng/g, with generally higher concentrations in the 64-202 $\mu\text{m}$  and  $>202\mu\text{m}$  size fractions. PCB congener distribution coefficients (*e.g.*,  $K_d$ , the ratio of the particle and dissolved concentrations) span several orders of magnitude, and are usually poorly correlated with PCB octanol-



water partition coefficients. PCB congeners with comparable  $K_{ow}$  values often have distribution coefficients which differ more than 10-fold. It is particularly intriguing that the observed partitioning behavior often differs considerably among the various particle sizes. For example, although the  $K_d$  values of the more hydrophobic PCB congeners ( $K_{ow} > 10^7$ ) are comparable for all size fractions collected from the surface waters in October, 1990, the  $K_d$  values for the less chlorinated congeners vary widely, with the smallest particles having the smallest  $K_d$  values.

The partitioning behavior of certain sized particles varies considerably from surface to bottom waters and between seasons. Surface water zooplankton samples ( $< 202 \mu\text{m}$ ) collected in October and March had elevated levels of PCBs and lipid, while those collected near the bottom in the fall had significantly lower lipid concentrations, including triacylglycerol, and an order of magnitude lower PCB concentrations. While the extent of PCB partitioning is poorly correlated to the bulk organic carbon content of the particles, our initial data suggest that total lipid is a better correlative parameter. We interpret these zooplankton data as strong evidence for the linkage between lipid levels and HOC partitioning into the estuarine food web. HOC partitioning is highly variable and particle-size dependent in Chesapeake Bay.

**ROLE OF PLANKTON IN CONTROLLING THE PARTITIONING AND TRANSPORT OF HYDROPHOBIC ORGANIC CONTAMINANTS IN CHESAPEAKE BAY: ZOOPLANKTON GRAZING AND EXCRETION**

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**PROGRESS TO DATE**

We began research (9/90 - 12/92) to elucidate the role of zooplankton in the transport of HOCs in Chesapeake Bay. Our research objectives were to measure zooplankton abundance and fecal pellet production. Using this data in collaboration with Baker and Harvey we proposed to measure the amount of lipids and HOCs in zooplankton (>200  $\mu\text{m}$ ) and zooplankton fecal pellets in order to assess the inventory of HOCs in the water column and to estimate the flux of HOCs to the bottom via zooplankton fecal pellets.

We had proposed three cruises in 1990-1991. Because the project was scaled back due to budget reductions, we only participated in cruises in October 1990. We have just begun our second year of funding (1/1/92). We will participate in cruises this spring, summer and fall.

Our cruise to the Hooper Island Station, in the mesohaline portion of Chesapeake Bay on 18 October 1990 was abbreviated because of high winds. A second cruise on 30 October 1990 was calmer, allowing us time to conduct day/night sampling, fecal pellet production experiments and sample from three depth strata. Zooplankton were collected with a pump sampler. Zooplankton biomass was determined from direct measurements with a C-H-N analyzer.

Table 1. Zooplankton Biomass at Hooper Island Station

Date	Time	Depth ( $\text{mg C m}^{-3}$ )			Integrated ( $\text{mg C m}^{-2}$ )
10/18/90		0 - 7m	8 - 16m		0 - 16m
	1300	10.8		18.8	244.6
10/30/90		0 - 7m	8 - 13m	14 - 16m	0 - 16m
	1240	0.5	0.9	2.9	17.5
	1850	1.5	3.6	7.8	55.6

The average weight of the dominant copepod, Acartia tonsa was 5  $\mu\text{g}$  C. Thus the estimated abundance of zooplankton was 49,000, 3,600 and 11,200 animals per  $\text{m}^2$  on 10/18 (1300), 10/30 (1240) and 10/30 (1850). The higher zooplankton abundance on 10/30 may be due to the different tidal stages sampled (nearly slack high at 1240 and slack low at 1850), the water possessing more "upstream" zooplankton at 1850 and being more "diluted" by lower Bay waters at 1240.

Analysis of copepod fecal pellets during October were as follows: 0.16  $\mu\text{g}$  dry weight/pellet, 0.11  $\mu\text{g}$  C/pellet, 69% C/dry weight, C/N of pellets averaged 7.7. We conducted fecal pellet production experiments on October 30 by incubating 10 Acartia in 1 liter jars containing surface Bay water for various time periods (Figure 1). We found that approximately 1 pellet/copepod/hour are produced under these conditions. Using the average pellet C biomass and our estimates of zooplankton abundance, we estimate that the production of fecal pellets was 130 and 20  $\text{mg}$  C/ $\text{m}^2$ /day on 10/18 and 10/30. These potential fecal pellet production rates are roughly 10% of the carbon flux estimated at the station with sediment traps by Baker and Harvey during our cruise. Comparing the ratio of C/dry weight of the ambient seston to that found in the traps, they found the trap ratios to be more similar to sediments rather than suspended particulate matter. Thus resuspension during our cruises in October likely dominated the catch in the sediment traps resulting in high apparent flux rates and low contributions from fecal pellets.

As part of the monitoring program conducted by the Maryland Department of the Environment, zooplankton are measured each month at a number of stations in Chesapeake Bay. We have graphed their abundance estimates of Acartia at the mid-Bay station (MCB4.3C) near our Hoopers Island station for 1985 and 1986 (Figure 2). If we assume a 16m water column, an average fecal pellet production rate of 1 pellet/copepod/h and an average fecal pellet C of 0.11  $\mu\text{g}$  C/pellet, we can estimate the potential flux of carbon via fecal pellets (Figure 3). Potential flux rates over the two years range from 11 to 1616  $\text{mg}$  C/ $\text{m}^2$ /day. Maxima in potential pellet production occur in July and September (Figure 3). These rates can be the major source of carbon flux measured in sediment traps (Boynton et al. 1988) over the same period.

Clearly these approximations are over simplifications of fecal pellet production rates. Other copepod species ( e.g. Eurytemora, Centropages) can also be abundant and contribute to fecal pellet flux. The production rate of fecal pellets is influenced by temperature, food quality and food quantity. At the higher concentrations of phytoplankton that occur in Chesapeake Bay in spring and summer, fecal pellet production rates would likely be greater than we found in October (Figure 4). In the remaining year of the grant we will measure fecal pellet

# Fecal Pellet Production

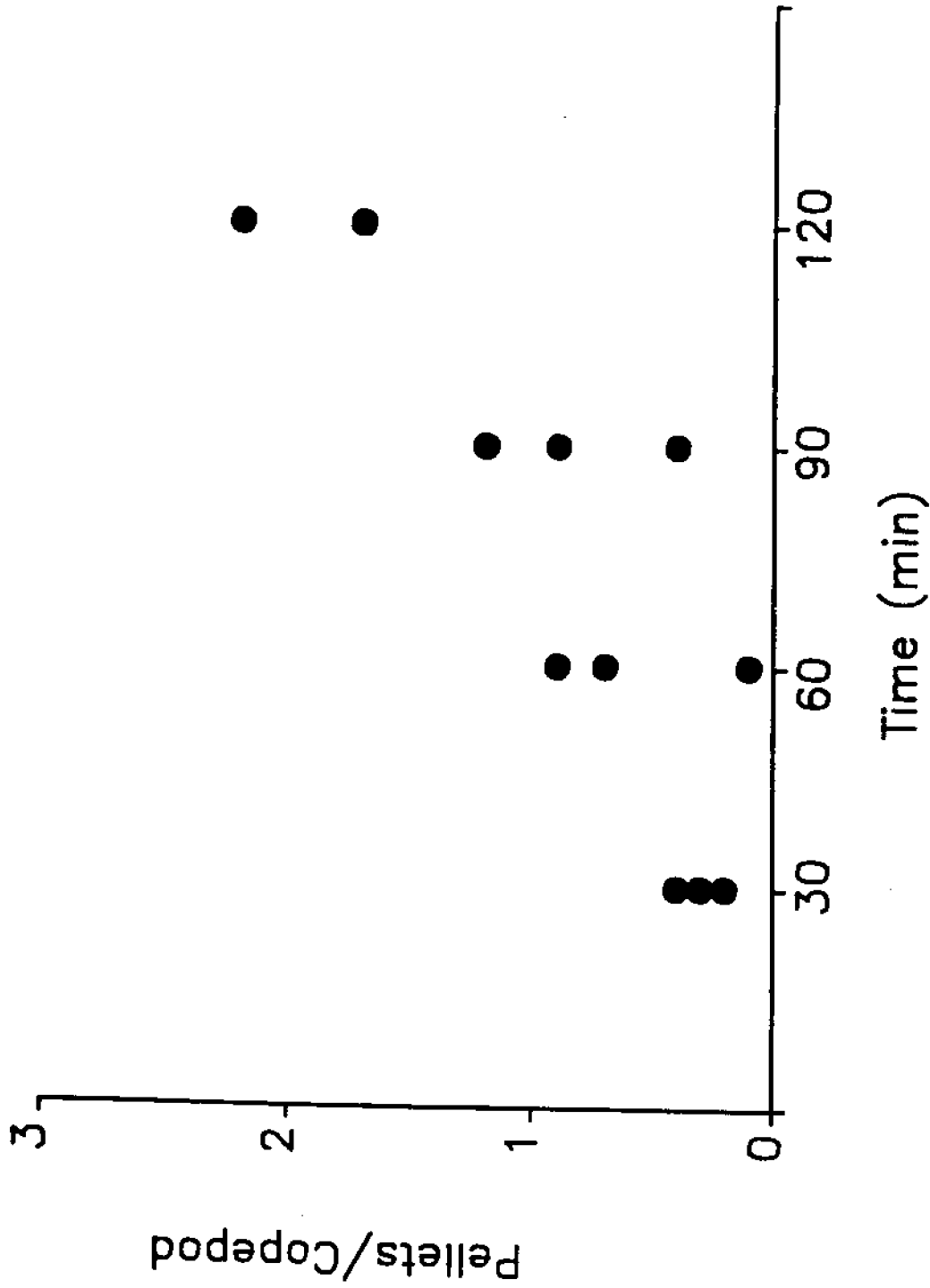


FIGURE 1. Fecal pellet production over time of *Acartia tonsa* incubated in surface seawater from Chesapeake Bay on 10/30/90.

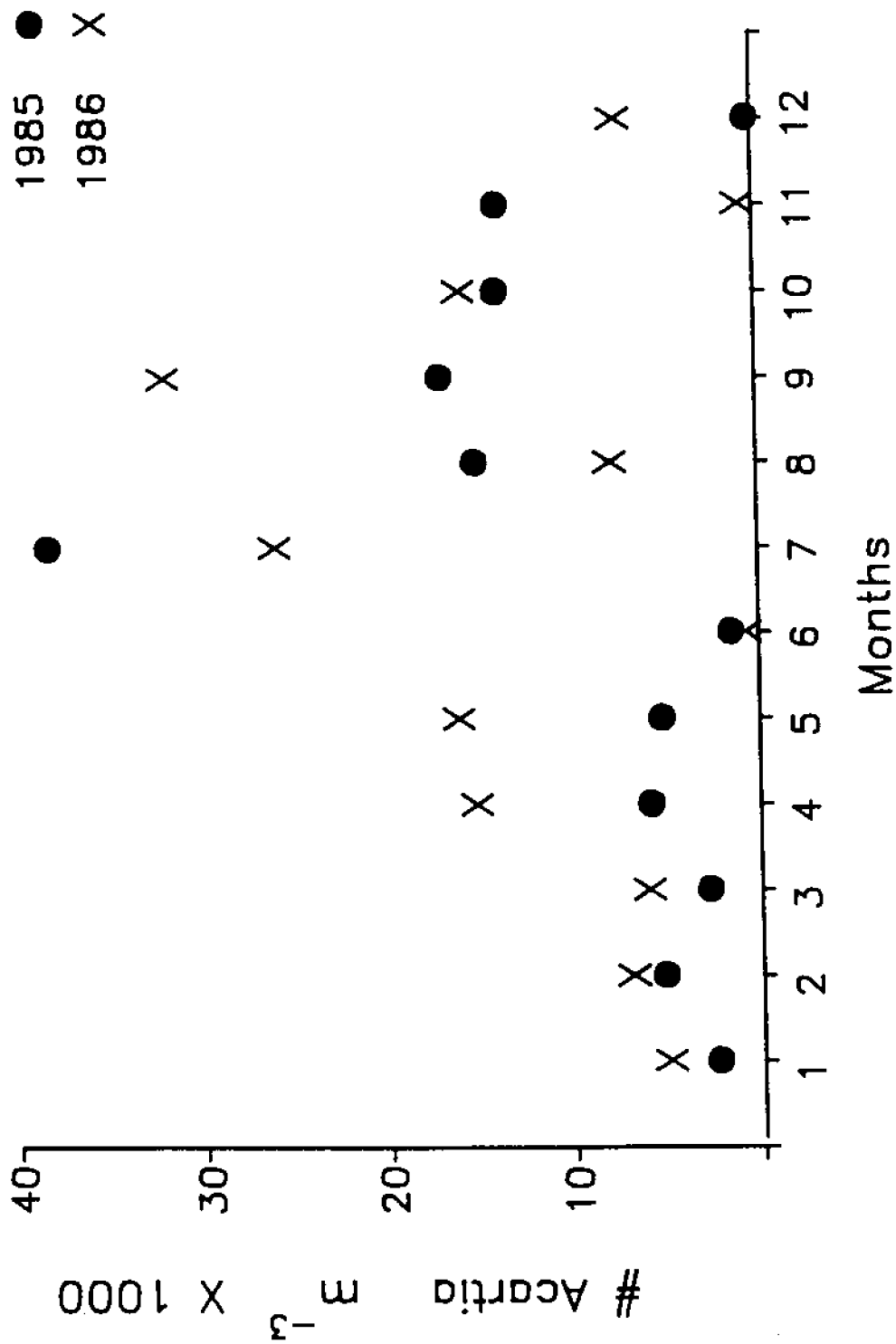


FIGURE 2. Abundance of *Acartia* from the mesohaline portion of Chesapeake Bay in 1985 and 1986. Data from Maryland Department of Environment monitoring program, prepared by Versar Inc..

