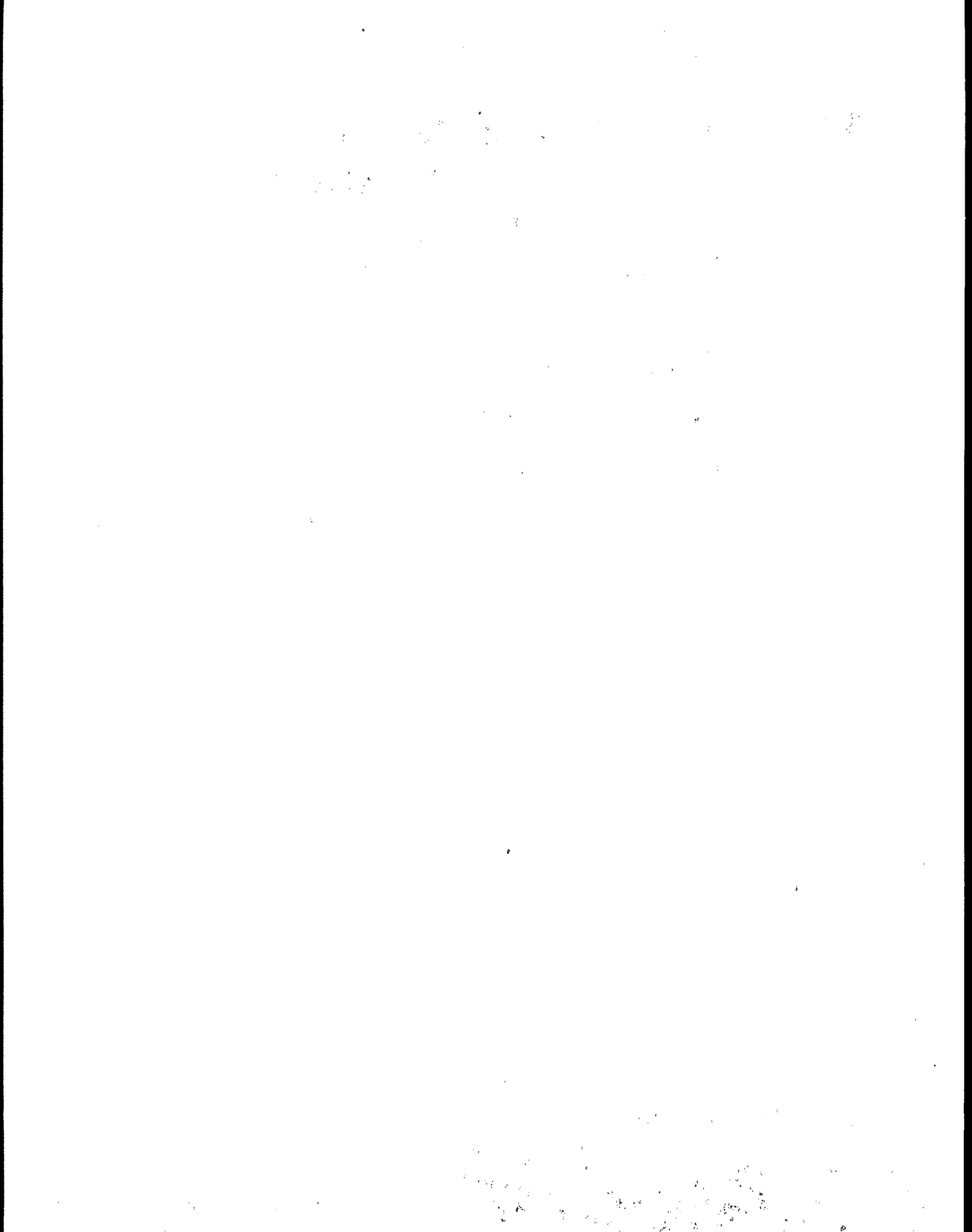




Fate and Effects of Pollutants on Aquatic Organisms and Ecosystems:

**Proceedings of USA-
USSR Symposium,
Athens, Georgia,
October 19-21, 1987**





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ON AQUATIC ORGANISMS AND ECOSYSTEMS:
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Edited by
Robert C. Ryans

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GEORGIA 30613

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FOREWORD

For a decade and a half, cooperation and exchange of scientific information under the USA-USSR Agreement on Cooperation in the Field of Environmental Protection has helped both countries in their efforts to control environmental pollution. These efforts are pursued in recognition of the international nature of the problem: pollution knows no boundaries.

Three projects are carried out under the joint USA-USSR Agreement's Working Group on Cooperation in the Area of Water Pollution Prevention. These are: Project 02.02-11 "River Basin Water Quality and Management," Project 02.02-12 "Protection and Management of Water Quality in Lakes and Estuaries," and Project 02.02-13 "Effect of Pollutants on Aquatic Organisms and Ecosystems: Development of Water Quality Criteria."

Over the years, scientific delegations and individual scientists have traveled to each other's countries to visit scientific institutions, perform joint research, and exchange technical information. This Proceedings presents associated with the most recent formal symposium, which was held in Athens, Georgia USA, in 1987.

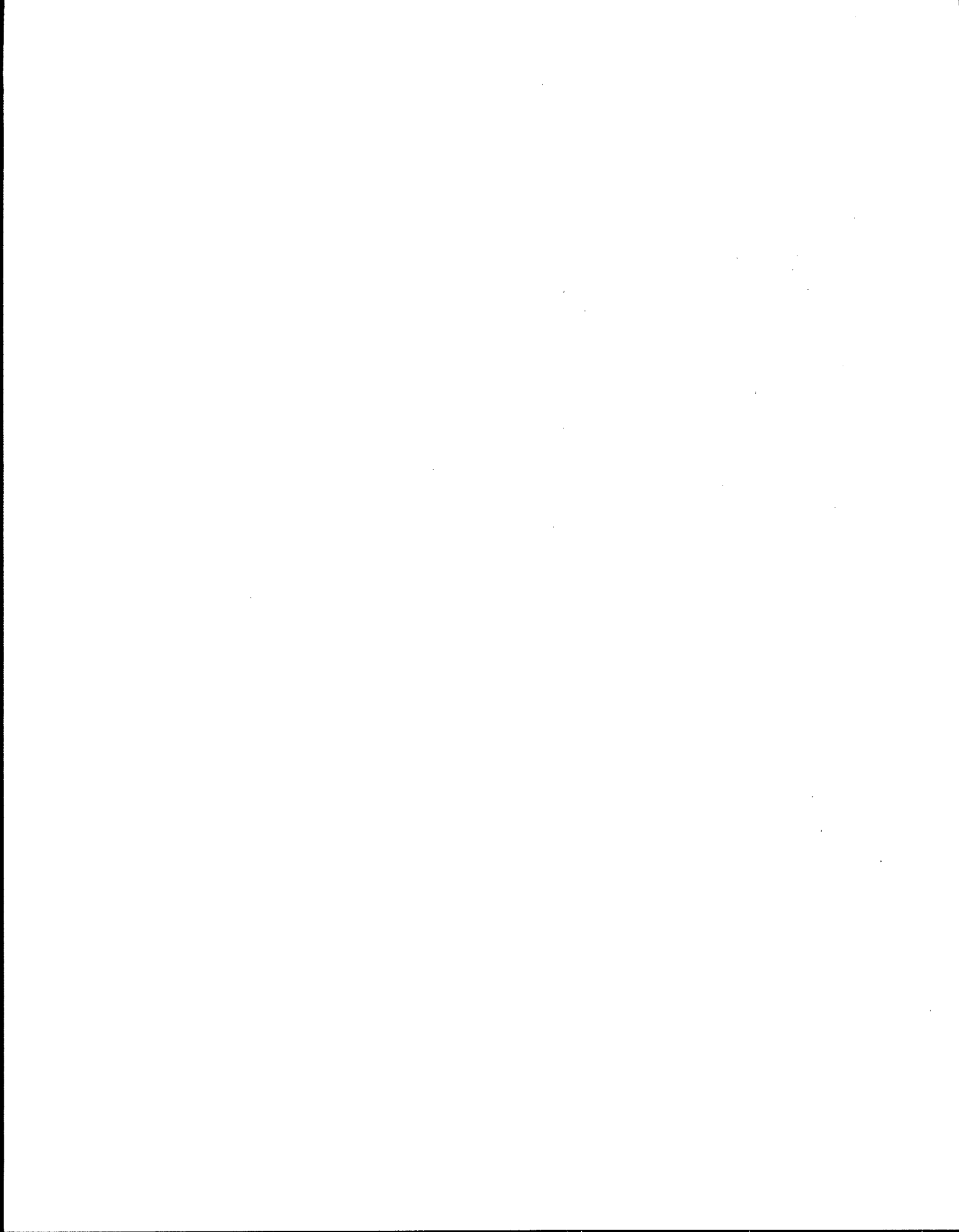
Rosemarie C. Russo
Director
Environmental Research Laboratory
Athens, Georgia

IN MEMORIAM

This document is dedicated to the memory of Dr. Nikolai V. Butorin. Dr. Butorin was among the first USSR scientists involved in the USA-USSR Agreement on Cooperation in the Field of Environmental Protection. He was intimately involved with the program over 15 years. His scientific expertise and enthusiasm for cooperative work between the two countries were invaluable contributions to the success of the Working Group on Cooperation in the Area of Water Pollution Prevention.

ABSTRACT

The 14 papers in this proceedings present research by scientists and engineers of the USA and USSR in three projects under the Working Group on Cooperation in the Area of Water Pollution Prevention. The Working Group is a component of the USA-USSR Agreement on Cooperation in the Field of Environmental Protection. Included among the papers are reports of modeling of runoff of substances from agricultural watersheds, of modeling lacustrine systems, of modeling toxic pollutant risk to aquatic organisms, and of modeling tributyltin exposure. Social and economic aspects of water quality management are examined and an integrated system for controlling water use and conservation is discussed. Effects of ammonium ions on mineral exchange in fish and ammonia distribution and excretion by fish are examined. The first use of a uniform toxicity test in both countries is described and a system for remote monitoring of ecosystem conditions is presented. Pesticide exposure is examined through aquatic community studies and in studies of resistance mechanisms in carp and perch. Buffer capacities of freshwater ecosystems for metals is examined and the relationship of trace metal body burdens and gill damage in fish to surface water acidification from atmospheric deposition is explored.



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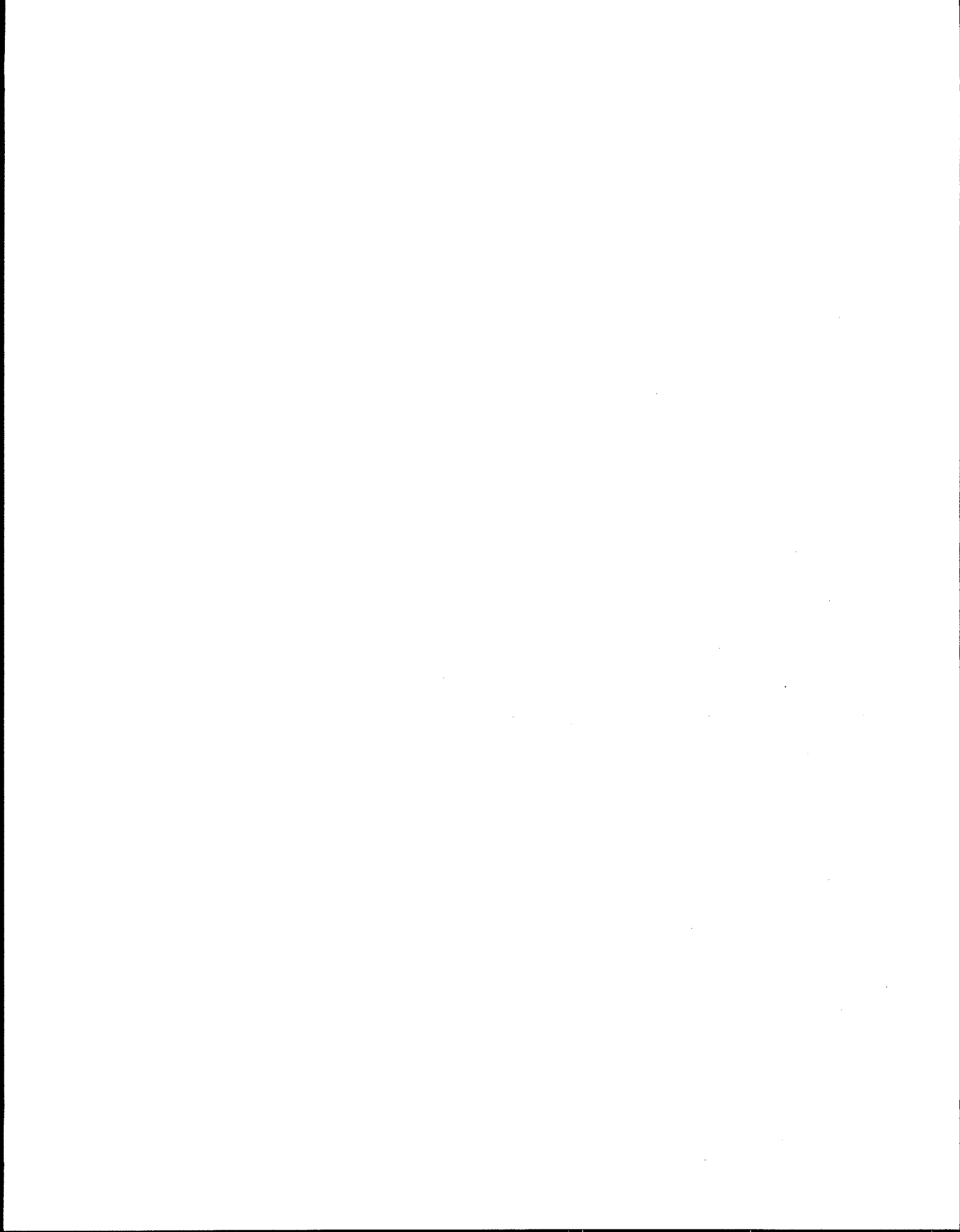
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ACKNOWLEDGMENTS

Organizing and presenting a symposium and preparing a proceedings is frequently a complex task, particularly when participants are from two countries that are widely separated geographically and have different languages. The dedication and hard work of Athens Environmental Research Laboratory staff--particularly that of Ms. Joan I. Price and Mr. J. Mac-Arthur Long--in taking care of the myriad arrangements for the symposium are greatly appreciated. The contributions of Ms. Martha M. Wilkes of Computer Sciences Corporation who typed the final document are gratefully acknowledged.

The scientists, engineers, and environmental managers who participated in the symposium, of course, are deserving of primary recognition. Co-chairmen of the Working Group on Cooperation in the Area of Water Pollution Prevention are Mr. Valdus V. Adamkus, Regional Administrator of USEPA Region V, and Dr. Alexander K. Kuzin, Deputy Director of the All-Union Research Institute for Water Protection. The symposium was divided into three sessions. Presiding over the session entitled "River Basin Water Quality Planning and Management" were Mr. Vacys J. Saulys of the Great Lakes National Program Office of USEPA Region V and Dr. Kuzin. Presiding over the session entitled "Effects of Pollutants on Aquatic Organisms and Systems" were Dr. Richard A. Schoettger, Director of the National Fisheries Contaminant Research Center, Columbia MO, and Dr. Nikolai V. Butorin, Director of the Institute of Biology of Inland Waters, Borok. Presiding over the session entitled "Protection and Management of Water Quality in Lakes and Estuaries" were Dr. Rosemarie C. Russo, Director of the Environmental Research Laboratory, Athens GA, and Dr. Anatoly M. Nikanorov, Director of the Hydrochemical Institute, Rostov-on-Don. Finally, the contributions of those who took time away from their busy research schedules to prepare and present papers at the symposium are gratefully acknowledged.



A SCREENING LEVEL MODEL FOR TRIBUTYLTIN CRITERIA

by

L.E. Fink¹

ABSTRACT

Some portions of the Great Lakes ecosystem are exposed to significant concentrations of tributyltin, a compounds that is acutely toxic to aquatic life. This paper reports on an environmental risk assessment to recommend maximum release rates.

INTRODUCTION

Tributyltin (or TBT) compounds are used, among other applications, in antifoulant pesticides (USEPA 1987). Of particular environmental concern is their incorporation into paints that are applied to submerged surfaces in aquatic environments to prevent the attachment of algae, barnacles, and other encrusting organisms. As a result of the use of TBT-containing paints on recreational and commercial vessels, the compound has accumulated in water and sediment of a number of Great Lakes harbors and connecting channels (Maguire 1983) and in fish from one harbor (R.J. Maguire, Canada Center for Inland Waters, personal communication). Thus, there is widespread exposure to TBT in some portions of the Great Lakes aquatic ecosystem.

TBT is acutely toxic to aquatic life, particularly molluscs. This is not surprising, because one important target pest is the barnacle. For example, the 15-day LC50 for mussel larvae is about 0.1 ug/L. The 96-hour LC50 for the juvenile chinook salmon is 1.5 ppb, and the 48-hr EC50 for the water flea, daphnia magna, is about 1.7 ppb.

Concentrations measured in the water column near the sediments in some Great Lakes harbors are within an order of magnitude of levels determined to be acutely toxic to embryo-larval and juvenile fish (Maguire and Tkacz 1985). Thus, potentially toxic levels are accumulating in some portions of the Great Lakes ecosystem. Because of its widespread distribution in the aquatic ecosystem and its extreme toxicity to many forms of aquatic life, TBT may pose a

¹Great Lakes National Program Office, U.S. Environmental Protection Agency, Region V, Chicago, IL, USA.

substantial risk to sensitive aquatic populations when used in anti-foulant paints.

The above considerations have prompted the U.S. Environmental Protection Agency to undertake a 2-year review of the registration of TBT anti-foulant paints. The regulatory policy question at issue was: Should the registration of tributyltin-based anti-foulant paints be revoked or modified to assure protection of aquatic life in fresh and salt water aquatic ecosystems? Recently, EPA completed its review and has recommended that:

1. The registration of TBT anti-foulant paints on recreational vessels less than 65 feet in length should be revoked.
2. The release rate of TBT from anti-foulant paints cannot exceed 168 ug/cm²-day during the 14-day initial release phase immediately after freshly painted boats are put into the water. After the initial phase, the release rate cannot exceed 4 ug/cm²-day.
3. TBT anti-foulant paints are to be applied by licensed pesticide applicators only.
4. TBT paint wastes are to be disposed of in an environmentally sound manner.
5. TBT concentrations in fresh waters should not exceed 20 ng/L at any time.

The purpose of this screening level analysis is to evaluate the environmental consequences of the regulatory proposals outlined above using an analytical methodology that EPA refers to as risk assessment.

At this juncture, it is necessary to briefly summarize what is meant here by risk assessment. In evaluating the ecological risks posed by a man-made chemical, two distinct analyses must be conducted: 1) hazard assessment and 2) exposure assessment. In a hazard assessment, the toxicological effects of the substance are studied, and no-effect levels or acceptable risk levels are derived for the most sensitive organisms and the most sensitive toxicological endpoints. In an exposure assessment, the rate at which the most sensitive organism is dosed is calculated. The rate at which an organism is dosed in its natural setting is determined by the concentration of biologically available toxicant in each environmental medium with which it comes into contact, the duration of contact, and the rate of uptake during that contact. Accumulation of the toxicant within the organism is determined by the rate of uptake in competition with the rates of metabolism and depuration.

In an exposure assessment, one or both of two distinct approaches can be taken:

1. The exposure assessment can be based on measured concentrations in the various media with which the organism comes into contact, and measured loading rates to each medium; or

2. The exposure assessment can be based on estimated concentrations and loadings using conservative assumptions and simple models.

The latter approach is often referred to as a mass balance approach. The essence of the approach is summarized in Figure 1. The former approach suffers from two drawbacks:

1. It requires a great deal of environmental and source data. For diffuse sources, these data are often hard to obtain.

$$\text{LOAD IN} = \text{LOAD OUT} - \text{LOAD STORED} - \text{LOAD LOST}$$

LOAD LOST

- . VOLATILIZATION
- . SEDIMENTATION (BURIAL)
- . CHEMICAL REACTION
 - .. HYDROLYSIS
 - .. PHOTOLYSIS
 - .. REDOX
 - .. COMPLEXATION
- . BIOCHEMICAL REACTION
 - .. BIODEGRADATION

LOAD STORED

- . WATER COLUMN
 - .. DISSOLVED
 - .. SUSPENDED SOLIDS
- . SEDIMENT
 - .. DISSOLVED
 - .. SUSPENDED SOLIDS
- . BIOTA

Figure 1. The mass balance approach.

2. It has no predictive capability beyond simple projection of existing trends.

Although the latter approach is also very data intensive, it incorporates a predictive capability. With this predictive capability, it is possible to evaluate the response of the aquatic ecosystem to a variety of source control and cleanup options. Within the framework of this predictive approach, the gathering of environmental data serves two purposes:

1. To identify emerging problems.
2. To allow an evaluation of the accuracy of model predictions (model validation).

For many chemicals, the data needed for a detailed analysis of the sources, transport, transformation, environmental distribution, and effects are not available.

Fortunately in the case of TBT, studies conducted by scientists at the Canada Centre for Inland Waters in Burlington, Ontario, provide much of the data needed to evaluate TBT transport, transformation and distribution in the Great Lakes aquatic ecosystem. The data on the distribution of TBT in the Great Lakes ecosystem also permits a comparison between model predictions and actual environmental conditions.

To perform a regulatory analysis of the proposed changes to the TBT pesticide registration, it is necessary to answer five questions:

1. What are acceptable levels of TBT in water, sediment, and biota?
2. What are the sources of TBT?
3. What are the loading rates from each source category?
4. What is the loading rate-concentration relationship?
5. Which source category(ies) need to be reduced by how much so as not to exceed acceptable levels?

To help crystallize the issues, attention is focused on the St. Clair River-Lake St. Clair - Detroit River System, one of the most densely industrialized waterways in the United States and a heavily used corridor for commercial shipping. But perhaps most important, there are enough boat slips on the Michigan side of Lake St. Clair to accommodate 14,334 vessels of various sizes, more than for any of the other Michigan Great Lakes.

Returning to the first of the five questions, EPA has proposed that the concentration of TBT not exceed 20 ng/L in the water column at any time. (The method of derivation of the fresh water quality criterion for aquatic life or its adequacy will not be discussed here.)

It is now necessary to quantify the loading rates to the system from recreational and commercial vessels to see whether these sources can account for the observed concentrations in the Detroit River. The data used to quantify recreational and commercial sources are summarized in Table I. The results of that analysis are indicated in Table II.

Next it is necessary to evaluate the fate of TBT in Lake St. Clair, which acts like a shallow retention pond for the St. Clair River and has a retention time of about 8 days. The limnological data used to calibrate the model were obtained from Dr. Thomas Fontaine III (National Oceanic and Atmospheric Administration, Ann Arbor, MI, (personal communication). Important physiochemical and fate rate data for TBT are summarized in Table A-1 of the Appendix.

Before getting to the focus of the modeling analysis, it is important to appreciate the significance of the coefficient describing the distribution of the compound between particles and water at thermochemical equilibrium, the so-called K_p value. When this value is divided by the fraction of organic matter present in the sediments, we have the so-called K_{oc} value. If the total organic carbon (or TOC) value of any particular sediment is known, then its K_p value can be estimated from the K_{oc} value. The K_{oc} value, in turn, can be estimated from the n-octanol/water partition coefficient, which itself can be estimated from quantitative structure-activity relationships (Leo et al. 1971). Because it is the truly dissolved fraction of the compound of concern that drives volatilization, diffusion into the sediments and biological uptake, and because the truly dissolved fraction is calculated from K_p and concentration values for inorganic, organic and colloidal particles, the importance of an accurate value for K_{oc} cannot be overstated.

