WATER QUALITY CRITERIA RESEARCH OF THE U.S. ENVIRONMENTAL PROTECTION AGENCY Proceedings of an EPA-sponsored Symposium ...



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WATER QUALITY CRITERIA RESEARCH OF THE U.S. ENVIRONMENTAL PROTECTION AGENCY

Proceedings of an EPA-sponsored Symposium on Marine, Estuarine and Fresh Water Quality -presented at the 26th annual meeting of the AIBS, August 1975

compiled by

Technical Information Office Corvallis Environmental Research Laboratory Corvallis, Oregon 97330

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FOREWORD

The mission of the Environmental Protection Agency (EPA) is primarily one of a regulatory nature, with responsibility for establishing and enforcing environmental standards. The establishment of standards must be preceded by, and based on, sound, defensible research data. The Office of Health and Ecological Effects within the Office of Research and Development administers a variety of research programs to develop information necessary for the establishment of such standards. The major emphasis of this research has been directed toward the development of scientific information for the establishment of water and air quality standards. More recently, however, research expertise increasingly is being directed toward the total environmental picture (holistic or ecosystem approach), to develop a sound basis for evaluating the ecological consequences of all aspects of environmental pollution.

Proceedings of the two symposiums appearing in this text were organized under the National Environmental Research Center managerial mode. Subsequent reorganization has rendered each laboratory (exception noted on title page of papers) an independent entity with its own central research theme; in most cases similar to the one under the NERC mode. Therefore, questions concerning research activities of the EPA, in research areas appearing in these proceedings, should be made directly to the laboratories. Inquiries concerning other aspects of water and air related ecological effects research are invited. These may be made to the EPA Office of Health and Ecological Effects, 401 M Street, SW, Washington, D.C. 20460 (RD-683).

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PREFACE

Early in 1975, the American Institute of Biological Sciences (AIBS) invited the National Environmental Research Center (NERC), Corvallis to participate in its 26th Annual Meeting to be held on the Oregon State University campus during 17-22 August 1975. A. F. Bartsch, Director of the Center, accepted the invitation and Spencer A. Peterson, NERC staff ecologist, was charged with organizing a oneday symposium on the NERC research program.

At the time the invitation was extended, a diversity of research work was being conducted by the nine laboratories associated with NERC Corvallis. Research programs included ecological effects of various pollutants on freshwater, marine, and terrestrial ecosystems. Presentation of research papers in all of these areas during one day was considered to be impractical. Therefore, a decision was made to limit the presentations to marine and freshwater research areas since they were dominant at the time and to focus on water quality criteria research. The symposium was divided into a freshwater and a marine segment. Each was designed to present a cross-sectional representation of the types of research being conducted at the NERC-associated laboratories and was not meant to be all-inclusive. The freshwater program centered around the transport and biological modeling capabilities of the laboratories, cold climate aquatic biology, trophic status of lakes in the Eastern United States, and the impact of toxic substances on the freshwater environment. marine program centered on microbial and abiotic degradation processes, the problem of trace metals, the effect of toxic organics on the marine environment and the feasibility of new stress-measuring methodology.

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MARINE AND ESTUARINE WATER QUALITY RESEARCH OF THE ENVIRONMENTAL PROTECTION AGENCY

Eric Schneider, presiding Director, Environmental Research Laboratory--Narragansett

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Structural Analysis of Stressed Marine Communities

R.C. Swartz, J.D. Walker, W.A. DeBen, and F.A. Cole*

ABSTRACT

Pollution often causes major changes in the structure of marine communities. The impact of sewage sludge on macrobenthic assemblages in the New York Bight and in experimental microcosms is described as an illustration of the effects of stress on species composition, density, diversity and heterogeneity. Structure analysis provides an exceptionally good method for assessing ecological alterations at specific sites, but quantitative criteria such as diversity indices should not be used as universal regulatory standards. Field surveys should be closely coordinated with laboratory investigations of the toxicity and accumulation of pollutants from those species which dominated community structure and function prior to human perturbation.

INTRODUCTION

Variations in species composition, density, diversity, and spatial-temporal heterogeneity of multispecies assemblages are often used as indicators of the effects of pollution on marine community structure. Sometimes only one aspect of structure, usually diversity, is presented as the sole biological criterion of stress. We will review the need for more comprehensive structural analyses and their relationships with other branches of pollution ecology, especially multispecies bioassays. For illustrative purposes, data are given from field and laboratory investigations of the effects of sewage sludge on the marine macrobenthos.

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METHODS

NEW YORK BIGHT SAMPLES

To illustrate different methods of structural analysis, two representative samples were selected from a macrobenthic survey of the New York Bight. Sample S was collected in the apex of the Bight near the center of the sludge dumping site $(40^{\circ}23.8^{\circ}N, 73^{\circ}42.5^{\circ}W)$ on 24 August 1973 and sample A at a relatively clean site approximately 23 km south of Fire Island, New York $(40^{\circ}25.6^{\circ}N, 73^{\circ}11.1^{\circ}W)$ on 23 August 1973. The samples were collected with a $0.05m^{2}$ Smith McIntyre grab and sieved through a 1.0 mm screen. Animals retained on the screen were preserved in formalin and later identified to the species level.

INDICES OF COMMUNITY STRUCTURE

Density:
$$\sum_{i=1}^{S} n_i/0.05m^2$$

Diversity:

Areal Species Richness:
$$S/0.05m^2$$
 Simpson's (1949) Index of Dominance (S.I.):

1- S.I. = 1 - Σ

i=1 $\overline{N(N-1)}$

Information Theoretical Diversity (Shannon-Weaver Equation):

$$H' = \frac{1}{N}(N \log N - \sum_{i=1}^{S} n_i \log n_i)$$

Faunal Heterogeneity:

Czekanowski or Bray-Curtis Dissimilarity Index:

$$D.I. = 1 - W$$

where W = sum of lesser n_i/N for each species found in both samples n_i = number of individuals of the i species

N = total number of individuals in a sample

S = total number of species in a sample.

SLUDGE-BENTHOS EXPERIMENT

Digested municipal sewage sludge was obtained from the Bay Park Sewage Treatment Plant, East Rockaway, New York. Sediments and test specimens were collected in the lower Yaquina Bay, Oregon. The sediments were autoclaved and placed in a 3 cm deep layer at the bottom of a polyethylene box (25 l capacity, 1200 cm² bottom area). The tanks received a continuous flow of seawater entering at the surface at one end and exiting through a stand pipe at the opposite end. Animals were introduced to the tanks 48 hr before the sludge. The seawater was turned off for 45 min while the sludge was added and allowed to settle. Dissolved oxygen concentration reached a mimimum of 3 mg/l during this period.

The same sludge sample was used in the first two experiments, conducted 11-25 February 1974 and 1-15 April 1974. In the first, the polychaetes <u>Eupolynmia crescentis</u> (5 individuals) and <u>Glycinde polygnatha</u> (17); the molluscs <u>Clinocardium nuttallii</u> (11), <u>Macoma nasuta</u> (40), and <u>Transanella tantilla</u> (25); and the amphipod <u>Corophium spinicorne</u> (50) were placed in two control tanks (no sludge) and three test tanks in which sludge layers of 4, 20, and 45 mm were deposited. In the second experiment the same number of individuals of all of the above species except <u>E. crescentis</u> were placed in two control and four test tanks receiving 1, 4, 5, and 8 mm layers of sludge. In both experiments sediments were sieved 14 days after the sludge was deposited and all living individuals were recorded.

The third experiment was conducted 1-15 July 1974 with a different sludge sample from the same treatment plant. The polychaete <u>Glycinde</u> polygnatha (20 individuals); the molluscs <u>Clinocardium nuttallii</u> (10), <u>Macoma nasuta</u> (40), <u>Transanella tantilla</u> (15), and <u>Cryptomya californica</u> (10); the amphipods <u>Corophium spinicorne</u> (50) and <u>Paraphoxus epistomus</u> (17); and the cumacean <u>Lamprops quadriplicata</u> (6) were placed in two control tanks and six test tanks each of which received a 4 mm sludge layer. One of the test tanks was sacrificed 1, 2, 4, 7, 10, and 14 days after the sludge was deposited. Both controls were sacrificed after 14 days.

RESULTS AND DISCUSSION

SPECIES COMPOSITION

The species composition, density, diversity, and dissimilarity of macrobenthic collections at the sludge ground (station S) and a relatively clean station (A) are given in Table 1. With the exception of <u>Capitella capitata</u>, at least one individual of all species found at S was also present at A. The fauna at S appears to be composed of the stress-tolerant remnants of a more diverse benthic assemblage found in clean sandy sediments throughout much of the New York Bight. In particular, the gammarid amphipods were abundant at A, but absent at S. The extreme dominant at S, <u>Capitella capitata</u>, has never been found in several hundred grabs taken in the vicinity of A.

Total reliance upon indicator species as criteria of marine pollution is undesirable, but the concept should not be ignored. the polychaete, C. capitata, is an opportunistic species that can rapidly increase in abundance during environmental disruptions. It is a cosmopolitan species often found in areas of dredging, marine construction, cannery wastes, and sewage deposits (Reish 1959, Wass 1967, Eagle and Rees 1973). Surveys by the National Oceanic and Atmospheric Administration (1972) also indicated that the absence of amphipods was a good indicator of the effects of sludge dumping in the Bight.

TABLE 1. SPECIES COMPOSITION, DENSITY, DIVERSITY, AND DISSIMILARITY OF MACROBENTHOS COLLECTIONS AT THE SLUDGE GROUND (STATION S) AND A RELATIVE-LY CLEAN STATION (A) IN THE NEW YORK BIGHT

Station S		Station	Α
	umber of dividuals	<u>Taxon</u>	Number of Individuals
Capitella capitata Cancer irroratus Unid. Nemertean Cerebratulus sp. Unicola irrorata Nucula proxima	916 7 3 2 1	Trichophoxus epistomus Spiophanes bombyx Acanthohaustorius intermedius Foraminiferan No. 1 Acanthohaustorius spinosus Pseudunicola obliquua Unicola irrorata Cerebratulus sp. Nucula proxima Phyllodoce maculata Acanthohaustorius millsi Echinarchnius parma Unid. Nemertean Clymenella zonalis Plus 11 separate species represented by one individual	36 29 8 6 4 4 3 3 3 2 2 2 2
Total No. of Species	6		25
Total No. of Individuals	930		119
Species Diversity (H	1') 0.04		1.03
1- Simpson's Index of Dominance	0.03		0.84
Dissimil	arity Index	between Stations S and A = 0.98	

It is difficult to define the exact relationship between indicator species and specific environmental factors. These species may not be tolerant to all forms of pollution. The success of stress tolerant species may be due to the elimination of less resistant competitors or predators rather than a preference for altered habitats. The disappearance of stress sensitive indicators may be caused by factors other than human perturbation. However, if the more abundant organisms at a site are typically associated with stressed ecosystems, it is probable that environmental conditions have deteriorated. Wass (1967) suggested a pollution index based on the ratio of the number of individuals of tolerant and intolerant species. Application of the indicator concept at the multi-species level is preferable to reliance upon a single species such as Capitella capitata.

DENSITY

The higher density of individuals at station S is due to the great abundance of <u>Capitella capitata</u>. Excluding that species only 14 specimens were collected at S, whereas 119 were found at A (Table 1).

Density comparisons based on the total number of individuals in entire collections can be misleading if different phylogenetic and trophic assemblages are combined. Many of our samples from station A are dominated by a very large (1-4 mm) arenaceous foraminiferan (Astrorhiza sp.?). It seems unreasonable to include this species when comparing macrobenthic densities. Changes in the abundance of individual or closely related groups of species can be sensitive to minor ecological changes. Watling et al. (1974), for example, found that sludge dumping off Delaware Bay had not caused serious environmental damage, although the density of Nucula proxima, a deposit feeder, had increased substantially due to organic enrichment of the sediment

DIVERSITY

Species diversity is a function of the number of species (richness) and the distribution of individuals among the species (evenness) (Lloyd and Ghelardi, 1964). This is a very broad ecological concept for which a plethora of quantitative indices have been proposed.

Areal species richness or species density can be expressed as the number of species (S) collected per unit effort or area. This is the most basic concept of relative niche diversity. As a richness estimate, species density is preferable to catch of species per unit number of individuals (numeric species richness) because the latter is strongly influenced by evenness patterns. Species density obviously is not an estimate of the total number of species in a community and it is valid only for comparative study. Constant sampling effort can usually be incorporated into survey designs and S's for different samples can be directly compared.

The degree of dominance by the more abundant species is an important characteristic of the evenness of distribution of individuals among the species. As dominance increases, "effective" diversity will decrease even when the species density does not change. Simpson's (1949) index gives the probability that two individuals drawn at random and without replacement from a multispecies assemblage will belong to the same species.

It is a good measure of dominance and its complement is positively related to diversity.

To many ecologists species diversity implies an integrated measure of both richness and evenness. The most popular index of "overall" diversity is the Shannon-Weaver equation (H'). Because richness and evenness are not necessarily correlated and have basically different theoretical significance, H' may not always provide an adequate diversity analysis.

All aspects of diversity were substantially less at station S than at station A (Table 1). Species density decreased from 25 to 6 species, H' from 1.03 to 0.04, and the complement of Simpson's Index from 0.84 to 0.03. These data demonstrate a major deterioration in benthic community structure. The analysis of species composition and density indicate the differences in diversity are due to the absence at S of many stress intolerant species and the presence of a very large number of Capitella capitata.

FAUNAL HETEROGENEITY

The Bray-Curtis index is sensitive to differences in species composition and the relative abundance of individual species. The extremely high value (0.98) between S and A clearly demonstrates the major difference between these assemblages (Table 1).

Analysis of faunal heterogeneity is more useful when applied to surveys which include a large number of stations. Dissimilarity between all possible pairs of samples can be calculated and the results expressed in dendrograms which show hierarchial relationships between site clusters. Species clusters can also be identified from the interspecies similarity of distributions between stations. A variety of dissimilarity indices and clustering strategies are discussed by Clifford and Stephenson (1975). Boesch (1973) gave a good example of the application of this kind of analysis in marine pollution research.

SLUDGE-BENTHOS EXPERIMENT

In the first two experiments, the survival of all species was reduced when exposed to sludge layers >8 mm for two weeks (Table 2). Recovery of living Corophium spinicorne, Clinocardium nuttallii, and Transanella tantilla in test tanks receiving 4 or 5 mm sludge layers was substantially less than in the controls. Only 4 C. spinicorne survived when exposed to 1 mm of sludge while 21-37 of the 50 seeded specimens were recovered from the control tanks. These results show that 1) the response of the macrobenthos is proportional to the quantity of sludge deposited, 2) all species are not equally sensitive to sludge, and 3) a very thin layer of sludge (1 mm) can affect some species over a short period of time (14 days). It is not certain whether the impact is due to toxicity or indirect effects such as burial or changes in sediment size distribution. The design only crudely simulates the deposition of the settlable sludge fraction on the bottom. Under field conditions, currents or wave action might keep a larger proportion of the sludge in the water column.

TABLE 2. SURVIVAL IN A MACROBENTHIC SPECIES ASSEMBLAGE EX-POSED TO SEWAGE LAYERS OF 1-45 mm FOR TWO WEEKS

	Individuals Seeded				Indi	ividuals	Reco	vered				
			Cont	rols			;	Sludge	e Laye	er (m	n)	
Species		I	II	III	IV	1	4	4	5	8	20	45
Eupolynmia crescentis	5	4	2*	_	_	_	_	2	_	-	0	0
Glycinde polygnatha	17	15	17	16	14	13	10	15	12	8	6	1
Corophium spinicorne	50	35	42	21	37	4	0	5	0	1	1	0
Macoma nasuta	40	39	37	39	3 9	37	35	19	29	9	1	1
Transanella tantilla	25	18	21	24	21	20	15	2	3	0	0	0
Clinocardium nuttallii	11	9	9	11	11	7	0	0	0	0	0	0

^{*}Only 4 <u>Glycinde</u> seeded in Control II.

The third experiment was designed to determine if there was a temporal pattern of mortality following exposure to a 4 mm sludge layer. Interestingly, there was no substantial difference in survival of all species between control and test tanks after 14 days (Table 3). Failure to reproduce the results of the first two experiments might be attributable to variations in the toxicity of sludge from the same treatment plant since a different sample was used in the third experiment. If this is true, source control of toxicants in some sewage sludges might significantly reduce their environmental impact.

These experiments demonstrate the feasibility of conducting multispecies bioassays with ecologically important species collected from ocean disposal sites. This permits a much closer coordination between field and laboratory investigations than is possible with many conventional bioassay organisms.

EFFICACY OF COMMUNITY STRUCTURE ANALYSIS IN POLLUTION RESEARCH

No single aspect of community structure provides an unequivocal criterion of biotic response to stress. In particular, total reliance on diversity indices should be discouraged because of their insensitivity to changes in the species composition. Further, the assumption that diversity always decreases in response to ecological alteration is not always true. Fish species diversity sometimes increases in the vicinity of ocean outfalls and thermal discharges (Grimes and Mountain, 1971; Turner, Ebert and Given, 1966). It is thus impossible to establish a particular diversity index value as a universal regulatory standard for an unacceptable level of pollution. However, diversity should be employed as an important part of a more comprehensive investigation of community structure.

Analysis of the condition of biotic assemblages in stressed areas has several advantages over other methods in pollution ecology. The biotic resource to be protected is examined directly. There is no uncertainty about extrapolating laboratory results to field situations. Structural characteristics such as species composition, density, diversity, and heterogeneity are sensitive to individual and synergistic effects of all forms of natural and pollutional stress, some of which may not be immediately apparent. Spatial-temporal community patterns can indicate both environmental impact and recovery following pollution abatement.

We do not advocate community structure analyses as the "best" method of assessing ecological alterations. They should be closely coordinated with experiments on the toxicity and bioaccumulation of specific pollutants. Similarly, bioassay organisms should represent the dominant taxocenes which would occur in the absence of pollution at the stressed site. Neither field nor laboratory studies by themselves can provide an adequate basis for regulatory decisions.

TABLE 3. SURVIVAL IN A MACROBENTHIC SPECIES ASSEMBLAGE EXPOSED TO A 4 mm LAYER OF SEWAGE SLUDGE FOR 1 - 14 DAYS.

	Individuals Seeded			Individuals	Recov	ered			
	000 00 1			Exposure Tim	e (da	ys) .			
		14	14	1	2	4	7	10	14
Species		Cont	rols			4 mm :	S1udg	e Lay	er
Glycinde polygnatha	20	19	17	17	20	20	14	17	17
Corophium spinicorne	50	48	46	40	44	37	43	31	40
Paraphoxus epistomus	17	15	14	14	15	13	14	14	15
Lamprops quadriplicata	6	5	6	6	5	4	4	3	6
Macoma nasuta	40	36	34	36	35	34	30	33	32
Transanella tantilla	15	15	14	15	15	13	14	13	13
Clinocardium nuttallii	10	9	10	10	9	6	9	9	8
Cryptomya californica	10	10	10	10	9	10	10	10	9

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Trace Metals in the Oceans: Problem or No?

Earl W. Davey*

ABSTRACT

Increased input of mercury to the estuarine environment resulted in bioaccumulation in marine food chains that affected man (Irukayama, 1966). Toxic effects of other metals on marine animals have been demonstrated under laboratory conditions. However, cause and effect between elevated environmental metals levels and toxicity to marine animals has yet to be conclusively demonstrated under field conditions. Municipal waste water treatment plants, dredging and spoiling activities, and the dumping of sewage sludge and industrial wastes are the major sources of metals to the marine environment. These sources are likely to increase in the near future unless the Federal Water Pollution Control Act Amendments of 1972 (PL-92-500) are carefully enforced.

INTRODUCTION

Estuaries, because of the fact that they are landward extensions of the sea, have become centers of industrial, commercial, and related activities. As a consequence, estuaries have received an increasing input of metals due to the result of by-products of modern industry and technological advancement. Metals can be introduced indirectly from contaminated rivers and land runoff or directly by pumping from land based industries and municipalities, ship or barge discharges and aerial fallout (Merlini, 1971). When viewed as a whole, ocean systems appear to be beyond compromise in relation to its ability to dilute elemental introductions due to man's activities -- after all, the continental masses are continually bathed in their oceans and seas. Where then do problems occur?

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Ocean waters, especially estuaries, are not uniformly mixed and lack of uniform dilution can cause local concentrations of metals. Metals tend to be concentrated at air-sea, sediment-water, or freshwater-saltwater interfaces and boundaries between water and living or dead particles (Fig. 1). Some metals discharged even in small quantities can be accumulated to alarming and lethal levels by certain marine biota. Seafoods harvested by man can become extensively impacted when excessive metals are added to the sea. A classic example of the human aspect of the problem first received considerable attention when mercury poisoning occurred in Japan in 1953 through consumption of contaminated fish and shellfish (Irukayama, 1966).

It must also be recognized that it is not necessarily the total amount of a metal present in seawater or marine sediments but the form of the metal which may be important to consider with respect to the effects metals may manifest on marine biota. Metals in seawater can be operationally characterized as particulate (metals associated with particles larger than 0.45μ) or dissolved metals (<0.45 μ). Dissolved metals can be categorized further as in organically associated, organically bound, i.e. chelated, or metal-organic compounds. Dissolved metal forms are likely to interact with most marine biota; however, the effects may differ if the metals are organically bound. If a metal such as copper is chelated, there may be a reduction in metal toxicity response by organisms such as marine phytoplankton; whereas, if the metal is an organometallic like methyl-mercury, this compound is more toxic than the inorganic form and can also be concentrated in food chains. Particulate metals, probably occurring in high levels near industrial outfalls or ocean dumping activities, are likely to affect filter feeding organisms which ingest and concentrate particulate matter. Consequently, the form of the metals may be the dictating factor in the response of marine biota to heavy metals.

METHODS AND MATERIALS

Trace elements are essential to all life systems; yet excess amounts are toxic. Also, non-essential elements such as mercury, cadmium, lead, etc., can be toxicants and bioaccumulated to large quantities to affect organisms within marine food chains including man. Therefore, a matrix of existing toxicity and body burden data using marine species (including various life stages) as one axis and metals (including various chemical states and modes of application) as the other has been formulated in order to assess, broaden, and validate the data base needed for criteria decision making. The metals matrix helps to point out information gaps, thereby defining research goals; and it provides a basis for comparing metal levels and their modes of application in laboratory toxicity and bioaccumulation studies with levels and pathways defined in metal-problem areas in the natural environment.

A summary of two metals matrices which were constructed mainly from literature reviews by Ketchum et al. (1972), Eisler (1973), more recent additions from the open literature, and in-house experiments performed

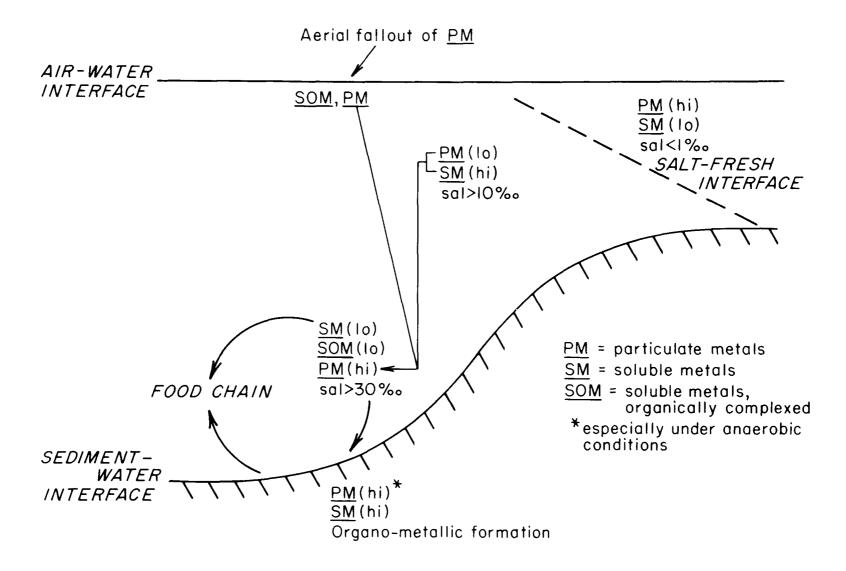


Figure 1. Generalized diagram for sites of metal concentration and transformation of metal forms in the marine environment.

at the National Marine Water Quality Laboratory (NMWQL) are presented in Tables 1 and 2.

RESULTS

The metals matrix indicates that there is information on only 36 elements and of these only 18 have toxicity data listed and of the 18 perhaps only four (Cd, Cu, Hg, and Zn) are sufficiently documented to formulate good criteria. Since the NMWQL has had to respond to unexpected requests for elemental toxicity and bioaccumulation data, in order to anticipate future requests, we have undertaken an in-house program to develop acute and chronic marine bioassay information on a wide spectrum of elements.

However, because there is infinite variety of combinations of marine biota versus elemental compounds, a number of elements can be eliminated from consideration in the following categories:

- 1. Elements such as mercury with sufficient information for good water quality criteria
- 2. Major constituents of seawater s.a. Na, Mg, C1, SO₄
- 3. Major constituents of marine organisms s.a. C, H, N, O
- 4. Noble gasses, i.e. He, Ne, etc.
- 5. Elements which are short half-life isotopes
- 6. Rare earths

The remaining, approximately fifty elements, can be listed in priority according to the following considerations:

- 1. Known toxicity to man
- 2. Information indicating elemental impact in the marine environment
- 3. The form of the element in seawater
- 4. No information available

On the basis of these considerations, elements are chosen for short-term, acute bioassays. Acute bioassays involve a rapid response of a single species to increasing concentrations of a toxicant. The results of the acute bioassay are reported as the median tolerance limit (TL_m of TL_{50}) which signifies the concentration of toxicant that kills 50% of the organisms within a specified time span, usually in 96 hours. Organisms for acute bioassay are being selected from a wide range of representative marine phylla and growth stages.

TABLE 1. MATRIX OF ELEMENTS VERSUS MARINE BIOTA RESPONSE

Element	Environmental Oceans Clean	Spp. (Phyla) Tested	Organism	Most Sensitive Level	Response
Aluminum	0.01	4 (3)	Redfish	88*	Death
Antimony	0.0005	2 (2)	Algae	3.5	Inhib. cell div.
Arsenic	0.003	6 (4)	Copepod	0.1	72hr LC ₅₀
Beryllium	0.0000006	1 (1)	Mummichog	0.0001	Decr. enz. act.
Cadmium	0.0001	34 (7)	Oyster	0.015	Slow sex. devel.
Chromium	0.000005	13 (5)	Algae	0.0001	Decr. culture yield
Cobalt	0.0001	1 (1)	Copepod	0.01	72hr LC ₅₀
Copper	0.003	48 (9)	Diatom	0.001	Inhib. growth Inhib. growth Death Cell clumping Inhib. growth LC ₅₀ of embryos
Germanium	0.00006	2 (1)	Diatom	1.0	
Gold	0.000004	1 (1)	Pinfish	0.069	
Iron	0.0013	1 (1)	Diatom	0.027	
Lead	0.00003	14 (7)	Ciliate	0.15	
Manganese	0.005	2 (2)	Oyster	16.0	
Mercury	0.00003	43 (8)	0yster	0.0056	48hr LC ₅₀ of emryos
Nickel	0.002	17 (4)	Algae	0.0902	Inhib. growth
Selenium	0.0004	5 (2)	Copepod	0.01	96hr LC ₅₀
Silver	0.00004	9 (5)	Copepod	0.0033	72hr LC ₅₀
Yttrium	0.003	1 (1)	Oyster	0.001	Abnormal larvae (98%)
Zinc	0.01	28 (8)	Annelid	0.05	Abnormal larvae

 $[\]mbox{\ensuremath{\star}}$ all concentrations expressed in mg/kg

TABLE 2. MATRIX OF ELEMENTS VERSUS MARINE BIOTA BIOACCUMULATION

Element	Spp. (Phyla) Tested	Organism	Level Reached	Toxic to Man
Aluminum	7 (1)	Phytoplankton	5000*	_
Antimony	42 (1Ó)	Octopus	0.92	+
Arsenic	88 (12)	Squid (gills)	198	+
Barium	3 (1)	Phytoplankton	262	-
Beryllium	1 (1)	Phytoplankton	8.4	+
Bismuth	1 (1)	Phytoplankton Phytop	7.7	+
Cadmium	136 (12)	Abalone (digest, gland)	1162.7	+
Cerium	16 (5)	Fish	64	-
Cesium	20 (6)	Algae	0.64	-
Chromium	30 (4)	Zooplankton	260	+
Cobalt	34 (7)	Zooplankton	110	_
Copper	101 (8)	Squid (liver)	15,160	_
Gold	3 (1)	Mollusc ´	282	_
Iron	73 (8)	Annelid	42,800	-
Lanthanum	4 (2)	Fish	Ś7	-
Lead	102 (7)	Algae	3100	+
l anganese	51 (5)	Algae	226	_
lercury	198 (15)	Algae	7400	+
Molybdenum	5 (3)	Zooplankton	36	_
Nickel	45 (6)	Zooplankton	480	_
Plutonium	38 (7)	Algae	21,000 (CF) #	+
olonium	1 (1)	Fish	61 pCi/gm wet wt	+
Rubidium	6 (3)	Algae	2.3	_
Ruthenium	11 (7)	Sponge	10,000 (CF)	_
Samarium	15 (3)	Annelid	3.6	_
Scandium	20 (4)	Annelid	26.4	_
Selenium	11 (5)	Octopus	71	+
Silver	18 (4)	Squid (liver)	1044	-
Strontium	18 (5)	Algae	4160	_
horium	5 (3)	Octopus	9.2	+
in	2 (2)	Phytoplankton	101	_
itanium	6 (2)	Phytoplankton	940	_
Jranium	i (i)	Fish	21	+
/anadium	6 (2)	Pteropod	290	_
ttrium	2 (2)	Mollusc	1000 uCi	_
Zinc	130 (10)	Mollusc	99,220	_

^{*} all values in mg/kg, except where noted # CF - concentration factor Toxic to Man: + yes; - no

Elements having low TL50 are in turn chosen for long-term chronic bioassays. Chronic bioassays involve a continuous exposure to a sublethal concentration of the toxicant. In the chronic bioassay, any biological response, such as reduction of growth or reproduction, behavior change, histopathological change, etc., can be used to monitor the effect of the element or the species. Also, test organisms are analyzed to determine possible bioaccumulation of the element which could in turn indicate a potential pathway back to man.

DISCUSSION

A definite need exists to carefully inventory all natural and man-made element sources which might impact the marine environment. Table 3 is a generalized inventory. Assessing potential ocean pollutants (Robinson, et al., 1974) has presented an extensive and important approach for budgeting pollutants; however, the report deals only with the metals iron, copper, and plutonium and concludes that plutonium is the only element of potential global pollution. Similar assessment should be made for all elements; however, these assessments should be focused at more localized areas, such as coastal or estuarine areas as well as on a global scale. These inventories would highlight elements of major environmental concern which should be carefully bioassayed in the laboratory. Also, these budgets should point out specific areas of high metal impact in the United States.

Field investigations of metal impacted areas throughout the U.S. are necessary in order to determine the extent, fate and effects of metals on marine biota. Have metals per se directly or indirectly caused environmental damage and, if so, to what extent? What are the inputs, rates, routes, and reservoirs of metals within impacted areas? Special consideration should be given to areas of:

- 1. Mining activities
- 2. Smelters
- 3. Industrial outfalls, especially metal plating industries
- 4. Sewage outfalls
- 5. Desalinization plants
- 6. Offshore ocean disposal areas for industrial wastes, sewage sludge, and dredge spoils

However, Cross and Duke (1974) have emphasized that it is essential that present efforts be continued and new efforts initiated to determine baseline levels of trace metals in marine organisms and the environmental variables that affect them. These studies should be conducted not only in contaminated environments such as Long Island Sound, New York Bight, and the Southern California Bight, but also in relatively pristine or uncontaminated environments. The concentration of any trace metals can

TABLE 3. INORGANIC CHEMICALS TO BE CONSIDERED AS POLLUTANTS OF THE MARINE ENVIRONMENT

Element	Natural conc in sea water µg/l	World production metric tons/year (1968)	Routes of entry into the sea	Pollution categories
H (acids)	pH=8 (alk=0.0024)	?	D,A	III c
Be	0.001	250	U	IV c ?
Ti	2	1,000,000	A ?	IV b ?
V	2	9,000	Α	IV a ?
Cr	0.04	1,500,000	R(U)	IV c ?
Fe	10	480,000,000	D,R	IV c
Cu	7	5,000,000	D,R	IV c
Zn	2	5,000,000	D,R	III c
Cd	0.02	15,000	A,R	ΙΙ c
Hg	0.1	9,000	A,R	Ιb
ΑĬ	10	8,000,000	D,R	IV c
CN	-	?	D,R	III c
Pb	0.02	3,000,000	A,R	I a
Р	_	?	D	IV c
As	2	60,000	D	ΙΙ c
Sb	0.45	60,000	U	IV c
Bi	0.02	3,800	U	IV c ?
Se	0.45	1,000	Ü	III c ?
F	1,340	1,800,000	Ď,R	IV c ?

D dumping, A through atmospheric pollution, R through rivers (runoff) or pipelines U unknown

I-IV order of decreasing menace; a worldwide, b regional, c local (coastal, bays, estuaries, single dumping). Referenced from FAO Fisheries Reports, No. 99 Suppl. 1. Report of the seminar on methods of detection, measurement and monitoring of pollutants in the marine environment: Inorganic chemicals, Panel 3. Dyrssen, D., C. Patterson, J. Ui and G. F. Weichart

be highly variable both within and between species and influenced by a number of environmental variables. Until we understand the variability that exists in healthy ecosystems, it may be difficult to identify a contaminated ecosystem. Also, because trace metals occur naturally in the marine environment as a result of weathering and volcanic activity, the problem of determining the contribution of anthropogenic additions of trace metals to natural levels in marine organisms is more difficult than with halogenated hydrocarbons or refined petroleum products.

Other questions concerning potential metal pollutants which need to be answered are as follows:

- 1. Are certain industries, such as power plants, producing excessive metal inputs which should be controlled?
- 2. Can elemental transformations occur within marine areas to produce more lethal and/or bioaccumulated compounds such as methyl-mercury? If so, which elements are capable of transformation and under what circumstances?
- 3. Dredge spoils removed from navigational channels are often taken from areas which act as traps for sediments laden with river and estuarine bourne waste. What are the long-term effects of these ocean dumped dredge materials upon the cleaner shelf areas? How should ocean dumped materials be handled to lessen environmental impact in disposal areas?
- 4. Liquid effluents from waste water treatment plants probably will be a major contribution of trace metals to estuarine and coastal waters during the next several decades. Efforts should be made to evaluate the impact that these discharges will have on concentrations of trace metals in harvestable marine species that complete a major portion of their life cycle in coastal areas.

According to Schroeder (1973) environmental pollution by toxic metals is a much more serious and insidious problem than is pollution by organic substances such as pesticides, weed killers, sulfur dioxide, oxides of nitrogen, carbon monoxide, and other gross contaminants of air and water. Most organic substances are degradable by natural processes; no metal is degradable. Elements in elemental form or as salts remain in the environment until they are leached by rains into rivers and into the sea. Therefore, every effort must be made to slow down the environmental build-up of those elements which are toxic and can cause degenerative diseases.

The solution to problems of metal waste disposal might be expected to be dilution into the vastness of sea. However, because metals can be concentrated by geological, chemical, and especially biological processes in the sea, the solution to metal disposal problems is not dilution. The solution must be to stop pollution at its source by the development of the proper technology to control and recycle metal wastes. Hopefully, metal wastes entering the marine environment should be reduced if application of the Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) to apply the best available technology to minimize environmental pollutants are carefully enforced.

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Persistence in Marine Systems

Kenneth T. Perez*

ABSTRACT

When various stressors and/or disturbances are applied to a system, regulatory agencies are confronted with the problem of determining what resulting systems changes are "acceptable". In general, previous studies have been arbitrary or unrealistic. We have attempted to overcome the above inadequacies by: (1) viewing systems as holistic, (2) assuming that some systems can be miniaturized for experimental purposes, and (3) attempting to define the persistence limits of a system.

Experimental microcosms simulating a complex marine coastal system are described. Some preliminary results of such systems to different artificial sewage stresses are also presented.

Ecologists today more than ever before are being asked to predict the consequences of changes in total systems caused by various disturbances. A possible strategy for establishing limits for such changes is the subject of this paper.

Conceptually, two general system responses are possible when a disturbance of some intensity and duration is relaxed: the system either recovers its "original" structural and functional state, i.e., it persists or it does not recover, i.e., the changes due to the disturbance are irreversible. This view is similar to that of Holling (1973) but more explicitly stated by Innis (1975). Given that the system persists, one is also interested in the speed of recovery. Thus, the limits for systems change proposed in this communique are the ability to recover to some previously defined state or control condition. If system changes were confined to the limits for recovery then the resource or system would be maintained by definition.

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Co-investigators in this study are Scott Nixon, Candice Oviate and Jan Northby of the University of Rhode Island.

The establishment of persistence limits based upon previous theoretical studies is subject to question. The data base and principles from which most complex models are formulated is derived from components of a system (May, 1973; Patten, 1971). These components are usually experimentally isolated from the system as a whole before dynamical studies are performed. The point is, if systems are holistic (Gallopin, 1971), then even given a detailed knowledge of its parts will not enable the description of the total system. It had been shown (Walters & Efford, 1972) that a complex model derived from isolated components of a system provided limited dynamical information.

Experimental field studies of the recovery of disturbed systems are (1) few in number and (2) difficult to perform and interpret. First, it is extremely difficult to impose or relax disturbances on natural marine systems. Second, one is usually not allowed to jeopardize the system for experimental purposes. Third, because of the problems in replicating systems and/or knowledge of other uncontrolled disturbances, the establishment of cause and effect relationships is difficult.

Previous studies of laboratory microcosms have had major shortcomings. To my knowledge, no persistence measures as described above have been made. In fact, most of the microcosms lacked a full complement of species (see Levandowsky, in press); those that did (e.g., Odum and Chestnut, 1970; Whittaker, 1961) failed to provide sufficient physical properties (e.g., turbulence, water turnover) resulting in systems changes not observed in similarly impacted areas in the field. One of the unique properties of natural systems is their complexity. I would ask, "Why has this property been minimized by the majority of microcosm studies?" Presented below is an experimental marine system which attempts to overcome many of the inadequacies of previous studies.

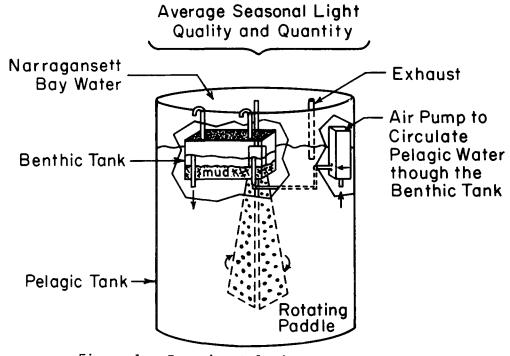


Figure 1. Experimental microcosm.

Our microcosms consisted of an interconnected pelagic and benthic phase (Fig. 1). Pelagic water was continuously circulated over the benthic community. The size of the pelagic phase (150 1) was dictated by our resources. However, the surface area of the benthos (167 cm²) was based upon the surface area to volume ratio in Narragansett Bay. All container surfaces were scrubbed daily so that the only surface area available for settling was the benthic sediments (i.e., the 167 cm²). Natural changes in surface temperatures in the microcosms were reproduced by continuously passing Bay water on the outside of the microcosms. Salinity was monitored weekly. However, the West Passage of Narragansett Bay, the system being simulated, exhibits small salinity changes (≤2 o/oo). Natural turbulence levels in each tank were simulated by adjusting the speed and reversing time of paddles such that the dissolution rates of "sour ball" candy was approximately equal to that of the Bay (Table 1).

TABLE 1. DISSOLUTION RATES (gm/min) OF "SOUR BALL" CANDY IN NARRAGANSETT BAY (NB) AND RHODE ISLAND SOUND (RIS) DURING CALM AND WINDY PERIODS AND IN THE EXPERIMENTAL MICROCOSMS

0	NB cm wave height	RIS 30-60 cm wave height	Experimental microcosms
X	0.174	0.246	0.153
RGE	0.168-0.178	0.233-0.264	0.150-0.160
N	6	6	4

As a result of the continuous mixing, no differences in water chemistry existed between the top and bottom of the tanks. This condition is similar to that found in the West Passage of the Bay. Water turnover (10 1/48 hrs) was based upon the flushing time of the Bay (Kramer, 1975) and was accomplished by the removal and replacement of 10 liters of water every 48 hours. All water was hand-carried so as to eliminate mechanical damage due to pumping. Light regimes were based upon the quality and quantity of light found at 3 m, the depth at which the average light intensity for the water column occurred in West Passage during early spring. Because light is effectively extinguished on the bottom of the Bay, all benthic chambers were dark.

The biotic composition of the microcosms was based upon densities per unit volume for the pelagic phase and per unit area for the benthic phase. This meant, for example, that fish larvae were experimentally excluded from our systems since the highest densities found in West Passage was $5 \times 10^{-3}/1$. However, some larvae were observed in our tanks and probably entered during the egg stage for we screened our water to 1000μ for purposes of reducing replicate variability. It should be noted that the inclusion of pelagic macroscopic forms such as ctenophores and fish larvae

is possible; while ctenophores are major predators in the Bay they were not present in any significant numbers during this time of the year (early spring). The benthic organisms were collected from an anchor dredge, screened of large living and dead material through ½" mesh, diluted with seawater and mixed uniformly, allowed to settle in the benthic chambers with flowing seawater for five days prior to place in the pelagic tanks. Animal macrofauns (<1 mm) in the benthic chambers were counted at this time and any large organisms not found in the boxes due to sampling error were added in appropriate densities to each box. The seawater in the tanks was intermixed for three weeks before any experiments were performed.

The objectives for our first experiment were to (1) compare different variables in the microcosms to the field, and (2) to determine the persistence (as defined above) of the microcosms exposed to fixed (i.e., time independent) levels of domestic sewage (the disturbance). The sewage was collected locally in large volume, partitioned to 500 ml fractions and then frozen. The sewage was added, following the three week intermixing period, to the tanks initially at three concentrations, 0.01, 0.1 and 1.0%; control tanks received deionized water in proportions equal to the high sewage tanks. However, the amount of sewage added thereafter only took into account the 48 hour seawater additions, i.e., the simulated influx water volume. There were three replicates for each test condition and the control.

Some of the variables in the microcosms were measured continuously, others discretely. The latter were the structural descriptions for the benthos (macro- and meiofauna) and plankton. Specific size $(1-50\,^{\mu})$ frequency distributions of "particles" were made three times a week using a modified Coulter counter. Continuously measured variables in the water column were ATP, nutrients (NH3, NO3, NO2, PO4) and chlorophyll (in vivo fluorescence and extracted). Measures of ATP, S=, CO2, particulate organic carbon (POC), and trace metals in sediments, and POC, DOC, dissolved organic carbon (DOC), total organic nitrogen, total metabolism, nitrogen, and carbon fluxes in the pelagic phase are in progress. As a general comment, we have found that the methods for measuring ATP in the sediments and DOC, POC in the water column require close attention with respect to accuracy.

