The Fate & Effects Of Pollutants

A Symposium

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Of Pollutants
A Symposium

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Acknowledgements

Introduction

To answer questions about the transport and behavior
of waterborne pollutants--especially in estuaries such
as the Chesapeake Bay--scientists from the University
of Maryland and elsewhere convened for a symposium on
"The Fate and Effects of Pollutants." The symposium,
held on April 26 and 27, 1985, was sponsored by the
University of Maryland's Sea Grant College and Marine-
Estuarine-Environmental Sciences Program. This
proceedings, a compilation of the invited papers and
of abstracts of contributed papers and posters, is a
record of that effort.

Pollution of the sort addressed here--chronic,
invisible pollution whose effects are felt slowly and
in concert with other causes--calls for both new
research methods and insights by experienced experts
in the field if we are to understand and control it.
Such pollution does not avail itself of easy analysis,
and causes and effects may remain difficult to
identify. The symposium presentations, and the papers
of this proceedings, thus represent a diversity of
widely varying approaches.

Because of the lack of simple answers, research
in this field must be open--as is much of science--to
progress and insight from unanticipated quarters. It
is this thought that motivated the Maryland Sea Grant
College and the Marine-Estuarine-Environmental
Sciences Program to call for this symposium--the
desire to gather together experts and to listen and
watch for novel and promising directions in pollution-
related research.

Out of such sharing of insight will come the best
understanding of environmental degradation--of its
scale and intransigence. And out of such
understanding will come better methods for tracing the

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causes of pollution and for detecting their effects--
methods needed to help guide our efforts to protect
and restore our invaluable water resources.

Invited Papers

Nutrient Enrichment Effects in Chesapeake Bay: The Nitrogen vs. Phosphorus Controversy

Christopher F. D'Elia, Chesapeake Biological Laboratory

Sanitary engineers often use the term "secondary BOD" to refer to the biochemical oxygen demand (BOD) of the organic matter resulting from the nutrient enrichment of receiving water by "point-source" sewage effluent. Phytoplankton, the primary producers that typically account for the major portion of the organic matter produced, are fertilized, and their growth is thus enhanced by these nutrients. Problems develop when this organic matter reaches a concentration so high that, upon its decay, it depletes oxygen from the water faster than it can be resupplied by other processes. The oxygen content of the water then reaches levels too low to support the survival of fish and other organisms we deem important to the "health" of natural waters and we say that "water quality" is poor.

Anoxia in the mainstem of the bay is believed by many scientists to be a manifestation of the enrichment process. Tributary estuaries to the Chesapeake Bay are presently over-enriched by nutrients derived not only from sewage effluents, but also by so called "non-point" sources, or runoff from the land. Thus, there is an oxygen demand in excess of the secondary BOD from sewage that results from organic matter produced by phytoplanktonic growth stimulated by runoff-derived nutrients.

Now at issue in the Chesapeake are: (1) what percentage of the nutrients are derived from point and non-point sources, (2) how much, when, and where do these nutrients stimulate the excess production of the organic matter that increases biochemical oxygen demand, (3) which nutrient limits phytoplanktonic primary productivity and when, and (4) how do we control nutrient inputs to the bay to reduce

secondary BOD to levels that maintain a "water quality" acceptable to the public?

Here I review some recent evidence about nutrient-limited phytoplanktonic growth in the Chesapeake, using the Patuxent River as a case study. Specifically, I consider what is becoming a major issue for this and other estuaries: does nitrogen, phosphorus or a combination of the two nutrient elements limit primary productivity by phytoplankton in the estuary? The extent to which this primary productivity and secondary and other BOD can be regulated by nutrient-control strategies is of obvious practical importance.

I also wish to consider the role that scientists play in the process that leads to the making of public policy. This topic is in many ways a greater concern than that about water quality in a given estuary. As we discuss the fate and effects of pollutants in this conference, it will be useful to keep in perspective how scientific findings may be interpreted and used in the course of determining public policy.

I shall take these two issues in sequence.

Nutrient Limitation in the Chesapeake Bay

A considerable controversy has arisen about whether the nutrient element phosphorus or nitrogen limits plant growth in the Chesapeake system. In general, state and federal agencies, citing in particular, evidence derived from mathematical water quality models, have identified phosphorus as the critical nutrient element to control to reduce phytoplankton blooms--primarily in the freshwater reaches of tributaries such as the Potomac and the Patuxent.

While officials acknowledge that phytoplankton blooms in the freshwater reaches of tributaries are only part of the "water quality" problem of the system, they have publicly expressed the belief that transport of organic material from these freshwater areas is responsible for the oxygen consumption in the estuary downstream. Most research scientists familiar with the problem agree that phosphorus

limitation is likely in freshwater sections, but
contend that more attention needs to be paid to the
role of nitrogen in downstream estuarine areas,
where most modelers agree that the models are con-
siderably less reliable.

Before I discuss evidence suggesting that the
nutrient element nitrogen and not phosphorus limits
algal growth throughout most of the "growing season"
in the estuarine portion of the Patuxent River, I
will present some simple calculations showing that
despite the occurrence of higher concentrations of
algal organic matter upstream than downstream, the
total mass of algal organic matter is much larger
downstream than that upstream. Thus, downstream
algal biomass is likely to have been derived from in
situ primary productivity rather than from imported
organic matter. Accordingly, control of algal
growth and organic matter production in the estuary
must require consideration of which nutrient is
likely to limit primary productivity downstream.

Figures 1 and 2 illustrate this point. Figure 1
shows surface and bottom chlorophyll a concen-
tration, an indicator of phytoplanktonic biomass,
versus river segment during a fairly low-flow period
in August, 1978. The segments are those used by the
State of Maryland in its "HydroQual" model of the
river and represent approximately 5-kilometer divi-
sions starting about 100 km upstream (segment 1) and
extending downstream to Drum Point at the river
mouth (segment 19).

Clearly, the major chlorophyll a concentration
peak occurred between segments 6 and 11 (approxi-
mately 50-77 km upstream of the river mouth), in the
freshwater-low salinity (<5 o/oo) region of the
river. The mesohaline, estuarine portion of the
river—i.e. segments 13-15 (26-39 km upstream),
which ranged from 5 to 12 o/oo salinity during
August, 1978—showed considerably lower chlorophyll
a concentrations. This zone of the river is some-
times referred to as the "salinity-transition zone"
because of the sharp salinity gradient with longi-
tudinal distance. Because of historical changes in
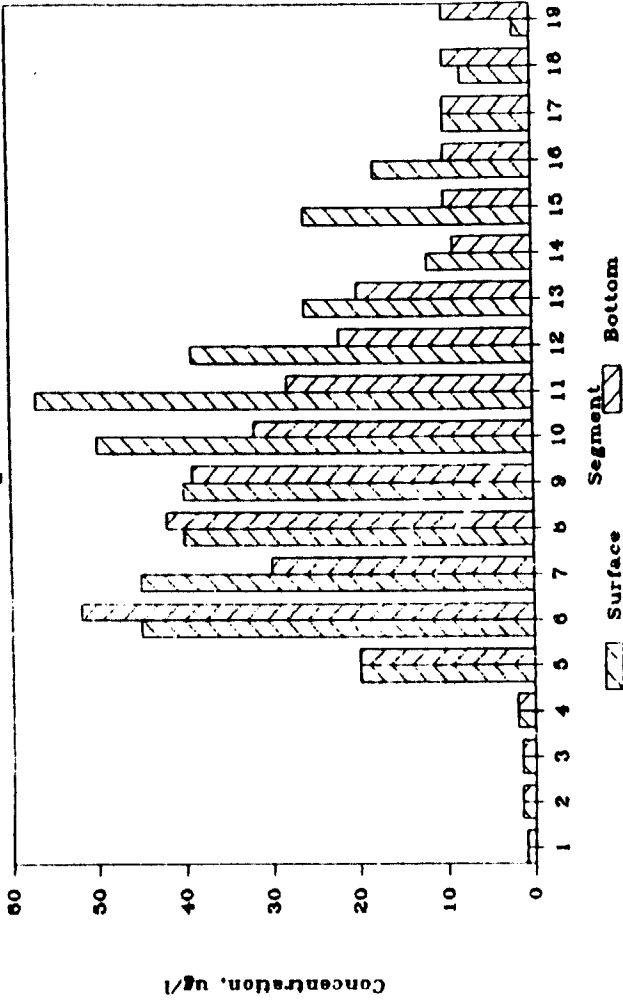dissolved oxygen concentrations in that zone, during

Figure 1. The chlorophyll a concentration peak in the Patuxent River from 100 km upstream (segment 1) to the mouth (segment 19).
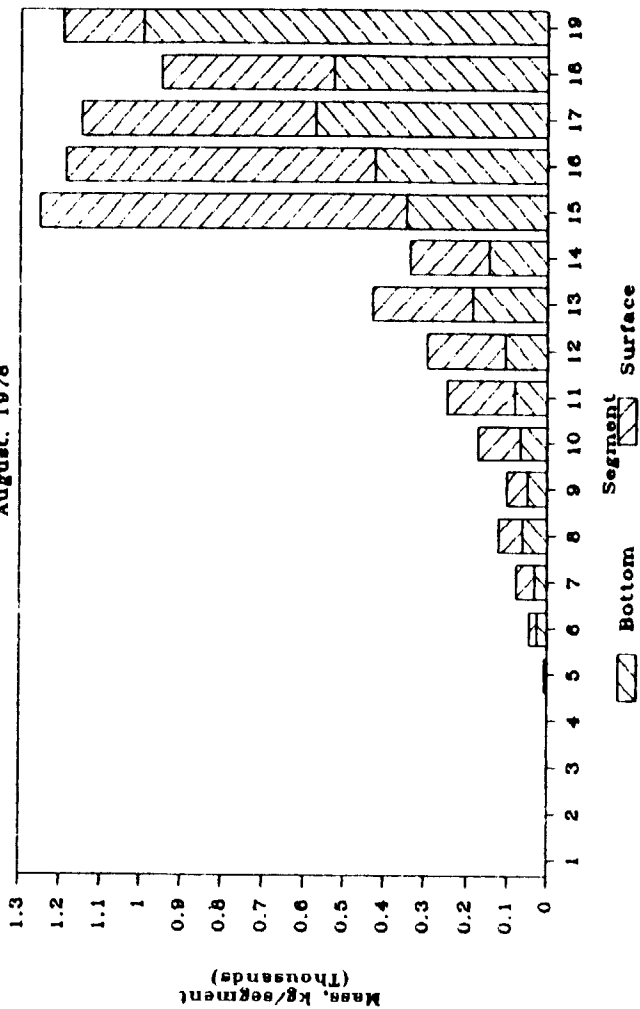
Figure 2. Chlorophyll a mass in the Patuxent River from 100 km upstream (segment 1) to the mouth (segment 19).

a "charette" organized by the state in 1981, it was
designated as a focal point of "clean up" efforts by
consensus of public officials, watermen, citizens
and scientists.

A chlorophyll a concentration peak such as is
shown in Figure 1 is misleading because it does not
account for the enormous increase in river volume
that occurs with distance downstream. Figure 2
illustrates the effect of including volume in calcu-
lations: total chlorophyll a biomass per segment
(i.e. concentration x segment volume) is much
greater in the lower estuary, despite the fact that
the chlorophyll a concentrations are lower than in
upstream segments.

Estuarine Nutrient Limitation

The previous figures were included simply to show
the importance of understanding not only what con-
trols organic production in upstream areas, but also
of understanding what controls it in downstream
areas. What evidence is now available about nut-
rient limitation in the critical salinity-transition
zone? I believe that two lines of evidence, vari-
ations in the seasonal availability of nutrients,
and the response of natural phytoplankton to nut-
rient enrichment in outdoor cultures provide par-
ticularly important evidence.