Partition coefficients were based on a K_{oc} value of 9.2×10^4 reported by Maguire and Tkacz (1985) and the assumption that algae were 35% TOC (Connolly 1987), colloidal material was 35% TOC (Hassett, J., State University of New York at Syracuse, personal communication) and that the concentration of colloidal material was equal to that of the algae.

TBT TRANSPORT-FATE IN FRESHWATER AQUATIC ECOSYSTEMS

Based on the properties summarized in Table A-1 of the Appendix, the following tentative conclusions can be drawn. Given its relatively slow rates of biodegradation, photodegradation, and volatilization, and its only moderate affinity for particles, TBT is only slowly removed from the water column by natural processes in the freshwater aquatic ecosystem relative to simple hydraulic dilution. Under steady state conditions, the potentially most significant routes of removal of TBT from the water column after hydraulic dilution are photodegradation, biodegradation, and association with settling particles and subsequent degradation and burial beneath the active sediment layer. In turbulent systems having very slow rates of sediment accumulation, burial would not be a significant route of removal from the system.

TBT is only slowly converted to dibutyltin (DBT) and then monobutyltin (BT) via biodegradation, with the most significant rate of conversion occurring in the sediments. Whether the rate of biodegradation determined in a

TABLE I. TBT RELEASE RATE DATA

Component	Measurement	Reference
Existing Release Rate	20 ug/cm ² -day	Anderson (1987) ^a
Number of Recreational Vessels in L. St. Clair	$\frac{95\%}{100\%} \times 14,334$	Holecek and Brothers (1983)
Number-weighted Average Painted Surface Area	19 m ²	Author's calculation.
Percentage of TBT Users on Recreational Vessels	14% X 30% (U.S. average)	Anderson (1987) ^a
Number of Ocean-Going Vessels That Pass Through The System	2.6/day	Papineau (1987) ^b
Transit Time	5 hours	Papineau (1987) ^b
Number of Ocean-Going Vessels Docked in The System	$\frac{5\%}{100\%} \times 5$	Armitage (1987) ^c
Average Painted Surface Area	9.4 X 10 ³ m ²	Author's calculation
Percentage of TBT Users on Commercial Vessels	27% (U.S. average)	Anderson (1987) ^a

^aAnderson, E., U.S. Environmental Protection Agency, personal communication.

^bPapineau, P., Canadian Coast Guard, personal communication.

^cArmitage, K., Harbor Master, Port of Sarnia, Ontario, personal communication.

TABLE II. ESTIMATED LOADINGS OF TBT (kg/day) TO THE LAKE ST. CLAIR SYSTEM FROM RECREATIONAL AND COMMERCIAL USES OF TBT-BASED ANTI-FOULING PAINTS

TBT Uses	Rate	
	4 ug/cm ² -day	20 ug/cm ² -day
Recreational Boats	0.44	2.2
Paint Chips in Sediments from wet scraping (assume 20% of TBT users scrape down hull over water)	0.175	@ 0
Precipitation Runoff contribution from dry dock scraping (assume 80% of TBT users scrape down hull in dry dock)	0.35	@ 0
Ocean-going Commercial Vessels	0.6	0.38
TOTAL	1.0	2.6

sediment slurry in vitro is applicable to river or lake sediments in situ cannot be ascertained with certitude at present, but it would appear from the observed ratios of TBT to DBT and DBT to BT that the rates of biotransformation of TBT to DBT and DBT to BT are slower in natural sediment. Whether photolysis of TBT yields DBT and thence BT or other photoproducts cannot be determined from the available data.

Given the tendency of TBT to accumulate in the sediments due to its partitioning behavior, and given the relatively higher rate of biodegradation in the sediments versus the water column, it would appear that the most significant route of removal from the aquatic ecosystem is biodegradation in the sediment. Once degraded from TBT to DBT and thence to BT, the rates of release of these species from the sediments could be greater than for TBT, both because their sediment/water partition coefficients would be correspondingly

smaller and their diffusion coefficients correspondingly greater. Thus, it could well be argued that the sediment is a significant source of the DBT and BT found in aquatic ecosystems.

The hydraulics and biodegradation rate constants for water and sediment and the photolysis rate constant for water, as well as desorption kinetics data, also were obtained from the studies of Maguire and Tkacz (1985). To quantify the relationship between the loading rate and the biologically available concentration in the water column, a simplified lake model was calibrated to the important limnological parameters describing Lake St. Clair and site-specific adaptations of the fate rate coefficients. The simplified lake model was developed by HydroQual, Inc., in Mahwah, N.J. (DiToro et al. 1980). Simple algebraic solutions to the time-dependent and steady state equations were obtained by the authors at the expense of model accuracy. The most important simplifying assumptions and approximations used in developing the model were:

1. Water flow is constant.
2. Water column is homogeneous.
3. Suspended and settled particles are of uniform size, shape and chemical composition:
 - o one settling, resuspension and sedimentation velocity
 - o one particle/water partition coefficient
 - o one rate constant for each particle associated process
4. Suspended and settled particle concentrations are constant.
5. Homogeneous active sediment layer of constant depth.
6. The bed is stable.
7. Rates of adsorption and desorption are so rapid relative to other processes that particle/water sorption equilibrium exists locally.
8. All toxicant concentration-driven rate processes are first-order with respect to toxicant concentration.
9. No speciation of dissolved and/or partitioned toxicant occurs.
10. There is no contribution of organisms in direct contact with contaminated sediments (e.g., bottom feeding fish and benthic invertebrates) to the food chain biomagnification of toxicant in top predators.

The model equations, the general algebraic solution for the steady state condition, the model input data, and the model results are described in the appendix. The results of this assessment tend to support the conclusion that, in systems having a low sedimentation rate and short retention times, there are no significant routes and rates of removal relative to simple hydraulic dilution. Thus, for the Lake St. Clair example, the assumption of conservation of mass will introduce an error of only about 10% into the calculation of the loadconcentration relationship for TBT.

MASS BALANCING TBT IN THE ST. CLAIR-DETROIT RIVER SYSTEM

Maguire et al. (1985) studied the distributions of TBT, DBT, and BT in the St. Clair River and Detroit River water and sediment. The Detroit River was sampled in June 1983; the St. Clair River was sampled in October, after the recreational boating season. The fast-flowing St. Clair River is not nearly as popular as Lake St. Clair for recreational boaters, however, so the difference may not be too great. Both rivers were sampled during the commercial shipping season, however.

It is highly unlikely that a single sample of water collected and analyzed from a few stations along these rivers could adequately characterize the TBT loads entering and leaving Lake St. Clair. On the other hand, with diffuse and relatively constant sources of TBT, DBT and BT in the system, the heterogeneity in loadings should not be nearly as great as that associated with point source industrial cycles or storm water runoff events. Thus, while the calculation of a mass balance for TBT in the system from so few data could not be used for purposes of regulating sources, it can be used to gain insight into relative source strengths in this screening level analysis.

TBT was not detected in subsurface samples in the St. Clair River during the study by Maguire and co-workers. DBT and BT were detected. If the ratio of the concentration of TBT to BT at the headwaters of the Detroit River (the mouth of Lake St. Clair) is the same as at the mouth of the St. Clair River (the headwaters of Lake St. Clair), then the concentration of TBT can be inferred for the St. Clair River from that ratio and the concentration of BT detected there. A concentration of 8.1×10^{-12} moles Sn/L is calculated. Using a flow rate for the system of 4.7×10^{11} L/day, an upstream TBT loading rate of about 1.1 kg/day is calculated. The concentration of TBT as organic tin at the headwaters of the Detroit River was reported to be 6.90×10^{-11} moles/L, corresponding to a downstream TBT loading of 9.4 kg/day. The difference between downstream and upstream loadings indicates a source strength of about 8.3 kg/day in Lake St. Clair in June 1983.

It should be noted here that the estimate of the opening season release rate from recreational vessels on Lake St. Clair, assuming one-third of the 14,300 vessels put in during any 2-week period for the first 6 weeks of the season, is about 6.2 kg/day. The estimate of the opening season release rate for commercial vessels, assuming that one-sixth of the vessels are re-painted in any given year and that 50% of the newly painted boats travel to the Port of Sarnia during the initial release rate period, the commercial vessels contribution increases to about 0.6 kg/day. The time of sampling in June of 1983 may have been early enough to quantify the impact of this early release rate phenomenon on Lake St. Clair and Detroit River water quality.

Whether the initial release rate phenomenon discussed above for commercial vessels could account for the upstream loading rate observed in June of 1983 cannot be determined. An evaluation of the maximum contribution that could be made to upstream loadings from sediment particle resuspension, pore water exchange and desorption can account for only a fraction of the 1.1 kg/day estimated loading. The possibility of an upstream point source cannot be ruled out.

Due to the relatively short retention time in Lake St. Clair, the lake rapidly approaches steady state conditions in response to this early season loading. On the other hand, the sediment lags behind the water column, approaching steady state only towards the end of the recreational boating season of 180 days duration. The 0.6 kg/day loading rate would be sufficient to raise the concentration in the water column above the 1 ng/L level of concern and keep it there for the duration of the opening season, perhaps as long as 30 to 45 days. Under the proposed 4 ug/cm²-day release rate limit, the initial phase loading contribution from commercial vessels drops to about 0.27 kg/day, just above the loading rate necessary to cause the Detroit River to exceed a 1 ng/L concentration under once in 10-year, 7-day low flow conditions.

CONCLUSIONS

Based on the above analysis, to assure that susceptible harbors and connecting channels in the Great Lakes system not exceed the proposed 20 ng/L level of concern, the use of TBT anti-foulant paints on the vast majority of recreational vessels should be discontinued. Although the proposed maximum release rate of 4 ug/cm²-day at steady state is not likely to pose a threat to rivers and harbors having short retention times, the maximum initial release rate of 168 ug/cm²-day from freshly painted vessels that put into the water only shortly before entering the Great Lakes system could present an unacceptable risk to aquatic life during the months of April and May. Follow-up studies should track the concentration profiles of TBT, DBT, and BT in the water column and sediment from the opening of the commercial shipping season to its close. If levels exceeding 1 ng/L are observed for any significant period of time subsequent to virtually eliminating the recreational uses of TBT anti-foulant paints, additional controls on commercial uses may be necessary.

RECOMMENDATIONS

1. Recreational uses of TBT-based anti-foulant paints in the Great Lakes Basin should be virtually eliminated.
2. The effect of continued commercial uses of TBT-based anti-foulant paints under the proposed restrictions should be carefully monitored over the next 2 years.
3. Over the next 2 years, additional toxicological studies should be undertaken to evaluate the adequacy of the proposed 20 ng/L TBT criterion to protect aquatic life, particularly with respect to the food chain contribution to bioaccumulation.

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APPENDIX

TABLE A-1. PROPERTIES OF TBT₀ AND TBT^a

Species	Sol. H ₂ O ^b	log K _{ow} ^c	t _{1/2} bi ^d	t _{1/2} vol	t _{1/2} hydro ^d	t _{1/2} photo
TBT ₀	0.75 - 4.0 1 mg/L at pH = 7.8		?	?	?	?
<hr/>						
TBT	?	3.2 ^e	20+/- 5 wks (H ₂ O) 16 +/- 2 wks (sed)	@ 0	@ 0	> 89 d

^aMaguire and Tkacz (1985) in Toronto Harbor water and sediment at 20°C.
(Note: All measurements were made at 20°C unless otherwise indicated.)

^bpH = 6.0-7.8 in phos. buffer (mg/L).

^cpH = 6.0.

^dpH = 2.9-10.3.

^eLaughlin et al. (1986) report a log K_{ow} value for TBT of 3.845

LAKE ST. CLAIR LIMNOLOGICAL CHARACTERISTICS

Q	=	flow	=	5400 M ³ /s
			=	4.7 x 10 ¹¹ l/day
H ₁	=	average depth of the water column	=	3.6 M
H ₂	=	average depth of active sediment layer	=	0.05 M
A	=	surface area of the lake	=	1250 km ²
			=	1.25 x 10 ⁹ M ²
V	=	volume of lake	=	3.7 x 10 ⁹ M ³
t _H	=	hydraulic retention time	=	V/Q
			=	8 days
m _{1a}	=	the concentration of abiological particles in the water column	=	11.2 x 10 ⁻⁶ kg/l
m _{1b}	=	the concentration of biological particles (algae, etc.) in the water column	=	20 x 10 ⁻⁶ kg/l
m _{1c}	=	the concentration of colloidal (non-filterable organic) particles in the water column	=	20 x 10 ⁻⁶ kg/l
m ₂	=	concentration of particles in the active layer of the sediment	=	0.42 kg/l
w _a	=	settling velocity of inorganic particles	=	1.2 M/day
w _{rs}	=	resuspension velocity of particles from the active sediment layer	=	3.2 x 10 ⁻⁵ M/day
w _s	=	velocity of burial of inorganic particles beneath the active sediment layer	=	0 0 M/day

LAKE ST. CLAIR LIMNOLOGICAL CHARACTERISTICS

TOC = total organic carbon

DOC = "dissolved" organic carbon

TOC of the inorganic particles in the water column and sediment is assumed to be the average of the TOC values for the St. Clair River and Lake St. Clair stations, roughly 0.35%.

TOC of the biological particles in the water column is assumed to be roughly 35% (Connolly, 1987).

TOC of the colloidal particles in the water column is assumed to be equal to that for biological particles, or 35%.

$$K_{oc} = 9.2 \times 10^4 \text{ l/kg}$$

$$\eta_{1a} = 9.2 \times 10^4 \text{ l/kg oc} \times 0.0035 = 3.2 \times 10^2 \text{ l/kg}$$

$$\eta_{1b} = 9.2 \times 10^4 \text{ l/kg oc} \times 0.35 = 3.2 \times 10^4 \text{ l/kg}$$

$$\eta_{1c} = 9.2 \times 10^4 \text{ l/kg oc} \times 0.35 = 3.2 \times 10^4 \text{ l/kg}$$

$$k_{1bio} = \frac{0.693}{20 \text{ wks} \times 7 \text{ days/wk}} = 4.95 \times 10^{-3} \text{ day}^{-1}$$

$$k_{2bio} = \frac{0.693}{16 \text{ wks} \times 7 \text{ days/wk}} = 6.2 \times 10^{-3} \text{ day}$$

$$k_{1pho} = \frac{0.693}{> 85 \text{ days}} < 8.15 \times 10^{-3} \text{ day}$$

LAKE ST. CLAIR LIMNOLOGICAL CHARACTERISTICS

fd_1 = apparent dissolved fraction in the water column
(non-filterable TBT)

fd_1^* = truly dissolved fraction in the water column

fp_{1a} = fraction of TBT associated with inorganic particles in
the water column

fp_{1b} = fraction of TBT associated with biological particles in
the water column

fp_{1c} = fraction of TBT associated with colloidal particles in
the water column

$$fp_{1a} = \frac{\eta_{1a} \times m_{1a}}{1 + \eta_{1a} \times m_{1a} + \eta_{1b} \times m_{1b} + \eta_{1c} \times m_{1c}} = 0.0015$$

$$fp_{1b} = \frac{\eta_{1b} \times m_{1b}}{1 + \dots} = 0.280$$

$$fp_{1c} = \frac{\eta_{1c} \times m_{1c}}{1 + \dots} = 0.280$$

$$fd_1^* = 1 - (fp_{1a} + fp_{1b} + fp_{1c}) = 0.4385$$

$$fd_1^* = fd^* + fp_{1c} = 1 - (fp_{1a} + fp_{1b}) = 0.7185$$

LAKE ST. CLAIR LIMNOLOGICAL CHARACTERISTICS

$$\text{assume } \eta_{1a} = \eta_{2a} = \eta_2$$

$$fp_2 = \text{fraction of TBT associated with sediment particles}$$

$$= \frac{\eta_2 \times m_2}{1 + \eta_2 \times m_2}$$

$$= \frac{3.2 \times 10^2 \text{ l/kg} \times 0.42 \text{ kg/l}}{1 + 3.2 \times 10^2 \text{ l/kg} \times 0.42 \text{ kg/l}} = 0.9926$$

$$fd_2 = 1 - fp_2 = 0.0074$$

VOLATILIZATION RATE CALCULATIONS

$$K_v = 1/L \left[\frac{1}{K_l^0 (D_l^r)^m} + \frac{RT}{H K_g^w (D_g^r)^n} \right]^{-1} \quad \text{Smith et al. (1981)}$$

where:

D_l^r = the ratio of the molecular diffusivity of the chemical to that of air in water

D_g^r = the ratio of the molecular diffusivity of the chemical to that of water in air

K_g^w = mass-transfer coefficient for water vapor in the air phase

K_l^0 = mass-transfer coefficient for oxygen in the water phase

m, n = In the range from 1.0 for stagnant conditions and 0.5 for very turbulent conditions

H = Henry's Law Constant, generally calculated as the ratio of the vapor pressure to the solubility

R = the universal gas constant (0.082 l-atm/mole-°)

T = the absolute temperature on the Kelvin scale

L = the depth of the water column

PARAMETER VALUES FOR VOLATILIZATION RATE COEFFICIENT CALCULATION

$$K^0_1 = 0.43 \text{ M/day} \quad \text{Smith et al. (1981)}$$

$$K^W_g = 504 \text{ M/day} \quad \dots \quad \dots$$

$$m = 0.7 \quad \dots \quad \dots$$

$$n = 1.0 \quad \dots \quad \dots$$

$$H = 8.42 \times 10^{-10} \text{ atm} / 1.38 \times 10^{-2} \text{ mole/M}^3 = 6.1 \times 10^{-8} \text{ atm/mole-M}^3$$

$$D^{\text{air}}_{\text{H}_2\text{O}} = 0.239 \text{ cm}^2/\text{s} (80^\circ\text{C}) = 2.1 \text{ M}^2/\text{day}$$

$$D^{\text{H}_2\text{O}}_{\text{H}_2\text{O}} = 2.1 \times 10^{-5} \text{ cm}^2/\text{s} = 1.8 \times 10^{-4} \text{ M}^2/\text{day} \quad (\text{Weast, 1977})$$

$$D^9_{\text{TCDD}} = 4.7 \times 10^{-2} \text{ cm}^2/\text{s} = 0.41 \text{ M}^2/\text{day} \quad \text{calculated by Smith et al. (1981)}$$

$$D^1_{\text{TCDD}} = 5.1 \times 10^{-6} \text{ cm}^2/\text{s} = 4.4 \times 10^{-5} \text{ M}^2/\text{day}$$

$$\begin{aligned} D^{\text{O}_2}_1 &= D^{\text{H}_2\text{O}}_1 \times \left(\frac{\text{MW}_{\text{H}_2\text{O}}}{\text{MW}_{\text{O}_2}} \right)^{2/3} = 1.8 \times 10^{-4} \text{ M}^2/\text{day} \left(\frac{18}{32} \right)^{2/3} \\ &= 1.2 \times 10^{-4} \text{ M}^2/\text{day} \end{aligned}$$

$$D^r_1 = \frac{4.4 \times 10^{-5} \text{ M}^2/\text{day}}{1.2 \times 10^{-4} \text{ M}^2/\text{day}} = 0.37$$

$$D^r_g = \frac{(0.42 \text{ M}^2/\text{day})}{2.1 \text{ M}^2/\text{day}} = 0.2$$

$$\begin{aligned} K_v &= 1/3.6 \text{ M} \left[\frac{1}{0.43 \text{ M/day}} (0.37)^{.7} + \frac{0.82 \frac{\text{L-atm}}{\text{mole}^\circ} \times 10^{-3} \text{ M}^3/\text{l} \times 293^\circ\text{K}}{504 \text{ M/day} (1.8 \times 10^{-7} \frac{\text{atm-M}^3}{\text{moles}})(0.2)^1} \right]^{-1} \\ &= 0.36 \times 10^{-3} \text{ day}^{-1} \end{aligned}$$

SIMPLIFIED STEADY STATE TRANSPORT-FATE MODEL OF LAKE ST. CLAIR

$$W_T = C_{T1}(00) \times Q_L [1 + K_T V_L/Q_L]$$

$$K_T = K_1 + B \times (r_2/r_1) (K_2 + k_s)$$

$$k_s = \frac{w_s \times fp_2}{H_2} = 0$$

$$K_1 = k_{d1} \times f_{d1} + k_{p1} \times fp_1$$

$$k_{d1} = k_{1bio} + k_{1pho} + k_{vol}$$

$$k_{d1} = 4.95 \times 10^{-3} \text{ day}^{-1} + 8.15 \times 10^{-3} \text{ day}^{-1} + 0.36 \times 10^{-3} \text{ day}^{-1}$$

$$k_{d1} = 1.35 \times 10^{-2} \text{ day}^{-1}$$

$$\begin{aligned} K_1 &= 1.35 \times 10^{-2} \text{ day}^{-1} \times 0.4385 + 6.2 \times 10^{-3} \text{ day}^{-1} \times 0.0015 = \\ &= 5.9 \times 10^{-3} \text{ day}^{-1} \end{aligned}$$

$$\begin{aligned} K_2 &= k_{d2} \times f_{d2} + k_{p2} \times fp_2 = 0 + 8.15 \times 10^{-3} \text{ day}^{-1} \times 0.9926 \\ &= 8.1 \times 10^{-3} \text{ day}^{-1} \end{aligned}$$

$$B = \frac{fp_1 \times m_1 \times H_2}{fp_2 \times m_2 \times H_1}$$

It is assumed that the biological particles do not settle in Lake St. Clair but are carried on through the system to the Detroit River, because the settling time of biological particles is longer than the retention time. Thus, the only communication between the sediment and the overlying water column is via inorganic particles. Therefore, $fp_1 = fp_{1a}$, $m_1 = m_{1a}$, and $\eta_1 = \eta_{1a}$

$$B = \frac{0.0015 \times 0.42 \times 10^3 \text{ kg/M}^3 \times 0.05 \text{ M}^3}{0.9926 \times 11 \times 10^{-3} \text{ kg/M}^3 \times 3.6 \text{ M}} = 0.8$$

$$\text{If } \eta_{1a} = \eta_{2a}, \text{ then } r_2/r_1 = @ 1$$

$$\begin{aligned} K_T &= K_1 + B \times (r_2/r_1) (K_2 + k_s) \\ &= 5.9 \times 10^{-3} \text{ day}^{-1} + 0.8 \times 1 \times (8.1 \times 10^{-3} \text{ day}^{-1} + 0) \\ &= 1.2 \times 10^{-2} \text{ day}^{-1} \end{aligned}$$

$$\begin{aligned} W_T &= C_{T1(\infty)} \times Q_L [1 + K_T \times V_L/Q_L] \\ &= 20 \text{ ng/l} \times 10^3 \text{ l/M}^3 \times 4.7 \times 10^8 \text{ M}^3/\text{day} \times [1 + 1.2 \times 10^{-2} \text{ day}^{-1} \times 8 \text{ days}] \\ &= 9.4 \text{ kg/day} [1 + 0.1] \\ &= 10.3 \text{ kg/day} \end{aligned}$$

Under design drought flow conditions, $Q_L = 108,000 \text{ cfs} = 2.64 \times 10^8 \text{ M}^3/\text{day}$, and:

$$\begin{aligned} W_T &= 20 \text{ ng/l} \times 10^3 \text{ l/M}^3 \times 2.6 \times 10^8 \text{ M}^3/\text{day} [1 + 0.1] \\ &= 5.2 \text{ kg/day} [1 + 0.1] = 5.7 \text{ kg/day} \end{aligned}$$

If only 10,000 cfs is given over for dilution of any particular source category in the Detroit River, as it would be if the source category were point sources regulated under Michigan's NPDES Permit Program, then:

$$\begin{aligned} W_T &= 20 \text{ ng/l} \times 10^3 \text{ l/M}^3 \times 2.45 \times 10^7 \text{ M}^3/\text{day} [1 + 0.1] \\ &= 0.49 \text{ kg/day} [1 + 0.1] = 0.54 \text{ kg/day} \end{aligned}$$

SOCIAL AND ECONOMIC ASPECTS OF WATER QUALITY MANAGEMENT

by

A.K. Kuzin, O.I. Kovaleva, and L.S. Garibova¹

ABSTRACT

Economic feasibility is an important component of the decision-making process in the water management area. In this paper, some suggestions are advanced for determining the economic effectiveness of water management programs.