The species richness of our microcosms prior to sewage addition was representative of field levels using the above density criteria. The number of phytoplankton species ranged from 10-12. While we did not count the number of holo and meroplanktonic species at the start of the experiment, Martin (1964) averaged 19 such species during the early spring over a three year period in West Passage. The benthic macrofauna consisted of 10 species. The largest organism in the benthos was a polychaete worm, Nephtys, 4-5 cm in length. The meiofauna (<1 mm) and bacteria were not enumerated at this time.

We found a reasonable correspondence between the Bay and control ATP levels (Fig. 2), thus suggesting realism of our microcosms with respect to the pelagic bacteria and phytoplankton. The reason for the slightly higher ATP concentrations in the controls as compared to the Bay during the intermixing period (Table 2) is unknown; this relative difference remained, however, during the sewage exposure despite increases in Bay concentrations,

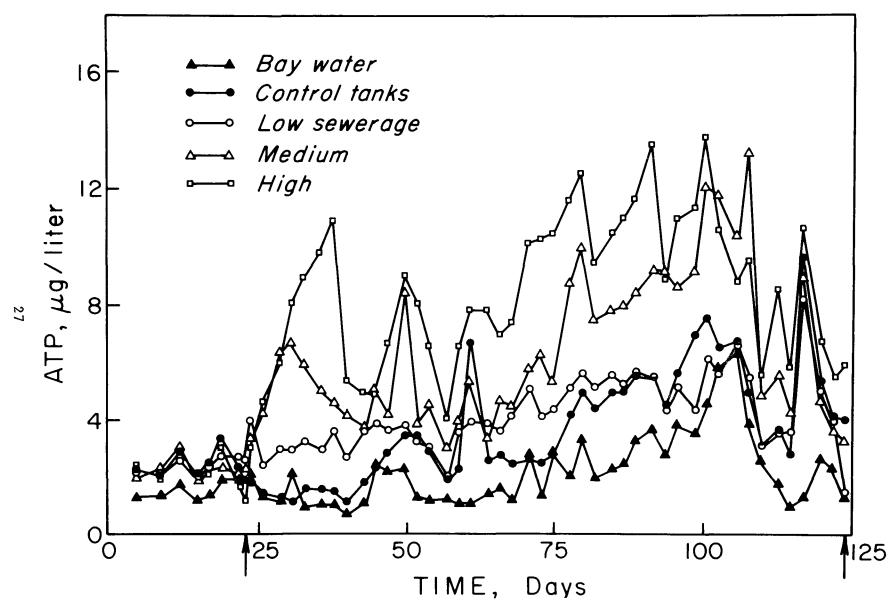


Figure 2. Mean pelagic ATP changes in Narragansett Bay and experimental microcosms prior to and during sewerage addition.

i.e., the controls appeared to follow the Bay but slight "constant" differences existed. Differences between the sewage tanks treated alike also existed. However, it was possible to detect significant (\approx = 0.05) nonlinear changes in ATP for all sewage levels over time. During the intermixing period all tanks had equal ATP concentrations. A direct relationship between ATP and sewage addition was observed most of the time following the intermixing period. Chlorophyll concentrations (Fig. 3) showed similar results although the differences between the Bay and the control tanks were greater.

TABLE 2. AVERAGE ATP CONCENTRATIONS (µgm/1) FOR NARRAGANSETT BAY (NB) AND LABORATORY MICROCOSMS PRIOR TO AND DURING EXPOSURE TO DOMESTIC SEWAGE

	"Intermi	xing period" (17 days)	Sewage e	xposure period	(98 days)
	\overline{x}	Sx	n	\overline{x}	$S\overline{x}$	n
NB control	1.54 2.52	0.135 0.178	5 7	2.27 3.71	0.200 0.309	42 43
0.01% sewage 0.1% sewage	2.40 2.31	0.119 0.114	, 7 7	4.26 6.46	0.194 0.410	43 43 43
1.00% sewage	2.40	0.168	7	8.39	0.334	43

The "sinks" for the high productivity in the pelagic phase were (1) the 48 hour losses (i.e., flushing) and (2) the benthos. After 98 days of sewage, the benthic communitites exposed to high sewage were characterized by high organic layers at the sediment surface (36.9 mgC/l) as compared to the controls (24.9 mgC/l). Polydora lignae, a polychaete worm, occurred in moderate density due perhaps to high sediment sulfide concentrations (a sulfide bacterium almost completely covered the surface). It should be noted that such a community was the result of organic loading and not low water column oxygen levels, since oxygen concentrations near or exceeding saturation (67-107%) of pelagic water was continuously circulated over the surface of the sediments. The benthic communities treated with intermediate sewage were dramatic; high densities of Polydora were immediately evident. densities of 20-30/cm² were found. Presumably, lower organic loads with lower sediment anaerobiosis possibly either (1) provided "optimal" conditions for Polydora to dominate and/or (2) excluded competitors and/or predators. The real contrasts to the high and intermediate sewage levels were found in the control and low sewage tanks. Almost no Polydora were present (1 tube/ cm²) in the control and low sewage tanks, but rather the initially stocked community represented by Nephytys and Yoldia. As a result of these findings, cursory surveys of the benthos along a sewage gradient were made in Narragansett Bay. Areas suspected of high pollution were devoid of most living material in the sediments. However, in slightly polluted areas densities (5-25 tubes/cm²) of Polydora similar to that found in our intermediate sewage microcosms were observed. Unpolluted locations showed benthic communities similar to that of the control tanks with Polydora at very low densities

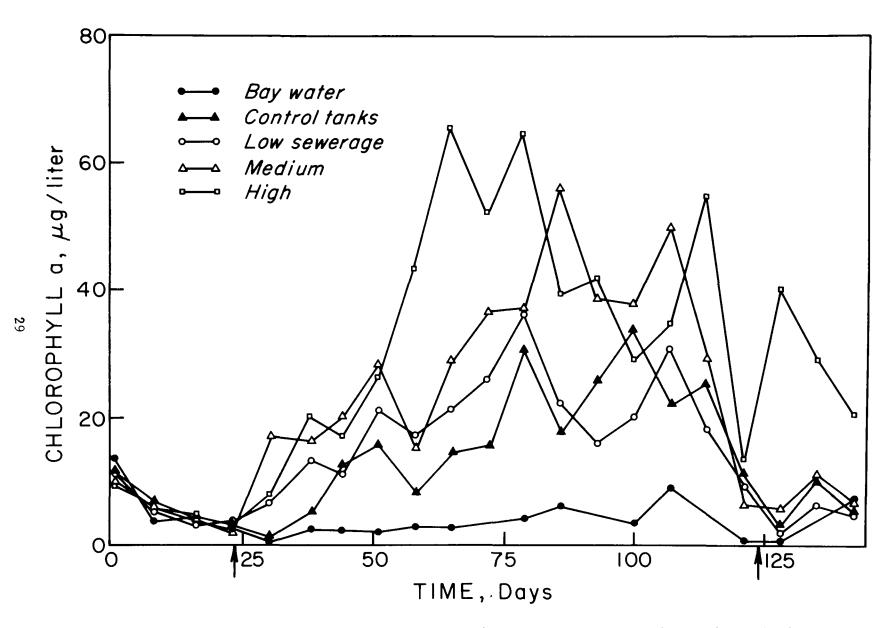


Figure 3. Mean pelagic chlorophyll \underline{a} changes in Narragansett Bay and experimental microcosms prior to and during sewerage addition.

 $(0-1 \text{ tube/cm}^2)$. This preliminary result suggests that the laboratory simulation of this marine system is somewhat realistic. Field determinations of nutrient and organic loading and its relationship to benthic communities is required before any further conclusions are made.

The main objective of this study is yet to come. Systems changes, as described above, have occurred as a result of the disturbances applied. The question now is, will the disturbed systems return to the structural and functional state of the "control" systems once the sewage input is relaxed? If so, then what is the time course? -- weeks, months, years? We will continue to monitor the systems and follow their recovery since the recent cessation of sewage.

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Criteria for Marine Microbiota

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INTRODUCTION

The examination of estuarine and coastal waters for microbial indicators of quality can be and, in some instances, already is important in assessing the ecological and human health impact of industrial, agricultural and sanitary pollutants discharged therein. Such pollutants may affect microbial activities in marine ecosystems in a number of ways. Toxic organic and inorganic chemicals can destroy those microorganisms responsible for essential biological transformations such as mineralization, nitrification, etc. or those which act as food sources for higher life forms. Nutrients discharged into the water from sewage or industrial wastes or man-induced changes in the physical environment may permit the multiplication of pathogens for fish or other marine fauna. On the other hand, toxicants and changes in the physical conditions may affect the susceptibility of the fauna to microbial infection and disease. The activities of marine microorganisms themselves are important in that some species degrade pollutants such as pesticides, detergents and other organic molecules, some accumulate pollutants and pass them up through the food chain, and some activate certain chemicals to more toxic forms, i.e., methyl mercury.

Unfortunately, in most of the interactions noted above, the relation-ships among the pollutant, the adverse ecological effect and some microbial indicator thereof have not been quantified sufficiently; and, hence, microbial guidelines and standards are not available. This, of course, is understandable because of the complex interrelationship involved.

Pollution associated effects on human health are more amenable to quantification. There are a number of microbial pathogens of man which can be discharged into receiving waters via fecal wastes or which can multiply therein under the influence of nutrient pollution. However, in terms of microbial activity, there is only one target species (man), two routes of transmission (recreational use of marine waters and consumption of marine biota as food), and two basic processes (infectious disease and bionitoxication). The above factors notwithstanding, a major constraint in quantifying health effects and modeling dose-response relationships stems from the logistic and ethical restrictions placed on studying the target species, man.

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Because of the above considerations, the directness and immediacy of the impact on man via his health and well being, and man's egocentricity as a species, it is not surprising that human health effects guidelines and standards for water quality generally have antedated those for ecological effects by a number of years. Furthermore, it is both understandable and defendable that such microbial guidelines and standards have been set forth based upon a limited quantity of epidemiological data. The reality is that the construction of waste disposal systems will continue and that receiving water criteria are needed so that they may be translated into effluent guidelines and standards, including the degree of treatment required, the siting of sewage outfalls, and the locating of sludge disposal areas.

As used in the studies to be described, a health effects, recreational water quality criterion may be defined as a scientific or objective requirement of a condition to be fulfilled for the protection and promotion of the health and safety of the public. It is a set of facts or data upon which a decision or judgement may be based. Many such criteria are developed through intensive and extensive epidemiological studies^{1,2}. The criteria may be used in two ways. They can be extrapolated into guidelines and standards for posting or closing beaches as "unsafe" for use. A more desirable use of the criteria, since it increases rather than decreases the available resource, is their translation into effluent guidelines and standards as noted above.

Figure 1 is a graphic representation of the health effects, recreational water quality criteria as defined above. It is a slightly modified version of that described by Cabelli and McCabe³. The salient point is that a criterion is expressed as a quantitative relationship between some index of health effects among swimmers to some measure of the quality of the water. Once an "acceptable risk" is determined, an appropriate guideline can be extrapolated from the criterion. The setting of an "acceptable risk" has social and economic implications as well as the health effects input inherent to the criterion. Therefore, the two translations may, and probably will, have different "acceptable risk" levels and, hence, different guidelines and standards.

Existing criteria, guidelines, and standards at the local, state and national level have been reviewed elsewhere as have the data base required for their development, the types of experimentation or observation which can be used to produce the data, available information, and the shortcomings of this information^{2,5}. As of 1969 when the present study was designed or even 1972 when it was initiated, the available epidemiological data came primarily from Stevenson's prospective studies⁶, Moore's restrospective study⁷ and some scattered case reports^{8,9}. The analysis of a recreation associated outbreak of shigellosis along the Mississippi River below Dubuque, Iowa¹⁰ provided some additional data. For a number of reasons none of these studies individually or together provided the totality of the required epidemiological and microbiological data.

The United States Environmental Protection Agency has responded to the need for additional data by a long term epidemiological-microbiological program whose objective is to define the relationships noted earlier. The overall program calls for (1) a three year study at selected New York City beaches to define the relationships (including a pretest of the epidemiological and microbiological methods), (2) trials at some "subtropical"

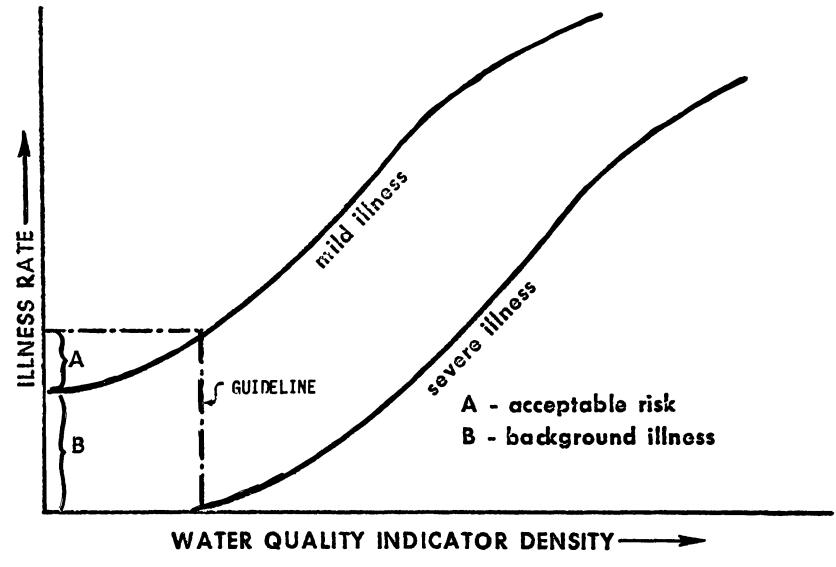


Figure 1. Graphical illustration of health effects water quality criteria and their extrapolation to guidelines.

location to examine the variable of climate, (3) the development of a mathematical model (the regression line and confidence limits of the relationship described in Figure 1), and (4) spot testing of the model at a number of geographically distinct sites. The findings to be presented summarize the data obtained during the first two years of the program.

EXPERIMENTAL DESIGN

The study being conducted at the New York City beaches is a prospective epidemiological investigation in which (1) the potential participants (primarily family groups) are approached at the beach in the course of weekend trials, and individuals who swim in the midweeks immediately before and after a trial are eliminated from the study, (2) swimming is rigorously defined as significant exposure of the head and face to the water, (3) measurements for a number of potential water quality indicators are made during the course of the trials at the test beaches, and (4) follow-up information concerning symptomatology and demography is solicited by phone some 8-10 days after a trial (Table 1). The experimental design and the rationale for its

TABLE 1. SEQUENCE OF EVENTS FOR EPIDEMIOLOGICAL-MICROBIOLOGICAL TRIALS

Day of Week	Day Number	Activity	Function
Saturday	1	(Beach Interview, Water Sampling)	(a) Obtain name,address, phone, etc.
		Sallip (1119)	(b) Reject pretrial midweek swimmers
			(c) Query on beach activity
			(d) Assay of water samples
Sunday	2	(Beach Interview, Water Sampling)	As Above
Monday	3	Reminder Letter	(a) Provide name of physician
			(b) Reminder to note illness
Monday	10	Phone or mail Interview	(a) Obtain illness information
			(b) Reject post-trial midweek swimmers
			(c) Obtain demographic information

use have been described elsewhere 5 . In the first two years of the New York study two sites (beaches) were used. The first beach, located at Coney Island around 22-24th Street (Figure 2), was designated as "barely acceptable" (BA) and was the most polluted beach available which was not posted as unsafe for swimming. The second, located at Arverne or Riis Park at the Rockaways, was designated as "relatively unpolluted" (RU) and was the least polluted beach available at which the populations were demographically similar to the BA beach. Thereby, attack rates for symptoms, symptom groups (i.e., gastrointestinal, respiratory, "other") and a "severity index" (stayed home, stayed in bed, sought medical advice) was obtained for the four groups (swimmers and nonswimmers at both beaches) and for the various demographic subgroups (sex, age, ethnicity, socioeconomic status). The symptoms for which information was solicited are given in Table 2. The soliciting of health effects information in the context of symptoms rather than specific disease is consistent with the first basic tenant of the experimental design, i.e., there would be no prejudgement as to which diseases were "important" in the context of swimming associated health effects.

TABLE 2. SYMPTOMS FOR WHICH QUERIES WERE MADE

<u>Gastrointestinal</u>

Vomiting Diarrhea Stomachache Nausea

"Other"

Fever (>100°C) Headache (more than few hours) Backache

General

Sunburn Skin rash, itching skin Red, itchy. or watery eyes

Respiratory

Sore throat
Bad cough
Chest cold
Runny or stuffed nose
Earache or runny ears
Sneezing, wheezing, tightness
in chest

"Severity" Index

Home because of symptoms
In bed because of symptoms
Medical help because of symptoms

The second tenant of the study was that the "correct" indicator would be treated as an unknown; this required density measurements and, at times, the development of enumeration methods for a number of potential water quality indicators. Water samples, used to obtain the density measurements, were collected at "chest level" from two sites at each beach about every two hours during the period of maximum swimming (11:00 a.m. to 5:00 p.m.). A number of potential indicators are listed in Table 3 along with designations as to those for which measurements have or will be made. A review of potential health effects water quality indicators and the methods used for

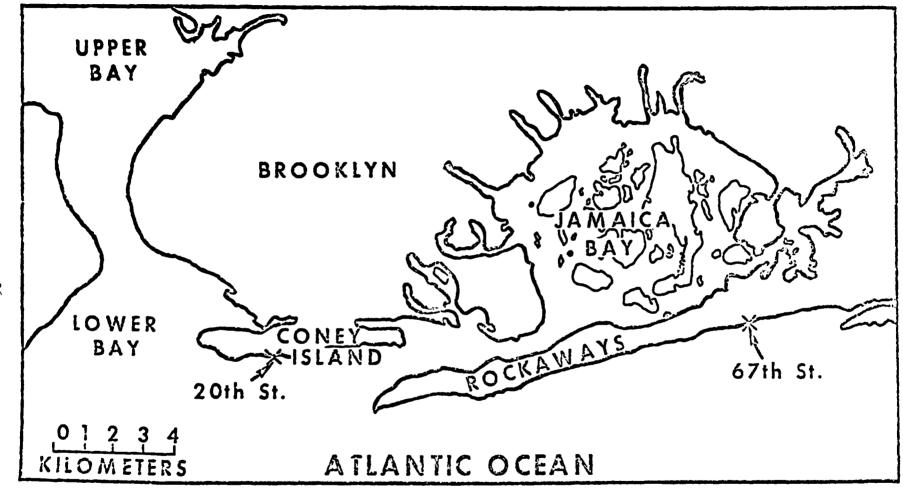


Figure 2. Test beaches at Coney Island ("barely acceptable") and the Rockaways ("relatively unpolluted") in New York City.

their enumeration is beyond the scope of this report. This has been done by Bonde 11 . Such a review, including usage rationales is being prepared for publication. Papers describing the enumerative methods used in or developed for this program have been published $^{12-17}$, and others are in preparation.

TABLE 3. POTENTIAL HEALTH EFFECTS WATER QUALITY INDICATORS

Indicator	Status	Indicator	Status
Total Coliforms	a	Enteroviruses	d
Fecal Coliforms	a	Coliphage	С
E. coli	a	Salmonella	
Klebsiella	a	Shigella	d
Enterobacter- Citrobacter	a	P. aeruginosaA. hydrophila	a a
Enterococci	a		
C. perfringens	b	V. parahemolyticus	b
C. albicans	С		
Bifidobcateria	С		

a - examined in 1973 and 1974

RESULTS

The pretest (Phase I) trials conducted during the summer of 1973 confirmed the applicability of the epidemiological and microbiological methodology 5. Although the study population contained only 1300 individuals, a statistically significant increase in the rate of gastrointentinal (GI) symptoms for swimmers relative to nonswimmers was observed at the "barely acceptable" but not the "relatively unpolluted" beach (Table 4). Cochran's chi square method as descrived by Fleiss 18 was used for the statistical analysis. Increases in respiratory, "other" and "severe" symptoms also were obtained at the Coney Island beach, but these were not statistically significant at the P=0.05 level. With the exception of respiratory symptoms, smaller increases (swimmer minus nonswimmer) were obtained at the Rockaways beach. The microbiological findings were described previously 5.

b - examined in 1974

c - to be examined in 1975

d - may be examined in future

e - examined in 1973, discontinued

TABLE 4. SYMPTOM RATES BY CATEGORY FOR 1973

	Symptom Rate in Percent at					
Symptom Type	Con S	ey Islam NS	nd Δ	Roo S	ckaways NS	Δ
	474	167		484	197	
Resp.	12.9	10.2	2.7	18.0 ^{a,b}	11.7	6.3
GI	7.2 a	2.4	4.8	8.1	4.6	3.5
Other	9.9	6.6	3.3	9.1	8.6	0.5
"Severe"	5.9	4.2	1.7	6.0	5.6	0.4

aSignificantly (P = 0.05) higher than nonswimmers.

S-Swimmers; NS-nonswimmers; Δ -difference; Resp.-respiratory; GI-gastro-intestinal; Other-general symptoms; "Severe"-stayed home, stayed in bed or sought medical help.

The 1974 findings (Table 5) essentially confirmed the 1973 results.

TABLE 5. SYMPTOM RATES BY CATEGORY FOR 1974.

	Symptom Rate in Percent at					
Symptom Type	Co S	ney Isla NS	and ∆	S	Rockaways NS	δ Δ
	1961	1185		2767	2156	
Resp.	7.2	6.4	0.8	8.3	7.8	0.5
GI	4.2 ^a	2.6	1.6	3.9	3.5	0.4
Other	7.3	6.7	0.6	8.6	7.7	0.9
"Severe"	3.8	2.9	0.9	3.0	2.6	0.4

^aSignificantly (P=0.05) higher than nonswimmers.

 $^{^{}b}$ Significantly (P = 0.05) higher than other beach.

^bSignificantly (P=0.05) higher than other beach.

S-Swimmers; NS-nonswimmers; Δ -Difference; Resp.-respiratory; GI-gastro-intestinal; Other-general symptoms; "Severe"-stayed home, stayed in bed or sought medical help.

Although the differential rates for most of the symptom categories were lower in 1974, because of the larger study population a statistically significant increase in the rate of GI symptoms among swimmers relative to nonswimmers again was obtained at the "barely acceptable" beach. In addition, the most sensitive portions of the Coney Island population were identified as children, Latin Americans and low to middle socioeconomic status individuals. Finally, the validity of the responses obtained as to gastrointestinal symptomatology was examined by calculating the rates of those symptoms considered highly reliable (all instances of vomiting; diarrhea only when "severe" or with fever; stomachache and nausea only with an accompanying fever) for each of the subgroups and comparing these to overall GI rates for the corresponding groups. The trends, and in most cases the statistical significance, were comparable. These findings were important in demonstrating that certain differences probably were not spurious, in confirming the acceptability of the methodology, and in identifying the sensitive portions of the population for future studies. In addition, there are aspects and implications of the data relating the health effects of swimming per se, year to year variability in the nonswimming ("Background") rates of gastrointestinal symptomatology, and demographic differences in reporting symptoms which will be considered in a later publication. However, this type of analysis does not speak to the overall objective of the program, that is, defining the relationship or association of health effects to water quality indicators as described in Figure 1.

In the context of the present experimental design, the data can be analyzed to yield the criteria in two ways. It can be obtained from regression analysis of the data obtained during a given summer by considering the symptom rates and the corresponding indicator densities for each trial (day) as a single point on the line; in this instance, one capitalizes on temporal (day to day) and spacial (distance) variability in pollution levels reaching the beaches. The second approach is to analyze the data across summers. Thereby, the overall symptom rates and associated indicator densities for all the trials at each beach during a given summer are combined to yield a single data point.

Correlation coefficients for the differential rate of gastrointestinal symptoms against the various water quality indicators were obtained from the 1974 data as shown in Table 6. The regression lines for \underline{E} . \underline{coli} , $\underline{Klebsiella}$ and fecal coliforms, the indicators with the highest correlation coefficient, are shown in Figure 3. Another set of regression lines should be obtained from the 1975 data.

When the data were examined across summers, four points were obtained for each indicator (Figure 4). Since an additional two points should be obtained from the 1975 trials, a statistical analysis was not attempted. However, inspection alone confirms the close relationship of GI symptomatology to \underline{E} . \underline{coli} densities, although fecal streptococci, $\underline{Klebsiella}$ and $\underline{Aeromonas}$ $\underline{hydrophila}$ also produced close fitting lines. The regression lines for both total and "severe" GI symptoms against \underline{E} . \underline{coli} densities are shown in Figure 5. It is of interest that the " \underline{E} . \underline{coli} lines obtained by both methods of analysis were quite similar; the differential rates for total GI symptoms associated with mean \underline{E} . \underline{coli} densities of 200/100 ml were 3.8 and 3.6%.

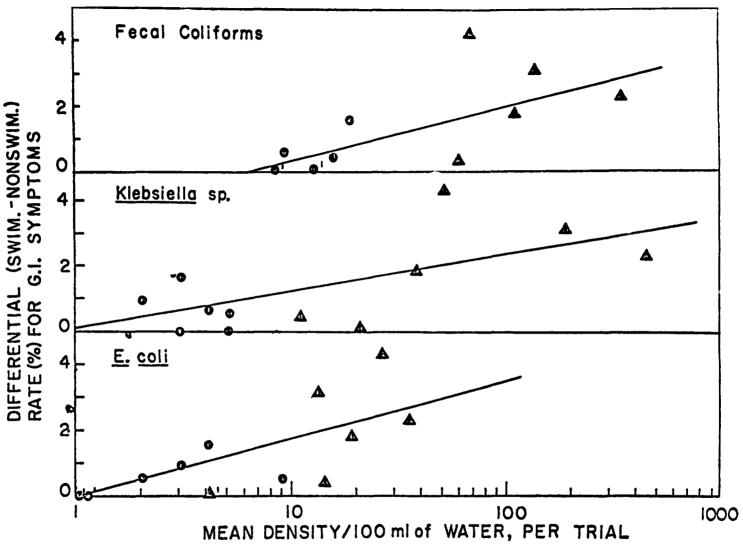


Figure 3. Relationship of the differential rate of gastrointestinal symptoms (swimmers minus nonswimmers) to the mean density of the water quality indicators as obtained from the trial by trial analysis of 1974 data. The lines were drawn from a least squares analysis. The three regression lines are for the three indicators which gave the best correlation coefficients: E. coli, 0.771; fecal coliforms, 0.673; Klebsiella, 0.664; Reconey Island.

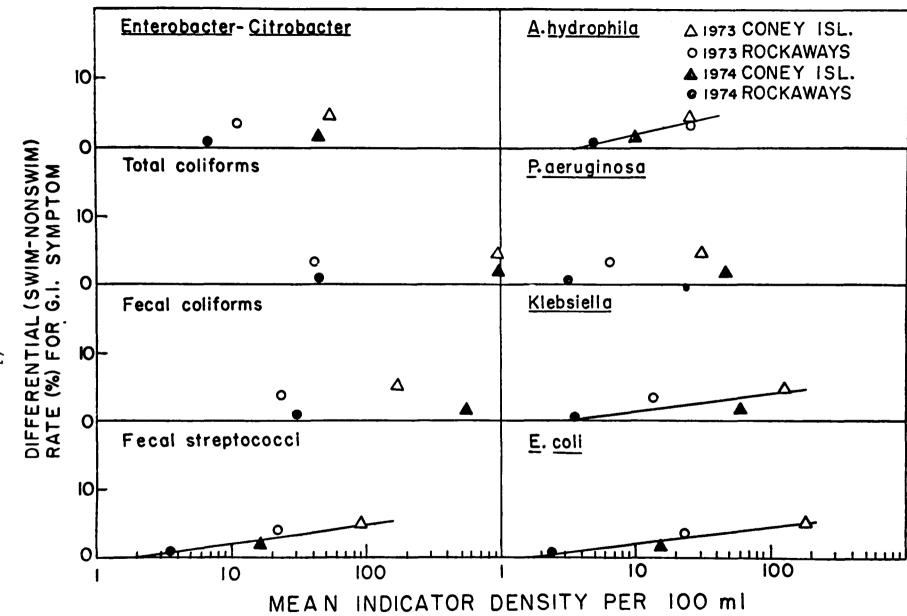


Figure 4. Relationship of the differential rate of gastrointestinal symptomatology to indicators densities as obtained from the analysis of 1973 and 1974 data. Each point represents the overall GI symptom rate and mean indicator density for all the trials conducted at the beach during that summer.

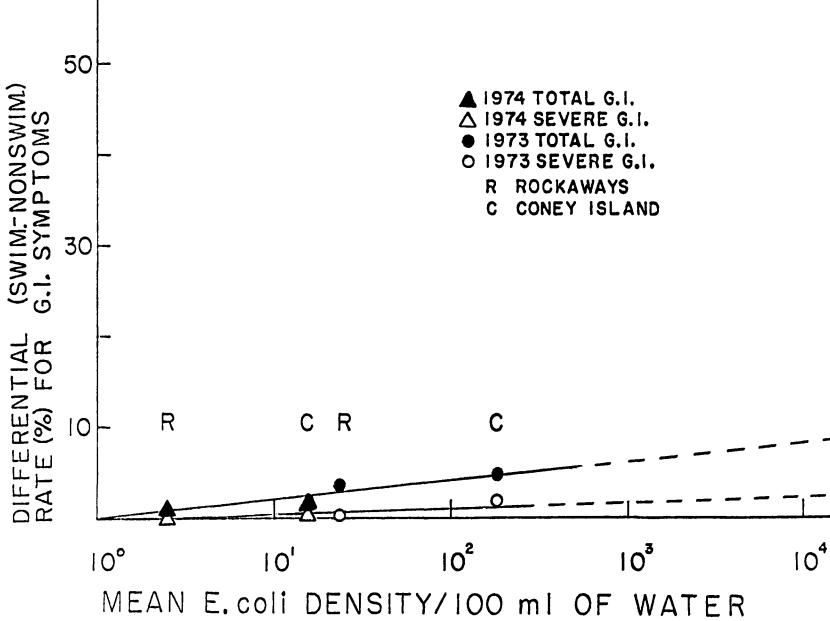


Figure 5. Differential rates for total and "relatively severe" gastrointestinal symptoms in relation to the mean \underline{E} . \underline{coli} density as obtained from 1973 and 1974 data.

TABLE 6. RELATIONSHIP OF INDICATOR DENSITY TO THE DIFFERENTIAL (SWIM-NON-SWIM) ATTACK RATE FOR GASTROINTESTINAL SYMPTOMS (1974)*

Indicator	Correlation Coeff.(r)
E. coli	0.711
Klebsiella	0.664
Fecal Coliforms	0.673
Total coliforms	0.549
Fecal streptococci	0.453
Pseudomonas aeruginosa	0.191

^{*}Obtained from six trials at Coney Island (BA) and Rockaways (RU) beaches.

The high attack rate of 3-4% above background (nonswimmers) appears to be somewhat disturbing. However, it must be borne in mind that the individuals in question neither died or required hospitalization. In all probability most of these cases would not have been reported to public health authorities except in an "outbreak" situation. Nevertheless, they do represent a measureable and, hopefully, predictable health effect whose economic and social import must be considered in setting an "acceptable risk". As noted previously, additional data should be forthcoming from trials being conducted at the New York City beaches during the summer of 1975 and at a "subtropical" site the following year. Therefore, a complete statistical analysis of the health effects vs indicator data obtained to date was not attempted; and the information to follow is meant to be descriptive and indicative of the relationships which can be expected.

The overall program to develop health effects recreational water quality criteria is far from complete. However, the data obtained thus far are quite encouraging. E. coli and fecal streptococci appear to be the best indicators examined thus far; and, if the data being obtained this summer are consistant with the findings to date, interim criteria should be available in 1976. "Subtropical" site selection is in progress; and the nature of the model is envisioned, that is, the regression line of GI symptomatology vs E. coli or fecal streptococci densities and the confidence limits around the line.

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Impact of Chlorination Processes On Marine Ecosystems

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ABSTRACT

The use of chlorine as a disinfectant and antifouling agent is reviewed. Chemical reactions of chlorine in aquatic environments are discussed, with particular emphasis on the formation of halogenated organic constituents in freshwater and marine systems. Studies of the effect of chlorinated sewage effluents and cooling water from generating stations on marine organisms and ecosystems are summarized.

INTRODUCTION

Chlorine gas has been used as an industrial bleaching agent since 1800 and has become one of the most versatile chemicals known. In freshwater it is used in drinking and recreational water as a disinfection agent, a biocide for slime and fouling control, and in the treatment of municipal wastes to control pathogens. In these applications, vast quantities of chlorine are used, and find their way into natural ecosystems. The toxicity desired in disinfection and biocide applications can continue on with undesirable effects on wildlife and the environment. Recent detection of halogenated organics in the drinking water of 80 cities underscores the need for responsible assessment of the management and effects of our chlorination processes, and the environmental costs incurred.

Some of the most accurate statistics on the rate of chlorine use exist for the State of Maryland. Chlorine discharge from Maryland into the Chesapeake Bay is presently estimated to be 1.1 x 10^{10} g/yr from municipal sewage treatment plants and 0.1 x 10^{10} g/yr from power generating facilities (Block and Helz, 1975). It is estimated (but still to be confirmed experimentally) that 1 percent of these totals may become halogenated organic compounds which would persist in the environment (Jolley, 1973). Thirty-three other states border marine ecosystems where some form of chlorine discharge currently persists.

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The purpose of this paper is to compile the scarce data presently available for chlorine effects upon aquatic life relevant to estuarine and marine ecosystems. The chemistry of chlorine is briefly reviewed to point out some of the unique features of chlorination in marine waters. Although some data exist on the effects or residual chlorine and a limited number of by-products upon specific organisms, virtually no information is available on transport processes, persistence, bioaccumulation, and the fate of halogenated compounds from chlorination processes.

CHEMISTRY OF CHLORINE

Chlorine is presently manufactured by a variety of methods, including: the electrolysis of brine,

$$2NaC1 + 2H_2O + \frac{electric\ current}{} 2NaOH + Cl_2 + H_2$$

the salt process,

$$3NaC1 + 4HNO_3 \longrightarrow 3NaNO_3 + Cl_2 + NOC1 + 2H_2O$$

and the hydrochloric acid oxidation process,

$$4HC1 + 0_2 \xrightarrow{450-650^{\circ}C} 2C1_2 + 2H_20.$$

CHLORINE IN FRESHWATER SYSTEMS

Chlorine gas dissolves rapidly in water and hydrolyses,

$$C1_2 + H_20 \longleftrightarrow HOC1 + H^+ + C1^-$$
.

This hydrolysis is nearly complete and only when the pH is below 3.0, or the chlorine concentration over 1000 mg/l is there any measurable quantity of molecular chlorine present. The oxidizing capacity of chlorine is retained in the hydrolysis product, hypochlorous acid. Hypochlorous acid dissociates to form,

$$HOC1 \longleftrightarrow H^{+} + C10^{-}$$

This reaction is pH dependent. For a neutral pH (7.0) at 20° C, the equilibrium is approximately 75 percent HOCl and 25 percent ClO⁻. For a pH of 8.0, the reverse is true with approximately 25 percent HOCl and 75 percent ClO⁻ (Sawyer and McCarty, 1969).

The addition of hypochlorite salts to water forms hypochlorite ions followed by hypochlorous acid,

Ca
$$(C10)_2 = Ca^{++} + 2 C10^{-},$$

 $H^{+} + C10^{-} \longleftrightarrow H0C1.$

and

If ammonia or organic amines are present in the water, they will react with hypochlorous acid to form

chloramines,

$$NH_3 + HOC1 = NH_2C1 + H_2O.$$

Like the ionization of hypochlorous acid to $\mathrm{H}^++\mathrm{ClO}^-$, the reaction rate between ammonia and hypochlorous acid is pH dependent, occurring most rapidly in solutions with a pH of 8.3. This reaction is also dependent upon temperature and the ratio of ammonia to hypochlorous acid.

Monochloramines react with hypochlorous acid to form di- and tri-chloramines,

$$NH2C1 + H0C1 = NHC12 + H20$$
,

and

 $2NH_2C1 + HOC1 = NC1_3 + H_20.$

Low pH favors a shift in equilibrium toward the formation of di- and tri-chloramines. Fair et al. (1948) determined that at pH 5.0, the ratio was 16 percent monochloramine and 84 percent dichloramine. For a pH of 8.0, the ratio was 85 percent monochloramine and 15 percent dichloramine. Tri-chloramine is found in significant quantities only at pH values of less than 4 (McKee and Wolf, 1963).

Ingols et al. (1953) determined that hypochlorous acid and monochloramine in freshwater will react with various organic constituents. Some of these reactions resulted in the formation of organic monochloramines although none were persistent (Table 1). The formation of chlorinated organic

TABLE 1. SUMMARY OF REACTIONS OF CHLORINE WITH ORGANIC COMPOUNDS IN FRESHWATER (MODIFIED FROM INGOLS ET AL. 1953)

Organic Substrate	Hypochlorous Acid	Monochloramine
Alanine	Pyruvic Acid	Organic Monochloramine
Cysteine	RS0 ₃ H	RSSR
Glycylglycine	0xidative	w
Glycylglycylglycine	Hydrolysis and Deaminization	Terminal Organic Monochloramine
Tyrosine	Ketone	Organic Monochloramine
Hemin	Violent Change	Irreversible Addition or Oxidation

compounds during chlorination of sewage effluents and power plant cooling waters has recently been documented (Jolley, 1973; Jolley et al. 1975). Isotopic ³⁶Cl tracers and high-resolution anion-exchange chromatography were used to separate over 50 chlorine containing constituents from chlorinated secondary effluents. Seventeen of these were tentatively identified and quantified (Table 2).

TABLE 2. TENTATIVE IDENTIFICATIONS AND CONCENTRATIONS OF CHLORINE CONTAINING CONSTITUENTS FROM CHLORINATED SEWAGE EFFLUENTS (MODIFIED FROM JOLLEY, 1973)

Identification	Conc. of Organic Compound µg/l
5-Chlorouracil 5-Chlorouridine 8-Chlorocaffeine 6-Chloroguanine 8-Chloroxanthine 2-Chlorobenzoic Acid 5-Chlorosalicylic Acid 4-Chloromandelic Acid 2-Chlorophenol 4-Chlorophenylacetic Acid 4-Chlorobenzoic Acid 4-Chlorobenzoic Acid 4-Chlorophenol 4-Chlorophenol 4-Chlororesorcinol 3-Chloro-4-Hydroxybenzoic Acid 4-Chloro-3-Methyl Phenol	4.3 1.7 1.7 0.9 1.5 0.26 0.24 1.1 1.7 0.38 0.62 0.69 1.2 1.3
4-Chioro-3-Methyi Phenoi	1.5

CHLORINE IN MARINE SYSTEMS

Major sources of chlorine contamination in the marine environment are related to postchlorination of secondary sewage effluents with outfalls located on coastal and estuarine waters, and chlorination of seawater used for cooling of thermal electric generating plants (White, 1972, 1973; Markowski, 1959).

The addition of chlorine to seawater results in a complex series of chemical reactions, the most obvious one frees bromine,

$$Cl_2 + 2Br^- = 2Cl^- + Br_2$$
.

This reaction goes to completion and is the basis for the manufacture of bromine from seawater (Lewis, 1966).

The industrial extraction of bromine from seawater requires that the pH be reduced below 3.0, so that molecular chlorine can release molecular

bromine. The hydrolysis products from adding chlorine to seawater, HOC1 and ClO, will also release bromine from the bromide ion in the form of hypobromous acid and hypobromite ion,

and
$$C10^- + Br^- = Br0^- + C1^-,$$
 $Br0^- + H^+ \xrightarrow{\longleftarrow} HOBr.$

Houghton (1946) has also suggested that chlorination of water containing free ammonia and bromine may result in the formation of bromamines. Johanneson (1958) added chlorinated water to a sodium-ammonium salts solution buffered to pH 8.3. This resulted in the formation of monobromamine and some monochloramine. The addition of sodium hypochlorite solution produced mostly monochloramine. The hypochlorite in solution apparently reacts with both the bromine and ammonia,

and
$$C10^{-} + Br^{-} = Br0^{-} + C1^{-},$$
 $C10^{-} + NH_{3} = NH_{2}C1 + OH^{-}.$

Injection of chlorine gas may result in localized acidity, favoring the first reaction above, which is rapid at pH values of less than 8.0. The second reaction is favored when chlorine is added as sodium hypochlorite since there is no accompnying reduction in the normal pH of 8.0-8.3.

When ammonia is present in seawater, it will react with hypobromous acid to form monobromamine. Monobromamine in turn will react with hypobromite ion to form dibromamine,

In addition, monobromamine at near neutral pH will form monobrom-ammonium which dissociates into ammonium ion and free bromine (Johanneson, 1960).

Block and Helz (1975) have prepared a reaction series model to illustrate the theoretical degradation processes occurring after the addition of chlorine to natural, saline waters (Figure 1). Compounds in each successive level can give rise to ones on a lower level. In general, compounds occurring on lower levels will not contribute to the formation of those in the levels above.

The reaction occurring between levels I and II is a result of chlorine decay from a diatomic gas to hypochlorous acid, hypochlorite ions and sodium hypochlorite. As pointed out by Moore (1951) and Lewis (1966), this reaction occurs rapidly and goes to completion within seconds after the addition of chlorine. The inclusion of sodium hypochlorite within level II is based on the results of work by Sugam and Helz (1975, unpublished manuscript).

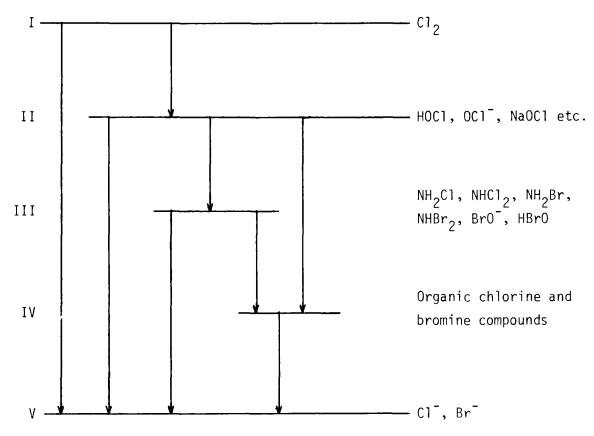


Figure 1. Degradation processes for chlorine in saline waters (modified from Block and Helz, in preparation)

The chemical composition and abundance of products formed from level II to level III is a function of physical and chemical parameters of the water including but not limited to temperature, pH, ammonia, and bromine, available as reaction components. In seawater it is possible that the predominant species would be bromamines, especially if NH₄ ions are less abundant than Br ions.

Level IV includes halogenated organic constituents which may be formed by level II or level III species, including chloramines, hypobromite and bromamines. The stable end products in level V occur through a diverse group of mechanisms taking place in steps I-IV.

Charge balance results in one atom of CI passing from level I to level V to each atom passing from level I to level II. Reduction of hypochlorite by Br or Fe²⁺ and Mn²⁺ may release CI from level II to level V. Movement of Cl from level III to level V can also occur in a number of ways, the most obvious, suggested by Laubusch (1971), involves the destruction of chloramines when the OCl $^{-}$ /NH4 ratio is large.

Some of the chlorinated organics identified by Jolley (1973) are persistent and the decay from level IV to level V is probably a slow process, relative to decay from levels I through III to level V.