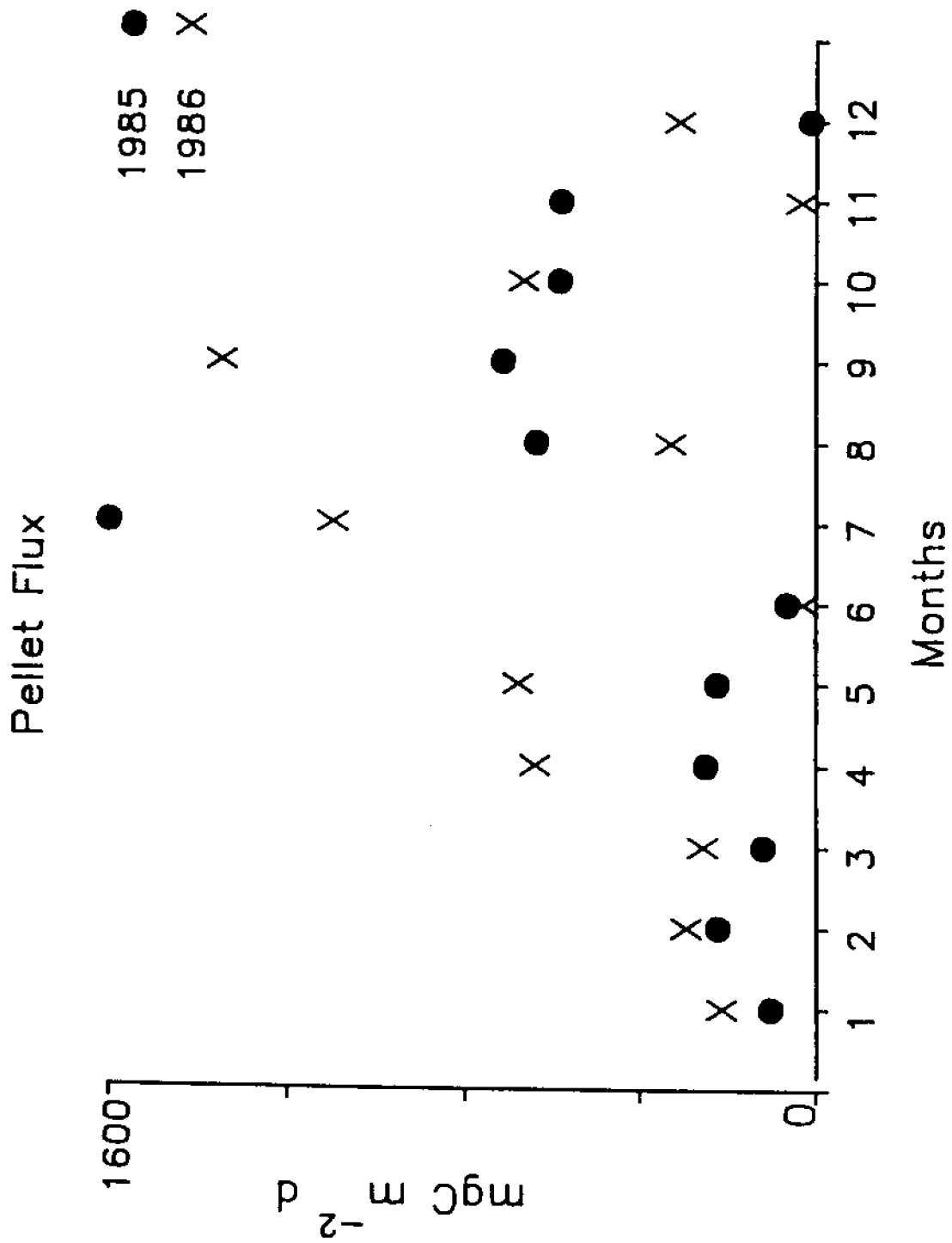


FIGURE 3. Potential fecal pellet production rates in mesohaline portion of Chesapeake Bay, assuming a 16 m water column, a production rate of 1 fecal pellet/hour and an average fecal pellet biomass of 0.11  $\mu\text{g C/pellet}$ .

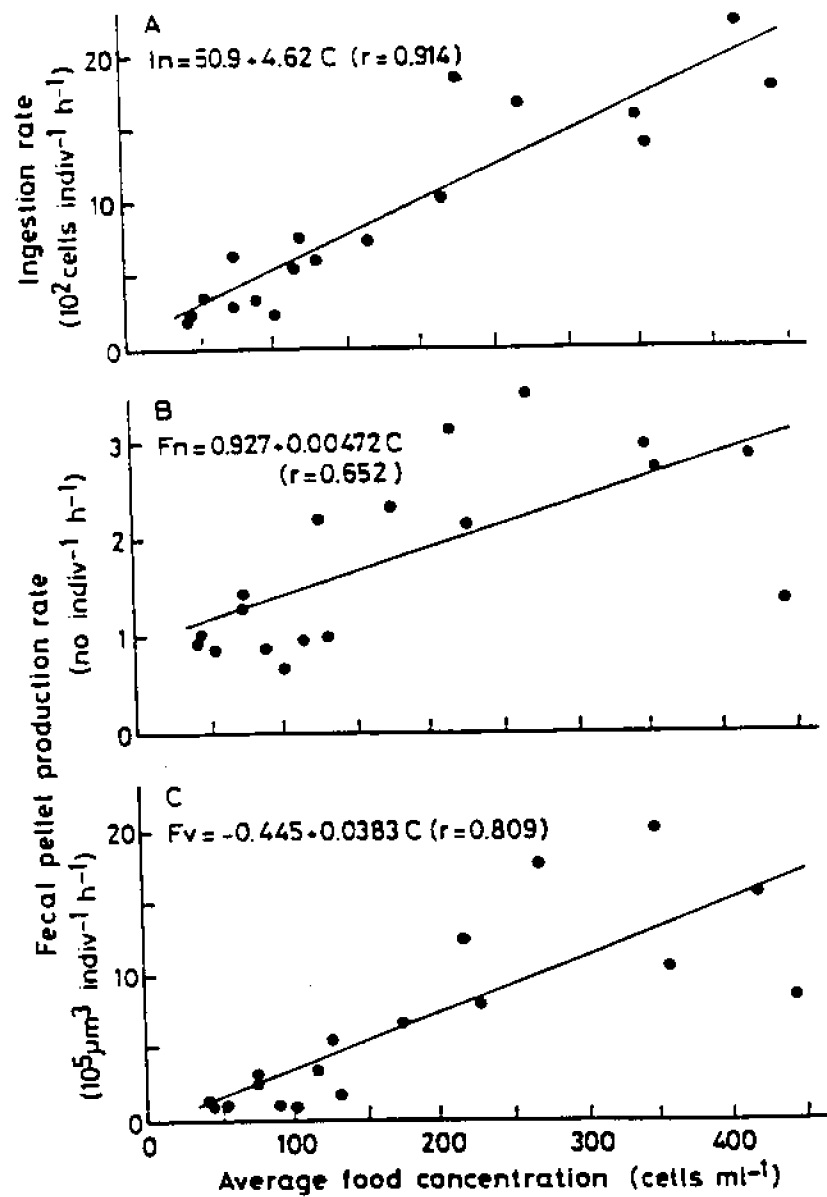


Fig. 4. Relationship between the concentration of *Thalassiosira decipiens* and (A) the number of cells ingested, (B) the number and (C) total volume of fecal pellets voided by adult female *Calanus pacificus pacificus*. From Ayukai and Nishizawa 1986.

production rates under a variety of conditions so that we can better understand the factors which influence fecal pellet production rates. We hope to produce algorithms which predict fecal pellet production rates from data on particle concentration and temperature. These predictive equations could then be used with data on zooplankton abundance such as that from the zooplankton monitoring program of the Maryland Department of the Environment, to estimate the potential flux of fecal pellets in different areas of Chesapeake Bay over the year.

Preliminary data on HOC distributions in plankton size fractions (see Baker and Harvey's proposal) indicate increasing concentrations with larger particles. Thus the zooplankton are bioaccumulating HOCs from smaller sized particles (Table 2). Increased amounts of neutral lipids, principally as triacylglycerals (see Baker and Harvey's proposal) are found in larger particles, particularly the > 200  $\mu\text{m}$  zooplankton. HOC associations will be most closely related to these neutral lipid concentrations rather than the polar lipids which predominate in the small size particles (< 10  $\mu\text{m}$ ). Harvey found an average of 7.3 ng lipid/fecal pellet in our October study. Our fecal pellet flux rates during the 2 cruises could thus be extrapolated to estimate lipid fluxes via fecal pellets of from 0.6 to 8.6 mg lipid/m<sup>2</sup>/day.

Table 2. HOC concentrations in plankton size fractions in October, 1990 (data from Baker).

HOC Component	64 - 200 $\mu\text{m}$ (ng/g dry wt)	> 200 $\mu\text{m}$
Phenanthrene	74	236
Anthracene	48	200
Fluoranthene	284	581
Pyrene	325	509
Benzo-a-Anthracene	336	588
Benzo-e-Pyrene	607	994



## RESUSPENSION AND TRANSPORT OF OF SEDIMENT ASSOCIATED TOXICS IN THE NORTHERN CHESAPEAKE BAY

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### OBJECTIVES

This project is the physical component of an integrated group of three projects addressing physical, geochemical, and biological processes controlling transport, fate, and bioavailability of suspended and dissolved toxic compounds in Chesapeake Bay waters. The present project concentrates on physical forcing, sedimentary particulate response, and trace metal contaminants. Companion projects under the direction of J. Baker, R. Harvey, and R. Dawson, and the direction of G. McManus and M. Roman, examine the contributions of phytoplankton and zooplankton populations, and concentrate on hydrophobic organic contaminants (HOCs). The overall objectives of this study are:

1) To investigate the resuspension and transport of fine sediments in the northern Chesapeake Bay, characterizing temporal and spatial (vertical) variability in resuspension processes through a sequence of combined moored and in situ observations.

2) To investigate the influence of resuspension on the time varying flux of toxics across the sediment-water interface, and to examine how resuspension affects partitioning of toxics between continuously suspended particulates, tidally resuspended particulates, bottom sediments, and dissolution.

3) To relate resuspension and transport of sediment associated toxics to more easily measurable or predictable sediment and physical forcing characteristics, in order to facilitate the incorporation of our results in improved toxics transport models.

### APPROACH AND PROGRESS TO DATE

A series of field observations have been carried out on a site in mid-Chesapeake Bay, just off the mouth of the Patuxent River. The site is located in the center of a broad depositional area of silty clays on the western shelf of the Bay, at 17 m water depth on the western flank of the deep center channel. The field observations have taken two forms: short-term (1-2 weeks) moored observations leading up to multi-investigator anchor station observations, and more limited but more frequent sediment trap deployments with no associated anchor station. Physical program efforts have been concentrated on the mooring/anchor

station observational periods. Two mooring/anchor station cruises were carried out during October of 1990, and one during October of 1991. The first of the October, 1990, anchor stations was canceled after only a few hours due to rough weather, but the second 1990 anchor station and the 1991 anchor station lasted for 20-22 hours and covered almost two full tidal cycles. A final anchor station cruise is scheduled for August, 1992, when bottom waters at the site are expected to be anoxic, offering maximum contrast to our previous observations.

The philosophy of the experimental design is to lead up to an anchor station cruise with 1-2 week deployments of current meters, transmissometers, and auxiliary sensors. Sediment traps are deployed 1-2 days prior to an anchor station, and all gear is recovered shortly after the end of the anchor station. The anchor station is scheduled to be occupied during predicted spring tides to maximize the tidal resuspension signal. The anchor stations are designed as 24 hr cooperative efforts from large, stable research platforms at 2 or 3 point anchor. Detailed vertical profiles of temperature, salinity, velocity, turbidity, and suspended sediment are acquired each hour, and information from real-time displays is used to guide sampling for particulate and dissolved toxics and zooplankton. Axial and lateral hydrographic surveys are performed in a crossed pattern centered on the site when the moorings are deployed and again immediately after the anchor station, and sediment cores are obtained for surface sediment sampling. Meteorological data are acquired from the nearby National Weather Service station at Patuxent Naval Air Station. In reality, of course, all of the observational periods have not included all of these components, but we have been quite successful at covering the basics in one form or another.