Seasonal availability of nutrients. The standing
stocks of inorganic nutrients available to support
phytoplanktonic growth in the Chesapeake system vary
greatly with season, such that, in the saline por-
tions of major tributaries, nitrogen is much more
available than phosphorus in the late-winter, high-
flow season. Conversely, in the late-summer, low-
flow season the opposite is true.

Table 1 shows seasonal variations in concentra-
tions of different nutrient forms and elemental
ratios typical for the Patuxent River in the sali-
nity-transition zone near Benedict, MD. In the
March, 1984, nitrate was extremely abundant relative
to other nutrients and the N:P ratio, by atoms, was

Table 1. Typical monthly concentrations (in uM) of different nutrient forms and elemental ratios (by atoms) for the Patuxent River near Benedict, Maryland. December and January data were unavailable at the time this table was made.

Month	Nitrate	Nitrite	Ammonium	Phosphate	N:P
Feb	53.1	0.57	11.5	0.92	70.9
Mar	65.0	0.70	5.90	0.94	76.2
Apr	54.8	0.84	5.30	1.09	55.9
May	33.7	0.46	0.90	0.50	70.2
Jun	15.9	0.61	1.70	1.24	14.7
Jul	5.71	0.09	2.10	1.70	4.65
Aug	0.75	0.05	0.30	1.47	0.75
Sep	2.88	1.72	8.40	4.00	3.25
Oct	5.20	1.90	4.50	2.54	4.57
Nov	59.3	0.66	10.3	1.42	49.5

well in excess of the approximately 15:1 stoichio-
metric requirement of the "average" phytoplankter—
the so-called Redfield ratio. In August, 1984,
phosphate was extremely abundant relative to other
nutrients and the N:P ratio was considerably below
that required by phytoplankton. Major transitions
in nutrient regimes occurred in July and November.

Based simply on the ratios of inorganic nutrients
available to support algal growth, one easily con-
cludes that nitrogen is more likely to limit primary
productivity than phosphorus during the summer
season and vice versa.

Why are such great seasonal variations observed
in nutrient standing stocks? The high-flow abun-
dance of nitrate-N is easily explained. Nitrate is
abundant in winter runoff, but phosphorus is not.
During this season, the non-point-source term of the
Patuxent River nutrient budget seems to exceed all
other terms.

The low-flow abundance of phosphate-P is less
easily explained. During the low-flow season,
runoff and non-point sources are low; this reduces
the magnitude of the nitrogen input. The major
external nutrient input to the system is now sewage,
which is typically phosphorus-rich, relative to
phytoplanktonic needs. Deep water from the
Chesapeake Bay proper, during this season is
similarly low in N:P ratio. This may explain the
relative abundance of P.

The absolute increase in P abundance in the water
column during the summer seems to be related to
sediment processes. Factors affecting summer N
abundance are also believed to be controlled by
sediment processes, but are less clearly understood.

Research recently supported in part by the
Maryland Sea Grant Program has shown that (1) deni-
trification in the sediments leads to a substantial
loss of combined nitrogen from the sediments and
overlying water, (2) nitrogen fixation in the sedi-
ments and water column is inconsequential in offset-
ting this loss, and (3) phosphate is conserved in
the system and cycles seasonally between the sedi-
ments and water column, with the net effect that

phosphate is "buffered" at high levels in the water column during the summer season.

It is the buffering of phosphate at high concentrations in the water column by the sediments, even under oxic conditions in the water column, that constitutes what I consider to be a difficult-to-control, if not uncontrollable non-point source of phosphate to the estuary. No amount of terrestrial point- or non-point-source phosphorus control will be able to reduce phosphate below naturally high concentrations in the estuary.

Enrichment experiments. Recent enrichment experiments in the Benedict region of the Patuxent estuary, also supported in part by Maryland Sea Grant, have confirmed the seasonal patterns of nutrient limitation that one would predict from N:P ratios of available nutrient stocks. Table 2 summarizes the results of these experiments in which continuous-flow cultures of freshly inoculated, natural phytoplankton from the river were enriched with various forms of N and phosphate-P, and the growth response noted.

Relative to phosphorus enrichments and unenriched controls, nitrogen enrichments yielded an approximately one order-of-magnitude increase of biomass obtained in the cultures during the low-flow summer season. Conversely, weak increases in biomass yield by phosphate enrichment was observed during the high-flow winter months (Table 2).

Note that the shifts between phosphorus and nitrogen responses shown in Table 2 correspond closely to the changes in nutrient regime shown in Table 1. The shifts from a weak phosphorus to a strong nitrogen enrichment potential with season is consistent with that expected from the available standing stocks given in Table 1.

Implications. It seems clear from the discussion above that a phosphorus-control strategy for the Patuxent Basin is unlikely to have a significant effect on the in situ production of organic matter in the salinity-transition zone. During the warmer,

Table 2. Ratio of biomass levels attained in experimental cultures enriched with nutrients to levels attained in unenriched control cultures at the Benedict "microcosm" study site. Biomass was determined as relative in vivo chlorophyll fluorescence. NA = Not available.

Experimental:Control Ratio

Date	Phosphate to Control	Ammonium to Control	Nitrate to Control	Comment
June, 1983	1.5	3.3	NA	Weak N Response
Aug., 1983	1.0	7.3	NA	Strong N Response
Nov., 1983	2.6	5.0	2.3	Unstable Response
Feb., 1984	3.1	1.1	1.1	Weak P Response
Mar., 1984	1.0	1.6	1.1	No Response
May, 1984	1.3	1.8	1.1	No Response
Jul., 1984	1.4	4.3	5.9	Moderate N Response
Aug., 1984	1.0	7.1	9.3	Strong N Response
Sep., 1984	1.1	13.5	11.7	Strong N Response
Oct., 1984	2.0	1.3	1.4	Weak P Response

low-flow months, primary productivity in this zone is more likely to be limited by nitrogen than phosphorus. Whether stringent phosphorus controls can reduce concentrations in that zone to levels low enough to be limiting is uncertain, but this seems unlikely, because the sediment seems to constitute an uncontrollable non-point source of phosphorus.

Nitrogen control seems, in theory at least, to be the better option to control in situ primary productivity in the salinity-transition zone in the warm, low-flow season. However, aside from the important engineering concerns about the expense and technical feasibility of nitrogen removal from sewage, important scientific concerns remain as well. For example, how closely in time is primary production and its decay coupled? Will control of primary productivity in the summer season alone be sufficient to reduce oxygen deficits in the lower river, or must some attempt be made to control productivity in the spring and winter season as well? How far downriver are fluvial and sewage-derived nutrients important relative to the nutrients that enter the estuary in deep waters from the Chesapeake Bay proper?

Such questions will be difficult to answer, but are critical ones if the enrichment process is to be understood and controlled. I believe that the answers to the questions can only be obtained by use of all the "tools" at hand, from basic research on algal production and decay, to mathematical modeling and monitoring.

Scientists and the Policy-Making Process

After having covered only the bare essentials of the scientific issues confronting scientists and policy makers concerned with the Patuxent River and the Chesapeake system in general, I would like to consider briefly the roles that science and scientists play in the process that leads to the making of policy.

I have spent a great deal of time in the last decade, not only as a research scientist studying

how nutrients affect estuaries, but also as the
Chairman of the State's Patuxent River Technical
Advisory Committee, considering how scientists like
me fit into the policy-making process. With regard
to the latter, my conclusion is that scientists, the
lay public, and public officials feel compelled by
circumstances to comment on issues outside of their
technical expertise. Consequently, these groups
often find themselves needlessly at odds.

Scientists often fail, or are perceived to fail,
to make the distinction between their roles as
brokers of scientific information and their roles as
citizen advocates of certain public policies. Like-
wise, the distinction is poorly made in the other
direction: non scientists who are simply unqualified
to speak to scientific issues are severely inter-
fering with the scientific process and consequently
putting at great risk the knowledge-gathering acti-
vities needed to determine public policy.

Officials faced with adversarial relationships
with environmental interest groups seem compelled to
deemphasize scientific evidence that might imply the
need to adopt some unattractive (to them) courses of
action such as nitrogen removal at sewage treatment
plants.

The motivation behind such an action is often
most noble: the solutions implied by the scientific
evidence will simply be too costly for the public to
bear, or may involve unreliable, unfamiliar or
untested technology. However, instead of focusing
on the issues of cost, difficulties of implementa-
tion, etc., which justifiably are important concerns
at which they are expert, regulatory and resource
managing officials often find themselves facing
legal exigencies that put them in the awkward posi-
tion of arguing scientific issues that are outside
their scope of expertise. The results can be ludi-
crous and lead to the development of policy based on
erroneous "scientific" facts.

The most notorious example of this occurred
several decades ago in the Soviet Union, when the
state adopted, as policy, the geneticist Lysenko's
belief that acquired plant traits could be

inherited. Science was forced to conform to the dominant ideology of the state, with the result that crops failed badly from the practice of pre-Darwinian approaches to plant breeding.

Such a situation appears to have occurred recently, although on a much lesser scale, at an adjucatory hearing involving a wastewater-discharge permit at one of the treatment plants on the Patuxent River. During the course of the hearing, at least a score of engineers, state officials and scientists were called to testify by the lawyers of the state and the county running the sewage treatment plant, and by the citizen's group opposed to the present permit limitations, which call for phosphorus and not nitrogen removal from the effluent.

The witnesses called in defense of the existing permit testified how the mathematical water quality model of the Patuxent River showed that the state's phosphorus-control strategy would cause a significant reduction in the algal biomass concentration (cf. Fig. 1) particularly in the freshwater section of the river. Most scientists agreed that this is plausible. Several witnesses called in defense of the existing permit expressed their beliefs that it is the transport of this algal material to the lower estuary that ultimately exacerbates the oxygen-depletion problem, and that phosphorus inputs to the river and estuary can be reduced substantially enough to make phosphorus limiting even if it were not presently so.

On the other hand, at least ten active and experienced research scientists testified about their concerns that a phosphorus-control strategy is less likely to be effective in the saline regions of the river—in particular in the critical salinity-transition zone where the nutrient enrichment experiments described above were conducted. Several scientists discussed the role of the sediments in maintaining high water-column phosphorus concentrations; several discussed the importance of denitrification and relative unimportance of nitrogen fixation; and several discussed evidence that phyto-

plankton in the estuary showed evidence of nitrogen, but not phosphorus limitation.

The major conclusion of the hearing examiner, who vitually ignored the experience and credentials of the scientists who testified, was "it is obvious that one would go with the most cost-effective control for solving the problem; in this instance phosphorus control." I can hardly argue against the wisdom of saving the taxpayer money, certainly an appropriate concern of the hearing examiner, but I have grave concerns about the the probable efficacy of the phosphorus-control solution for the lower estuary, based on the evidence I presented above.

In any case, it is most disconcerting to a scientist to see statements such as those in the hearing examiner's conclusion and recommendation document like "algae itself is not necessarily bad. It is useful in that it creates dissolved oxygen and it can create food for the various organisms, and plant and marine life. The idea is not to destroy it completely, but to control it."

No wonder scientists become advocates.

Sediment-Molecule Interactions of Hydrophobic Organic Compounds: Implications for Bioavailability

Jay C. Means, Chesapeake Biological Laboratory

The interactions of organic compounds with various particulate materials in the environment are considered to be of prime importance in determining their ultimate fate and to some degree their toxicity to target species. Although several studies have detailed the occurrence of a wide variety of organic pollutants including polynuclear aromatic hydrocarbons (PAH) and pesticides in Bay sediments, these data tend to give an integrated but stop-action view of the organics in the estuarine environment. They do not indicate the rates of movement, rates of degradation or final deposition of these compounds, nor do they indicate the potential bioavailability of the toxic substances. Adsorption/desorption equilibria are more highly indicative of the latter processes.