TOXICITY OF CHLORINE IN ESTUARINE ENVIRONMENTS

The relative toxicity of chlorine in water is related to the amount and proportions of free and residual chlorine. Several investigators have found that free chlorine is generally more toxic to freshwater organisms than chloramines (Douderoff and Katz, 1950; Merkens, 1958), even though the toxicity of the various forms of chlorine were of the same order of magnitude. Rosenberger (1971) and Basch and Truchan (1973), found that dichloramine was more toxic than monochloramine in freshwater. A comprehensive review paper by Brungs (1973) summarizes the toxic effects of residual chlorine on freshwater aquatic organisms.

In seawater, Holland et al. (1960) determined that dichloramine is apparently more toxic than monochloramine and that the chloramines were more toxic than free chlorine. These findings may reflect the complex chlorine-bromine reaction kinetics suggested by Johanneson (1958, 1960) and Lewis (1966).

CHLORINE TOXICITY TO MARINE PHYTOPLANKTON

The effects of chlorination and thermal pollution on phytoplankton productivity have been investigated in some detail (Table 3). Carpenter et al. (1972) observed an 83 percent decrease in the productivity of phytoplankton passed through the cooling system of a nuclear generating plant on Long Island Sound.

TABLE 3. SUMMARY OF TOXIC EFFECTS OF CHLORINATED WASTES AND WATER ON MARINE PHYTOPLANKTON.

Species	Toxicant used	Measured residual chlorine mg/l	Duration of Test	Effect(s)	Reference
Phytoplankton	Cl ₂ injection	0.05-0.40	12 hrs + 4 hrs incu- bation	50-98% loss Of productivity	Carpenter et al. (1972)
Chlamydomona sp.	hypochlorite solution	0.69-12.9	5 min	Reduced growth rate	
Skeletonema costatum		0.18-2.4	5 min	None up to 0.29 mg/l; greater amounts inhibit- ed growth	Hirayama and Hirano (1970)
Phytoplankton	hypochlorite solution	0.32	2 min	55% decrease in ATP	Gentile et al. unpublished data
	201051011	0.01	45 min	77% decrease in ATP	(1972, 1973)
		0.075-0.25	24 hrs	50% decrease in growth	
Phytoplankton	Cl ₂ injection		15 min	91% reduction in photosynthesis	Hamilton et al. (1970)

Intake water was chlorinated at a rate of 1.2 mg/l with a residual of 0.4 mg/l measured at the discharge. Addition of 0.1 mg/l chlorine at the intake with nondetectable residuals at the outfall decreased productivity by 79 percent. Essentially no decreases in productivity were observed when phytoplankton passed through the cooling system without addition of chlorine. Hirayama and Hirano (1970) measured the effect of chlorination on the photosynthetic activity of Skeletonema costatum and found that cells were killed when subjected to 1.5 to 2.3 mg/l chlorine for 5 and 10 minutes.

Gentile (1972, 1973 unpublished data, National Marine Water Quality Laboratory, West Kingston, RI) observed a 55 percent decrease in the ATP content of marine phytoplankton exposed to 0.32 mg/l residual chlorine for two minutes and a 77 percent decrease after 45 minutes of exposure to chlorine concentrations as low as 0.01 mg/l. A 50 percent depression in the growth rates of 10 species of marine phytoplankton exposed to chlorine concentrations ranging from 0.075 to 0.25 mg/l for 24 hours was also measured.

Morgan and Stross (1969) used photosynthetic rates to evaluate the response of estuarine phytoplankton passed through the cooling system of a steam electric power station on the Patuxent River, Maryland. The photosynthetic rate increased with an 8°C rise in temperature when ambient water temperatures were 16°C or less. Inhibition occurred when ambient temperatures were above 20°C. In a related study, conducted at the same site, Hamilton et al. (1970) measured a 91 percent decrease in primary productivity during intermittent chlorination.

CHLORINE TOXICITY TO INVERTEBRATES

Muchmore and Epel (1973) investigated the effects of chlorination of was tewater on fertilization in marine invertebrates (Table 4). Unchlorinated sewage (from the Pacific Grove, California STP) was a weak inhibitor of fertilization in the sea urchin, Strongylocentrotus purpuratus. Exposure of gametes of the sea urchin to a 10 percent unchlorinated sewage-seawater mixture typically reduced fertilization success by 20 percent. A 0.5 percent dilution of moderately chlorinated sewage (11 mg/1 TRC undiluted) significantly reduced fertilization. It was also determined that chlorination had more effect on sperm cells than on eggs. Eggs incubated for 5 minutes in a 0.77 mg/l hypochlorite solution and subsequently washed to remove the hypochlorite showed no reduction in fertility. Incubation of sperm at a 0.07 mg/l hypochlorite concentration resulted in a loss of fertilization ability. This was attributed to a loss of sperm motility which was not restored after washing to remove the hypochlorite. Gametes of the echiuroid, Urechis caupo, and sperm of the annelid worm, Phragmatopoma californica, were not as sensitive to chlorine toxicity.

A number of power plant related studies have been conducted to determine the effect of chlorination of seawater on fouling organisms. Waugh (1964) observed no significant difference in the mortality of oyster larvae, Ostrea edulis, exposed to 5 mg/l chlorine for 3 minutes at ambient temperature, computed to control mortality. Exposure of larvae to thermal stress (10°C above ambient) and 10 mg/l chlorine for 6 to 48 minutes also had no significant effect on survival 64 hours after treatment. Barnacle

nauplii, Eliminius modestus, showed more acute sensitivity to chlorine. Residual chlorine concentrations in excess of 0.5 mg/l caused heavy mortality and reduced growth for survivors.

TABLE 4. SUMMARY OF TOXIC EFFECTS OF CHLORINATED WASTES AND WATER ON MARINE INVERTEBRATES

Species	Toxicant used	Measured residual chlorine mg/l	Duration of Test	Effect(s)	Reference
Strongylo- centrus purpuratus	chlorinated sewage effluents	0.02 0.11	5 min 5 min	None 100% inhibition of fertilization	Muchmore and Epel (1973)
(gametes)		0.03 0.13	5 min 5 min	None 99% inhibition of fertilization	
<u>Urechis</u>		0.2	5 min	22% inhibition	
(gametes)		1.0	5 min	of fertilization 100% inhibition of fertilization	
Phrogmatopoma		0.2	5 min	22% loss of	
(sperm)		1.0	5 min	motility 86% loss of motility	
Elminius	residual	2.0	10 min	Death and inhib-	Waugh (1964)
nodestus	chlorine	5.0	3 min	ited growth None	
Melita nitida	Cl ₂ injection	2.5	5 min 3 hrs 48 hrs 96 hrs	None 27% mortality 72% mortality 97% mortality	McLean (1972, 1973)
<u>Gammurus</u> <u>sp</u> .		2.5	3 hrs	25% mortality 96 hrs after exposure	
Bimaria franciscana		4.5	4 days	None	
Balanus sp. Acartia tonsi		2.5	5 min 5 min	80% mortality 90% mortality	
Anemones	residual chlorine	10.0	1, 2, 4, 8 hrs/day for 10 days	None	Turner et al. (1948)
		2.5 1.0	8 days 15 days	100% mortality 100% mortality	
Mussels		10.0	1, 2, 4, 8 hrs/day for 10 days	None	
		2.5 1.0	5 days 15 days	100% mortality 100% mortality	
Barnacles		10.0	1, 2, 4 hrs/ day for 10 days	95-100% mortality	
		2.5 1.0	4 days 7 days	100% mortality 100% mortality	
Mytilus edulis	Cl ₂ injection	0.02 0.05	A few hrs	Detachment and migration	James (1967)

McClean (1973) simulated the conditions encountered by marine organisms passing through a power plant on the Patuxent River, Maryland. Intake chlorination to 2.5 mg/l residual, entrainment for approximately 3 minutes and sustained exposure to elevated temperatures for up to 3 hours were used as experimental parameters. While barnacle larvae, Balanus sp. and copepods, Acartia tonsi, were not affected by a 3 hour temperature stress of 5.5 and 11°C above ambient; exposure to 2.5 mg/l residual chlorine for 5 minutes at ambient temperatures caused respective mortality rates of 80 and 90 percent. The amphipod, Melita nitida, and the grass shrimp, Palaemonetes pugio, showed a delayed death response after exposure to 2.5 mg/l TRC for 5 minutes. Near 100 percent mortality was observed for both species 96 hours after exposure to the chlorine residual. McLean (1972) showed that established colonies of the euryhaline colonial hydroid, Bimeria franciscana, were not greatly affected by 1 and 3 hours of exposure to 4.5 mg/l TRC.

Turner et al. (1948) determined that continuous treatment of seawater conduits with 0.25 mg/l chlorine prevented fouling during a 90 day interval when the flow velocity was 52 cm/second or less. Intermittent treatment with 10 mg/l residual chlorine for 8 hours a day was ineffective in preventing fouling by anemones, mussels and barnacles.

James (1967), working in Great Britain, observed that residual chlorine concentrations of 0.02 and 0.05 mg/l caused detachment and movement of mussels in the direction of water flow through an aquarium with eventual elimination of the mussels. He concluded that the most effective way to prevent fouling by mussels was not to kill, but to discourage settling in cooling water systems by continuous low level chlorination.

Markowski (1960) compared the occurrence of marine organisms on concrete slabs placed in the intake and outfall canals of an electric generating plant. Chlorine was injected into the condensors of this plant for two hours a day at a concentration between 1 and 2.5 mg/l. No vegetation was observed growing in the intake canal where dense animal populations occurred (predominantly invertebrates, Coelenterata and Polyzoa). The outfall canal contained a prolific growth of algae, Enteromorpha sp. but fewer invertebrates. Balanus improvisis, which was collected with some regularity from the intake canal was never observed in the outfall canal. The mollusk, Eubranchus sp. was more abundant on the intake slabs than in the outfall.

CHLORINE TOXICITY TO ESTUARINE FISH

Tsai (1968, 1970, 1975) has observed decreases in the abundance and occurrence of brackish water fish species in certain areas of the Upper and Little Patuxent Rivers receiving chlorinated sewage effluent. Tsai suggests that chlorinated sewage effluent may also block the upstream migration of such semi-anadromous species as the white catfish and white perch. He attributed the "blocking effect" to chlorination products rather than reduced dissolved oxygen or pH resulting from organic decomposition of the effluent (Table 5).

Tsai (1973) measured the diversity index of fish upstream and downstream of 98 sewage treatment plants in Virginia, Maryland and Pennsylvania. Sewage treatment plants were categorized as Type I engineering facilities (sludge

TABLE 5. SUMMARY OF TOXIC EFFECTS OF CHLORINATED WASTES AND WATER ON MARINE AND FRESHWATER FISHES

Species	Toxicant used	Measured residual chlorine mg/l	Duration of Test	Effect(s)	Reference
Cyprinus carpio eggs (Freshwater)	4-Chlororesor- cinol 5-Chlorouracil (0.001 mg/l)		3-7 days	Reduced hatch	Gehrs et al. (1974)
Freshwater and brackish fishes	chlorinated sewage effluents	0.6-2.0	Long-term	Decreased popn. size and diver- sity	Tsai (1968, 1970 1973)
L. xanthurus Morone sp. Pomatomus saltatrix C. regalis Brevoortia tyrannus	chlorinated sewage effluents	0.07-0.28	May-June, 1973	Probable kill 5-10 million fish	Virginia State Water Control Board (1974)
L. xanthurus	sodium hypo- chlorite	0.09 0.14 0. 28	96 hrs 24 hrs 6 hrs	50% mortality 50% mortality 50% mortality	Virginia Inst. Marine Science for VSWCB (1974)
0. nerka 0. gorbuscha (Freshwater)	chlorinated sewage effluents	0.02-0.026 0.16	24 hrs 72 hrs	100% mortality 100% mortality	Servizi and Martens (1974)
0. gorbuscha 0. tshawytscha	residual chlorine	0.5 0.5	80 min + 10°C 10 min + 10°C thermal shock	50% mortality 50% mortality	Stober and Hanson (1974)
Morone	residual	0.08	10 min	Avoidance	Meldrim et al.
americana Menidia	chlorine	0.08	10 min	Avoidance	(1974)
menidia F. hetero-		0.03	10 min	Avoidance	
Clitus Trinectes maculatus		0.03	10 min	Avoidance	
Pleuronectes platessa eggs	free chlorine?	0.04-0.08 0.70 0.12	8 days 72 hrs 96 hrs	None 50% mortality 50% mortality	Alderson (1972)
larvae		0.032 0.026	48 hrs 96 hrs	50% mortality 50% mortality	

activation, aeration, sedimentation and filtration) with effluent chlorination; Type II engineering facilities with chlorination and an effluent holding lagoon and Type III engineering facilities with a lagoon and effluent chlorination at the lagoon outlet. Reductions in the number of fish, number of species and the species diversity index were significant downstream of Type I and III plants. These reductions were attributed to total residual chlorine levels and turbidity. Diversity indices showed no significant changes in downstream areas associated with Type II plants.

Massive fish kills occurred on the James River, Virginia during May-June, 1973 (Virginia State Water Control Board, 1974). Species affected by the kill included spot, Leiostomus xanthurus; white perch, Morone americana; bluefish, Pomatomus saltatrix; grey seatrout, Cynoscion regalis and menhaden, Brevoortia tyrannus. A majority of the fish kill in the James River occurred adjacent to sewage treatment plants. Total residual chlorine (TRC) levels as high as 0.7 mg/l were observed in the James. Effluents from both plants showed more than 3.0 mg/l TRC.

Distress symptoms of fish dying included, spiral swimming patterns, broken vertebral columns, listless floating, inverted swimming, distension of the air bladder in some, loose body scales, mucous on the skin and hemorrhaging along the fins and body surface.

Live box tests conducted adjacent to the James River sewage treatment plant (STP) demonstrated a correlation between rates of effluent chlorination and mortality of juvenile spot and croaker. With an average daily chlorine feed of 1200 pounds (total flow of water was approximately 10 mgd during tests) and a measured residual chlorine level of 3.0 mg/l, caged fish suffered 100 percent mortality within 20 hours. After a cutback to a chlorine feed rate of approximately 400 pounds per day, only 20 percent mortality was observed among caged fish after 20 hours.

On-site aquaria tests confirmed the results of the cage tests. Water from an area adjacent to the outfall of the James River (STP) was pumped through aquaria containing juvenile spot. Mortalities ranged from 91 to 100 percent after 40-85 minutes of exposure prior to the cutback in chlorination. After chlorination rates were reduced, mortalities were 0-26 percent after 120 minutes of exposure.

Continuous flow laboratory bioassays were also conducted. The 96 hour LC50 for juvenile spot was estimated at 0.09 mg/l TRC. The estimated 24 hour LC50 was 0.14 mg/l and the 6 hour LC50, 0.28 mg/l TRC.

Separate field studies on the spot, <u>Leiostomus</u> <u>xanthurus</u>, found up to 40 percent of juveniles from the 1973 <u>year class</u> <u>exhibited</u> deformities in the vertebral column. These abnormal forms are identifiable as a distinct year class in 1975 population samples from the Chesapeake Bay, (Chao Labbish, personal communication).

A study of the effect of chlorinated sewage effluents on sockeye salmon, Onchorhynchus nerka, and pink salmon, O. gorbuscha, has been conducted by Servizi and Martens (1974). They used three study sites to conduct cage bioassays. The first, Site I, was adjacent to a primary treatment plant with effluents chlorinated following settling and discharged through a 600' pipe line directly into the receiving stream. Site II was on a stream receiving wastes from an activated sludge plant in which chlorinated effluents were discharged into a large effluent holding lagoon and retained for 30 to 60 days. Site III was located on a stream receiving effluents which were chlorinated as they left a non-aerated lagoon.

Measured chlorine residuals in the receiving stream at Site I ranged from 0.02-0.26 mg/l. These concentrations resulted in 100 percent mortality of caged sockeye fingerlings placed 30, 60 and 250 feet below the effluent discharge point. Additional tests indicated that the primary effluent without chlorination was also toxic. However, fish exposed to the unchlorinated effluent lived ten times longer than ones exposed when effluents were being chlorinated. Toxicity of the unchlorinated effluents was attributed to MBAS and ammonia.

Tests at Site II indicated that chlorinated effluents retained for 30 to 60 days were not toxic to sockeye fingerlings and alevins and pink salmon alevins after 26 days of exposure.

In tests at Site II, with fingerling sockeye salmon, chlorinated sewage effluents (measured TRC 0.85 mg/l) resulted in 50 percent mortality after 48 minutes. Fifty percent mortality occurred after 13 hours of exposure to the unchlorinated effluents. Sublethal exposures of fingerling sockeye salmon to the effluents from Site III (1-3 hours of exposure to 0.22 mg/l TRC) resulted in gill damage, including hyperplasia, swollen epithelial cells, and separation of epithelium from pillar cells.

The toxicity of chlorine and heat to pink, <u>Oncorhynchus gorbuscha</u>, and chinook salmon, <u>O. tshawytscha</u>, has been determined by Stober and Hanson (1974). Juveniles of each species were tested in seawater at five residual chlorine concentrations, ranging from 0.05-1.0 mg/l, and four temperatures from t $0\text{-}10^{\circ}\text{C}$. Salmon were exposed to each matrix for 7.5-60 minutes. A decrease in the tolerance of both species to residual chlorine was observed with increased temperature and exposure time. The most toxic effect was observed at a t of $9.9\text{-}10^{\circ}\text{C}$ where the LT₅₀ (lethal time for 50 percent mortality) ranged from approximately 10 minutes at 0.5 mg/l TRC for chinooks to 80 minutes for pinks.

Meldrim et al. (1974) in flowing water bioassays studied the effect of chemical pollutants on estuarine organisms. They found that white perch, Morone americana, consistently avoided TRC levels as low as 0.08 mg/l at temperatures from 7-17°C. Silversides, Menidia menidia, also avoided 0.08 mg/l TRC at temperatures from 8-28°C but showed a preference for 0.08 mg/l TRC when fish acclimated to 7°C were exposed at 12°C. Mummichogs, Fundulus heteroclitus, and hog chokers, Trinectes maculatus, avoided TRC levels as low as 0.03 mg/l.

Alderson (1972) found that the 48 and 96 hour Tl_m of free chlorine for plaice larvae, <u>Pleuronectes platessa</u>, was 0.032 and 0.026 mg/l respectively. Eggs were not affected when exposed to 0.075 and 0.04 mg/l free chlorine for 8 days, indicating that the egg membrane gives considerable protection over long periods. The 72 and 192 hour Tl_m for eggs was 0.7 and 0.12 mg/l TRC respectively.

Gehrs et al. (1974) tested the sensitivity of carp eggs, <u>Cyprinus carpio</u>, to two of the compounds identified by Jolley, 4-Chlororesorcinol and 5-Chlorouracil. Significant reductions in the hatchability of non-water hardened carp eggs were observed in concentrations of each compound as low as 0.001 mg/1.

In California, Young (1964) observed tumor-like sores around the mouth of white croakers, <u>Genyonemus lineatus</u>, collected near the Hyperion sewage outfall in Santa Monica Bay. While there was no direct evidence to link the occurrence of lesions with chlorinated sewage effluents, a general decline in fitness of croakers and other species found in close proximity to the outfall area was observed.

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Techniques to Assess the Effects of Toxic Organics on Marine Organisms

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ABSTRACT

Acute static or flow-through bioassays generally have been used to set marine water quality standards, but few new bioassay techniques are available to determine long-term effects of one or more toxicants on survival, growth and reproduction of individual species of mollusks, arthropods or fish and on communities of estuarine organisms. Not only has the duration of bioassays increased from 96 hours or less to periods of from one month to two years, but the complexity has increased as well. Effects of toxicants on the entire life-cycle of an oviparous estuarine fish, Cyprinodon variegatus, can now be studied; one bioassay with endrin has been completed. This fish typically develops from an embryo to maturity in 10 weeks, with about 70% survival overall. Females produce an average of eight eggs per day and fertilization success exceeds 90%. Effects of a polychlorinated biphenyl, Aroclo 1254, and a pesticide, toxaphene, on developing communities of estuarine animals have been investigated. These studies provide data for prediction of pollutioninduced shifts in composition of estuarine animal communities.

INTRODUCTION

Bioassays are probably the most useful technique available to the biologist for predicting the potential hazard of a chemical. Bioassays vary considerably in complexity and utility and each procedure has its own particular advantages and disadvantages. They range from relatively simple acute static and flow-through bioassays, to complex chronic entire life cycle and community bioassays. Flow-through acute bioassays usually provide a more sensitive measure of stress than do static bioassays whereas entire life cycle and community bioassays provide a better estimate of "safe" concentrations from which water quality criteria can be derived.

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In spite of the importance of developing sound marine water quality criteria to protect aquatic life, the quantity and quality of sound research aimed at evaluating effects is limited. Results of a recent survey conducted by the Water Quality Committee of the American Fisheries Society indicated that the funds and manpower spend on research to develop water quality criteria were comparatively small and that bioassays were of short duration and predominantly used freshwater fishes. The Committee on Water Quality Criteria of the National Research Council summarized marine bioassay data for a total of 70 organic chemicals in Table 6, pages 484 to 508 of the Blue Book, 1972 (NAS-NAE Committee on Water Quality Criteria, 1972). A summary of this appendix (Table 1) helps to quantify the findings of the American Fisheries Society Committee. All of the 317 experiments with phytoplanters were static tests. Of the 332 experiments with estuarine animals only 12 percent were flowing water bioassays, only 16 percent included statistical treatment and few received chemical analyses to determine the actual concentration of the chemical in the test water. Significantly, less than two percent of all of these bioassays upon which water quality criteria may be recommended were dynamic tests lasting longer than 96 hours and no tests were on a complete life cycle of an animal or on communities of organisms.

TABLE 1. BIOASSAY METHODS USED TO OBTAIN TOXICITY DATA ON THE EFFECTS OF ORGANIC CHEMICALS ON MARINE ORGANISMS AS REPORTED IN APPENDIX III, TABLE 6, P. 484-590 OF "WATER QUALITY CRITERIA," 1972 - THE BLUE BOOK

Organism		Kinds and Numbe	ers of Bioassays	
	Sta	tic	Dynam	1 i C
	<96 hrs.	<96 hrs.	<96 hrs.	<96 hrs.
Plants Animals	37 290	280 53	0 29	0 13
Totals	327	333	29	13

The purpose of this paper is to describe some recent improvements in bioassay procedures used at the Gulf Breeze Environmental Research Laboratory (GBERL) to test the effect of toxicants on estuarine animals. These are: (1) improved techniques for conducting constant-temperature and-salinity acute bioassays in which the concentration of the toxicant is measured and the data are treated statistically; (2) in-house and extramural bioassays on sensitive larval stages of crabs and shrimp; (3) development of methods to bioassay a portion, or the entire life cycle, of grass shrimp (Palaemonetes pugio) and the sheepshead minnow (Cyprinodon variegatus) and (4) development of methods to assess the effects of toxicants on entire communities of benthic macroinvertebrates.

CONCLUSIONS

- 1. Acute 96-hour flow-through bioassays should be conducted using uniform methods on representative species from several phyla of estuarine organisms. Use of uniform methods with appropriate statistical and chemical analyses makes comparisons between tests reliable. Recent acute bioassays indicate that previous tests have underestimated acute toxicities of many organic chemicals.
- 2. In addition to acute bioassays, information is needed on the effects of chemicals on sensitive life-stages and entire life-cycles of estuarine organisms, as well as on communities of organisms, in order to set sound water quality criteria. Some methods necessary to conduct these experiments are available and additional procedures are presently being developed.

BIOASSAY TECHNIQUES

ACUTE BIOASSAYS

Acute toxicity experiments are usually conducted to determine the quantity of chemical that will adversely affect a certain percentage of the test organisms in a short period of time. This information is used to make comparisons of relative toxicity and relative sensitivity. Comparisons become most reliable if bioassay methods are uniform and the tests are conducted to obtain statistically valid data supported by chemical analyses of the test water. Data from this type of bioassay, although more difficult and costly to obtain than data from simpler screening tests, are required by EPA because of the Agency's regulatory responsibilities.

Acute bioassay methods used at GBERL have changed since joining EPA. When our laboratory was part of the Bureau of Commercial Fisheries, Jack I. Lowe was in charge of the acute bioassays. From 1963 to 1972 he conducted flow-through bioassays that usually lasted 48 hours on over 200 chemicals on oysters, penaeid shrimp, fishes and occasionally crabs. His data were used to help in pesticide registration and to develop label restrictions. Acute flow-through bioassays are now being repeated on some of these chemicals to provide 96-hour LC50 data backed by statistical and chemical analyses. The results of recent experiments continue to show that panaeid shrimp are usually more sensitive to the chemicals tested than oysters, grass shrimp or estuarine fishes (Table 2). The acute toxicity of these chemicals, except methoxychlor, in our tests exceeded that of acute bioassays published in the Blue Book (NAS-NAE Committee on Water Quality Criteria, 1972).

Recent acute bioassays have been conducted using water of constant temperature and salinity to improve comparisons of the results of these tests. Bioassays of DDT, heptachlor (99%), heptachlor epoxide, lindane and methoxychlor in Table 2 were all conducted at 25°C and 20 % oo salinity. The salinity was controlled by an inexpensive device in which appropriate amounts of fresh and saltwater were added through solenoid valves that were controlled electrically by a photocell that sensed changes in water density detected by a floating hydrometer (Bahner and Nimmo, 1975a). This device has been used successfully for periods of up to 9 months to maintain constant (± 1 % oo) salinity in bioassays.

TABLE 2. NINETY-SIX HOUR LC50'S AND 95% CONFIDENCE INTERVALS
FOR THE SPECIES OF ESTUARINE ORGANISM MOST SENSITIVE
TO SELECTED ORGANIC CHEMICALS IN FLOW-THROUGH BIOASSAYS. USUALLY THE AMERICAN OYSTER, TWO FISHES AND
TWO ARTHROPODS WERE TESTED. CONCENTRATIONS IN WATER
WERE MEASURED BY ELECTRON-CAPTURE GAS CHROMATOGRAPHY

CHEMICAL	SENSITIVE SPECIES	96 HOUR LC50 (μg/l)	REFERENCE
Chlordane	Pink Shrimp	0.4(0.3-0.6)	Parrish <u>et al</u> ., 1975
DDT*	Brown Shrimp	0.1(0.1-0.2)	Schimmel et al., unpubl.**
Dieldrin	Pink Shrimp	0.7(0.4-1.2)	Parrish <u>et al.</u> , 1973
Endrin	Pink Shrimp	0.04(.0205)	Schimmel <u>et al.</u> , 1974a
НСВ	Pink Shrimp	>25	Parrish <u>et al</u> ., 1974
Heptachlor (74%)	Pink Shrimp	0.1(0.07-0.1)	Schimmel <u>et al</u> ., unpubl.**
Heptachlor (99%)*	Pink Shrimp	0.03(0.02-0.04)	u n
Heptachlor Epoxide*	Pink Shrimp	0.04(0.001-0.1)	11 11
Lindane*	Pink Shrimp	0.2(0.1-0.2)	II II
Methoxychlor*	Pink Shrimp	3.5(2.8-4.4)	Bahner and Nimmo, 1975b
Toxaphene	Pinfish	0.6(0.5-0.7)	Schimmel et al., unpubl.**

^{*}Less than five species of estuarine animals tested.

SENSITIVE LIFE STAGE BIOASSAYS AND ENTIRE LIFE CYCLE BIOASSAYS

Chronic bioassays on sensitive life stages and on entire life-cycles of estuarine organisms are usually conducted to determine the quantity of chemical that can be tolerated by an organism throughout its life or during a critical portion of its life. Data from this type of bioassay are especially important in deriving water quality criteria. Water quality criteria are most frequently obtained by multiplying the 96-hour LC50 of the most sensitive species tested by an arbitrary application factor, to protect that species—and hopefully, the ecosystem—from chronic effects of a pollutant. The arbitrary application factor for persistant pollutants

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is usually about 0.01 (NAS-NAE Committee on Water Quality Criteria, 1972). Scientifically derived application factors can be obtained by comparing data from acute bioassays and bioassays in which a fish or invertebrate is exposed to the chemical throughout its entire life cycle. The factor is obtained by dividing the concentration not affecting survival, growth or reproduction in entire-life-cycle bioassays by the 96 hour LC50 for that species (Mount and Stephan, 1967; Eaton, 1973).

Sensitive Life Stage Bioassays

Marine toxicologists have not been able to experimentally derive application factors based on exposures throughout a marine animal's life cycle because techniques for maintaining cultures throughout entire life cycles were lacking. Therefore, it is necessary to develop and use methods that provide toxicity data on sensitive stages of the life-cycle of saltwater species. Our laboratory has funded grants or contracts to look at the effects of pesticides on larval development of dungeness crabs, Cancer magister; blue crabs, Callinectes sapidus; and a mud crab, Rhithropanopeus harrisii. Chemicals that are being or have been investigated include captan, carbofuran, chlordane, DEF, malathion, methoxychlor, mirex, propanil, trifluralin, 2,4-D and juvenile hormones. We also supported research on the effects of methoxychlor and mirex on embryo, larval, juvenile and adult striped mullet, Mugil cephalus (Lee et al., 1975).

Research on sensitive stages of estuarine organisms at GBERL is primarily on larval and postlarval grass shrimp (Palaemonetes pugio), and embryos and fry of the fishes Cyprinodon variegatus, Fundulus similis, F. heteroclitus, Leiostomus xanthurus, Menidia menidia and Morone saxatilis. Recently published papers on this research include those of Hansen et al., (1975), Middaugh et al., (1975), Parrish et al. (1975) and Schimmel et al. (1974a, b). This research has primarily been on the effects of toxicants in water on development and survival of early life-stages. Recent research (Hansen et al., 1973) on the effects of a PCB, Aroclor 1254 in the eggs of the sheepshead minnow, C. variegatus, indicated that certain concentrations of PCB in eggs are lethal to embryos and fry (Figure 1). If this PCB affects other fishes similarly, residues exceeding 5 parts per million in eggs would decrease survival of fry.

Entire Life Cycle Bioassays --

Chronic, entire life-cycle bioassays are routinely conducted by freshwater toxicologists, but saltwater toxicologists have only recently developed similar procedures. Freshwater chronic bioassays can be conducted with bluegills (Lepomis macrochirus), fathead minnows (Pimephales promelas), brook trout (Salvelinus fontinalis), water fleas (Daphnia magna) and other fishes and invertebrates (Eaton, 1973).

Chronic bioassays using the estuarine fish <u>Cyprinodon variegatus</u> are possible (Schimmel and Hansen, 1974). This oviparous fish develops from an embryo to maturity in about 10 weeks, with about 70% survival overall. The fish spawns readily in an aquarium, producing about 8 eggs per day (Figure 2). Total egg production seems unrelated to fish size but frequency of spawning and egg fertility appear to be size-dependent (Schimmel and Hansen, 1974). Females begin producing eggs at 27 mm standard length.

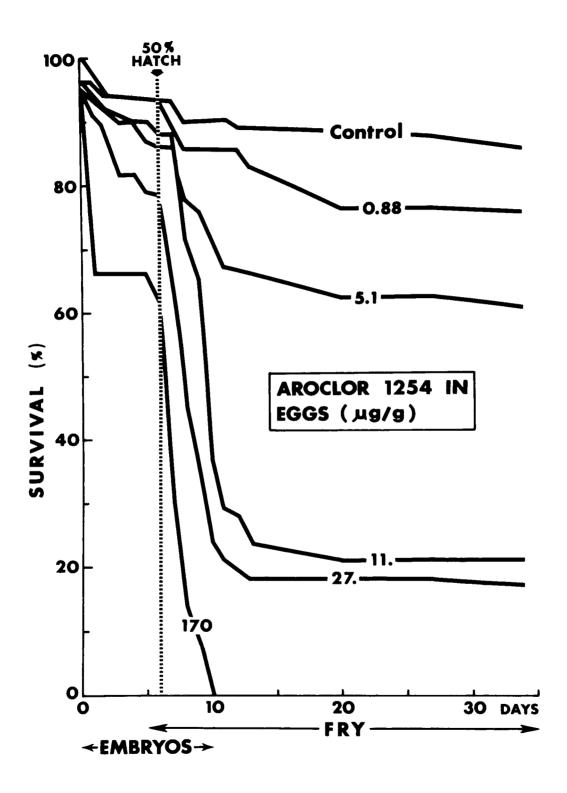


Figure 1. Effect of Aroclor® 1254 in eggs of sheepshead minnows on the survival of embryos and fry.

In one experiment, 19 fish less than 35 mm long produced an average of 8.2 eggs per day, and 15 fish 35 mm and longer averaged 7.8 eggs per day. The smaller fish produced eggs more consistently (50% of the days vs. 31%) with greater fertility (94% fertility vs. 79%) than the larger fish. As a result of this and other information, a tentative method for entire lifecycle bioassays using this fish has been suggested (Hansen and Schimmel, 1975). Recently, sheepshead minnows were exposed to endrin and to heptachlor to determine the effect of these pesticides on reproduction.

Sheepshead minnows were exposed to 0.025, 0.077, 0.12, 0.31 or 0.77 $\mu g/l$ of endrin measured in water during an entire life cycle bioassay that lasted 25 weeks. This bioassay consisted of three parts: (1) the exposure began with embryos and continued through embryonic development, hatching of fry and growth of the fry to adulthood; (2) continued exposure of adult fish to monitor spawning success, including egg production and fertility; and (3) the bioassay ended following a 28-day exposure of embryos and fry obtained from spawning fish. The apparatus used was that of Schimmel et al., (1974b) and the methods were similar to those of Hansen and Schimmel (1975).

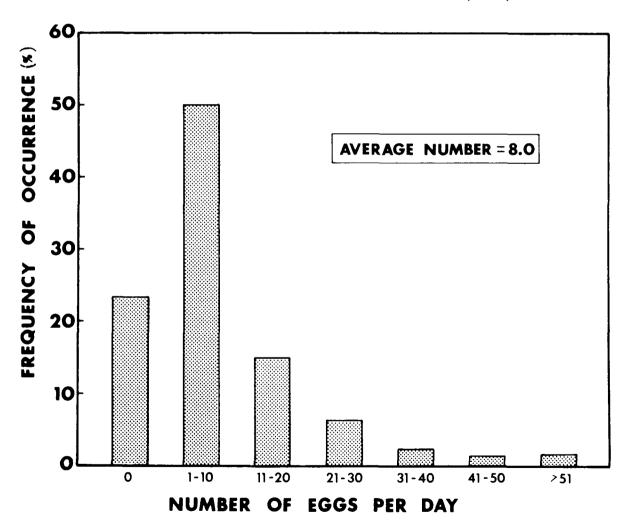


Figure 2. Number of eggs spawned by breeding pairs of sheepshead minnows (Cyprinodon variegatus).

Sheepshead minnows were affected by endrin in this entire life cycle bioassay (Table 3). Embryos in 0.31 and 0.72 μ g/1 of endrin hatched sooner than embryos in water free of endrin. Fry in 0.72 μ g/1 began to die one day after hatching and all were dead by day 9. Fry in 0.31 μ g/1 began to die two days after hatching and over half were dead by day 12. Survival of juvenile fish was unaffected. Survival of spawning females was reduced in 0.31 μ g/1 and their eggs were less fertile than were those of control females. Survival of fry from eggs spawned by fish exposed throughout their life to 0.31 μ g/1 - and possibly 0.12 μ g/1 - was decreased.

TABLE 3. EFFECTS OF ENDRIN ON SHEEPSHEAD MINNOWS (CYPRINODON VARIEGATUS) EXPOSED THROUGHOUT THEIR ENTIRE LIFE-CYCLE. CONCENTRATIONS OF EXPOSURE WERE: CONTROL, 0.025, 0.077, 0.12, 0.31 and 0.72 µg/1

Generation	Life Stage	Effect	Concentration, µg/l
F ₂	Embryo	Early hatching	0.31, 0.72
	Fry	Death	0.31, 0.72
		Decreased growth	0.31
	Juveniles	No effect	
	Adults	Death of spawning females	0.31
		Decreased fertility of eggs	0.31
F ₂	Embryos and fry	Death	0.31

The effects of technical heptachlor on reproduction and development of Cyprinodon variegatus was studied in a similar experiment, except that it began with juvenile fish rather than embryos. Measured concentrations of exposure were 0.71, 0.97, 1.9, 2.8 and 5.7 $\mu g/l$ of technical heptachlor (heptachlor and trans-chlordane) and a control. In the first four weeks of the experiment, some juvenile fish died in 2.8 and 5.7 $\mu g/l$ of technical heptachlor. Thereafter, few fish died until the reproductive portion of the experiment began at week 8. Heptachlor also affected reproduction by reducing number of spawnings, number of eggs, fertility of the eggs and survival of fry from fertile eggs.

Experiments are being conducted to determine techniques required to conduct entire life-cycle bioassays with the grass shrimp (Palaemonetes pugio). The effect of light and temperature on initiation and success of spawning has been investigated. Larval and postlarval shrimp have been used in bioassays to determine effects of certain PCB's on larval development and metamorphosis. Results indicate that grass shrimp will spawn readily, larvae will develop successfully, the species will be sensitive to toxic chemicals and, therefore, would be excellent for entire life-cycle bioassays.

Bioassays can be used to predict how communities of estuarine organisms will respond to a toxicant. Bioassays in which only one species or organism is exposed to a chemical can be used to predict how a community may respond if a number of species from various phyla have been tested under similar conditions. Predictions from this type of data are questionable, particularly if little is known about how species interact in the community. Predictions can also be made using data obtained from field studies, but these predictions may also be questioned because of problems with inadequate controls and lack of replication. An alternative approach is to conduct laboratory studies in which communities of organisms are exposed to a chemical and effects determined. This approach can be valuable if laboratory communities resemble ones in the field and if enough replicates and concentrations are used so that statistical analyses can be made and trends observed.

I have completed two bioassays to determine the effects of Aroclor® 1254, a polychlorinated biphenyl (PCB), and toxaphene, an insecticide, on the development of estuarine communities. The numbers, species and diversity of animals that grew from planktonic larvae in contaminated aquaria were compared with those that grew in identical aquaria that were not contaminated. In each bioassay, sea water with its natural complement of plankton flowed into each of 10 replicate sand-filled aquaria for each of three toxicant concentrations and a control. Planktonic larvae colonized the sand and walls of each aquarium. At the end of the experiments--4 months for the PCB, 3 months for toxaphene--organisms were collected in a lmm-mesh sieve, preserved and later identified.

Aroclor \$\text{\$\text{\$\text{\$P\$}}\$1254 altered the composition of communities of estuarine animals that developed from planktonic larvae in salt water that flowed through 10 aquaria contaminated with 1 or 10 \$\mu g/1\$ (Hansen, 1974). Communities that developed in 10 control aquaria and 10 aquaria that received 0.1 \$\mu g/1\$, of PCB for four months were dominated (>75%) by arthropods, primarily the amphipod Corophium volutator (Figure 3). In aquaria receiving 1 and 10 \$\mu g/1\$, the number of arthropods decreased and the number of chordates, primarily the tunicate, \$\text{Molgula manhattensis}\$, increased; over 75% of the animals in 10 \$\mu g/1\$ aquaria were tunicates. Numbers of phyla, species, and individuals (particularly amphipods, bryozoans, crabs, and mollusks) were decreased by the presence of this PCB, but there was no apparent effect on the abundance of annelids, brachipods, coelenterates, echinoderms or nemerteans (Table 4). The Shannon-Weaver index of species diversity was not altered by Aroclor 1254.

TABLE 4. EFFECT OF AROCLOR® 1254 ON THE NUMBER OF PHYLA, SPECIES AND INDIVIDUALS AND ON THE SHANNON-WEAVER INDEX OF SPECIES DIVERSITY IN COMMUNITIES OF ESTUARINE ORGANISMS THAT DEVELOPED IN SAND-FILLED AQUARIA IN A 4 MONTH BIOASSAY

		Aroclor®1254 (µg/1)			
	Control	0.1	7	10	
Phyla	9	7	7	5*	
Species	52	34	43	25*	
Individuals	1776	2043	1421	657	
Species diversity	1.82	1.26	2.21	1.70	

^{*}Statistically different from controls, $^{\circ}$ = 0.05.

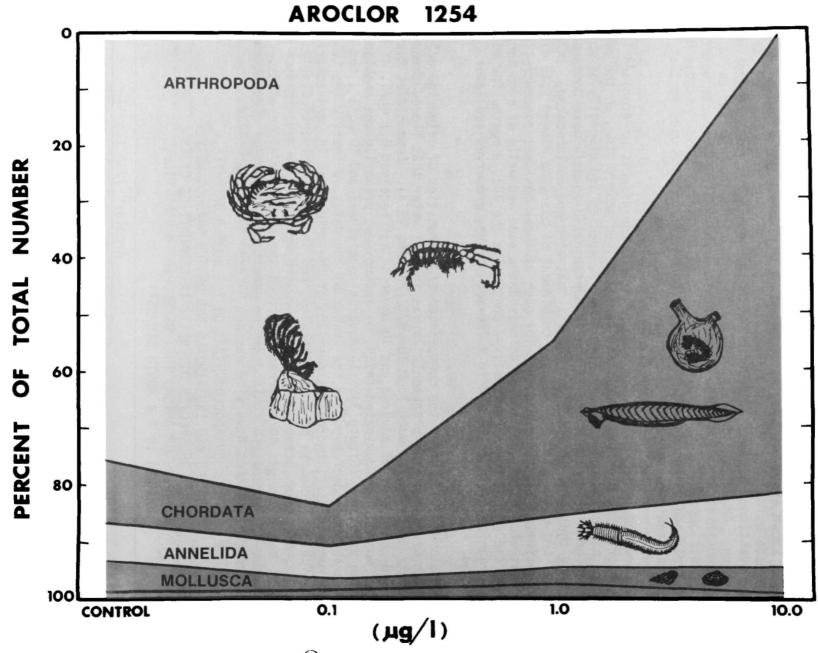


Figure 3. Effect of Aroclor 1254 on the structure of communities of estuarine organisms.

In a similar experiment, the insecticide toxaphene also altered the structure of communities that developed in sand-filled aquaria. Concentrations of exposure were 0.1, l and 10 μ g/l. The number of mollusks (primarily gastropods) tripled, annelids (primarily capitellids) doubled and arthropods were almost eliminated in aquaria contaminated by 10 μ g/l of toxaphene (Table 5). Similar numbers of pelecypods were found in all aquaria, however, the height (distance from hinge to distal valve edge) of Morton's cockles (Laevicardium mortoni) was significantly reduced by 10 μ g/l of the insecticide (Figure 4).

TABLE 5. AVERAGE NUMBER OF ANIMALS IN 10 CONTROL AQUARIA AND 10 AQUARIA THAT FOR THREE MONTHS RECEIVED 0.1, 1 OR 10 µg/1 OF TOXAPHENE. RANGE IN PARANTHESIS

		Toxaphene (µg/1)			
Phylum	Control	0.1	1.0	10.	
Mollusca	124(65-146)	170(98-274)	142(65-237)	373(245-489)	
Annelida	56(19-97)	62(33-90)	66(31-126)	110(82-182)	
Arthropoda	32(2-257)	155(1-523)	9(1-63)	0.4(0-1)	
Coelenterata	3(0-21)	3(0-19)	10(0-44)		
Other	0.1(0-1)	0.1(0-1)	- -		

EFFECT OF TOXAPHENE ON HEIGHT OF COCKLES

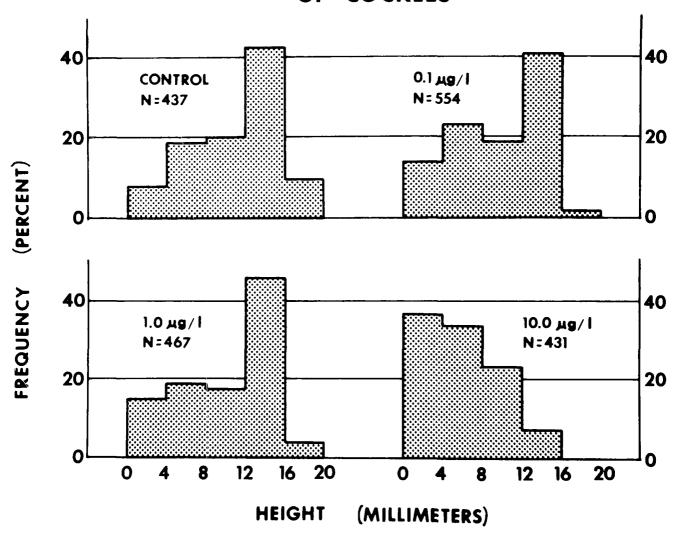


Figure 4. Effect of toxaphene on the height (distance from hinge to distal edge of valve) of Morton's cockles collected from a community of estuarine organisms.