WATER QUALITY MANAGEMENT

As self-financing continues to be developed in the USSR, the role of economic support for good water quality programs is increased. This is due to the high outlays of funds for construction and exploitation of water management facilities. Several published scientific articles, recommendations, and instructions are devoted to methodological issues in this area (Anon. 1981; 1983a,b; 1986a,b; 1987). Economic factors for the support of water management programs are often carried out to the detriment of social and economic programs, which creates erroneous assumptions for decision-making. The role of economic feasibility within the decision-making process in the water management area is often unclearly defined. In this paper, some suggestions for determining the economic effectiveness of water management programs are advanced as component parts in the larger issue, taking into account the social and ecological factors.

The components of social well being--living conditions, social environment, living environment--are derived to a lesser or larger degree from the quality of water. Living conditions, which are determined by the degree to which the population is supplied with material goods, are dependent on water quality on two levels. On the one hand, when there are extremely high outlays of funds for the provision of high standards of water quality, there is a reduction in the production of material goods and, as a rule, there is a drop in the quality of life. On the other, when outlays to protect water quality are low, water quality may deteriorate to the point that both capital

¹All-Union Research Institute for Water Protection, Kharkov USSR.

and operating costs for water processing will rise sharply to the point that this will also result in decreased allotments to the production of material goods. Consequently, from the point of view of providing the best conditions of life, a compromise on the state of water quality must correspond to the optimum outlays to protect water quality.

The state of the social environment also is tied to water quality on two levels. First, when water quality is poor, the health of the population declines, which results in decreased income of the population and increased costs for public insurance and preventive measures, as well as other negative effects. Second, when water quality costs are high, closures of enterprises may result because of their diminished effectiveness as a result of the high-cost purifying facilities, or employment opportunities may be reduced because of a reorientation of the enterprises. Thus, as mentioned above, a search for a compromise on positions is necessary.

Water quality is also an important component of the state of the natural environment, which serves as a source of aesthetic pleasure and a source of satisfaction to man both spiritually and culturally. Thus, to a large degree, the issue of establishing a specific category of natural water is reduced to the development of an optimal correlation between the components that make up social well-being--a state characterized by economic, social, and ecological parameters. The determination of this correlation is difficult to formalize, however, and the formalization process is imbalanced at different stages of the decision-making process.

Let us note that the water quality category and the category of the water body are determined by their purpose, because indicators for water composition and properties have been defined accordingly (drinking and household, general use, fishing industry). Thus placement of water bodies in the appropriate category--or in other words, the procedure for establishing usage standards for water protection activity--is carried out jointly at the state, republic, regional, and local levels.

Water quality on the state level is established for major water bodies that have national significance, such as Lakes Baikal, Sevan, and Ladoga. The basis for placing water bodies in this category may be their extremely important economic significance, their exceptional value as natural environments, or their unique water quality. Also examined are such indicators as a particular territory's supply of water, its agroindustrial potential, population density, condition of the environment in the region, and other factors.

Concerning such priority bodies of water, end use is determined by the water protection guidelines that take into account the management factors as well as socio-economic values. When necessary data are available, the economic feasibility of reaching the appropriate water quality category can be determined and taken into account as a component for substantiating this category. Also determined on the state level is water quality on boundary sites of principal rivers that border with Union republics, as well as on state boundaries (on the basis of inter-government agreements).

The principal documents that contain decisions or substantiations for the protection of water bodies of national significance are the decrees of the USSR Council of Ministers, the General Plan for Utilizing and Protecting USSR Water Resources, Basin Maps of Large Water Bodies, and intergovernmental agreements on the protection and utilization of water adjacent to borders.

On a republic level, the end use standards for water quality are determined at the water body sites that form boundaries between territories, and that are within the purview of neighboring basin management authorities for water use and protection thereof, as well as at individual priority water sites of significance to the republic.

End-use standards for water quality are determined in a similar fashion on a regional level by a regional basin management that sets standards for the boundaries between autonomous republics, as well as at water sites that have the greatest significance for the region.

And finally, there are standards for all bodies of water that have management or socio-economic importance. These standards, which are set at the local territorial level, are determined by administrative allotment (oblast, krai, or autonomous republic).

The substantiations and decisions for setting end use water quality standards for selected priority water bodies are maintained in the decrees of the Council of Republic Ministers, the decrees of local management bodies, and republic-level basin and oblast plans for the use and protection of water resources. Decisions are made on the basis of management or socio-economic factors. As the evaluations are substantiated, the accuracy for determined economic feasibility in achieving the corresponding water quality levels is improved, which makes it possible to include this component as well.

Calculation of economic feasibility for achieving the corresponding water quality category and end use standards involves the comparison of results and outlays involved with improving water quality, i.e.

$$\begin{aligned} \mathcal{O}_{\delta+i} &= \Delta \mathcal{O}_{\delta+i} - (\Pi_{\delta+i} - \Pi_{\delta}), \\ i &= 1, 2, \dots, n, \end{aligned} \tag{1}$$

where: $\mathcal{O}_{\delta+i}$ is the general economic effect as a result of improved water quality, from δ to i -category, millions of rubles per year; $\Delta \mathcal{O}_{\delta+i}$ is the total effect for water consumers with improved water quality, from δ to i -category; millions of rubles per year; Π_{δ} , $\Pi_{\delta+i}$ is the adduced costs for the achievement of water protection measures, for maintaining the base water quality category, and for achieving the i -category quality, millions of rubles per year; n is the number of quality categories that are possible to be attained.

Component indicators included in Formula 1 are selected on the basis of the following considerations. It is presumed that necessary water protection facilities have been established previously at this particular site, or a part

of it, and that the operation of these facilities is tied to outlays C_b to operate them. It is thanks to them that δ level water quality is maintained presently.

To maintain water at this level in the future, it is necessary to allocate capital investments K_b for the development of new facilities and to anticipate increased exploitation costs of ΔC_δ . Thus, maintenance of the base water quality is tied to the cited μ_δ , that is,

$$\mu_\delta = C_\delta + E_\Delta K_\delta + \Delta C_\delta \quad (2)$$

where E is the normative efficiency coefficient for capital investments, taken to be 0.12 with a 7-year amortization period.

If there are plans to achieve water quality above the i -category in the future, it is necessary to take into account additional capital investments $\Delta K_{\delta+i}$ and the exploitative expenditures of $\Delta C_{\delta+i}$, that is,

$$\mu_{\delta+i} = \mu_\delta + E_\Delta K_{\delta+i} + \Delta C_{\delta+i} \quad (3)$$

$$a = 1, 2, \dots, b; e = 1, 2, \dots, k,$$

At the same time with the change in water quality category (as compared to base), it may be possible to improve the economic effect as a result of improved conditions of water usage. This effect is defined as the sum total of the types of water utilization, each of which is calculated accordingly as a sum total of benefits for individual sites or facilities, i.e.

$$\Delta \mathcal{P}_{\delta+i} = \sum_{a=1}^b \sum_{e=1}^k \Delta \mathcal{P}_{(\delta+i)ae}, \quad (4)$$

$$a = 1, 2, \dots, b; e = 1, 2, \dots, k,$$

where: b is the number of usage types; k is the number of a -type usage facilities and $\Delta \mathcal{P}_{(\delta)ae}$ is the economic effect for the e -facility/site with a -type water usage, when the water quality category is raised (compared to base), millions of rubles per year.

Although the determination of the economic effect of improved water quality for various types of usage--household and drinking, fish industry, general use--has its particular requirements, the common efficiency indicator is the annual increase in income or the reduction of adduced costs. For example, with household and drinking usage, changes in the water quality indicators within the allowable limits results in changes in adduced costs

relating to various high-cost water purifying equipment and the expenditures to service it.

After a decision has been made relative to the water quality at a given water site, there arises an economic problem in determining a set of measures that will assure the type of water quality indicators that will involve minimum outlays. A number of modifications exist to deal with this problem, depending on the details of the original data, familiarity with a particular water resource, types of models utilized to transform the water quality, and other conditions. A general view of the economic effect following an extensive examination of the contamination sites and sources, and the selection of an optimal system of measures is determined by the expression:

$$\mathcal{D}_j = \sum_{i=1}^n \text{ind.}_{ij} - \min. \sum_{i=1}^n \mu_{ij}(P_{ij}), \quad (5)$$

$$i = 1, 2, \dots, n; j = 1, 2, \dots, m,$$

where \mathcal{D}_j is the economic effect following the development of a network of inter-connected measures for the purpose of bringing a water body to a normative state, according to contamination indicator j , millions of rubles per year; n is the number of sites at which water protection measures are being implemented; m is the number of contaminating substances that are being studied; ind._{ij} , μ_{ij} are the adduced costs for the i -site for the j -contaminant, according to individual checks for sources of water contamination, and the development of a system of inter-connected measures, millions of rubles per year; P_{ij} is the reduction level of contaminants at the i -site, j -contaminant in percent, determined by the expression:

$$P_{ij} = \frac{u_{ij}^H - u_{ij}^{\text{OCT}}}{u_{ij}^H} \cdot 100 \quad \text{at:} \quad p_{ij}^{\min} \leq P_{ij} \leq p_{ij}^{\max},$$

where u_{ij}^H , u_{ij}^{OCT} are the initial and residual concentration of j -type contaminating substance (prior to runoff into the water body) for the i -site [Note: Cyrillic letters "H" and "OCT" above formula indicate initial and residual concentrations, respectively]; p_{ij}^{\max} - the minimal acceptable and maximum possible degree of contamination reduction of j -contaminant at the i -site, respectively.

Limitations of contaminating substances may be defined according to:

- extent of contaminants in the runoff into the water body:

$$\sum_{i=1}^n u_{ij}^{\text{OCT}} g_{ij} \leq W_j^{\text{don}}, \quad (6)$$

- based on observations of runoff conditions for the contaminants in the gaging section of a water body:

$$u_j^2(P_{1j}, P_{2j}, \dots, P_{nj}, B) \leq u_j^{rdon}; \quad (7)$$

- based on observations for contaminant runoff in each gaging section where runoff is contaminated:

$$u_{ij}^2(P_{ij}, B) \leq u_{jj}^{2don}; \quad (8)$$

where: g_{ij} is the runoff flow at i-site containing j-contaminant; W_j^{don} - the allowable amount of contaminants in the runoff into the water body [Note: Cyrillic "don" is abbreviation for allowable]; u_j^2 , u_j^{2don} are the calculated and allowable concentrations of j-contaminant in the gaging section of a water body, respectively; β are the parameters of the water body that are necessary to construct a water quality transformation model.

There has been extensive experience in solving the problem that has been formulated (equation 5). Data and software for various calculation needs have been developed. In particular, solution of equation 5 defines the maximum allowable runoff [MAR] for contaminating substances.

An industrial enterprise that has been given a MAR restriction may achieve the economic effect, according to the water protection regulation, by reducing the cost of purification (without increasing the volume of contaminant in runoff), increasing the profitability of utilizing beneficial substances, and utilizing the payment factor for discharge of water effluent in instances where payment has been established and where size depends on purification effectiveness. The dimensions of such an effect may be determined according to the expression:

$$\mathcal{O}_{npj} = S_{\delta_j} - \min. [\mu_j(P_j) + C_{c\delta_j} - C_{ymj}], \quad (9)$$

where: \mathcal{O}_{npj} is the economic effect derived by a company as a result of rationalizing water-protection actions to reduce the j-contaminant, S_{δ_j} is the principal outlays for protecting water against the j-contaminant, μ_j is the adduced costs for reducing j-contaminant runoff; $C_{c\delta_j}$ is outlays for discharge of j-contaminant; and C_{ymj} is income from utilizing the j-contaminant.

A well-thought-out combination of MAR and payments for discharge of effluents may interest a company financially to improve the results of water protection activities.

Thus, when water protection programs are being developed, the economic effect may be achieved through establishment of a water quality level for a site, or part of it, thorough the development of a system of water protection measures that assure that the desired wate quality is achieved, and also through determination of the effectiveness for rationalizing water protection

facilities. Thus, if in the first instance, the economical effectiveness indicators are only one of the factors for the decision-making process, then in the second and third instances, the economic calculations can serve as the basis for implementation of water protection measures. Taking into account the economic factors, along with social and ecologic factors, when establishing water protection parameters makes it possible to heighten the effectiveness of water quality management.

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INTEGRATED SYSTEM OF STATE CONTROL FOR WATER USE AND
CONSERVATION BASED ON THE EXAMPLE OF THE
AZOV-BLACK SEA DIRECTORATE

by

L.P. Yarmak¹

ABSTRACT

The Principles of Water Legislation in the USSR are discussed. These Principles establish that all water bodies are subject to protection from any pollution, contamination, or depletion that could be harmful to the health of the population. Specific information is provided concerning water pollution monitoring and control activities in the Azov-Black Sea Basin.

THE INTEGRATED SYSTEM

The state system of water conservation includes legal, organizational, technical, and economic activities. Water use regulation in the USSR is based on the Principles of Water Legislation of the USSR and the Union Republics (December 1970), which took effect on September 1, 1971, and on other acts passed in agreement with them.

The state water use and conservation directorate is composed of the Councils of Ministers of the USSR, of the union republics, the autonomous republics, the executive committees of the local Councils of Deputies, and specially empowered organs, such as the Ministry of Melioration and Water Management of the USSR, similarly named ministries and other Union-Republic organs of melioration and water management of the union republics, basin directorates and inspectorates named by them, as well as other local organs of the system "MINVODKHOZ" of the USSR.

The legal basis of water conservation in the USSR is a statute of the Constitution to the effect that all natural resources including water, are the exclusive property of the state and are for its exclusive use. The statute also forbids any acts that directly or indirectly infringe upon the state's right to natural resources, including water.

¹Azov-Black Sea Basin Directorate, Inspector of Use and Preservation of Water, Krasnodar USSR.

All waters of the USSR constitute the common state water resources. The common state water resources include rivers, reservoirs, lakes, other surface bodies of water, as well as the waters of canals and ponds, subsurface waters and glaciers, internal seas and other internal sea waters of the USSR, and territorial waters (the territorial sea) of the USSR.

Legal water conservation in the USSR includes preserving the state's exclusive water rights and establishing the legal responsibility of water users to use water rationally and protect it from pollution, contamination and depletion.

The Principles of Water Legislation in the USSR and the Union Republics establishes that all water (water bodies) is subject to protection from any pollution, contamination, and depletion that could be harmful to the health of the population. This applies as well to any acts that could cause a reduction of fish stocks, worsen the condition of the water supply, or have other unfavorable manifestations as a result of changes in the physical, chemical, and biological properties of the waters, lowering their natural purification ability, or disturbing the hydrological and hydrogeological regime of the waters. Such protection is provided not only for water flowing into the economic cycle, but also for unused waters.

The Principles of Water Legislation prohibit discharge of industrial, domestic, and other types of water and refuse into water bodies. Use of water bodies for discharge of wastewater is only permitted subject to all requirements and rules reviewed by the legislature of the USSR and its republics. Discharge of wastewater into water bodies can occur only with permission from the water use and conservation regulatory agencies, after their agreement with the agencies of state sanitary supervision and conservation of fish resources and with other interested agencies.

Water users, utilizing bodies of water for industrial purposes, are required to take measures for the reduction and elimination of emissions of wastewater by means of state-of-the-art production technology.

The Principles forbid initiating operations of facilities affecting local water quality that are not equipped with systems to prevent pollution and contamination. This must be coordinated with special agencies, the executives of local Soviets of Deputies of workers, and other interested agencies.

According to water use and conservation regulations, geological survey organizations are required to inform the agencies that monitor water use and conservation immediately upon introducing exploratory efforts and to take measures for the conservation of subsurface waters. Self-pumping wells must be equipped with regulators and are subject to temporary or permanent shut-downs.

The Principles provide for the payment of special water use fees according to a fee schedule established by the Soviet of Ministers of the USSR.

The Principles also establish criminal or administrative responsibility (in accordance with legislation of the USSR and union republics) for pollution

and contamination of waters by public utilities and other facilities lacking treatment equipment to prevent pollution and contamination of the waters or their harmful effects. Organizations and citizens may be required to provide compensation for damages resulting from violation of water legislation. Guilty officials in such cases must bear material responsibility for their acts. Insofar as the Principles are the fundamental legislative act, all other standard setting acts are viable only so far as they do not contradict the Principles. The Principles of Water Legislation of the USSR and the union republics are the basic document for the development of all water codes by all republics in the union.

The Directorate of Water Quality in the USSR exists in accordance with specially developed rules--"Rules for preventing surface water pollution by wastewater" and "Rules for the prevention of coastal water pollution." These rules establish the main requirements of water quality for two uses--for water supplies for cities and population centers and for fisheries.

Water quality in bodies of waters is evaluated using physical-chemical, biological, and microbiological indicators. The analysis of these establishes compliance or noncompliance of a tested body of water as to water use requirements according to functioning legislative acts. Criteria for evaluating allowable polluting substance loads for water sources are the maximum allowable concentration (MAC) of harmful substances in bodies of water, as well as their general sanitary characteristics. Requirements applying to water quality for rivers, lakes, and seas are developed in view of the MAC for water supply sources located near population centers and also for bodies of water significant as fisheries. In the Soviet Union, there is a single rule for wastewater discharge into bodies of water for rivers, for internal reservoirs, and for seashores. These rules state the MAC for a large number of harmful substances (over 500) as well as the calculated hydrological conditions for water quality evaluation.

To provide for the needs of the population, the economy, and the preservation or establishment of water quality and quantity in the USSR according to the requirements of water legislation, a general plan of integrated use and conservation of water resources of the USSR was developed. Also developed were plans for integrated use and conservation of water resources by basins (for basins of rivers and other bodies of water) and by territories (for republics, areas, regions).

The general plan will serve as the basis for water management for planning development and distribution of industry of the USSR. The plan is developed in relation to its interaction with the plan for industry and is the interdepartmental document on which the distribution of water resources is based. It also establishes the norms for maximum allowable discharge (MAD) of wastewater pollutants into bodies of water in a given water management region.

The integrated plan outlines measures for: (1) the management of rational and economic water use based on improved production technology application of low water and no water processes; (2) limiting irreversible water losses in irrigation and water supply systems; (3) maximum possible use of local water

resources for water control; (4) interbasin redistribution of river flows; (5) limiting the discharge volume of untreated wastewater; and (6) the prevention of flooding and submerging of cities, populated centers, agricultural lands, and other areas.

Integrated plans are being developed for no less than 15 years (by 5-year plans, with more emphasis on the first 5-year plan) according to river basins as per the water management regionalization of the USSR. MINVODKHOZ of the USSR provides for all integrated plans of national significance, determines the managerial developers, and confirms the technical plan for development.

The technical plan for development should include: (1) indicators of basic directions of economic and social development of the USSR for the next 5-year plan and for the long term for the given project as presented to the directing agencies, (2) the conception of development and distribution of industry of the USSR, (3) the options for development and distribution of production, and (4) the management of technical policy. All of these activities are to be resolved by the Central Committee (CC) of the Communist Party of the Soviet Union (CPSU) and the Council of Ministers of the USSR.

Under the development of the general plan for integrated use and conservation of water resources of the USSR and other plans of national significance, the ministries and agencies of the USSR, based on their branch plans, present data on production and distribution of water use and water transfer to MINVODKHOZ according to specific categories of wastewater and discharge of pollutants into bodies of water and to the type and volume of discharge into territories of basins.

Water management activity of water use facilities is regulated by permits of special water use given to basin directorates according to the requirements of water legislation and confirmed by the plans for integrated water use and conservation. These permits establish the limits of taking of water from natural sources and norms for maximum allowable discharge of pollutants with wastewater.

In the Azov-Black Sea Basin Directorate Zone, there are more than 2000 special water use facilities.

Besides normalizing water use conditions and organizing observation and information collection, the factual conditions of use and quality of natural surface waters are also the function of the basin directorate. For analysis of water management conditions, information about actual water expenditure in the Kuban River Basin is collected and systematized as are the quality of water at permanent observation points and the quality and quantity of wastewater by the water-use facilities.

For this, the basin directorate establishes systematic laboratory monitoring of wastewater composition in industrial and agricultural facilities using territorial hydrochemical laboratories. They also monitor the effectiveness of purifying facilities and stations, and the activity of departmental

laboratories for research of wastewaters in industrial enterprises. Hydrochemical observation is carried out at 600 points set up on the water bodies near the points of use. All complexes of treatment facilities are registered and are the responsibility of the basic hydrochemical laboratories. According to plan, the departmental laboratories (there are approximately 360 of them in the zone of activity) must submit written analysis of the treatment facilities' work. The volume of analytic work for each departmental laboratory is set in relation to the quantity of wastewater and the degree of its pollution.

By analytic groups, the basin directorate annually takes more than 3000 samples of waste and natural waters, these samples contain up to 80 water quality indicators, on which more than 50,000 determinations are made, including determinations for more than 60 specific pollutants (metals, pesticides, petroleum products, furfural, methanol, formaldehyde, cyanides, phenols, and others.)

Hydrochemical laboratories run these tests utilizing contemporary methodology, using such instruments as spectrophotocolorimeters, spectrophotometers, polarographs, and gas chromatographs.

The collection of initial information on water source quality is carried out with varying frequency depending upon the purpose and importance of the source--hydrochemical indicators are determined every 24 hours, every 10 days, monthly, or by season. Because of this, it is also necessary to determine the indicators of water composition such as suspended particles, color, odor, temperature, pH, mineral composition, oxygen content, biochemical requirements in oxygen, electroconductivity, as well as specific pollutants characteristic for the given type of production. A full analysis of the background area water quality for water sources and rivers that are practically free of economic activity or production wastewaters is done every 3 months and more often for polluted areas, depending upon the work regime of the polluting sources and the significance of the water source to the local economy.

A system of state assessment for water use has been developed in order to evaluate the status of water resources use. In accordance with this, every enterprise annually submits a special form with a complete account including data on the volume of water taken, how the water was used, and of the water quality of the resulting wastewater.

These data are systematized and computer-processed according to branches of industry, to river basins, and to regions. The results of the generalization are used to determine the direction of water management development, comparing it with the basic proposals of the plans for integrated water use and conservation, the status of the area, the disturbances of special water use, etc.

Based on the analysis of all information about water management and water conservation activity of every water use facility so as to determine its compliance with norms established by the basin directorate, a decision is taken about the necessity of taking further measures for the improvement of water use and the quality of discharged wastewater.

Based on the orders of the basin directorate, the water using facility develops a plan of organizational and technical measures including the introduction of more progressive technical and technological advances in the area of rational water use and conservation in order to meet the established norms. After agreement with the basin directorate, these plans are introduced into the state economic development plan and are provided with the necessary capital.

To provide the economic stimulus for resolving the issues of rational water use and prevention of water pollution in the USSR, provisions for economic sanctions have been made.

Thus, an industrial enterprise pays for the water it uses from the water management system. In a case where the established use limits are exceeded, the payment is increased by a factor of five. For discharging pollutants with wastewater in excess of the allowable norms, the enterprise is charged with compensation for damages from pollution of water sources. Thus, for a one-time discharge of 1 ton of pollutants over the allowable norm, the fine varies from 8 to 200,000 rubles; for a steady discharge, from 2 to 72,000 rubles. In a case where the discharge of pollutants may lead to serious consequences, or in a case of systematic non-use of water conservation measures, the enterprise may be shut down.

Provision also is made for criminal and administrative responsibility for specific officials found to be in violation of water legislation. To provide timely implementation of water conservation measures in various significant regions, the USSR is issuing a legislative decree, establishing concrete assignments to ministries and managements to construct facilities for water recycling systems.