The experimental design and sampling apparatus have evolved and expanded during the course of the field programs to date. A centerpiece of the physical sampling efforts has been a profiling rig equipped with a Marsh-McBirney electromagnetic current meter mounted in front of, and at the same height as, a Sea Tech 5 cm pathlength transmissometer, a D&A OBS suspended solids monitor, and the opening of a sampling tube. The current meter is oriented into the flow by a large vane on the after end of the rig, which is ballasted to hang vertically under water; two 10 kg weights are also attached at the bottom of the central vertical axis. The sampling tube leads to a teflon-lined centrifugal pump at the surface, which pumps at a rate of about 8 l/min and is used for suspended particulate and metals sampling. A Datasonics acoustic altimeter gives a direct readout of height above the bottom, accurate to within a few cm. The profiling rig has allowed us to measure the vertical structure of suspended sediment and velocity, and collect concurrent water samples from 0.25 m above the bottom to 5 m below the surface throughout the anchor stations, and has also allowed us to construct reasonable calibrations of the turbidity sensors against total suspended particulates. These calibrations are also applied to the output of the moored turbidity sensors, which are all cross-calibrated

in a formazin standard. Moored sensors are either mounted as part of the taut-wire sediment trap arrays or on a bottom tripod for detailed near-bottom observations. An InterOcean S4 current meter is used for moored current, temperature, conductivity, and pressure measurements, and an Endeco Pulsed Dissolved Oxygen (DO) Sensor is used for moored DO measurements.

The results of our efforts to date have allowed us to achieve three important objectives. We have begun to understand the magnitude and variability of fine sediment resuspension in the mid-Bay, and the processes that control it. We have been able to provide sampling guidance, a physical context, and physical interpretation for the geochemical and biological measurements collected by the other members of our group. We have also been able to obtain samples for suspended metals analysis with a good knowledge of the immediate environment (e.g., suspended sediment, temperature, salinity, and velocity).

We believe that we have been able to identify five previously undocumented aspects of fine sediment resuspension in the mid-Bay:

1. Sediment resuspension occurs on a regular tidal basis, but a critical erosion velocity that in our observations is very close to typical tidal velocities causes a marked asymmetry in tidal resuspension. Data from the October, 1990, tripod deployment show that tidal resuspension is most notable on the strongest flood tide of each day, and is weak at other times.

2. Wind/storm generated resuspension occurs less frequently than tidal resuspension, but is much larger than tidal resuspension. This storm related resuspension is probably not due to surface waves, since our 17 m site is below effective wave base in the mid-Bay, but rather it is due to persistent higher current speeds associated with the wind-driven response of the Bay.

3. Temperature/salinity stratification in the water column can play an important role in resuspension by limiting the height to which eroded sediments can be resuspended. For example, the total suspended particulate concentration (TSP) data from the first, aborted anchor station on October 18, 1990, show that tidally resuspended sediments were elevated through the entire water column, though still concentrated near the bottom. During periods of comparable tidal velocity on October 30-31, sediments were resuspended but were not elevated further than 2-4 meters above the bottom. The water column was relatively well mixed on October 18, but on October 30-31 a near-bottom pycnocline was present between 2-4 meters height above the bottom. Thus, the stratification effectively capped the resuspended layer on October 30-31, but did not on October 18. The stratification can also occasionally be close enough to the bottom that it limits local resuspension by reducing bottom shear stress.

4. Resuspended bottom sediments settle quite rapidly out of suspension in the mid-Bay, resulting in relatively short-lived periods of high suspended sediment concentration. The rate of TSP decrease observed during the anchor stations implies settling rates of roughly 20-40 m/day, which are approximately an order of magnitude faster than settling rates of the elementary particles that comprise the silty clays at our site, implying that resuspended particles are in some way flocculated or agglomerated into much larger aggregates. Furthermore, the background TSP concentrations that remain after resuspension episodes are much lower than we originally anticipated on the basis of previous observations in the turbidity maximum of the upper Bay.

5. The depth of erosion that results from tidal resuspension in the mid-Bay is on the order of mm thick. If the difference between the maximum and the minimum total suspended load on October 30-31, 1990, is taken to represent the amount previously eroded, then redeposited sediment, and the porosity of the surface layer of sediment is estimated as 0.9, and the equivalent thickness of erosion is approximately 4 mm. A similar estimate from the October 18 TSP data yields an estimate of 2 mm thickness. It is important to note that these resuspended masses/depths are much greater than estimates of the equivalent masses/depths of newly sedimented material in the same amount of time. It is also important to note that these estimated erosion depths are very similar to the thickness of the "floc layer" observed at the very surface of bottom sediments from mid-Bay sites, when sediment samples are obtained by careful box coring.

Working as a tightly integrated group with our biological and geochemical colleagues has greatly enhanced the value of all of our sampling efforts. We have been able to provide guidance as to predicted times of spring tides, bottom sediment characteristics, observed real-time pycnocline depths, and observed real-time current speeds and suspended sediment levels. The latter has been particularly important, since tidal resuspension events are so short-lived and near-bottom concentrated that obtaining pumped samples of resuspended sediment for hydrophobic organic contaminant (HOC) analyses is extremely difficult, even with real-time data on resuspension processes. We have come far enough in our data analysis that we are beginning to be able to offer physical explanations for some of the variability observed in our colleagues' samples, and we are continuing these efforts. In a logistical sense, we have also been able to provide access to large, relatively stable NSF ships for the anchor stations at greatly reduced cost to CBEEC, since one of us (LPS) is a PI in an ongoing NSF funded Land-Margin Ecosystem Research (LMER) program with objectives closely related to our group's contaminant work. A side benefit of this association has been the attraction of investigators from the LMER program to participate in the anchor station cruises in 1991 and 1992.

In turn, our colleagues' biological and geochemical programs and expertise inform and benefit our efforts by establishing a

clear connection between our observations and our goal of examining contaminant fluxes. We are not equipped to sample or analyze for HOCs or plankton influences, but expect to be able to combine our estimates of sediment flux (resuspension) with their concurrent estimates of contaminant loading and settling rates, to derive meaningful estimates of contaminant fluxes.

Finally, our metals analyses are well underway and we have begun examining relationships between metals variability, resuspension, and advection of subpycnocline water. For example, Mn, which is virtually entirely found in the particulate phase, is strongly influenced by longitudinal velocity and altitude from the bottom. Concentrations increase at velocities greater than  $\pm 20$  cm/sec, and with proximity to the bottom. Cu, on the other hand, is found primarily in the aqueous phase. Although variations occur, they are not as large as for Mn and there is no consistent pattern evident. We will expand on this work during our summer, 1992, anchor station cruise, when bottom waters at our mid-Bay site are expected to be anoxic. Under anoxic conditions, changes in the behavior of the metals can be expected. For example, Mn is expected to remobilize under anoxic conditions. This remobilization may bring an additional flux of dissolved species into the water column due to the release of associated metals from the oxy-hydroxide grain coatings.

## DYNAMICS OF SEDIMENT RESUSPENSION: BAY STEM PLAINS OF THE LOWER CHESAPEAKE BAY

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### OBJECTIVES

The bay stem plains environment of the lower Chesapeake Bay is the most aerially extensive and has considerable economic importance as a region of previous and projected dredged material disposal and of significant benthic resource value. In this study, we are attempting to gain insights into the rates and frequencies of sediment fluxes across the sediment-water interface and the processes responsible for those fluxes. To this end, the specific objectives for 1991 have been: (1) to determine hydraulic roughness and bed stress; (2) to determine the sediment resuspension potential; (3) to determine the roles of physical vs. biological sediment resuspension processes; and (4) to assess the appropriateness of existing models for predicting sediment resuspension.

### APPROACH

Field measurements were made in winter, spring, summer, and autumn to assess seasonal variability. A bottom-mounted tripod supporting arrays of electromagnetic current meters, turbidity sensors, a pressure sensor, and a sonar altimeter was used to obtain time series of near-bottom currents, wave activity, bed stress, and suspended sediment concentrations at five elevations. Box coring provided samples for determinations of benthic biologic activity. Bottom micromorphology and details of sediment column layering and bioturbation were determined using a sediment profiling camera and a conventional camera. A seabed flume, recently developed at VIMS, was used to obtain in situ measurements of the critical shear stress required for sediment entrainment. Stress and roughness estimates were made by applying the "law of the wall," the Kolmogorov spectrum (inertial dissipation) method, and the Grant and Madsen wave current boundary layer model.

### RESULTS

Biogenic micromorphology dominates bed roughness at the Wolf Trap experiment site. Velocity profiles as well as Kolmogorov spectra indicate that the bed is hydraulically very smooth in winter with a roughness length,  $k_b$ , of only 0.5 cm (equivalent to a  $z_0$  value of 0.017 cm). Biological roughness was considerably greater in spring and summer with  $k_b = 2.0$  cm ( $z_0 = 0.067$  cm). Interactions of swell and wind waves with tidal currents in the

presence of a biologically-roughened bottom caused the hydraulic roughness height sensed by the mean flows to be significantly increased at times when wave orbital velocities were significant. It is important to note that for much of the time, low amplitude but long period swells from the Atlantic affect the bottom boundary layer. In addition, oscillations related to internal waves at frequencies close to the Brunt Vaisala frequency were often present.

No local resuspension was observed for most of the time. Only when "storm" waves interacted with strong tidal currents were skin friction shear stresses large enough to entrain sediment. This is attributable in part to the cohesiveness of the sediment and in part to biological binding and armoring of the bed at certain times of the year. Enhanced bioturbation in summer significantly reduces the critical shear stress at that time. The results from two deployments of the seabed flume indicated a high critical shear stress value of 0.18 Pa in late spring (June 1991). In contrast, in early autumn (October 1991) after a summer period of intense bioturbation, the critical shear stress at which resuspension occurred was reduced to 0.13 Pa.

#### CONCLUSIONS TO DATE

- 1) Hydraulic roughness is biologically dominated.
- 2) The roughness height,  $k_b$  ( $= 30 z_0$ ) ranges from 0.5 cm in winter to  $> 2.0$  cm in spring and summer.
- 3) Waves, including long-period swell, enhance hydraulic roughness and shear stress.
- 4) Critical shear stress is reduced in summer by biological activity.
- 5) Currents alone do not resuspend sediments.
- 6) The critical shear stress required for sediment entrainment is only exceeded when strong currents interact with moderate waves.

These conclusions suggest that the flux of particulates from the floor of the bay stem plains into the water column cannot be modeled simply in terms of physical processes. Account must be taken of seasonally-varying biological effects as well as of the contributions made by episodic wave agitation of the bed.

#### PROJECTED ACTIVITY FOR 1992

The same approach used in 1991 will be employed in 1992 to obtain data on the sediment dynamics of the Old Plantation Flats region of the lower Chesapeake Bay. This study region is near to the Wolf Trap site but is shallower, and subject to more intense physical agitation of the bed. We expect flow-induced form-drag to prevail here. Two field experiments are planned for 1992.

## MANUSCRIPT IN REVIEW

The following paper reports results from this study and is currently undergoing review for journal publication. An additional paper on sediment dynamics is in preparation.

Wright, L.D., Boon, J.D., Xu, J.-P., and Kim S.C., in review.  
The bottom boundary layer of the Bay Stem Plains  
environment of lower Chesapeake Bay. Submitted to  
Estuarine, Coastal, and Shelf Science.



# THE ROLE OF BENTHIC INFAUNA AND FLUCTUATING OXYGEN CONCENTRATIONS IN THE FLUX OF TOXIC TRACE ELEMENTS FROM CHESAPEAKE BAY SEDIMENTS

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## RATIONALE

Large reservoirs of toxic trace elements reside in Chesapeake Bay sediments. Their effect on the Bay depends on the extent to which they are able to leave the sediment. This study addresses important processes in the movement of toxic trace elements out of the sediment.

## OBJECTIVES

The purpose of this research program is to understand the processes by which trace elements are transported into and out of sediments, how benthic organisms or their activities regulate the transport of such elements between the sediments and the remainder of the ecosystem, and how these processes are altered by periodic changes in the oxygen concentrations of bottom waters. To meet these objectives, we designed a two-year study which began with laboratory experiments under carefully controlled conditions. These experiments build in complexity in the second year with manipulations on essentially intact natural sediments in the laboratory.

### 1990-91 Objectives

In the first year, using manipulated sediments under laboratory controlled conditions with carefully selected fauna, our objective was to examine the changes in fluxes due to anoxia and changes in fauna under optimal conditions. This experiment allowed us to test hypotheses concerning the effects of anoxia and associated changes in faunal abundance on trace element flux.

### 1992 Objectives

In the second year, using techniques refined in the first year, we will study the effects of anoxia on trace element fluxes in natural sediments with intact fauna. In this portion of the study our objective is to measure changes in trace element flux under the most realistic conditions we can maintain in the laboratory.

## RESULTS

Trace element fluxes and distributions have been measured in sediment/water microcosms with treatments consisting of combinations of benthic infauna and oxygen levels. Experiments

to date have used manipulated (screened, defaunated) sediments with monospecific benthic fauna. Experiments planned for the future will utilize intact sediments and fauna. We have examined fluxes of arsenic, copper and manganese to date. Results for iron are pending.