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The Effect of Subtle Temperature Changes on Individual Species and Community Diversity

William C. Johnson II and Eric D. Schneider*

ABSTRACT

Decisions about the regulation of thermal additions in aquatic systems have often been based on acute or chronic high temperature effects on individuals from various life stages of selected species, but rarely on populations or communities (Mihursky, 1969). This paper offers a synthesis from a variety of data bases that demonstrated consistent response of biological systems to long-term, low level temperature change. Profound effects of subtle prolonged temperature displacement are demonstrated at the species, and community levels of biological organization.

INTRODUCTION

For the past decade there has been a controversy as to whether or not artificial temperature alteration should be considered a type of pollution. It is of interest that Congress (SR 92-500) considers artificial thermal perturbations as pollution and requires the United States Environmental Protection Agency to develop regulations which assure maintenance of balanced and indigenous populations within the area of thermal discharge. Temperature is known to be a key physical controlling parameter of biological systems. Latitudinal distributions of organisms is usually a direct reflection of the temperature gradient that exists between the poles and the equator. Therefore, one might hypothesize that in any locale, a persistent temperature change may lead to a biotic change with the possible loss of desirable species and replacement by others. This paper identifies the data base which substantiates this hypothesis. These data have been generated previously by studies related to abundance of commercially valuable species, power plant impact studies, and pelagic foraminiferal studies.

METHODS

In order to demonstrate consistent response of biological systems to long-term, low level temperature change, it is necessary only to look at existing models derived from commercial species abundances and power plant impact studies with a new point of view. However, utilization of foraminiferal data requires some manipulation.

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Analyses of the foraminiferal data were designed to determine the relationship between species diversity of trigger core tops and piston core tops and the surface water temperatures overlying those cores. These core top samples represent recent sediments. A history of marine geology has established the fact that the conditions during deposition generally correlate well with the present environmental conditions.

Foraminiferal species diversity is calculated from relative abundance for the data sets of Kennett (1967) and Imbrie and Kipp (1971). Using these data the Shannon-Wiener index, \bar{H} , was calculated according to the formula:

$$\vec{H} = -\Sigma \text{ pi log pi}$$

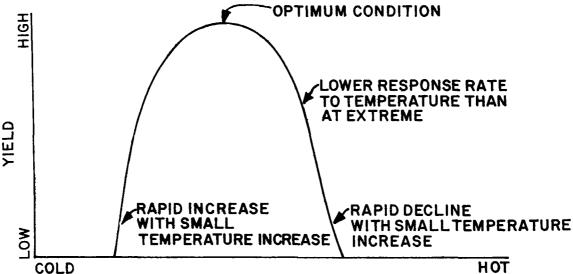
$$\frac{i=1}{N}$$

where s = the number of species, pi = the proportion of the ith species in the total number of species, and <math>N = the total number of individuals. The diversity values were taken directly from Williams and Johnson (1975).

The summer-winter average temperatures presented by Williams and Johnson (1975) were used. A simple arithmetic mean was calculated from the summer and winter temperatures presented by Imbrie and Kipp (1971). For each of Kennett's (1967) sediment core locations the same temperature term was calculated by averaging summer and winter values from the ocean-ographic atlas of Schott (1935). Regressions of temperature and diversity values were made by the least squares method of linear regression.

DISCUSSION

Figure 1 depicts a hypothetical relationship between success or abundance of an individual, a population, or community assemblage, and temperature. The determination of the upper and lower thermal limits, of the



TEMPERATURE (DURING A CRITICAL PERIOD)

Figure 1. The hypothetical relationship between temperature and an individual's, a species', or community success. Different rates of response for the different levels of biological organization within their tolerated range are suggested.

optimum, and of the temperature range that can be tolerated by the individual, a species, or the community are of ecological importance. Bradshaw (1961), through experiments on foraminifera, suggested that such a curve is skewed toward the warmer temperatures at the species level. Indeed, data presented herein indicate a similar tendency toward skewing at the community level.

Temperature may have intensified effects during particular life history stages of different species. Such effects are often a result of direct relationships between critical biological processes and physiological effects of temperature. Rates of processes or timing of critical events are two types of biological variables affected (Jeffries and Johnson, 1974).

Another important consideration with respect to temperature change is the alteration of community structure and composition. Consider a hypothetical assemblage of five species which have different ranges, optima, upper and lower limits, and rates of response to temperature (Figure 2). Community structure is predicted at two points within the temperature range by measuring the relative heights of the individual curves at these temperatures, with species interaction not taken into account. The resulting prediction shows very different community structure at the two temperatures. The magnitude of temperature change required to cause such dramatic biotic shifts is the question which will be treated here.

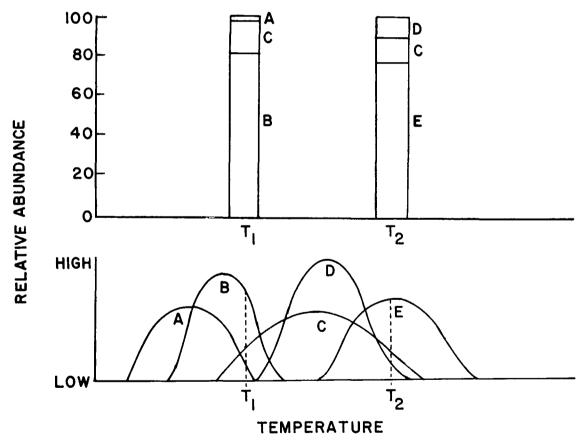


Figure 2. Hypothetical temperature ranges for five species and their relative abundances throughout their respective ranges. Theoretical community composition at two temperatures is predicted by the relative species' abundance at the two temperatures.

Direct prediction of community composition from this type of figure would not be warranted if significant species interaction were to occur. Species interaction is nearly always present, although the amount and kinds of such interaction have been difficult to predict in natural situations. An example of this difficulty is the effect that predation by the green crab, Carcinus maenas, had on soft clams, Mya arenaria, in Maine (Glude, 1954). Here, a slight climatic warming of approximately 2°C led to the introduction of the green crab, which eliminated entire year classes of the soft clam.

COMMERCIALLY VALUABLE SPECIES DATA

A valuable source of information concerning temperature-biotic relationships may be found in the analysis of fishery catch data. Table 1 (Jeffries and Johnson, 1975) summarizes the responses of eight marine species to temperature change when univariate models (Dow, 1973) and a bivariate model (Flowers and Saila, 1972) are applied to catch statistics for these species. Figure 3 demonstrates the extreme thermal sensitivity of Hawaiian corals' reproductive success (Jokiel et al., 1974). A generalized two compartment temperature model is presented in Figure 4 (Jeffries and Johnson, 1975). Their specific winter flounder model (Figure 5) demonstrates how temperature may affect a species abundance through two independent mechanisms.

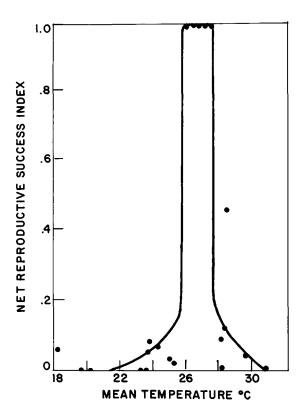


Figure 3. Net reproductive success of Hawaiian corals over an experimental temperature range. Note the limited temperature range for the optimal reproductive success. (Figure from Jokiel, et al., 1974)

TABLE 1. CHANGES IN ABUNDANCE OF SEVERAL SPECIES PREDICTED FROM A 1°C INCREASE IN THE GRAND MEAN, ANNUAL SEA-SURFACE TEMPERATURE (MAINE). (TABLE FROM JEFFRIES AND JOHNSON, 1975)

Author	Species	% Change	Basis of annual comparison; total yield relative to mean temperature	Average catch (metric T)	Observation period	r [†]	Effect
		· · · · · · · · · · · · · · · · · · ·	- UNIVARIATE MODELS	-			
Dow (1973)	hard clam <u>Mercenaria</u> <u>mercenaria</u>	+73.4	Same year	83.3	1939-1967	.770**	Winter survival,
	oyster <u>Crassostrea</u> <u>virginica</u>	+51.0	3 yr later	1.2	1951-1967	.822**	near N limit
	lobster Homarus americanus	+15.2	same year	8.3×10^3	1939-1967	.627**	molting, recruitment
	shrimp <u>Pandalus</u> <u>borealis</u>	-75.0	4 yr later	139	1939-1949 1954-1967	505*	spawning, early survival, near S limit
	scallop <u>Placopecten</u> magellanicus	-37.5	6 yr later	135	1941-1965	743**	
	soft clam <u>Mya</u> <u>arenaria</u>	-36.8	5 yr later	1.9 x 10 ³	1940-1966	643**	predation on spat
	sand worm Nereis virens	-32.5	same year	239.2	1949-1967	812**	spawning, early
	bloodworm Glycera dibranciata	-22.4	same year	179.7	1949-1967	669**	survival
			- BIVARIATE MODEL	-			
Flowers and Saila (1972)	lobster <u>Homarus</u> <u>americanus</u>	+14.6	T _o & T ₋₆₇₈ ‡	9.4 x 10 ^{3†}	1947-1967	.889**	T _o : molting, recruitmer T ₋₆₇₈ : early winter mortali

^{*}significant at the 95% level of probability;

^{**}significant at the 99% level of probability;

tcalculated from data presented by Dow (1973);

to is the mean annual sea-surface temperature of the present year;

 T_{-678} is the sum of the mean annual sea-surface temperatures for 6, 7, and 8 years previous to T_0 .

TEMPERATURE EFFECTS ON ENTIRE LIFE OF A SPECIES

ABUNDANCE

EARLY PERIOD

DIRECT TEMP EFFECTS

- I SPAWNING ACTIVITY
- 2. EGG VIABILITY
- 3. DEVELOPMENT
- 4. SUCCESS OF METAMORPHOSIS
- 5. CRITICAL TIMING OF MET.

REMAINDER OF LIFE

DIRECT & INDIRECT TEMP. EFFECTS A.IF AT LIMIT OF RANGE

- I.MAX OR MIN TEMPERATURES BEYOND ACCEPTABLE LEVELS
- 2. MATURATION (REPRODUCTIVE)

B. AND IN GENERAL

- 3. SUCCESS IN COMPETITION
- 4. GROWTH RATE & FEEDING RATE
- 5. PREDATOR RELATIONS (CRAB & CLAM)
- 6. MATURATION TO ADULT (LOBSTER)
- 7. LONGEVITY
- 8. MIGRATIONAL PATTERNS
- 9. EFFECT ON HABITAT

Figure 4. Biological evaluation of a generalized bivariate temperature model of species abundance. Climatic temperature change is the basis for this model. (After Jeffries and Johnson, 1975)

Taylor et al. (1957) noted a close relationship between shifts of the geographic ranges in marine fishes and other species in the Northwestern Atlantic and climatic warming. Dow (1964, 1967, 1969, 1971, 1973) has been a key contributor on this topic by observing a relationship between temperature and catch statistics of eight commercially valuable marine species.

Considering the response model of Figure 1, the logical question is, at what rate does species abundance respond to a given prolonged temperature change. Jeffries and Johnson (1974, 1975) have attempted to quantify the abundance of several single species with respect to temperature change (Table 1). These data suggest that as little as a one degree centigrade positive displacement from the long-term mean coastal surface temperature, may result in significant changes in species abundance, ranging from +73.4% to -75%. The extreme response rates are for populations near their thermal limits, while those living closer to their temperature optimum generally show smaller change with this temperature rise.

Other models of abundance for marine fish species have been developed which use temperature as an influential term. Sissenwine (1974, 1975), for instance, developed fisheries models for yellowtail flounder in New England which incorporated an important temperature effect. His models indicate extreme sensitivity of recruitment and growth to minor temperature change $(+1^{\circ}\text{C})$.

Temperature can play an exaggerated role during the early life history of many species. Figure 3 demonstrates this sensitivity in Hawaiian corals (Jokiel et al., 1974), where an optimum reproductive range of only 2°C was observed. Baird (1953) suggested that there was a similar sensitivity during the spawning of the giant scallop, Placopecten magellanicus, a temperate species. A similar effect has been identified by Jeffries and Johnson (1975) in modeling the winter flounder population, Pseudopleuronectes americanus, in Narragansett Bay, Rhode Island. Thus, data from both temperate and tropical locations support the hypothesis of ecologically significant early life history temperature sensitivity for a variety of species.

A quantitative bivariate population model can give more information, in some instances, than univariate counterparts by offering more insight into the effects of temperature at different times of a species life history. A generalized and a specific model are presented in Figures 4 and 5. Flowers and Saila (1972) employed a similar bivariate temperature model to describe lobster abundance in Maine. These two different types of models are applied here only with respect to their value in pointing out apparent temperature sensitivity of life stages and without bias toward any particular scheme of modeling.

TEMPERATURE EFFECTS ON WINTER FLOUNDER (PSEUDOPLEURONECTES AMERICANUS) JEFFRIES AND JOHNSON (1975)

ABUNDANCE

APRIL TEMP.
30 MONTHS PRIOR
TO CATCH

TEMP. HISTORY FROM MAY, 29 MONTHS PRIOR TO CATCH THRU SEPT., FIRST MONTH OF CATCH

DIRECT EFFECTS

I. DEVELOPMENT RATE 2.SURVIVAL RATE **INTERACTIONS**

I.COMPETITION FOR RESOURCES 2.PREDATION

Figure 5. A specific bivariate temperature model for the abundance of winter flounder (<u>Pseudopleuronectes americanus</u>) developed by Jeffries and Johnson (1975). Possible biological interactions are suggested.

POWER PLANT STUDIES

A second source of data on the effect of temperature on populations and communities is that found in the literature concerning power plant impact. Figure 6 depicts the effect of temperature on the relative abundance of benthic microalgae in Hawaiian waters (Jokiel et al., 1974). Figure 7 (Jokiel et al., 1974) shows that in selected species systems, Hawaiian macroalgae standing crop drops nearly five fold with an increase in temperature of $4.3\,^{\circ}\text{C}$.

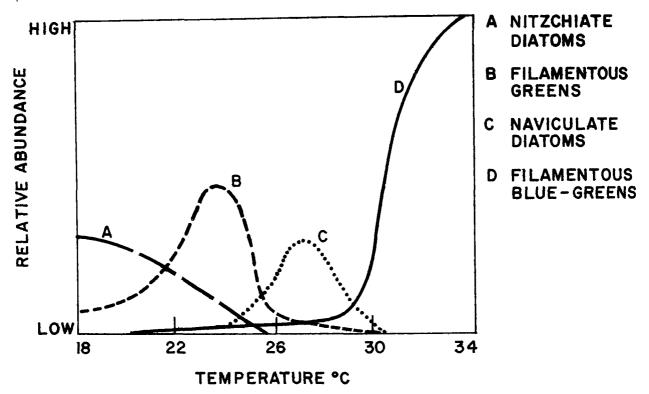
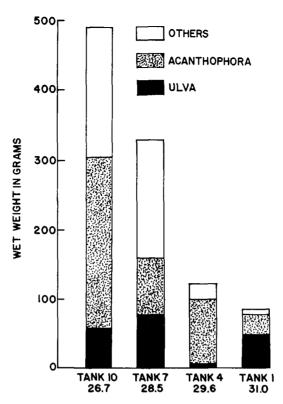


Figure 6. The effect of temperature on the abundance of benthic microalgae on Hawaiian waters. This figure resembles Figure 2 and demonstrates the theorized community shift. (Figure from Jokiel et al., 1974)

From Figure 6 one can see that two of the subtropical algal types have optimal ranges of less than 5° C. It is also of interest to note that this figure resembles Figure 2 and that temperature displacement results in community shifts as hypothesized. Beyond these algal species, the entire marine communities in Hawaii and Florida have been observed to undergo major species compositional changes as a result of prolonged local warming from heated power plant discharge (Jokiel et al., 1974, Roessler et al., 1974). Caution should be applied when using a tropical response to thermal stress as indicative of a general pattern, as this biota typically lives close to their upper thermal limit. However, these data agree with the temperate examples already cited (Taylor et al., 1957, Jeffries and Johnson, 1974).

A marked increase or decrease in net macroalgal production resulting from persistent temperature displacement could be responsible for some of the observed faunal changes (Roessler et al., 1974). Although the direction of change is probably not typical, limitations of macroalgal production



AVERAGE TEMP °C DURING STRESS PERIOD

Figure 7. Hawaiian macroalgae standing crop at four experimental temperatures. Note the dramatic decrease in biomass with only a 4.3°C shift. (Figure from Jokiel et al., 1974)

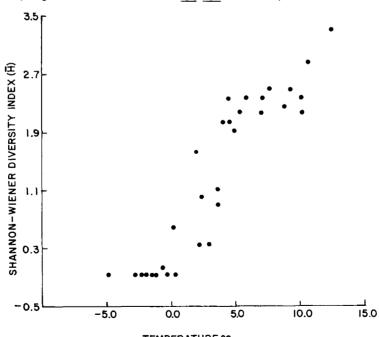


Figure 8. Scatter diagram of Shannon-Wiener diversity values, calculated for the Kennett data set (1967), plotted versus the summer-winter average temperature. Note the linear trend of increasing diversity with increasing temperature.

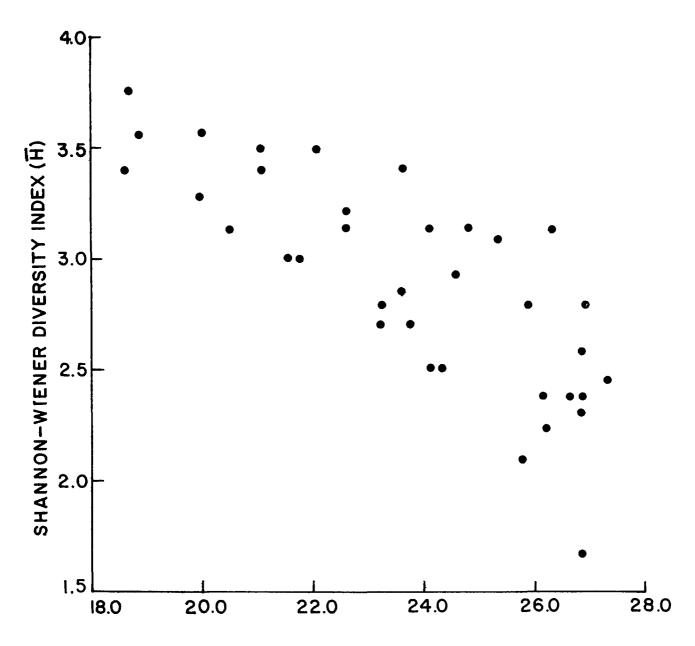
with increased ambient temperatures in the tropics provide an example (Figure 7). It is worth noting from this figure that there is a significant shift in relative abundances of the three different groups of algae over the observed temperature range (4.3°C). Thus, in addition to altered productivity, a shift in species composition occurs which affects the amount and quality of algal habitat afforded to a segment of the animal community.

FORAMINIFERAL INVESTIGATIONS

Another data source showing sensitive temperature-faunal interaction is the foraminiferal data base. The optimal and total temperature ranges for eighteen species of foraminifera are presented in Table 2 (Be' and Tolderlund, 1971). The effect of temperature as an independent variable on the Shannon-Wiener diversity index values (H) for the foraminiferal abundance data of Kennett (1967), Imbrie and Kipp (1971), and Williams and Johnson (1975) are shown in Figures 8, 9, and 10. Figure 10 also shows the faunal composition of three cores with average temperatures near the mean of the diversity data set. Figure 11 summarizes those data by drawing in the individual regression lines.

TABLE 2. AVERAGE TOTAL AND OPTIONAL SURFACE TEMPERATURE RANGES FOR EIGHTEEN SPECIES OF PLANKTONIC FORA-MINIFERA IN THE ATLANTIC AND INDIAN OCEANS (BASED ON DATA FROM BE AND TOLDERLUND 1971)

	Average Range		
Species Name	Optimum °C	Total °C	
Globigerina pachyderma G. quinqueloba G. bulloides Globorotalia inflata G. truncatulinoides G. crassaformis G. hirsuta G. menardii Globigerinita glutinata Globoquadrina dutertrei Orbulina universa Globigerinella aequilateralis Hastigerina pelagica Globigerinoides ruber G. conglobatus G. sacculifer Pulleniatina obliquiloculata	8.2 7.9 9.2 5.4 2.5 - 1.0 8.0 3.4 2.3 2.5 5.7 3.0 7.0 7.5 4.4 3.0	19.4 18.9 26.0 23.5 16.7 8.5 8.2 12.4 25.7 16.7 17.5 15.4 12.2 14.8 11.8	
<u>Candeina nitida</u> Grand Average	5.1	7.4 ————————————————————————————————————	



DIVERSITY VS. SUMMER-WINTER AVERAGE TEMPERATURE IMBIE & KIPP (1971)

Figure 9. Scatter diagram of Shannon-Wiener diversity values, calculated for the Imbrie and Kipp data set (1971), plotted against the summer-winter average temperature. Note that at summer-winter average temperature greater than 18.5°C, there is a decline in species diversity.

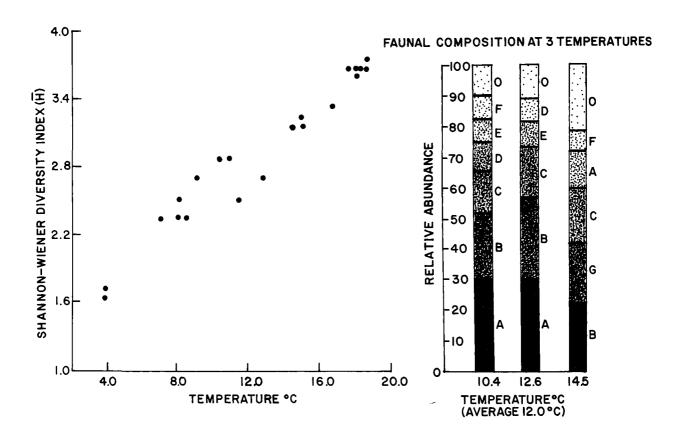


Figure 10. Scatter diagram of Shannon-Wiener diversity values of Williams and Johnson (1975) plotted with respect to the summer-winter average temperature. Here, as in Figure 8, there is an increase in species diversity with increased temperature. Faunal composition at three temperatures is presented as well. The faunal composition at 14.5°C was calculated by averaging data from two cores. Note the faunal shifts, additions, and deletions of species as the temperature changes.

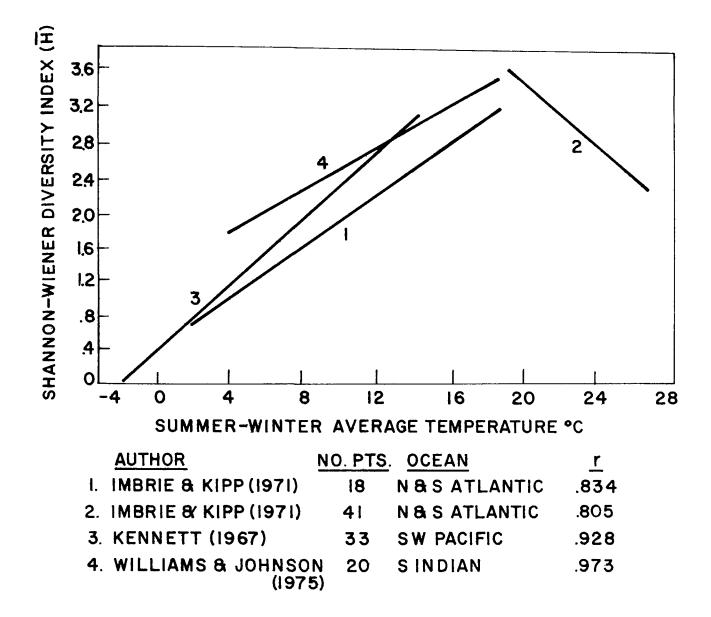


Figure 11. Individual regression lines of diversity versus summer-winter average temperature. Note their close correspondence despite different sources of data. These lines approximate the shape of the hypothetical community response curve demonstrated in Figure 1.

Investigators in the micropaleontological field pioneered the investigation of the effects that small scale temperature fluctuations have on the abundances of individual species. As early as 1935, Schott made the observation that pelagic foraminifera could be utilized as markers of climatic change. Other early investigators (Ericson, 1959; Ericson and Wollin, 1956) noted faunal changes in response to climatic trends. For those species examined in Table 2, the range for the optima is 5.1°C and the average total range is 15.5°C.

Kennett (1970), Ruddiman (1971), Imbrie and Kipp (1971), and Hecht (1973) are but a few of the investigators who have developed sophisticated paleotemperature models from relationships observed between temperature and living foraminiferal species assemblages. Although developed to satisfy quite another need, these models and their data bases underscore impact on living foraminiferal populations resulting from minor, but persistent, temperature change.

The foraminiferal data possibly demonstrate community structure sensitivity to long-term temperature changes. This ubiquitous data base was chosen because it lends itself to global comparisons. Species diversity is used as an index of community structure. Although species diversity should not be considered a panacea for community studies, it can serve as a simple common denominator for comparing the Voluminous foraminiferal data sets.

The scatter diagrams (Figures 8, 9, and 10) show how well diversity approximates linear trends with respect to temperature. There is a rapid rate of change for each of the data sets. It is notewrothy that significant shifts of relative species abundances (Figure 10) occur even within the 4.0°C range examined. This type of faunal shift persists throughout the data sets and is assumed not to be fortuitous in this example.

Figure 11 demonstrates that a break in diversity occurs generally at a summer-winter average temperature of 18.5°C. Thus, species diversity is not linearly related to temperature throughout the entire temperature range studied. The overall shape of these lines approximates the theoretical shape of temperature's effect on community success (Figure 1) with the modification of slight skewing toward the warmer temperatures. This would imply that species at their southern limits and tropical or subtropical communities would have greater sensitivity to warming trends than species well within their temperature ranges and temperate or polar communities.

In summation, by applying available modeling tools to completely different existing data sets, we demonstrate appreciable effects of long-term, low level temperature change on species abundance and community structure and composition. This demonstration is achieved in a manner which is amenable to regulatory requirements generated by Public Law 92-500 (1972) in sections 304 and 316a. These laws direct the United States Environmental Protection Agency to develop regulations to control thermal discharge with limitations more stringent than necessary in order to assure the protection and propagation of a balanced, indigenous population of shellfish, fish, and wildlife in and on the body of water into which the discharge is made.

Jeffries and Johnson (1974, 1975) have employed natural fluctuations of temperature as the stressor in their models. As mentioned earlier, part of the east coast of North America has undergone short-term warming trends, giving rise to changes in species abundance (Table 1). With the building of large scale thermal nuclear power plants on estuarine and coastal waters, we may see regional temperature rises in the ranges discussed in this paper (\pm 1°C). Broecker (1975) has projected that, because of atmospheric CO increase, there will be a global warming of 1.1°C by the year 2010 A.D. Such man induced warming coupled with nature's unpredictable fluctuations should have appreciable effects on indigenous marine populations.

It is apparent that the biota is very sensitive to slight long-term temperature alteration. Seasonal cycles and daily fluctuations of temperature tend to obscure long-term temperature trends and their biological effects, which perhaps explains why many investigators have overlooked this delicate, but dramatic relationship. Data obtained from a global spectrum form a basis of support for this suggested relationship. Although these are preliminary findings, the same overbearing theme persists.

In the future, we would hope to achieve predictive models. At present, the changes which have occurred, due to thermal pollution or climatic changes, have been somewhat unpredictable. As mentioned earlier, newly introduced predators may cause significant changes in the indigenous populations.

CONCLUSIONS

Responses due to thermal perturbation, seen at the species level of organization, include:

- 1) Species often have average yearly thermal ranges of about 5° C when in natural surroundings. However, subtle shifts of $\pm 1^{\circ}$ C give rise to marked changes in population abundances.
- 2) Response to temperature displacement is appreciable in the resident biota. Some species benefit by temperature change while others are adversely affected by the same.
- Early life history stages may be particularly sensitive to temperature changes.

The community level of organization appears, also, to be very much affected by temperature change, as shown by:

- 1) Entire communities have undergone significant change when prolonged low level warming occurs because of the discharge of heated effluents
- 2) Prediction of community changes is confounded by unsuspected interaction between species, as in the case of the green crab and soft clam in Maine.
- 3) Species diversity changes with ambient temperature for certain community types. Diversity in foraminiferal communities respond appreciably to temperature change with an apparent maximum at 18.5°C summer-winter average.

ACKNOWLEDGMENTS

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FRESHWATER QUALITY CRITERIA RESEARCH OF THE ENVIRONMENTAL PROTECTION AGENCY

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Models for Transport and Transformation Of Malathion in Aquatic Systems

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ABSTRACT

A mathematical model has been developed for predicting the fate and transport of malathion in riverine aquatic ecosystems. Two competing degradation pathways were modeled--alkaline hydrolysis and microbial breakdown. Incorporating data obtained from previous laboratory studies, the model was used to verify proposed degradation mechanisms by predicting the behavior of malathion in the AEcoS, a physical system designed to simulate environmental conditions as closely as possible. Although in general results were similar for the two systems, rates measured in the environmental simulator were slower than those measured in laboratory studies.

INTRODUCTION

The fate and transport of toxic substances in aquatic ecosystems has been the subject of numerous studies over the years. Field studies are undertaken to estimate the persistence of the toxic materials under natural conditions and laboratory studies are undertaken to study the persistent pollutants. In recent years mathematical modeling has also become a useful technique in the study of environmental pollution. As modeling capabilities have improved, mathematical models have been applied with increasing frequency to interpret the results of both laboratory and field experiments and to extrapolate results obtained to other ecosystems.

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Such a model was developed to describe the fate and transport of malathion {0,0-dimethyl S-(1,2-dicarbethoxy)ethylphosphorodithioate}, an organo-phosphorus pesticide widely used for control of mosquitos and agricultural insect pests. A number of laboratory studies have been done to determine the pathways and rates of chemical and biological degradation of the insecticide. Ferguson (1975) reviewed the available literature concerning malathion including its chemistry, pharmacology, toxicity, fate and significance in the environment, and production and use.

Koivistoinen and Aalto (1970) have reported pseudo-first-order rate coefficients for chemical hydrolysis of malathion as a function of pH ranging from 1 to 9 and of temperature ranging from 20°C to 70°C. Under alkaline conditions, malathion hydrolyzes to form predominantly dimethyl phosphorodithioate and dimethyl phosphorodithionate. Wolfe et al. (in press) have done a detailed study of chemical degradation pathways and have estimated rate coefficients for intermediate product degradation as well as for malathion hydrolysis. They note that at low temperatures malathion monoacid is formed as an intermediate product that is more stable than the parent compound and consequently has a potential environmental impact.

Paris et al. (1975) completed a microbial degradation study in which mixed bacterial cultures isolated from the field were inoculated into medium containing malathion as a sole carbon source. From the rate data obtained, malathion degradation was modeled using Monod kinetics (Stumm-Zollinger and Harris, 1971), and maximum degradation rate, half-saturation constant, and yield factor were obtained by least squares fit.

All laboratory studies are simplifications of the actual phenomona occurring in nature. They are well-defined and controllable, but suffer from the fact that they contain only a few compartments and consequently important systems interactions may be unobserved. In field studies, however, the extreme variability and uncontrollability make mechanistic studies of the ecosystem difficult. A physical model, the Aquatic Ecosystem Simulator (AEcoS), has been developed to bridge the gap between laboratory and field studies. The facility was designed to simulate the complexity of natural field systems as closely as possible, thus providing the realism of a field study with the controllability of a laboratory system.

To test the mathematical model, results obtained by Wolfe et al. (in press) for chemical hydrolysis of malathion and results obtained by Paris et al. (1975) for microbial degradation were incorporated into the model. Based on simulations using laboratory coefficients a series of AEcoS experiments were run to verify the proposed mechanisms.

MATERIALS AND METHODS

The facility used in the experiments consisted of a channel, 19.5 m long by 46 cm wide by 46 cm deep, enclosed in an environmentally controlled chamber. A detailed description of the facility has been presented by Sanders and Falco (1973).

Bacterial cultures were kindly supplied by Doris F. Paris, Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens.

Georgia. In all experiments, bacteria were continuously inoculated into the channel inlet from a chemostat as shown in Figure 1. Bacterial cultures were maintained in the feed chemostat on 1/100 strength nutrient broth to which was added malathion in quantities to sustain a nominal chemostat effluent concentration of 0.5 mg/l.

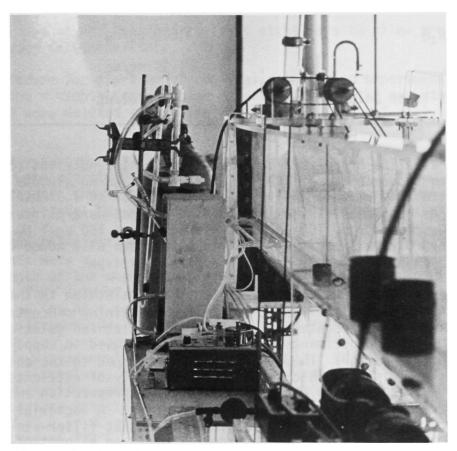


Figure 1. End view of the channel showing bacteria feed system.

The water supplied to the channel was once deionized and once distilled. In microbial degradation experiments, compounds were added in the ratios shown in Table 1, and in quantities designed to sustain the inlet concentration of o-PO₄ phosphorus at 90 μ g/l, NO₃ nitrogen at 300 μ g/l, NH₃ nitrogen at 450 μ g/l, glucose at 6.0 mg/l, and malathion at 1.0 mg/l. Secondary reagent grade (97% pure) malathion, provided by American Cyanamid Co., was used. All other compounds were reagent grade.

TABLE 1. RELATIVE AMOUNTS OF COMPOUNDS IN NUTRIENT MEDIA

Compound	Ratio to Amount of $(NH_4)_2SO_4$ Added
Na ₂ HPO ₄ •7H ₂ O	0.195 mg/mg
KH ₂ PO ₄	99.4 µg/mg
KNO ₃	1.02 mg/mg
MgS0 ₄ •7H ₂ 0	10.3 µg/mg
Glucose	1.39 mg/mg
Hunter's Trace Solution	0.938 μl/mg

In the alkaline hydrolysis experiments, the same nutrient composition was used with two exceptions: the solution contained no glucose and the ratio of nitrate to ammonia was increased from 0.667 to 1. Absolute concentrations of nutrients at the inlet to the channel were maintained at 30 $\mu g/l$ o-PO $_{4}$ phosphorus, 150 $\mu g/l$ NH $_{3}$ nitrogen, and 150 $\mu g/l$ NO $_{3}$ nitrogen during the hydrolysis experiments. Tris buffer was also added continuously in the channel inlet to maintain desired inlet pH.

The feed system that supplied nutrients and malathion to the channel consisted of two closed 40-liter carboys, one containing concentrated nutrient solution and one containing concentrated malathion solution. For alkaline hydrolysis experiments a third carboy was used to supply the channel with tris buffer. These solutions were pumped to the channel inlet by peristaltic pumps, which regulated the supply of nutrients and malathion. Nutrient stocks were autoclaved after preparation and malathion solutions were filter-sterilized after preparation. A bacterial contaminant, however, was found in some malathion stocks that filter-sterilization did not eliminate. To eliminate this contaminant, an aliquot of acetone was mixed with the malathion sample and the mixture was allowed to stand for approximately one hour, during which the bacteria cells were lysed. Acetone was removed by evaporation.

The nutrient feed system for the chemostat was similar to the channel feed system with the exception that only one carboy containing both nutrient and malathion was used. Influent nutrient broth concentration was selected to yield approximately 1×10^8 bacteria/ml in the chemostat effluent. Flow rate through the chemostat was set at 1 ml/min and consequently the bacteria count in the channel influent was $1.9 \times 10^5 \text{ cells/ml}$.

The procedure for start-up of microbial degradation experiments was as follows:

1. Filled chemostats were inoculated with bacteria and allowed to

stand for 24 hours to develop the culture.

- 2. Channel flow was set at 0.525 liters/min and paddle wheel rotation speed was set at 2 rpm.
- Chemostat flow was started and effluent stream was directed into channel inlet.
- 4. Twenty-four hours after the start-up of chemostat flow, nutrient and malathion flows into the channel inlet were started.
- 5. The channel was operated at least eight days to allow the system to come to steady-state.

The procedure for start-up of chemical degradation experiments was the same as for the microbial degradation experiments with the exception that steps 1 and 3 were deleted and nominal channel flow was set at 1.31 liter/min.

In the first microbial degradation experiment, both air and inlet water temperatures were set at 22°C. In the second experiment, temperatures were set at 27°C, and in the third and fourth experiments, temperatures were set at 32°C. All chemical degradation experiments were carried out at 27°C.

During the transient period of all tests, chemical determinations and bacteria counts were measured at nine equally spaced sampling locations along the length of the channel at least once a day. During the steady-state period, four sets of chemical determinations and bacteria counts were made at each of the nine sampling stations. Determination of o-OP4 phosphorous, NO_3 nitrogen, NH_3 nitrogen, and glucose were accomplished by an automated auto-analyzer system described by Kollig (in preparation). Malathion analysis was accomplished by extracting water samples with 2,2,4-trimethylpentane (isooctane) and analyzing the extract by gas-liquid chromatography. Determinations were performed using a Tracor MT550 GC with a nickel 63 electron capture detector. A 1.8 meter long by 0.64 cm diameter column packed with a 3% S.E. 30 on 80/100 mesh Gas Chrom Q was used at a column oven temperature of 220° C.

Viable bacteria concentrations were estimated by plate counts (Standard Methods, 1965). Tryptone-glucose-extract agar was used as plating medium and the cultures were incubated at 32°C. Species existing in water samples taken during two microbial experiments were confirmed as

- Flavobacterium meningosepticum
- Xanthomonas species
- Comanonas terrigeri
- Pseudomonas cepacia

A low background level of other bacteria (three Bacillus species) was observed during the experiment.

Water temperatures were recorded at the nine sampling stations at least once per day during each experiment.

Water flow rate and relative humidity were also recorded daily.

MATHEMATICAL MODEL

The continuity equation describing the movement and transformations of material is well known. For one dimensional incompressible flow describing the flow regime in our channel experiments and in many natural riverine ecosystems, the equation is

$$\frac{\partial C_{i}}{\partial t} = \frac{D}{\partial x^{2}} \frac{\partial^{2} C_{i}}{\partial x^{2}} - \frac{v}{\partial x} \frac{\partial C_{i}}{\partial x} + S_{i} \pm \sum_{j} R_{ij}$$
 (1)

where

C = concentration of constituent i

D = dispersion coefficient

Rij = rate of production or elimination of constituent i
by pathway j

S: = source strength of component i

t = time

x = distance in the direction of flow

In equation 1, no distinction is made between point source loads and non-point source loads. A point source load is simply described by a Dirac delta function.

The major effort in modeling is usually directed toward development of an adequate representation for R_{ij} . In the case of malathion, two competing processes occur, namely, alkaline hydrolysis and bacterial degradation.

Wolfe et al. (in press) modeled the degradation of malathion by alkaline hydrolysis as a second-order reaction, i.e.,

$$R_{hydrolysis} = k_1 C_{OH} C_{M}$$
 (2)

where

k_i = second-order rate coefficient

 C_{OH} = concentration of hydroxide ion

 C_{M} = concentration of malathion

They note that two competing temperature dependent reactions occur. An elimination reaction favored at elevated temperatures results in the production of diethyl fumarate and 0,0-dimethyl-phosphorodithioic acid. The

second reaction, favored at low temperatures, results in an intermediate malathion monoacid product that has environmental significance because of its persistence in the environment.

In modeling alkaline degradation, therefore, we have separated the rate coefficient into two contributions

$$k_1 = k_{elim} + k_{hydrol}$$
 (3)

Using the data provided by Wolfe $\underline{\text{et al.}}$ (in press), we fit each of the coefficients to the following equations:

$$k_{elim} = A_1 \exp \{-\frac{A_2}{T}\}\$$
 (4)

$$k_{hydrol} = B_1 \exp \{-\frac{B_2}{T}\}$$
 (5)

where A_1 , A_2 , B_1 , and B_2 are fit coefficients and

T = Temperature (°K)

Paris et al. (1975) proposed two models to describe the bacterial degradation of malathion. For the first they used the standard Monod expression for growth of an organism and limiting substrate utilization. The malathion degradation equation for this model is

$$R_{Mal} = \frac{-\mu_{m} \cdot C_{B} \cdot C_{M}}{Y(K_{m} + C_{M})}$$
 (6)

where

Y = yield coefficient

 $^{\mu}$ m = maximum degradation rate

 K_m = half saturation constant

 C_{p} = bacteria concentration

The corresponding equation for bacterial growth on malathion is

$$R_{\text{Bacteria}} = \frac{\mu_{\text{m}} \cdot C_{\text{B}} \cdot C_{\text{M}}}{K_{\text{m}} + C_{\text{M}}}$$
 (7)

The second model proposed is a simple second-order equation, which assumes that microbial degradation can be described by the equation

$$R_{Ma1} = -k_2 \cdot C_B \cdot C_M \tag{8}$$

where

 k_2 = specific microbial degradation rate

In the model we have developed, equation 6 has been generalized to account for degradation by any number of species i as follows:

$$R_{ij} = -\sum_{i}^{\mu_{ij}} \frac{C_{i} C_{j}}{Y_{ij} (K_{ij} + C_{j})}$$
(9)

and microbial growth has been generalized to account for utilization of j carbon substrates simultaneously as follows:

$$R_{ij} = \sum_{j}^{\mu_{ij}} \frac{C_{j} C_{j}}{K_{i,j} + C_{j}}$$
 (10)

A flow sheet of the computer program developed for the model is shown in Figure 2. Input data include length of river reach, average velocity, and longitudinal dispersion coefficient. For the finite difference equation used to approximate equation 1, the river reach is divided into 56 equally spaced segments. First- and second-order spatial gradients at all interior points are approximated by a third-order central difference approximation (Salvadori, 1961). Spatial derivitives are approximated in the first segment of the reach by a sixth-order forward difference equation and in the last segment of the reach by a sixth-order backwards difference equation. Time integrations are accomplished by a Runge-Kutta technique developed by Shampine and Watts (1974). Calculations of chemical reaction rates are accomplished in a separate subroutine as are calculations of microbial growth and degradation rate. Thus, other mechanisms for kinetic rates can be substituted into the program with a minimum of effort.