Thus, in 1976, the CK of the CPSU and the Union of Ministers of the USSR issued decree #42 "Regarding the Measures for the Prevention of Pollution of the Basins of the Black and Azov Seas. In order to effect the decree, 182 purification complexes with a total capacity of 936,000 mz/day were constructed and put into operation in practically every city and town of the Krasnodar and Stavropol regions. In addition, for rational water resource use, 49 recycling systems with a total capacity of 700,900 mz/day were put into operation. As a result of this, discharge of polluted wastewater in the Azov-Black Sea basin has been practically eliminated, and the saving of fresh water reached nearly 7.8 billion mz. The quality of the shoreline of the Azov and Black Seas has improved in the Sochi, Adler, Bzugu, Anapa, Gelendzhik, Eiskares, in the rivers of the Adagum in the area of Krymsk, and of the Kuban River in the area of Armavira and others.

The preservation of small rivers that flow, as a rule, in areas of intensive agricultural productivity, from depletion and pollution presents a particular problem.

In the USSR, a special decree was issued, "On the Strengthening of the Preservation of Small Rivers from Pollution, Contamination, and Depletion and on the Rational Use of their Water Resources." This decree acknowledged the usefulness of establishing shorelines and water conservation zones along the

shores of all small rivers, ravines, and creeks. Conditions were confirmed for these shorelines whereby a special regime was established in order to prevent pollution, contamination, depletion, and buildup of sludge in the water bodies.

To this end, the shorelines are planted with long-living grasses. Along the shores, forest belts are planted. Facilities with the potential for negative effects on the water bodies are removed. Work is underway to clear the rivers of sludge layers and brushwood.

The system of state control for the prevention of pollution of the seas has some specific aspects, the main ones being the regular aerial visual and instrumental observation of monitored zones. This system allows for providing effective control of the condition of the sea waters in order to discover practically all incidents of pollution in a timely manner and stop their sources, to take energetic measures to liquidate the pollution, and also to receive and register initial data and evidence for the application of sanctions.

Systematic aerial monitoring using aerial photography was instituted to detect and register petroleum pollution. The introduction of severe sanctions against guilty parties provides for significant reductions in total discharge of petroleum products into the territorial waters and waters of the economic zones of the USSR.

Thus, in 1981, 55 cases of pollution, discharging almost 38 tons and accounting for 60 percent of all discharges of petroleum products were accounted for. But in 1985, 23 cases, discharging a total of only 5 tons, and 95 per cent of all petroleum products was accounted for.

In the next two years, the USSR will establish measures for improving the system of managing the use of natural resources and protecting them from pollution. Cooperation with other countries is of no small importance in dealing with these tasks insofar as in recent years, the problem of protecting the environment has taken on an international character.

MATHEMATICAL MODELING OF RUNOFF OF SUBSTANCES
FROM AGRICULTURAL WATERSHEDS INTO BODIES OF WATER

by

L. M. Bondarenko, V. Z. Kolpar, and Yu. M. Plis¹

ABSTRACT

An approach to the creation of a mathematical model of the runoff of nutrients and pesticides from an agricultural watershed is presented. The model takes into account the inhomogeneity of the underlying surface, the application of chemicals in fields, the spatial inhomogeneity of precipitation, and other important simulation factors.

MODELING AGRICULTURAL WATERSHEDS

At the present time, the problem of contamination and silting of bodies of water by surface runoff from agricultural areas has assumed great urgency. Agriculture is suffering major losses as a result of the washout of fertile topsoil with the fertilizers and toxic chemicals introduced into it.

Efficient planning of antierosion measures during the establishment of water conservation complexes of small river basins should be based on estimates of soil erosion and evacuation of nutrient elements and pesticides with the surface runoff, allowing for the nonuniformity of distribution of the intensity of nonpoint sources of contamination over the agricultural watershed. One of the effective methods of estimating the evacuation of substances from a watershed by surface runoff is mathematical modeling, the use of which makes it possible to consider a large number of natural and anthropogenic factors and to ensure the formulation of important practical recommendations in relatively short periods of time.

This paper discusses an approach to the creation of a mathematical model of formation of the surface runoff of storm waters and evacuation of substances from an agricultural watershed with a dissected topography. Essentially, this approach consists in the following. The data of a topographic map of the watershed are used to construct a geometric model on the basis of which the routes of the runoff to a given contour, for example, the left bank

¹All-Union Research Institute for Water Protection, Kharkov USSR

of a river or the edge of lake water, are determined. Then the storm water paths obtained are used to calculate the runoff hydrograph and the concentration of suspended matter, which in turn constitute the starting data for calculating the evacuation of chemical substances into a body of water.

Also considered is the possible variety of runoff routes over the planes comprising the geometrical model of the watershed, and the movement of the flow over the thalweg system if such exists. This approach also makes it possible to take into account a variety of important factors, including the inhomogeneity of the underlying surface, application of fertilizers and pesticides in fields, spatial inhomogeneity of precipitation, and so on.

A general diagram of the software used for the problem is shown in Figure 1. Block 1 is the steering program; blocks 2, 3, and 4 implement the computational algorithms for constructing a geometric relief model, finding the runoff routes of storm waters along the planes of the relief model, and finally, considering the relationships of water flows moving along different runoff paths. These blocks have the most complex software. They are standardized, therefore, and the user need not change them. Blocks 5, 6, 7, and 8, as follows from their names, implement the computational algorithms for calculating the runoff hydrograph, concentration of suspended matter in the flow, and evacuation of nutrient elements and pesticides from the slope. As the mechanism of formation of storm water runoff and evacuation of substances from the slope is studied, these blocks can be improved and introduced into the software without changing Blocks 2, 3, and 4.

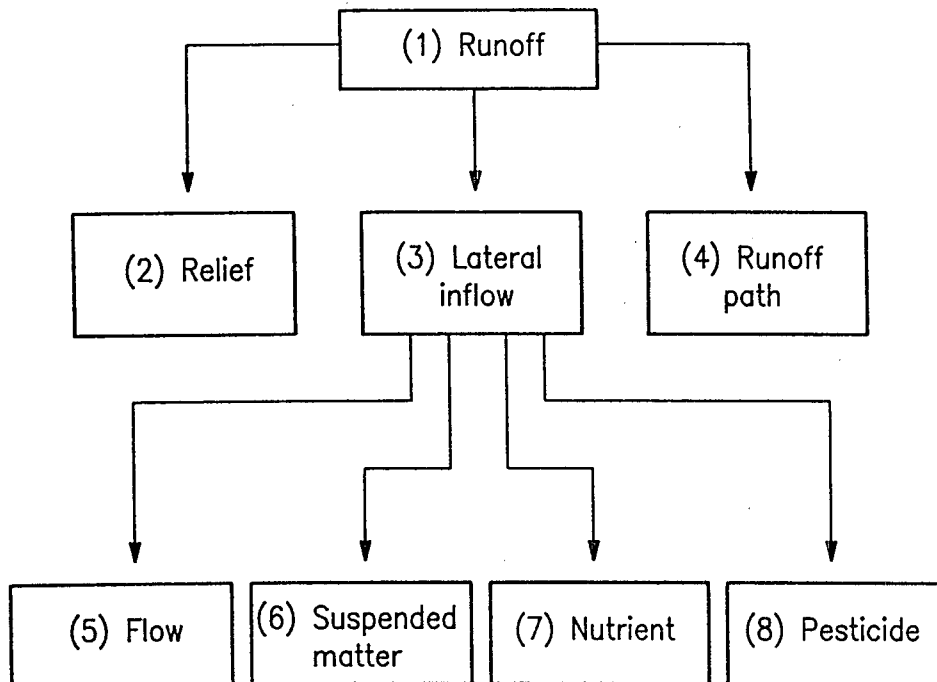


Figure 1. Module scheme of software.

Evacuation of substances from the watershed is accomplished by the liquid and solid components of the storm runoff. In turn, other things being equal, the discharge of liquid runoff predetermines the solid runoff, i.e., the products of soil erosion. Therefore, the most significant part of the problem is the accuracy and reliability of the modeling of the liquid component of the runoff. There are various approaches to the calculation of the runoff volume, runoff hydrograph, and maximum discharge (Kuchment et al. 1983, Gudzon 1974). The accuracy of the estimate depends substantially on the consideration of the variety of factors involved in the formation of the runoff and on the reliability of the initial data. In our view, the most acceptable method of solving practical problems is the use of unidimensional differential equations describing the motion of a water flow down a slope with allowance made for the roughness of the underlying surface, infiltration of water into the soil, and changing rate of precipitation.

The mathematical model of formation of the liquid phase of surface runoff is based on the unidimensional continuity equation (Moskovkin et al. 1983).

$$\frac{\partial \omega}{\partial t} + \frac{\partial q}{\partial x} = (R-I) \frac{B}{6 \cdot 10^4} + q_0 \quad (1)$$

where: ω is the cross-sectional area of the flow, m^2

q is the water discharge, m^3/sec

R, I are, respectively, the rates of rain precipitation and infiltration, mm/min

B is the average slope width, m

t is the time, sec

x is the coordinate measured downslope, m

q_0 is the lateral inflow per unit length of slope, m^2/sec

Integrating Eq. 1 over the length of the slope X from 0 to l and representing the water discharge at the exit from the slope by q_f with the aid of the Chezy and Manning formulas,

$$q_f = \frac{1}{\eta} \omega^{\frac{5}{3}} B^{-\frac{2}{3}} \quad (2)$$

we obtain the following nonlinear ordinary differential equation in $\bar{\omega}$

$$\frac{d\bar{\omega}}{dt} = \frac{q_s}{\ell} - \frac{R-1}{6 \cdot 10^4} \frac{\bar{\omega}}{\bar{B}} - \frac{i}{\eta \ell} \bar{\omega}^{\frac{5}{3}} \bar{B}^{-\frac{2}{3}} \quad (3)$$

where: q_s is the water discharge at the entrance to the slope, m^3

i is the average slope angle

η is the roughness coefficient

ℓ is the length of the slope

$\bar{\omega}$ and \bar{B} are, respectively, the cross-sectional area and flow width averaged over length ℓ

$$q_s = q_{x=0} + \int_0^{\ell} q_{\delta} \cdot dx$$

To describe the filtration rate I , use was made of the Holton-Overton equations, given by Beasley and Huggins (1982).

$$I = I_s + I_m (P_v / T_p)^P \quad (4)$$

where: I_s is the steady rate of infiltration (filtration coefficients),
mm/min

I_m is the maximum rate of inhibition, mm/min

T_p is the total volume of pairs in the confines of the control zone considered, mm

$P_v = T_p - W$ is the layer of water that can accumulate in the control zone before its saturation, mm

W is the flowing layer of water accumulated in the control zone during precipitation, mm

P is a coefficient relating the rate of decrease in infiltration rate to the increase in the moisture content of the soil

In determining P_v , use may be made of the equation

$$\frac{dP_v}{dt} = D_z - I \quad (5)$$

$$D_z = \begin{cases} 0, & \text{for } P_v > G \\ I_m(1 - P_v/G)^3, & \text{for } P_v \leq G \end{cases} \quad (6)$$

where: D_z is the rate of drainage of water from the control zone, mm/min

$G = T_p - W_i$ is the gravitational moisture capacity of the soil within the confines of the control zone, mm

W_i is the initial moisture capacity in the control zone, mm

The calculation of the evacuation of soil particles from the slope is based on the equation of sediment balance in the flow in the form (Moskovkin et al. 1983)

$$\frac{\partial}{\partial t} (c\omega) + \frac{\partial}{\partial x} (cq) = -K_s(C - C_{tr})\omega + C\delta q\delta \quad (7)$$

where: C , C_δ are, respectively, the concentrations of suspended matter in the flow and intermediate inflow, g/m³

K_s is the sedimentation coefficient, L/sec

C_{tr} is the concentration of suspended matter corresponding to the transporting capacity of the flow, g/m³

Integrating Eq. 7 over the length of the slope x from 0 to l and expressing the average concentration of suspended matter in the flow in terms of the concentration at the entrance C_0 and exit C_L from the slope by the relation $\bar{C} = (C_0 + C_L)/2$, we obtain the following linear ordinary differential equation in \bar{C} :

(8)

$$\frac{d\bar{C}}{dt} + \bar{C} \left(\frac{q_s + q_f}{\bar{\omega}} + \frac{\bar{q}_\delta}{\bar{\omega}} + \bar{K}_s + \frac{R-I}{6 \cdot 10^4} \cdot \frac{\bar{B}}{\bar{\omega}} \right) = \frac{q_s + q_f}{\bar{\omega}} C_0 + \frac{q_s}{\bar{\omega}} \bar{C}_\delta + \bar{K}_s \bar{C}_{tr}$$

where: \bar{K}_s , \bar{C}_{tr} , \bar{C}_δ , \bar{q}_δ are, respectively, the quantities K_s , C_{tr} , C_δ , and q_δ averaged over the length of the slope.

\bar{K}_s is determined from the formula

$$\bar{K}_s = \frac{u}{\bar{h}} \left(1 + \frac{M \cdot C_{Ch} u}{4gv} \right) \quad (9)$$

where: u is the particle fall velocity, m/sec

g is the gravitational acceleration, m/sec

\bar{h} is the average depth of the flow, m

$$M = \begin{cases} 0.7 \cdot C_{Ch} + 6, & \text{for } C_{Ch} < 60 \\ 48, & \text{for } C_{Ch} > 60 \end{cases}$$

$C_{Ch} = \frac{1}{n} h^{-1/6}$ is the Chezy coefficient, $m^{1/2}/\text{sec}$

$v = \frac{1}{n} h^{-2/3} \sqrt{i}$ is the speed of water down the slope, m/sec

The concentration \bar{C}_{tr} is calculated from the formula

$$\bar{C}_{tr} = \frac{v^2}{\bar{h}} E \quad (10)$$

where E, in accordance with Zubkova (1977) may be calculated from the formula
 $E = 9.85 C_{Ch}^{1.75}$.

Thus to calculate the liquid and solid phases of surface runoff, we arrive at a closed system of ordinary differential Equations 3, 5, and 8, the solution of which is carried out numerically by means of the Runge-Kutta method. The characteristics of the liquid and solid runoffs obtained by calculation may be used to estimate the magnitude of the evacuation of agricultural chemicals (fertilizers and pesticides from farm lands as a result of washout by surface runoff).

The evacuation of agricultural chemicals by surface runoff is determined by the results of the interaction of the water flowing down the incline of the watershed with the top (active) layer of the soil and with the chemicals present therein. The depth of the active layer (h_a) is determined by the thickness of the saturation zones, where a moisture content equal to the total moisture capacity is established in the course of precipitation. According to Rode (1965), the saturation zone is about 10 mm thick.

At the present time, there is no definitive theory providing a reliable estimate of the evacuation of chemicals from a watershed having a complex relief structure and a nonuniform soil fertility. At the same time, for practical purposes, an attempt has been made, on the basis of an analysis of factors affecting the rate of evacuation of agricultural chemicals from farm lands, to establish the relationships permitting quantitative estimates of the magnitude of evacuation of nutrient elements and pesticides with the solid and liquid phases of runoff. These relationships relate the concentration of the indicated substances to their content in the arable layer and to the physical parameters and characteristics of hydrological conditions in the watershed.

The evacuation of dissolved agricultural chemicals can be determined from the following formulas.

$$D_s = 10^{-3} \frac{m}{P \cdot h_{ar}} A \frac{1 - e^{-D}}{D_s} \cdot h_k \quad (11)$$

$$A = \begin{cases} 0.717 \left(\frac{3}{4} \right) \frac{Q}{Ph_a \left(\frac{2}{3} - \frac{W_a}{\Pi} \right)}, & \text{for } W_a < \frac{\Pi}{\zeta} \\ 0.717 \left(\frac{3}{2} \frac{W}{P} \right) \frac{Q}{Ph_a \left(\frac{2}{3} - \frac{W_a}{\Gamma} \right)}, & \text{for } \frac{P}{\zeta} \leq W_a < \frac{2}{3} \Pi \\ 0.717, & \text{for } \frac{2}{3} P \leq W_a < \\ -1 & \text{for } W_a = \Pi \end{cases} \quad (12)$$

$$D = \frac{H}{h h_a} - \frac{Q}{h h_a} + \frac{W_a}{h} - 1,274 \quad (13)$$

where: D_s is the evacuation of dissolved agricultural chemicals by the surface runoff, kg/ha

m is the initial (before the start of rain) content of dissolved agricultural chemicals in the arable layer of the soil, kg/ha

h_{ar} is the depth of the arable layer of the soil (in the calculation of the evacuation of nutrient elements) or the depth of the soil layer in which most of the pesticide is localized (in the calculation of the evacuation of pesticides), m

P is the porosity of the arable layer, fraction of unity

h_x is the layer of surface runoff, mm

H is the layer of rain precipitation, mm

W_a is the initial moisture content of the soil in the active layer, fraction of unity

W_c is the moisture content of the soil in the control zone before its humidification, fraction of unity

Q is the volume of water expended in changing the moisture content in the control zone before the appearance of surface runoff, mm

$$Q = Ph_c \left(-\frac{1}{3} - \frac{W_c}{2P} \right),$$

h_c is the depth of the control zone, mm.

The quantity h_c is assumed equal to the depth of soaking of the soil before the appearance of surface runoff, i.e., when the rate of imbibition in the active layer of the soil ($h_a = 10$ mm) becomes numerically equal to the filtration coefficient ($I = I_c$). According to Rode's scheme of the infiltration process (1965), the depth of soaking varies between 30 cm and 75 cm.

The evacuation of agricultural chemicals with the solid phase of surface runoff may be estimated from the following equations.

for nutrients

$$D_b = \frac{m_s^b \cdot M}{10^4 \gamma h_{ar}}, \quad (14)$$

for pesticides

$$D^b = \frac{m_s^p \cdot M}{10^4 \gamma h_{ar}^2}, \quad \left(2h_{ar} - \frac{M}{10^4 \gamma} \right), \quad (15)$$

where: D_b and D^b are, respectively, the evacuation of nutrient elements and pesticides with the solid runoff, kg/ha

m_s^b and m_s^p are, respectively, the content in the arable layer of nutrient elements in exchange-absorbed form and of pesticides in sorbed form, kg/ha

M is the rate of solid runoff, t/ha

γ is the volume weight of the soil of the arable layer, g/cm³.

Let us give a more detailed description of the software used in solving the stated problem. We note that the literature gives a description of the algorithmization of the solution by computer of the problem of runoff formation and soil erosion in a watershed, for example, the ANSWERS program

(Beasley and Huggins 1982). When calculations are made according to this program, the direction of water flow down the slopes of the schematized watershed is specified by the user. This visual specification of the direction of the water runoff down a slope oriented arbitrarily in space does not preclude the occurrence of subjective errors capable of resulting in an appreciable redistribution of runoff over a watershed with a dissected topography.

In this paper, in order to determine the formation and movement of a storm runoff over a watershed with a dissected topography, a programmed realization of the solution of this problem is proposed that eliminates the user's participation in the determination of the runoff path.

Let us consider a watershed G , shown on the map, enclosed by a rectangular contour Γ (Fig. 2). We fix the surface of the specified watershed in a rectangular coordinate system $OXYZ$, superimpose the horizontal plane XOY onto the map reference plane, and direct the Z axis vertically upward through the left upper top of contour Γ . We draw vertical planes in this coordinate system parallel to the XOZ and YOZ planes, respectively, with step ΔX along the X axis and step ΔY along the Y axis. We thus obtain a grid region G'

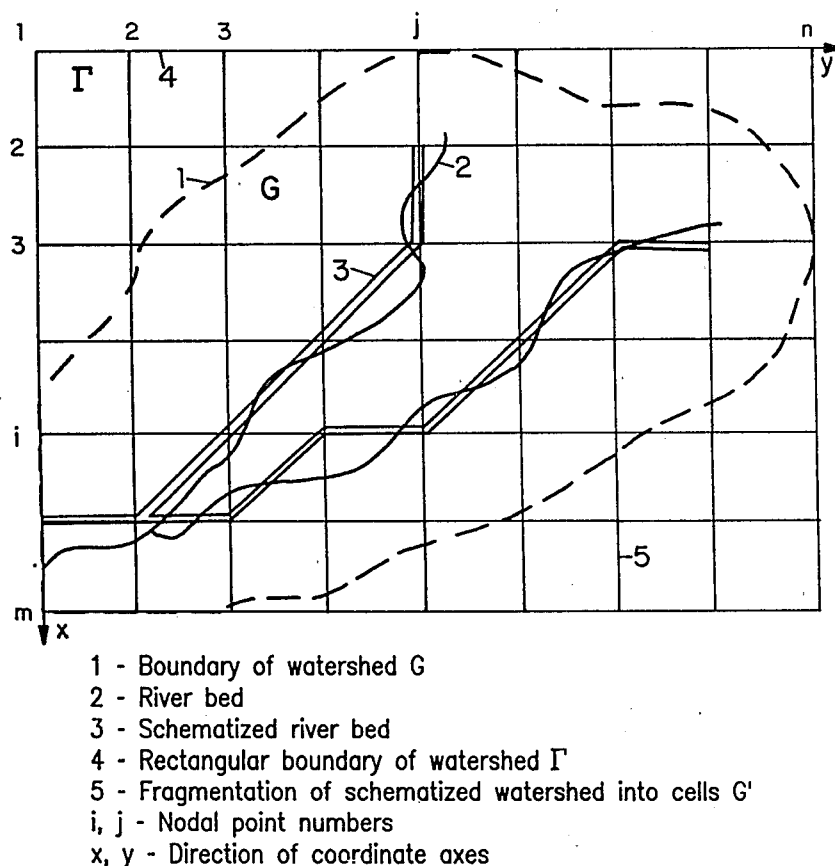


Figure 2. Schematization of a watershed and river bed.

consisting of nodes formed by the intersecting straight lines in the XOY plane. From the data of the topographical map, using the method of least squares, we calculate the heights of the relief at the nodes of grid region G', the totality of which determines the geometric relief model. Naturally, the smaller ΔX and ΔY are, the more accurately the geometric model will correspond to the actual relief. The module implementing the solution of this problem is called the RELIEF module.

The RUNOFF PATH module determines the path of a water flow for a contour L specified in advance. In general, this contour is a broken line consisting of sectors connecting the two adjacent nodes of grid region G'. For each of the sectors of the contour, the RUNOFF PATH module plots the runoff-forming chains of triangular planes and thereby defines the individual watersheds, the runoff from which reaches contour L in a distributed manner, i.e., uniformly along the length of a sector. The nodes of the contour are also analyzed. If the runoff from a thalweg enters the node of a contour, a runoff-forming chain is formed (which may include a graph of the thalwegs), and in this case, a concentrated discharge to contour L is considered. In the computer representation, this will be an ordered recording of the numbers of the triangles (this recording will be called the runoff-forming chain of triangles RCT), which consists of four types:

$$(a) \emptyset A, \quad (b) BC, \quad (c) D\emptyset, \quad (d) \emptyset l \quad (16)$$

where A, B, C, and D represent the coded number of the triangle.

In Expression 16, the meaning of the symbols is as follows.

- (a) The runoff from triangle A arrives at the triangle located underneath;
- (b) The runoff from B arrives at C (among the elements of the RCT, there must be one more symbol of type EC, $B \neq E$);
- (c) The runoff from D enters either a thalweg or a sector of contour L;
- (d) Indication of the end of RCT in sector L.