In the first year study, we examined the effects of oxygen concentration and benthic infauna on trace metal flux in experimental microcosms with defaunated sediments collected from Baltimore Harbor. Seven treatments were examined:

1. Sediment held anoxic (bubbled with pure N<sub>2</sub>), with no organisms,
2. Sediment held at 5-10% O<sub>2</sub> saturation, no organisms,
3. Sediment held at 5-10% O<sub>2</sub> saturation, Macoma (a small, common burrowing clam) added,
4. Sediment held at 5-10% O<sub>2</sub> saturation, Nereis succinea, a common burrowing worm) added,
5. Sediment held at saturating O<sub>2</sub>, no organisms,
6. Sediment held at saturating O<sub>2</sub>, Macoma added,
7. Sediment held at saturating O<sub>2</sub>, Nereis added.

Each treatment had three replicates. Microcosms were operated in continuous flow mode with a turnover of 50% volume per day, except that two stopped flow experiments were carried out to examine metal fluxes. The experiment was carried out over a period of about six weeks. Other than continuous flow experiments, microcosms were sampled twice weekly. At the end of the experiment, sediments, pore waters, and organisms were collected for analysis.

### Arsenic Flux

Arsenic in treatment 1 (anoxic) exhibited a substantial flux from the sediment into the water column in both the continuous flow mode and the first (and to date only analyzed) stopped flow experiment.

Arsenic in treatments 2 (5-10% O<sub>2</sub> saturation, no organisms) showed no significant flux under any condition. However, when Macoma or Nereis were present (Treatments 3 and 4), substantial fluxes (9 and 5 ng/cm<sup>2</sup>/day) were observed. Using flux rates from the stopped flow experiment (8 ng/cm<sup>2</sup>/day), the concentration of arsenic in average Bay sediments, and the area of the Bay, we have computed that a potential seasonal flux of 13 kg/day of arsenic due to anoxia and organisms could occur during periods of anoxia, resulting in 1 to 1.5 Mtons of arsenic flux per year.

Arsenic in treatment 5 (No organisms, saturated O<sub>2</sub>) showed no measurable flux out of the sediment. In fact, a slight decrease in the arsenic between these tanks compared to the inflowing water suggests that there was a slight negative flux of arsenic (arsenic fluxing into sediment). Similarly, Macoma and Nereis (Treatments 6 and 7) caused no apparent flux out of the

water, and Nereis showed some evidence of causing flux into the sediment.

### Copper Flux

Unlike arsenic, anoxia (Treatment 1) caused a substantial loss of copper from the water column (a negative flux of 1.2 ng/cm<sup>2</sup>/day).

In the low O<sub>2</sub> treatments, no flux was seen in the absence of organisms (Treatment 2), but a negative flux was observed with Macoma (about -0.3 ng/cm<sup>2</sup>/day) and Nereis (about -1.2 ng/cm<sup>2</sup>/day).

In the O<sub>2</sub> saturated treatment without organisms (Treatment 5), a substantial flux out of the sediment was observed (about 4 ng/cm<sup>2</sup>/day). However, in the presence of organisms, the flux was reversed, back into the sediment at about 0.4 ng/cm<sup>2</sup>/day for Macoma (Treatment 6) and 4 ng/cm<sup>2</sup>/day for Nereis (Treatment 7).

### Manganese Flux

Manganese behaved very similarly to arsenic, except that the concentrations involved and the resulting flux rates were much greater. No flux was seen for either low or saturated O<sub>2</sub> or without organisms. However, high flux was observed in the anoxic treatment (about 1.3 μg/cm<sup>2</sup>/day). Nereis in low or saturated O<sub>2</sub> water caused large fluxes (about 4 and 9 μg/cm<sup>2</sup>/day respectively), while Macoma had little or no effect on flux under the same conditions.

### **FUTURE STUDIES**

In the second year study, we will collect intact cores from Baltimore Harbor, and carry out similar experiments with three treatments:

1. No anoxia
2. Episodically anoxic (anoxic 1 week, oxic remainder)
3. Seasonally anoxic (anoxic 2 months, oxic remainder)

After anoxia, treatments will be exposed to raw water to allow recolonization with natural fauna.

Sampling will be similar to the first years study, with sampling focusing on times of transition (e.g. oxic to anoxic, anoxic to oxic, defaunated to populated).

### **SUMMARY**

Anoxia plays a considerable role in the flux of trace elements from contaminated Chesapeake Bay sediments, causing a flux of both arsenic and manganese out of the sediment, and copper into the sediment. The fluxes of arsenic are considerable, and represent a significant source of arsenic to

the Bay. Even the presence of small amounts of  $O_2$  largely negated these effects. However, the presence of organisms had a similar effect, stimulating flux in the presence of low, and sometimes even saturating  $O_2$ . Copper fluxes from contaminated sediments under saturating  $O_2$  conditions are also significant. We will focus special effort on this potential source during year two.

## **DIRECT MEASUREMENTS AND BIOGEOCHEMICAL CONTROLS OF SEDIMENT-WATER FLUX OF TRACE METALS FROM ESTUARINE SEDIMENTS**

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### **INTRODUCTION**

The affinity of dissolved organic and inorganic species (especially metals) for solid phases in natural waters often limits their solubility and can provide a mechanism for the removal of toxics from the aquatic water column to sediments. Sediment diagenesis can influence both pore water and solid phase profiles of trace metals, but the direct influence of such processes on fluxes across the sediment-water interface is only poorly understood. This proposed research is designed to determine the biogeochemical factors which influence burial, remobilization and sediment-water exchange of selected trace elements in Chesapeake Bay sediments.

Previous trace metal studies of Chesapeake Bay sediments have provided an extensive data base for concentrations and mass balances of metals in sediments. Increased concentrations of Mn and Fe in bottom water demonstrate Mn and Fe fluxes from anoxic sediments, but little is known about fluxes of other metals and nonmetals. The dynamics of metal fluxes at the sediment-water interface have not been studied. Our current work on Fe, S and P biogeochemistry show Chesapeake Bay sediments to be spatially and temporally variable and we expect similar variability in trace element diagenesis and sediment-water fluxes. The purpose of this research program is to determine the quantitative importance of metal fluxes from representative Chesapeake Bay sediments and to identify 1) the underlying mechanisms which result in trace element flux across the sediment-water interface and 2) processes which enhance trace element burial fluxes.

### **Relevance to the Problem**

This research program will be of value to the overall Chesapeake Bay program because it will provide, for the first time, a realistic measure of sediment fluxes of trace metals, specifically Cu, Zn, Cd, Mn, Fe and As in a broad range of sediment types, salinities and degrees of contamination. Because the work will be carried out in coordination with ongoing Chesapeake Bay biogeochemical studies, the results will fit in

well with the ecosystem-oriented toxics modelling efforts. Both Cd and Cu are on the Toxics of Concern List, with Zn being considered for inclusion (Joint Toxics Subcommittee Report, 1990).

Within the context of the CBEEES Toxics Research Program, our proposed studies provide overlap with the macrofauna-oriented metal flux program at the Academy of Natural Sciences, the sediment resuspension work of the University of Maryland and Maryland Geological Survey and the metal speciation work of at Old Dominion University. We will choose year 2 sites to correspond, where possible, to other sites used by CBEEEC Toxics Research Program investigators. This program will 1) examine processes which result in diagenetic metal enrichment at the sediment-water interface where sediment resuspension occurs and 2) provide additional spatial and temporal information on sediment processes responsible for water column anoxia and nutrient regeneration.

## **OBJECTIVES**

### Hypotheses

1. Manganese and iron oxyhydroxides are important for the retention of trace metals via adsorption, with both chemical and microbiological processes controlling such hydrous oxide surface area.

2. Reducing conditions within surficial sediments limit the sediment-water exchange of Cu, Cd and Zn and enhance the flux of Mn, Fe and As; the occurrence of sulfide in near-surface sediments is a key factor in the direction of sediment-water fluxes.

### Overall Objectives/Approach

The overall objectives of this program include measuring 1) the first direct dissolved metal fluxes from sediments across estuarine and trophic gradients, 2) temporal variability of metal fluxes, and 3) the importance of Mn, Fe and S redox cycling on trace element production and consumption and on fluxes across the sediment-water interface. Such studies will include the measurement of 1) "pool sizes" of pore water and solid phase trace metals, metal oxides, sulfides and organic matter, 2) direct sediment-water exchange of metals and 3) rates of sulfate and Mn and Fe oxyhydroxide reduction.

# **MICROBIAL DEGRADATION OF CHLORINATED HYDROCARBONS UNDER ALTERNATING REDOX CONDITIONS IN CHESAPEAKE BAY**

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## **BACKGROUND**

The Chesapeake Bay, the largest estuary in the United States, receives inputs of anthropogenic contaminants from numerous industrial, agricultural, urban, and municipal sources. Organic contaminants deposited to the sediments may undergo several fates, including their microbiological degradation. While anaerobic pathways of reductive cleavage of mono-aromatics are known (Evans, 1977; Evans and Fuchs, 1988; Cerniglia, 1982; Young 1984), significant breakdown of non-halogenated aromatic contaminants in the environment appears restricted to aerobic zones (Atlas, 1981; Hambrick et al. 1980; Bauer and Capone, 1985).

Hence, alternating redox may result in more complete degradation of chlorinated hydrocarbons than what might occur under strictly aerobic or anaerobic conditions. Halogenated organics, which are susceptible to alteration under both oxic and anoxic conditions, may be expected to be degraded differently (perhaps more rapidly) than under either strict anaerobic or aerobic conditions. For example, Pfaender and Alexander (1976) found DDT to require anoxic dechlorination before further oxic degradation occurred by a second microbial consortium. Likewise, Fogel et al. (1982) observed that methoxychlor underwent 70-fold greater mineralization under sequentially anoxic and oxic conditions than under strict anoxic or oxic conditions.

## **RATIONALE**

There is little information on the microbial degradation of chlorinated contaminants in the Chesapeake Bay. Microbial degradation is an important component of understanding the fate of these compounds. Also, recent observations suggest that dechlorination of chloroaromatics occurs under anoxic conditions. Dechlorination is often required before a compound is a good substrate for aerobic degradation. The seasonal anoxia in the Chesapeake Bay may provide an excellent environment for this.

## **HYPOTHESES**

1) Exposure of chlorinated aromatic hydrocarbons to reducing conditions in sediments increases their potential for mineralization under subsequent oxic conditions. This is "The Redox Facilitation Hypothesis."

2) Sustained exposure to organic contaminants and seasonally varying anoxia increases the capacity of surficial sediments for degradation and mineralization of these compounds. This is "The Acclimation/Conditioning Hypothesis."

#### OBJECTIVES

1) To examine the importance of microbial degradation in determining the fate of a suite of chlorinated hydrocarbons in estuaries.

2) To demonstrate the significance of alternating redox conditions in modifying the rate or extent of mineralization.

#### EXPERIMENTAL DETAIL

The effect of experimental manipulation of redox conditions upon degradation and mineralization rates of selected model chlorinated hydrocarbons and their non-chlorinated analogs will be examined in laboratory studies. These studies will be initiated during the Spring of 1991 and will run through the end of the year.

For each site, several liters of surficial sediments (0-2 cm) will be returned to the laboratory where they will be gently homogenized in an anaerobic hood, and combined in an approximately 1:1 ratio with deoxygenated water from the site. Homogenized sediment will be dispensed to experimental flasks according to the experimental scheme given in Fig. 1. Assay procedures are similar to the protocols of Bauer and Capone (1985, 1988), with the modification of using Teflon faced, butyl stoppers (Pierce) for sealing assay flasks.

For each site, and for each experimental level (each model compound at a specific initial concentration), two types of assays will be initiated. A set of 4 to 5 small (60cc) assay flasks with serum crimp closures containing about 50 ml of slurry will be amended with a defined level of the model compound, as well as a  $^{14}\text{C}$  trace (about 0.1 uCi) of the compound and sealed. After sealing, each flask will be regassed with  $\text{O}_2$  free  $\text{N}_2$ . After discrete intervals (e.g. 2, 4, 8 wks), individual flasks will be purged with  $\text{N}_2$  and evolved  $^{14}\text{CO}_2$  or  $^{14}\text{CH}_4$  trapped and quantitated. Also, at each interval, one flask will be made aerobic by purging with air, and the extent of  $^{14}\text{CO}_2$  monitored weekly. Killed controls will serve to correct for abiological losses (see Bauer and Capone, 1985). As time and the complexity of the experiment permits, tracer experiments will also be conducted on sediments which have not been amended with exogenous substrate as a control.

In parallel to small flask assays, a larger "batch" slurry (500 to 1000 ml in appropriate flask) will be amended with the unlabelled compound at the same concentration and held anoxic over the entire time course (Fig. 1). This flask will be used for subsampling for parent disappearance and daughter product





(and particularly dechlorinated forms) appearance over the same time course as the small flasks. For PCB's, disappearance of substrate and appearance of major intermediates will be determined by GC/ECD. The identity and/or authentication of predominant intermediates will be determined by GC/MS as necessary. Reverse phase HPLC will be employed as the analytical procedure in chlorophenol studies with GC/MS used as necessary. A binary gradient system with UV detector is available in the PI's laboratory.