Initial conditions are read in for each of 56 segments of the river reach. Two different inlet boundary conditions can be applied. The first assumes no dispersion upstream of the inlet reach. This boundary condition gives reasonable results when large non-point source or point source loads are simulated. The second set of boundary conditions assumes that the concentration at the inlet is a known constant. This second assumption appears to give reasonable results when small downstream inputs are simulated. No dispersion at the end of the river reach is always assumed. Source strengths are assumed to be constant in the current version of the program and are read in at the beginning of the execution for each of the 56 segments.

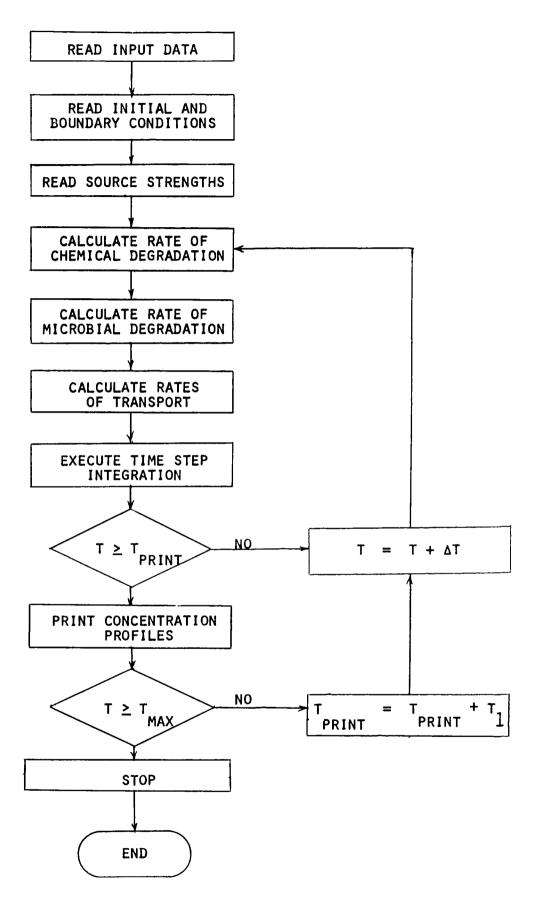


Figure 2. Flow diagram for malathion degradation program.

To compare results obtained from AEcoS experiments with laboratory results, the data had to be fit to the mathematical model. Assuming that steady-state has been attained, equation 1 can be rewritten as

$$\sum_{j} R_{ij} = \frac{-D \frac{\partial^{2}C_{i}}{\partial x^{2}} + v \frac{\partial C_{i}}{\partial x} - S_{i}$$

To obtain a satisfactory least squares fit of the data, malathion concentration data and bacteria counts were averaged over the steady-state period. The averaged values were substituted into a finite difference approximation to equation 11 to calculate a rate for bacterial growth and malathion degradation at each of the seven interior sampling stations. Since only nine data points were available, a second-order central difference was used to approximate first and second spatial derivatives at the five most interior points. A fourth-order forward difference approximation was used at the second sampling location, and fourth-order backward difference approximation was used at the eighth sampling location.

The seven rates were then fit to either equation 2 or equation 7 by a nonlinear least squares fit using a Marquardt-Levenberg iterative curvefitting algorithm (Knott, 1972).

RESULTS AND CONCLUSIONS

Typical simulation results are shown in Figures 3, 4, 5, and 6. Figure 3 is a plot of malathion concentration versus time of travel that would result under flow conditions in which longitudinal dispersion is small and degradation is attributable to alkaline hydrolysis. The effect of temperature variation is quite large. Figure 4 shows the effect of pH on malathion concentration profiles. A change in pH has a dramatic effect on the rate of hydrolysis. Figure 5 shows malathion concentration profiles as a function of the glucose concentration at the inlet of the reach. All of these model simulations were obtained using coefficients reported by Paris et al. (1975) and Wolfe et al. (in press).

By comparing the rates of malathion degradation by alkaline hydrolysis and microbial action, combinations of environmental conditions can be defined in which either hydrolysis or microbial degradation is the dominant pathway of malathion breakdown. Figure 6 illustrates this comparison. At high pH and low bacteria counts, alkaline hydrolysis is the major degradation pathway. At low pH and high bacteria counts, microbial degradation is the major degradation pathway.

Typical results from alkaline degradation experiments (pH 8.25) conducted in AEcoS are shown in Figure 7. Second-order rate coefficients for malathion degradation calculated from least squares fit of AEcoS data are compared in Table 2 with coefficients determined in the laboratory. Rate coefficients calculated from AEcoS experiments are approximately 26% lower than those obtained in the laboratory.

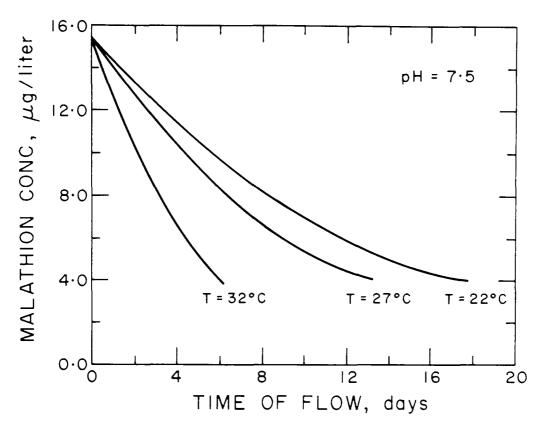


Figure 3. Effect of variation in temperature on alkaline degradation of malathion.

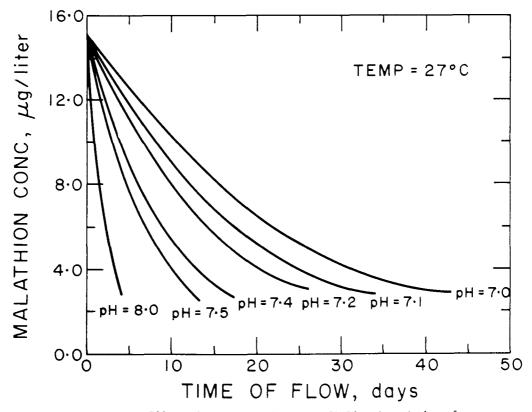


Figure 4. Effect of variations in pH on alkaline degradation of malathion.

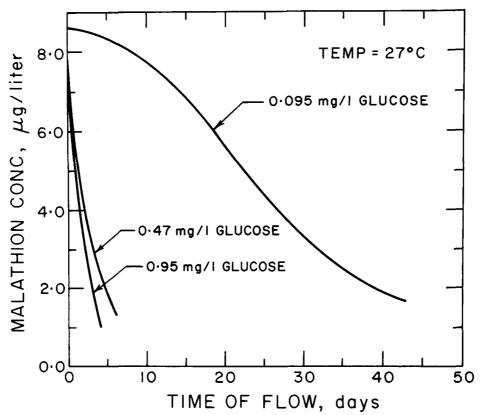


Figure 5. Effect of variations in utilizable carbon loads on microbial degradation of malathion.

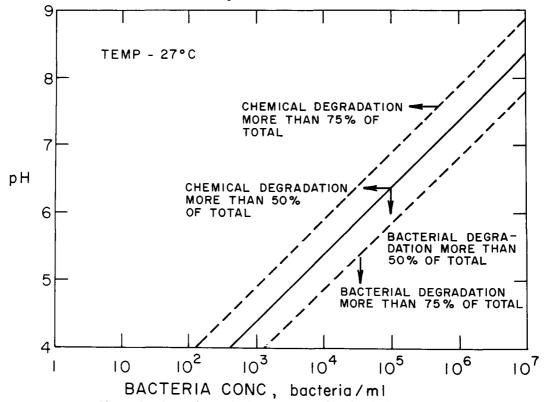


Figure 6. Comparison of microbial and alkaline hydrolysis degradation pathways.

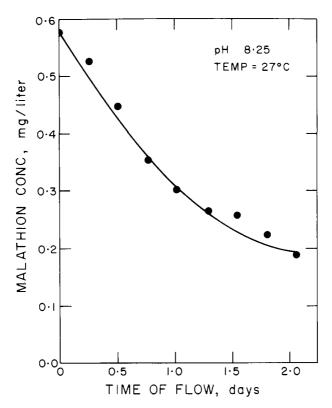


Figure 7. Typical steady-state malathion concentration profile observed in AEcoS during alkaline degradation study.

TABLE 2. COMPARISON OF RATE COEFFICIENTS FOR ALKALINE DEGRADATION BETWEEN LABORATORY AND AECOS STUDIES

рН	k ₁ (M•sec ⁻¹) (AEcoS Study)	k ₁ (M∙sec ⁻¹) (Laboratory Study)
7.5	3.86 ± 0.11	5.4 ± 0.1
8.25	4.12 ± 0.47	5.4 ± 0.1

Typical results for microbial degradation are shown in Figures 8 and 9. The decline of bacteria concentration down the length of the channel indicates that the rate of utilization of malathion as an energy source is too slow to fulfill the metabolic requirements of the organisms. Consequently, to describe the dynamic behavior of the microbial population, a death term was added to the model

$$R_{BAC} = -k \cdot C_{B}$$
 (12)
= specific death rate

where

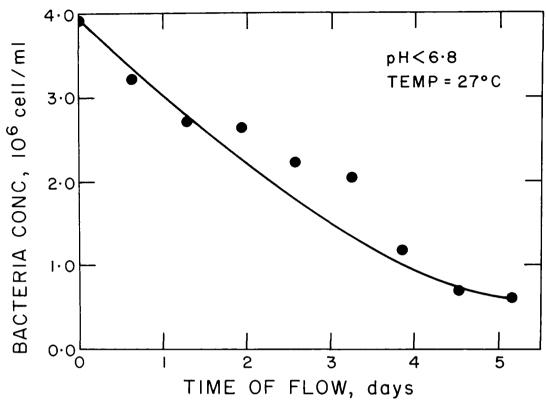


Figure 8. Typical steady-state bacteria concentration profile observed in AEcoS during microbial degradation study.

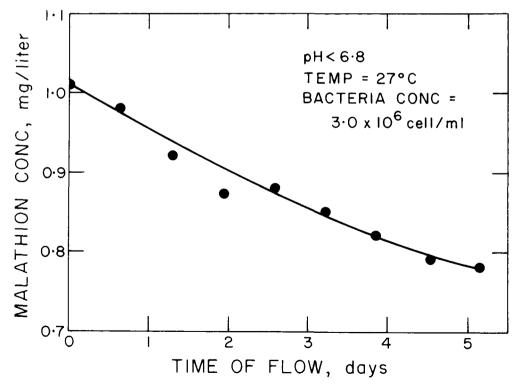


Figure 9. Typical steady-state malathion concentration profile observed in AEcoS during microbial degradation study.

Values obtained for specific death rates by a least squares fit of bacteria data from each experiment are shown in Table 3.

TABLE 3. SPECIFIC DEATH RATE FOR BACTERIA CULTURES USED IN AECOS MICROBIAL DEGRADATION EXPERIMENTS

Temperature	k (min ⁻¹) x 10 ⁻⁴	
22°C	0.98	
27°C	1.86	
32°C	0.10 0.72	

Glucose fed into the channel inlet was effectively utilized at the point of injection. Consequently, equation 12 described the total change in bacteria concentration down the length of the channel. The only apparent effect of variation in glucose input was in regulating the size of the bacterial population at the channel inlet. Second-order rate coefficients for microbial degradation of malathion calculated from least squares fits of AEcoS data are compared in Table 4 with coefficients evaluated in the laboratory. The values calculated from AEcoS experiments are again lower than values obtained in laboratory studies. Reproducibility of results was fair for the one test replicated at 32°C.

TABLE 4. COMPARISON OF RATE COEFFICIENTS FOR MICROBIAL DEGRADATION BETWEEN AECOS AND LABORATORY STUDIES

Temperature	K ₂ (AEcoS Study) (1 org- ¹ hr ⁻¹) x 10 ⁻¹²	k ₂ (Laboratory Study) (1 org ⁻¹ hr ⁻¹) x 10 ⁻¹²
22°C	0.59 ± 0.31	
27°C	1.3 ± 0.52	4.9 ± 2.1, 2.5 ^a
32°C	0.77 ± 0.46 1.38 ± 0.58	

^aCoefficient calculated from Monod constants reported by Paris <u>et al</u>. (1975) and malathion concentration of 0.8 mg/l.

Flask experiments and background tests conducted in AEcoS, indicated that bacteria entering the system from chamber air and inflowing water supply made no significant contribution to malathion degradation. Their contribution to the total bacterial population was also small (less than 10% of the total population).

The difference in degradation rates between chamber experiments and laboratory experiments cannot be attributed to changes in non-limiting nutrient concentrations in the case of microbial degradation; in flask experiments varying the amounts of non-limiting nutrients produced no detectable effect on the rate of degradation. The difference in rate of degradation in the case of hydrolysis reaction could be due to differences in the buffers used.

We suggest an alternative explanation. In laboratory studies reported, solutions were well-mixed, i.e., systems were characterized by high turbulence levels. In AEcoS experiments, the turbulence levels were low. The low level of turbulence introduces the possibility of mass transport limitations to the degradation of malathion by bacteria. Hydrolysis of malathion may be similarly affected, although it is less likely because of the molecular nature of the reaction. Further experimentation would be required to determine the source of the differences in these experiments.

A few further tests must be done to gather additional background data for the microbial system under study. The next major system scheduled for testing includes an algal component. In this series of experiments, a green and a blue-green algae will be added to the bacterial system and its effects on malathion degradation rate will be studied.

The results of the experiments completed in the AEcoS were similar to those obtained in laboratory studies. However, the rates of the two processes studied in the AEcoS were significantly lower than those obtained in laboratory studies. For valid extrapolation of laboratory results to field situations, phenomena causing this reduced rate should be studied. If it is due to mass transport limitations, the effect will be even more important for fast processes, e.g., phosphorus cycling.

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Shagawa Lake Recovery Characteristics As Depicted by Predictive Modeling

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ABSTRACT

Predictions obtained using several mass balance models describing changes expected in lake phosphorus concentrations resulting from an external phosphorus supply reduction to Shagawa Lake were compared with observations. Two of the models predicted a rapid recovery of the lake and underestimated present wintertime phosphorus concentrations by about 50%. A third model which includes an algal biomass component projected similar wintertime total phosphorus concentrations but showed how internal sources of phosphorus can delay the attainment of this level. Two of these models were used to project lake phosphorus concentrations expected if wastewater phosphorus concentrations were allowed to increase from the present 50 μ g/1 to 400 μ g/1 and 1.0 mg/l. Both suggest that at effluent concentrations of 1.0 mg/l, the lake would exhibit phosphorus concentrations often associated with a eutrophic state.

INTRODUCTION

The use of mathematical models as tools to assist in understanding the dynamics of aquatic ecosystems as well as to predict their responses to man induced perturbations has increased dramatically in recent years. A partial listing of aquatic ecosystem models includes those developed and used by 85 investigators responding to a survey inquiry conducted during 1974 (Parker and Roop, 1974); many others exist. Models which describe lake trophic state and algal dynamics (reflecting trophic state) have been developed at several levels of complexity. Vollenweider (1969, 1975) has advocated single compartment phosphorus mass balance models on the premise that lake phosphorus concentrations provide an estimate of trophic state and algal concentrations. Others have expanded and elaborated this type of model with good success.

Slightly more complex phosphorus lake models have dealt with a two compartment (particulate and dissolved), vertically stratified (epiliminion and hypolimnion) system (Snodgrass and O'Melia, 1975; Imboden,

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1973, 1974). These models are more effective when considering seasonal changes in phosphorus levels and might be more effective when predicting average phosphorus concentrations (usually taken as values observed at vernal circulation). More complex models describe the interrelationships between various components of aquatic ecosystems including nutrients, algae, herbivores, carnivores, and decomposers (Chen, 1970; Park, et al., 1974; Thomann, et al., 1975; Baca, et al., 1974). These models may have three spatial dimensions, but are often one or two dimensional.

At Shagawa Lake, Minnesota, an opportunity exists to test the predictive capabilities of representatives of these models of several levels of complexity in describing the lake's response to a large-scale, man induced, environmental perturbation: the phosphorus supply to Shagawa Lake was reduced to about 20% of its former level by removing essentially all of the wastewater phosphorus which could enter the lake. This report compares results of predictions using models developed by Vollenweider (1969, 1975), Snodgrass and O'Melia (1975), and a simplified epilimnetic algal model similar to those developed by Thomann, et al. (1975), and Baca, et al. (1974) with observations in the lake. In addition, since it is unlikely that the wastewater phosphorus removal efficiency will continue at its present level because the operation is expensive, projections using higher wastewater phosphorus concentrations, up to 1.0 mg/l (the Minnesota State Standard) are included.

Shagawa Lake, a shallow (mean depth 5.7m) lake located in northeastern Minnesota, has received wastewater from the city of Ely since about 1880 when the development of mining and logging industries attracted hundreds of settlers. As a result the lake became eutrophic. A tertiary wastewater treatment plant designed to reduce effluent phosphorus concentrations to $50~\mu g$ P/l, (a 99% reduction) became operational in early 1973. Since wastewater accounted for approximately 80% of the total supply of phosphorus to Shagawa Lake from surface sources, (the remainder originating primarily from natural sources), its removal should cause a dramatic change in lake conditions. Detailed background of the project and documentation of nutrient loads and limnological characteristics of Shagawa Lake can be found in Larsen and Malueg (1975), Larsen, et al. (1975), Malueg, et al. (1973), Malueg, et al. (1975), and Schults, Malueg, and Smith (1975).

VOLLENWEIDER MODEL

Based upon earlier work (Biffi, 1963; Piontelli and Tonolli, 1964) Vollenweider (1969, 1975) developed a mass balance model for total phosphorus in lakes to include external supplies, loss through the outflow and sedimentation. He chose to describe sedimentation as a function of the amount of phosphorus in the lake, proposing the following equation:

$$\frac{d[P]}{dt} = \ell_p - (\rho_w + \sigma_p)[P]$$
 (1)

where [P] = total phosphorus concentration in the lake (M L⁻³) $\ell_{p} = \text{volumnar phosphorus supply (M L}^{-3} \text{ T}^{-1})$ $\ell_{w} = \text{hydraulic washout coefficient (T}^{-1})$ $\ell_{p} = \text{sedimentation rate constant (T}^{-1})$ $\ell_{p} = \text{time (T)}.$

Assuming constant ℓ_p , ρ_w , and σ_p , a time dependent solution to equation (1) can be obtained analytically as

$$[P(t)] = [P_0]e^{-(\rho_W + \sigma_p)t} + \frac{\ell_p}{\rho_W + \sigma_p} (1 - e^{-(\rho_W + \sigma_p)t}) (2)$$

Assumptions are: a well-mixed lake, constant lake volume, outflow concentration equivalent to lake concentration, equivalent inflow and outflow rates, and no net supply from the sediments. An important point is that this model is essentially an accountability statement, i.e., material in the lake occurs as a balance between supplies and losses. The only hypothesis contained in equation (1) is that sedimentation is a function of the amount of phosphorus in the lake (Vollenweider, 1975). Models of this general nature have been described often (Dillon, 1974).

The solution, equation (2), to equation (1) depends on an experimentally difficult to determine sedimentation rate coefficient, σ_p . Dillon and Rigler (1974) and Sonzogni, et al. (1975) have proposed alternative means to obtain its value. These methods were used to estimate σ_p ; the results are summarized in Table 1. Other variables and coefficients can be determined experimentally.

Equation (1) was solved using flow and phosphorus loading data for 1973 and 1974 (see Malueg, et al., (1975) for flow and loading calculation methods). For projections beyond 1974, projected wastewater flows and phosphorus concentrations were added to average natural flow and phosphorus concentrations (based upon data obtained during 1972 and 1973). Model response was compared with wintertime total phosphorus values. Springtime concentrations are usually used for comparisons because a lake is likely to be well mixed at this time, but in Shagawa Lake, concentrations change rapidly shortly after ice-out. For example, during the three weeks subsequent to ice-out in 1973, mean total phosphorus concentrations declined from 63 $\mu g/l$ to 44 $\mu g/l$. During the interval from mid-December to mid-January each year, mean concentrations changed

only slightly, and hence, were taken as better representatives of mean conditions. These mean values were determined as follows. Each week a volume-weighted average lake concentration was calculated from vertical profiles (1.5 m depth interval) located at three stations in the lake. These weekly values were then averaged over the interval from mid-December to mid-January.

Figure 1 compares the expected response of Shagawa Lake to reduced phosphorus input using this model with the wintertime total phosphorus values. One run displays the expected lake response treating total phosphorus as a conservative substance ($\sigma_{\rm p}$ =0; termed the hydraulic washout model); the second run includes the deposition term ($\sigma_{\rm p}$ =0.852 yr^{-1} ; termed the phosphorus washout model). Both runs suggest that Shagawa Lake should respond rapidly to the reduced phosphorus supply, attaining a stable state within two years. The expected time required to reach 95% of a steady state value can be used as a measure of the responsiveness of lakes to changed inputs. This is usually given as three times the phosphorus retention time $(\tau_p=1/(\rho_w+\sigma_p))$ or 1.3 yr for Shagawa Lake using the values summarized in Table 1. Hence, this model suggests that a new stable state should have occurred by mid-1974. The phosphorus washout model suggests that mean lake concentrations should be 10-12 $\mu g/1$ when a steady state is attained if phosphorus deposition is similar to that observed during pretreatment years. The hydraulic washout model suggests a mean lake concentration of 17-20 μg/l, equivalent to the mean influent concentration. Sufficient time has elapsed for the lake to have achieved a new stable state. Figure 1 suggests that the lake responded rapidly; however, mean concentrations have not declined to expected levels. In fact, mean concentrations are approximately twice as high as those predicted from the phosphorus washout model and are higher than those suggested by the hydraulic washout model alone. There is an indication that the lake may have achieved a stable state, since late 1974 winter time total phosphorus concentrations are similar to those during late winter 1975 (Figure 1). This lake concentration is higher than mean influent concentrations, hence must be maintained by an internal supply of phosphorus.

Although the lake has not responded entirely as predicted by these washout models, it is instructive to speculate on what can be expected if the wastewater phosphorus concentration is altered from its present level of 50 $\mu g/l$ to a higher level. The steady state solution to equation (1) can be written (Larsen and Mercier, 1975) as

$$[P] = [\bar{p}] (1 - R_p) \tag{3}$$

where $[\bar{p}]$ = average influent phosphorus concentration (M L⁻³) and R_p = phosphorus retention coefficient = $\frac{\sigma_p}{\rho_W + \sigma_p}$ (Vollenweider, 1975).

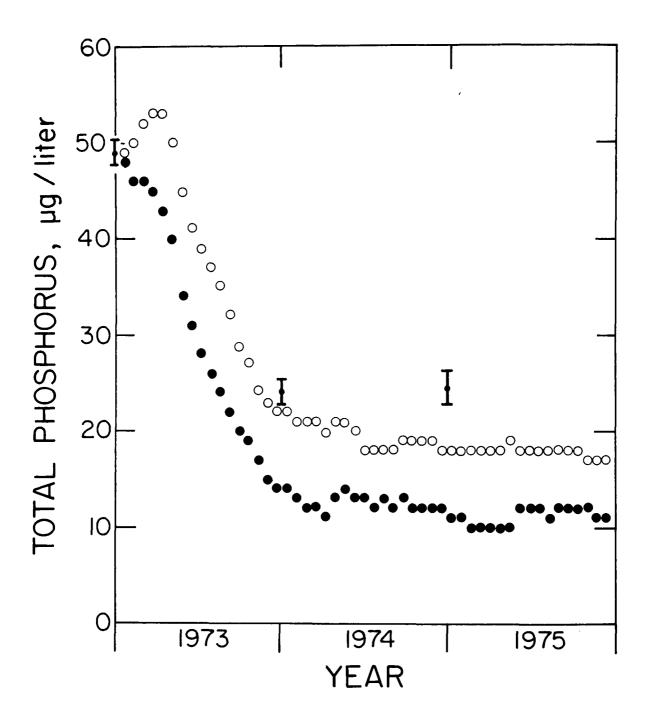


Figure 1. Comparison of response of Vollenweider mass balance model with lake observations. Solid circles represent model run with phosphorus deposition; open circles represent no deposition. Lake observations are mean wintertime values (see text) + 1 standard deviation.

TABLE 1. ESTIMATES OF ρ_W AND σ_D FOR SHAGAWA LAKE

	-1 (yr)	σ _p -1 (yr)
1971	1.85	0.67 ^a
		0.88 ^b
1972	1.26	0.82 ^a
		0.93 ^b

- a) determined from $R_p = \frac{\sigma_p}{\rho_W + \sigma_p} = 1 \frac{Annual\ Export \pm Lake\ Change\ Annual\ P\ Import\ }{Annual\ P\ Import\ }$ (Dillon and Rigler, 1974).
- b) determined from steady state solution of mass balance model (Equation 1). (Sonzogni, et al., 1975).

TABLE 2. POTENTIAL EFFECT OF DIFFERENT WASTEWATER EFFLUENT PHOSPHORUS CONCENTRATIONS ON MEAN LAKE CONCENTRATIONS

Wastewater Effluent Conc.	% of Natural Supply	Mean Influent Conc.	Expected Mean Lake Conc.
<u>μ</u> g/l		μ g /l	μg/1
50	6	18	12 Meso-
200	22	20	13
400	45	24	trophic 16
700	7 9	30	20
1000	113	35	Eutrophic 23

This relationship expresses the concept/that the steady state lake concentration will be equivalent to the mean influent phosphorus concentration in the absence of deposition of phosphorus (i.e. if phosphorus were a conservative substance). The effect of phosphorus deposition is to reduce the mean influent concentration and this effect can be expressed as the phosphorus retention coefficient, that fraction of incoming phosphorus which is retained by the sediments.

Equation (3) was used to project the effect of alternative wastewater effluent total phosphorus concentrations upon mean lake concentrations. The results, using total phosphorus effluent concentrations up to 1.0 mg/l, are summarized in Table 2. This analysis suggests that wastewater effluent phosphorus concentrations of 700 $\mu g/l$ or greater might produce a eutrophic lake while the present effluent concentrations of 50 $\mu g/l$ might produce a lake of lower mesotrophic classification. A 400 $\mu g/l$ effluent concentration, equivalent to about a 90% secondary wastewater phosphorus reduction, might produce a mid-mesotrophic lake. It is interesting to note that an effluent concentration of 1.0 mg/l would provide a supply of phosphorus approximately equivalent to the supply from all other sources. The classification of lakes into trophic categories is difficult; here the guidelines suggested by Vollenweider (1968) and Dillon (1975) have been adopted.

These projections provide an estimate of the state toward which the lake might stabilize and are based upon the assumption that the sediments will act as a net sink for phosphorus as they did prior to 1973. If this basic model is correct the recent wintertime total phosphorus concentrations might typify lake characteristics at an effluent of 1.0 mg/l after stable conditions have been attained.

SNODGRASS - O'MELIA MODEL

Snodgrass and O'Melia (1975) proposed a more complex mass balance model which includes particulate and ortho-phosphorus, divides the lake into epi- and hypolimnia, each well mixed, and incorporates two seasons, each 180 days. One represents summer conditions during which stratification occurs and the other hypothesizes a well mixed lake. Lake processes include: conversion of ortho-phosphorus into particulate phosphorus, sedimentation of particulate phosphorus, decomposition of particulate phosphorus into ortho-phosphorus, and vertical exchange of material across the epilimnion-hypolimnion boundary. An effect of flocculation was developed such that the net sinking velocity in deep lakes was greater than that in shallow lakes. Although they specifically state that the model is applicable to lakes whose hypolimnia remain aerobic throughout the year, it was instructive to apply the model to Shagawa Lake, in which anaerobic conditions have regularly developed each year during late winter (before ice-out) and during late summer.

The equations and model coefficients are summarized in Table 3. Snodgrass and O'Melia estimated coefficients from the literature and calibrated the model using Lake Ontario data. The coefficients they presented were used for the Shagawa Lake runs except those that were site specific (e.g., mean depth, volume, etc.). External water and phosphorus supplies used were those observed for Shagawa Lake.

Predicted year end total phosphorus concentrations were compared with lake observations obtained during mid-December to mid-January as before (Figure 2). This interval was also selected to minimize the effects of sediment phosphorus supply during anaerobic periods thereby potentially minimizing the model constraint of aerobic conditions throughout the year. For the years prior to treatment (1968-1972), the model results are quite close to observed values with the exception of the single value for 1967-1968 when the model projects total phosphorus concentrations of about 46 $\mu \rm g/l$ and the lake mean during the only week for which data were obtained was 28 $\mu \rm g/l$.

It is particularly encouraging that the lake observations and model response for the last three pretreatment years (1970-1971, 1971-1972, 1972-1973) are in close agreement when sampling frequency had been increased. This agreement might occur because the phosphorus pulses which occur in the lake during anaerobic intervals deposit rapidly subsequent to circulation periods, hence, their effect on wintertime averages is minimized. However, model projections subsequent to treatment are similar to those predicted by the Vollenweider model, suggesting total phosphorus concentrations near 10 $\mu \rm g/l$, substantially below observed values.

EPILIMNION MODEL

A three compartment model was constructed to describe the seasonal changes in total phosphorus and algal phosphorus within the well mixed epilimnion (5.25 m) of Shagawa Lake and to predict recovery of the lake subsequent to treatment. The model is a simplified version of those developed by Thomann, et al. (1975) and Baca, et al. (1974). The following is a general description of the model structure; equations and coefficient values are summarized in Table 4.

The specific rate of growth of algae was related to solar radiation, temperature, and soluble reactive phosphate; loss rates included the effects of sinking, conversion into non-algal particulate phosphorus (lumping the effects of zooplankton grazing and cell death) and washout. A specific growth rate reduction factor, as a function of total daily radiation, was generated by averaging Vollenweider's (1964) expression, relating photosynthesis to light intensity, over a 24 hour day and the mixed zone as elaborated by Fee (1973). This integral can be used to evaluate relative photosynthesis over the euphotic zone for particular values of physiological "constants" and various amounts of total daily

TABLE 3. EQUATIONS AND COEFFICIENTS FOR SNODGRASS-O'MELIA MODEL (1975) AS APPLIED TO SHAGAWA LAKE

Summer

Epilimnion ortho- and particulate phosphorus

$$V_{e} \frac{d[OP]_{e}}{dt} = \Sigma Q_{j}[OP]_{j} - Q[OP]_{e} - p_{e}V_{e}[OP]_{e} + \frac{k_{th}}{\overline{Z}_{th}} A_{th}[OP]_{h} - \frac{k_{th}}{\overline{Z}_{th}} A_{th}[OP]_{e}$$

$$V_{e} \frac{d[PP]_{e}}{dt} = \Sigma Q_{j}[PP]_{j} - Q[PP]_{e} + p_{e}V_{e}[OP]_{e} - g_{e}A_{th}[PP]_{e} + \frac{k_{th}}{\overline{Z}_{th}} A_{th}[PP]_{h} - \frac{k_{th}}{\overline{Z}_{th}} A_{th}[PP]_{e}$$

Hypolimnion ortho- and particulate phosphorus

$$V_{h} \frac{d[OP]_{h}}{dt} = r_{h}V_{h}[PP]_{h} + \frac{k_{th}}{\overline{Z}_{th}} A_{th}[OP]_{e} - \frac{k_{th}}{\overline{Z}_{th}} A_{th}[OP]_{h}$$

$$V_{h} \frac{d[PP]_{h}}{dt} = g_{e}A_{th}[PP]_{e} - g_{h}A_{s}[PP]_{h} - r_{h}V_{h}[PP]_{h} + \frac{k_{th}}{\overline{Z}_{th}} A_{th}[PP]_{e} - \frac{k_{th}}{\overline{Z}_{th}} A_{th}[PP]_{h}$$

Winter

Ortho- and particulate phosphorus

$$V \frac{d[OP]}{dt} = \Sigma Q_{j}[OP]_{j} - Q[OP] - P_{eu}V_{eu}[OP] + rV[PP]$$

$$V \frac{d[PP]}{dt} = \Sigma Q_{j}[PP]_{j} - Q[PP] + P_{eu}V_{eu}[OP] - rV[PP] - gA_{s}[PP]$$

(Continued)

TABLE 3. EQUATIONS AND COEFFICIENTS FOR SNODGRASS-O'MELIA MODEL (1975) AS APPLIED TO SHAGAWA LAKE (continued)

Summer Stratification

$$g_{e} = 0.1 \text{ mg/day}$$

$$g_{h} = g_{o}(1 + f\overline{Z}_{h})$$

$$g_{o} = 0.05 \text{ m/day}$$

$$f = 0.05/m$$

$$\frac{k_{th}}{\overline{Z}_{th}} = \hat{k} = 0.005 \overline{Z}$$

$$p_{\Delta} = 2.0/day$$

Winter Circulation

$$g = g_0 [1 + f(\overline{Z} - \overline{Z}_{eu})]$$

$$g_0 = 0.05 \text{ m/day}$$

$$f = 0.05/m$$

$$\overline{Z}_{eu} = 10 \text{ m for } \overline{Z} \ge 10 \text{ m}$$

$$\overline{Z}_{eu} = \overline{Z} \text{ for } \overline{Z} < 10 \text{ m}$$

$$p_{eu} = 0.06/day$$

r = 0.03/day

Coefficients Specific to Shagawa Lake

$$V_e = 39 \times 10^6 \text{ m}^3$$
 $A_{th} = 5.5 \text{ km}^2$
 $V_h = 14 \times 10^6 \text{ m}^3$

$$\overline{Z}_h = 2.54 \text{ m}$$

$$A_s = 5.5 \text{ km}^2$$

 $V = 53 \times 10^6 \text{ m}^3$
 $V_{eu} = 39 \times 10^6 \text{ m}^3$

$$\overline{Z} = 5.25 \text{ m}$$

List of Symbols

- A_s Surface area of the sediment water interface (L^2)
- A_{th} Horizontal cross-sectional area of a lake at the thermocline (L^2)
- f Flocculation coefficient (L^{-1})
- g Sedimentation coefficient of entire lake (L/T)
- g_h Sedimentation coefficient in the hypolimnion (L/T)
- $g_{\rm p}$ Sedimentation coefficient in the epilimnion (L/T)
- g_0 Sedimentation coefficient in the absence of flocculation (L/T)
- k_{th} Vertical transport coefficient in the thermocline (L²/T)
- p_{e} Production rate coefficient in the epilimnion (T^{-1})

Table 3 (continued). List of Symbols

```
Production rate coefficient in the euphotic zone, circulation
     model(T^{-1})
     Volumetric rate of discharge from a lake (L^3/T)
Q
     Volumetric rate of inflow to a lake from source j(L^3/T)
Q,
     Decomposition rate coefficient for entire lake (T^{-1})
r
     Decomposition rate coefficient for the hypolimnion (T^{-1})
     time (T)
t
     Volume of entire lake (L^3)
٧
     Volume of the epilimnion (L^3)
     Volume of the euphotic zone in circulation model (L3)
     Volume of the hypolimnion (L^3)
Z
     Mean lake depth (L)
     Mean depth of the euphotic zone, circulation model (L)
     Mean depth of the hypolimnion (L)
    Mean depth of thermocline region (L)
[OP] Concentration of orthophosphate (M/L<sup>3</sup>)
[PP] Concentration of particulate phosphorus (M/L<sup>3</sup>)
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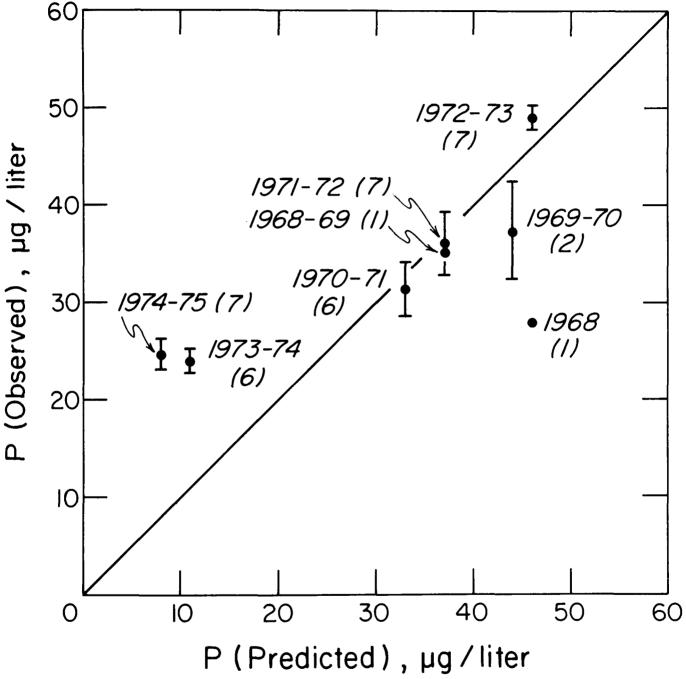


Figure 2. Comparison of predicted total phosphorus concentrations using Snodgrass-O'Melia model with lake wintertime concentrations. Solid line is 1:1 correspondence between predictions and observations. Dates mean wintertime values + 1 standard deviation and numbers of observations making up the mean are indicated for lake observations. See text for calculation methods.

TABLE 4. EQUATIONS AND COEFFICIENTS FOR SHAGAWA LAKE EPILIMNION PHOSPHORUS MODEL

Algae:

$$\frac{d[A]}{dt} = G_{MAX}(T).CLITE. \underbrace{[SRP]}_{[SRP]} + K_{p} [A]$$

$$-(N_1 + \sigma_1 + \rho_w) [A]$$

Soluble Reactive Phosphorus:

$$\frac{d[SRP]}{dt} = \frac{SRPIN}{V} - G_{MAX}(T).CLITE.\frac{[SRP]}{[SRP]} + K_{P}[A]$$

$$+N_{2}[PP] - \rho_{w}[SRP]$$

Non-Algal Particulate Phosphorus:

$$\frac{d[PP]}{dt} = \frac{PPIN}{V} + N_{1}[A] - (N_{2} + \sigma_{2} + \rho_{w})[PP]$$

Model Coefficients

$$G_{MAX}(T) = 0.59 (1.066^{T})$$

CLITE = $\frac{0.172 (1 - e^{-0.007TDR}) + 0.000451TDR}{K_{e}}$

$$K_e = 30[A] + 0.75$$
 $K_p = \mu g SRP/1$
 $N_1 = 0.05 day^{-1}$
 $N_2 = 0.005 day^{-1}$
 $\sigma_1 = 0.01 day^{-1}$
 $\sigma_2 = 0.007 day^{-1}$
 $V = 40 \times 10^6 M^3$

TABLE 4. EQUATIONS AND COEFFICIENTS FOR SHAGAWA LAKE EPILMNION PHOSPHORUS MODEL -- LIST OF SYMBOLS