The RCT having a runoff into the node formed by two adjacent sectors is similarly constructed. The construction of the RCT considers all possible cases of direction of motion of the flow at the models of the watershed:

- runoff from one triangle to another
- runoff from one triangle to the two adjacent to it
- the triangle has an inflow from the two adjacent to it
- the two adjacent triangles form a thalweg, and the system of such pairs of triangles forms the graph of thalwegs

- two (three) thalwegs have a runoff into one node of contour L
- two (three) thalwegs originate from the same node
- the runoff from a thalweg (graph of a thalweg) reaches a triangle

The system of runoff-forming chains is the initial information in the calculation of runoff hydrographs and concentration of substances in the runoff with the use of the LATERAL INFLOW module. The RUNOFF PATH and LATERAL INFLOW modules realized in the YeS computer system in PL/1 language were set up by the use of the principle of structural programming. The module construction makes it possible, without changing the hierarchic structure of the programs, to replace one module by another. For example, the runoff of water from a slope can be described by the NESHA equation, the kinematic water equation, and hydrodynamic equations. On the basis of each of these equations, one can construct a FLOW submodule that can easily be connected to the LATERAL INFLOW module.

The RELIEF, RUNOFF PATH and LATERAL INFLOW modules are combined by the RUNOFF basic steering program. The RUNOFF program functions as the software for modeling the formation of storm runoff from agricultural watersheds. In combination with two files of initial data, the program employed can be used to consider the following.

- the spatial nonuniformity of the underlying surface
- the space-time variability of sediments above the watershed
- the concentrated (over the ravine grid) and distributed (over the slopes) runoff of storm waters
- estimate of the effectiveness of antierosion measures (which include water conservation measures in the watershed).

As an illustration, we will consider the RCT on contour $L = \Gamma$ of a watershed fragment consisting of four cells (Fig. 3). Figure 3a shows the view of the watershed from above, and the numbers along contour Γ indicate the relief height at the nodes of region G' ; number 101, 102, ... denote the consecutive numbers of the triangles; the dashed line is the dividing line. Figure 3b shows a model of the watershed fragment in perspective geometry. It is evident from Figure 3 that the watershed has thalwegs, triangles with two outflows: 101, 102, 103, and triangle 202 with two inflows. The RCT elements are listed in Table 1.

It follows from Table 1 that the runoff from the watershed arrives in a distributed manner at the sector connecting nodes (1, 1) and (2, 1) and in a concentrated manner down a thalweg into node (2, 1). There is no runoff to the remaining sectors and nodes of contour L.

Let us consider the specification of information and the course of the computational process. Two files of initial data are specified. The first

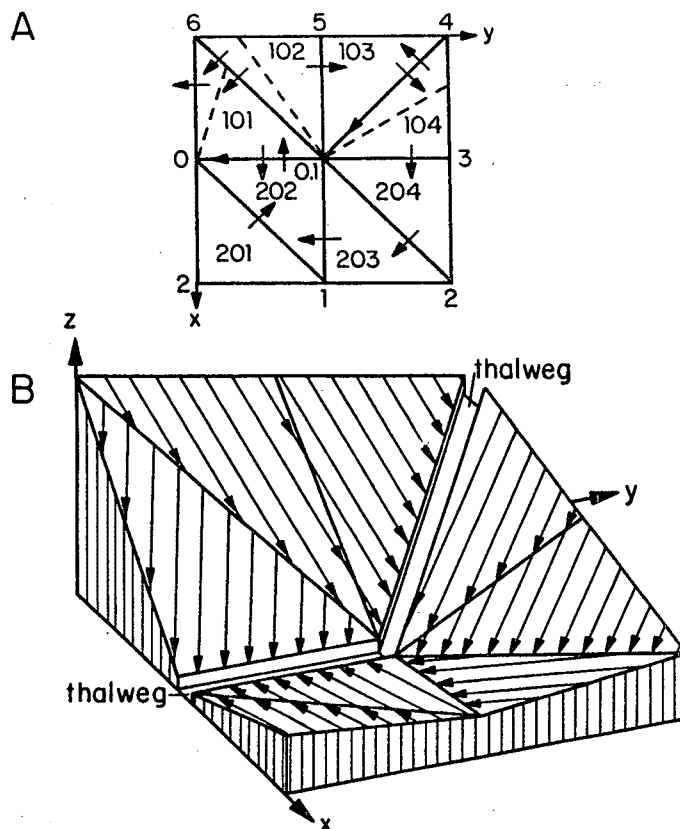


Figure 3. Direction of motion of water flow down the planes and thalwegs of the geometric relief model--A, view of watershed from above; B, perspective geometry of the watershed.

file constitutes a table of surface level marks, which is obtained from data of a topographic map. Steps ΔX , ΔY of grid region G' are established which, as the final result, determine the degree of detail in the description of the watershed relief. The greater the steps ΔX and ΔY , the more generalized the geometric model of the watershed will be. On the other hand, when the values of ΔX and ΔY are taken to be small, there is an increase in the number of cells of the watershed model and hence, in the investment of computer time in the solution of the problem. Therefore, steps ΔX and ΔY should be selected by considering the accuracy of representation of the actual watershed relief by its geometrical model as well as the cost of the computing. The second file also constitutes a matrix whose dimensions are determined by the number of cells covering watershed G . For each such cell, it is necessary to know the "passport," by which is meant a set of parameters: the roughness coefficient, rate of precipitation, filtration coefficient, pesticide content of the soil at the time of precipitation, etc., necessary for the calculation using Equations 3, 5, and 8 and Relations 11 through 15.

As a rule, the execution of practical calculations is preceded by calibration calculations, carried out for the purpose of determining the param-

TABLE 1. Runoff-forming chains of triangles on contour L

No.	RCT elements	No.	RCT elements	No.	RCT elements	No.	RCT elements
1	102	5	1030000	9	2030202	13	1010000
2	1010000	6	1040000	10	2010202	14	1
3	1	7	104	11	2020000		
4	102	8	204	12	102		

ters of the models, primarily, those of the hydrological model. In this case, the file of initial data will contain only the set of parameters for calculations of the runoff hydrograph. During the calculation, the parameters of the model are determined more accurately in order to achieve agreement between the calculated hydrographs (runoff volumes) and the observed values. Then, when necessary, calculations of soil erosion are performed until the observed and calculated masses of the soil introduced into the body of water are similar. Through an expansion of the second file of data, this procedure is repeated for the nutrient elements and pesticides being modeled.

The calculation of liquid and solid runoff by means of Equations 3 and 8 is carried out for all the RCT elements. The calculation of the evacuation of chemical substances from a watershed is performed as follows. One calculates the area of the partial watershed adjacent to the sector or node of contour L, the average content of the substance in the soil of the watershed, the rate of solid runoff, and the layer of liquid runoff. These quantities are substituted into Formulas 11 through 15 and thus is obtained the mass of substances evacuated by storm runoff from partial watersheds.

Such calculations, associated with the use of well known agricultural and hydraulic antierosion methods, make it possible to ensure the establishment of an efficient, cost-effective and efficient set of measures aimed at protecting bodies of water from contamination by surface runoff from farm lands.

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AMMONIA DISTRIBUTION IN AND EXCRETION BY FISHES

by

D.J. Randall¹, R.C. Russo², and R.V. Thurston³

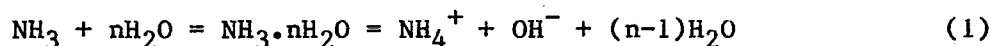
ABSTRACT

Ammonia is widely found in natural water systems in both ionized and un-ionized forms. This paper reviews research into the conditions affecting ammonia concentrations in water and the distribution of the compound in fish tissues. A discussion of ammonia excretion with emphasis on removal across fish gills is included. Elevated environmental ammonia levels will reduce excretion and result in ammonia accumulation in the body of the fish with deleterious consequences.

INTRODUCTION

Ammonia can enter natural water systems from several sources, including industrial wastes, sewage effluents, alternative fuel conversion processes, and agricultural discharges. It is a natural biological degradation product of nitrogenous organic matter.

To understand ammonia distribution in and excretion by fishes, it is important to understand its chemical equilibrium in water. In aqueous solutions ammonia assumes two chemical forms, illustrated by the following equation.



These species are the un-ionized form (NH_3), hydrogen-bonded to at least three ($n \geq 3$) water molecules (Butler 1964), and the ionized form (NH_4^+). Total ammonia is the sum of NH_3 and NH_4^+ , and it is total ammonia that is measured analytically in aqueous solution.

The relative concentrations of ionized and un-ionized ammonia in a given solution are principally a function of the pH, temperature, and ionic strength of that solution. As pH increases, the equilibrium is shifted toward the

¹Department of Zoology, University of British Columbia, Vancouver, BC, Canada;

²Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, GA, USA;

³Fisheries Bioassay Laboratory, Montana State University, Bozeman, MT, USA.

un-ionized species, and the concentration of NH_3 increases while that of NH_4^+ decreases. For example, in aqueous solution a pH increase from 7.0 to 8.0 within the temperature range 0 to 30°C results in a nearly tenfold increase in the concentration of NH_3 (Emerson et al. 1975, Thurston et al. 1979). Temperature increase also favors the NH_3 species, but to a lesser extent; a temperature increase of 5 degrees between 0 and 30°C at pH 7.0 results in an NH_3 concentration increase of 40 to 50% (Emerson et al. 1975). An increase in ionic strength, at low concentrations, favors the NH_4^+ species. In natural waters with low to moderate amounts of dissolved solids (200 to 1000 mg/L), this effect will slightly lower the concentration of NH_3 , and the magnitude of this effect will vary with the composition of the water (Thurston et al. 1979).

Ammonia is a toxic end-product of protein metabolism and, therefore, must be excreted or converted to less toxic compounds, such as urea or glutamine. Ammonia is, however, both a substrate and a product of protein metabolism and in some tissues it may be utilized rather than produced. Elevated concentrations of environmental ammonia will reduce excretion and result in ammonia accumulation within the body of the fish.

AMMONIA DISTRIBUTION

The pK of the ammonia/ammonium reaction is around 9.5, so at the pH of fish tissues nearly all of the ammonia will be as NH_4^+ . Cameron and Heisler (1983) found that ammonia was slightly more soluble in fish plasma than in water, and they also constructed a nomogram to describe the effects of ionic strength and temperature on the pK of the $\text{NH}_3/\text{NH}_4^+$ reaction (see also Kormanik and Cameron 1981, Boutilier et al. 1984).

Ammonia gas (NH_3) diffuses at about the same rate as, but is much more soluble than, CO_2 , so it will rapidly equilibrate between different tissue compartments and be excreted across the gills. As a result, the body concentrations of NH_3 are low. The concentrations of NH_4^+ , however, can be several orders of magnitude higher than those of NH_3 , bringing total ammonia levels into the mMol range. Concentrations of NH_4^+ often reflect the pH of the compartment (Randall and Wright 1987); tissues with a lower pH having higher total ammonia concentrations. In many instances, however, NH_4^+ is distributed according to membrane potential, indicating a considerable membrane permeability to NH_4^+ . For example, Wright et al. (1988b) have shown that the distribution of NH_4^+ in skeletal muscle, heart muscle, and brain of the lemon sole (*Parophrys vetulus*) is related to membrane potential rather than pH, indicating a relatively high NH_4^+ permeability across the barriers between these compartments and blood. Thus, NH_4^+ concentrations are greater than expected from that due to pH. The consequence will be a continual production of H^+ within the cell with the cycling of NH_4^+ into the cells and the diffusion of NH_3 out of the cell.

Wright et al. (1988c) also found that ammonia was in equilibrium across red blood cell membranes and that NH_4^+ was distributed between plasma and red blood cells according to membrane potential. In this case, however, the results need not indicate a high NH_4^+ permeability, as hydrogen ions also are distributed according to membrane potential.

AMMONIA EXCRETION

Most of the ammonia produced by the fish is excreted across the gills, and the amount is variable, depending on the state of the animal, environmental conditions, and the species. Ammonia excretion by the dogfish (Scyliorhinus stellaris) in seawater is unaffected by temperature change, exercise, hyperoxia, hypercapnia, or the infusion of HCl, NaHCO₃, or anything that induces acid-base stress (see Heisler, 1984, for review). Ammonia excretion tripled in sockeye salmon (Oncorhynchus nerka) following daily feeding (Brett and Zala 1975) but remained low and unchanging during 22 days of starvation.

In freshwater fishes, ammonia excretion increases in response to exercise (Sukumaran and Kutty 1977, Holeyton et al. 1983), long-term acid exposure (McDonald and Wood 1981, Ultsch et al. 1981), hypercapnia (Claiborne and Heisler 1984), and NH₄Cl infusion (Hillaby and Randall 1979). In contrast, short-term exposure to acid or alkaline water caused a decrease in ammonia excretion in trout (Wright and Wood 1985). It is not known whether these changes in excretion reflect changes in the rate of ammonia production or in the total ammonia content (NH₃ + NH₄⁺) of the body.

The total ammonia content of fish is likely to be about the equivalent of the ammonia excreted in 2 hours, most of the total ammonia being stored in muscle. Blood levels are around 0.2 to 0.3 mMol, but muscle has concentrations up to 1 mMol. Thus a 1-kg fish contains about 0.5 to 0.7 mMol of total ammonia and has an excretion rate of about 0.3 mMol per hour.

There is an increase in blood ammonia during starvation (Hillaby and Randall 1979, Morii 1979), which is perhaps surprising because at the same time ammonia excretion declines (Brett and Zala 1975). Carbon dioxide excretion is reduced during starvation and this may account for this reduction in ammonia excretion and concomittent elevation in blood ammonia concentration.

Blood ammonia concentrations also increase with increases in temperature (Fauconneau and Luquet 1979) and exposure to air (Gordon 1970), or to increased ammonia concentrations in water (Fromm and Gillette 1968, Guerin-Ancey 1976). This is associated with a rise in urea production in many fishes. Unlike the above studies, Buckley et al. (1979) found no change in total ammonia in the blood when coho salmon (Oncorhynchus kisutch) were exposed to elevated ammonia concentrations in the environment. They did observe a significant rise, however, in plasma sodium indicating some coupling between sodium uptake and ammonia excretion.

The excretion of ammonia is largely a function of the NH₃ gradient across the gills (Hillaby and Randall 1979, Kormanik and Cameron 1981, Cameron and Heisler 1983, Wright and Wood 1985), as is ammonia entry into the fish (Wuhrmann et al. 1947, Wuhrmann and Woker 1948, Fromm and Gillette 1968). The excretion of NH₄⁺ in freshwater fishes is strongly coupled to the movement of other ions. Membranes, including the gills, are not very permeable to cations, and NH₄⁺ is probably transferred across the gill epithelium via carrier-mediated processes. Potassium can be displaced by NH₄⁺ in many membrane processes,

for example in squid giant axon (Binstock and Lecar 1969), and this may be the reason that elevated ammonia concentrations cause convulsions in so many vertebrates.

In fish gills, it is possible that NH_4^+ can substitute for potassium in ouabain sensitive sodium/potassium exchange, and also substitute for protons in amiloride sensitive Na^+/H^+ exchange--the former moving NH_4^+ from blood into the gill epithelium, and the latter exchanging NH_4^+ for sodium on the outer surface of the gill epithelium (Maetz and Garcia-Romeu 1964, Evans 1977, Girard and Payan 1980, Wright and Wood 1985). Either acid conditions or amiloride in the water inhibit sodium influx across the gills, and both these conditions result in a reduction of ammonia excretion (Wright and Wood 1985, Randall and Wright, 1986). In addition, ammonia infusion will stimulate sodium influx, even in salt water fish (Evans 1977).

Cameron and Heisler (1983), however, could account for ammonia excretion in trout, under most conditions, by the diffusion of NH_3 , but in the presence of high external ammonia, $\text{Na}^+/\text{NH}_4^+$ exchange may counterbalance the diffusive uptake of ammonia. Indeed, this would explain the unchanged blood ammonia levels but increased sodium levels in coho salmon exposed to elevated ammonia concentrations (Buckley et al. 1979).

A more detailed understanding of ammonia excretion requires a more detailed analysis of pH gradients across the gills. The amount of CO_2 excreted across the gills usually exceeds that of ammonia. Water flow over the gills is laminar and there are boundary layers next to the epithelial surface. Mucus and dead cells contribute carbonic anhydrase to this boundary layer.

Fish excrete molecular CO_2 rather than HCO_3^- across their gills. The CO_2 entering the boundary layer will be rapidly hydrated to HCO_3^- , and this will acidify the water boundary layer next to the gill surface (Wright, et al. 1986). Ammonia entering the boundary layer will be trapped as NH_4^+ , maintaining the ammonia gradient across the gills. A reduction in CO_2 excretion will reduce the acidity of, and therefore raise ammonia levels in, the boundary layer and hence the blood. An elevation of blood ammonia is seen in starving fish and this is associated with a reduction in CO_2 production.

More recently Wright et al. (1988a) have shown that manipulations that reduce the acidity of the boundary layer have a marked effect on ammonia transfer. Thus, CO_2 and ammonia excretion are coupled in the fish gill as in the kidney, although the nature of the coupling is somewhat different.

Carbon dioxide in the water affects ammonia toxicity; if CO_2 levels are raised, total ammonia toxicity is decreased (Alabaster and Herbert 1954). This is because an increase in CO_2 causes a fall in pH and decreases the proportion of NH_3 in solution. The un-ionized form has a greater toxic effect because ammonia must enter the fish to exert its toxic action, and lipid membranes are much more permeable to ammonia as NH_3 (Wuhrmann et al. 1947, Wuhrmann and Woker 1948, Thurston et al. 1981).

Lloyd and Herbert (1960), however, found that although total ammonia toxicity was reduced at high CO₂ levels, the inverse was true when considering NH₃ alone. More NH₃ is required in low CO₂-high pH water to exert the same toxic effect as is seen in fish in high CO₂-low pH water. The explanation presented by Lloyd and Herbert (1960) for the decreased toxicity of NH₃ in low CO₂ water was that CO₂ excretion across the gills would reduce pH and therefore the concentration of NH₃ in water flowing over the gills. This is consistent with the conclusions of Wright et al. (1988a), with the addition that these effects are occurring in the boundary layer of water next to the gills rather than in the bulk flow.

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EFFECT OF AMMONIUM IONS ON MINERAL EXCHANGE IN
FRESHWATER FISH AND CRUSTACEANS

by

G.A. Vinogradov¹

ABSTRACT

The effects of ammonium salts (NH_4Cl) and $(\text{NH}_4)_2\text{SO}_4$ at different pH values of the medium on the regulation of sodium exchange in the crucian carp are examined. Results indicate disturbances in ion exchange at sublethal concentrations of total and ionized ammonium.

INTRODUCTION

Ammonia, the end product of protein metabolism, has a toxic effect during its accumulation in the fish organism. The percentage dissociation of free ammonia from ammonium salts in aqueous solutions is substantially dependent on the pH and temperature of the water. When the solution pH increases, the equilibrium shifts toward the formation of free ammonia (NH_3). In the range of pH acceptable to aquatic animals, a one-unit increase in pH raises the NH_3 concentration approximately ten-fold. Raising the temperature also promotes the formation of NH_3 , but to a lesser degree. Increasing the ionic strength at low concentration promotes the formation of the NH_4^+ species (Thurston et al. 1979).

The concentration of ammonium ions (NH_4^+) in fish blood normally amounts to 0.2 to 0.3 mmole/L. Most of the ammonia produced by a fish is eliminated through the gills (Para and Prekup 1960). At physiological pH values, practically all of the ammonia in the organism is in the ionized state. The gills of fish are not very permeable to NH_4^+ . At the present time, there is every reason to assume that ammonia is eliminated through the gills, not only because of passive diffusion of gaseous ammonia (NH_3), but also as a result of $\text{NH}_4^+/\text{Na}^+$ exchange. Most of the data indicating $\text{NH}_4^+/\text{Na}^+$ exchange in the gills of freshwater fish were obtained on the crucian carp and fish of the salmon family (Maetz 1973, Wright and Wood 1984, Randall and Wright 1986).

¹Institute of Biology of Inland Waters, USSR Academy of Sciences, Borok USSR.

RESULTS

Our experiments dealt with the effect of ammonium salts (NH_4Cl) and $(\text{NH}_4)_2\text{SO}_4$ at different pH values of the medium on the regulation of sodium exchange in the crucian carp (Carassius carassius). The introduction of ammonium salts into aquariums containing fish acclimated for 2 and 7 days at pH 5.5 and 4.5 to a concentration of 5 and 10 mmole/L did not cause any disruption in Na^+ uptake (Thurston et al. 1979).

The concentration of Na^+ and Cl^- ions in the blood of the crucian carp and pond carp placed in water with different concentrations of $(\text{NH}_4)_2\text{SO}_4$ up to the maximum tolerable value did not differ reliably from the control.

Sodium exchange in the crucian carp in alkaline medium (pH 7.8) changes insignificantly at a very high concentration of NH_4^+ (Figure 1). Immediately after the fish are placed in water containing 2.5 mmole/L NH_4Cl , the net uptake of sodium becomes negative as a result of an increase in the passive yield of this ion, which in our view is due to the ammonia stress factor. After 1 day and during the subsequent acclimation, the uptake of pure sodium became positive (Figure 1). Placing the fish after 4 days of acclimation to 2.5 mmole/L of NH_4Cl in water containing no ammonium ions slightly increased the sodium loss in distilled water, but the overall Na^+ balance remained positive. During the subsequent deacclimation, small variations in sodium exchange caused by a change in Na^+ loss were observed. Ammonium ions in high concentrations had no reliable effect on sodium exchange in the gills or in other species of freshwater fish--the perch (Perca fluviatilis) or the roach (Rutilus rutilus).

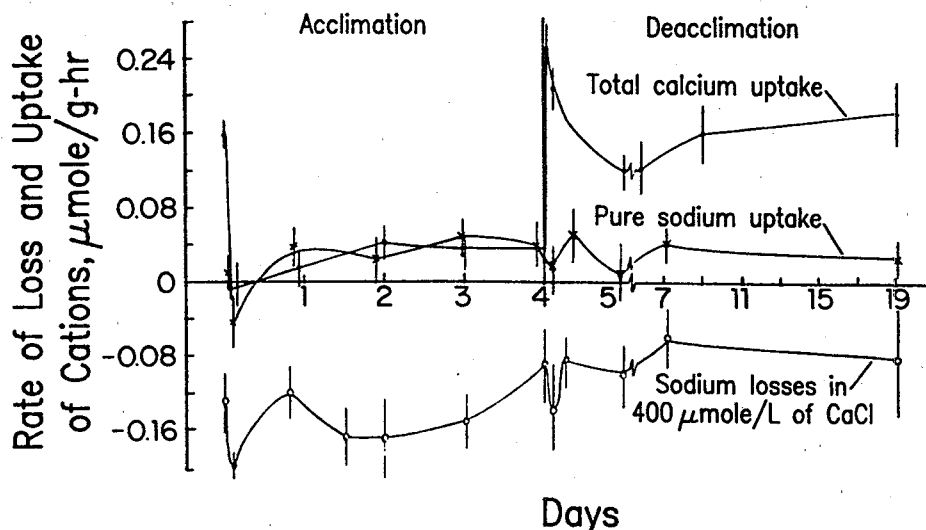


Figure 1. Effect of ammonium (2.5 mole/L NH_4Cl) on the uptake of calcium and sodium and loss of sodium in the crucian carp (pH 6.8, temperature 15 °C).

A possible cause of the discrepancy between our results and the data of other investigators may be the fact that injections into the organism of ammonium solutions, which were used to provide $\text{Na}^+/\text{NH}_4^+$ exchange, caused the development of appreciable acidosis (Cameron and Heisler 1983), which stimulated Na^+/H^+ exchange. In earlier studies, this fact was not considered in the interpretation of the results, and therefore, the increase in sodium transport after the injections was regarded as stimulation of Na/NH_4^+ exchange. Nevertheless, it should be noted that in fish of the salmon family, there is a relationship between the excretion of NH_4^+ and sodium uptake (Wright and Wood 1984, Randall and Wright 1986). In a weakly acidic or alkaline medium, the flow ratio of NH_4^+ and Na^+ is 1:1, and a substantial portion of the total ammonia is eliminated from the organism in the form of NH_4^+ (Randall and Wright 1986).