Also, subsamples at each time point (e.g. weeks 2,4,8,16) will be removed, placed in small serum flasks under air and amended with a radiolabelled trace of the non-chlorinated analog (i.e.  $^{14}\text{C}$ -biphenyl or  $^{14}\text{C}$ -phenol) and monitored for  $^{14}\text{CO}_2$  appearance with time. A single unamended batch will serve as a "control" for all levels of the experiment, with samples taken for  $^{14}\text{C}$  biphenyl or  $^{14}\text{C}$  phenol mineralization.

Mineralization of labeled compounds to  $^{14}\text{CO}_2$  will be determined after direct trapping in base (Bauer and Capone, 1985). In anaerobic assays, the production of  $^{14}\text{CO}_2$  and  $^{14}\text{CH}_4$  will each be determined by either gas proportional counting (GPC) after separation of gas phase samples by gas-solid chromatography (Nelson and Zeikus, 1974) or by sequential on-line trapping of  $\text{CO}_2$ , oxidation of  $\text{CH}_4$  and trapping of  $\text{CH}_4$  derived  $\text{CO}_2$ . Both systems are available and in use in our lab. The former (GPC) is more convenient and inexpensive (requires no scintillant), while the latter offers more sensitivity.

Whereas most previous studies of reductive dehalogenation have focussed on freshwater environments dominated by methanogenesis, we will be specifically evaluating this process in estuarine sediments which are dominated by sulfate reduction (Capone and Kiene, 1988). Depending upon the extent of reductive dechlorination observed, experiments will also be undertaken to assess the effect of specific inhibitors of sulfate reduction and methanogenesis (Oremland and Capone, 1988; Genthner et al. 1989).

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# ROLE OF BENTHIC COMMUNITIES IN SEDIMENT-ASSOCIATED TOXIC ORGANIC CHEMICAL FATE AND TRANSPORT IN LOWER CHESAPEAKE BAY

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## PROJECT

Recent studies of sediment transport and the stratigraphic record preserved in near-surface sediments demonstrate that benthic communities have major impacts on sediment dynamics in Chesapeake Bay. Thus benthic organisms have a high potential to influence toxic chemical fate as well as transport and recycling within the Chesapeake Bay estuarine system. In particular, estimates of rates of bioturbation and patterns of toxicant storage (especially accumulation in organisms or biogenic structures) within the sediment are essential for modelling transport probabilities in this environment and in other habitats where biological reworking of bottom sediments exceeds physical reworking. Furthermore, it is suggested that uptake of sediment-associated pollutants by macrofauna is limited by the rate of desorption of the toxic chemical from sediment. Our study will provide information necessary to predict the relative importance of biological versus physical controls on pollutant transport and fate.

We have three major objectives: (1) To identify and quantify the role of macrobenthic organisms on sediment associated organic contaminant (PAH, PCB) transport and fate for the main basin region of lower Chesapeake Bay. (2) To evaluate the seasonal variation in the rates and mechanisms of sediment associated organic pollutant fate and transport. (3) To evaluate the rates of organic pollutant sorption/desorption and equilibrium distribution on Chesapeake Bay sediment and relate these physical-chemical properties to the uptake and bioaccumulation of sediment associated organic contaminants.

Using a laboratory microcosm approach, we will investigate the mechanisms, pathways and rates of toxicant (i.e. PAHs - phenanthrene, benzo(a)pyrene; PCBs - 2,2',4,4'-tetrachlorobiphenyl, 2,2',4,4',5,5'-hexachlorobiphenyl) transport into sediments occupied by intact benthic assemblages. We will identify toxic chemical sinks within the organism-sediment complex and assess the importance of macrofauna in sediment-associated toxic organic pollutant fate and transport. We will compare these processes in microcosms with macrofauna to microcosms devoid of macrofauna, but with otherwise intact sediments. Simultaneously, we will assess the desorption kinetics of sediment-bound pollutants and compare the relative rates of these physical-chemical and biologically-mediated fate and transport processes. Our experiments will be conducted during two major seasonal periods - summer and winter - so that

we can characterize the maximum and minimum biological effects for the region.

Work on this project was initiated during January 1992. Laboratory microcosm systems are being constructed and tested. Laboratory protocols are being outlined and verified. Preliminary sorption-desorption studies are underway. A preliminary dosing experiment will be conducted in May. The first major experiment will begin in late June and will terminate in August 1992.

## UPTAKE OF DISSOLVED AND PARTICLE-ASSOCIATED TOXICANTS BY THE EASTERN OYSTER

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Our research addresses the physical/chemical partitioning of toxicants in marine systems and how this partitioning affects the uptake of toxicants by biota. Specifically, our objective is to establish how the partitioning of a polychlorinated biphenyl (PCB) among dissolved and particulate phases affects the rates and extents of bioaccumulation by a benthic suspension feeder, the oyster Crassostrea virginica. Uptake of some hydrophobic toxicants from ingested particles has been shown to be important for benthic deposit feeders, a finding that is not surprising given the fact that these animals normally feed by ingesting bulk sediment. Although benthic suspension feeders do not ingest bulk sediments, they do live in an environment where there is a high potential for ingesting toxic substances associated with resuspended sediments and settling particulates.

Our study involves three series of laboratory experiments to investigate how changes in the concentrations of dissolved organic matter (DOM), particulate organic matter (POM), and particulate inorganic matter (PIM) affect bioaccumulation of PCB by individual oyster spat. In Series 1 experiments we will examine the relative bioavailability of PCB in the freely dissolved form and in colloidal association with DOM. In Series 2 we will provide POM in the form of an algal food source for the oyster, and examine the availability of PCB associated with ingested material. In Series 3 we will add PIM as kaolinite clay, and we anticipate that the kinetics of uptake will be dependent upon filtration and ingestion rates as determined by clay concentration.

Since we are examining bioaccumulation processes, this research provides part of the critical link between the "fate and transport" studies and the "effects" investigations funded through the CBEES Toxic Research Program. In addition, since the oyster feeds upon suspended material (and associated toxicants), this work is a clear extension of the research by other investigators on toxicants associated with suspended particulates in Chesapeake Bay (Baker, Roman, Sanford). It is obviously complementary to those studies specifically examining toxic effects on the oyster itself (Chu).

The research will significantly increase our understanding of the routes by which benthic suspension feeders accumulate hydrophobic toxicants such as PCBs and polycyclic aromatic

hydrocarbons. The work will help to identify the most bioavailable fractions and should lead to the development of methods for quantifying those fractions. Understanding how benthic suspension feeders such as mussels and oysters attain their observed toxicant body burdens will also aid in the interpretation of monitoring data from on-going programs such as Mussel Watch. Finally, the proposed work will add to our understanding of both the potential for toxicant depuration and for biodeposition by suspension-feeding bivalves, processes that are important from fisheries, aquaculture and management perspectives.

# RELATIONSHIP OF POLLUTANTS TO THE ONSET OF DISEASE IN THE EASTERN OYSTER, CRASSOSTREA VIRGINICA

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## OBJECTIVES

1. Determine the effects of a complex pollutant mixture derived from contaminated sediments on specific cellular and humoral defense-related activities of the oyster.

2. Determine the relationship between pollutant exposure and P. marinus susceptibility in oysters.

## RATIONALE AND APPROACH

The relationship between pollutant induced stress and host-pathogen interaction is unknown. This research examines the relationship of stress, in the form of exposure to environmental contaminants, and susceptibility to disease. The chemicals examined consist of a complex mixture of aromatic hydrocarbons, heterocyclics, and other compounds derived from sediments from a contaminated area, the Elizabeth River subestuary of the Chesapeake Bay. Thus, the suite of toxicants is representative of those to which organisms may be exposed in the actual environment. The test organism, the eastern oyster (Crassostrea virginica), is a representative bivalve species. This organism is a valuable natural resource of the East Coast states, but has been severely impacted by disease in the environment. The disease organism, Perkinsus marinus, is one of the two major pathogens which have seriously decimated the oyster fishery in the Chesapeake Bay and other coastal estuaries. The research assesses whether pollution is a factor in the spread of infectious diseases in aquatic organisms in general, and this epizootic in particular. In addition, the study attempts to characterize the cellular and humoral responses of pollutant-stressed animals. This information will be used to determine cause-and-effect linkages between disease and exposure to environmental contaminants. This research addresses the Research Priorities Workgroup's recommendations on risk assessment and biomarker evaluation.

## PROGRESS TO DATE

### I. Evaluation of chemical test materials:

Sediments were collected from the Elizabeth River, near the Atlantic Wood site. Sediment and filtered estuarine water were mixed for one hour and the aqueous phase filtered after settling for approximately 12 hrs. This was used with dilution in



subsequent in vitro and in vivo experiments. Sediment, water and oysters were subjected to chemical analysis.

Sediment contained contaminants indicative of the nearby creosote plant source. Heavy metals and chlorinated hydrocarbons were present at relatively low concentrations. In contrast, mean total aromatic hydrocarbon and polar heterocyclic concentrations in the homogenized sediment were high, 3190 and 135 mg/kg (ppm), respectively. Dominant compounds were the PAHs, e.g. phenanthrene, fluoranthene, pyrene, chrysene, benzofluorenes, benzochrysenes and benzopyrenes. Filtered toxicant water contained much lower levels, 3-5 mg/l (ppm). This mixture was complex, consisting of over 100 individual organic compounds. A shift in the dominant compounds towards lower molecular weight aromatics, such as naphthalene, fluorene, dibenzofuran, acenaphthene, methyl naphthalenes and carbazole was evident. Dilutions of the aqueous stock (100% solution) were used in subsequent in vitro and in vivo experiments.

## II. In vitro effects of pollutants on oyster hemocyte activities:

Chemiluminescence (CL) and chemotactic responses of hemocytes exposed to different dilutions of a toxic mixture (100, 50 and 25% of the aqueous toxic extracts) extracted from contaminated sediments were measured. Chemiluminescence of hemocytes was measured at 0, 0.5, 1.0, 1.5 and 2.5 hrs after incubation at  $15 \pm 1^\circ\text{C}$ . Chemotaxis of hemocytes was determined at 2.0 and 3.0 hrs at  $20 \pm 1^\circ\text{C}$ . Results of three trials indicated the following: At 0 to 1.0 hrs, the highest peak CL was recorded for hemocytes exposed to 0 % of the toxic extract and declined with each increase in toxic extract concentration. However, CL responses measured at 2.5 hrs appeared to be higher in the hemocytes incubated in 100, 50, and 25% toxic extracts compared to the control (0% aqueous toxic extract). Similarly, chemotactic activity determined at 2.0 and 3.0 hrs showed enhanced zymosan stimulated chemotactic response in hemocytes exposed to toxic extracts. The hemocytes exposed to the 50% toxic extract had the highest percentages of chemotaxis. Aqueous extracts derived from contaminated sediments apparently modulate the CL and chemotactic responses in oyster hemocytes and these responses changed with time.

## III. Determination of pollutant concentrations which cause effective stress in oysters and the relationship between pollutant exposure and susceptibility to Perkinsus marinus in oysters.

Three experiments have been conducted to determine the concentrations of toxic mixtures extracted from Elizabeth River sediments which will cause alteration of cellular and humoral responses and also affect the oyster's susceptibility to P. marinus infection. In these experiments, oysters were inoculated (challenged) with a dose of  $10^6$  or  $10^3$  P. marinus infective particles (trophozoites) per oyster and then exposed to three concentration regimes of toxic mixtures (5 and 10%; 10 and 20% ;

and 10 and 25% dilutions). Oysters exposed to 0% of the aqueous toxic extract served as toxic exposure controls. Non-P. marinus challenged oysters served as disease susceptibility controls. The following summarized the findings of those experiments:

1. In the first and second experiments, oysters were challenged with a dose of  $10^6$  trophozoites per oyster. In these preliminary experiments, all P. marinus challenged oysters were determined to be infected by P. marinus, while the diagnosis on non-P. marinus challenged controls was negative. It was believed that the challenged dose of  $10^6$  trophozoites per oyster was too high, thus overwhelming any toxic effect. To test this hypothesis, in the third experiment oysters were challenged with either  $10^6$  or  $10^3$  trophozoites and the maximum pollutant exposure concentration was increased to 25%. Results of the third experiment support the hypothesis drawn from the previous experiments. An apparent dose response relationship for P. marinus incidence was observed in oysters challenged with  $10^3$  trophozoites; both prevalence (% of infection) and weighed incidence (sum of infection level/number of oysters) in oysters increased as a function of toxic exposure concentrations. Six to 10% of the non-P. marinus challenged oysters were detected to be infected by P. marinus. But, P. marinus infection in non-P. marinus challenged oysters was not correlated with toxic exposure concentrations. Thus it suggests that infection found in non-P. marinus challenged oysters must be acquired in the field prior to experimentations. No toxic dose response was observed for the oysters challenged with  $10^6$  trophozoites, in either disease prevalence or intensity. This further strengthens the hypothesis that overdosing occurred when challenged with  $10^6$  Perkinsus trophozoites per oyster; thus offsetting any related toxic effects on disease susceptibility in the oysters.