The Sorption Process

Sorption results when a component in solution is concentrated at an interface. For sediment/water systems the interface of primary concern is the liquid/solid interface. Sorption will occur when the forces of attraction between sorbing species and the solid surface are greater than the sum of the repulsive forces between the solid and the sorbate and the forces of attraction between the solute and the solvent. The sorbing species is referred to as the solute when it is in solution and the sorbate when it is in contact with the sorbent surface.

For organic molecules there are two general cases when the affinity of the sorbate for the sorbent is greater than the affinity of the solute for the solvent resulting in significant sorption. In the

first case, there is a relatively strong specific interaction between the sorbate and the sorbent such as coulombic attraction, ligand exchange or hydrogen bonding. These forces of attraction can be large and can overcome fairly strong solute-solvent attraction. The sorption of cationic or other polar molecules is an example of this type of sorbent-sorbate attraction. In the second case, sorption occurs due to a weak solute-solvent interaction rather than a large specific sorbate-sorbent interaction. Here, even very weak sorbate-sorbent attraction (e.g. Van der Waal forces) will overcome the weak solute-solvent interaction and result in the removal of the compound from solution. This type of sorption is characteristic or many hydrophobic organic molecules or those molecules having low water solubilities. A weak solute-sorbent interaction (low water solubility) is the result of a large decrease in the entropy of the system upon solvation and the absence of significant hydrophilic character in the molecule. This process can be defined as hydrophobic sorption because of the existence of the weak solute-solvent interaction. The sorption of aromatic hydrocarbons by sediment organic material is an example of this type of sorption. These experiments have demonstrated that for hydrophobic organics, a linear relationship exists between the log-water solubility of the compounds and the log of the equilibrium sorption constant for that compound normalized for the organic carbon content of the substrate (Koc). A linear relationship also exists between the log of thee octanol-water partition coefficient (Kow) and the log of the sorption constant (Koc). Only limited data are available on factors influencing the sorption of toxic organic compounds in estuarine and marine sediments. Recent work has shown that sediment-associated contaminants exposed to a salinity gradient are bound to the sediments even more tightly than would be predicted based on decreases in the solubility ("salting out") of the solute. This phenomenon could have important implications for the bioavailability of contaminants

in estuarine and marine systems.

The Desorption Process

Once organic contaminants are sorbed to sediments, the assumption of thermodynamics are that the sorption process is completely reversible and that the desorption isotherm will overlay the sorption isotherm. Several recent studies suggest, however, that the desorption process may be restricted in some way and that sorbed contaminants, particularly those with very low water solubilities, may become "locked in" to the gel matrix of organic matter associated with sediment aggregates. The net effect of this hysteresis in sorption vs desorption process has profound implications not only for the bioavailability of these types of contaminants in the field but also for the ways in which laboratory studies of bioavailability must be conducted.

Modifying Processes

Since organic matter is so important in controlling the sorptive behavior of many hydrophobic non-polar contaminants in sediment-water systems, it is not surprising that a number of recent studies have found that many insoluble compounds can form strong sorptive association with organic-rich colloidal sized particles in aquatic systems including estuarine and marine surface waters and interstitial waters. The data available suggest that the sorption of organics to colloids is controlled by the same mechanisms and forces and may be modeled using similar predictive equations. The net effect of this sorptive behavior on colloids is to increase the apparent solubility of the contaminant thus potentially increasing its mobility in the environment and thus also its bioavailability. Direct experiments on the influence of colloids on the availability and toxicity of a few compounds have yielded mixed results. Much more experimentation needs to be conducted in this area of research.

Biological Processes

It is becoming increasingly clear that the bioavail-
ability of contaminants is not only a function of
the physical-chemical processes described above, but
that biological processes such as feeding strategy,
burrowing behavior, and metabolism also contribute
to and to some degree control the levels of contami-
nants to which benthic organisms are exposed.
Critical gaps exist in our knowledge of the
relationship between concentrations of contaminants
bound to sediments and the residues of these contam-
inants accumulating in benthic organisms. Studies
of this relationship and the chemical and biological
factors which control it in different benthic commu-
nities together with an understanding of the poten-
tial for food chain transfers to higher trophic
levels and effects on community structure are major
areas of research needed in the immediate future.

Early Diagenesis of Transition Metals: A Study of Metal Partitioning Between Macrofaunal Populations and Shallow Sediments

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INTRODUCTION

Because estuarine sediments are major geochemical
sinks of anthropogenic trace metal pollutants, a
large amount of basic research during the past decade
has. focussed on the relationships between concentra-
tions of common pollutant metals in sediment particu-
lates, interstitial waters, and benthic organisms.
Although the general picture of metal partitioning
between biological and nonbiological components of
the benthic environment is materializing at a frus-
trating snail's pace, a few major advances have been
made.
    As D. A. Wright discusses in a companion paper
in this volume, we now understand that metal uptake
and retention by organisms is fundamentally related
to chemical composition and speciation in the
organismal environment and to certain biochemical and
physiological attributes of the organisms themselves.
Along with this important generalization, we have
developed the corollary that total concentration of a
particular trace metal in a sedimentary deposit is of
secondary importance compared to the concentration of
biologically available species of that trace metal.
In essence, most of what we have learned deals with
the relationship between trace metal bioaccumulation
and the physicochemical state of the immediate envi-
ronment of the organism. It is in this arena of
research that tremendous advances have been made in
our understanding of the relationship between an
individual's trace metal chemistry and that of its
environment.

Conversely, we have generally failed to consider how this chemical milieu, in which the benthos live and from which they assimilate material, evolves the physicochemical characteristics that are largely determinant in bioaccumulation -- i.e., the relationship between early diagenetic transformations in the bioturbated zone and trace metal uptake by the benthos. Because the chemical and physical evolution of bioturbated deposits is profoundly influenced by the densities and types of macrofauna present, one might expect that macrobenthic populations may exert indirect controls upon their own body burdens of natural and pollutant trace metals. In this paper I shall pursue this idea and present supporting evidence which hopefully will help bridge the gap between studies of trace metal bioaccumulation, benthic ecology, and sedimentary geochemistry.

MACROFAUNAL POPULATIONS AND TRACE METALS IN THE BIOTURBATED ZONE

The physical, geochemical, and ecological development of the bioturbated zone of a deposit is dependent upon a complex set of interacting transport phenomena, quasi-equilibrium and nonequilibrium reactions, and benthic community dynamics. In all three of these aspects the macrobenthos figure prominently as agents of physical transport and biogeochemical catalysis (Aller, 1982). For example, the feeding and burrowing activities of the macroinfauna may not only exert major effects upon the vertical and horizontal distribution of particulates and interstitial fluids but may also affects the standing crop, community composition, and physiological state of the benthic microflora, which in turn exert major controls upon the biogeochemistry of the deposit. Because of this intimate relationship, it is clear that the intensity and spatial distribution of their effect is dependent upon both the composition of the macrofaunal community and the density of constituent populations.

To date, studies of trace metal partitioning in the benthic environment have ignored the role of

macrofauna at the population level. The major field
studies relating trace metal distribution in marine
benthos to both environmental and biological (taxono-
mic and trophic) factors have not considered how
benthic population/community dynamics may figure
prominently in the biogeochemistry of the bioturbated
zone. Failure to consider metal uptake by the
benthos as a population-related phenomenon may also
explain why replicate individuals (of the same or
similar species) taken from geochemically similar
environments often do not exhibit similar trace metal
chemistries.

Although we are still ignorant of the intensity
of the impact of differential levels of macrofaunal
bioturbation (arising from different population
densities), enough information has become available
that we can say that the effect is significant.
Studies completed within the past fifteen years
suggest at least five ways that differential levels
of macrofaunal reworking of sediments affects trace
metal distribution in shallow deposits:

1. Mechanical bioturbation greatly affects
texture and other physical properties of sediments.
Infaunal bioturbation significantly influences grain
size distribution (especially by pellitization),
porosity, and surface stability. The associated
vertical redistribution of particulates and pore
water solutes is important in nutrient cycling and
may also be significant in trace metal distribution.
Consequently, mechanical activity not only changes
the amount of solid-water reaction interface for
reactive trace metals, it also provides a mechanism
for particulate and dissolved species advection
between bottom waters, the boundary layer, and deeper
deposits.

2. Bioturbation effectively extends near-
surface chemical conditions deeper into the sediment
column. Extensively reworked sediments exhibit Eh-pH
conditions similar to those of bottom water. In a
summary of his work on the effects of tube-dwelling
infauna upon the chemistry of the surrounding
deposit, R. C. Aller noted that dense colonization of

the seafloor essentially creates a highly invaginated
sediment-water interface (of high surface area)
across which chemical exchange between bottom waters
and deeper portions of the deposit is enhanced. Con-
sequently, the zone of iron and manganese reduction
is depressed further into the sediments if the
deposit is densely colonized. Moreover, those tran-
sition metals which readily associate with Fe and Mn
hydrous oxides and/or sulfides will be distributed
differently than they would be in the absence of or
at lower densities of macroinfauna.

3. Microbial cycling of trace metals may be
affected by the presence of macrofauna, especially
deposit-feeders. The activity associated with
feeding, metabolism, and mechanical bioturbation
appears to stimulate both meiofaunal and microbial
activity. The importance of sediment microbial com-
munities in the speciation and cycling of Fe, Mn, Hg,
and Sn is well known, and their significance for
cycling of other t.ansition metals (especially Cu,
Zn, and Cd) is implied although not well understood.
In a study of aerobic and anaerobic decomposition of
organic detritus, Roger Hanson and I have found that
increasing levels of bacterial activity variously
cause significant losses or gains of Fe, Mn, Cu, Zn,
and Cd from the decomposing particles. It is a
fairly common to observe that, simply by manually
stirring a sample of sediment that has remained un-
disturbed for several hours, one may cause an other-
wise sluggish microbial community to become extremely
active. The stimulatory effect of macrobenthic
deposit-feeders upon microbial activity may then be
of singular importance in the evolution of the trace
metal chemistry of a deposit.

4. Because ingestion and egestion activity by
deposit-feeders exposes particulate trace metals to a
sequence of differing chemical microenvironments
(i,e, pore waters and the gut), deposit-feeding
itself may effect trace metal speciation. The chem-
istry of ingested particulates may change drastically
during passage through the invertebrate gut. For
example, Boothe and Knauer found that _Pugettia_

producta concentrated seven out of nine trace
elements in its feces by a factor of more than two
times the levels of those metals in the kelp upon
which it fed. In a very interesting paper, W. A.
Pryor noted that during the passage of food and clay
through the digestive tract of the decapod
Callianassa major and the polychaete Onuphis
microcephala, chlorites and mixed-layer montmoril-
lonites were partially destroyed; moreover, the
organic matter included in the feces of these
organisms created microreducing conditions that so
effectively mobilize Fe that glauconitization of
clays was prompted. Consequently, passage of sedi-
ments through the invertebrate gut may result in
redistribution of trace metals in both exchange
(relatively labile) and crystallographic (relatively
non-labile) sites.
    5. The benthic macrofauna, like all organisms,
are themselves major reservoirs of trace metals.
Consequently, infaunal burrowers may variously
assimilate, chemically bind, and excrete metals --
effectively functioning as biogeochemical reservoirs
as well as agents. There is some evidence that the
relative ability of invertebrates to accumulate trace
elements depends upon the relative stability of com-
plexes formed in the animal. In one sense then, the
benthos compete physicochemically with interstitial
water and particulate reservoirs for the total
standing amount of metals in a deposit.