```
Concentration of algal phosphorus (M/L<sup>3</sup>)
[A]
           Fractional reduction in G_{\text{MAX}}(T) in epilimnion due to
CLITE
           availability of light
G_{M\Delta Y}(T)
           Maximum specific growth rate as a function of
           temperature (T<sup>-1</sup>)
           Extinction coefficient (L<sup>-1</sup>)
Ke
           Concentration of SRP at which specific growth rate is
K<sub>D</sub>
           reduced to 1/2 maximum (M/L^3)
           Conversion rate constant from algal phosphorus into
N_1
           particulate phosphorus (T^{-1})
           Conversion rate constant from non-algal particulate
N_2
           phosphorus into soluble reactive phosphorus (T^{-1})
           Concentration of non-algal particulate phosphorus (M/L<sup>3</sup>)
[PP]
           Supply of non-algal particulate phosphorus to epilimnion (M/T)
PPIN
           Hydraulic washout coefficient as a function of time (T^{-1})
\rho_{\mathbf{W}}
           Settling rate constant for algal phosphorus (corresponding
σı
           to a settling velocity of 0.05 m/day) (T^{-1})
           Settling rate constant for non-algal particulate phosphorus
σ2
           (corresponding to a settling velocity of 0.04 m/day) (T<sup>-1</sup>)
           Concentration of soluble reactive phosphate (M/L^3)
[SRP]
           Supply of SRP to epilimnion (M/T)
SRPIN
           Temperature as a function of time (°C)
Ţ
t
           Time (T)
           Total daily radiation as a function of time (gcal/L^2/T)
TDR
           Epilimnion volume (L^3)
٧
```

radiation distributed realistically throughout a daylight day. Values used for physiological "constants" were those reported by Fee (1973). The expression developed for the reduction factor is given in Table 3 and is similar in form to that presented earlier (Larsen, Mercier, and Malueg, 1973). Eppley's (1972) relationship between maximum specific growth rate and temperature was used. The hyperbolic expression commonly used to express the relationship between the rate of uptake of a nutrient and its concentration in the extracellular medium was used to express the fractional reduction in specific growth rate related to nutrient concentration. First order rate kinetics were used to express the loss of algal phosphorus to non-algal particulate phosphorus and through sinking out of the epilimnion.

External sources of soluble reactive phosphate were wastewater, tributaries, and precipitation. An internal supply was added to this, mimicking the sediment and hypolimnetic supply (this supply is discussed subsequently). Particulate phosphorus was converted to soluble reactive phosphorus using first order kinetics. Soluble reactive phosphorus losses were algal consumption and surface outflow. Particulate phosphorus originated from tributaries, wastewater and conversion from algae. Losses were sinking, conversion into soluble reactive phosphorus and outflow.

An average water year was constructed from flow data (from all sources) obtained during 1972 and 1973 to provide daily water input for model runs. Weekly soluble reactive and total phosphorus loads determined during 1972 and 1973 for all natural sources (all sources excluding wastewater) were averaged to produce weekly natural loads. Thus the flow and loading inputs to the model displayed the same cycles each year, representing average "natural" conditions. During 1972 observed wastewater loads were added to the natural loads; from 1973 onward, wastewater loads were calculated as the product of an assumed concentration in the effluent and the average wastewater flow.

The model was calibrated by manipulating the coefficients N₁, N₂, σ_1 , and σ_2 to fit the 1972-1973 average epilimnetic concentrations observed in the lake. Model coefficients were initially estimated from those presented in Thomann, et al. (1975) and Baca, et al. (1974) and references therein.

An initial estimate of the internal supply of phosphorus was available from mass balance calculations comparing supplies and losses of total phosphorus with lake changes for the years 1970-1973. This estimate was necessarily a net supply and thus provided a lower limit to the supply of phosphorus from internal sources. It was reasoned that the lake sediments act like a capacitor, accumulating phosphorus during the year and releasing it during the anaerobic intervals. For the purposes of this model it was assumed that the total internal supply for the year was proportional to the previous year's deposition. The supply

was evenly distributed during two weeks in late winter and ten weeks during the summer, intervals during which anaerobic conditions have developed in the lake. For post-treatment years it was reasoned that the sediment phosphorus would washout, hence a constant of proportionality greater than I was used. A value of 1.1 with an initial supply of 60 kg/day provided a good fit.

Figures 3 and 4 compare calibrated model runs with lake observations for total phosphorus and chlorophyll \underline{a} . Algal phosphorus was converted to chlorophyll \underline{a} using a factor chlorophyll $\underline{a} = \frac{\text{algal phosphorus}}{0.62}$ based upon regressions of chlorophyll \underline{a} on particulate phosphorus for lake observations. This conversion ratio is lower than the more commonly used 1:1 value (Thomann, et al., 1975; Baca, et al., 1974). The runs presented are not necessarily the best fit to the data in any statistical sense, but represent runs which approach the actual pattern observed. Other combinations of coefficients could be used to produce approximately the same results. The selection of coefficients used to produce these "final" runs is therefore somewhat arbitrary, and although techniques exist which provide parameter estimates based upon minimized deviation techniques, they are somewhat costly and thus have not yet been tried.

The model mimics the temporal pattern of total phosphorus and chlorophyll a although some differences occur both in timing and magnitude of pulses (Figures 3 and 4). These differences probably occur because year to year differences in timing of internal phosphorus pulses, initiation of algal blooms and other factors were not included in the model. The model is based upon average conditions and produces results which might be expected in an average year. The gradual decline in phosphorus concentrations in the lake is mimicked by the model up through mid-1975 as is a decline in the magnitude of the summer algal blooms. It is interesting that the model projects wintertime phosphorus levels of about 20 µg/1 during 1974-1975, and appears to stabilize at wintertime epilimnion levels similar to those projected by the previous models for the entire lake (Figures 3, 5 and 6), but the time required to reach this level is considerably longer than that projected by the other models. Mean values for the epilimnion during the mid-December mid-January are only slightly lower than the average lake levels used to compare the previous models.

The calibrated model projections of total phosphorus and algal concentrations expected if wastewater concentrations were altered are summarized in Figures 5 and 6. The model was run until a stable pattern occurred; the results displayed compared the effects of 50, 400, and 1,000 $\mu \rm g/l$ total phosphorus wastewater concentrations; (total phosphorus was supplied in a ratio of 30% soluble reactive phosphorus and 70% particulate phosphorus, consistent with observations based upon proportions in the present wastewater). Data obtained during 1974 are included for comparison. The model projections suggest that the total phosphorus

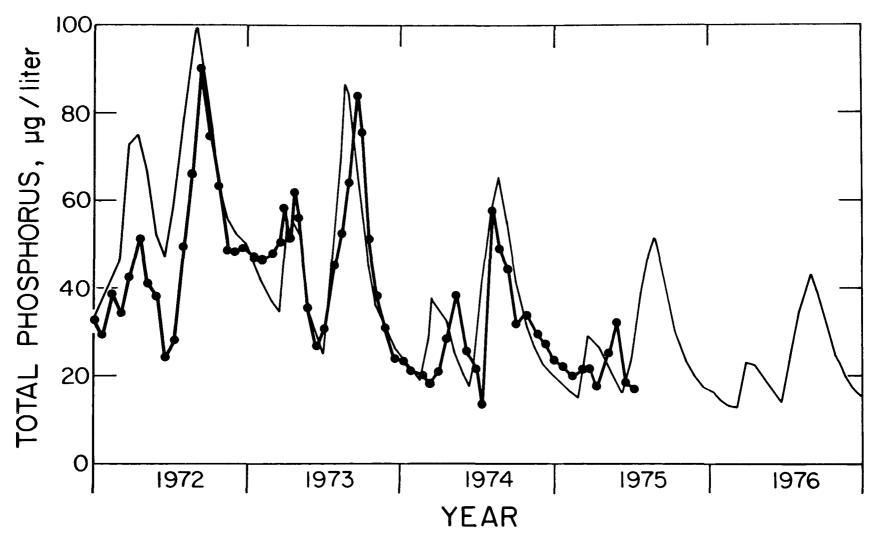


Figure 3. Comparison of predicted epilimnetic total phosphorus concentrations (light line) with lake observations.

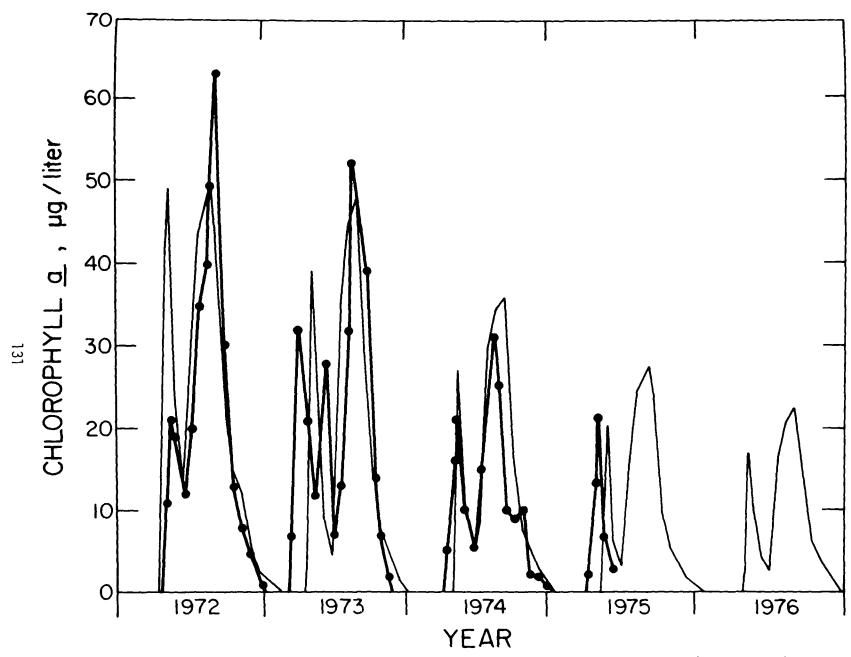


Figure 4. Comparison of predicted epilimnetic chlorophyll concentrations (light line) with lake observations.

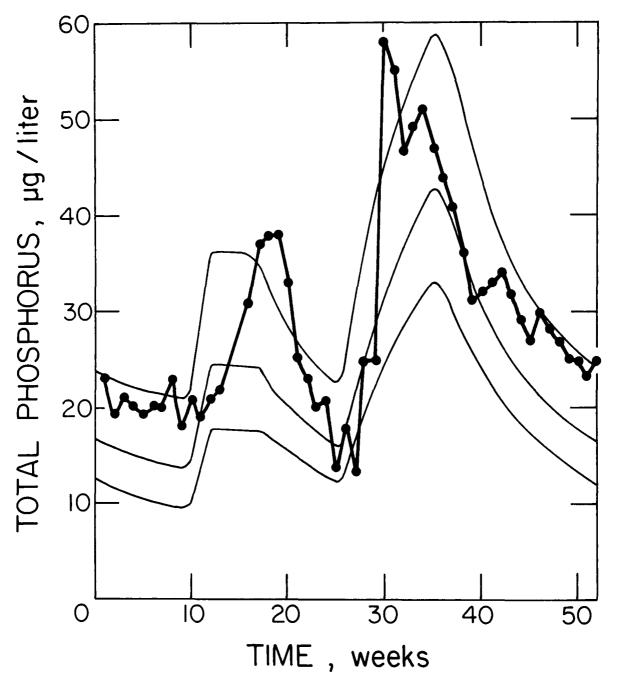


Figure 5. Sensitivity of epilimnion model response (total phosphorus) to different wastewater total phosphorus concentrations (50, 400, 1000 $\mu g/1)$ at model stable state (light lines) compared with 1974 lake epilimnion observations.

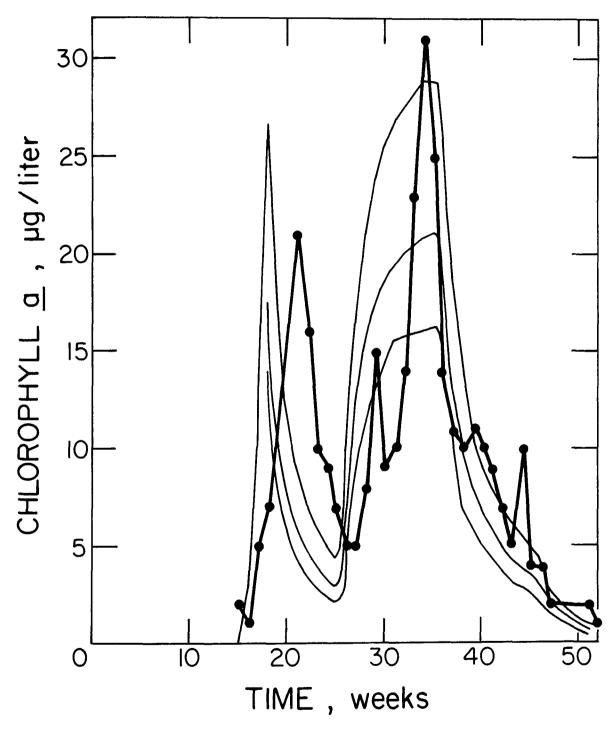


Figure 6. Sensitivity of epilimnion model response (chlorophyll \underline{a}) to different wastewater total phosphorus concentrations (50, 400, 1000 $\mu g/l$) at model stable state (light lines) compared with 1974 lake epilimnion observations.

pattern which might occur if wastewater effluent total phosphorus concentrations were 1.0 mg/l would be similar to that observed during 1974 with peak average values of about 60 µg/l and wintertime concentrations of about 20-25 µg/l. Chlorophyll a concentrations might similarly exist as they did during 1974 with peak average summertime concentrations of 25-30 μ g/l. A wastewater effluent concentration of 400 μ g/l might produce conditions where total phosphorus concentrations slightly exceed 40 ug/1 during the summer and wintertime concentrations would be approximately 15 μ g/l. Summertime chlorophyll a values might be about 20 μ g/l. These projections rely upon the assumption that the lake will respond in a fashion similar to the manner in which it has responded in the past. Of particular significance are the projected phosphorus pulses which drive the summer blooms. These seem to be related to the generation of anaerobic conditions in the bottom waters thus, if, at present wastewater effluent levels, the deeper waters cease becoming anaerobic, a different pattern might emerge. It is also unknown whether higher wastewater phosphorus concentrations (for example 400 µg/l) will continue to promote anaerobic conditions, hence provide stimulation for summer algal blooms.

DISCUSSION

The Vollenweider and Snodgrass-O'Melia models predict lake phosphorus concentrations considerably below observed values because these models do not include mechanisms by which phosphorus is supplied from internal sources, a feature which apparently controls the recovery of the lake to some extent. Vollenweider (1975) specifically stated that the mass balance model he developed is inapplicable to situations in which there is net annual internal supply of phosphorus; Snodgrass and O'Melia restrict the utility of their model to lakes whose hypolimnia remain aerobic throughout the year. Nevertheless, it was instructive to apply these models to compare their predictions with lake observations to obtain a measure of the deviation of the Shagawa Lake response from simple model predictions. Both models suggest that wintertime total phosphorus concentrations should be about 10 μ g/l. This value is a reasonable expectation since mean influent concentrations are presently about 18 µg/1, and lake concentrations are expected to be less than this value after a stable state has been achieved. An empirical expression which relates the retention of phosphorus by lakes to the hydraulic washout coefficient (Larsen and Mercier, 1975) suggests that 45% of Shaqawa's influent phosphorus should be sedimented annually; therefore, steady state concentrations should be approximately 10 ug/1 as suggested by the above two models. Also, total phosphorus concentrations in the upper 10m of Burntside Lake, upstream of Shagawa Lake and uninfluenced by urban activities, were approximately 9 µg/l during 1974. Thus these models likely provide good indications of the expected level at which the lake should stabilize.

The effect of the internal source of phosphorus has been to delay the attainment of these predicted levels. This effect has been incorporated in the epilimnion model by establishing the construct that the internal supply of phosphorus is proportional to the previous years deposition. A proportionality greater than I implies leeching from the sediments, i.e. a store which built over pretreatment years discharges for sometime subsequent. A value of I or less might also represent sediment leeching since it is likely that only a fraction of deposited phosphorus is converted into soluble form.

The observed wintertime phosphorus concentrations might be the result of an equilibrium between sediment phosphorus and lake phosphorus maintained above expected levels by high concentrations of phosphorus within the sediments. This store of sedimentary phosphorus might be depleted slowly, depending upon such characteristics as the size of the reservoir (both as available phosphorus within a unit volume of sediments, and the depth within the sediments to which this phosphorus can release into overlying water), hydrodynamic characteristics of the overlying water, mixing processes within the sediments themselves, or the extent to which the sediment-water interface continues to become anaerobic. there is indeed a temporary or permanent equilibrium, the epilimnion model does not include mechanisms to describe it or its effect on lake dynamics, as indicated by the fact that it predicts wintertime total phosphorus concentrations similar to those of the other models but the time taken to reach those levels is longer than simple models suggest. The epilimnion model does show how, by pulsed inputs of phosphorus from internal sources, average levels of phosphorus during wintertime can be higher than those predicted by other models and how pulsed phosphorus inputs during the summertime influence summertime algal biomass as is expected during phosphorus limited conditions.

There is a precautionary note which must be considered when evaluating models of complex systems which have been tuned by coefficient manipulation, particularly if the models are to be used for predictive purposes. The models are abstractions of processes thought to be important in controlling the response of ecosystem; however, the model calibration or tuning process can hide failure to include some of the important processes because model coefficients are often difficult to verify in natural systems. The experimental values of coefficients used often display such ranges that wide latitude is available in selecting values during calibration to provide an acceptable fit to observed data. Thus the determination of the validity of projections is a somewhat subjective process and predictive ability might be poor if important processes are not included.

Although models of the nature of those presented in this paper are simple representations of complex systems and often include only estimates of important rates or coefficients, they provide an indication of some of the characteristics which can be expected in a lake. Perhaps more important, they provide a framework against which processes within the lake can be identified, particularly as deviations from model results. This can assist in designing or revising experimental approaches to provide a more complete description of a lake's activity or response.

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A Mathematical Model of Pollutant Cause And Effect in Saginaw Bay, Lake Huron

William L. Richardson and Victor J. Bierman, Jr.*

INTRODUCTION

As part of the joint U.S.-Canadian Upper Great Lakes Study, the U.S. Environmental Protection Agency, Large Lakes Research Station at Grosse Ile, has undertaken an intensive evaluation of the water quality process in Saginaw Bay. The project includes field examination of water quality and development of cause and effect models for data interpretation. These models are designed to simulate the effect of nutrients on the growth, composition, and distribution of phytoplankton biomass and will eventually be used to simulate the effect of nutrient control alternatives.

The primary emphasis of this paper is the presentation of methodology. including the practical considerations of applying an existing model structure to a new physical system. The existing model is the phytoplankton chlorophyll-nutrient model developed by O'Connor, et al. (1973). This approach has evolved over the past decade largely through research support from the U.S. Environmental Protection Agency and has recently culminated in its application to Lake Ontario (Thomann, et al. 1975). The computer program, which implements the Lake Ontario model (LAKE-1), has been modified to represent the physical system of Saginaw Bay. First, model output using the Lake Ontario biological parameters will be shown. This output will then be compared to model output using a set of biological parameters determined for Saginaw Bay. These parameters were based on a series of numerical experiments. The results of this comparison are preliminary and do not necessarily represent the exact dynamics or kinetics of the bay.

SAGINAW BAY WATER QUALITY CHARACTERISTICS

Although small in comparison to Lake Huron, Saginaw Bay is an important water resource serving as a source of water supply for municipal and industrial uses, for sport and commercial fishing, recreation, waste disposal, and navigation. The Bay has a surface area of about 2500 square kilometers and a 21,000 square kilometer drainage basin (Figure 1). The basin supports a population of 1.2 million (1970 census) and a variety of land uses including large industrial and urban centers. The basin also contains extensive agricultural, recreational, and natural areas.

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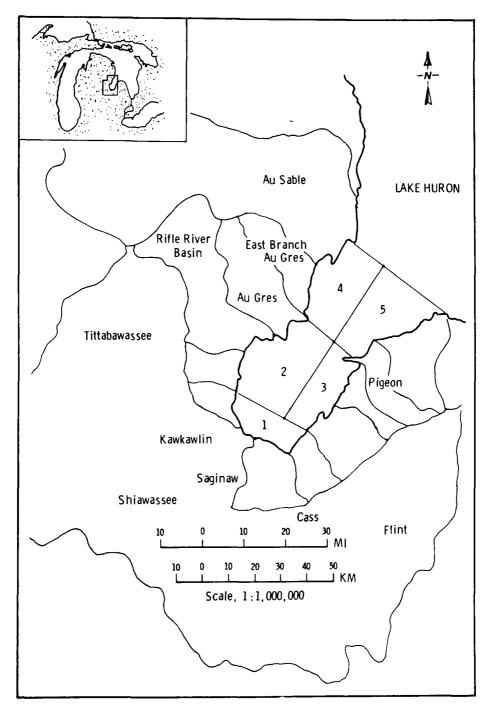


Figure 1. Saginaw Bay Basin and five model segments.

The hydrodynamics of the bay are such that Ayers et al. (1956) concluded that the bay acts like an estuary. Fish and Wildlife Service drift bottle studies concluded that circulation is variable and closely related to meteorlogical conditions. Northeast winds for example, can drive water into the bay which results in water level fluctuations near Saginaw River of over one meter (USDI 1956).

The physical, chemical, and biological dynamics in Saginaw Bay are very complex. Because of the dynamic interaction with Lake Huron, large water quality gradients extend from the Saginaw River, the primary source of material input, to the outer extremities of the Bay. Chloride levels in 1974 varied from 39 mg/l near the Saginaw River to 2 mg/l near Lake Huron. Chlorophyll <u>a</u> concentrations (an indirect indication of phytoplankton biomass) were recorded in the range of 1 to 82 mg/l in 1974 (Smith, 1975).

GENERAL MODELING PROCESS

The water quality processes for large, complex natural systems can be considered to consist of two primary components, 1) physical transport and 2) biological-chemical processes. A common approach is to develop separate process models independently and merge results into a final water quality management model (Figure 2). The resolution of either model component depends on the purpose or application of the model. For a general indication of future water quality trends for planning purposes, simple biological and chemical models averaged over space and time are appropriate. If more resolution is desired to answer other specific questions, then the model components must be sub-divided to provide more precise simulations.

Complex ecosystem models have been structured by several theorists but these have remained primarily research models with little or no field calibration or verification (Middlebrooks et al., 1973). Factors limiting the complexity of ecosystem models include computer size and execution time, as well as data acquisition and analysis. Expansion of the simple modeling framework to include more physical, chemical, and biological resolution is continuing as part of the EPA Great Lakes research program. Bierman (1975) has structured a four class phytoplankton model which contains more detailed nutrient-phytoplankton interaction kinetics. Thomann, et al. (1975), has structured a 67 segment model for Lake Ontario. These models represent the next generation of verified ecological models.

In the case of Saginaw Bay, the primary question concerns the effects of material load reduction on water quality parameters such as dissolved solids and biomass. The modeling approach applied herein is a simple evaluation tool for making such assessments. The space scale considered is on the order of 10-30 kilometers and the time scale on the order of seasons.

MODEL PRINCIPLES

The key principle used in the modeling of material transport is mass balance. The model equations for physical, chemical, and biological systems conserve mass in both space and time. The computer program which implements these equations accounts for and traces materials from their spatial

GROSSE ILE LAB MODELING PROCESS

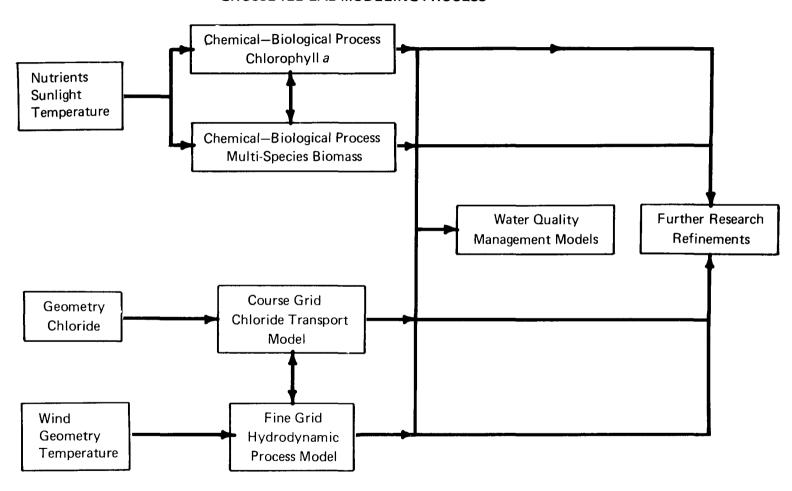


Figure 2. Mathematical modeling process diagram.

points of input to their final export points. If the material is conservative, the transport mechanisms are totally physical. If the material is non-conservative, such as nitrogen and phosphorus, the transport mechanisms also include chemical and biological reactions. A mass balance equation in finite difference form for a water body divided into n finite completely mixed segments is given by Thomann et al. (1975):

$$[V] \frac{d(s)_k}{dt} = [A] (s_k) \pm (S)_k \pm (W)_k$$
 (1)

where

 $v = n \times n$ diagonal matrix of volumes, (L)

 (s_{ν}) = n x l vector of material concentration

 $[A] = n \times n$ matrix of advective and dispersive transport terms

 $(S_k) = n \times 1$ vector of kinetic interaction terms

 $(W)_k = n \times 1$ vector of material s_k inputs

This system of equations accounts for the mass of a substance k in each model segment which is equal to the mass entering minus the mass leaving, plus or minus mass produced or lost within the segment.

PHYSICAL TRANSPORT

The first phase of model development for large, dynamic water systems is usually devoted to quantifying the circulation. This has been done for Saginaw Bay by tracing a conservative substance, chloride, through the system by adjusting transport parameters in equation 1 until a reasonable comparison is obtained between computed and measured chloride concentrations (Richardson 1975).

BIOLOGICAL-CHEMICAL PROCESSES

The general scheme of nutrient/chlorophyll a dynamics for a single segment has been adapted from O'Connor, et al. (T973) (Figure 3). The specific system scheme used for Saginaw Bay adapted from Thomann et al. (1975) includes eight state variables with their interactions (Figure 4). This model is a simplification of a complex biological-chemical system where phytoplankton biomass is represented by chlorophyll a which is used primarily because of the ease of measurement and availability of data. Phytoplankton carbon is specified using carbon-chlorophyll stoichiometry obtained by experimental data and is the element which zooplankton consume along with other nutrients contained in the phytoplankton. The nutrients, phosphorus and nitrogen, are also accounted for and traced through the phytoplankton and zooplankton by specifying stoichiometry relationships with carbon. The model assumes all other nutrients to be in sufficient supply so as not to limit phytoplankton growth.

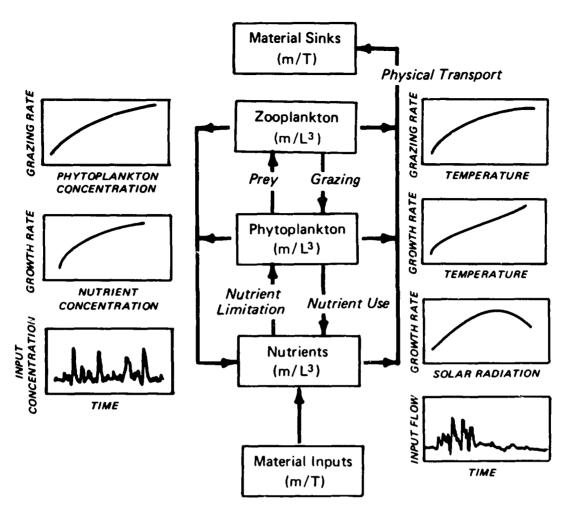


Figure 3. General nutrient-phytoplankton model interactions.

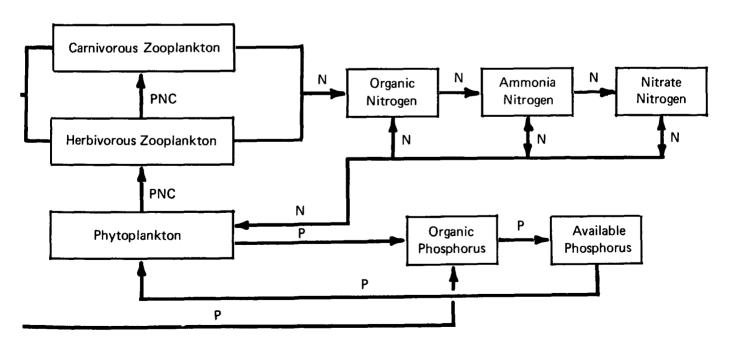


Figure 4. Specific model biological-chemical interaction diagram (Thomann 1975).

The biological-chemical equations have been developed and reported by Thomann et al. (1975) and the details will not be repeated here. However, in summary the key assumptions of the kinetic expressions will include:

- 1. Phytoplankton growth rate is a function of temperature, light and nutrients and uses Michaelis-Menton product kinetics. A maximum growth rate is computed from the temperature relationship and then reduced by the product of the nutrient and light limitation terms. The death rate is a function of zooplankton grazing and endogeneous respiration. Both of these processes are temperature dependent. The dead phytoplankton return to the non-living organic nutrient pools and the grazed phytoplankton become part of the zooplankton biomass. Phytoplankton can also leave the system by sinking to the sediment.
- 2. Herbivorus zooplankton growth rate is a function of the grazing efficiency, grazing rate, and available phytoplankton, and follows a Michaelis-Menton form (i.e., the growth rate reaches an asympote as phytoplankton concentration increases). The death rate is a function of temperature and the grazing rate of the carnivorous zooplankton. Grazed zooplankton biomass and nutrients become part of the carnivorous zooplankton biomass whereas the dead zooplankton biomass and nutrients return to the non-living organic pools.
- 3. The growth rate for carnivorous zooplankton is a function of grazing rate and efficiency and the death rate is a function of temperature only. Dead zooplankton return to the appropriate material pools.

APPLICATION TO SAGINAW BAY

SEGMENTATION

The bay was divided into five (5) segments shown in Figure 1. This segmentation scheme was chosen after considering such factors as water quality gradients, morphology, spacial resolution desired, and available research time.

MATERIAL LOADINGS

The primary source of material input to Saginaw Bay is the Saginaw River. The loadings provide the forcing functions, (W), to the mathematical model (Equation 1) and must be defined for each state variable during the entire period for which the model is run. For this investigation loadings were computed by the product of river discharge and material concentration. The U.S. Department of the Interior (1975) provides daily discharge information for the four major tributaries to the Saginaw River including the Cass, Tittabawassee, Shiawassee, and Flint Rivers. Meaningful flow measurements can not be made near the mouth of the Saginaw River since the river behaves like an estuary and reacts hydraulically to the fluctuations in the bay water levels. This can cause flow stagnation and reversals which make stage recordings meaningless for flow computations. Therefore, the daily measured flows from the four major tributaries were added along with a computed flow representing the ungaged portion of the basin (about 24% of the total basin).

The material concentrations were obtained from the Michigan Water Resources Commission bimonthly sampling station at Midland Street in Bay City about five miles upstream from the mouth of the river, the Cranbrook Institute of Science (1975) sampling stations at the Dow Chemical Co. water intake (samples about every two or three days) about a mile upstream from the mouth and from the Cranbrook Station at Midland Street (sampled once or twice per month). During low flow periods, June through December, the Dow intake is influenced by the diluting effect of the bay, therefore these data were used only for the peiod of January through June. For days when a sample was collected a daily load was computed as the product of the daily average flow and the grab sample concentration. These points were connected by straight line segments to provide a continuous time series for the entire year of 1974. These are shown in Figure 5 for each state variable including chloride.

Circulation --

The circulation pattern in the bay was obtained by mathematically tracing the transport of chloride from Saginaw River through the five segments. The details of this approach have been presented by Richardson (1975). In summary, having measured the chloride loads from the Saginaw River and the average segment concentrations, the transport dispersion and the advection terms in the mass balance equation are adjusted (Figure 6) until computed chloride concentrations match the measured in the five segments (Figure 7). The measured chloride time series is the cruise by cruise average of chloride measurements. A simulation is acceptable when the computed concentration falls within a range of plus and minus one standard deviation of the mean. Note that this criterion has not yet been met at all times in each segment. This is especially the case in segments 1 and 3, the smallest and most dynamic. However, these comparisons are sufficiently accurate during this initial phase. The degree of further refinement will depend on the results of biological-chemical modeling and the resolution obtained.

<u>Initial Results</u> --

As a starting point, an initial simulation was obtained from the modified Lake Ontario "LAKE-1" computer program. Only those parameters unique to Saginaw Bay in 1974 were changed. These included segmentation, advective and dispersive transport terms, boundary conditions, initial conditions, segment temperatures, segment light extinction, and segment depth. The Saginaw Bay physical characteristics are listed in Table 1. The first run was made using the verified Lake Ontario biological-chemical parameters (Thomann et al. 1975). To simplify this presentation only the results for Segment 3 are shown (Figure 8).

To compare the computed concentrations (model output) with those measured (actual data), the data for all sampling stations in a model segment (Figure 9) were combined for each sampling cruise and the mean and standard deviation computed. This was easily facilitated by the use of the EPA data system, STORET. The cruise means and standard deviations were inputted to the LAKE-1 graphics subroutine and plotted along with the computed results for each of comparison.

Saginaw River MATERIAL LOADS TO SAGINAW BAY

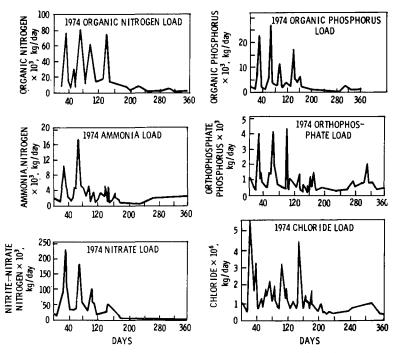


Figure 5. Saginaw River material loads to Saginaw Bay.

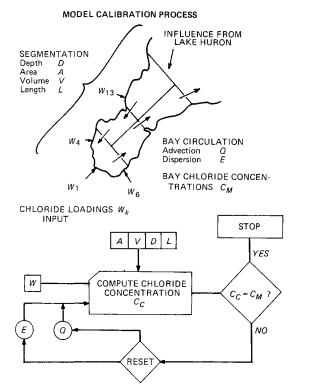


Figure 6. Physical transport model calibration process.

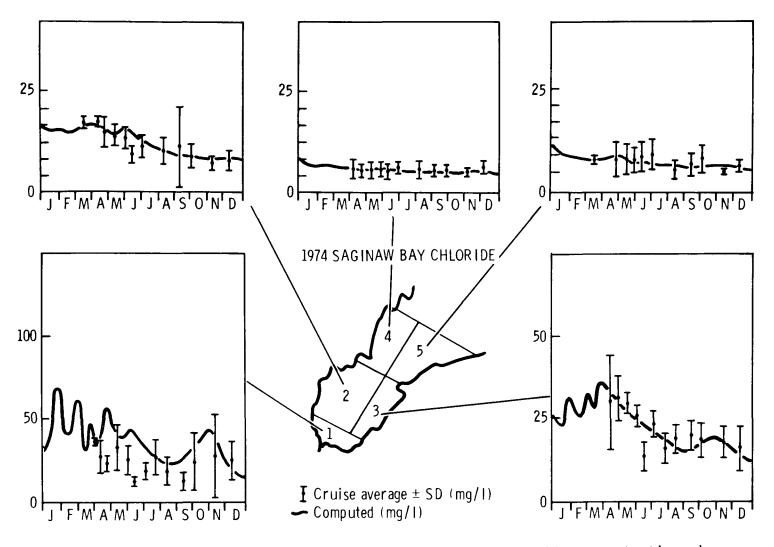


Figure 7. Comparison of 1974 computed and measured chloride concentrations in five model segments.

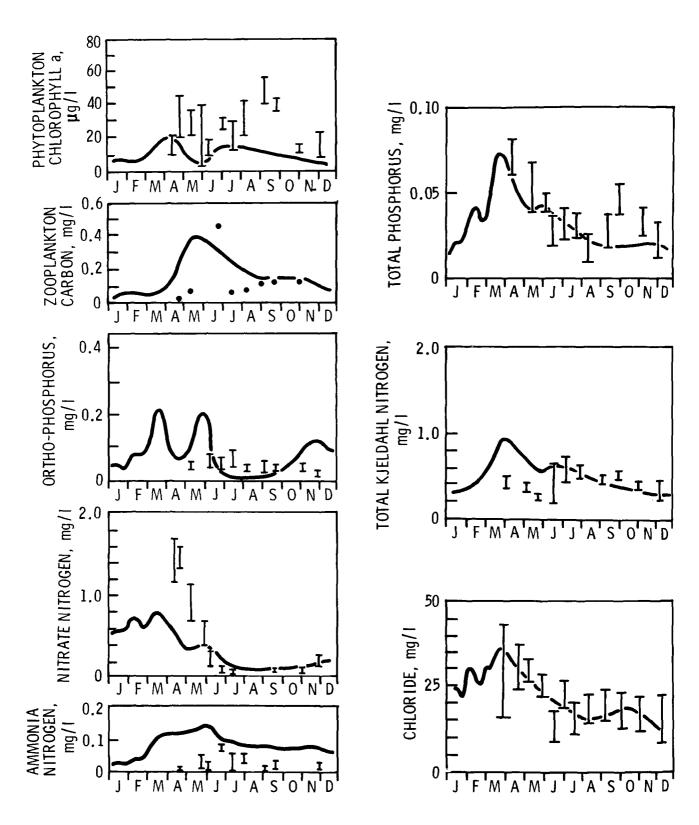


Figure 8. Comparison of 1974 computed and measured material concentrations in Saginaw Bay for initial model simulation using Lake Ontario model bio-chemical parameters.

TABLE 1. SAGINAW BAY MODEL PHYSICAL PARAMETERS

Segment	Interacting Segment	Segment Volume km ³	Average Depth m	Light Ext. Coef. m ⁻¹	Intersegment Area m ² x 10 ³
1	2	894	3.85	1.5	100
2	2 3 3	5890	7.33	1.0	123 35 137
3	3 4	1270	3.74	1.0	133
4	5 5	7880	13.22	.5	35 499
5	Lake Huron Lake Huron	9390	15.15	.5	323 769

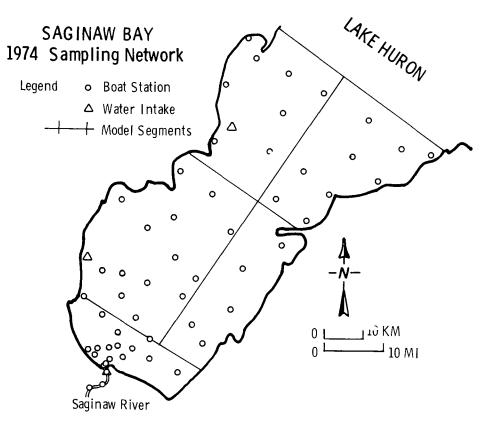


Figure 9. Saginaw Bay 1974 sampling network.

The initial results (Figure 8) reveal the following:

- 1. Computed phytoplankton grow too early in the year which results in bad timing for the spring and fall peaks as compared to the data.
- 2. As a result of the early phytoplankton growth, computed zooplankton appear too soon which shifts the entire zooplankton time series. Too much computed zooplankton biomass could be one of the factors which reduces the computed phytoplankton levels relative to the observed values.
- 3. The reaction rates for conversion of organic nitrogen and ammonia to nitrate are too low. This is apparent because the computed concontrations of total kjeldahl nitrogen and ammonia are higher than the measured and that for nitrate is too low.
- 4. The poor timing and insufficient growth of phytoplankton result in poor timing for orthophosphorus. Computed orthophosphorus appears to be another limiting factor for the computed phytoplankton peak during the summer.
- 5. Total phosphorus appears to be too low in the fall. This could be caused by incorrect loss rates and/or by an inaccurate total phosphorus load.

Calibration --

The calibration process proceeds similarly to that described previously for chloride except there are 16 biological-chemical parameters to adjust compared to only only two transport parameters. This process is not a curve fitting exercise in a statistical sense; rather, it requires an understanding of the cause and effect relationships inherent in the system and knowledge of a reasonable range of values for each parameter (0'Connor, et al. 1973). As each parameter is altered keeping all others constant, perception of the sensitivity and importance of each is obtained by the analyst which further increases his insight and intuition. One problem arising, however, is the practicality of assimilating all of the information generated. Computer output must be reduced to graphs, and graphs of simulations overlaid to depict the alterations. The analyst soon becomes overwhelmed having to perceive eight state variables, for five segment, for numerous calibration simulations.

To simplify this process the emphasis was given to chlorophyll \underline{a} in segment 3. This reduces the number of graphs from forty to just one for each simulation. A few of the more important initial sensitivity simulations are shown in Figure 10 compared to the base run. The results of these sensitivity runs revealed the following:

- 1. No single alteration of any of the principal parameters appears to have a significant effect on the magnitude of the computed phytoplankton chlorophyll a.
- 2. A reduction of 75% in the phosphorus-chlorophyll <u>a</u> ratio (from .001 to .00025 mg per μ g chlorophyll <u>a</u>) has the most significant single impact primarily in summer chlorophyll peak.

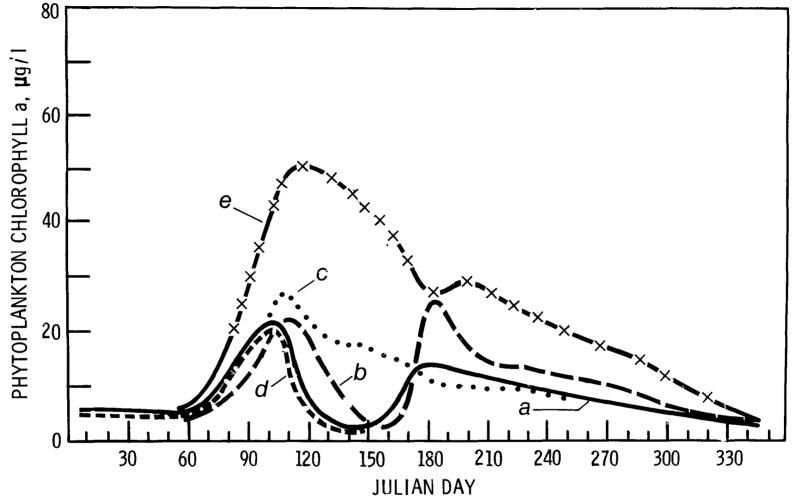


Figure 10. 1974 phytoplankton chlorophyll <u>a</u> concentration sensitivity simulations including:

- ----Phosphorus-chlorophyll a ratio of .00025
- • • •Carbon-chlorophyll ratio of .025 and herbivorous zooplankton grazing rate of .2
- d -----Organic nitrogen and ammonia nitrogen decomposition rates of .01
- e x-x-x-xAll above except phos-chlor ratio of .0005 and phytoplankton settling rate of .05

- 3. Only after altering the phosphorus-chlorophyll <u>a</u> ratio, carbon-chlorophyll <u>a</u> ratio, herbivorous zooplankton grazing rate, and nitrogen decomposition rates concurrently does the chlorophyll <u>a</u> increase significantly.
- 4. To fit the data, the organic nitrogen to ammonia, and ammonia to nitrate decomposition rates must be increased by an order of magnitude over those used for Lake Ontario.

Once these required alterations were determined, additional sensitivity simulations were made from this new base. The best comparisons (at the time of this report) of observed versus computed for the eight state variables and five segments are shown in Figures 11 through 17. As these show, more effort remains to obtain an acceptable calibration. The parameter values for this final run are listed in Table 2. In particular, as Figure 13 shows, computed levels of orthophosphorus are too high in all segments throughout the year. Also, it would be desirable to refine the chlorophyll \underline{a} simulation in Segment 3.

TABLE 2. BIOLOGICAL-CHEMICAL MODEL PARAMETERS

		Lake 1 Ontario	Saginaw Bay	Units
Nitrogen	Half-saturation constant Organic nitrogen decomposition rate Ammonia to nitrate nitrification rate Nitrogen-chlorophyll ratio	0.025 0.0175 0.002 0.01	0.025 0.007 0.015 0.01	mg/lldeg-lday-ldeg-lday-ldeg-l
Phosphorus	Half-saturation constant Organic phosphorus decomposition rate Phosphorus-chlorophyll ratio	0.002 0.007 0.001	0.005 0.007 0.00025	mg/l day ^{-l} deg ^{-l}
Zooplankton	Conversion efficiency Endogenous respiration rate Herbivorous zooplankton grazing rate Carnivorous zooplankton grazing rate	0.6 0.001 0.06 0.06	0.6 0.001 0.04 0.04	day ⁻¹ deg ⁻¹ 1/mg C day deg 1/mg C day deg
Phytoplankton	Chlorophyll half-saturation constant Endogenous respiration rate (at 20°) Settling velocity Saturated growth rate	10 0.1 0.1 0.58	20 0.1 0.05 0.50	µg/l day-l m/day day-l
Carbon	Carbon-chlorophyll ratio	0.05	0.025	a

 $^{^{}a}$ Ratio mg element to μg chlorophyll.

¹Thomann 1975.

Figures 11-17. Final comparison of 1974 computed and measured material concentrations.

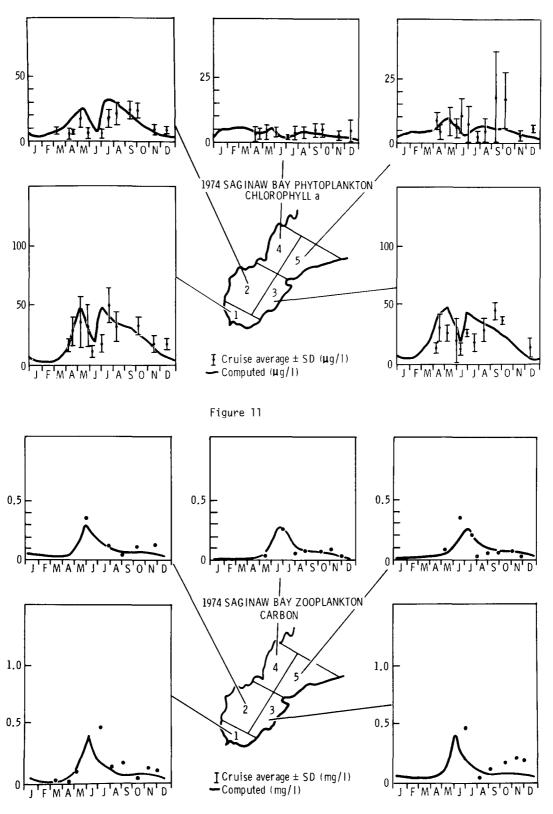


Figure 12

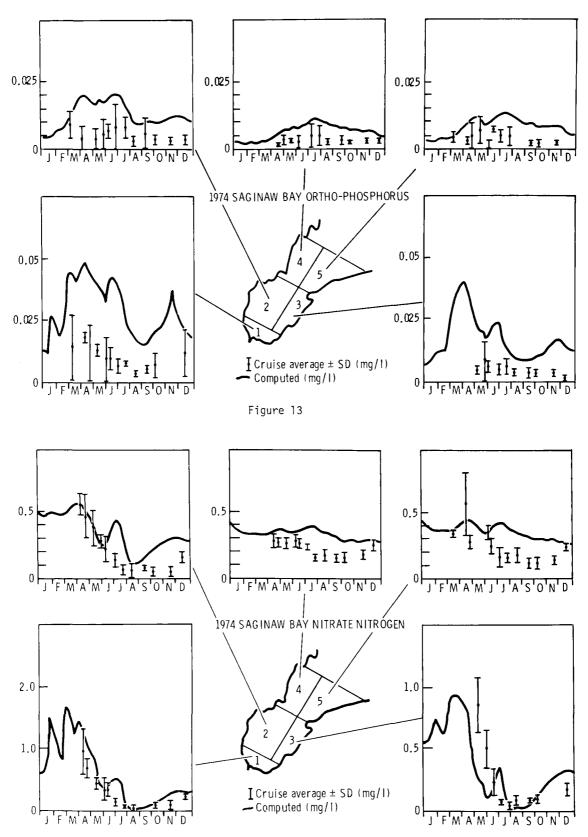


Figure 14

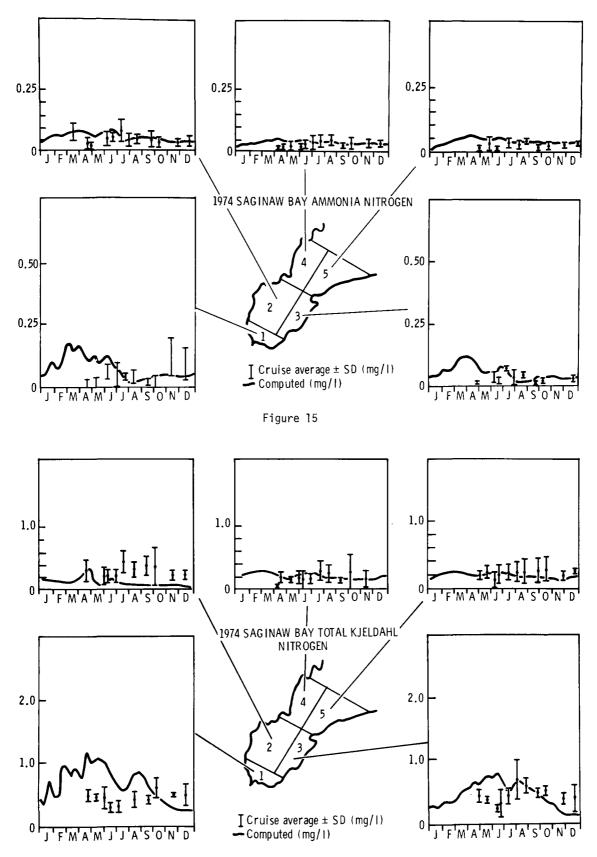
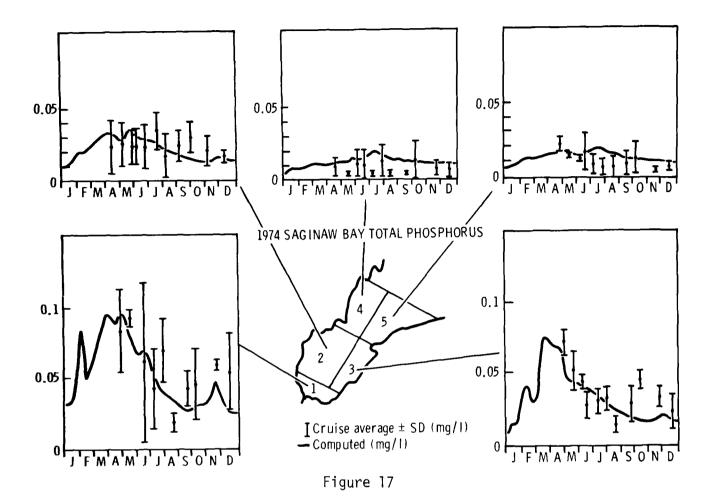


Figure 16



DISCUSSION AND CONCLUSIONS

Although additional effort remains to be expended, some general conclusions can be drawn from the work done to date. It is emphasized that the model parameter values reported herein (Table 2) have yet to be confirmed and checked and only represent order of magnitude estimates at this time.

It has been learned that substantial research resources are required to apply an existing computer program/model to a new physical system. The emphasis in modeling research is not on the writing of the computer program but rather on arriving at the basic workable kinetic structure and then calibrating this structure to a given data set. If a calibration can be obtained, the model must then be verified by comparing model results to an independent data set-ideally after the system has been perturbed (i.e., phosphorus loads altered).

Although this effort was initially considered to be an "application" project, calibration and verification for a new system require such a substantial effort, with no guarantee of success, that this work should be considered as applied research. Only after calibration and verification are obtained can a model be "turned over" to an engineering staff for use in making management decisions. The time required from project initiation to final transfer to manage-

ment of any new system is on the order of one to two years if all required data is available.

The calibration/verification research, itself, has side benefits which are useful during the course of the work. The modeling process requires a systematic approach to data collection and analysis. It helps structure a surveillance program and preliminary model results can be used to gain insight into the data and help in the management of surveillance and experimentation programs. The preliminary results reveal gaps in our knowledge for a particular system and are useful to direct new study and research. As an example, the Saginaw Bay model has revealed possible errors in total phosphorus loading in the fall. This has led to detailed inquiry of possible additional sources of phosphorus from diffuse sources, release from sediments, and from the atmosphere. Inquiry was made to regulatory agencies on possible seasonal loadings from waste sources. Additional work remains to be done to quantify the effect of dredging as a possible source of phosphorus and more effort needs to be made on the method of sampling the Saginaw River and accurately computing the loadings to the Bay.