2. Exposure to pollutants altered the cellular responses in oysters. In the second experiment, peak CL in oysters sampled 3 weeks after exposure to 20% toxic aqueous extract were lower than in oysters exposed to 0% toxic extracts. A similar phenomenon was observed in the third experiment in the group of oysters which were challenged with  $10^3$  trophozoites and exposed to 25% toxic extract for 2 weeks. However, no difference was observed in CL response between control and toxic exposed oysters sampled at the end of the experiment (5 weeks). It is interesting to note that in both toxic exposure and control groups, hemocytes from oysters challenged by P. marinus demonstrated higher CL than non-P. marinus challenged oysters. The observed higher CL in P. marinus challenged oysters is probably a result of parasitological and /or pathological response to P. marinus infection.

3. No difference was found in the measured humoral parameters, hemagglutination titers, lysozyme activities and protein concentrations between toxic exposed and control oysters.

4. No mortality occurred during in vivo toxic exposure experiments over the course of the experimental period.

5. Data analysis of the measurements of hemocyte chemotactic activities from the in vivo toxic experiments have not been completed, therefore results from this aspect can not be presented at this time.

6. Preliminary analysis of oysters subjected to 0, 10 and 20% dilutions of the stock have been conducted. Significant bioaccumulation of aromatic compounds have been observed. Concentrations in soft tissues of oysters exposed to the toxic extracts were ca 100 mg/kg (ppm). Chromatographic profiles resembled sediment rather than exposure water.

Results to date suggest that exposure of oysters to 25% or higher concentrations of toxic extracts may be required to weaken the oyster's defense system and increase their susceptibility to P. marinus. Currently, we are performing an experiment in which oysters are being exposed to 30% toxic extracts. To test disease susceptibility following stress, oysters will be exposed to toxicants for 5 weeks prior to P. marinus challenge.

It is not certain whether the stimulated CL and chemotaxis found in vivo and in vitro experiments are indications of additive reactivity of hemocytes to toxic chemicals or processes of acclimation/regulation of toxic chemicals in oysters. The mechanisms responsible for the CL and chemotactic stimulation in hemocytes after in vitro and in vivo exposure to toxic extracts are not known and need to be clarified.

## USE OF FISH AND OYSTER CELL CULTURES TO STUDY TOXIC EFFECTS OF CHEMICAL POLLUTANTS OF THE CHESAPEAKE BAY.

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### RESEARCH OBJECTIVES

To standardize cell culture systems from fish and oysters to assess the biohazardous effects of Elizabeth River sediments in areas that are dominated by polynuclear aromatic hydrocarbon contamination.

### RATIONALE AND APPROACH

The need for assessment of the toxicity of xenobiotics released into the aquatic environment of the Chesapeake Bay has stimulated the search for bioassays from which reliable information can be obtained in a short time. Teleosts, invertebrates, and unicellular microorganisms have been used as target organisms in the development of such assay. Whole animal toxicity tests are limited by the number of animals that can be economically and conveniently used, by problems in obtaining organisms of known background and parentage, and by the difficulties of extrapolating data from one species to another. Recently, attention has been paid to the great potentials and advantages of cultured fish cells in assessing toxic effects of xenobiotics. Since cultured cells do not possess the multiple defense mechanisms that are present in intact organisms, they are frequently more sensitive to the cyto- and genotoxic effects of a chemical than the whole organism.

As hepatocytes are the primary target of toxic chemical aggression, our laboratory has successfully developed protocols to culture hepatocytes of Chesapeake Bay fishes. Some of these cultures have developed to immortal cell lines. In the course of this study, cultured hepatocytes have been exposed to PAH-contaminated sediments and to selected PAH compounds.

Cells of the American oyster (*Crassostrea virginica*) were also assessed in the cytotoxicity assay. Despite the absence of mitosis in cultured oyster cells, several endpoints of cytotoxicity could be applied after some modifications.

### PROGRESS TO DATE

#### A. Comparison between the sensitivity of the different cell cultures:

The sensitivity of a variety of primary cultures as well as cell lines were compared in order to select the most sensitive cell(s) for further monitoring. This included: 1. Established fish cell lines; FHM, BF-2, BB (Brown bullhead), and carp

leucocyte cell line (CLC), Japanese medaka, SLW (spot hepatocytes), AML (Atlantic Menhaden hepatocyte), and MML (Mummichog hepatocellular carcinoma), 2. Primary, secondary, and line cultures of mummichog and spot liver, 3. Oyster primary culture of oyster hemocytes, adductor muscle, mantle epithelium, digestive gland, and heart.

Our results indicate that primary hepatocytes of spot (Leiostomus xanthurus) are very sensitive to PAH compounds and contaminated sediment. SLW and AML cell lines showed moderate sensitivity to PAH. Our further experiments therefore focussed on these three cell systems. Oyster hemocyte and digestive gland were very sensitive to the toxic effects of PAHs.

#### B. Comparison between the endpoints for cytotoxicity:

We compared between several endpoints that are routinely used as indicators of cytotoxicity. Such endpoints have included trypan blue exclusion (only cells with damaged membranes allow the entry of the dye), dye retention (only cells with undamaged lysosomal membranes can retain the supravital neutral red dye), leakage of soluble enzymes (e.g., lactate dehydrogenase) or release of radioactive chemicals (e.g., <sup>51</sup>Chromium), uptake of radioactive precursors (e.g., <sup>3</sup>H-uridine), cell attachment to or detachment from a substratum, and cell replication.

Our results have clearly showed that cell attachment to the substratum and staining by neutral red are superior to all other tested endpoints for cytotoxicity. In addition, readings by both techniques could be automated using a Photometer/ELIZA-plate reader. All conditions for primary hepatocytes, SLW, and AML were adjusted in order to maximize the attachment to the plate.

In case of oyster cells, the neutral red and the uptake of <sup>3</sup>H-uridine were superior to all other cytotoxicity endpoints.

#### C. Comparison between the endpoints for genotoxicity:

We compared between several techniques that are known as indicators of genotoxicity. This included sister chromatid, forward mutations, visible chromosomal damage, and anaphase aberrations.

The results indicated that anaphase aberration in the primary hepatocytes is the test of choice to assess PAH-induced genotoxic effects. This was followed by chromosomal macrolesions.

#### D. Assessment of Elizabeth River Sediment using cyto- and genotoxicity assays:

All Elizabeth River sediment were toxic to cultured fish and oyster cells. The degree of cytotoxicity differed, however, from one sediment to the other. The highest cytotoxicity was obtained with the Station 217-sediment ( $10^5$  TCCD<sub>50</sub>/ml of the

organic sediment extract). At high dilutions, two of the sediments (217 and Atlantic Wood) showed a significant increase in the cell proliferation. One other sediment (Craney Island) inhibited cell division at high dilutions and was cytotoxic at high concentrations. In general, a sediment extract was considered cytotoxic if it contained more than  $10^2$  TCCD<sub>50</sub>/ml of the sediment extract. By combining cytotoxic and genotoxic tests, we were able to demonstrate four different responses following exposure to contaminated sediment extracts: a) non-cytotoxic non-genotoxic (this was only found in the control York River site), b) cytotoxic genotoxic such 217 and Atlantic Wood sediments, c) genotoxic non-cytotoxic, d) cytotoxic non-genotoxic.

E. Determination of the relationship between TCCD<sub>50</sub> and PAH concentration:

A linear correlation was found between the total PAH and cytotoxicity ( $r^2=0.87$ ). This correlation was more evident with the concentrations of the low molecular weight PAH ( $r^2=0.96$ ). Similar correlation was also observed by using individual PAH compounds such as benzo(a)pyrene [B(a)].

F. Determination of the relationship between genotoxicity and PAH concentration:

No correlation could be found between genotoxicity and total PAH in the sediment. A barely significant correlation was found between the concentration of B(a)P and the visible chromosomal macrolesions ( $r^2=0.71$ ). In genotoxic sediment, a correlation existed between the sediment dilution and the number of cells with damaged chromosomes.

**ONGOING PROJECT**

Current experiments aimed at determining the relationship between the Elizabeth River sediment median tissue culture cytotoxic dose (TCCD<sub>50</sub>) and median lethal dose (LC<sub>50</sub>) are being carried out.

The overall conclusion of the results obtained to date suggests that assessing toxic effects of sediments using isolated cell culture techniques is accurate and cost effective in risk assessment of pollution with PAH.

## EFFECTS OF TRACE METALS AND ORGANIC POLLUTANTS ON STRESS-INDUCED PROTEINS AND METALLOTHIONEIN IN OYSTER LARVAE AND SPAT: A MOLECULAR APPROACH

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When most organisms are challenged with a thermal stress, they respond by producing specific proteins to metabolically compensate for high temperature exposure. These proteins have been called Heat-Shock Proteins; however, it is now recognized that there are many other proteins that are synthesized as a direct response to different physiological stresses. These kinds of proteins are best described as Stress-Responsive Proteins and they can be induced by a variety of parameters including trace metal exposure, pesticide exposure, and viral infections. In anthropogenically impacted areas, there is an apparent correlation between environmental stresses and disease susceptibility such that these environmental stresses may be an important component of disease etiology in marine organisms. Thus, the production of stress proteins in field populations can provide biomarkers of physiological compromise and may help to identify impacted populations that are at risk of infection before the irreversible onset of disease.

In the past, it has been difficult to quantify levels of physiological stress. This project will take a new approach and focus on the induction of stress proteins by measuring the transcription rates of their encoding genes. Gene transcription rates represent a metabolic commitment to produce stress proteins and can provide a sensitive measure of stress in response to experimental exposures. The eastern oyster, Crassostrea virginica, will be used as the model system because of its economic importance and recent population declines in Chesapeake Bay. Because the oyster ingests particulate matter originating from both the water column and the bottom sediments, it may serve as an ideal animal for assessing the general exposure of other organisms in its environment because it integrates both of these exposure compartments.

Preliminary work in the lab has demonstrated that oyster larvae synthesize several major proteins in response to thermal stress; the most dominant one has a molecular size of about 70 KD. Other animals have been shown to produce a 70 KD protein in response to thermal stress, and the cDNA sequences for these different proteins were aligned to design PCR oligonucleotide primers. These primers were used to successfully amplify a cDNA fragment from oysters and that fragment was then used in library screening to isolate a full length cDNA for the oyster HSP70. Thus, oysters have the capacity to produce stress proteins and can synthesize several in response to temperature, one of which is a homolog of the known HSP70s.

In order to identify other proteins that are produced in response to stress, we will use a "subtraction library" technique. Here, mRNA from a control group of larvae is labelled with Biotin while mRNA from a stressed group is reverse-transcribed to produce the complementary strand. The two pools of nucleic acids are mixed and all the mRNAs from the control group, which represent the expression of normal cell function genes, will bind to their complementary strands from the stressed group. The nucleic acid mixture is then passed through an Avidin column where the "Biotin -><- Control RNA -><- Complementary Stressed DNA" complexes are retained by the avidin/biotin interaction, allowing the cDNAs that were transcribed following the stress exposure to pass through. This produces a cDNA sample for the stressed group that is enriched in gene transcripts unique to the oyster's physiological response to the specific experimental stress. These unique transcripts will then be packaged into a cDNA library and then characterized.

Overall, the objective of this project is to isolate and characterize the cDNAs of Stress-Responsive (SR) proteins in oyster larvae and spat. In the long run, this information can then be used to: 1) **Identify Stressors** by characterizing changes in the transcription of these SR genes to a wide spectrum of known stressors (i.e., pesticides, infection, metals, temperature, oxygen); 2) **Identify Degree of Field Stress** in a field monitoring program to characterize the seasonal pattern of SR gene expression in natural oyster populations from different regions of Chesapeake Bay; and 3) **Identify Source of Field Stress** in a principal component analysis to correlate the patterns of SR gene expression under experimental conditions [in #1] to the patterns of SR gene expression in field populations from Chesapeake Bay [in #2].



**ECOSYSTEM PROCESSES RELATED TO TRANSPORT, PARTITIONING AND  
EFFECTS OF ORGANIC CONTAMINANTS IN CHESAPEAKE BAY: A SIMULATION  
MODELING STUDY**

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University of Maryland System CEES

There is mounting evidence that the fate and transport of hydrophobic organic contaminants (HOCs) in aquatic environments are significantly influenced by plankton and benthic trophic and metabolic processes via processes such as sorption, biomagnification and deposition to sediments. Many of these ecological processes may, in turn, be altered by toxic stresses associated with such contaminants. Indeed, there is a complex ensemble of biological, chemical and physical processes that control the dynamic behavior of HOCs in estuaries such as Chesapeake Bay. Simulation models, which incorporate key ecological interactions and appropriate chemical kinetics, equilibrium reactions and toxicological relations for such contaminants, represent a useful tool for sorting out this inherent complexity. With sufficient information on HOC inputs and chemistry and on ecological relations, such models can provide information needed for effective scientific integration and for risk assessment to establish sound management policies.