BENTHIC POPULATION - TRACE METAL DYNAMICS: EXPERIMENTAL EVIDENCE

Recent work by Rice and others (1981), suggests that
an important biogeochemical feed-back relationship
exists between populations of deposit-feeders and the
trace metal pools of bioturbated deposits. Conti-
nuous, open-system cultures of the deposit-feeding
polychaete Capitella capitata were maintained on
several rations of metal-rich organic detritus for a
period of time (3 months) sufficient for the worm
populations to reach a carrying capacity determined

by the rate of detritus addition. Larger stable
populations of _Capitella_ -- even though they received
proportionally larger rations of metal-rich food --
exhibited concentrations of Cu, Ag, Cdm Ni, and Zn
which were as much as 80% lower than concentrations
in smaller stable populations. The investigators
suggested several explanations for this surprising
result. First, the lower metal concentrations in
larger populations may reflect simply a higher level
of competition for an approximately limited benthic
trace metal pool (food, sediment, water). Secondly,
the higher organic input rates may have accelerated
microbially mediated metal transformations so that
transition metals in the high-ration, high
population-density cultures were solubilized by
organic complexation (and carried out of the sedi-
ments) or fixed as sulfides more effectively than in
the low-ration cultures. The results are provocative
because the experimental systems were open systems.
Even though the large cultures received a substan-
tially higher input of metal-rich detritus, metal
concentrations in the larger populations were lower.

Regardless of how one interprets the data of
Rice et al, it is clear that a population response,
not an individual response, was measured. We
hypothesize that populations of deposit-feeders may
so effectively redistribute (i.e., repartition) trace
metals among benthic reservoirs that they drastically
alter metal transfer kinetics and bioavailability.
Moreover, because large populations of deposit-
feeders may -- by mechanical bioturbation,
stimulation of microbial activity, or through
apportioning the available metal pool over a large
number of individuals -- depress the pool of
assimilable metals, these organisms at the population
level may exert major controls upon their own trace
metal chemistry as well as trace metal partitioning
and diagenesis in the bioturbated zone.

BENTHIC POPULATION - TRACE METAL DYNAMICS:
FIELD OBSERVATIONS

We have recently verified the existence of the popu-
lation density - early diagenesis - body burden para-
digm in a study of sediments inhabited by the
orbiniid polychaete Scoloplos spp. (Rice and Whitlow,
1985). In our field area in Lowes Cove, Maine, an
intertidal flat on the Damariscotta River near
Boothbay Harbor, sediment turnover, the rate of in-
corporation of organic matter to depth, porosity, and
a variety of other physical and chemical parameters
of the top several centimeters of the bioturbated
zone is controlled by populations of these poly-
chaetes. Scoloplos feeds at depth and defecates on
the sediment surface, thereby creating an orderly
type of sediment mixing which Donald Rhoads has
termed "conveyor-belt" mixing. One inportant result
of this feeding habit is that patches of this worm
are maintained at predictable densities from season
to season and year after year; that is, because the
population controls the subduction of fresh organic
matter to depth, each population patch is somewhat
self-sustaining.
    There is a marked inverse relationship between
standing biomass and copper (and several other
transition metals) content of Scoloplos. A standing
crop of ca. 500 mg worms (dry weight) per sq meter
was associated with a copper body burden of ca. 31
ppm or an absolute mass of ca. 15 ug Cu (in
Scoloplos) per sq meter. At a standing crop of ca.
4000 mg worms (dry weight) per sq meter, the
concentration in the worms was ca. 9 ppm, yielding an
absolute mass of ca. 36 ug Cu (in Scoloplos) per sq
meter. With increasing population density, the
concentration of Cu in Scoloplos decreased
significantly (by a factor of 4), although not as
rapidly as biomass increased (by a factor of 8).
There was no correlation whatsoever between average
individual biomass and metal concentration, as found
by Bryan and Hummerstone for Nereis diversicolor.

Metal concentrations in <u>Scoloplos</u> were also found to be directly proportional to the concentrations of ion-exchangeable (via ammonium acetate) particulate metals, and inversely proportional to pore water concentrations of metals. Using rather simple diagenetic models which divide the bioturbated zone into three compartments -- a box above the feeding zone of <u>Scoloplos</u>, a box containing the feeding zone (ca. 4 - 7 cm depth) at the redox potential discontinuity, and a box below the feeding zone -- we have calculated that at increasing population densities, the rates of trace metal release from the surfacemost sediment particulates and the rates of incorporation of metals into solid (sulfides presumably) phases just below the feeding zone likewise increase. Both observations can be explained by the differential rates at which populations of different sizes subduct fresh material from the sediment surface to depth. Larger populations bring down fresh material faster, thereby solubilizing more metals just below the sediment-water interface and indirectly enhancing sulfide production a few cm deeper in the deposit.

GEOCHEMICAL RAMIFICATIONS IN BENTHIC ECOLOGY AND STUDIES OF HEAVY METAL POLLUTION

The hypotheses and results discussed above have a number of important ramifications in benthic ecology and metal pollution studies, particularly in regard to modes of adaptation of benthic organisms to their chemical environment. The ability of dense deposit-feeding populations to exert such major controls on diagenetic transformations in sediments, and, in turn, to moderate their own chemistry, may partially explain why opportunistic species like <u>Capitella capitata</u> are able to colonize chemically hostile environments. R. C. Aller has already proposed that tubiculous macroinfaunal r-strategists may adapt to hostile sediments by building burrows close together, thereby reducing the amount of individual irriga-tional effort required to maintain surface conditions

in individual burrows. The data reported above support Aller's hypothesis, and furthermore indicate that his idea may be more generally significant than indicated in his original proposition (see Aller, 1982, for references). Our work has shown that dense populations not only reduce the level of potential toxicants in the benthic environment, but in the members of the population as well.

Our failure to consider the effects of biogeochemical partitioning associated with population effects in the hundreds of past studies of trace metal uptake by benthic organisms may explain why independent studies (attempting to relate trace metal levels in the benthos to concentrations in dissolved or particulate phases) using INDIVIDUALS of the same or similar species taken from chemically similar environments often yield "conflicting" results. For example, in estuarine environments there was no difference in metal levels in polychaetes living in sediments with different metal concentrations (Cross et al, 1970). Conversely, concentrations of Cu, Zn, and Cd in Nereis diversicolor were directly related to metal concentrations in sediments (Bryan and Hummerstone, 1973). Such studies have proven to be frustrating, possibly because population effects on chemical partitioning were not examined.

The biogeochemical relationships in a deposit reworked by populations of macroinfauna are complex. The mechanical and chemical effects of the macrobenthos upon the sediments in which they live may be expressed as a feedback into the somatic chemistry of the macrobenthos themselves. The complexity of such a system prefigures a difficult problem to be dismantled; nevertheless, it is a problem which must be solved if we are to understand the ecological and geological fates of pollutant metals.

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**Factors Affecting the Accumulation of Trace Metals
by Aquatic Invertebrates**

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Uptake of trace metals by aquatic organisms has been
the subject of an increasing number of investiga-
tions especially over the last 20 years. These have
generally been prompted by concern over the environ-
mental implications of the bioaccumulation of these
often highly toxic metals. Industrial sources
include mining, smelting, electroplating, paint and
plastic industries.

When we consider that animals evolved in an
aquatic (mainly marine) environment for several
hundred million years, it is not surprising that the
common ever-present components of seawater have
become incorporated into vital physiological
mechanisms. A corollary of this is that these
elements have evolved highly specific and sensitive
regulatory mechanisms.

On the other hand, man's influence on the
distribution of metals in the earth's crust can only
be counted in terms of a few thousand years. Only
recently, then, has it been possible to expose
animals to unprecedented amounts of metals to which
they have had very little time, in evolutionary
terms, to adapt.

It is, therefore, of interest to see if specific
regulatory mechanisms have been evolved for these
metals.

From a toxicological point of view research has
been directed along two main lines of investigation:
1)-What are the environmental and physiological
factors affecting trace metal accumulation by
organisms?
2)-What effects do metals have on animals at both
the individual and population level?

One particularly intriguing and important aspect of trace metal physiology is that there is, for some metals, a narrow window between what may be essential for normal metabolic functioning and levels which may be toxic e.g. copper.

Numerous studies have shown that the cupric ion may be particularly toxic to a variety of organisms, and yet in the right form it is an essential component of several different systems.

The body burden of a particular metal is the resultant between uptake rate on one hand, and excretion rate on the other. The overall exchange rate or turnover of a contaminant such as a trace metal may itself be the product of complex exchanges between different body compartments. Some structures such as skeletal elements may have slow turnover rates: blood on the other hand usually has a rapid turnover.

The regulation of major physiological ions, such as sodium, chloride, potassium, calcium and magnesium tends to be delegated to specialized epithelia such as the gill and portions of the gut. However, little evidence has emerged, so far, of specialized epithelial regulatory mechanisms for trace metals and most of the current work on trace metal regulation has been directed towards the characterization of specific metal binding proteins which are produced by animals often in response to trace metal exposure. In other words several of these proteins are inducible. So far, metal-binding proteins have been isolated from several widely divergent groups of organisms including mammals, fish, crustaceans, molluscs, insects, and even bacteria. The term metallothionein has often been used to describe these metal-binding proteins although since metallothionein was initially described in mammals (a low molecular weight, sulfur-containing, cadmium binding protein) most workers reserve the term for this particular protein, or class of proteins, and in other phyla reference is generally made to metallothionein-like proteins. Metal-binding proteins in the invertebrates have some different characteristics from standard

mammalian metallothioneins. For example Engel and
Brouwer (1984) have isolated a cadmium-binding
protein from the oyster Crassostrea virginica
apparently containing aromatic residues and having
<30% crysteine. However these authors have recently
reported a typical metallothionein-like protein from
this species.

Another form of specific cadmium-binding protein
of very low molecular weight (VLMW) has been
isolated from the European oyster, Ostrea edulis
(Fig.1) In a study of metal-binding proteins in two
populations of O. edulis from a metal-contaminated
environment (Restronguet Creek, Cornwall, England
and from a pristine environment (Conwy estuary,
Wales), Frazier and George (1983) found that after
an 83 day controlled exposure to cadmium a large
fraction of the cadmium taken up by the animals was
associated with the VLMW fraction. These authors
identified three potentially metal-binding protein
fractions in oyster cytosol:-
   a) VLMW fraction (eluting close to K^+ peak)
   b) Binding protein (BP) fraction (7,000-20,000
      MW metallothioneins and similar proteins)
   c) Non-specific (NS) high molecular weight
      (probably including metabolic enzymes).

In oysters from the metal-polluted Restronguet
Creek it was especially noticeable that nearly all
the cadmium was associated with the VLMW and
virtually none with the higher molecular weight
fractions.