According to our data, the presence of NH_4Cl in the water disturbs the K^+ balance. An excess of potassium loss over its uptake is observed during the entire acclimation period. The return of the fish to clean water normalizes the potassium exchange.

NH_4^+ ions depress the transport of calcium in the crucian carp starting at a concentration of 0.25 to 0.5 eq/L (Figure 2). The inhibiting effect of NH_4^+ also is preserved during the acclimation of the fish to water with an NH_4^+ concentration of 1 to 5 eq/L. Transferring the fish into clean water after their exposure to ammonia stimulates the uptake of calcium by 150 to

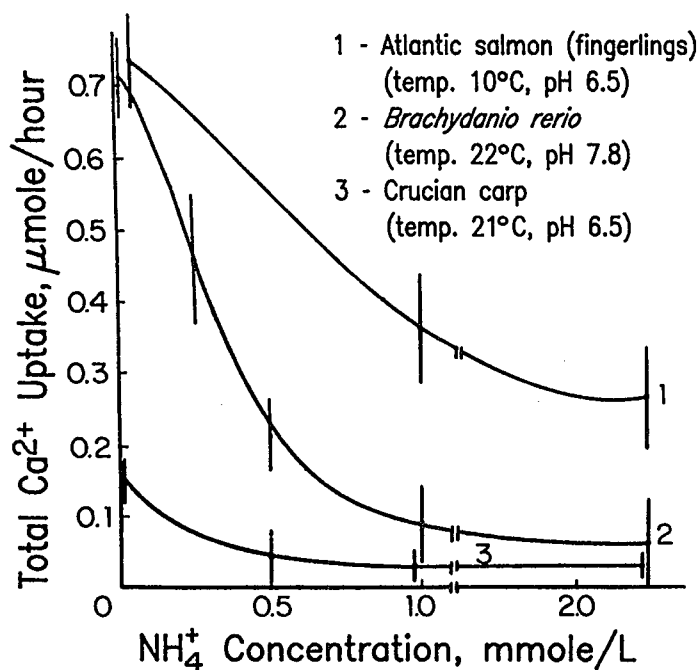


Figure 2. Effect of NH_4^+ on Ca^{2+} uptake in fish in 0.5 mmole/L CaCl_2 .

200% in comparison with the control. Lowering the pH of water to 4.0 to 4.5 does not appreciably affect the calcium exchange. The above results speak in favor of $\text{Ca}^{2+}/\text{NH}_4^+$ exchange. Apparently, this exchange is also characteristic of other bony fish living in fresh water.

The inhibition of calcium uptake by ammonium ions takes place in the immature Atlantic salmon - parr and "aquarium fish" (*Brachydanio rerio*). The $\text{Ca}^{2+}/\text{NH}_4^+$ exchange also is supported by the results of a study of the excretion of total ammonia in the perch. In distilled water, the yield of $\text{NH}_3 + \text{NH}_4^+$ is 0.057 ± 0.18 ueq/gh, in CaCl_2 solution 20 ueq/L 0.125 ± 0.046 , in 50 meq/L 0.163 ± 0.031 , and in 100 - 0.212 ± 0.044 . The calcium uptake in these solutions is 0.021 ± 0.010 , 0.06 ± 0.02 , and 0.130 ± 0.40 ueq/gh, respectively. As the calcium content of the water increases further, the yield of total ammonia either remains unchanged or decreases slightly. The results of this study show that the calcium ion may be exchanged for two ammonium ions. A breakdown of this ratio during an intensive uptake of calcium is probably due to an insufficiency of the ion exchange stock of NH_4^+ .

The acclimation of crucian carp to a higher content of ammonium ions revealed a number of significant aspects of calcium exchange. It was found that when the NH_4^+ content of the water is 2.5 and 5.0 meq/L, the calcium transport practically stops after 30 minutes of action. It then increases slightly during the next 16 to 24 hours of acclimation. Subsequently, the level of calcium uptake remains almost unchanged, and after 4 to 5 days, the acclimation amounts to 10 to 30% of the original value (Figure 1). At a lower concentration (1 meq/L of NH_4^+), the degree of the original inhibition of calcium inflow is about 40%. During the subsequent acclimation, the calcium uptake from water is not completely restored (Figure 3).

When the crucian carp are returned to clean water after acclimation to an increased ammonium content, a rapid increase in Ca^{2+} uptake is observed.

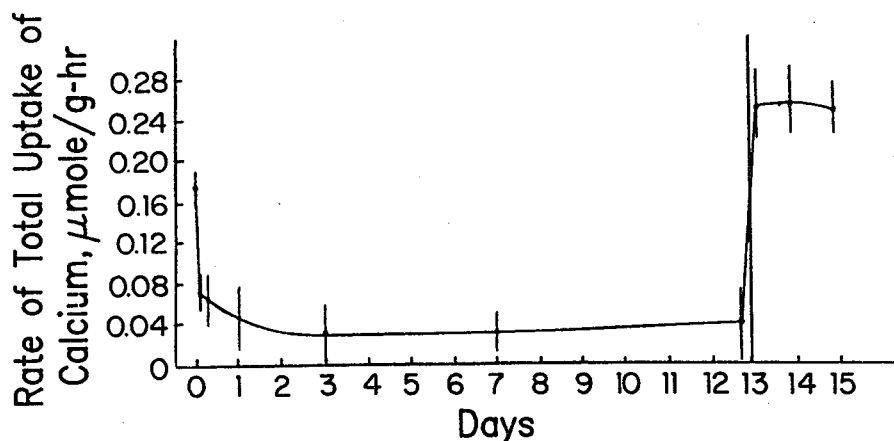


Figure 3. Effect of ammonium (1 mmole/L NH_4Cl) on the total uptake of calcium in the crucian carp (temperature 18 °C, pH 6.8, 0-13 days - medium with NH_4^+ , 13-15 days - pure water).

During the entire first hour of acclimation, the Ca^{2+} uptake from water increases substantially and reaches a value that is 1.5 times the level of normal calcium transport. After 3 to 4 hours of deacclimation, the calcium uptake by the organism decreases again. During the next 16 to 20 hours, the calcium exchange becomes normalized.

A study of the influence of ammonium salts on the dynamics of uptake and loss of sodium in the narrow-clawed crayfish (*Astacus leptodactylus*) showed that, at ammonium concentrations in excess of 1 meq/L of NH_4^+ , the equilibrium between the loss and gain of sodium is disturbed. In the first 2 to 3 hours, a depression of sodium uptake and an increase of its discharge into the surrounding medium are observed. The degree of deviation from the balanced state depends on the ammonium concentration (Figures 4 and 5). Subsequently, there is a gradual restoration of the rate of sodium transport and rate of its escape into the surrounding medium.

After 24 to 36 hours, both processes become stabilized, and do not change significantly for the next 3 days of acclimation. After the crayfish are put back in clean water (deacclimation), a marked increase in sodium uptake is noted, the magnitude of which substantially exceeds the initial level. Then the sodium transport gradually decreases, and after 48 hours the deacclimation reaches normal values. During the deacclimation, a reduction of total sodium loss is noted.

In the course of longer periods of acclimation to increased ammonium concentration, it was noted that an equilibrium in sodium exchange was estab-

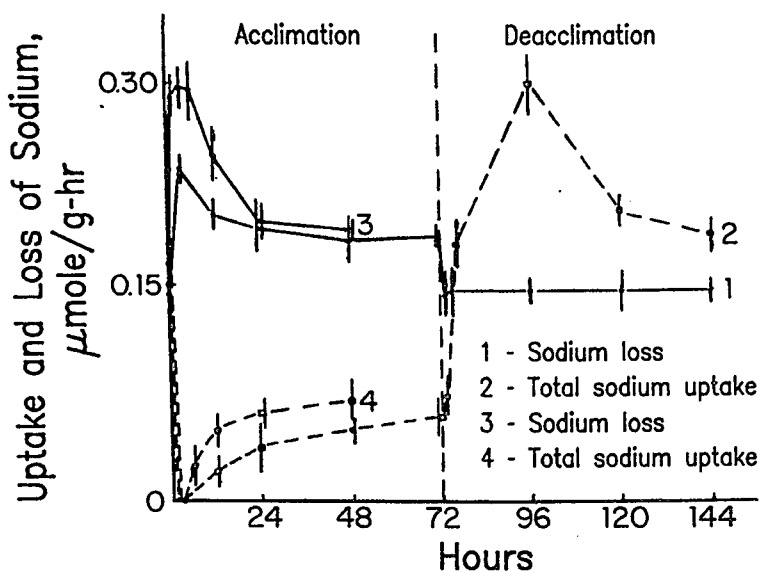


Figure 4. Na^+ exchange in the narrow-clawed crayfish (*Astacus leptodactylus*) during acclimation to 2.5 mmole/L NH_4Cl (temperature 12 °C, pH 7.2-7.4--lines 1 and 2) and 5 mmole/L $(\text{NH}_4)_2\text{SO}_4$ (temperature 18-21 °C, pH 7.2-7.4--lines 3 and 4).

lished at a level that was lower than the initial one. After 14 days, the inflow of sodium was equal to its loss. After the crayfish were transferred to clean water, as in the case of a shorter acclimation period, a manyfold increase in sodium uptake and decrease in its loss took place.

Placing the crayfish in an isotonic solution of NaCl (190 meq/L) increases the sodium transport three-fold during the first few hours of the experiment. After a day of exposure to the salt solution, the sodium uptake practically ceases. The Na^+ -dependent ammonium yield, calculated from the difference between the excretion in animals with maximum sodium transport and nontransporting animals, amounts to about 60% of the total ammonium excretion.

A study of the effect of dinitrophenol, which is a respiratory phosphorylation inhibitor, on sodium uptake and ammonium excretion made it possible to establish the interdependence of these processes. Inhibition of active transport of ions through the gills substantially reduces the level of cation-dependent ammonium excretion. Good agreement is observed between the degree of inhibition of ion transport and ammonium excretion. A three-fold depression of sodium transport and, apparently, other cations leads to an analogous reduction of cation-dependent excretion.

In the amphipod (*Gammaracanthus lacustris*), the effectiveness of the action of ammonium ions on the uptake and loss of sodium is somewhat lower than in the freshwater crayfish.

The results of experiments on the uptake of K^+ and Ca^{++} showed that, in solutions containing NH_4^+ in concentrations of 0.25 to 2.0 meq/L, a depression of potassium uptake from the medium and an increase of its yield from the organism are observed as early as the first 30 minutes. Similar, but more pronounced, changes take place in calcium exchange. The addition of 2

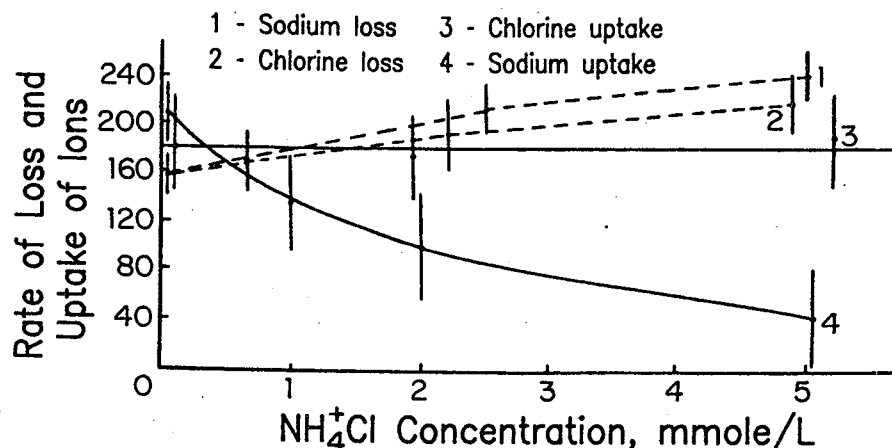


Figure 5. Effect of NH_4Cl on sodium and chlorine exchange in the narrow-clawed crayfish (temperature 18-21 °C, pH 7.6).

TABLE 1. EFFECT OF FUNCTIONAL ACTIVITY OF Na^+ -TRANSPORTING SYSTEM ON THE AMMONIUM EXCRETION OF THE CRAYFISH (after Vinogradov et al. 1982)

Time of exposure to isotonic solution (hours)	Surrounding medium	Total Na^+ uptake, ueq/gh	NH_4^+ excretion, ueq/gh	Na^+ -dependent NH_4^+ excretion, ueq.gh
Control (0)	0.2 mmole/L of NaCl distilled water	0.185 \pm 0.022	0.267 \pm 0.27	0.110
		0	0.157 \pm 0.036	0
0.5	190 mmole/L NaCl	0.540 \pm 0.030	0.384 \pm 0.039	0.229
	190 mmole/L NaCl + dinitrophenol	0.188 \pm 0.027	0.232 \pm 0.056	0.092
24	190 mmole/L NaCl	0	0.155 \pm 0.042	0
	190 mmole/L NaCl + dinitrophenol	0	0.140 \pm 0.061	0

\pm - confidence interval for $p = 0.05$

mmole/L of ammonium fluoride to the medium causes a three-fold increase in calcium loss, whereas its uptake is almost completely suppressed (Figure 6). When the crayfish are kept in a 2 mmole/L NH_4Cl solution for 7 days, uptake of calcium from water is lower than in the control and amounts to 33, 39, and 43% of the control in the 36th, 96th, and 168th hour, respectively.

The rate of ammonium excretion depends on the concentration of potassium and sodium in the ambient medium and correlates with their rate of uptake, indicating the existence in the crayfish of a mechanism of ammonium excretion associated with calcium transport (Figure 6). A comparison of the rates of sodium and calcium uptake and rate of ammonium excretion shows that calcium can be exchanged for ammonium in the ratio of 2:1.

Another factor in the transport of cations in addition to ammonium can be the hydrogen ion (Ehrenfeld 1974). In this case, an increase in the external concentration of hydrogen ions should cause a depression of calcium and potassium uptake. In our experiments, a decrease in water pH from 6.5 to 4.0 did not lead to any changes in the transport and escape of potassium or in the uptake of calcium. The passive loss of calcium on acidification of the medium sharply increases. This effect is probably due to an increase in the solubility at low pH values of calcium carbamate, which enters into the composition of the exoskeleton.

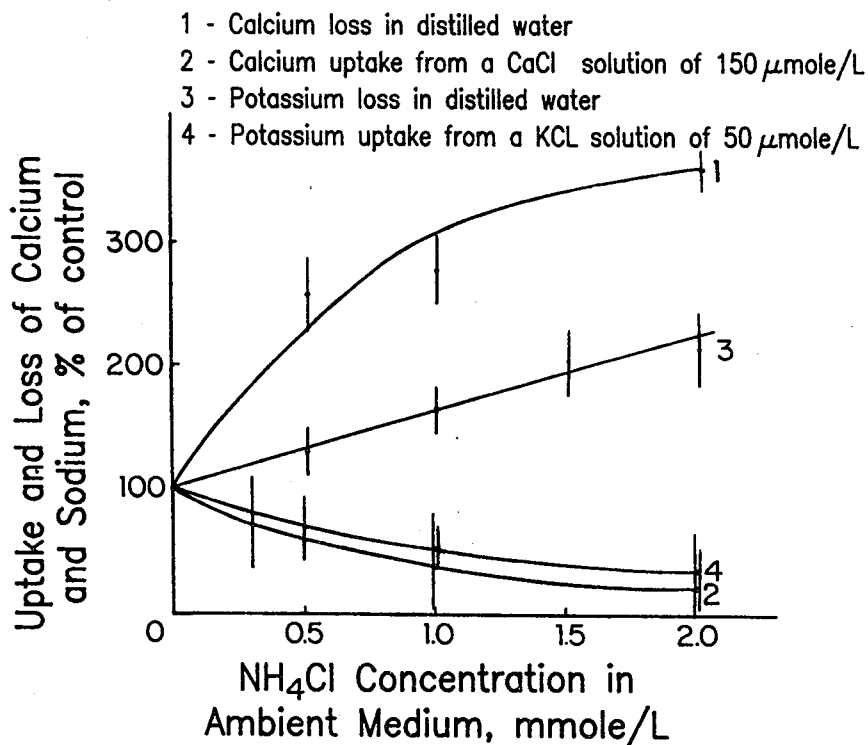


Figure 6. Effect of ammonium on potassium and calcium exchange in the narrow-clawed crayfish (temperature 18-21 °C, pH 6.5).

In crayfish placed in water at pH 4.5, the rate of the total loss of calcium increased by a factor of 8-9 in comparison with the control and remained unchanged during the entire experiment (7 days). The critical pH value at which the transport of calcium is unable to offset its losses amounts to 4.6 to 4.7. It should be emphasized that under standard conditions, the loss of calcium amounts to only 1/7 to 1/8 of its uptake. Thanks to this characteristic of calcium exchange, a constant accumulation of calcium in the organism is evidently ensured.

DISCUSSION

Numerous literature data generalized in review articles (Liebmann 1960, EPA 1977, Thurston et al. 1979 and 1982, EPA 1983) attest to a high toxicity of the NH_3 species. In this connection, the criterion of the European Consultative Commission on Fish Breeding in Inland Waters and of the U.S. Environmental Protection Agency is based on the premise that NH_4^+ is not very toxic to aquatic organisms. There is no question that the acute toxicity of ammonium ($\text{NH}_3 + \text{NH}_4^+$) is determined mainly by the concentration of NH_3 . In estimating water quality, however, it is necessary to consider the NH_3^+ content as well.

Our studies in fish showed that ammonium ions (NH_4^+) inhibit the uptake of calcium. This effect manifests itself when the concentration is only 4.5 to

18.0 mg/L NH_4^+ . It is well known that the normal course of many metabolic reactions depends on the availability of calcium to the fish organism (Romanenko et al. 1982).

It also is known that the concentration of calcium in water, and hence, the rate of its uptake by the organism determine the development and growth of fish to a considerable extent (Yeleonskiy 1932, Skadovskiy 1954). It was found that immature fish are most sensitive to a calcium deficiency. This applies particularly to crustaceans. A calcium deficiency decreases the growth of fingerlings by slowing down the mineralization of the skeleton (Kaplanskiy and Boldyreva 1934, Bodrova and Krayukhin 1962).

In this connection, it is interesting to note that a similar negative influence on fish is exerted by sublethal ammonium concentrations, as is manifested most clearly in juveniles (Thurston 1981, EPA 1983). A recalculation of sublethal NH_3 concentrations for different species of fish (0.05 to 0.15 mg/L) cited in literature sources, for the ionized form of ammonium indicates that the NH_4^+ content in these experiments usually amounted to 4 to 30 mg/L. That is, the NH_4^+ concentration in water was sufficient to disturb the calcium exchange. In our view, this fact accounts for much of the negative influence of sublethal ammonium concentrations on fish and invertebrates, especially in the early stages of ontogeny.

In discussing the toxicity of ammonium to aquatic animals, we would like to emphasize, in particular, that the results of our studies clearly indicate disturbances in ion exchange at sublethal concentrations of total and ionized ammonium. The results obtained and analysis of literature data regarding the effect of sublethal ammonium concentrations lead to the conclusion that the chronic toxicity of ammonium contamination and the negative influence of sublethal values of the total ammonium content of water are apparently determined not only by the NH_3 species but also by NH_4^+ .

Without belittling the value of the reported data and our own results for NH_4^+/Na exchange in fish and crustaceans (Shaw 1960, Maetz and Garcia 1964, Maetz 1973, Evans 1975, Payan 1978, Vinogradov 1981, Vinogradov et al. 1983, Randall and Wright 1986), we should note in conclusion that apparently, in stenohaline freshwater fish, sodium uptake is primarily associated with the excretion of H^+ , and the removal of ammonium ions from the organism may take place as a result of exchange for Ca^{2+} . A diagram supplementing the concept of ion exchange processes in the gills of freshwater fish and crustaceans is given in Figure 7.

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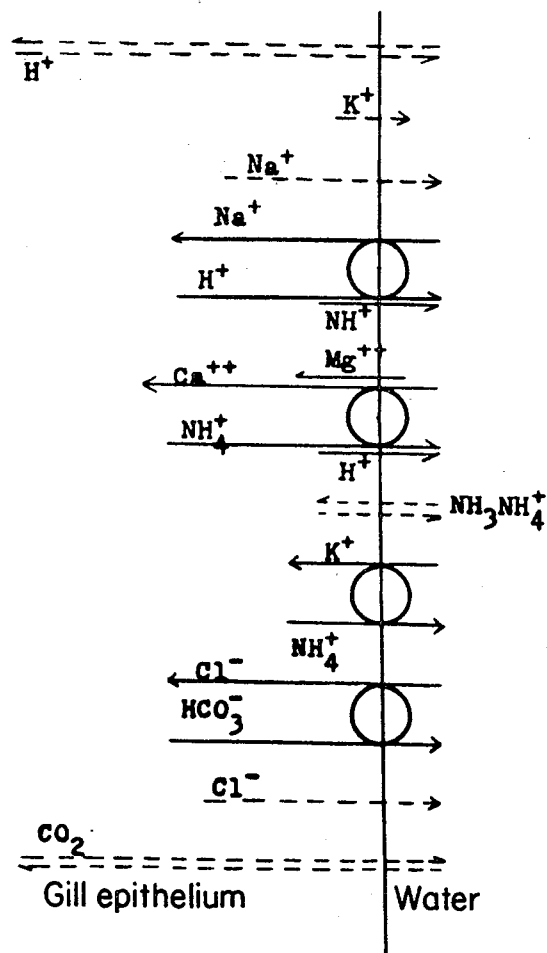


Figure 7. Diagram illustrating the participation of ion exchange in the gills of freshwater fish and crustaceans in the maintenance of acid-alkali and osmoionic homeostasis (-----ionic and molecular diffusion, ——ion exchange mechanism).

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ON-SITE TOXICITY TESTING: APPLICATIONS
IN THE UNITED STATES AND SOVIET UNION

by

M.G. Henry¹, B.A. Flerov², V.T. Komov², and
T.A. Heming³

ABSTRACT

On-site toxicity tests using the cladoceran Ceriodaphnia dubia were conducted in the USA and USSR by the same team of investigators. A non-point source situation (Detroit River, USA) and a point source spill situation (Rybinsk Reservoir, USSR) were assessed. The test method was successfully applied in both instances. The resultant compatibility of approach affords opportunities to accurately compare future data sets from both countries.

INTRODUCTION

One of the focuses of Project 13 of the USA-USSR scientific exchange program for cooperation in the field of environmental protection is the development of aquatic toxicity test methods that can be field applied in both countries. Species differences, changes in the life histories of similar species due to latitudinal differences, and inconsistencies in available equipment present formidable obstacles in the development and application of common methods. Use of the cladoceran Ceriodaphnia dubia in on-site assessments offers an opportunity to overcome these difficulties. C. dubia is widely distributed in both countries, has a short life-cycle, and is sensitive to low levels of contaminants. Moreover, the test protocol developed for this species by Mount and Norberg (1984) is relatively simple, requires no specialized equipment, and can easily be modified to compensate for temperature-related differences in life-cycle (McNaught and Mount 1986, Cowgill et al. 1985).

The objectives of this research were twofold: to establish healthy cultures of Ceriodaphnia dubia in the USSR and to use the same team of American and Soviet investigators to conduct on-site toxicity tests in both countries so that dissemination of the method and compatibility of approach could be accomplished.

¹National Fisheries Center-Great Lakes, U.S. Fish and Wildlife Service, Ann Arbor, MI USA.

²Institute of Biology of Inland Waters, USSR Academy of Sciences, Borok, Jaroslavl Oblast USSR.

³University of Texas Medical Branch, Galveston, TX USA.