Concerning model results, no specific conclusions can be drawn as yet. However, the model has revealed Saginaw Bay to be quite a different system than Lake Ontario which reinforces intuitive conclusions made from observing the data. Decomposition rates used in the model are higher as expected. The phosphorus-chlorophyll a ratio apparently must be lower, especially in the fall. This indicates a possible need to alter the model structure. Perhaps this ratio is time-variable due to a shift in the dominant plankton Phytoplankton settling velocity appears to be lower than that for Lake Ontario. This is reasonable because the hydrodynamics of the bay tend to keep materials in suspension. The initial phytoplankton growth was better using a saturated growth rate of .5 per day rather than .58 used for Ontario and the Potomac models (O'Connor, et al. 1973). This may be an artificial compensation for lack of information on exact levels of solar radiation and light extinction in the water under ice. Alternatively, it could be accounted for by species differences between the systems. The zooplankton kinetics are yet to be confirmed by experimental research so the zooplankton parameters remain to be adjusted over large ranges.

In conclusion, this effort represents a first EPA in-house attempt to apply an existing computer program/model which had been developed under previous and ongoing EPA grants. A close working relationship was established between the grantee staff and the EPA research staff which resulted in better communications and an overall enhanced program for all of the Great Lakes modeling research.

The average chlorophyll \underline{a} biomass model is a relatively economical research tool which can aid \overline{in} analyzing complex, limnological interactions and has been useful in guiding additional research and data gathering activities.

ACKNOWLEDGEMENTS

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Mathematical Model of Phytoplankton Growth and Class Succession in Saginaw Bay, Lake Huron

Victor J. Bierman, Jr. and William L. Richardson*

INTRODUCTION

Mathematical modeling techniques can provide a systematic basis for a research approach to the problem of cultural eutrophication and can greatly aid in the comparison of various management options. From an applied standpoint, the general techniques of O'Connor et al. (1973) have been brought to bear on a variety of different physical systems. In particular, Thomann et al. (1975) and Canale et al. (1973) have investigated phytoplankton-nutrient interactions in the Great Lakes. Chen and Orlob (1972) have also developed such techniques and have used them to investigate, among other cases, the effects of wastewater diversion from Lake Washington. From a research standpoint, work is progressing on a number of systems models and component models for purposes of gaining deeper insight with regard to chemical-biological processes that occur in natural systems (e.g., Middlebrooks et al. [1973]).

The present work is part of the International Joint Commission's Upper Lakes Reference Study involving Saginaw Bay, Lake Huron. The ultimate goal of this work is to develop a mathematical model which can be used both to describe the physical, chemical and biological processes that occur in Saginaw Bay and to predict the effects of reduced waste loadings. Specifically, the modeling effort will focus on phosphorus, nitrogen and silicon loadings to the bay and the resultant production of phytoplankton biomass.

Model development is proceeding along two parallel pathways. The first of these involves the development of research-oriented models which include biological and chemical detail but which, for simplicity, do not include any spatial detail. The second pathway involves the development of engineering-oriented water quality model which mimics, as closely as practicable, the actual physical system, including spatial detail. At any given point in time, the water quality model will contain those chemical and biological processes which have previously been investigated and developed using the spatially-simplified model. There is constant feedback between the above two pathways and constant interaction between the entire modeling effort and the ongoing sampling effort on Saginaw Bay.

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Previous work (Bierman [1976]) involved a preliminary calibration of a spatially-simplified, multi-class phytoplankton model to data from the inner portion of Saginaw Bay. Only chlorophyll and dissolved nutrient data were considered, and sensitivity analyses were presented for several important processes affecting the development of blue-green algae.

The present paper involves the use of the same spatially-simplified model. The purpose of this work is to obtain a more refined calibration using a data set that has been expanded to include total phosphorus, total nitrogen, and total zooplankton biomass. Also, finer time scales were used for external nutrient loads, boundary conditions, and water circulation rates. Ambiguities that can occur when calibrating an ecosystem model are discussed, in particular, those that can occur by using chlorophyll concentration as an indicator of phytoplankton biomass.

SUMMARY

A mathematical model of phytoplankton production has been applied to a set of physical, chemical, and biological data from Saginaw Bay, Lake Huron. The model includes four phytoplankton types, two zooplankton types, and three nutrients: phosphorus, nitrogen, and silicon. The phytoplankton types include diatoms, greens, and both nitrogen-fixing and non-nitrogen-fixing bluegreens.

The purpose of this study was to obtain the best possible calibration between model output and the existing data set. This is one of the many preliminary tasks which must be performed before such a model can ultimately be used as a tool for making management decisions.

The model output agreed reasonably well with the data for phytoplankton chlorophyll, total nitrogen, and dissolved forms of phosphorus, nitrogen, and silicon. The model output did not agree well with the data for total phosphorus during the latter part of the year, and the output showed a large discrepancy with the total zooplankton data.

Ambiguities persisted in the interpretation of the model output because insufficient data were available. The most serious problem was the lack of simultaneous measurements of phytoplankton biomass and zooplankton biomass. The existing phytoplankton data were available only in the form of chlorophyll concentrations, a lumped parameter which can not be used to distinguish among various functional groups of phytoplankton. Another problem was the lack of direct measurements for all of the rate coefficients in the model. Given the present state of the art, the latter problem is common to most ecosystems models

CONCLUSIONS AND RECOMMENDATIONS

Output from complex ecosystems models is difficult to interpret unless large amounts of experimental data are available. Frequently, more than one set of model coefficients will produce output which compares favorably with experimental data. For this reason, it is difficult to gain insight with regard to cause-effect mechanisms.

As the number of state variables for which there is comprehensive data is increased, many coefficients in a model become more tightly constrained. If an ecosystem model can be calibrated to a large number of simultaneous and independent variables, its reliability as a tool for drawing cause-effect inferences can be greatly increased.

Continued development of sophisticated phytoplankton production models will require detailed cell count and cell volume measurements. Chlorophyll measurements alone give no information with regard to the partitioning of phytoplankton biomass among various functional groups. In addition, system atic, comparative studies of phytoplankton-nutrient dynamics are required for various functional groups of phytoplankton in order to provide rate coefficients for such models.

MODEL CONCEPTS

The basic model framework and preliminary simulations appear elsewhere (Bierman [1976] and DePinto et al. [1976]). The compartments in the model are four phytoplankton, two zooplankton, higher predators, and three nutrients (Figure 1). The phytoplankton types include diatoms, greens, and bluegreens, both nitrogen-fixing and non nitrogen-fixing.

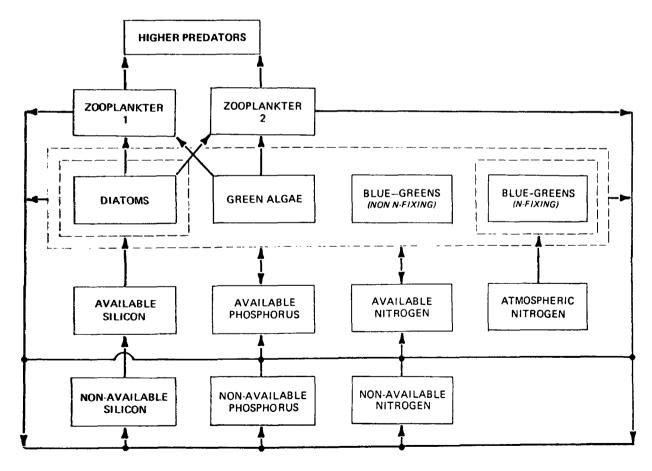


Figure 1. Principal compartments of the Saginaw Bay eutrophication model.

The motivation for a multi-class modeling approach is that different classes of algae have very different nutrient requirements, for example, diatoms need silicon and certain types of blue-greens can fix atmospheric nitrogen. In addition, at high concentrations, not all of these classes have the same nuisance characteristics from a water quality standpoint. Diatoms and green algae are grazed by zooplankton, but blue-green algae are not significantly grazed and can form objectionable floating scums.

A unique feature of the model is that cell growth is considered to be a two-step process involving separate nutrient uptake and cell synthesis mechanisms. The motivation for this variable stoichiometry approach is that an increasingly large body of experimental evidence indicates that the mechanisms of nutrient uptake and cell growth are quite distinct (e.g. Fuhs [1969, 1971], Droop [1973], Caperon and Meyer [1972a, 1972b]). The model includes carrier-mediated uptake of phosphorus and nitrogen using a reaction-diffusion mechanism, and possible intermediate storage in excess of a cell's immediate metabolic needs. Specific cell growth rates are assumed to be dependent on the intracellular levels of these nutrients, in contrast to the traditional Michaelis-Menten approach which relates growth rates directly to extracellular nutrient concentrations.

MODEL IMPLEMENTATION

A major problem in attempting to implement a complex chemical-biological process model is the lack of sufficient experimental data. It is often possible that more than one set of model coefficients could produce an acceptable fit between the model output and a given data set. In the transition from single-class to multi-class models, this problem becomes particularly acute because it is no longer sufficient to ascertain a range of literature values for a given coefficient. Multi-class models necessitate the definition of class distinctions within this range. Given the present state of the art of ecosystems modeling and associated experimental work, many of the coefficients in such models must simply be estimated.

The primary operational differences among the phytoplankton types in the model are summarized in Table 1. Principal phytoplankton coefficients are summarized in Table 2. The working equations of the model and sensitivity analyses of some of the most important coefficients have been presented in Bierman (1976).

One of the assumptions of the model is that cell biomass concentration is a more accurate indicator of standing crop than is chlorophyll concentration. In addition, chlorophyll is a lumped parameter and can not be used to distinguish between different functional groups of phytoplankton. For these reasons, chlorophyll concentration does not appear in any of the kinetic equations of the model. However, the only available field data for phytoplankton in Saginaw Bay at this time are chlorophyll concentrations. In order to relate the model output to these data, the output must be converted to chlorophyll concentration.

TABLE 1. OPERATIONAL DIFFERENCES AMONG PHYTOPLANKTON TYPES

		Phytoplankton Type		
Characteristic Property	Diatoms	Greens (Blue-Greens (non N ₂ -fixing)	Blue-Greens (N ₂ -fixing)
Nutrient Requirements	Phosphorus, Nitrogen, Silicon	Phosphorus, Nitrogen	Phosphorus, Nitrogen	Phosphorus
Relative Growth Rates Under Opti- mum Conditions at 20°C	High	Moderately High	Low	Low
Phosphorus Uptake Affinity	Low	Low	High	High
Sinking Rate	High	High	Low	Low
Grazing Pressure	High	High	None	None

TABLE 2. PRINCIPAL PHYTOPLANKTON COEFFICIENTS

			Phytoplankton Type		
Parameter	Diatoms	Greens	Blue-Greens (non N ₂ -fixing)	Blue-Greens (N ₂ -fixing)	
Maximum P Uptake Rate (day)-1	0.502	0.502	0.588	0.588	
Maximum N Uptake Rate (day)-1	0.125	0.125	0.125	0.125	
Saturation Light In- tensity (ft. candles	s) 1000	1000	500	500	
Maximum Growth Rate at 20°C (day)-1	2.0	1.9	1.2	1.2	
Milligrams Dry Weight per Cell).15x10 ⁻⁶	0.27x10 ⁻⁷	0.25x10 ⁻⁷	0.41×10 ⁻⁷	
Sinking Rate (meters/day)	0.20	0.10	0.05	0.05	

The computer program which actually implements the model is written in FORTRAN IV and is structured in a form such that any number of phytoplankton and zooplankton types can be simulated, along with any set of food web interactions among these groups. The version of the model in Figure 1 consists of 20 simultaneous differential equations. The solutions were obtained using a fourth-order Runge-Kutta method with a time step of 30 minutes for the nutrient kinetics equations and a time step of 3 hours for the growth equations. For a 365-day simulation, approximately 4 minutes of CPU time are required on an IBM 370/158 computer. For the same simulation, approximately 45 minutes of CPU time are required on the Grosse Ile Laboratory's PDP-8/e minicomputer with floating point hardware.

EXPERIMENTAL DATA

The chemistry and chlorophyll data used were collected by Cranbrook Institute of Science (Smith [1975]). During 1974, 12 cruises were conducted and samples were collected from 59 stations in Saginaw Bay. Samples were taken at 1 meter and at all depths from 5 meters to the bottom in 5-meter intervals. A total of 111 station-depth combinations were sampled on most of the cruises. Analyses were conducted for 21 chemical parameters, including phytoplankton chlorophyll. Since the present modeling study is restructed only to the inner portion of Saginaw Bay (Figure 2), only data from the 33 field stations in this region were used.

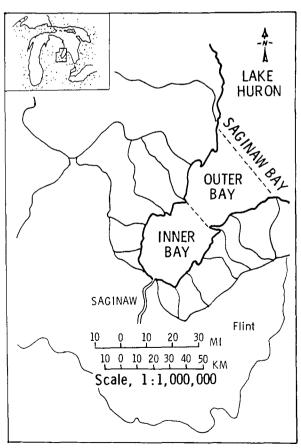


Figure 2. Saginaw Bay watershed indicating distinctions between inner and outer portions of the bay.

The zooplankton data used were collected on the above cruises at the same station-depth combinations as the chemical data. This work was conducted by the University of Michigan, Pellston Biological Station (Gannon [1975]). Zooplankton species counts were converted directly to dry weight concentrations and then integrated to the level of the two functional groups in the model. Work is progressing on phytoplankton species counts and cell volume measurements.

Nutrient loadings to Saginaw Bay from the Saginaw River, the primary source, were determined on the basis of a field sampling program. For the first half of the year, samples were taken at two- to three-day intervals at the Dow Chemical Company water intake plant at the mouth of the Saginaw River. From July to December, samples were taken from the Midland Street Bridge in Bay City every two weeks. During this period, the Dow intake plant was too strongly influenced by the bay itself. The Midland Street Bridge is approximately 5 miles upstream from the river mouth and is not influenced by the bay during this period. Concentrations were obtained for chloride and total and dissolved forms of phosphorus, nitrogen, and silicon. Daily flow rates were obtained from the U.S. Geological Survey.

BOUNDARY CONDITIONS AND FORCING FUNCTIONS

Since the physical system under consideration is only part of a larger physical system, Lake Huron proper, the interaction between Saginaw Bay and Lake Huron is extremely important. The predominant flow pattern in the bay is counterclockwise with Lake Huron water flowing in along the north shore and a mixture of Lake Huron water and Saginaw River water flowing out of the bay along the south shore (Figure 2). The concentrations of nutrients and biota in the water which flows across the indicated inner-outer boundary are examples of boundary conditions which must be specified. These concentrations were determined using the cruise data from two field stations nearest to the area of water inflow from the outer bay. Daily concentration values were calculated by linear interpolation between the cruise averages for these stations.

Before the model can be implemented, various quantities known as forcing functions must be specified. Conceptually, the physical system is described by a number of quantities called state variables (Figure 1). If, at a given time, values are specified for each of these state variables, then the complete state of the system is known. It is desired to use the model to calculate the state of the system at some future time. However, in order to do this for the present system, various quantities such as water circulation rates, light, temperature, and external nutrient loadings must be specified. These quantities are forcing functions and they are unique to the physical system under consideration.

External nutrient loads and water circulation rates are the most important forcing functions in the present study. Total daily flow from the Saginaw River was calculated by summing the primary tributary gauges and the estimated flow from the ungauged tributary area. Daily nutrient loading rates were calculated using the measured nutrient concentrations on that day. These daily loading rates were then plotted and time-series of loading rates were generated by linearly interpolating between all of the significant peaks and troughs. For example, for total phosphorus, a series of 46 loading rates/

time-breaks was generated. For orthophosphorus, a series of 46 loading rates/time-breaks was generated. Water circulation rates between the inner and outer bay were determined by modeling chloride concentrations in the bay and chloride loadings from the Saginaw River (Richardson [1976]). Time-variable flows were used which corresponded to hydraulic detention times ranging from 45 to 120 days for the inner bay.

RESULTS OF SAGINAW BAY SIMULATIONS

Calibration results are presented in Figures 3-10. Note that this model output is an attempt to describe an existing data set and is not intended to be predictive in nature.

To obtain model output for chlorophyll a, the total biomass concentration for all four phytoplankton classes in the model was converted to chlorophyll a concentration using 20 μg chlorophyll a/mg dry weight biomass. This conversion factor was based on fresh weight biomass and chlorophyll a data for Saginaw Bay (Vollenweider et al. [1974]), assuming that dry weight biomass is 20% of fresh weight biomass (Kuenzler and Ketchum [1962]). However, these data were collected at only one station in the inner part of the bay on eight separate cruises during the 1971 growing season. These data do not necessarily represent the average condition of the inner bay for 1974.

Preliminary simulations of chlorophyll a in Saginaw Bay (Bierman [1976]) showed that the model output was significantly higher than the data during the month of June. This problem has been eliminated in the present work (Figure 3) by using variable water circulation rates. Richardson (1976) has shown that two distinct flow regimes exist in Saginaw Bay, spearated by a turbulent transition period in June. Previously, this high June flushing rate was not modeled and only a constant, annual-average hydraulic detention time of 60 days was used.

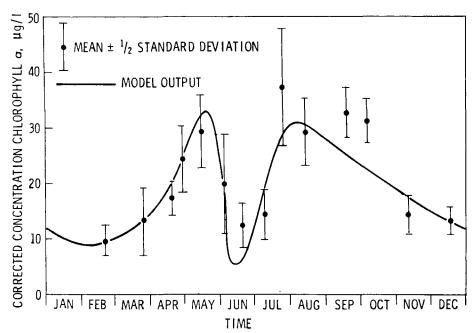


Figure 3. Corrected chlorophyll <u>a</u> distribution for 1974 in Saginaw Bay, inner portion, as compared to model output.

The class composition of the model output indicates that the early phytoplankton crops are dominated by diatoms and green algae and that the broad Summer-Fall peak is dominated by blue-green algae (Figure 4). A similar successional pattern was observed in the inner bay by Vollenweider et al. (1974). Chartrand (1973) reported significant late-Summer crops of Aphanizomenon, a filamentous, blue-green alga in the outer bay, which also corresponds to model output. It is not possible at this time to rigorously calibrate the model at the level of the four functional groups of phytoplankton. A more rigorous calibration depends on biomass data for each of the phytoplankton classes.

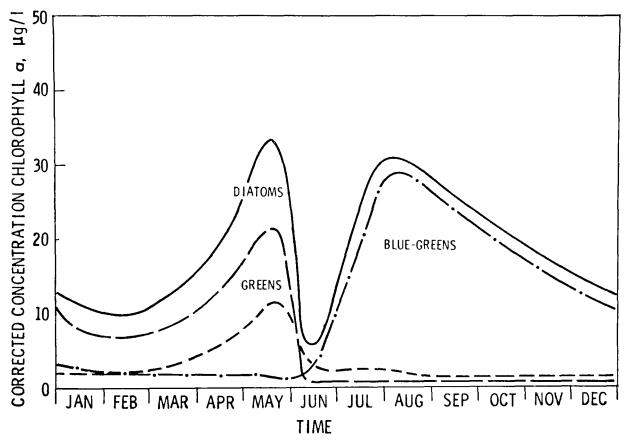


Figure 4. Phytoplankton class composition of model output in Figure 3.

The model output for total zooplankton biomass is much lower than the actual data (Figure 5). This might indicate that the zooplankton kinetics were modeled incorrectly because the model output for phytoplankton chlorophyll closely matches the actual data. However, chlorophyll does not appear in any of the kinetic equations of the model. The phytoplankton-zooplankton interaction is parameterized completely in terms of dry weight biomass. Since the only comprehensive phytoplankton data available at this time are chlorophyll data, neither the actual phytoplankton biomass nor the class composition of this biomass are accurately known. This uncertainty in the determination of phytoplankton biomass could be an alternative explanation for the discrepancy between the model output and the total zooplankton data.

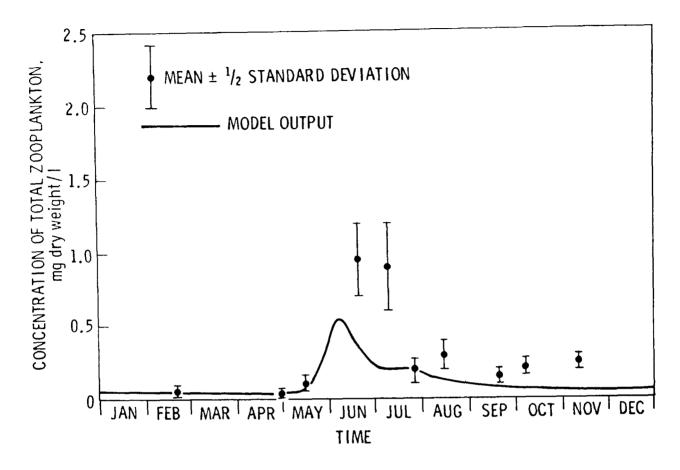


Figure 5. Total zooplankton biomass distribution for 1974 in Saginaw Bay, inner portion, as compared to model output.

Model output for total phosphorus (Figure 6) and total nitrogen (Figure 7) is reasonable, with the possible exception of the late-fall period for total phosphorus. Since the only external nutrient sources considered were the Saginaw River and Lake Huron, the present results must be considered preliminary in nature. The possible roles of sediments and atmospheric sources must be considered before a complete picture of the nutrient dynamics in Saginaw Bay can be obtained.

The general patterns of the model output for dissolved nutrients (Figures 8-10) agree reasonably well with the actual data. However, the above qualifications for total nutrients must also be applied to the dissolved forms.

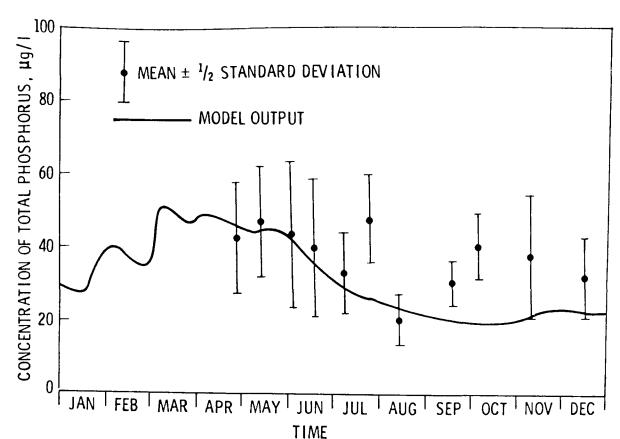


Figure 6. Total phosphorus distribution for 1974 in Saginaw Bay, inner portion, as compared to model output.

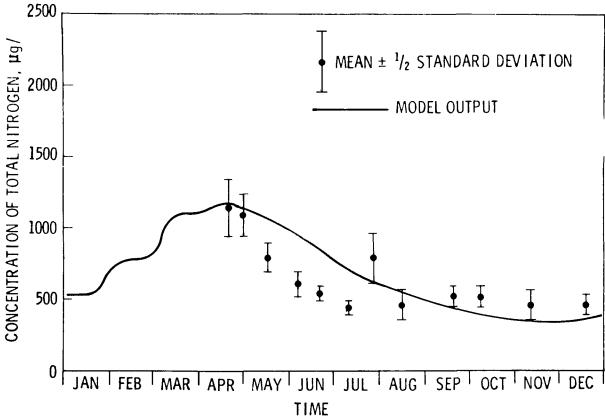


Figure 7. Total nitrogen (TKN plus nitrate/nitrite) distribution for 1974 in Saginaw Bay, inner portion, as compared to model output.

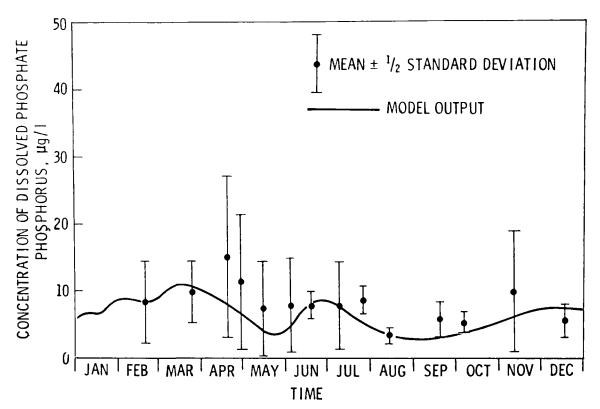


Figure 8. Dissolved orthophosphate phosphorus distribution for 1974 in Saginaw Bay, inner portion, as compared to model output.

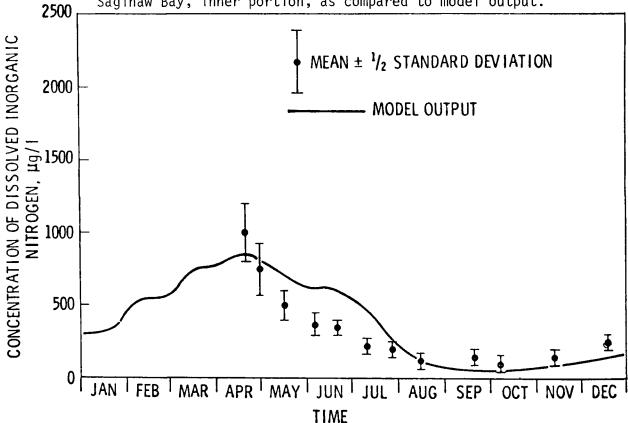


Figure 9. Dissolved inorganic nitrogen (ammonia plus nitrate) distribution for 1974 in Saginaw Bay, inner portion, as compared to model output.

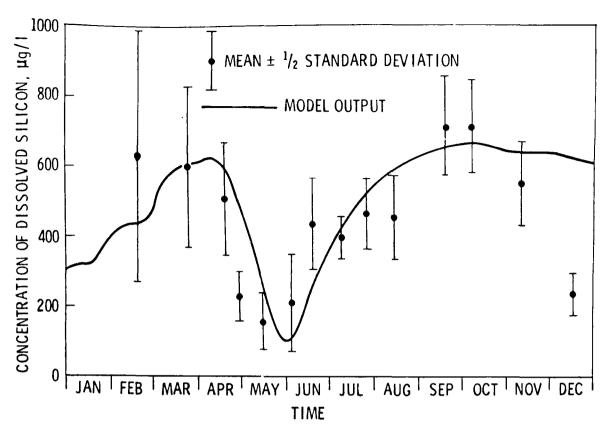


Figure 10. Dissolved silicon distribution for 1974 in Saginaw Bay, inner portion, as compared to model output.

DISCUSSION

In general, ambiguities can occur when attempting to calibrate a mathematical model if the model contains state variables or coefficients for which there are no direct measurements. This is usually the case with ecosystems models because the state of the art is still very primitive. There have been few comprehensive experimental programs designed to provide field data and rate coefficients for such models. The present model will be refined as measurements for additional state variables and rate coefficients become available.

One of the causes for the discrepancy between the model output and the total zooplankton data could be the lack of simultaneous measurements of phytoplankton biomass and zooplankton biomass. This problem is not necessarily unique to multi-class phytoplankton models, but can also occur with conventional chlorophyll models as well. A multi-class approach merely adds another dimension to this ambiguity because zooplankton are not considered to graze all of the phytoplankton classes. There is uncertainty in the partitioning of the total phytoplankton biomass among the various classes, as well as uncertainty in the total phytoplankton biomass itself. The only way to determine if resources should be expended to refine the phytoplankton-zooplankton interaction kinetics in the model is to first obtain comprehensive phytoplankton cell counts and cell volumes. Such a determination is being conducted for Saginaw Bay and the results will be incorporated in subsequent versions of the model.

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The lack of direct measurements for all of the independent rate coefficients in a model can still result in model output which corresponds closely to the actual data. However, cause-effect inferences can only be made with great caution in these cases. In such circumstances, a model can be valuable as a research tool if it is used to conduct sensitivity analyses for the purpose of determining the most important coefficients.

It should be noted that, as the number of state variables for which there is comprehensive data is increased, many coefficients in a model become more tightly constrained. For example, phytoplankton sinking rates of 0.15 to 0.40 meters/day were used in preliminary calibration work which involved only chlorophyll and dissolved nutrients (Bierman [1976]). Using the present expanded data set, it was found that phytoplankton sinking rates could not exceed 0.20 meters/day without causing a very significant discrepancy between the model output and the total phosphorus data. If an ecosystem model can be calibrated to a large number of simultaneous and independent parameters, its reliability as a tool for drawing cause-effect inferences can be greatly increased. The present model will eventually be calibrated to at least 12 simultaneous and independent parameters and tested against similar comprehensive data from the 1975 field sampling program on Saginaw Bay.

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Implications of Resource Development on the North Slope of Alaska with Regard to Water Quality on the Sagavanirktok River

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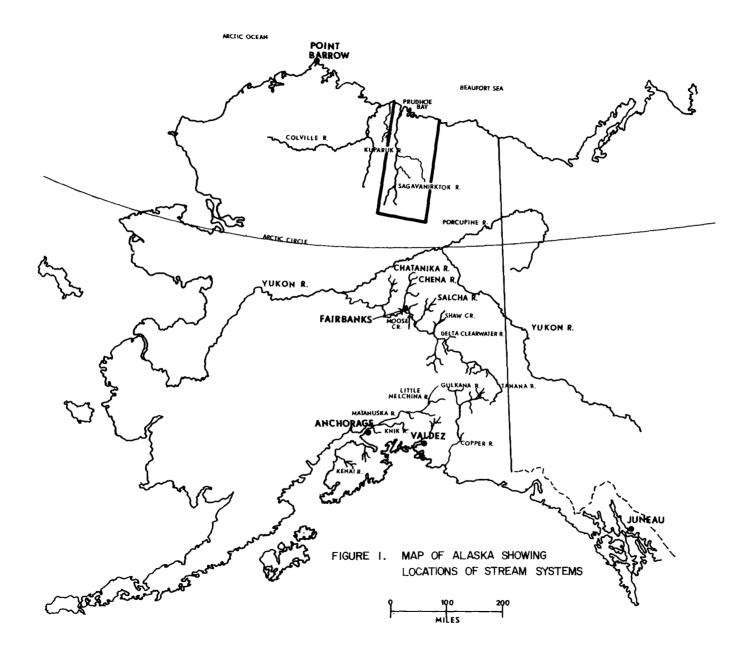
ABSTRACT

The Sagavanirktok (Sag) River, located on the North Slope of Alaska is undergoing a rapid transition from an isolated undisturbed river system to an accessible impacted watershed. Impact is caused by: 1. The demands of rapidly expanding industry drawing heavily upon some of the available resources such as water and gravel; 2. The extended arctic conditions that affect the environment which include 8 months of winter (October through May), permafrost a few centimeters beneath the surface, and annual precipitation in the coastal province of about 14 cm; and 3. The specific water quality characteristics of the river that are sometimes limited and critical. During winter, stream discharge virtually ceases, dissolved oxygen concentrations are low (1.2 mg/l), specific conductance may be high (1700 umhos), and nutrients may be high (0.76 mg/l nitrate as nitrogen and 12.5 mg/l silica). The impact of industry on these water quality characteristics may affect indigenous aquatic biota.

INTRODUCTION

The Sagavanirktok (Sag) River, located on the North Slope of Alaska, (Figure 1) is undergoing a rapid transition from an isolated, undisturbed stream system to an accessible impacted drainage. This transition started in 1968 with discovery of oil at Prudhoe Bay near the mouth of the river. It is continuing with the construction of the Trans-Alaska pipeline (Alyeska Pipeline) which traverses approximately 200 km (125 miles) through the heart of the Sag River Basin. Further transition is a promise for the future with the continued search and development of oil and as the quest for other natural resources begins. The anticipated completion of the bridge crossing the Yukon River will complete the all-weather road connecting the Alaskan Arctic to the existing State road system and will enable additional access to the Sag River.

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This new prominence in the world of resources, and the linked accessibility, is impacting a set of terrestrial and aquatic environmental conditions that are substantially different from those in the contiguous 48 states. It is impossible to discuss all of them with the interrelationships here, but a few pertinent factors will set the environmental scene and relate to implications of resource development.

CLIMATE

The Arctic climate may best be described as harsh when compared to climates of most other areas. Ambient air temperature, one of the dominant features, is characterized by a mean annual range of -12° C (10° F) to -7° C (19° F) (Watson, 1969) and by severe winter temperatures as low as -54° C (-65° F) in localized interior areas. As little as 10° C (10° C) and winter precipitation may collect along the coast (Johnson et al., 1969), and winter precipitation as snow is often redeposited by strong and persistent winds (Watson, 1969).

Another factor that contributes to the harshness is lack of solar radiation during the winter. Prudhoe Bay, which is near 70°N latitude, has no direct sunlight from the middle of November to mid-January, but during the summer has continuous daylight from the middle of May to early August.

The above factors affect permafrost which becomes unstable when the temperature equilibrium of the system is disturbed (Proceedings of the First International Conference on Permafrost, 1963). All of the Arctic is in the continuous permafrost zone (Ferrians, 1969) with the thickness ranging up to 396 meters (1300 feet).

Climate, permafrost, and geology of the area all affect the soil that has developed, and vegetation types that have adapted to this ecosystem. Several soil types have been described (Tedrow and Cantlon, 1958 and Tedrow et al., 1958). These soil types support different vegetative communities which may have as many as 300 different species of plants (Johnson et al., 1964). These plant communities in turn dampen the soil temperature extremes, retard heat penetration, reduce the rate of soil and frost erosion and thereby maintain the permafrost integrity (Johnson, 1963).

WATER QUALITY

A baseline water quality survey of the Sag River basin was conducted by the Arctic Environmental Research Laboratory in 1969-70. The water quality of the river at that time could be characterized as good during the summer open water period. Breakup and summer precipitation in the form of spates can cause temporary changes and deterioration in the quality of some parameters. This, however, is usually a short-lived phenomenon and does not create serious problems for the indigenous biota, or for the domestic and industrial users. Breakup occurs during early June although the timing, magnitude and related problems such as flooding are dependent upon a combination of factors and may vary widely from year to year.

Sag River water quality during winter differs substantially from summer. The differences are caused by a complex interaction of geologic and climatological factors that affect numerous water quality parameters. Selected summer and winter data are presented in Table 1. These data are similar to results obtained from the Colville, Kuparuk and Sag Rivers by the U.S. Geological Survey in 1964 and 1972.

TABLE 1. SELECTED WINTER AND SUMMER WATER QUALITY DATA FROM SAMPLES COLLECTED FROM THE SAGAVANIRKTOK RIVER 1969-1970

Parameter	Range During Summer	Range During Winter
Silica (mg/l)	0.6 - 2.7	3.6 - 12.5
Total phosphate (mg/l)	0.01 - 0.05	0.01
Nitrate (mg/l)	0.05 - 0.15	0.09 - 0.76
Ammonia (mg/1)	0.02 - 0.09	0.01 - 0.18
Calcium (mg/l)	10.0 - 42.0	89.0 - 95.0
Potassium (mg/l)	0.15 - 0.75	0.7 - 1.97
Sodium (mg/1)	0.40 - 1.3	2.6 - 9.0
рН	7.6 - 8.1	7.2 - 7.7
Specific conductance (umhos)	80 - 240	660 - 1700

Comparison of summer data to winter data in Table 1 shows that several water quality parameters deterioriated appreciably in winter. In many instances, the ranges found during the winter were significantly higher than those found during the summer. These trends are supported by dissolved solids and hardness data from the Colville and Sag Rivers by Feulner, et al., 1971. These higher concentrations during winter are probably caused by a combination of extrusion of salts during the freezing process, accumulating metabolites and salt water intrusion in coastal areas.

Dissolved oxygen (DO) is often considered to be one of the critical parameters affecting aquatic life but until recently was not considered to be a problem in Alaska. The data presented in Figure 2 indicate that DO ranges from 9.9 mg/l (91.7 percent saturation) to 13.3 mg/l (95 percent saturation) during the summer but extremely low concentrations may be found during the winter (1.2 mg/l; 8.2 percent saturation). These concentrations are comparable to other DO data on the rivers of the North Slope and to the general spatial and seasonal DO patterns in the Chena, Chatanika, Tanana, and Yukon Rivers of interior Alaska (Schallock and Lotspeich, 1974).

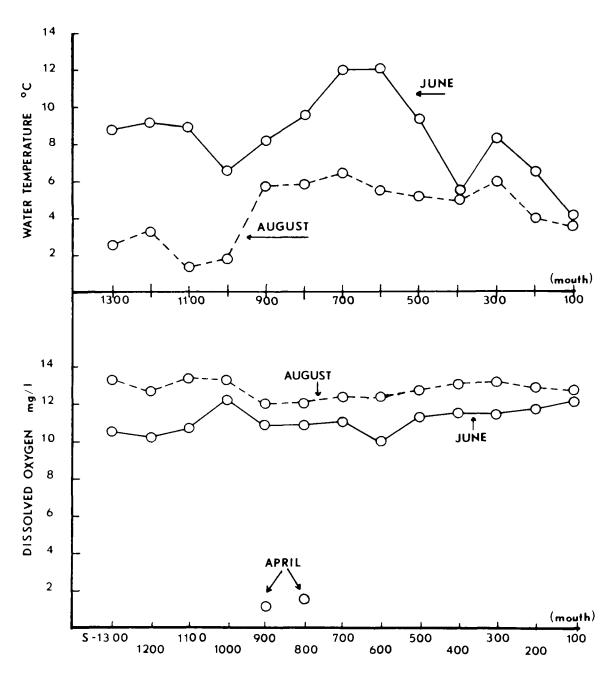


Figure 2. Dissolved oxygen and water temperature data from 13 stations on the Sagavanirktok River (1969-1970).

A consistent inverse relationship was found between water temperature and concentrations of DO. During the June study interval, the water temperature reached the recorded maximum of about 12°C (54°F). Water temperatures were generally highest in the foothill province near Sagwon (Station 700) about 104 km (65 miles) inland from Prudhoe Bay.

WATER QUANTITY

Stream discharges and seasonal timing of these discharges are characteristics causing great concern both in industry and in the agencies charged with resource management. Long periods of low discharge during winter followed by an increase during spring and rapid decline after breakup are the "normal" discharge patterns of the Sag and Patuligayak (Put) Rivers (Figure 3).

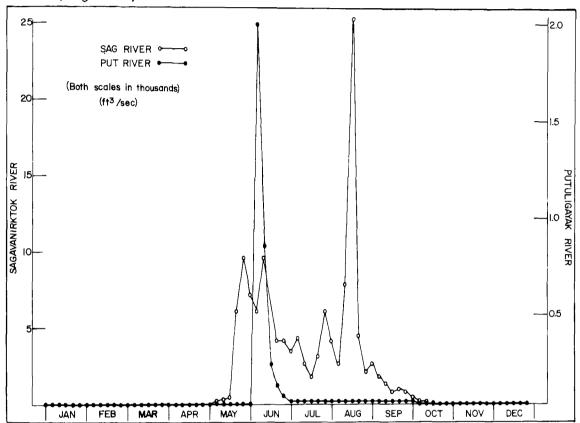


Figure 3. Seasonal discharge in the Sagavanirktok (Sag) and Putuligayak (Put) Rivers from October 1973 through September 1974 (U.S.G.S. Data).

Spring breakup accounts for the majority of the annual discharge. In the Put River, over 71 percent of the annual volume is discharged between June 1st and June 15th and approximately 94 percent of the annual volume by June 30th. In the Sag River, the results are not as dramatic if the same comparisons are made because the seasonal high discharge pattern is bimodal. Between June 1st and June 15th, over 16 percent of the total is discharged while 10 percent is discharged between June 16th and June 30th. A higher peak with shorter duration occurred between August 16th and August 31st and accounts for 20 percent of the total. The short term, high volume discharges of both the Put and Sag Rivers rapidly decrease to smaller volumes that apparently originate from ground water sources. This smaller volume is reached in July and October, respectively. The Colville River, the largest drainage on the North Slope, may discharge as much as 43 percent of the annual runoff in a 3-week period (Alexander, et al., 1974).

Some debate has focused on whether the discharge of North Slope rivers during the winter is just extremely low or whether discharge actually ceases in some instances. In either case, a limited volume of water is available for man's use.

AQUATIC BIOLOGY

Prior to discovery of oil at Prudhoe Bay, little information has been published on the life history patterns of the indigenous fish and only occasional data were available on microbiological or macrobenthic communities. Since 1968, moderate effort has gone into examining various characteristics of specific biological populations and communities.

Spawning areas, migration patterns and overwintering areas were chosen as possible limiting factors to any population of fish inhabiting the Sag River. The two most important fish in the Sag River are the Arctic Char, Salvelinus alpinus, and the Arctic Grayling, Thymallus arcticus. Lake Trout, Salvelinus namaycush, are also found in the river basin.

Arctic char and grayling are generally distributed throughout the Sag drainage but may be concentrated in localized areas of the Sag main stem or its tributaries during the summer. Some migrations such as the upstream migration of adult and subadult char during early summer are well documented while other migrations are suspected but are not well documented.

Spawning areas utilized by char and grayling are difficult to locate because the char spawn in autumn when ice cover is beginning and grayling spawn during the high water of spring. Both fish establish redds in gravels with specific characteristics.

Overwintering of young-of-the-year and juveniles are also difficult to determine. Studies by the Alaska Department of Fish and Game and the U.S. Fish and Wildlife Service documented overwintering populations in spring areas that are primarily located in the upper Sag drainage and tributaries. However, Furniss (1975) recently demonstrated that young-of-the-year and/or juvenile fish are also utilizing the deep pools of the Sag River from Franklin Bluffs to the coast.

Members of the macrobenthic community are ubiquitously distributed along the length of the river and are sensitive to water quality parameters because the organisms are relatively immobile. This community consists principally of Plecoptera (stoneflies), Ephemeroptera (mayflies), Chironomidae (midges), Trichoptera (cadisflies), and oligochaetes. These organisms may number as high as 400 per square meter (330 per square yard) during summer conditions (Schallock and Mueller, 1970) and are the primary food items for most life stages of fish.

Unpublished data collected by Gordon during 1969-1970 showed that the number of local coliforms present in the Sag River was low at that time. However, his recent work (Gordon, 1975) on the survival of enteric microorganisms in the Tanana River near Fairbanks reveals that the addition of these microorganisms into a limited and closed system such as the Sag River could be extremely dangerous to users. This danger appears where numerous activities are located along the drainage and the river is utilized as a source of potable water.

RESOURCE AND MANAGEMENT IMPLICATIONS

WATER APPROPRIATIONS