One particular theory concerning the toxicity of
certain trace metals may be termed the 'spillover'
theory, whereby the capacity of a particular
organism to sequester metals by the production of
specific metal-binding proteins becomes saturated
and metals become associated with non-specific high
molecular weight proteins including metabolically
important enzymes. Supporting evidence for this
theory and a summary of other evidence is contained
in Roesijadi's (1982) study of mercury-binding
proteins in the gills of Mytilus edulis. The impli-
cations for this theory contained in Frazier and
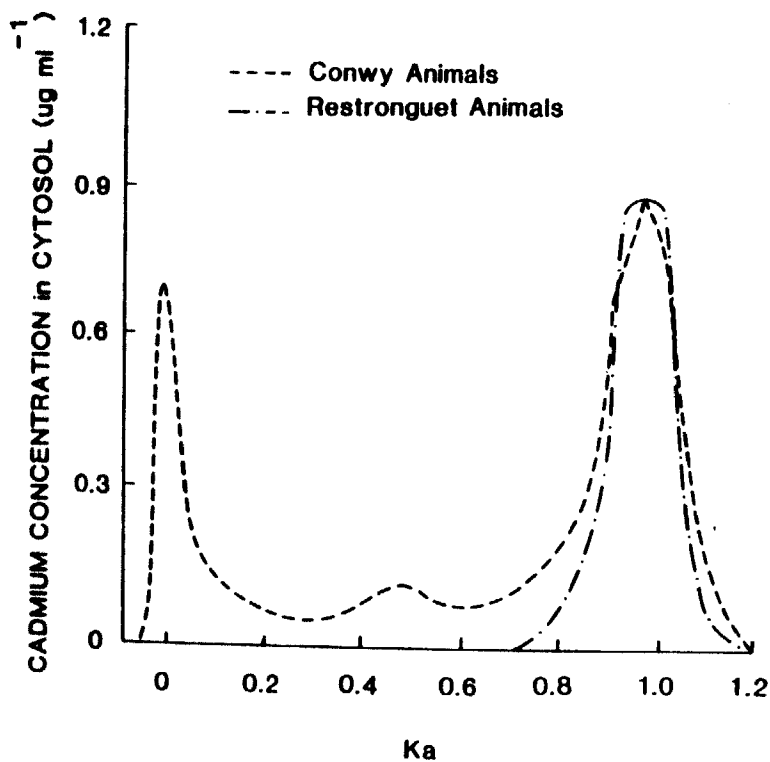George's (1983) study are that over a period of 83

Fig. 1 Cadmium profiles following gel-permeation chromatography (Sephadex G-75) of Ostrea edulis from a metal-polluted river (Restronguet Creek) and a metal-free river (Conwy). Ka = normalized elution volume. (after Frazier and George, 1983)

days the non-specific high molecular weight fraction
is being protected by the VLMW fraction. It might
be speculated that the development of this protec-
tive capability in chronically metal-exposed ani-
mals, such as those taken from Restronguet Creek
(Frazier and George, 1983) may be a genetic adapta-
tion resulting in a metal-tolerant population. The
incidence of metal tolerant animal populations in
chronically polluted environments has been reported
several times in the literature and has involved
fish (Weis, et al. 1981), polychaete worms (Bryan
1976), crustaceans (Brown 1976, 1977) and molluscs.
Studies such as those outlined above demonstrate
that the ability of an organism to deal with an
excess of toxic metal may not necessarily depend on
the absolute amount of metal entering the animal;
rather, the partitioning of the metal once it has
been accumulated. The distribution of metals and
metal-binding proteins may vary according to the
source of the metal. In the blue crab (_Callinectes
sapidus_) for example, Engel and Brouwer (1984) have
shown that cadmium from food is accumulated mainly
in the digestive gland, and cadmium from seawater is
mainly accumulated in the gills. Gel-permeation
chromatography of digestive gland from crabs exposed
to cadmium in food showed the presence of proteins
in the 10,000MW range that bound copper, cadmium and
zinc. Further purification of fractions in this
range yielded two metal-binding proteins, one
containing cadmium and zinc and another containing
only copper. Only cadmium-binding protein was found
in the gills of crabs exposed to cadmium in solu-
tion. Both this and the cadmium-binding protein
from the digestive gland showed true metallothionein
characteristics.

In addition to biochemical adaptations to high
metal environments it seems likely that certain
adaptive changes may involve actual permeability
changes. The work of Bryan (1976) demonstrated an
apparent low zinc permeability in _Nereis diversi-
color_ from a high zinc environment, and it is also
interesting to note that, under controlled
conditions, the rate of cadmium uptake by _Ostrea_

edulis from a metal-polluted environment (Restronguet Creek) was lower than in animals collected from a metal-free estuary. (Frazier and George 1983). A similar pattern was established for populations of the amphipod crustacean Gammarus marinus collected from four different estuaries in England: (Fig. 2) Restronguet Creek, and the rivers Gannel, Hayle and Coquet. When exposed to 1mg L^{-1} Zn, Cu and Pb in seawater under controlled conditions, animals from the River Coquet, the only river unpolluted by metals, showed consistently higher rates of metal uptake than the other populations (Wright, unpublished). Zinc seemed to be better regulated than the other two metals, and recent work on the shrimp Palaemon elegans by White and Rainbow (1984), suggested that for this metal, regulation may be effected by an integumentary mechanism. Using $^{65}Z_n$ White and Rainbow (1984) demonstrated a doubling of zinc flux for every 4^{0}C rise in temperature. This suggested an active component to the uptake mechanism. It seemed unlikely that increases in metabolic rate which might secondarily bring zinc across body surfaces and increases in simple physical transmembrane transport processes would result in such a high temperature coefficient. Respiratory rates in crustaceans for example have a Q^{10} of only 2-3. White and Rainbow's study showed a maximum rate of zinc exchange of 14.4% of total zinc content of the shrimp per day although the total zinc concentration did not significantly alter at all. As total body zinc was well regulated in the face of a high rate of uptake, there must be an efficient system of zinc excretion in this species. Earlier work by Bryan (1964, 1966, 1967) had suggested an efficient excretory system for zinc in crustaceans, either through the antennary gland or through the gills. Other than these investigations, there are virtually no existing demonstrations of specific epithelial regulatory mechanisms for trace metals in aquatic animals.

In several cases salinity effects have been reported in the literature, usually manifest as an increased rate of trace metal accumulation at low
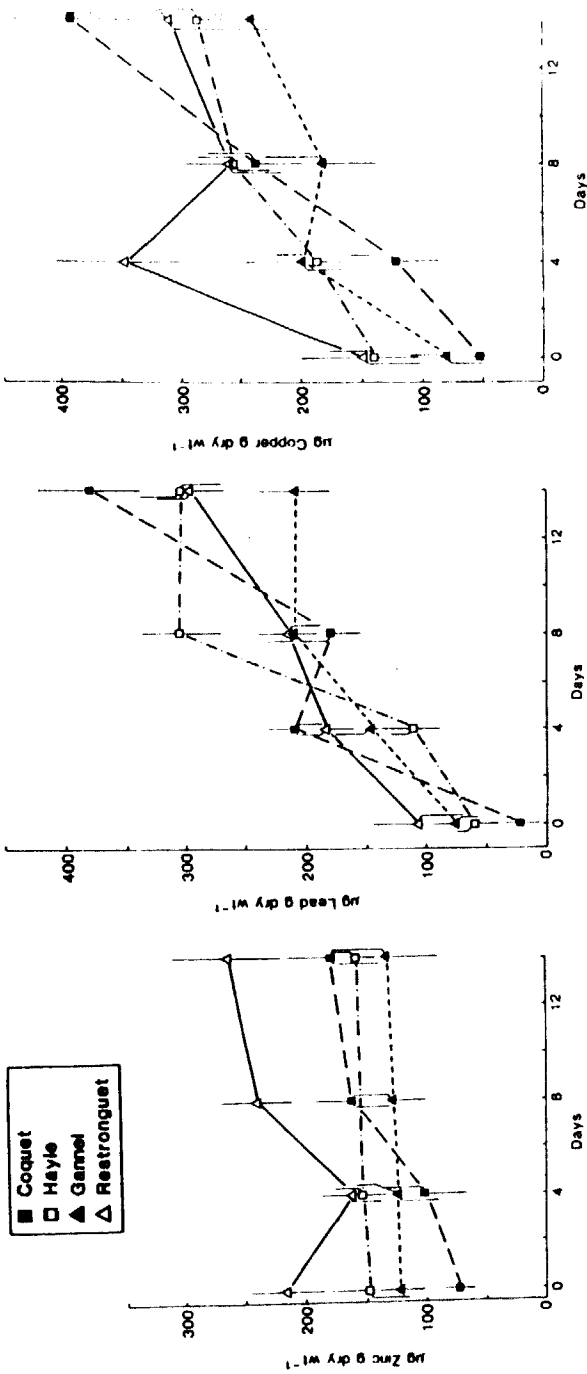
Fig. 2. Trace metal uptake (from 1 mg L^{-1} trace metal solutions in 100% seawater) by the amphipod crustacean <u>Gammarus</u> <u>marinus</u> from three metal-polluted (Restronguet, Gannel, Hayle) and one metal-free river (Coquet).

salinity. Both physicochemical and physiological explanations have been advanced for this. Sunda et al. (1978) ascribed lower cadmium uptake by the shrimp *Palaemonetes pugio* at high salinities to the complexation of cadmium with the chloride ion. At lower salinities a greater proportion of cadmium was present in the more bioavailable, free ionic form. Another relatively straightforward physical explanation of the salinity effect is simply that the freshwater input to any system often carries the highest trace metal load. In such a case a salinity gradient may co-correlate with a contamination gradient. In the Chesapeake system such a phenomenon may contribute significantly to salinity influences on metal accumulation in oysters (Huggett et al. 1973; Phelps et al. 1985). However, it is clear that this fails to provide the full explanation, as laboratory studies indicate significantly increased copper accumulation by the oyster *Crassostrea virginica* and the soft-shelled clam *Mya aremaria* under low salinity conditions (Zamuda and Wright unpublished) even when cupric ion activity is controlled using a Nitrilotriacetic Acid Metal Buffer Chelator system.

Physiological explanations for the salinity effect tend to imply the mediation of major ionic regulatory mechanisms which function at an increased capacity in more dilute waters in order to maintain ionic balance (e.g. O. Hara 1973; Phillips 1977). However, positive proof of a link between trace metal accumulation and an ionic pump is almost entirely lacking, with the possible exception of a connection between cadmium accumulation by the decapod crustacean *Carcinus maenas* and the calcium regulatory mechanism in this species. Experiments showed an increase in cadmium uptake by *Carcinus* at lower salinities, but similar results could be obtained by artificially manipulating the calcium concentration of the medium (Fig. 3, Wright 1977 a,b). In other experiments it was found that both calcium and cadmium accumulation increased dramatically following molt and results could be interpreted as the involvement of cadmium with an active
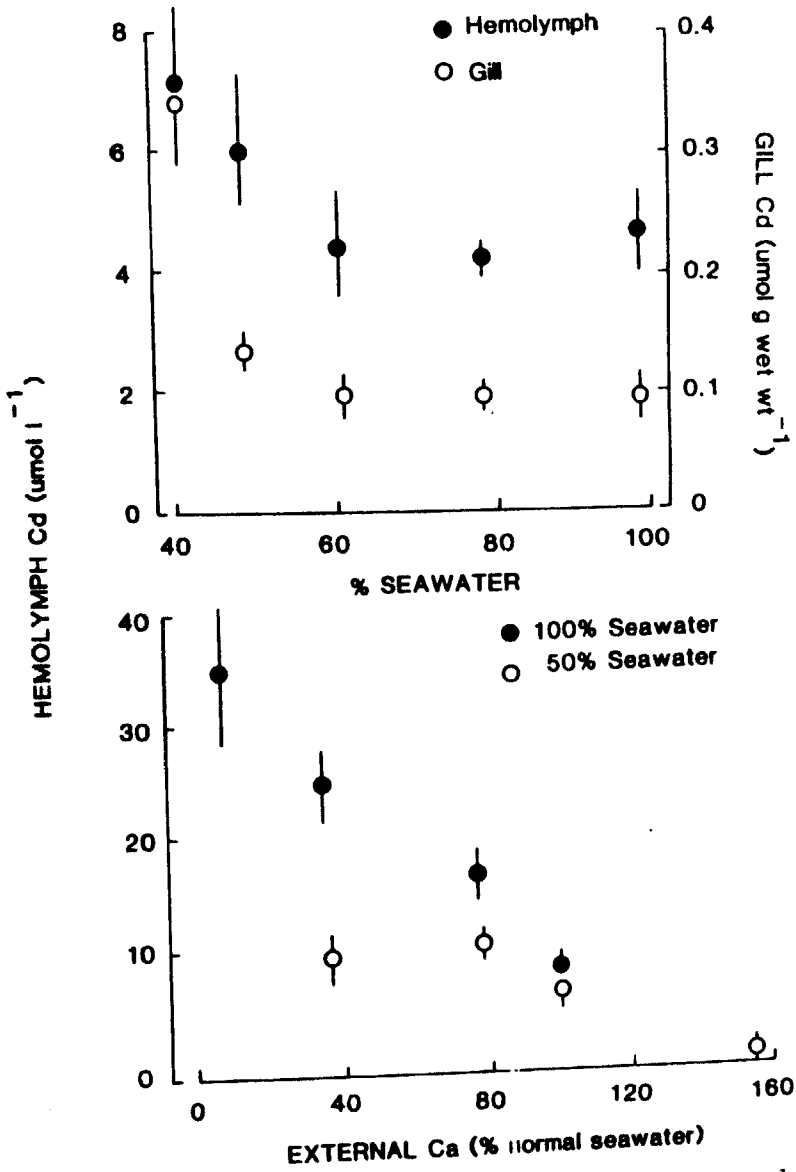
Fig. 3. Relationship between cadmium uptake, and external salinity/Ca in the decapod crustacean <u>Carcinus</u> <u>maenas</u>. (after Wright 1977 a, b).

calcium regulatory mechanism. The term accidental active uptake might reasonably apply to such a phenomenon.