MATERIALS AND METHODS

The Great Lakes and their connecting channels are located in the north central part of the United States. They constitute an important commercial and recreational resource and are heavily used by industries. The Detroit River, which connects Lake St. Clair and Lake Erie, is no exception. Several chemical and steel manufacturing plants are located along the banks of the Detroit River. Numerous organic and inorganic contaminants have been detected in Detroit River sediments but the toxicity of Detroit River water (DRW) needs closer examination. We selected a representative site in the Trenton Channel of the Detroit River (Figure 1) as our test site. This site was located downstream from steel and concrete manufacturing plants. Sediments collected at this site have been found to contain elevated concentrations of certain polyaromatic hydrocarbons and metals (Giesy et al. 1988).

The on-site toxicity test was conducted during August 1986. Because of the nonpoint source nature of contaminants in the Detroit River, a continuous water sampling scheme was established at the test site. Samples were taken 3.5 m below the water surface with a shore-mounted Masterflex Composite Sampler. A 500-ml aliquot of DRW was sampled every 15 min for 7 days. Integrated 24-h samples were collected each morning for use in the static renewal Ceriodaphnia test.

The Ceriodaphnia test followed methods outlined by Mount and Norberg (1984). The test was conducted in a constant temperature (24-25°C) environmental chamber at the USEPA Large Lakes Research Station, Gross Ile, Michigan. Test animals were cultured in reconstituted dilution water. The dilution water was a mixture of well water and reverse-osmosis water with approximately the same hardness as Detroit River water. Ten beakers with one neonate (less than 24-h old) in each were used at each exposure level. Six exposure levels were assessed: 100% Detroit River water, 50% DRW; 25% DRW, 12.5% DRW, 6.25% DRW, 0% DRW (100% dilution water). Mortalities and number of neonates produced were monitored daily. The results were statistically analyzed using methods developed by Kaiser and Finger (1986).

On test days 1, 3, and 6, aliquots of the integrated 24-h water sample were prepared for organic analysis by fixing 3-liter subsamples with 150 ml of dichloromethane. Two 200-ml samples were also taken on each of these days for inorganic analysis. One was filtered and the other was left unfiltered. Both were fixed with 2 ml of ultra-pure nitric acid. Organic samples were to be analyzed by gas chromatography/mass spectroscopy and inorganics analyzed using atomic absorption spectrophotometry.

USSR TEST

In January 1987, a wastewater spill occurred at a metallurgical plant located on the northern shores of the Rybinsk Reservoir at Tcherepovets, adjacent to station 1 (Kabachino, Figure 2). Thousands of gallons were released, causing immediate fish mortality and water quality problems (Pant-zirev 1987). At the first available opportunity after ice melt, grab samples

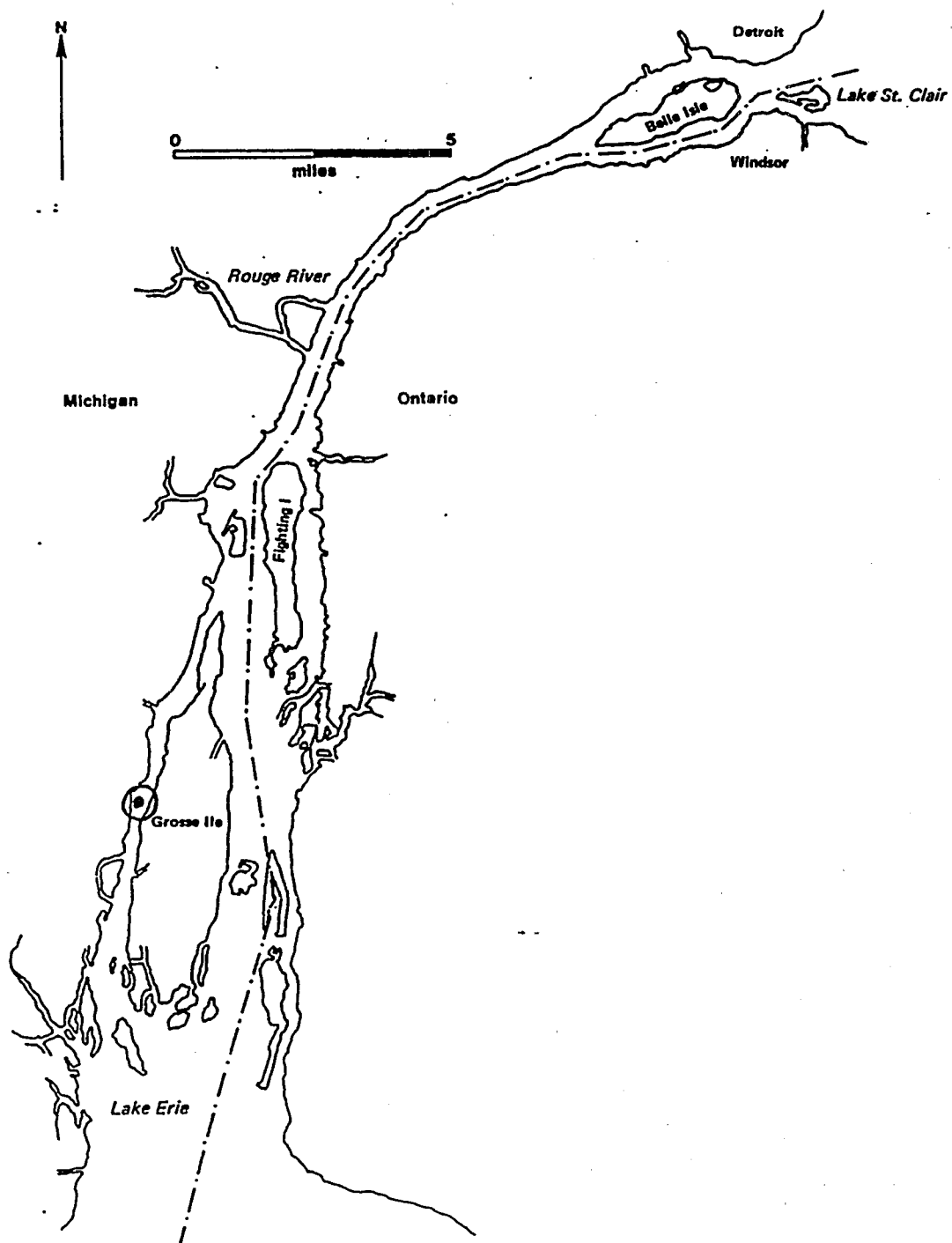


Figure 1. Sampling station location in the Detroit River for the USA on-site toxicity test conducted in 1986.

of water were taken at nine stations along a north-south transect moving away from the spill site to assess the persistent effects of the spill. Water samples were taken 4 m below the surface using a van Dorn bottle.

The Ceriodaphnia test was conducted at the Freshwater Institute for the Biology of Inland Waters at Borok in June 1987. Static renewal was used and, because of the lower-than-recommended temperature of available reservoir water (21 to 22°C), the test was run for 10 days. All other methods were those recommended by Mount and Norberg (1984). Water from the southernmost tip of the Rybinsk Reservoir at Borok below station 10 (Volga, Figure 2) was used as control and culture water. Chemical analyses of water, fixed and prepared as described above, were conducted using atomic absorption spectro-



Figure 2. Location of sampling stations in the Rybinsk Reservoir for the USSR on-site toxicity test conducted in 1987.

photometry and gas chromatography. Results of the toxicity test were analyzed using analysis of variance.

RESULTS

A 48-hr acute lethality bioassay conducted in conjunction with the USA test indicated that 81% DRW induced mortality in 50% of the adult test population. Complete mortality also was induced during the 7-day on-site test in the 100% and 50% DRW treatments. Results of the 7-day reproduction test were considered to be inconclusive because the requirement for production of three broods of at least nine young in the control (Mount and Norberg 1984) was not achieved.

Despite the lack of protocol-required reproduction, the data suggest that there was a dose-response relationship in mortality and reproduction associated with DRW dilution (Table 1). Complete mortality was induced in the two highest dilutions, 100% and 50% DRW within 2 and 4 days, respectively. The 25% DRW treatment induced 30% mortality and, of the remaining survivors, two broods were produced with only a mean number of 3.1 neonates in each. Mortality in the remaining three treatments was insignificant and statistically indistinguishable from each other. Three broods were produced in the 12.5% DRW treatment, whereas four were observed in both the 6.25% and control treatments. Due to lower neonate/brood production, the results of the bioassay were considered incomplete and water samples were not chemically analyzed.

Initial cultures of C. dubia were established in the USSR in July-August 1984, using animals collected from the Rybinsk Reservoir. These cultures were subsequently found to be contaminated with C. reticulata. Stable cultures of pure C. dubia were achieved at the Freshwater Institute for the Biology of Inland Waters by August 1986.

Results of the Rybinsk Reservoir on-site test were more complete than the USA test. A definite dilution effect was apparent, even 4 months after the spill (Table 2). Complete mortality was induced by water collected at four sites; partial mortality was induced by water from the other six sites. Three sites where 100% mortality was induced were upstream from the spill site. Control reservoir water did not induce any mortality. Reproduction, of course, was non-existent in treatments where 100% mortality occurred but, of the survivors in other treatments, reproduction was completely truncated in water from station 1 and was statistically indistinguishable from control levels in waters from stations 5, 6, 7, 8, and 10. Neonate production approximated the protocol-recommended levels. Chemical analyses of water samples are currently being completed.

DISCUSSION

Although some of the test results were inconclusive, this does not diminish the significance of the research. This is the first time identical species have been used in common bioassays conducted in the USA and the USSR. Because pollution abatement and monitoring is a global problem, the compati-

TABLE 1. EFFECTS OF DETROIT RIVER WATER ON CERIODAPHNIA SURVIVAL AND REPRODUCTION.

% Detroit River Water	\$ Mortality/Mean Neonates per Adult Day						
	1	2	3	4	5	6	7
100%	60/0	100/0					
50%	20/0	20/0	50/0	100/0			
25%	10/0	10/0	30/0	30/0	30/0	30/0	30/3.1
12.5%	0/0	0/0	0/3.0	0/6.2	0/0	0/0	0/1.0
6.25%	0/0	0/0	10/3.4	0/6.2	0/0	0/11.7	0/5.7
0%	10/0	10/0	10/3.1	10/6.5	10/0	0/12.4	10/6.6

bility of approach used here affords us opportunities to accurately compare future data sets. It further emphasizes that this on-site method can be applied successfully in point source and non-point source situations.

Establishment of healthy cultures of test organisms is paramount if the required number of broods and neonates per brood are to be produced. Transport stress to animals may impede reproductive capability and, consequently, should be minimized. On the other hand, diet and culture water quality also have been implicated in determining the health of test organisms (DeGraeve and Cooney 1987). Because brood production is species- and temperature-dependent, maintaining pure cultures under recommended conditions is important. Furthermore, although taxonomic distinction between C. dubia and C. reticulata can be difficult, culture purity must be periodically monitored because a lack of culture purity can influence the test results.

Despite the lack of protocol-required reproduction in the Detroit River test, the data indicate that Detroit River water is toxic to C. dubia. This emphasizes the need for further research.

Mortality patterns observed in Ceriodaphnia exposed to water from the Rybinsk Reservoir spill appear to have been influenced by the hydrology of the reservoir. The flow patterns of water in the northern portion of the reservoir are such that the plant wastewater moved slightly north before moving south through the central basin (Flerov 1987). The mortality observed in animals exposed to water from station 9, however, is not explainable on the basis of water currents. Perhaps results of chemical analyses will aid in

TABLE 2. RESULTS OF THE ON-SITE Ceriodaphnia TEST OF THE RYBNSK RESERVOIR WATER AFTER A METALLURGICAL PLANT SPILL NEAR STATION 1.

Station	Days	% Mortality, (n=10)										% Final survival	Mean broods per female	Mean young per female
		1	2	3	4	5	6	7	8	9	10			
1. Kabachino	80	80	80	90	90	90	90	90	90	90	90	10	-	-
2. Jagorba	100	-	-	-	-	-	-	-	-	-	-	0	-	-
3. Koschta	90	90	90	100	-	-	-	-	-	-	-	0	-	-
4. Suda	70	80	80	90	100	-	-	-	-	-	-	0	-	-
5. Kargach	10	10	10	10	20	20	20	20	20	20	20	80	3.0	8.2+4.5
6. Lubez	0	0	0	20	20	20	20	20	20	20	20	80	2.9	8.7+3.7
7. Mjaksa	0	0	0	20	20	20	20	20	20	20	20	80	3.25	8.0+5.3
8. Dvor	0	20	20	20	20	20	20	20	20	20	20	80	3.0	7.4+4.1
9. Central	40	100	-	-	-	-	-	-	-	-	-	0	-	-
10. Volga	0	10	10	10	10	10	10	10	10	10	10	90	3.3	7.8+4.2
11. Control	0	0	0	0	0	0	0	0	0	0	0	100	3.0	8.4+3.5

the interpretation of this portion of the test results. Areas requiring further development are 1) adapting available technology in the Soviet Union for taking integrated water samples and 2) writing a manual for circulation in the USSR so that personnel associated with water management offices and sewage treatment facilities also can employ this versatile method.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the field assistance and cooperation of Steve Smith, NFRC-GL. Without his help, this project would never have been possible. Additional thanks go to Susan Finger for her assistance with test protocol recommendations and data analyses and to Mark Kaiser for data manipulation and statistical analyses.

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VARIOUS RESISTANCE MECHANISMS OF CARP (Cyprinus Caprio L.) AND
PERCH (Perca Fluviatilis L.) TO DDVF ORGANOPHOSPHORUS COMPOUNDS

by

G.M. Chuyko¹

ABSTRACT

Differences in the resistance of carp and perch to the effects of dichlorofos in acute tests are examined. The experiments demonstrate that differences are determined by the toxin's different rate of penetration into the fish and the uneven intensity of subsequent detoxification processes.

INTRODUCTION

An increase in world-wide farming production implies a greater reliance on pesticides, among which insecticides and acaricides play a major role. The principal volume of these falls in the organophosphorus category that, in comparison to other types of chemical substances has a broader selectivity range for animals (Melnikov et al. 1977, Melnikov, 1981). The synthesis of compounds that are highly selective and narrowly directed in their effects is based on a thorough knowledge of the resistance mechanism of various animal groups (O'Brien 1964, Rozengart and Sherstobitov 1978).

Fish have varying degrees of resistance to organophosphorus. As data of various authors indicate, the most resistant to a majority of compounds in this group are members of the Cyprinidae family, and specifically, the Salmonidae and Percidae families (Gantverg 1985, Macek and McAllister 1970, Johnson and Finley 1980). The selective effect mechanisms of organophosphorus on fish is practically unknown. Current understanding has been based on the research on mammals and arthropods (Rozengart and Sherstobitov 1978). According to their work, the most probable causes of varying resistance levels in fish may be type-specific characteristics of the toxicant's rate of penetration into the organism and their sensitivity to the "target" acetylcholinesterase (ACE), and its metabolic intensity. No complete study of the selectivity of organophosphorus on fish has been done to date, although certain aspects of this issue have been examined in a number of studies (Gantverg 1985, Murphy, 1966, Macek and McAllister, 1970, Fujii and Asaka 1982). For

¹Institute of Biology of Inland Water, USSR Academy of Science, Borok USSR.

this reason, the intent of this paper is to study the primary reasons for the varying degree of resistance to one of the organophosphorus compounds, "dichlorophos" (DDVF).

DATA AND METHODOLOGY

Two types of fresh water fish were utilized in the experiments, each with varying degrees of resistance to organophosphorus compounds--the carp, Cyprinus carpio L. (genus Cyprinidae) and the perch, Perca fluviatilis L. (genus Percidae). For the tests, carp were obtained from the All-Union Fish Experimental Facility, (Moscow Oblast); the perch were caught by net from the Rybinsk Reservoir. The carp were 1-year and 2-year old fingerlings (weight 5.7 ± 0.4 , 10.1 ± 1.4 and 65.0 ± 6.1 g); the perch were 2-year and 4-year old fingerlings (weight 3.6 ± 0.3 , 22.7 ± 0.8 and 75.2 ± 9.4 g). When studying the ACE sensitivity to DDVF, fish were selected immediately after catching. For other experiments, fish were adapted to laboratory conditions for no less than 7 to 10 days prior to the start of the experiments.

The toxic compound consisted of purifying 97% DDVF preparation: 0.0-dymethyl-0-(2.2-dichlorovinyl)phosphate. Concentration was calculated according to the active ingredient.

Fish resistance to the effects of the toxin was evaluated in acute tests using assay-analysis inherent modification (Nepomnyashchikh and Chuyko 1986), based on the lethal concentration LK_{50} or LD_{50} dosage, causing 50% mortality of the test fish over a 48-hour period. Six or eight fish were placed in 30-L aquariums, with settled river water at 8.1 to 8.3 pH, 16 to 18°C, and 8.7 to 9.8 mg/L oxygen content. The toxic compound was preliminarily dissolved in acetone, and then, depending on experimental conditions, was placed into the water or into the physiological solution for the fish. End volume concentration of the acetone in each aquarium did not exceed 0.1%. To determine LD_{50} the DDVF physiological solution was introduced intraventrally into the abdominal cavity, calculated per 1 kg of live weight. The injected solution was 0.5 ml, with the amount of acetone per fish not exceeding 0.05 ml. Fish injected with a physiological solution with acetone, but without the toxin, served as control.

Sensitivity of fish ACE to DDVF was evaluated in vitro according to magnitude of the biomolecular constant of the inhibition rate k_{11} (Yakovlev 1965). Ferment activity was determined in brain homogenates using Ellman's method (Ellman et al., 1961) and the Maslova and Reznik modification (1976). Acetylthiocholine bromide served as substrate. Homogenates were prepared using a phosphate buffer with a 7.5 pH, 1:10 ratio. After homogenization, the samples were centrifuged at 5000 rpm for 10 minutes. The supernatant fluid was analyzed.

The content of DDVF in the blood and liver of the fish was determined by chromatographic self-modification. DDVF extraction was carried out using hexane with additional evaporation of the extract under vacuum at 40°C. DDVF extraction from blood comprised $91.6 \pm 0.6\%$ and $87.2 \pm 2\%$ from liver. Quantitative content of DDVF was evaluated according to peak level, using absolute

calibration methods. A Gazokhrom-1109 liquid gas chromatograph with an electron-grip detector, and a packed glass spiral column 1000 x 3 was utilized. Nitrogen served as gas carrier. Five percentile SE-30, N-AW chromatone was utilized as stationary phase. Chromatography conditions were an electrometer scale 2×10^{-10} A, column temperature 110°C, detector 130°C, evaporator 200°C, nitrogen blow-through velocity 73 cm³/min, speed of recording unit 200 mm/hr, hold time for DDVF 2 minutes and 35 seconds. Sensitivity detection was 0.5 ng. One to two ml of the extract were placed into the chromatograph.

Two series of tests were conducted in order to study the rate at which DDVF enters the fish organism from the time they are kept in the toxic solution, as well as the concentration of the toxin in water. In one series, the fish were kept from 5 to 60 minutes in a 21.9 mg/L DDVF solution; in another, the fish were placed for 5 minutes in solutions containing 5, 10, 15, and 21.9 mg/L of toxin and a measured amount of DDVF in the blood of the fish. Blood was taken from tail blood vessels after caudotomy.

Fermentative destruction of DDVF was determined on the basis of differences in toxin content after incubation at 30°C for 2 hours with 2 ml of intact and inactivated fish liver homogenates (thermal processing for 10 minutes at 80°C). Original content of DDVF in sample was 45 mkg. Rate of the fermentative destruction of the toxin was expressed in DDVF mkg, 1 g raw tissue destroyed in 1 hour. Liver homogenates were prepared like the brain homogenates--1:5 ratio for perch and 1:10 for carp.

All data were statistically processed at $p=0.05$ and represented in the form of means (\bar{x}), their errors ($m\bar{x}$) and confidence interval boundaries. Accuracy of results were calculated according to (Stedent's) criteria (Lakin 1969). Each experiment was repeated no less than 2 times, and the number of fish per point (n) was no less than 5.

RESULTS AND DISCUSSION

COMPARATIVE RESISTANCE OF FISH TO DDVF

The toxicological experiments established that the carp is significantly superior to the perch in its resistance to DDVF. The value LK_0 comprised 21.9 and 0.59 mg/L, respectively (Table 1). Our data correspond to results derived by other researchers on the same types of fish (Gantverg 1985, Johnson and Finley, 1980, Svobodova 1980). The carp is also more resistant than the perch when the toxin is injected intra-abdominally. LD_{50} values are 292.0 mg/kg for carp and 30.4 mg/kg for perch (Table 2).

When resistance of fish to the effects of the toxin is compared, the selective coefficient K_s is utilized which is represented by the relationship of values LK_{50} (LD_{50}) for the more resistant fish, to LK_{50} (LD_{50}) for the less resistant fish (Perevoznikov 1979, Gantverg 1985). It is believed that the comparison of K_s in direct contact with the toxin and intra-abdominal or intravenous injection makes it possible to evaluate separately the role of penetration processes, and the "internal" reasons for the toxic selectivity

TABLE 1. VALUES OF DDVF LK₅₀ FOR PERCH AND CARP FOR 48-hr EXPOSURE

Type of Fish	Number of Fish	LK ₅₀ , mg/L	Boundary of confidence interval LK ₅₀ , mg/L	K _s
Carp	38	21.9	10.2 - 23.8	37.1
Perch	42	0.59	0.54 - 0.64	

effects that are connected with the fate of the toxin inside the organism. Apparently, if the toxin's rate of penetration into the organs of the fish does not differentiate, when it is injected intra-abdominally or intravenously, which eliminates the toxin's penetration through the external tissues, then the K_s value must remain close to that of the value that results from external contact with the toxic medium.

In many other cases, when K_s is increased or decreased, one of the causes of selectivity appears to be the inter-genus differences in the toxin's rate of penetration. This method is widely utilized in the study of the selectivity of organophosphorus in mammals and arthropods (O'Brien 1964, Rozengart and Sherstobitov 1978). Use of this method with respect to fish has proven that the determining factor of higher toxicity in the Amur lamprey (Misgurnus anguillicaudatus) to DDT and Dieldrin, in comparison to "monokrotofos" and "dikrotofos" is the higher speed of penetration of the former into the fish organism (Yang and Sun 1977).

TABLE 2. VALUES OF DDVF LK₅₀ FOR PERCH AND CARP FOR 48-hr EXPOSURE

Type of Fish	Number of Fish	LK ₅₀ , mg/L	Boundary of confidence interval LK ₅₀ , mg/L	K _s
Carp	20	292.0	254.0 - 336.0	9.6
Perch	42	30.4	23.0 - 40.1	

In our tests, the value K_s for carp and perch when placed in a toxic solution was 37.1, and 9.6 when injected intra-abdominally (Tables 1 and 2), that is, K_s is reduced by four times when DDVF is introduced ventrally. It follows then that the higher resistance of carp in comparison to the perch may be explained by the inter-genus differences in the DDVF penetration process into the fish organism.

PENETRATION OF DDVF INTO FISH ORGANISMS

Results derived from experiments to determine DDVF content in the blood of carp and perch after being kept in a toxic solution confirm our explanation. It has been established that 5 minutes after fish are placed into a 21.9 mg/L toxin solution, which corresponds to value LK_{50} for carp when exposed for 48 hours, there is a significant amount of DDVF in the blood--1.3 mg/L for the carp and 5.1 mg/L for the perch (Figure 1). Note that the content is 4.5 times higher for the perch than for the carp. This value is close to the one derived by comparing K_s for the different methods by which toxin is acquired.

As exposure time for the fish in a DDVF solution is extended, DDVF content in the blood rises and the established differences are maintained for the duration of the entire period of observation (60 min.). For the perch, the 21.9 mg/L concentration was extremely lethal because fish died 45 minutes after start of tests. This, apparently, explains the fact that during the period immediately preceding death, when breathing in fish becomes less active, the amount of DDVF in the perch's blood stops rising.