The objective of this study is to develop a simulation model to test the hypothesis that planktonic and benthic trophic dynamics and benthic-pelagic coupling control the speciation, transport, bioavailability, bioaccumulation and toxic effects for synthetic organic contaminants in Chesapeake Bay. We propose to develop a numerical simulation model including the key ecological processes and kinetic parameters for representative HOCs in the estuary. The goals of this modeling study include the following: to integrate data collected by various investigators in the Bay region; to test hypotheses about interactions between trophic dynamics and contaminant fate/effects; and to provide information needed for ecological risk assessment. The portion of this model dealing with ecosystem processes will be adapted from existing simulation systems developed for Chesapeake Bay. HOC kinetic relations and toxicological interactions will be added to this modeling structure with the assistance of collaborators experienced in these empirical fields of research. To the extent possible, data collected within the CBEEC Toxics Program will be used in calibrating and validating our models. The model conceptualization, calibration and sensitivity phases of this study will help to identify significant gaps in fundamental scientific understanding of these processes and in the existing

data bases. Initial models will be developed using a simulation software package (Stella) on accelerated microcomputers (Macintosh FX) available at our research facilities. Integrated simulations in future years will employ mainframe computers. Initial models will be calibrated for the mesohaline Bay, and simulation experiments will be conducted to represent other estuarine regions experiencing greater contamination.

This research will provide a framework for combining existing, current, and future ecosystem process data (e.g., planktonic trophic dynamics, sediment geochemistry, benthic-pelagic coupling) with data on HOC dynamics (e.g., chemical kinetics, surface chemistry, equilibrium relations, toxicological effects) generated from CBEEC. While current information is insufficient for a rigorous risk assessment, this simulation model will provide a mechanism for integrating scientific results into such an analysis with improved data in the future.

## SYNOPSIS OF PANEL PRESENTATIONS AND DISCUSSION

Six members of state and federal agencies that have responsibilities in research and management of toxic substances in Chesapeake Bay were invited to participate in a panel session on the second day of the workshop. The purpose of convening the panel session was to increase communication between TRP researchers and representatives of management agencies. The panel members were invited to attend the presentations of investigators on the first day of the workshop and asked to address the following questions during the panel session:

- 1) What is your agency's role in the research or management of toxic substances, particularly in the Chesapeake Bay?
- 2) Is the Toxic Research Program supportive of your agency's mission and in what ways does your agency envision using results from the program?
- 3) What kind of research would your agency most like to see conducted, and what are your recommendations for redirecting the Toxics Research Program to better fit the responsibilities of your agency?

The panel session was moderated by Mr. Richard Batiuk of the Environmental Protection Agency's Chesapeake Bay Liaison Office. (The panel members are listed in Appendix 5.) Presentations by panel members and the discussion that followed among panel members and other attendees were transcribed from tape recordings and are summarized below. The summary has been organized around three main topics that dominated the discussions.

### **Are toxic contaminants a significant problem in Chesapeake Bay?**

■ With the exception of a few "hot spots" (notably the Elizabeth River and Baltimore Harbor), concentrations of toxic substances within the Chesapeake Bay are generally within water quality standards. Considering the other anthropogenic influences that are sources of mortality for Chesapeake Bay species (e.g., fishing, nutrient input, and habitat loss), one panel member did not consider toxics, which are actively regulated, a priority issue for allocation of limited funds within his state agency.

■ It was noted that a particular substance is not considered a "problem" by management agencies until levels of that substance exceed a water quality standard set for that compound. This may not be a sound approach in that 1) water quality criteria may be established without firm scientific backing, and 2) the effects of low levels of toxics substances on ecosystem function are poorly known. For example, arsenic, which is found at elevated levels throughout much of the Bay, causes a shift in phytoplankton community structure, but it is not known how (or if) this effect is transmitted through the food webs to affect

"more visible" species in the Bay. It is difficult, if not impossible, to quantify the significance of the toxics problem in the Bay without understanding these linkages.

■ Much of the resources of the state water quality agencies are devoted to implementation of the Clean Water Act and, to a lesser extent, identification of unregulated toxics that may pose a health problem. Water quality criteria have generally been based on single substance/single species bioassays, and while these criteria give little insight into "real world" effects, they have been an important tool for reducing toxic discharges into the Bay (i.e., effective in reducing the "problem").

■ The responsibility of identifying toxic problems in the Chesapeake Bay appears split among state and federal agencies and the research community. Although the state water quality agencies have ultimate regulatory authority, much of the water quality criteria are developed by EPA and "handed down" to the states pursuant to the Clean Water Act. Toxic monitoring programs are maintained by state and federal agencies (NOAA's Status and Trends Program and EPA's EMAP Program). The Virginia and Maryland water quality agencies have some research programs, mostly in applied aspects of water quality management. It was agreed that the academic research community should supply information to the regulatory agencies, but the exact nature of that information was debated. The TBT issue was given as a good example of the research community identifying a toxic problem and providing information that regulatory agencies were able to use in promulgating codes restricting the use of TBT.

#### **What is the role of the Toxics Research Program?**

■ The three representatives from state regulatory agencies did not see how TRP results would meet their immediate needs of establishing and enforcing water quality criteria, though the findings could likely be used in writing regulations and in setting priorities. Meeting the demands of the Clean Water Act, mostly through the permitting process, on a day-to-day basis requires the vast majority of their resources. Several specific needs of these agencies were: development of water quality criteria for "new" substances, criteria validation, development of management protocols, and development of improved technology for detecting low level compounds and treating effluents.

■ Panel representatives from the federal agencies envisioned the results of the TRP tying in with existing monitoring programs, supporting development and reassessment of water quality criteria, and providing an understanding of the pathways by which toxics interact with the ecosystem. Other regions that face similar questions and problems as the Chesapeake Bay would also benefit from the TRP findings. It was noted that both state and federal agencies examine effects of toxics, but may not have the expertise or resources to investigate the processes that lead to the effects.

■ The value of the TRP is that it takes an integrative approach to the movement, incorporation, and impact of toxic substances at an ecosystem level. It was argued that support activities for regulatory agencies, such as monitoring or technology development, should be done "in house" or contracted to consulting firms. However, some research needs expressed by the agencies, such as defining the relationship between sediment and water column toxics or modeling the transport of toxics in estuarine mixing zones, should be addressed by the research community.

■ The findings of the TRP would have greater utility to the regulatory agencies if the research were more focused on particular species or particular compounds that were known to be a problem.

■ The role of the TRP as a supplier of information to the agencies is not wholly functioning because it is not clear to the researchers what the agencies need, and the results that are produced are not effectively communicated to the agencies. This has proved frustrating for both groups.

■ It was noted that the research/regulatory community as a whole has a societal responsibility to act as a safety net for the species of the Bay: we must define what the toxics problem is in the Chesapeake Bay and take the appropriate steps to remedy the problem. However, in application, there is a process by which the costs of regulating a particular substance is weighed against the potential benefit of regulation.

### **Recommendations**

Panel members were asked to comment on the type of research that would be most useful to their agencies and to make recommendations concerning the content and direction of the TRP. Other recommendations expressed during the discussion are also summarized here.

■ While the TRP has adopted a sound approach in looking at interactions of toxics and ecosystem processes, the TRP should be more focused. Most importantly, there needs to be greater structure to the selection of substances, species, locations and processes that are studied. A more coherent package of research projects would facilitate integration of results among projects. Several "tools" were suggested for focusing the research direction:

- 1) There should be an established method of prioritizing among the many substances and species available for study. Prioritization could be based on the stated needs of the water quality agencies or the relative degree of substance/species problems. Also questions of transport and exposure could be generated by the effects component of the program.

- 2) The modeling effort funded under the TRP should provide a framework for tying together the projects within the program. Sensitivity analyses will facilitate identification of strengths and weaknesses in our understanding and setting program goals. The effects component of the program should not only be the output from the model, but should be used to direct the research and adjust the model framework. Other models, such as structural models, should also be utilized.
- 3) Risk assessment is an ultimate use of the TRP findings and the process of developing risk assessment protocol should begin. Choose one or two species, go through the process, and discover if we have the information necessary to evaluate the risks to particular species from toxic contaminants in the Bay.
- 4) The critical issues approach could also be applied to focus TRP research. Choose a particular species, substance, or process and put all the pieces together to find out what our level of understanding is.

■ There was an evident need for greater communication among individuals and groups that have research and/or management responsibilities for toxics in Chesapeake Bay. It was felt that increased communication would be important for addressing the other points of concern.

- 1) There should be greater aggregation of individual researchers. Increased interaction among researchers will help focus the program through collaborative investigations and accelerate the flow of information among the research community.
- 2) A strong need was expressed for greater dialogue between the TRP and the state water quality agencies. Currently both groups feel a level of frustration because the research community believes it is producing valuable information, yet the state agencies expressed doubts that the information was useful to them. If a goal of the TRP is to provide information to the state agencies, then the needs of these agencies should be factored in to the goals and directions of the program. In addition, there is a need for more effective communication of TRP findings to the management agencies and the Chesapeake Bay Program (CBP). It was agreed that a liaison group, possibly embedded within the structure of the CBP Toxics Subcommittee, could be an important avenue for this dialogue.
- 3) Two toxics monitoring programs, NOAA's Status and Trends Program and EPA's EMAP Program, should be included in the dialogue. These, as well as other monitoring programs are in position to feed information, such as changes in levels of substances over time, to the research and

management groups. Such information could be important for identifying concerns and setting research directions.

■ Findings from the TRP should be tied into the 2-D and 3-D hydrological models that have been developed for Chesapeake Bay and its tributaries. This is a real challenge, but one that should not be ignored. Tying these together could be extremely important in risk assessment.

■ From the management agencies' point of view, research on substances that are already banned from use is of little utility to their mission. For example, chlordane is present in the environment and is affecting the health of Bay species, but chlordane is already banned from use. There is no further action the regulatory agency can take regardless of what research is done. Therefore, it was suggested that research be focused on substances that are not already banned. It was argued, however, that understanding the pathways by which such substances move through the system and their effects on particular species could be of great value in other management arenas, such as fisheries.

■ There is, in general, a need for more research on synergistic effects of multiple chemicals that are presently in the environment. The use of single substance criteria has been effective in reducing the input of toxics to the Bay, but interactive effects of chemicals at low levels could have important, but presently unknown, impacts on the health of Bay species.

## OVERVIEW OF TOXIC STUDIES IN CHESAPEAKE BAY WATERSHED

Rich Batiuk  
EPA, Chesapeake Bay Liaison Office

The Basinwide Toxics Reduction Strategy, a commitment under the 1987 Chesapeake Bay Agreement, was signed by the Chesapeake Executive Council in December 1988. The Strategy recognized the need to build upon existing toxics control regulatory programs and legislative mandates. The 80 strategy commitments focused on assessment of the Bay's toxics problems but also included specific implementation and prevention actions.

The Strategy set forth a long term goal of working "towards a toxics free Bay by eliminating the discharge of toxic substances from all controllable sources." An interim strategy goal was stated as "by the year 2000, the input of toxic substances from all controllable sources to the Chesapeake Bay will be reduced to levels that result in no toxic or bioaccumulative impact on the living resources that inhabit the Bay or on human health."

As part of the process for implementing the Strategy's 80 commitments, the Chesapeake Bay Program's Toxics Subcommittee identified seven areas of emphasis:

- Build on existing regulatory programs;
- Define the nature and extent of toxics problems in the Bay;
- Assess non-traditional sources of toxics and toxicity;
- Develop knowledge base necessary for risk-based decisions;
- Target toxics of concern;
- Develop institutions for pollution prevention actions;
- Develop multi-agency resources base for assessment/implementation.

Overall, the Toxics Subcommittee has:

- \* focused on assessment and definition of the problem;
- \* placed parallel emphasis on source prevention; and
- \* recognized that management/regulatory agencies are the ultimate users of the resultant information and tools.

A broad overview of the scope and current activities underway within the Chesapeake Bay toxics program is provided below in the form of informational bullets under a series of topical headings.



### Chesapeake Bay Toxics of Concern List

- \* Initial list developed by joint Toxics and Living Resources Subcommittees' Criteria and Standards Workgroup.
  - Identified 14 toxics of concern and 10 secondary toxics for further information gathering.
  - Toxics of Concern List Report published in May 1991.

### Chesapeake Bay Toxics Data Base

- \* Data base design developed by Chesapeake Bay Program Office/CSC staff working through joint Toxics and Living Resources Subcommittees' Criteria and Standards Workgroup.
- \* Built around a comprehensive list of Bay basin toxics, list of Bay species, ambient data and toxicity data file for Bay basin species.
- \* Ongoing data base focus on ambient data acquisition and documentation (historical, ongoing TSC funded work).

### Basinwide Toxics Loading and Release Inventory

- \* Being developed through Toxics Subcommittee's Toxics Loading Inventory Workgroup.
- \* Focuses on point (industrial, municipal) and nonpoint (urban, agricultural, shipping, atmospheric, fall-line, groundwater) loadings and releases.
- \* Objectives are to establish comprehensive baseline for point/nonpoint loadings of toxic substances to the Bay system and provide a mechanism to measure progress by source category.
- \* Draft report reviewed by the Toxics Subcommittee; final report by summer 1992; loading database accessible now.

### Chesapeake Bay Atmospheric Deposition Network

- \* Three station network established in 1990 operated by University of Maryland, University of Delaware, Virginia Institute of Marine Science and Old Dominion University.
- \* Designed to provide data required to estimate annual loadings of organic contaminants and trace elements to the surface of Chesapeake Bay.
- \* Weekly-integrated precipitation samples analyzed for trace elements; every two week precipitation samples

analyzed for organics; week-long aerosol particulate samples analyzed for trace elements and major ions.