In summary, existing information suggests that the principal mechanisms of trace metal regulation operate to control metal form and distribution once the metals have entered the organism. Evidence for integumentary control mechanisms, whether metal-specific or through the mediation of major ionic pathways is sparse. Indeed, such mechanisms may have limited value in view of the small amounts of metals involved. Trace metals are rarely likely to be limiting and it seems reasonable that their control should be geared towards sequestration and excretion rather than accumulation. In fact it is likely that much of their accumulation may be through food. Zamuda and Sunda (1982) demonstrated that copper accumulation from seawater by the oyster _Crassostrea virginica_ was a function of the cupric ion activity of the medium although subsequent studies (Zamuda and Wright unpublished) have indicated that, in fed animals, copper accumulation from food organisms (phytoplankton, _Thallasiosira pseudonana_) represents the major source of metal to the oyster. It is clear that the form in which the metal is presented to the organism greatly affects its bioavailability. Complexation of metal with soluble organic ligands in the water body, for example, may lower its bioavailability (Ahsannulah and Florence 1984, Zamuda _et al._ 1985).

Current dogma concerning metal-binding proteins is that they essentially represent a detoxification mechanism. While this is no doubt true it is important to consider the roles which these molecules play in the normal regulatory physiology of the animal and it is encouraging to see this view expressed in recent literature (Engel and Brouwer 1984). Figure 4 shows a schematic for most of the topics discussed in this paper. Several topics have been omitted, simply through lack of time and space. Physicochemical characteristics affecting bioaccumulation have been barely addressed and the detrimental effects which metals may have on

FOOD - WATER

skeleton

gut

WATER

liver
(hepato-
pancreas)

gill

kidney
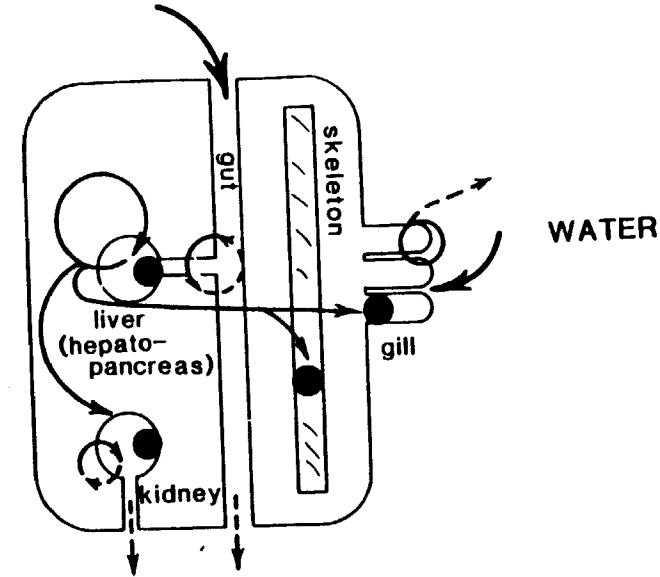
POSSIBLE ACTIVE UPTAKE OR EXCRETORY
MECHANISMS, METAL-SPECIFIC (ZINC) OR
ASSOCIATED WITH MAJOR IONS

METAL STORAGE, PERMANENT OR UNTIL EXCRETION,
METALLOTHIONEIN, PROTEIN COMPLEXES,
ELEMENTAL METAL, INORGANIC CONCRETIONS

TRANSPORT BY CIRCULATING BODY FLUIDS
HEMOCYANIN, RED BLOOD CELLS (VERTEBRATES),
PLASMA PROTEIN, METALLOTHIONEIN

EXCRETORY ROUTES

UPTAKE ROUTES

Fig. 4. Schematic of organismal trace metal regul-
atory mechanisms (vertebrate and invertebrate).

organisms are outside the scope of this paper.
Although no mention has been made of the implica-
tions which these topics may have for monitoring
trace metals in the biosphere it is clear that we
need a far clearer understanding of trace metal
physiology if we are to usefully interpret informa-
tion from such monitoring studies.

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Stress and Recovery of Aquatic Ecosystems and the Use of Fish to Measure Biological Integrity

Charles H. Hocutt, Horn Point Environmental
Laboratory

I was pleased to be invited as a guest speaker to
the inaugural Sea Grant/MEES Symposium on "The Fate
and Effects of Pollutants", with emphasis on the
Chesapeake Bay region. I reviewed the topics of the
other guest speakers, and as often the case, found
my presentation to be an example of applied research
as opposed to their more basic research topics. I
do not want to digress too far on this topic, but I
do believe that it warrants consideration by this
audience, which is composed of students as well as
professional ecologists. Graduate students, like
all organisms, are a product of their environment,
and in this case I mean their mentor's philosophy to
problem solving!

My point is that there is constant discussion in
academic circles as to whether a scientist's
research is meritorious, particularly if it is of
applied nature. I argue that science is science
regardless of whether it is applied or basic, and
that it is the question which is asked that deter-
mines whether the science performed is good or
bad. Indeed, a basic or an applied research program
may well be the extension of the other, as I will
show in my presentation.

My talk will differ from the material presented
in this abstract, the purpose of which is to broadly
review environmental stress and the mandate for
monitoring biological integrity. My seminar will be
concerned with the laboratory capabilities I have
developed to mitigate fish loss from industrial
impacts.

Environmental Stress

Stress in the aquatic environment is usually viewed
as man-related. However, stress may also be a
natural phenomenon; examples are (1) elevated sea-
sonal temperatures with a corresponding decrease in
satured oxygen levels. (2) shifting substrates, and
(3) fluctuations in salinity regimes. Stress can
act on aquatic organisms either directly through
toxic modes or indirectly through alterations in the
food chain or reproductive behavior, for example.
Also, stress can be viewed as being selective or
non-selective in its nature. If selective, the
elimination of target species with low thresholds
may be observed, however this could be accompanied
by increased productivity of surviving taxa. If the
stress is non-selective, species richness may not
decrease although overall biomass would be expected
to decline.Stress levels are usually determined by
the intensity (i.e., concentration), nature (e.g.,
the half-life or bio-degradableness of a pollutant),
mode (e.g., temperature, pH, heavy metal, pesticide,
etc.), duration and rate of exposure of the organism
or community to the stress. From a biological per-
spective, stress will be dependent upon the species,
its life stage and sex, and the presence of other
flora and fauna. A low-intensity stress may result
in little damage even over a prolonged period of
time, however, if the stress is increased either by
intensity, rate of exposure or the introduction of a
synergist, the probability of ecosystem damage is
increased. It is recognized that physical,
chemical, radiological and biological perturbations
can have a deleterious, sometimes irreversible,
impact on the structure and function of impacted
systems. However, it is also recognized that the
environment can be used as an extension of the water
treatment facility if the assimilative capacity of
the system is not exceeded. Thus, environmental
assessment can be viewed by two central themes: (1)
water quality assessment in terms of stress and
recovery of a damaged ecosystem, and (2) water
resource management. It is always preferable,

however, to operate within the limitations of the latter to aviod the former.

Ecological Integrity

The quantification, description and comparison of terrestrial plant communities preceded similar advances for aquatic communities. Many of the biological techniques used to assess aquatic ecosystems evolved from Kolwitz and Marsson's (1908,1909) saprobien system and Margalef's (1951) diversity index based on information theory, and resulted from the need to assess the effects of pollution. More recently there has been an attempt by James Karr and his associates (Karr 1981; Karr and Dudley 1978, 1981) to quantify "biological integrity" using fish communities. Frey (1975) defined biological integrity as "the capability of supporting and maintaining a balanced, integrative, adaptive community of organisms having a species composition similar to that of the natural habitat of the region."The emphasis of ecologists to measure "biological integrity" has been a direct consequence of the Federal Water Pollution Control Act of 1972 (PL 92-500), the stated intention of which was to "...restore and maintain the chemical, physical and biological integrity of the Nation's waters." The law set effluent limitations on point-source discharges, and specified that the discharge of any pollutant would be prohibited unless authorized by a permit as administered by the U.S. Environmental Protection Agency (USEPA) under Section 402 of the Act (National Pollutant Discharge Elimination System). PL 92-500 was amended in 1977 as the Clean Water Act (PL 95-217) which broadened the regulations to monitor and improve water quality. PL 95-217 defined pollution as "...the manmade or man-induced alteration of the chemical, physical, biological, and radiological integrity of water" (Hocutt 1981). PL 95-217 is now before Congress for reauthorization and is expected to lose some of its power. The USEPA's use of "representative important species" (RIS) to assess point source effluents

provides a legal mandate to assess biological
integrity of site-specific receiving waters.
Specifically, RIS are species "...representative in
the terms of their biological requirements of a
balanced, indigenous community of shellfish, fish
and wildlife in the body of water, into which the
discharge is made" (USEPA 1977). Ideally, RIS are
representative of all the trophic levels which occur
at the specific site (Dickson et al. 1976).
Stauffer and Hocutt (1980) equated community
structure and function and argued that information
gathered on tolerance levels of RIS can, as a rule,
be used to extrapolate the ecological thresholds of
phylogenetically related taxa. The attempt by Karr
and his colleagues to develop an index of
"biological integrity" using fish communities takes
the mandate of PL 92-500 a step further in ecosystem
assessment. Karr's objectives were not all together
different that those of Cairns and Dickson (1977) or
Stauffer and Hocutt (1980), i.e., to develop a
system which would have predictive value for
determining the amount of stress a system could
assimilate, and the potential of a system to recover
once it was stressed. Indeed, Karr's work (and that
of others, e.g., Stauffer and Hocutt 1980) adds
emphasis to the poineer aquatic ecology inves-
tigations of Ruth Patrick and John Cairns in the
United States, who stressed the importance of commu-
nity assemblages in data interpretation. I (Hocutt
1981), like Karr (1981), contend that fish communi-
ties should be given preference when assissing man-
related impacts in freshwaters. The most compelling
reason is that structurally and functionally diverse
fish communities directly and indirectly relfect
water quality conditions at a give locality in that
their community stability is indicative of past and
present enviornmental perturbation (Hocutt 1981).
The value of fishes in environmental assessment of
estuarine and marine systems is more limited when
one takes into account the large-scale migrations of
many species, however, fish continue to have great
utility when their seasonality of occurence is con-
sidered in relation to their life history aspects.