Quantity and water quality are problems on Alaska's North Slope. Seasonal discharge patterns and changes in the water quality of North Slope rivers have been presented during early discussion. The demands for water for both domestic and specific industrial activities are stressing the limited supplies. This is causing industry to travel some distance to obtain water and also to consider alternative sources and techniques for obtaining water.

The customary method for collecting water has been to set up a pump station at the river or to drill a hole in the ice and utilize a tanker truck to collect and transport the water. Pipeline construction activity has resulted in the demand for water to increase drastically; consequently some "watering holes" have been pumped dry.

Initially water was collected from the river immediately adjacent to the particular use. However, this past winter water was hauled as far as 72 km (45 miles) when it was not available in the immediate area. In one instance, holes were drilled through the river ice on a grid system with holes as close as 15 meters (50 feet). Whenever water was found, radio communications to identify the specific location were made to the water truck. The water truck then came to the water hole and pumped until that particular hole was dry and then the search for another water hole began.

Tundra lakes have been considered as an additional source but these lakes generally have small volumes of poor quality water that must be treated to be potable.

GRAVEL MINING

Gravel mining is presently causing tremendous concern, for this activity has not been given adequate regulation. One has only to examine the variety of endeavors utilizing gravel and the magnitude of its use is brought into focus. All roads, airstrips, pads for building, drill rigs and pipelines require large amounts of gravel. It is of particular important in those areas where a permanent gravel foundation is needed to maintain permafrost integrity.

An accurate estimate of the gravel requirements for pipeline construction was impossible before construction began. Early estimates, however, placed the amount near 4.6 million cubic meters (6 million cubic yards) for the entire pipeline while some Federal resource managers at the time estimated the amount to be closer to 7.6 million cubic meters (10 million cubic yards). At the present time, nearly twice this amount has been extracted from the lands administered by the Bureau of Land Management on the North Slope alone (Dean, 1975). It is now estimated that as much as 161 million cubic meters (210 million cubic yards) have been used along the pipeline and about 18 months of construction are still remaining.

Adequate amounts of suitable gravel are not readily available in many areas of the North Slope. However, the Sag River and its tributaries provide a permafrost free "thaw bulb" wherein it is economically feasible to borrow gravel. As a result, gravel used for airstrips, roads, pipeline pads and drill pads is being removed only from these frost-free areas.

Limited availability and resultant overhauls have increased the cost of gravel. Gravel purchased from the material site for approximately 18 cents per cubic meter (14 cents/cubic yard) may cost as much as \$52 per cubic meter (\$40/cubic yard) by the time it is purchased, loaded, hauled, deposited and spread at the deposition site. The shortage of gravel and its increasing cost is causing industry to consider other methods and materials as a substitute

Gravel mining can adversely affect the water quality. It may cause excessive suspended sediment and increased stream bed load if the mining operation is improperly placed and an effective settling pond is not provided. The addition of sediment to a stream system may in turn prevent primary production, cover the macrobenthic community and cuase the fish to outmigrate or smother the developing eggs and young-of-the-year. Continued gravel mining from the flood plain of the Sag River may also cause hydrologic instability that would require a long time to equilibrate. During this period of reestablishment, suspended sediment with its attendant problems would likely continue at above normal levels.

WASTE DISCHARGE

Waste discharges from permanent camps, temporary camps and drilling sites are a serious threat to water quality of the Sag River. The addition of oxygen demanding substances to an already severely depressed dissolved oxygen system would be disastrous. Toxic substances, such as residual chlorine or chloramines, heavy metals and hydrocarbons, if released into the water course, particularly during the low flow periods, could rapidly eliminate desirable fish and macrobenthic organisms. In addition, effluent containing enteric microorganisms from human waste that enters the river may well become a part of a downstream user's water supply.

BIOLOGICAL IMPLICATIONS

The Sag River is now experiencing the full impact of man's development of a nonrenewable resource in arctic Alaska. What are the implications of water appropriations, gravel mining and waste discharge on the river system? The most obvious implication is an adverse effect on the aquatic resources of the river. Overwintering populations of fish and macrobenthos will be impacted by water use in the Franklin Bluffs to Prudhoe Bay area. Reliable reports have been received of fish being found in water holding tanks. Other reports describe instances where the operator pumping water into the tank truck would have to stop and clean the intake screen of fish carcasses. Still other reports describe invertebrates contained in water supplies.

Low discharge during winter also magnifies the impact on the stream when it is used as the receiving water for domestic or industrial effluent. Small volumes of water, low winter dissolved oxygen and high concentrations of dissolved constituents all combine to create a system that is highly sensitive to an effluent containing oxygen demanding materials and/or toxic substances such as residual chlorine. With the addition of enteric microorganisms into this limited and closed system, public health becomes a serious consideration where activities are located along the drainage and utilize the river as a source of potable water.

Finally, aquatic organisms within the river system may be deleteriously affected by gravel mining operations either through the direct addition of sediment to the system or indirectly by hydrological instability.

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Lake Eutrophication: Results from The National Eutrophication Survey

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INTRODUCTION

In early 1972, the U.S. Environmental Protection Agency (EPA) initiated the National Eutrophication Survey (NES) program to: (1) identify those lakes and reservoirs in the contiguous United States that receive nutrients from the discharges of municipal sewage treatment facilities, and (2) determine the significance of these point-source nutrient inputs to the nutrient levels and the primary productivity of each system. After the program began, additional federal legislation was passed (Public Law 92-500), and NES objectives were broadened to include an assessment of the relationships of non-point sources; e.g., land use, to lake nutrient levels and also to assist in establishing water-quality criteria for nutrients.

SELECTION CRITERIA

Freshwater lakes and impoundments in the Survey were selected through consultation with EPA Regional Offices and state pollution control agencies, as well as related state agencies managing fisheries, water resources, or public health. EPA established selection criteria to limit the type and number of candidate water bodies, consistent with existing Agency water goals and strategies. For 27 states of the eastern United States where lakes were selected prior to passage of P.L. 92-500, strongest emphasis was placed on lakes faced with actual or potential accelerated eutrophication problems; i.e., an artificially increased rate of algal and/or aquatic plant production. As a result, the selected lakes:

- 1. were impacted by one or more municipal sewage treatment plants, either directly or by discharge to an inlet tributary within approximately 25 miles of the lake;
- 2. were 100 acres or larger in size; and
- 3. had mean hydraulic retention times of at least 30 days.

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However, these criteria were waived for a number of lakes of particular interest to the states.

In the western states, these criteria were modified to reflect revised water-research mandates, as well as to address more prevalent non-point source problems in agricultural or undeveloped areas. Thus each state was requested to submit a list of candidate lakes for the Survey that:

- were representative of the full range of water quality (from oligotrophic* to eutrophic*);
- 2. were in the recreational, water supply, and/or fish and wildlife propagation use-categories; and
- 3. were representative of the full scope of nutrient pollution problems or sources (from municipal waste and/or nutrient-rich industrial discharges, as well as from non-point sources).

The size and retention time constraints applied in the eastern states were retained as was the waiver provision.

In all cases, listings of potential candidate lakes or reservoirs, prepared with the cooperation of the EPA Regional Offices, were made available to the states to initiate the selection process.

In total, the Survey includes 812 lakes and reservoirs across the contiguous 48 United States. Figure 1 shows the distribution of the lakes and reservoirs by state and the year during which each water body was sampled.

GENERAL SURVEY METHODS

Several kinds of information are required as a basis for management decisions regarding the need for point or non-point source control of phosphorus and perhaps other nutrients as well. The Survey purpose is to collect the type of data which will provide a basis for such decisions or at least to provide a data base which can be supplemented with more detail, if required. First, an annual nutrient budget is estimated for each water body, differentiating between inputs originating from point and non-point sources; second, the existing trophic condition of the water body is evaluated by sampling; and third, an algal assay is performed to determine whether phosphorus, nitrogen, or some other element is limiting primary productivity of the water body. The methods used to gather this information are described below.

The operations aspects of the Survey are shared by branches of two EPA laboratories (46 people) and a small headquarters staff (3 people). The Environmental Monitoring and Support Laboratory at Las Vegas, Nevada (Las Vegas-EMSL) is responsible for sampling each lake, doing the associated analyses, evaluating a portion of the data, and reporting results. The Corvallis Environmental Research Laboratory (CERL) at Corvallis, Oregon is responsible for coordinating the sampling of streams and sewage treatment plants, analyzing the samples, and performing the algal assay on lake samples.

^{*} Oligotrophic--low nutrient concentrations and primary productivity. Eutrophic--high nutrient concentrations and primary productivity.

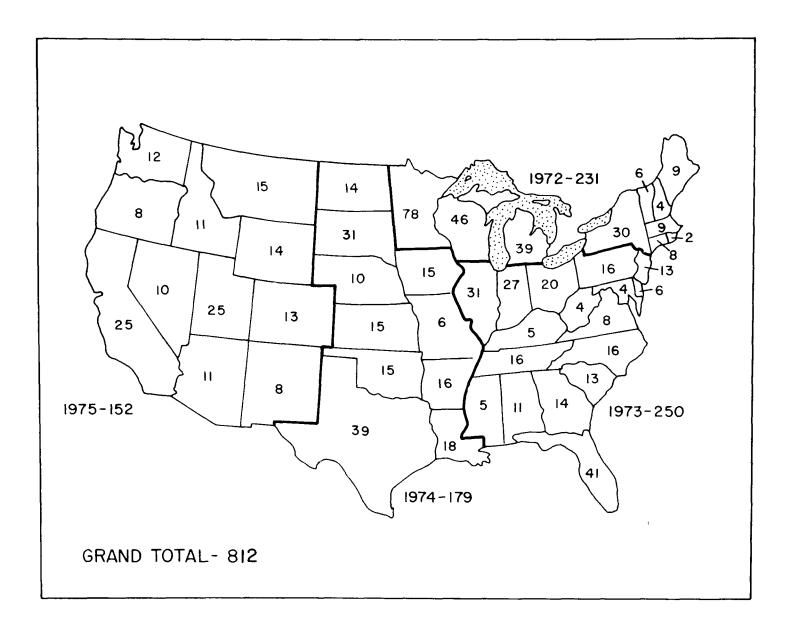


Figure 1. Number of lakes and reservoirs sampled in each state and year of sampling by the National Eutrophication Survey.

CERL also has major responsibility for evaluating the lake, stream, and point-source data and incorporating these data into a report on each lake. The headquarters staff (Washington, D.C.) makes the initial contact with each state water pollution control agency to explain the function of the Survey and to cooperatively determine which lakes and reservoirs will be They also contact each State National Guard to explain the function of the Survey and to request their assistance in meeting Survey objectives by collecting monthly samples from selected tributaries to surveyed lakes. In addition, the headquarters staff provides general coordination and guidance to the operational aspects of the program.

Because the Survey has to cover a large geographical area in a relatively short period of time, pontoon-equipped UH-IH Bell helicopters with automated and manually-operated instruments are used to measure the water quality of each lake. Two helicopters - carrying a limnologist and a technician - are operated simultaneously, and a third helicopter is used for ferrying parts, equipment, and people. The sampling teams from the Las Vegas-EMSL are supported by a mobile analytical laboratory, chemistry technicians, electronic specialists, and other staff involved with helicopter maintenance or program coordination. The total staff in the field usually ranges from 12 to 14 people.

Operating procedures involve establishing a work center at an airport and then sampling all lakes within a 100-mile radius. When all of the water bodies within the area are sampled, the support staff moves to a new central location, and sampling begins on a different set of lakes. In this manner, 150 to 250 lakes have been sampled three times each year, and the sampling will be completed on all of the 812 lakes in a four-year period.

Table 1 depicts the routine water-quality parameters which were selected to characterize each lake and assess its trophic condition. Parameter selection was based on the relevance of each parameter as a measure of potential and existing primary production. Both the number and the type of parameters measured were also limited to a certain extent by the operational aspects of the Survey.

TABLE 1. WATER-QUALITY CHARACTERISTICS MEASURED

Physical-Ch	emical
Alkalinity Conductivity* pH* Dissolved oxygen Phosphorus: Ortho Total	Nitrogen: Ammonia Kjeldahl Nitrate Secchi depth Temperature*
Biologi	cal
Algal assay Chlorophyll <u>a</u>	Algal count and identification
*Determined on-site with e	lectronic probes.

Concurrent with the lake sampling, the significant tributaries and outlet(s) of each lake are sampled monthly, totaling about 4,200 sampling sites nationwide. Volunteer National Guardsmen of each state, trained onsite by EPA or state agency staff, collect and preserve the samples at sites pre-selected by EPA personnel. The samples are shipped to CERL for analysis of the various forms of nitrogen and phosphorus (see Table 1).

Through an interagency agreement, the U.S. Geological Survey estimates flows for each sampled stream. These data are used in conjunction with concentration values to determine nutrient loadings.

A voluntary sampling program was established through the respective state water pollution control agencies to have plant operators collect effluent samples from those municipal sewage treatment plants which impact Survey lakes—about 1,000 treatment plants. The effluent samples are collected monthly, preserved, and shipped to the Corvallis laboratory for nitrogen and phosphorus analyses.

Specific procedures used in collecting, preserving, shipping, and analyzing the various kinds of samples collected by the Survey are described in National Eutrophication Survey Working Papers No. 1 (1974) and 175 (1975).

Presently, the field portion of the Survey is almost completed with the last samples scheduled for collection in November, 1975. Data analysis is scheduled for completion in December, 1976.

RESULTS AND DISCUSSION

LIMITING NUTRIENTS

For each of the surveyed lakes, an algal assay is performed on a sample of lake water and, to supplement the assay findings, inorganic nitrogen to dissolved orthophorus ratios are determined from the lake sampling results. For the 623 surveyed lakes in states east of the Rocky Mountains, the assay demonstrated that with respect to algal growth requirements, 67% were phosphorus-limited, 30% were nitrogen-limited and 3% were either limited by an element other than phosphorus or nitrogen or the results were not conclusive (Table 2).

TABLE 2. SUMMARY OF ALGAL ASSAY RESULTS FOR SURVEYED WATER BODIES IN THE 37 STATES EAST OF THE ROCKY MOUNTAINS

Limiting Nutr	ient	Number of Lakes	% of all Lakes
Phosphorus Nitrogen Other		417 186 <u>20</u>	67 30 <u>3</u>
	Total	623	100%

A higher percentage of phosphorus limited lakes would probably have been found had the Survey not been mostly concerned with lakes which were impacted by municipal wastes. The algal assay results should, therefore, be evaluated with some caution because they reflect existing conditions which often include man's impact on the nutrient regime.

Municipal waste treatment plant effluents, for example, have an average total nitrogen to total phosphorus ratio of about 2.5 to 1 whereas natural waters usually have a ratio in excess of 15 to 1. The relative abundance of phosphorus provided in municipal effluents could change a lake from phosphorus-limited to nitrogen-limited. Such a lake could theoretically be changed back to phosphorus-limited by reducing phosphorus inputs.

Figure 2 is an indication of the significance of municipal wastes to the total annual phosphorus load to some of the eastern lakes and reservoirs. Of the 234 water bodies included in the frequency histogram, 135 receive more than 20% of their annual total phosphorus load from municipal sources.

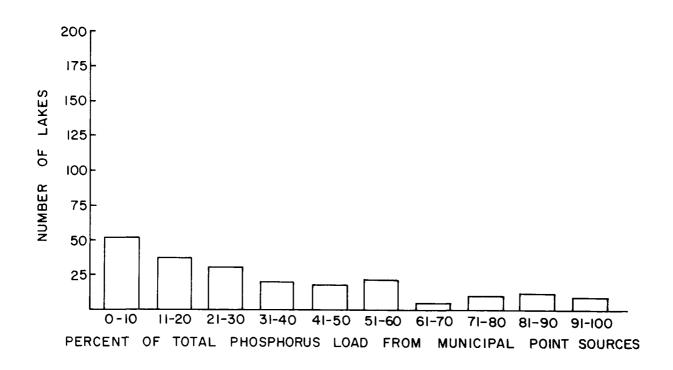


Figure 2. A frequency histogram representing the percent of total annual phosphorus load attributable to municipal wastes for a number of eastern U.S. lakes and reservoirs.

If 80% of the phosphorus were removed from these discharges by treatment, only 9 of the lakes would still receive more than 20% of their total phosphorus load from municipal wastes as shown in Figure 3.

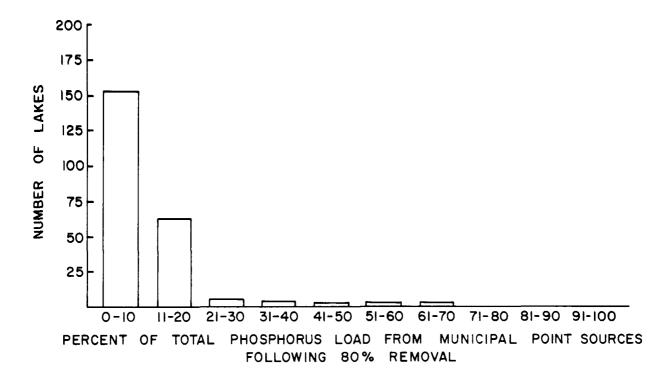


Figure 3. A frequency histogram representing the percent of total annual phosphorus load attributable to municipal wastes after 80% effluent phosphorus reduction for a number of eastern U.S. lakes and reservoirs.

The reduction or removal of phosphorus originating from municipal sources does not guarantee that the trophic status of the receiving lake will be significantly improved. That determination can only be made on a case-by-case basis in which many factors, such as background phosphorus levels, the limiting nutrient, lake morphometry, etc., are considered. It is apparent, however, that in many cases, eutrophic conditions are either the direct result of phosphorus from municipal wastes or at least are worsened by phosphorus inputs from these sources which could be readily controlled.

TROPHIC CONDITION OF SURVEY LAKES

About 80% of the lakes and reservoirs included in the first two years of the Survey in the eastern United States were eutrophic. This was not unexpected since a large number of these water bodies were impacted by municipal wastes.

The classical terms, oligotrophic, mesotrophic, and eutrophic were used to describe the trophic condition of each water body. Based partly on observations during the first year of the Survey and partly on literature values, some general guidelines were developed for each of four key parameters to assist us in assigning a trophic classification to each lake. These values are listed in Table 3.

TABLE 3. KEY PARAMETER VALUES ASSOCIATED WITH THREE LAKE TROPHIC CONDITIONS

Parameter	Oligotrophic	Mesotrophic	Eutrophic
Total Phosphorus (µg/l) Chlorophyll a (µg/l) Secchi depth (meters)	<10 <4 >3.7	10-20 4-10 2.0-3.7	>20-25 >10 <2.0
Hypolimnetic Dissolved Oxygen (% saturation)	>80	10-80	<10

If each of the four parameters from a given lake were within the range of a specific trophic condition (e.g., oligotrophic) then it was fairly certain that the indicated trophic condition appropriately described the lake. Unfortunately, in many cases, all the parameter values did not neatly fall within one trophic classification; therefore, a relative index or ranking system was also used. This index included the four parameters shown in Table 3 (except that minimum dissolved oxygen concentrations were used) plus inorganic nitrogen and dissolved orthophosphorus concentrations. The index was based on percentile rankings for each of the six parameters which were then added together to produce a single index number. Using this system, a large number of lakes could be ranked in general order from most oligotrophic to most eutrophic. There were enough well-studied lakes included in the Survey to allow us to determine approximately where the transition from oligotrophic to mesotrophic and from mesotrophic to eutrophic occurred in the ordered list of lakes. This system was not without exception but did prove useful. The index is discussed in detail in National Eutrophication Survey Working Paper No. 24 (1974).

PHOSPHORUS LOADING - TROPHIC CONDITION RELATIONSHIPS

Another of the Survey objectives was to estimate annual phosphorus and nitrogen loadings for each of the study lakes and to examine relationships between these nutrient inputs and the resulting trophic conditions. Such relationships are needed by lake managers to predict trophic responses which would result from either increasing or decreasing phosphorus loads. They

would also give regulatory agencies a firmer basis for allocating total phosphorus loads from point or non-point sources so that the desired trophic condition of a lake or reservoir could be maintained or achieved.

The Survey has not developed any original nutrient loading-lake response relationships. However, the data have been applied to models recently developed by other investigators.

Prior to 1968 there were no models of general applicability which related total phosphorus load to trophic condition in the receiving lake. Now, however, there are at least three which seem very promising. These models are presented and compared using data collected by the Survey from twenty-three lakes and reservoirs. These twenty-three water bodies represent a cross-section of trophic conditions, mean depths, and mean hydraulic retention times. All are located in northeastern and north-central states except for two reservoirs in Georgia and two in South Carolina. In this group of lakes, six are oligotrophic, nine are mesotrophic, and eight are eutrophic.

The three relationships (or models) which will be compared were developed by Vollenweider and Dillon (1974), Dillon (1975), and Larsen and Mercier (1975), respectively.

Vollenweider (1968), using existing data from a number of European and North American lakes, was the first to relate total phosphorus loading to lake trophic condition. He plotted annual total phosphorus loadings $(g/m^2/yr)$ against lake mean depths and empirically determined the transition between oligotrophic, mesotrophic, and eutrophic loadings.

Although this approach worked reasonably well for lakes with detention times of several months or longer, it did not account for the fact that two lakes with identical mean depths could have quite different hydraulic retention times and therefore different trophic responses to the same loading rate. Subsequently, Vollenweider modified his initial relationship and based his revised model on considerations of a mass balance equation for phosphorus. The application of Vollenweider's revised model to the Survey lakes is illustrated in Figure 4.

The observed loadings and trophic conditions of the 23 Survey lakes did not fit the Vollenweider relationship very well. Phosphorus loadings for five of the eutrophic lakes plotted clearly within the eutrophic zone of the Vollenweider relationship while loadings of two eutrophic lakes plotted within the mesotrophic zone and one within the oligotrophic zone. Loadings for five of the mesotrophic lakes fell within the oligotrophic zone while the remainder were within the mesotrophic portion of the Vollenweider relationship.

Vollenweider's work was extremely important not only because he was the first to investigate the loading-response relationship but also because his original ideas interested others in this type of approach.

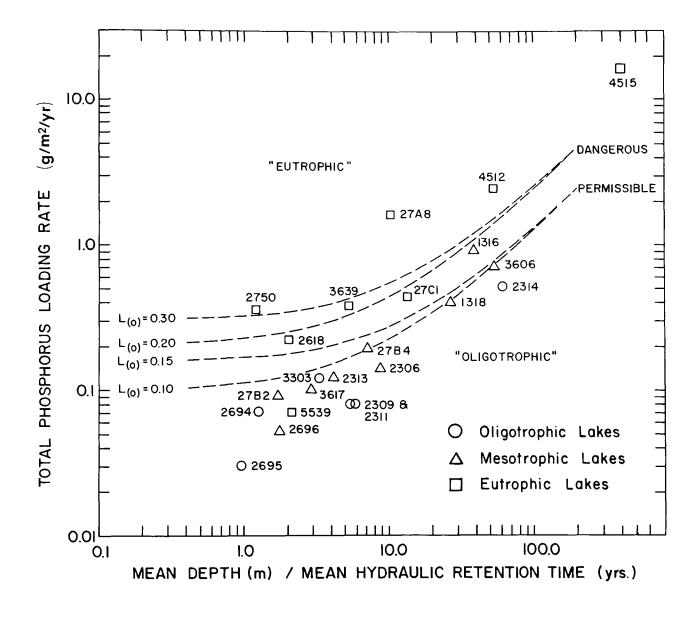


Figure 4. The Vollenweider relationship applied to a number of eastern U.S. lakes and reservoirs sampled by the Survey.

Stimulated by Vollenweider's earlier work, Dillon (1975) used the mass balance modeling approach to derive the relationship illustrated in Figure 5. Dillon's approach relates lake mean depth to a factor which includes total annual phosphorus loading, the phosphorus retention coefficient, and hydraulic flushing time. The 23 Survey lakes fit the Dillon relationship quite well as illustrated in Figure 5. Two oligotrophic lakes plotted in the mesotrophic zone and two mesotrophic lakes plotted in the oligotrophic zone; however, observed conditions for the other lakes were as predicted by the Dillon relationship.

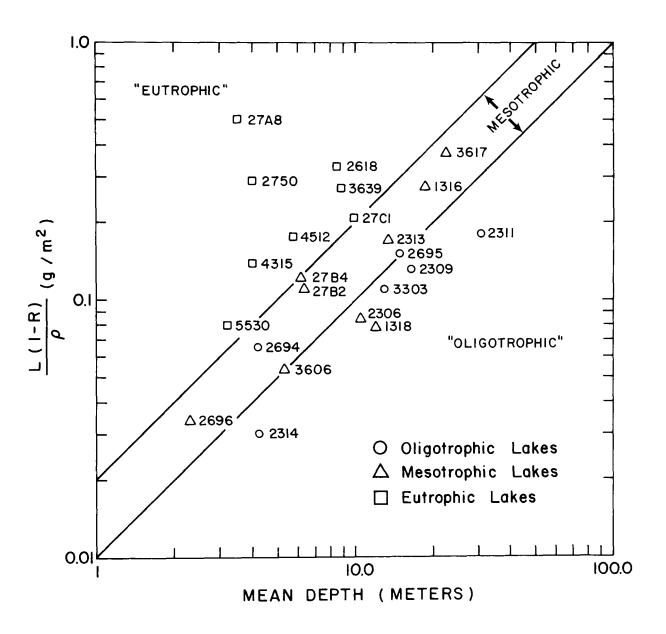


Figure 5. The Dillon relationship applied to a number of eastern U.S. lakes and reservoirs sampled by the Survey.

Larsen and Mercier (1975), working independently of Dillon, also solved a mass balance equation for phosphorus to develop a relationship between the average incoming phosphorus concentration and the phosphorus retention coefficient. The average incoming phosphorus concentration is defined as the total annual phosphorus load divided by the total hydraulic inflow which is also equivalent to:

where, L = annual total phosphorus areal load $(g/m^2/yr)$ Q = hydraulic flushing time (exchange/year)

 \bar{z} = mean depth (meters)

The Larsen and Mercier relationship therefore incorporates the same variables as the Dillon relationship although the graphical solution of the mass balance model for phosphorus is different. Figure 6 depicts the 23 Survey lakes plotted against the Larson-Mercier relationship. The fit is very good and the relative location of each point on the graph is very similar to Figure 5, the Dillon relationship.

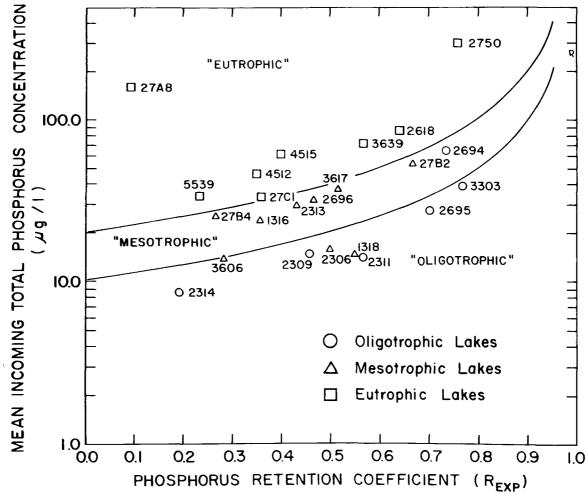


Figure 6. The Larsen-Mercier relationship applied to a number of eastern U.S. lakes and reservoirs sampled by the Survey.

Since both the latter two models predict in-lake concentrations of total phosphorus, the vertical distance from an observed point, representing a lake, to one of the transitional lines is at least a semiquantitative measure of the degree of oligotrophy or eutrophy.

The vertical distance from a given point to a transitional line in the Vollenweider relationship has less meaning in terms of the degree of oligotrophy or eutrophy because the model does not directly relate total phosphorus loading to in-lake phosphorus concentrations.

In summary, the models developed by Dillon and Larsen-Mercier, which relate total phosphorus loads to lake phosphorus concentrations, should prove to be useful lake management tools. The Vollenweider model, at this time, is probably less precise because it considers only total phosphorus loading without regard to in-lake processes which reduce the effective phosphorus concentration; however, the model can be used to determine approximate acceptable total phosphorus loads.

THE RELATIONSHIPS OF LAND USE TO NUTRIENT LEVELS

Another of the Survey objectives is to examine, on a National scale, the relationships of land use and other draining area characteristics to stream nutrient levels and subsequently lake trophic status.

Of the 4,200 sub-drainage areas sampled by the Survey across the United States, about 1,000 were selected for a detailed study of land use and other drainage area characteristics (see Figure 7). Criteria for selecting the 1,000 stream sampling sites and associated drainage areas were:

- 1. Absence of identifiable point sources.
- 2. Availability of usable aerial photography (scale 1:40,000 to 1:80,000) or exising land-use data.
- 3. Availability of accurate topographic maps for drainage area delineation.
- 4. Sufficient land relief for clear delineation of drainage area limits.
- 5. The need to encompass a variety of geographic and climatic areas.

Note that few, if any, of the selected drainage areas were in Florida, the Atlantic and Gulf coastal plains, or northern Minnesota. These areas were excluded from consideration because of the difficulty of accurately defining drainage area boundaries due to low topographic relief, and, in many cases, because of the strong influence of ground water.

At the present time only the data from the eastern United States (east of the Mississippi River) have been compiled, but the analysis of these data is not complete. Therefore only general results are presented.

198

Figure 7. The distribution of stream drainage areas selected by the National Eutrophication Survey for land use studies.

Figure 8 summarizes the data collected from 473 eastern U.S. drainage areas for total phosphorus and total nitrogen concentrations originating from different land use categories. The categories are defined as follows:

- 1. Forest; other types negligible
 - a. >75% forested (including forested wetland)
 - b. < 7% agriculture
 - c. < 2% urban
- 2. Mostly forest; other types present
 - a. >50% forest
 - b. not included in the forest category
- 3. Mostly agriculture; other types present
 - a. >50% agriculture
 - b. not included in the agriculture category
- 4. Agriculture; other types negligible
 - a. >75% agriculture
 - b < 7% urban
- 5. Urban

>39% urban

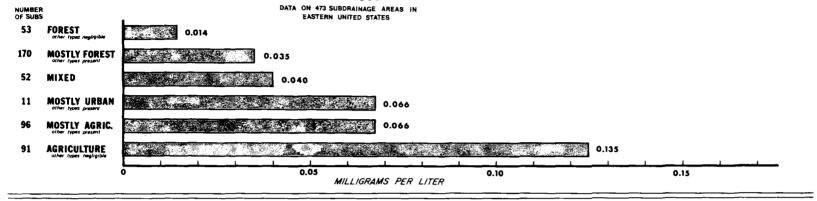
6. Mixed; not included in any of the other categories

Streams draining predominately agricultural areas have total phosphorus concentrations averaging about 10 times higher than those draining forested areas (Figure 8). The difference between total nitrogen concentrations was not as marked. Streams in agricultural areas averaged nearly 5 times higher total nitrogen concentrations than those draining forested areas. It is interesting to note that, based on the mean concentration values, phosphorus would be expected to be limiting in surface waters draining either forested or agricultural areas. The total nitrogen to total phosphorus ratio changes from 60 to 1 for forested areas to 31 to 1 for agricultural areas. Generally phosphorus is the limiting nutrient when the N:P ratio exceeds 14:1.

The nutrient loads per unit area of drainage for total phosphorus and total nitrogen are shown in Figure 9. The differences in exports for the different land use categories are not as pronounced as the nutrient concentrations were. Total phosphorus export from agricultural lands was only 317 times greater than from forested lands and total nitrogen export only 2.2 times greater. The differences in magnitude between stream loads and stream concentrations are due to the differences in stream flows resulting from the two types of land use. The data suggest that stream flow per unit of drainage area is somewhat higher for forested than for agricultural areas This seems logical since forested areas frequently are those which are unsuitable for agricultural purposes because of steeper slopes and relatively thin soils.

MEAN TOTAL PHOSPHORUS CONCENTRATIONS

LAND USE



MEAN TOTAL NITROGEN CONCENTRATIONS

LAND USE

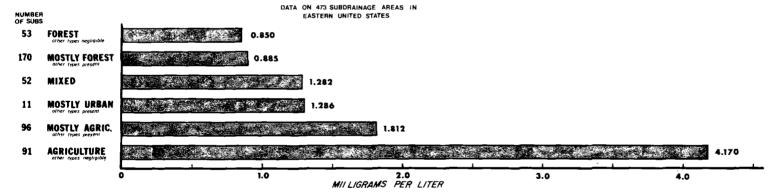


Figure 8. The relationship between total phosphorus and total nitrogen concentrations in streams and land use in the eastern U.S.

MOSTLY AGRIC.

AGRICULTURE

0

91

TOTAL PHOSPHORUS EXPORT LAND USE NUMBER OF SUBS DATA ON 473 SUBDRAINAGE AREAS IN EASTERN UNITED STATES 53 FOREST 170 **MOSTLY FOREST** 52 MIXED **MOSTLY URBAN** 11 30.1 MOSTLY AGRIC. AGRICULTURE 91 30.8 10 20 30 0 40 KILOGRAMS PER SQUARE KILOMETER PER YEAR TOTAL NITROGEN EXPORT VS LAND USE DATA ON 473 SUBDRAINAGE AREAS IN NUMBER OF SUBS EASTERN UNITED STATES 53 **FOREST** 440.1 **MOSTLY FOREST** 170 52 MIXED **MOSTLY URBAN** 788.6

Figure 9. The relationship between total phosphorus and total nitrogen export in streams and land use in the eastern U.S.

500

KILOGRAMS PER SQUARE KILOMETER PER YEAR

630.5

982.3

1000

The pattern for orthophosphorus concentrations was very similar to that for total phosphorus as shown in Figure 10. Except with predominately urban drainage areas, of which there were only eleven, mean orthophosphorus concentrations represented 40 to 43% of the total phosphorus concentrations regardless of overall land use. Orthophosphorus concentrations in streams draining agricultural areas were nearly 10 times the concentrations in streams draining forested areas.

Inorganic nitrogen exhibited quite a different pattern from total nitrogen in that substantially higher (13.7X) concentrations were observed in streams draining agricultural lands than in forested lands (Figure 10).

In streams draining forested areas, inorganic nitrogen constituted about 27% of the total nitrogen, however, this increased to 76% in streams draining predominately agricultural areas. Although the sample size (11 drainage areas) was relatively small, inorganic nitrogen made up about 98% of the total nitrogen in streams draining mostly urban drainage areas. Inorganic nitrogen export was also significantly higher (5.6X) from agricultural areas than from forested areas as shown in Figure 11. The difference probably reflects the use of inorganic nitrogen fertilizers and the high water solubility of inorganic nitrogen compounds.

What conclusions can be drawn from these general results? First, these data suggest that streams draining agricultural watersheds have higher nutrient levels and therefore would be expected to be more productive than those draining forested watersheds. The increase in nutrient levels is generally proportional to the increasing percent of the land in agriculture.

Second, the data indicate that the inorganic portion (orthophosphorus) of the total phosphorus component stays roughly at the 40% level regardless of land use type, whereas, the inorganic portion of the total nitrogen component increases markedly from 27% for forested areas to 75% for agricultural areas. Inorganic nitrogen in streams draining mostly urban areas represented a substantially larger fraction of the total nitrogen (98%), however, the number of test areas was relatively small (11).

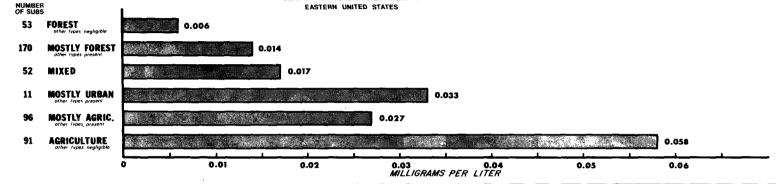
Lastly, what uses can be made of the data derived from this segment of the survey? Other than elucidating the land use-nutrient level-eutrophication relationships, probably the two most important uses will be: (1) to provide a basis for a quick and relatively accurate method of determining nitrogen and phosphorus concentrations and loadings based on land use and other non-point source types of geographical characteristics, and (2) to provide a large nationwide collection of watershed data for testing other methods of estimating nitrogen and phosphorus levels in streams from non-point sources.

SUMMARY

The National Eutrophication Survey, which was initiated in 1972 by the U.S. Environmental Protection Agency, is in the first stage of collecting data from over 800 lakes and reservoirs in the contiguous United States. In the eastern U.S., a large percentage of the surveyed water bodies are impacted by municipal sewage treatment plant effluent and are in various

MEAN ORTHOPHOSPHORUS CONCENTRATIONS

LAND USE DATA ON 473 SUBDRAINAGE AREAS IN EASTERN UNITED STATES



MEAN INORGANIC NITROGEN CONCENTRATIONS

LAND USE

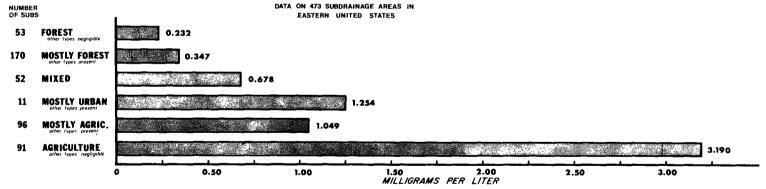


Figure 10. The relationship between orthophosphorus and inorganic nitrogen concentrations in streams and land use in the eastern U.S.

LAND USE DATA ON 473 SUBDRAINAGE AREAS IN EASTERN UNITED STATES NUMBER OF SUBS **FOREST** 53 170 **MOSTLY FOREST** MIXED 52 7.9 MOSTLY URBAN 15.0 11 MOSTLY AGRIC. AGRICULTURE 13.3

KILOGRAMS PER SQUARE KILOMETER PER YEAR

10

15

ORTHOPHOSPHORUS EXPORT

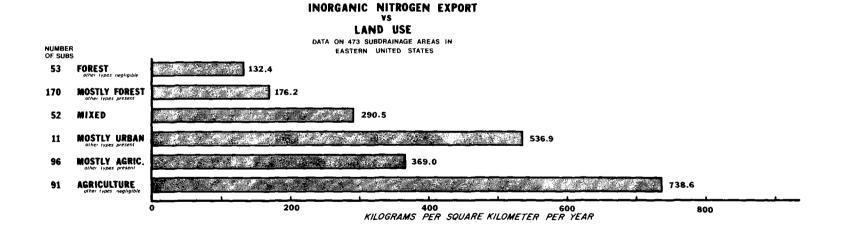


Figure 11. The relationship between orthorphosphorus and inorganic nitrogen export in streams and land use in the eastern U.S.

states of enrichment. Phosphorus loads to a significant number of these impacted lakes and reservoirs could be substantially reduced by controlling phosphorus inputs from municipal sources.

Primary production in 67% of the water bodies surveyed east of the Rocky Mountains was phosphorus-limited and 30% were nitrogen-limited according to algal assay results. It is believed that the apparent nitrogen-limited condition was frequently the result of excessive phosphorus inputs from municipal sources.

Land use in the watershed was shown to be a significant factor in determining levels of phosphorus and nitrogen in streams in selected areas studied in the eastern United States. Average total phosphorus concentrations were about 10 times greater in streams draining agricultural areas than in streams draining forested areas; total nitrogen concentrations were about 5 times greater. The percentage of total nitrogen in the inorganic form was substantially higher in streams draining agricultural lands than in those streams draining forested lands.

Phosphorus loading data for 23 selected survey lakes were applied to three general models relating annual total phosphorus loading rates to lake trophic conditions. The "fit" of observed conditions to predictions made by each model was compared and discussed.

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PAPERS PRESENTED BUT NOT AVAILABLE FOR PUBLICATION

A Method of Predicting Bioaccumulation Potential of Chemicals Gilman Veith. Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, MN

Adverse Effects of Chlorine Disinfection on Aquatic Organisms William A. Brungs. Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, MN

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16. ABSTRACT

These proceedings include a cross-sectional representation of the broad base ecological effects research programs conducted by research laboratories of the EPA Office of Health and Ecological Effects. The presentations focus on microbial and abiotic degredation processes, the problem of trace metals, the effects of toxic organics, and the feasibility of new stress-measuring methodologies in the marine environment. The freshwater segment of the symposium addresses the transport and biological modeling capabilities of the laboratories, cold climate aquatic biology, lake trophic states in the eastern United States, and the impact of toxic substances on freshwater systems.

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