#### Chesapeake Bay Fall line Toxics Monitoring Program

- \* Expanded fall-line program to include monitoring at Susquehanna, Potomac and James fall-lines in 1991.
- \* Monthly base flow and hi-flow event sampling conducted by U.S. Geological Survey, joined by Occoquan Watershed Monitoring Laboratory and George Mason University in 1992.
- \* Target compounds include the Chesapeake Bay Toxics of Concern, metals, selected organics and pesticides.
- \* Joint initiatives with USGS research program to further refine field sampling techniques, modeled load calculation techniques.

#### Chesapeake Bay Ambient Toxicity Assessment Program

- \* Assessment program involves investigators from University of Maryland and Old Dominion University focused on water column toxicity, sediment toxicity and biomarkers.
- \* Pilot phase of the program (1990-91) focused on sites in the Patapsco, Elizabeth, Potomac and Wye rivers to attempt to cover the range of habitats and habitat conditions.
- \* Toxicity protocols include standardized test protocols/species as well as species (and protocols) which are in field validation stages of SOP development.

#### Chesapeake Bay Basinwide Pesticide Use Survey

- \* Pesticide use surveys were conducted in Pennsylvania, Maryland and Virginia reporting a consistent set of information at the county level.
- \* Follow-up efforts directed at specific crops and within the District of Columbia are planned or being implemented.
- \* Data accessible through the Chesapeake Bay Program's toxics data base.

#### Chesapeake Bay Watershed Pesticide Monitoring Programs

- \* Pesticide watershed monitoring ongoing or planned for Bay states.

- Pesticides intensively monitored over the last several years within Virginia's Owl Creek/Nomini Creek demonstration watershed.
- Pennsylvania planning to initiate pesticide monitoring program within the Conestoga watershed within the Susquehanna River basin.
- Maryland planning pesticide monitoring program for the Monocacy watershed within the Potomac River basin.

- \* Pesticides included on the parameter list for the baywide fall-line toxics monitoring program.

#### Chesapeake Bay Basin Urban Toxics Load Estimations

- \* Estimated loads developed by Metropolitan Washington Council of Governments.
- \* Methodology estimates average pollutant loads on the basis of land use reported by major subbasins for 35 toxic substances.

#### Toxics Reduction Strategy System for Measuring Progress

- \* Focuses on defining milestones towards achievement of the Strategy's interim goal: "By the year 2000, the input of toxics substances from all controllable sources will be..."
- \* Sets measures against which results from strategy implementation are matched and progress is gauged.
- \* An example...

Milestone 5: Reduce ambient levels of toxic substances within the waters and sediments of Chesapeake Bay to concentrations where there are no toxic impacts on Bay living resources.

- \* Key is defining "toxic impact" from a risk-based perspective.

#### Chesapeake Bay Toxics Reduction Strategy Reevaluation

- \* Commitment in 1988 Strategy to reevaluate by 1992.
- \* Produce a comprehensive progress report on strategy implementation.
- Progress towards defining the nature, extent and magnitude of Bay toxics problems.

- Progress towards the Strategy's interim and long term goals.
  - Progress towards the Strategy commitments.
- \* Evaluate and recommend refinements to the Strategy; areas to receive increased/decreased emphasis.

**CHESAPEAKE BAY TOXICS RESEARCH PROGRAM - FUNDED PROJECTS****Flux and Speciation**

Air/water partitioning and mass transfer properties of toxic organic chemicals. R. M. Dickhut. 1991-1992.

Determination of the volatile/absorptive exchange of hydrophobic organic contaminants across the air/water interface of lower Chesapeake Bay. R. M. Dickhut. 1993-1994\*\*.

Particle-reactive radionuclides as analogues of particle-reactive pollutants in Chesapeake Bay. G. T. F. Wong. 1991-1992.

Particle-reactive pollutants in southern Chesapeake Bay: accumulation, resuspension and flux into the bottom. D. J. P. Swift. 1991-1992.

Temporal and spatial variability of the chemical speciation of dissolved copper and cadmium in Chesapeake Bay. J. R. Donat. 1992-1993.

**Water-column Bioprocessing**

The importance of dinoflagellate blooms in the transport of carbon and toxic trace elements in Chesapeake Bay. J. G. Sanders and K. G. Sellner. 1992-1993.

Role of plankton in controlling the partitioning and transport of hydrophobic organic contaminants in Chesapeake Bay. J. E. Baker, H. R. Harvey and R. Dawson. 1991-1992.

Role of plankton in controlling the partitioning and transport of hydrophobic organic contaminants in Chesapeake Bay: zooplankton grazing and excretion. G. McManus and M. R. Roman. 1991-1992.

Resuspension and transport of sediment associated toxics in the northern Chesapeake Bay. L. P. Sanford, J. P. Halka and J. M. Hill. 1991-1992.

**Benthic Processes**

Dynamics of sediment resuspension: Bay-stem plains of the lower Chesapeake Bay. L. D. Wright, J. D. Boon, J. P.-Y. Maa, and L. C. Schaffner. 1991-1992.

The role of benthic infauna and fluctuating oxygen concentrations in the flux of toxic trace elements from Chesapeake Bay sediments. G. F. Riedel, J. G. Sanders, R. W. Osman, and C. C. Gilmour. 1991-1992.

Direct measurements and biogeochemical controls of sediment-water flux of trace metals from estuarine sediments. J. D. Cornwell, D. J. Burdige and W. R. Boynton. 1992-1993.

Microbial degradation of chlorinated hydrocarbons under alternating redox conditions in Chesapeake Bay. D. G. Capone, J. W. Gooch and J. E. Baker. 1992- 1993.

Role of Benthic communities in sediment-associated toxic organic chemical fate and transport in lower Chesapeake Bay. L. C. Schaffner and R. M. Dickhut. 1992-1993.

Uptake of dissolved and particle-associated toxicants by the eastern oyster. D. P. Weston, D. L. Penry, R. I. E. Newell, and J. E. Baker. 1992-1993.

### **Effects**

Relationship of pollutants to the onset of disease in the eastern oyster, Crassostrea virginica. F.-L. Chu and R. Hale. 1991-1992.

Use of fish and oyster cell cultures to study toxic effects of chemical pollutants of the Chesapeake Bay. M. Faisal. 1991-1992.

Effects of trace metals and organic pollutants on stress-induced proteins and metallothionein in oyster larvae and spat: a molecular approach. T. P. Chen and G. Roesijadi. 1992-1993.

Contaminant flux from sediments: impact on Chesapeake Bay food webs. G. F. Reidel, J. G. Sanders and C. C. Gilmour. 1993-1994\*\*.

Interaction of copper and cadmium with microbial benthos biofilm and effects on oyster larvae set. R. Weiner and M. Walch. 1993-1994\*\*.

### **Modeling**

Ecosystem processes related to transport, partitioning and effects of organic contaminants in Chesapeake Bay: A simulation modeling study. W. M. Kemp, J. Gooch and J. E. Baker. 1992-1994.

\* second year funding is pending successful completion of first year work plan

\*\* projects scheduled to start in 1993

**CHESAPEAKE BAY ENVIRONMENTAL EFFECTS STUDIES  
TOXIC RESEARCH PROGRAM**

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## AGENDA

## CHESAPEAKE BAY ENVIRONMENTAL EFFECTS STUDIES

## TOXICS RESEARCH PROGRAM WORKSHOP

19 - 20 February 1992

**Wednesday 19 February**  
**Project Results and Direction**

- 0800 - 0830 Continental Breakfast at VIMS
- 0830 - 0845 Welcome and Introduction  
 \* **W. L. Rickards**, Virginia Sea Grant College Program  
 \* **D. E. Taylor**, Virginia Institute of Marine Science
- 0845 - 0900 Opening Remarks  
 \* **J. G. Sanders**
- 0900 - 1010 PI Presentations: Flux and Speciation  
 \* **R. M. Dickhut**  
 Air/water partitioning and mass transfer properties of toxic organic chemicals. (O)  
 \* **J. R. Donat**  
 Determination of the chemical speciation of dissolved copper and cadmium in Chesapeake Bay. (N)  
 \* **G. T. F. Wong**  
 Particle-reactive radionuclides as analogues of particle-reactive pollutants in the Chesapeake Bay. (O)  
 \* **D. J. P. Swift**  
 Particle-reactive pollutants in southern Chesapeake Bay: accumulation, resuspension and flux into the bottom. (O)
- 1010 - 1030 Coffee Break
- 1030 - 1140 PI Presentations: Water Column Bio-processing  
 \* **J. G. Sanders** and **K. G. Sellner**  
 The importance of dinoflagellate blooms in the transport of carbon and toxic trace elements in Chesapeake Bay. (N)  
 \* **J. E. Baker**, **H. R. Harvey** and **R. Dawson**  
 Role of plankton in controlling the partitioning and transport of hydrophobic organic contaminants in Chesapeake Bay. (O)  
 \* **M. R. Roman** and **G. B. McManus**  
 Role of plankton in controlling the partitioning and transport of hydrophobic organic contaminants in Chesapeake Bay: zooplankton grazing and excretion. (N)  
 \* **L. P. Sanford**, **J. P. Halka** and **J. M. Hill**  
 Resuspension and transport of sediment associated toxics in the northern Chesapeake Bay. (O)

- 1140 - 1230 Discussion  
 \* **J. G. Sanders** (Moderator)
- 1230 - 1330 Lunch at VIMS
- 1330 - 1450 PI Presentations: Benthic Processes
- \* **L. D. Wright, J. D. Boon, J. P. -Y. Maa, and L. C. Schaffner**  
 Dynamics of sediment resuspension: Bay-stem plains of the lower Chesapeake Bay. (O)
- \* **G. F. Riedel, J. G. Sanders, R. W. Osman, and C. C. Gilmour**  
 The role of benthic infauna and fluctuating oxygen concentrations in the flux of toxic trace elements from Chesapeake Bay sediments. (O)
- \* **J. C. Cornwell, D. J. Burdige, and W. R. Boynton**  
 Direct measurements and biogeochemical controls of sediment-water flux of trace metals from estuarine sediments. (N)
- \* **D. G. Capone, J. W. Gooch, and J. E. Baker**  
 Microbial degradation of chlorinated hydrocarbons under alternating redox conditions in Chesapeake Bay. (N)
- \* **L. C. Schaffner and R. M. Dickhut**  
 Role of benthic communities in sediment-associated toxic organic chemical fate and transport in lower Chesapeake Bay. (N)
- \* **D. P. Weston, D. L. Penry, R. I. E. Newell, and J. E. Baker**  
 Uptake of dissolved and particle-associated toxicants by the eastern oyster. (N)
- 1450 - 1510 Coffee Break
- 1510 - 1600 PI Presentations: Effects
- \* **F.-L. Chu and R. Hale**  
 Relationship of pollutants to the onset of disease in the eastern oyster, Crassostrea virginica. (O)
- \* **M. Faisal**  
 Use of fish and oyster cell cultures to study toxic effects of chemical pollutants of the Chesapeake Bay. (O)
- \* **T. P. Chen and G. Roesijadi** (presented by A. Marsh)  
 Effects of trace metals and organic pollutants on stress-induced proteins and metallothionein in oyster larvae and spat: a molecular approach. (N)
- 1600 - 1700 Discussion  
 \* **J. G. Sanders**, Moderator
- 1700 - 1715 Concluding Remarks  
 \* **J. G. Sanders**
- 1715 - 1900 Social at VIMS
- 1900 - Dinner on your own

**Thursday 20 February  
Program Integration and Management Needs**

- 0800 - 0830 Continental Breakfast at VIMS
- 0830 - 0840 Opening Remarks  
\* **R. Lippson**, NOAA-NMFS
- 0840 - 0910 Integration and Modeling  
\* **W. M. Kemp, J. W. Gooch, and J. E. Baker**  
Ecosystem processes related to transport, partitioning and effects of organic contaminants in Chesapeake Bay: a simulation modeling study. (N)
- 0910 - 0940 Overview of Toxic Studies in Bay Watershed  
\* **R. Batiuk**, EPA Chesapeake Bay Liaison Office
- 0940 - 1020 Panel Discussion: Management Needs & Research Direction  
\* **R. Batiuk**, EPA Chesapeake Bay Liaison Office  
\* **H. Coulombe**, U.S. Fish and Wildlife Service  
\* **P. Massicot**, Maryland Dept. of Natural Resources  
\* **A. Pollock**, Virginia Water Control Board  
\* **A. Robertson**, NOAA - NOS  
\* **P. Tinsley**, Maryland Dept. of the Environment  
\* **R. Menzer**, U. S. Environmental Protection Agency
- 1020 - 1040 Coffee Break
- 1040 - 1220 Panel Discussion: Management Needs & Research Direction (Continued)
- 1220 - 1230 Concluding Remarks and Adjourn  
\* **R. Batiuk**, EPA Chesapeake Bay Liaison Office
- 1230 - 1330 Lunch at VIMS and Depart

NOTE: (O) indicates ongoing research projects (initiated Sept. 1990)  
(N) indicates new projects (initiated Jan. 1992)

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Publication of this report is supported by grant NA90AA-D-SG803 from the National Oceanic and Atmospheric Administration to the Virginia and Maryland Sea Grant College Programs. The views expressed herein are those of the authors and do not necessarily reflect those of NOAA or any of its sub-agencies.

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