Stauffer and Hocutt (180) summarized the value of
using fish data in assessment of ecological integ-
rity, noting that (1) fishes occupy the upper
trophic level in most aquatic systems, and as such,
the "healthiness" of the fish community implies the
"healthiness" of lower trophic levels and phyletic
groups, (2) in their development from larvae to
mature adults, fishes pass from the primary consumer
stages to subsequently higher levels, (3) fish are
relatively easy to identify, thus the use of fish
data is made more readily available, and (4) more is
generally known for the life histories of fishes
than other phyletic groups, thus it is more easy to
relate structural and functional relationships in
fish community assemblages.A final point which
should be emphasized is that the use of mathematical
indices to assess biological integrity should be
done so with a degree of caution (Hocutt 1981).
Indices of integrity suffer many inherent difficul-
ties similar to the deficiences of their earlier
analogs, diversity indices, which I have critized
elsewhere (Hocutt 1975, 1978). A calculated number
can not (at this time) replace professional judge-
ment when assessing the effects of stress on aquatic
communities.

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Abstracts of
Contributed
Papers

Arsenic Transport, Reactivity, and Toxicity in the Chesapeake Bay

James G. Sanders

Arsenate, the primary inorganic form of arsenic in oxidized natural waters, is highly reactive in productive estuaries, actively taken up by phytoplankton, transformed into reduced and methylated forms, then released into the surrounding water column. The degree of arsenic methylation that takes place is proportional to the rate of primary production and the chemical form of arsenic produced is dependent on the species of phytoplankton present. For example, one particular form of arsenic (methylarsonate), which is common only during late summer, appears to be the product of one dominant algal genus, <u>Chroomonas</u>.

The various chemical forms of arsenic differ in their stability, reactivity, and toxicity; thus, the observed variations have considerable geochemical and ecological significance. Very low levels of arsenate are inhibitory to some species of phytoplankton; chronic inputs lead to marked changes in community structure and temporal succession of dominant species. Algal incorporation of arsenic and subsequent transformation of chemical form leads to an increase in reduced and methylated arsenicals which are less available (and, therefore, less toxic) to phytoplankton, but are much more toxic to higher organisms. It is important, therefore, that we understand how these biological and geochemical processes are coupled in productive estuaries like the Chesapeake Bay before we can predict the impact of a toxic compound.

Tin Methylation in Estuarine Sediments

Cynthia C. Gilmour, John H. Tuttle and Jay C. Means

Methylation of tin significantly increases the
toxicity of this virtually non-toxic metal.   In the
estuary, tin methylation is favored in anoxic sedi-
ments. Methyltin production with depth was measured
in reducing sediments from Chesapeake Bay.   Samples
collected with depth (0-15 cm) from three sites in
syringe minicores and incubated for 21 days with 10
ug Sn/cc as $SnCl_4$ formed methyltins in all cases.
Monomethyltin (MMT) accumulated up to 3 ng/gm sedi-
ment and accounted for greater than 95% of methyltin
production.   Dimethyltin was formed at 10-fold lower
concentrations and trimethyltin, even when found,
did not exceed 50 pg/gm sediment. MMT was also the
dominant methyltin species in freshly collected
sediments.   Total methyltin production increased
with bacterial numbers, and correlated best with
numbers of acetate-utilizing sulfate-reducing bacte-
ria (SRB). Axenic SRB cultures are also capable of
tin methylation in medium without added sediment.
However, methyltin production in these sediments was
negatively correlated with sulfate reduction rates,
and production was higher in sediments with lower
sulfide concentrations.   The sulfate-reducing bacte-
ria appear to be responsible for in situ Sn methyla-
tion in estuarine sediments, although, paradoxi-
cally, sulfide produced by these organisms inhibits
the methylation process.

Chemical Characterization of Coal Leachate

Nick J. Fendinger, Jay C. Means, Joann C. Radway and
S. L. Medley

Laboratory leaching experiments were conducted using
a low sulfur Pennsylvania bituminous coal. Leaching
chambers were constructed from 19 L glass carboys
and contained 6.8 kg of coal. Air saturated distil-
led water (pH-5.6) was used in simulated 2.5 cm
rainfalls at 10-day intervals for 70 days. The
leachate was analyzed for inorganic components (Fe,
Mn, SO_4^{--}, pH, and conductivity), and organic compo-
nents (DOC, TOC, total aromatic, total aliphatic,
and selected polynuclear aromatic hydrocarbons).
Iron, Mn, and SO_4^{--} concentrations increased for 40
days, stabilized, then decreased; pH decreased from
3.2 to 1.8 in the first 30 days and remained con-
stant for the duration of the experiment. Dissolved
organic carbon concentrations increased from 0.2
mg/L to 4.5 mg/L over 40 days then decreased. Total
organic carbon concentrations were variable but
generally decreased from concentrations as high as
170 mg/L to concentrations near 20 mg/L. The aver-
age total aliphatic concentration of the particle
fraction ranged from 1.3 to 2.0 ug/g to as high as
120 ug/g. Total aromatic concentrations for the
soluble and particle fractions ranged from 1.3 to
25.5 ug/L and 22.7 to 409.2 ug/g, respectively.
Concentrations ranging from 0.05 to 0.5 ug/L of
naphthalene, flourene, acenaphthene, and pyrene were
found in the dissolved fraction of the leachate.
Concentrations of PAH associated with the particle
fraction ranged from 0.67 ug/g acenaphthene to as
high as 11.20 ug/g chrysene.

Control of Oyster Settlement and Metamorphosis by L-DOPA, Epinephrine and Other Related Compounds

Stephen L. Coon, Dale B. Bonar and Ronald M. Weiner

Larvae of the Pacific oyster, Crassostrea gigas, exposed to L-dihydroxy-phenylalanine (L-DOPA) progress through a complete repertoire of normal searching behavior, eventually culminating in attachment and metamorphosis. Pretreatment of larvae for 15 minutes with 10^{-4}M L-DOPA prior to exposure to cultch results in rapid attachment, although the final percentage attaching is not higher than controls after 3 days. This technique may allow a shorter turnaround time for hatchery settlement tanks.

In contrast, larvae exposed to the catecholamines, epinephrine or norepinephrine, metamorphose without settlement behavior or attachment. Treatment of larvae with 10^{-4}M epinephrine efficiently induces more than 95% of the larvae to metamorphose with more than 90% of these being unattached. Mortality is negligible and spat reared for more than 6 weeks appear normal. This technique provides an easy, economical method for producing cultchless spat.

Similar findings have been obtained with the American oyster, C. virginica, although the percentage of larvae responding is not as great. The results of testing with other compounds will be presented. A model of control of settlement and metamorphosis and its implications for hatcheries and natural recruitment will be discussed.

A First Look at Hydrogen Peroxide in Estuarine Waters

Robert J. Kieber and George R. Helz

The first measurements of hydrogen peroxide in sur-
face waters of the Chesapeake Bay and Patuxent River
are presented. The peroxide content of the samples
was determined using a sensitive fluorescence decay
technique. The values ranged from 0.3×10^{-7} to
17×10^{-7}M. It is believed that the peroxide is pro-
duced in a natural water by a photochemical mechan-
ism involving organic matter. The seasonal and
diurnal fluctuations observed in H_2O_2 concentrations
support this hypothesis. Because it can act as both
an oxidant and a reductant, the peroxide will most
likely be involved in environmental redox processes,
some of which are suggested below: (1) During the
summer of 1983 Chesapeake Bay waters contained
enough H_2O_2 to reduce roughly 10% of a typical est-
uarine power plant chlorine dose, thus it consti-
tutes a potentially significant chlorine demand
component. (2) Evidence is presented which indica-
tes that hydrogen peroxide is involved in the redox
chemistry of dissolved Cr in natural waters.
Approximately 30% of an added peroxide spike was
destroyed in 4 hours in the presence of 1.2×10^{-6}M
Cr(III). (3) Hydrogen peroxide may be involved in
the degradation of certain xenobictic compounds,
specifically organosulfur pesticices. In 5 hours
half the peroxide content of a sample was reduced by
10^{-7}M of the pesticide parathion.

Immunoassy for Maleic Hydrazide

Robert O. Harrison and Judd O. Nelson

Maleic hydrazide (MH) is a plant growth regulator
which has been used in American agriculture for over
thirty years as a sprouting inhibitor on potatoes
and onions. Acute toxicity of MH to animals is
minimal, but chronic effects are uncertain due to
three decades of conflicting bioassay results. MH
forms conjugated metabolites in many organisms, but
the importance of these to detoxification or toxic
effects remains unknown. Analytical methods for MH
have focused on free MH until this decade and are
generally inadequate for detecting conjugated metab-
olites. One potential solution to this problem is
to develop an immunoassy for MH capable of detecting
bound or free forms.

An immunoassy for MH was demonstrated using MH
specific antisera raised in mice against two differ-
ent MH-protein conjugates. Antiserum titer and
specificity were analyzed by enzyme immunoassay (EIA)
and competitive inhibition EIA (CIEIA). Specificity
for MH was demonstrated by CIEIA and the position of
attachment to the MH ring structure determined the
specificity of the resulting antisera. Maleic
hydrazide was detected in an MH-spiked sample of
potato juice by CIEIA. The CIEIA detection limit
was calculated to be 2.8 ppm of MH in potatoes,
which is well below the legal tolerance of 50 ppm.

Offshore Oil Leasing: An Overview of Environmental Issues

Stephen J. Jordan

Project OCSMAPS is responsible for providing reviews and analyses of environmental information to be used by the Department of the Interior in making decisions on 5-year oil leasing schedules. Large-scale leasing decisions are based on several crit-eria, including relative biological "productivity" and environmental "sensitivity" of large areas of the continental shelf. The potential impacts of offshore oil development on marine biological resources and coastal habits are important factors in these criteria. Our analyses will consider the fate and effects of crude oil spills, as well as the potential for long-term impacts due to disturbance and chronic low-level pollution associated with offshore petroleum development. A number of acute oil spills have been well-documented, and compar-isons of fate and effects can be made over gradients of latitude, distance offshore, coastal geomorpho-logy, etc. Long-term effects are much less well-known, but experimental and monitoring studies are beginning to provide critical information.

Petroleum in Coastal Environments: What Do We Know?

David F. Ludwig, Cathy J. Womack, Stephen J. Jordon
and Wayne Bell

As part of an ongoing review of literature pertinent
to potential environmental effects of offshore pet-
roleum rights leasing, we have assembled (to date)
1196 key references. This data base consists of
recent material from a variety of sources, including
various map series, government documents, referreed
journals, review volumes, and symposia papers. The
data base is reasonably representative of available
information, and with this as an assumption, anal-
ysis of our catalogue suggests regional topics that
require additional study, are controversial and/or
critically important, or have been sufficiently
reported. Preliminary analysis of our data base
indicates that the Atlantic, Pacific, and parts of
the southern Alaskan coasts have been thoroughly
investigated, and that the U.S. Gulf of Mexico
coast, despite its developed drilling industry, is
deficient in ecological study. A relatively large
amount of information exists on phytoplankton and
finfish, less on seabirds, mammals and endangered
species. Nearly 25% of our references pertain to
coastal environments, 20% to phytoplankton, and less
that 10% to benthic habitats. Our conclusions are
tentative and subject to change as we accumulate
additional references, but we feel that analysis of
published data can contribute substantially to envi-
ronmental management.

Environmental Effects of Pollutarts Associated With
Marina Development: A Synthesis of Existing
Research

William A. Jenkins

Marina development in a natural, undeveloped estua-
rine setting has the potential to severely impact
the existing environment, not only through the pro-
cesses of construction and development, but through
continual daily use and operation. One of the major
environmental impacts associated with marina deve-
lopment is pollution of the waterway in which the
marina is placed. This is the topic of this paper.
    The findings presented here are highlights of a
report discussing the environmental and planning
considerations of marina development in estuarine
areas. The research methodology used both in the
larger report and this paper was a compilation of
established literature review techniques. Secondary
(or historical) analysis, content analysis, and
grounded theory building were integrated with a
review process utilizing practicing professionals.
    Based on existing literature, pollution from
marinas can be assembled into five general categor-
ies:
(1) Nutrient enrichment: such as N and P from
upland fertilizers and sanitary wastes.
(2) Organic wastes: such as sewage effluent from
marine septic systems and boats.
(3) Biocides: such as pesticides, insecticides,
herbicides, etc.
(4) Sediment: as supplied from upland areas
through erosion forces.
(5) Petro- and organic- chemical wastes: such as
fuels, oils, and anti- fouling paints, heavy metals,
etc.
    Numerous authors have described the environ-
mental effects of these pollutants and have studied
the effects of nutrients on the aquatic ecosystem.

The environmental effects of the specific pollu-
tants contained within the five general categories
cited above will be presented. Synergistic effects
and management implications will be discussed where
applicable. This paper is not intended to be all
encompassing in terms of literature reviewed, or
effects discussed. It is intended to provide the
reader with an understanding of the major or best
known pollution related impacts of marina develop-
ment.

Poster Session Abstracts

Mutagenicity of Leachates from Model Coal Piles

Sandra H. Baksi, Carol R. Daniels and Jay C. Means

Coal is often stockpiled at freight yards, factories
and power plants. The runoff that results from the
action of rain and snow fall on these piles contains
a wide range of environmental pollutants. Experi-
ments were performed to determine the mutagenicity
of leachate from artificial coal piles using the
Ames Salmonella/microsomal assay. Four carboys
containing 6.8kg of low sulfur coal were subjected
to 2 L of air saturated distilled water (pH 5.6) to
simulate rainfall. Rainfall events occurred every
14 days. Two coal piles were held at 4°C and two
were held at room temperature. Each leachate was
extracted five times at a pH of 2, and five times at
a pH of 10. The 10 extracts were combined, taken to
dryness, and the residue dissolved in DMSO. Resi-
dues from two successive rainfall events were com-
bined. Doses were based on ug residue/plate.
Salmonella strains TA 98 and TA 100 were exposed to
50, 100, 300, and 500 ug residue/plate using the
Ames assay with preincubation, both in the presence
and absence of the S-9 microsomal preparation. Each
assay was duplicated. TA 98 exhibited greater mut-
agenicity in the presence of the metabolic activa-
tion system, but some unactivated extracts were also
mutagenic. At the lower dose levels in the absence
of S9, the extracts were mutagenic to TA 100.
Higher dose levels were toxic. The addition of S-9
preparation decreased both mutagenicity and toxicity
to TA 100. These findings indicate that runoff from
model coal piles contains both base pair substitut-
ing and frame shift mutagens.

N and P Inputs and Transformations in Chesapeake and Delaware Bays and the Hudson River Estuary

Thomas R. Fisher

Longitudinal profiles of salinity, total and inorganic N and P were made in the Chesapeake and Delaware Bays and Hudson River estuary. Losses and gains of N and P were inferred from plots of N and P vs. salinity. In the Hudson, mid-estuarine sewage inputs from New York City dominated the TN, NH_4, NO_3, TP, and PO_4 distributions, and the freshwater concentrations of N and P in the upper Hudson were relatively low (TN=90, TP=2 uM). Most N and P appeared to be exported to the shelf plume. In the Delaware, sewage inputs from Philadelphia occurred principally in freshwater; concentrations varied inversely with river flow and were quite high (TN=260-360, TP=6-10). Both N and P were trapped in the Delaware, especially in the ca. 5 ppt region in the case of P. Inorganic N was abundant, and nitrification was an important feature of the DIN distributions. Occasional algal blooms near the mouth resulted in conversion of P and N, but most material appeared to be exported to the shelf. In the Chesapeake, freshwater concentrations varied inversely with flow rate (TN=110-170, TP=0.5-?), and losses of N from the water column were proportional to temperature. Nearly complete removal of inorganic N occurred at all seasons, although TN distributions varied from conservative at low temperature (2 C) to strongly concave at the highest temperature (25 C), indicating conversion to DON and P and seasonal export to the shelf plume. Freshwater and shelf TP concentrations were similar, and occasional import of TP from the shelf apeared to occur. In spite of the large lateral freshwater input from the Potomac River, no influence of the sewage N and P from Washington, D.C. was observed in the main bay axis, suggesting that the inputs were trapped in the Potomac itself.

Metabolism of Carbofuran by a Pure Bacterial Culture

Jeffrey S. Karns, Walter W. Mulbry, Judd O. Nelson
and Phillip C. Kearney

A bacterium WM111, isolated by soil enrichment and
identified as an Achromobacter species, was capable
of rapidly utilizing the insecticide carbofuran
(2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcar-
bamate) as a sole source of nitrogen. The doubling
time was 4 hr, and carbofuran was degraded to nonde-
tectable levels within 42 hr. The reaction proceed-
ed by hydrolysis of carbofuran and concomitant for-
mation of the 7-phenol metabolite (2,3-dihydro-2,2-
dimethyl-7-benzofuranol) as measured by high-perfor-
mance liquid chromatography. Resting cell suspen-
sions of WM111 hydrolyzed carbofuran at an excep-
tionally rapid rate and also rapidly hydrolyzed
several other $\underline{N}$-methylcarbamate insecticides.

The Release of Trace Metals by Dechlorination

Phillip J. Kijak and George R. Helz

The fate of residual S(IV) from the use of sulfur
dioxide in dechlorination is being studied. The
concentration of S(IV) in the discharge of the WSSC
Western Branch sewage treatment plant was found to
range widely between 0 and 36 uM, reflecting the
poor control in the addition of SO_2. The role of
sediments in the removal of residual S(IV) has been
explored by measuring the decay of S(IV) in the
presence of a standard sediment. Ionic strength,
pH, and sediment concentration were held constant.
The concentration of S(IV) was varied and the exper-
iments were done with and without O_2 present.
Samples were also taken for trace metal analysis.
In all experiments copper was released from the
sediment into solution in the presence of S(IV). We
hypothesize that the release of Cu involves the
dissolution of Fe oxyhydroxide coatings on
particles. This reaction of S(IV) with sediment
coatings, while important in releasing trace metals,
only oxidezes a fraction of the available S(IV).
The major oxidant is O_2. Preliminary evidence sug-
gests that sediment can catalyze the oxidation of
S(IV) by O_2.

Nutrient Fluxes and Sediment Oxygen Associated with the Sediment-Water Interface of the Choptank River

Lesley K. Smith

In estuarine systems sediments are reservoirs of organic material, which consume oxygen and can act as sources or sinks of nutrients. My goal was to measure these exchanges across the sediment-water interface and to evaluate the mechanisms by which they occur. Fluxes of oxygen, ammonium, nitrate, phosphate, and iron between the sediments and overlying water were measured on the Choptank River, a sub-estuary of the Chesapeake Bay. Two methods were used: 1) a chamber which measured the in situ rates and, 2) an interstitial water sampler which measured the nutrient concentration gradient; fluxes were calculated assuming molecular diffusion. The nutrient fluxes measured with the chambers were consistently higher than those measured with the interstitial sampler. Transport coefficients were calculated and found to be about two orders of magnitude higher than the molecular diffusion coefficients used to calculate the fluxes from the concentration gradients. The influence of bioturbation and tidal pumping are postulated to be the advective processes overriding the diffusive fluxes. A strong correlation between water temperature and sediment oxygen demand (SOD) as well as between SOD and ammonium fluxes into the overlying water were found. Implications are made referring to the eutrophication of a system with the onset of summer-time anoxia and the warming of the water-column.

Processes Controlling the Regional Distribution of
^{210}Pb, ^{226}Ra and Anthropogenic Zinc in Estuarine
Sediments

George R. Helz

The concentration of ^{226}Ra in Chesapeake Bay bottom
sediments is lower than in incoming sediments and
decreases systematically in the seaward direction,
reflecting displacement of Ra from sediments as
salinity increases. The amount of ^{226}Ra lost from
sediments approximately balances that gained by the
water. In the seaward 150km of the estuary, where
atmospheric deposition is the dominant ^{210}Pb$_{ex}$
source, the ^{210}Pb$_{ex}$/Org-C ratio is virtually con-
stant in surface samples. This indicates that
organic matter becomes the aquatic carrier of atmos-
pherically derived ^{210}Pb. It further implies that
the production of carbon per unit area is
constant. From independent productivity estimates,
about 10% of the carbon is found to survive remin-
eralization in the estuary long enough to be incor-
porated into surface sediments. All cores display a
zone of Zn enrichment near the surface. The
Zn$_{ex}$/Org-C ratio decreases systematically southward,
probably reflecting a regional decline in deposition
of anthropogenic Zn from the atmosphere. A negative
^{210}Pb anomaly is observed in most cores from the
river-dominated northern third of the Bay. This is
concluded to be associated with a major flood and
illustrates the importance of such events in estua-
rine sedimentation.

Crabmeat Spoilage and Plant Sanitation

John Pace, Ralph R. Cockey and Tuu-jyi Chai

Pasteurized crabmeat is heat-processed in hot water (186-190° F) to an internal temperature of 185°F for at least one minute in a hermetically sealed container. The shelf-life of pasteruized crabmeat under refigeration is normally more than six months. However, spoilage incidence during storage often occurred if crabmeat was improperly processed or if any mechanic flaw existed in processing, particularly in machine-picked meat. To identify and evaluate the possible spoilage causes, four plants which were equipped with picking machines were subject to sanitation survey. Spoiled cans of both machine-picked and hand-picked meat were collected for microbiological, chemicals and physical examination. The sanitation survey indicated that four processing plants were contaminated with bacterial count of 10^3 to 10^7 per square inch. Pseudomonas, Acinetobacter, Streptococcus, and Clostridium were the major microorganisms which were found on the surfaces of plant equipment. The major microorganisms in the machine-picked meat were Clostridium, Acinetobacter, Pseudomonas, and Flavobacterium, and in the hand-picked meat were Pseudomonas, Acinetobacter, Streptococcus, Enterobacteriaceae and Clostridium. Plant sanitation and defects in can seaming were the causes of spoilage.

The Modulation of Membrane Proteins of Deep Ocean Hyphomonas in Response to Growth Temperatures

Levent Dagasan and Ronald M. Weiner

We tested the hypothesis that Hyphomonas strain VP-1, isolated near Pacific Ocean thermal vents at 3000 m, would modulate membrane protein synthesis in response to shifts in temperature. Standard growth conditions in marine broth (2216) were aerobic, pH 7.6, and one atmosphere and 3.5% salts. Generation times were 390 min at 15C, 145 min at 30C, 80 min at 37C and 210 min at 45 C. SDS-PAGE was used to separate purified membrane proteins which were identified by their apparent mol. wt. (app mol wt) and characterized by their approximate percent, total wt of total membrane proteins (% tot wt). A major protein of 65000 app mol wt was synthesized in proportionately greater amounts as growth temperatures were increased. It comprised 1.4% tot wt of the membrane proteins at 15C and 24% tot wt at 45C. Conversely, a 20000 app mol wt protein was detected in amounts of 2% tot wt or greater only at temperatures 45 and 37C. An 88000 app mol wt protein was detected at temperatures below 45C. It is also interesting that many of Hyphomonas membrane proteins, like those of another prosthecate bacterium Caulobacter, are high molecular weight.

Hyphomonas VP-1 tolerates a wide range of environmental conditions. Its ability to modulate its membrane protein composition may contribute to its adaptibility.

Biochemical Effect of Cadmium on Sterol Biosynthesis by Soybean Suspension Cells

Sihua Xu and Woon J. Yang

Air pollution and the application of sewage sludge to agricultural lands have led to increasing exposure of plants to cadmium. This heavy metal has been reported to accumulate in plants, particularly in root tissue. Even low concentrations of cadmium have been shown to cause serious physiological problems. As little as 18uM CD in nutrient solutions inhibits soybean fresh weight, photosynthesis, nitrogenase activities and protein productions.

The purpose of this study was to examine growth and sterol biosynthesis by soybean suspension cultures in the presence of different levels of cadmium.