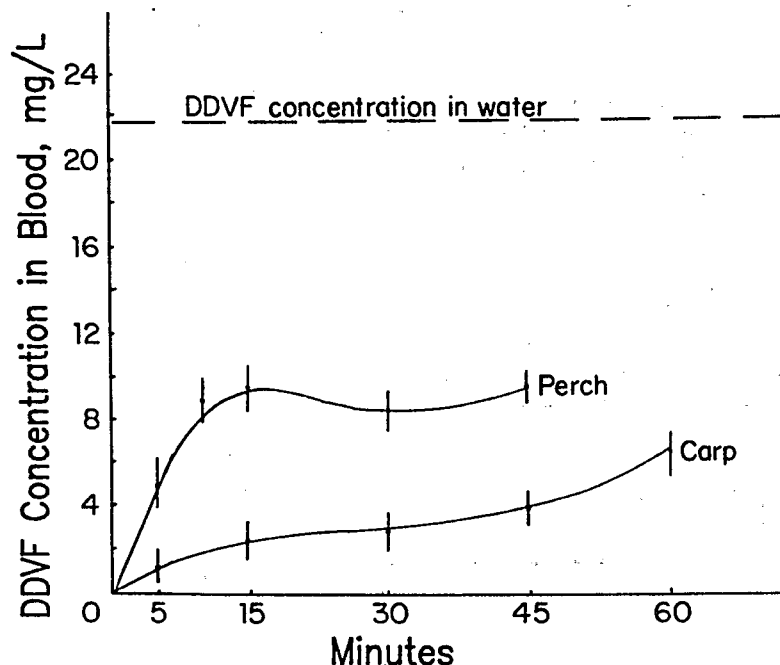


Figure 1. Dynamics of DDVF accumulation in blood of perch and carp in a 21.9 mg/L solution.

Also studied was the relationship of the initial content of DDVF in the blood of carp and perch to DDVF concentration in water. For this purpose, extreme lethality data for a 48-hour exposure period to the toxin was selected. The lowest possible concentration is taken as being a bit higher than LK_{50} values for the perch, because with lower concentrations, a precise determination of DDVF concentration in the blood by LGC methods is somewhat complicated. It has been established that with all the researched toxin concentrations in water, DDVF content in the blood of the perch is definitely higher than in the carp (Table 3). These data, shown as a graph, indicate that the relationship of toxin content in the blood to toxin content in the water has a linear nature (Figure 2).

Thus, the results attest that one of the reasons for the varying resistance to DDVF for the carp and perch is the unequal rate of penetration of the toxin into the blood of the fish. This rate is four to five times higher for the perch than for the carp. The established pattern is maintained for the lethal range (LK_{50} for 48 hours) of concentrations, 5 to 21.9 mg/L.

The discovery of the differences in DDVF penetration rates for the perch and carp may be explained from the point of view of the laws of permeability. It is known that organic-origin toxins, which include organophosphorus compounds, penetrate the fish directly from the water through tissue barriers (Tinsley 1982, Marcelle and Thome 1984). Penetration of these toxins through

TABLE 3. CONTENT OF DDVF IN CARP AND PERCH BLOOD 5 MINUTES AFTER START OF EXPERIMENT, WITH TOXIN CONCENTRATIONS OF 5, 10, 15, AND 21.9 mg/L IN THE WATER

Type of fish	Amount of DDVF in blood (mg/L) with following toxin concentrations in water			
	5 mg/L	10 mg/L	15 mg/L	21.9 mg/L
Carp	0.19 ± 0.03 (0.13-0.25)* n = 7	0.46 ± 0.03 (0.40-0.53) n = 5	0.61 ± 0.05 (0.52-0.70) n = 6	1.30 ± 0.12 (1.06-1.54) n = 8
Perch	1.69 ± 0.07 (1.56-1.82) n = 5	2.40 ± 0.19 (2.03-2.77) n = 5	3.48 ± 0.13 (3.23-3.73) n = 4	5.11 ± 0.23 (4.66-5.56) n = 5

*Parentheses indicate boundaries of confidence interval at $p = 0.05$

n - number of fish per section

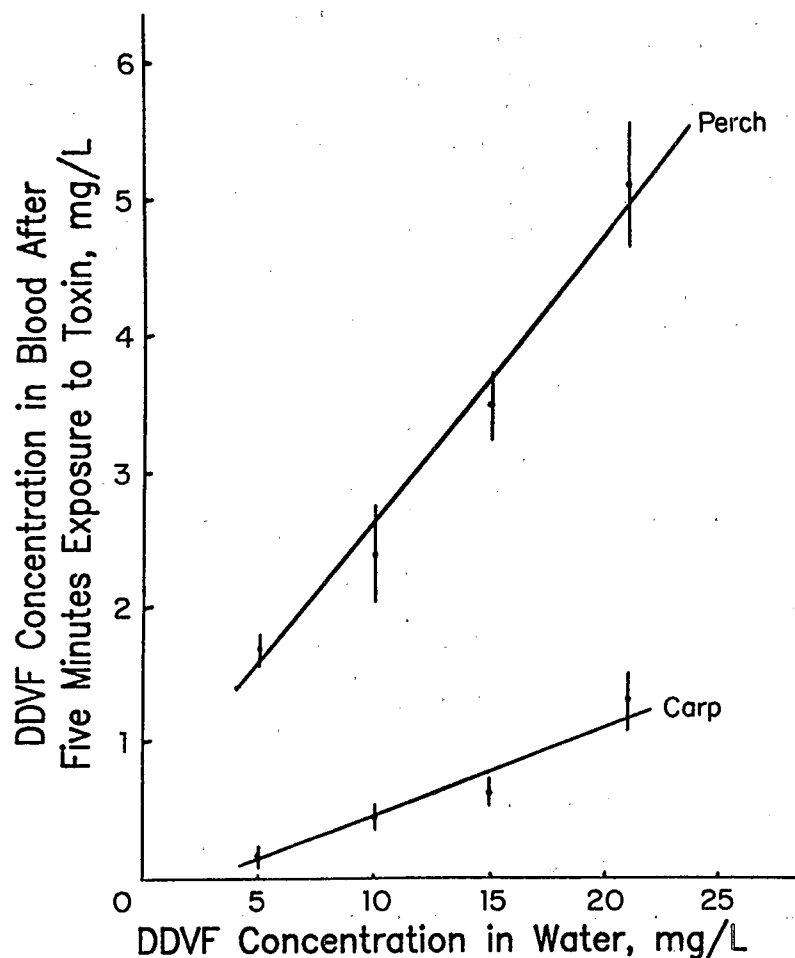


Figure 2. Relationship of DDVF accumulation in perch and carp blood as a result of the toxin concentration in water.

biologic membranes is determined by the ability of these compounds to dissolve in lipids; this occurs through the means of ordinary diffusion according to Fick's law.

According to this law, the rate of diffusion of a particular compound, in the presence of a stable concentration in an external medium, depends on the area and thickness of the barrier through which diffusion occurs--the larger the area, and thinner the barrier, the more rapid the diffusion of the compound (Tinsley 1982). The principal tissue barriers in the fish that separate the internal medium (blood) from the external medium through which toxic compounds found in the environment may be transported are the epithelia of the gills and the skin. Due to their morphofunctional peculiarities, the gills are the point of principal contact between the internal and external media of the organism (large surface area, thin tissue barrier and high degree of vascularization); the skin is of secondary importance. Consequently, gills have an important role in such processes as osmoregulation and ion ex-

change (Evans 1979). Based on the morphofunctional features of the gills, and the nature of the diffusion process, it can be considered that the penetration of organic toxins into fish, including organophosphorus compounds, occurs primarily through the gills. Other researchers have similar beliefs (Tinsley 1982, Yang and Sun 1977).

Gills in different types of fish have varying characteristics. In particular, it has been established that the overall surface of the gills in highly active, fast swimming fish are larger than in slow-swimming bottom fish. Differences can be measured by many factors of ten. The differences in tissue barrier thickness are also on the same order (Amineva and Yarzhombek 1984, Hughes 1984). It is precisely these differences that may be the cause of the unequal rate of DDVF penetration into the perch and carp organisms. The fact that the more active fish are less resistant to toxins, as compared to less active ones, may serve as an indirect confirmation of this conclusion.

The derived results only partially explain the selective effects of DDVF on the perch when toxin contact is external, and do not explain at all the higher resistance of the carp when toxin is injected intra-abdominally. In this case, the selectivity is determined only by internal causes, which in turn determine the fate of the toxic substance in the body of the animal. Some of the main reasons are the different levels of sensitivity to the toxic substance by the fish's ACE in the nervous system, and unique features of its metabolism.

DDVF INHIBITION OF FISH BRAIN ACE IN VITRO

Organophosphorus compounds are neuromuscular poisons. ACE serves as a principal target of their effects inside animal organisms with "cholinergic" systems. The symptoms of acute poisoning in animals by organophosphorus compounds are tied to the depression of this ferment (O'Brien 1964, Rozengart and Sherstobitov 1978).

Various researchers have expressed the opinion that differences in ACE sensitivity of the nervous system in fish may be a determining factor in their different resistance to organophosphorus compounds (Lukyanenko 1983, Macek and McAllister 1970). For this reason, the sensitivity of the brain of the two fish to DDVF also was examined. It was established that the value k_{11} for both fish is close in magnitude and is on the same order, which attests to the fact that both are equally sensitive to the toxin (Table 4). There are small differences ($p = 0.05$), but these are not important enough to be the cause of the resistance difference in the fish.

The absence of inter-genus differences of brain ACE sensitivity to a number of organophosphorus compounds, including DDVF, by other types of fish is supported by several authors (Hogan and Knowles 1968a, Hogan 1971), and our own efforts (Chuyko 1987). Thus the sensitivity of brain ACE in the examined fish does not play a significant role in the DDVF selective mechanism in the perch. A study of the nature of resistance in fish to "karbofos" brought identical results (Gantverg 1985).

TABLE 4. RATE OF INHIBITION CONSTANTS (k_{11}) FOR DDVF IN VITRO IN BRAIN ACE OF CARP AND PERCH

Type of fish	Number fish	mole ⁻¹ x l x min ⁻¹
Carp	7	9.1 ± 0.3
Perch	7	5.6 ± 0.1

DDVF DESTRUCTION BY FISH LIVER HOMOGENATES IN VITRO

As we know, organophosphorus compounds may undergo metabolic transformations inside the fish organism, as a result of which detoxification occurs (Gantverg 1985, Fujii and Asaka 1982). This process generally occurs in the liver, and DDVF is not an exception. It has been established that, in the liver of the canal catfish, Ictalurus punctatus, and another type of perch, Lepomis macrochirus, DDVF is destroyed at a rate that significantly exceeds the rate of spontaneous destruction. Here the variances in the efficiency of fermentative DDVF destruction are insignificant; the rate of toxin deterioration is only 1.3 times higher for L. macrochirus, than for I. punctatus (Hogan and Knowles 1986b).

Tests were carried out on the detoxifying system of the carp's and perch's liver showed the presence of fermentative systems in both fish, ones capable of destroying DDVF. The content of toxin in the samples after incubation with intact homogenate was significantly lower than with inactivated homogenates (Table 5).

Based on the data, the specific rates of DDVF destruction by liver homogenates of these two fish were shown to be 12.7 for the perch, and 38.8 mg/g-hr for the carp. These data attest that the specific rate of DDVF destruction by the carp liver homogenates is three times higher than that of the perch. As some researchers indicate, in comparison to other types of fish, the carp also has a higher rate of destruction of such organophosphorus compounds as "diazokson" and "karbofos" (Gantverg 1985, Fujii and Asaka 1982). At the same time, the fact of a higher specific rate of DDVF destruction in the carp does not completely explain the almost 10-fold difference in the resistance of this fish when toxin was injected intra-abdominally. Apparently, the absolute detoxifying capability of the liver depends both on the specific activity of its fermentative systems, as well as on its overall mass. Study of the absolute and relative mass of the carps' and perchs' livers (rounded off to unit of body weight) showed that for the carp this factor is two times higher than for the perch. Table 6 shows morphometric indicators of the fish, which were used in the DDVF detoxification experiments.

TABLE 5. DESTRUCTION OF DDVF BY INACTIVATED AND INTACT CARP AND PERCH LIVER HOMOGENATES

Type of fish	Number of Fish	DDVF content, % of original		Specific rate of fermentative destruction, mkg/g/hr
		Inactivated homogenate	Intact homogenate	
Carp	6	80.0 \pm 4.7	45.2 \pm 7.9	38.8 \pm 5.1
Perch	6	75.9 \pm 1.9	54.5 \pm 2.6	12.7 \pm 1.4

Other authors show that the relative mass of the liver of these two types of fish varies depending on the metabolic activity of the liver, the season of the year, and the degree of ontogenesis; however, mass is greater in the carp than in the perch (Makarova 1973, Dobrinskaya 1984). It can be thus concluded that the absolute capability of the carp's liver to destroy DDVF is six times higher than for the perch. This information makes it possible to explain the differences that were established with the intra-abdominal toxin injections.

CONCLUSION

As a result of the experiments, it has been established that the differing resistance of the carp and perch to the effects of DDVF in acute tests does not depend on the variant peculiarities of fish brain ACE sensitivity to the toxin but, rather, is determined by the toxin's different rate of penetration into the fish, and the uneven intensity of processes of the subsequent detoxification.

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TABLE 6. MORPHOMETRIC INDICATORS FOR CARP AND PERCH

Indicators	Number of fish	Carp	Perch
Body length, mm	12	141.0 \pm 4.0	160.0 \pm 6.0
Body weight, g	12	64.0 \pm 5.9	73.6 \pm 10.9
Liver weight, mg	12	1293.0 \pm 77.0	745.0 \pm 12.0
Relative liver mass, mg/g	12	21.6 \pm 1.5	9.9 \pm 0.7

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RELATION OF TRACE METAL BODY BURDENS AND GILL DAMAGE IN FISH
TO SURFACE WATER ACIDIFICATION FROM ATMOSPHERIC DEPOSITION

by

T.A. Haines¹, C.H. Jagoe², F.J. Dwyer³, and D.R. Buckler³

ABSTRACT

The possible relationship between trace metal body burden in fish and various physical and chemical factors in lakes was examined. The effect of acidity-related variables on body burdens in brook trout was determined. Also investigated were the effects of aluminum on gill structure of Atlantic salmon under laboratory conditions to determine whether a link exists the form and concentration of aluminum and damage to gill structures involved in ion regulation.

INTRODUCTION

Atmospheric deposition is a major source of the strong acids and trace metals reaching surface waters in the northeastern United States (Chan et al. 1986, Summers et al. 1986). Deposition of the acids may also increase the translocation of some metals, especially aluminum, from terrestrial to aquatic systems (Campbell and Stokes 1985, Goyer et al. 1985). Such metals may be directly toxic to fish or may be accumulated by fish to produce body burdens that are toxic to tertiary consumers including humans.

A number of investigators have reported that body burdens of trace metals are higher in fish from acidic lakes than in those from neutral or alkaline lakes (Dickson 1980, Fjerdingstad and Nilssen 1983, Hakanson 1980). Fish may accumulate metals directly from the external environment through the body integument (especially through the gill), or by way of the diet. Food chain uptake is especially important for metals occurring in organic form, such as methylmercury (Komarovskiy and Polishchuk 1981). Uptake across body membranes depends on the chemical form of the metal.

¹U.S. Fish and Wildlife Service, National Fisheries Contaminant Research Center, Orono Field Station, Department of Zoology, University of Maine, Orono, Maine, USA;

²Department of Zoology, University of Maine, Orono, Maine, USA;

³U.S. Fish and Wildlife Service, National Fisheries Contaminant Research Center, Route 1, Columbia, Missouri, USA.

Free ions are apparently more readily transported across membranes than are ions complexed to various ligands, and are generally more toxic (Campbell and Stokes 1985; Hutchinson and Sprague 1987). In acidic lakes the metal most toxic to fish appears to be aluminum; it is accumulated in the gills (Brumbaugh and Kane 1985, Karlsson-Norrgren et al. 1986), where it seemingly disrupts ion transport processes essential to osmoregulation (Leivestad et al. 1987, Neville 1985).

In the present study we investigated the possible relation between fish trace metal body burden and various lake physical and chemical factors, to determine whether acidity-related variables affect body burdens in brook trout (Salvelinus fontinalis), a common species in lakes in the northeastern United States. We further investigated the effects of aluminum on gill structure of Atlantic salmon (Salmo salar) under laboratory conditions, to determine whether there is a link between the form and concentration of aluminum and damage to gill structures involved in ion regulation.

MATERIALS AND METHODS

Six lakes were selected in Maine and New Hampshire along a southwest to northeast deposition pH gradient. The lakes were similar in size and elevation, and in having low specific conductance, but differed in acidity (Table 1). Each lake was visited twice; water samples were collected during both visits, and fish only during the second.

Water samples were collected with a plastic Van Dorn-type bottle at a depth of 0.1 m and at 1 m above the bottom in the deepest area of the lake.

Table 1. Physical and chemical characteristics of lakes examined. Color, specific conductance, and pH values are means of four samples per lake (two samples on two dates).

Lake	Area (ha)	Max. Depth (m)	Elevation (m)	Color (Hazen Unit)	Sp. Cond. ($\mu\text{S}/\text{cm}^3$)	pH
East Chairback	18	18	466	0	18	5.18
Ledge	3	6	911	48	17	5.43
Mountain Coburn	2	3	871	20	19	6.63
Mountain Rangeley	17	12	733	15	23	5.80
Solitude	2	6	729	33	20	4.95
Speck	4	8	999	22	18	5.08

They were transferred to polyethylene bottles that had been acid-washed and distilled water-rinsed, placed on ice, and returned to the laboratory for analysis. One aliquot of each sample was preserved with nitric acid and stored for later determination of metals. The pH was measured with a digital meter (Orion model 611) equipped with a liquid-filled glass combination electrode (Orion Ross). Specific conductance was measured with a temperature-compensating meter (Markson model 10). Apparent color was obtained by visually comparing the color of a 25-ml unfiltered water sample to platinum cobalt standards. We determined alkalinity by inflection point titration, following the method of Gran (Strumm and Morgan 1981). All analyses were performed in duplicate. Concentrations of elements were determined as follows: Na, K, Mn, and Zn by air-acetylene flame atomic absorption spectrophotometry (AAS; Perkin Elmer model 703); Ca and Mg by nitrous oxide-acetylene flame AAS; and Pb and total Al by graphite furnace AAS (Perkin Elmer model HGA 2200). Concentrations of SO_4 , NO_3 , and Cl were determined by ion chromatography (Dionex model 2110i). Anion samples were analyzed within 24 hr after collection.

Brook trout were collected with experimental (graded mesh) nylon gill nets fished overnight in the deepest area of each lake. After fish were removed from the net, they were placed on ice and returned to the laboratory, weighed (to the nearest gram), measured (total length, to the nearest millimeter), scale sampled for age estimation, and frozen individually in plastic bags. Whole 1-year-old fish were pooled in groups of three for homogenization, digestion, and analysis. The fish were chopped into small sections with a large knife and blended for 20 min in a polypropylene container fitted with a Teflon blade assembly. All equipment was washed in the following sequence between samples: detergent and tap water, 10% HCl, ultrapure water, distilled acetone. About 100 g of homogenate was lyophilized and then dry-blended for 10 min. Samples were stored in polyethylene bags in a desiccator until digested. Duplicate 0.5 g subsamples of dry homogenate were digested in 3 ml of 16 M HNO_3 in sealed pressure reaction tubes heated to 70°C for 48 hr. Digestates were diluted to 50 ml with 1% HCl.

We determined aluminum, cadmium, lead, and manganese in fish by graphite furnace AAS; selenium by graphite furnace AAS following hydrogen selenide formation in an automated hydride generator; mercury by automated cold vapor AAS; and copper and zinc by routine flame AAS. The quality assurance program involved analysis of U.S. National Bureau of Standards certified reference materials (tuna, oyster, pine needle, orchard leaves), in-house reference materials, and spiked samples. The results were within accepted limits for all metals. Fish trace metal concentrations were log transformed to approximate a normal distribution. Analysis of variance and Duncan's New Multiple Range Test were used to determine if trace metal concentrations in fish differed among lakes, and stepwise multiple regression was used to determine if lake physical or chemical factors were correlated with trace metal concentrations.

Laboratory exposures were conducted with a flow-through proportional diluter system supplied with reconstituted soft water as described by Cleveland et al. (1986). Total alkalinity of the test water was 200 ueq/L and calcium concentration about 3 mg/L. A 0.206 N mixture of sulfuric and

nitric acids (2:1) was added with an automated pipetting system to maintain the desired pH in the experimental aquaria. In the first year (1986) eggs and fry of Atlantic salmon were continuously maintained without aluminum at pH 7.2, 6.5, 6.0, 5.5, 5.0, and 4.5 in one diluter system. Simultaneously, other groups were maintained in a second diluter system at pH 5.5 with nominal aluminum concentrations of 38, 75, 150, and 300 ug/L. Aluminum was added as aluminum sulfate, and pH was adjusted as described above. Controls for this series were exposed to pH 5.5 with no aluminum, and unacidified test water at pH 7.2. All aquaria were maintained at 8°C. Eyed Atlantic salmon eggs were obtained from the Craig Brook (Maine) National Fish Hatchery. Eggs and the resulting fry were held under test conditions until 60 days past the median hatch date. Exposure procedures followed those described by Cleveland et al. (1986). Beginning at swim-up, the fish were fed an Atlantic salmon diet (ASD2-3 of the U.S. Fish and Wildlife Service) ad libitum three times daily, supplemented twice daily with live nauplii of brine shrimp (Artemia). Because the fish developed slowly at this low temperature, they did not swim up and begin feeding until near the end of the study. Five fish from each replicate were sampled for histological examination at 15, 30, and 60 days after the median hatching date.

In the second year, a series of four sequential replicated experiments were performed with post swim-up fry of Atlantic salmon to evaluate the effects of dissolved organic acids on aluminum toxicity. Fish were exposed to water at pH 5.7, without aluminum and with nominal aluminum concentrations of 52, 86, 140, and 24000 ug/L. They were sampled after 6 days of exposure. For the second experiment, 10 mg/L humic acid (Aldrich Chemical Co.) was added to the stock water. Fish were exposed to water at pH 5.7, without aluminum and with nominal aluminum concentrations of 780, 1300, 2160, and 3600 ug/L. They were sampled after 6 days of exposure. For the third experiment, 5 mg/L humic acid was added to the water, and fish were exposed to pH 5.7 water with nominal aluminum concentrations of 0 or 780 ug/L. The final experiment replicated the first (no humic acid added) to allow correction for the effects of increasing fish age on sensitivity for aluminum. Observed mortalities during the first and fourth experiments did not differ significantly.

Only live fish were selected for histological examination. Heads were severed just posterior to the opercular coverings, and immediately fixed in an ice cold mixture of 1% gluteraldehyde and 4% formaldehyde in 0.1 M phosphate buffer (pH 7.4), containing 10% sucrose (McDowell 1978). Tissues were stored under refrigeration in this solution until used. Two or three individuals from each treatment at each sampling date were randomly selected for examination by scanning electron microscopy (SEM).

Individual gill arches were dissected free of the branchial basket under a dissecting microscope, rinsed in 0.1 M phosphate buffer (pH 7.4) with 10% sucrose, and then postfixed in cold 1% osmium tetroxide in the same buffer for 1 hr to increase specimen conductance. Tissues were dehydrated through a graded ethanol series, and critical point dried under carbon dioxide. The arches were then glued to stubs with silver paste, and sputter coated with a gold palladium mixture to a nominal thickness of 250 angstroms. Specimens were examined with an AMR 1000A scanning electron microscope operating at 5 KV, and photographed on Polaroid film.

RESULTS AND DISCUSSION

The lakes ranged from 5.0 to 6.6 in pH and from -9 to 45 ueq/L in alkalinity (Table 2). The major cation was calcium and the major anion was sulfate, in contrast to many remote lakes where the major anion is bicarbonate (Wright and Henriksen 1983). The most likely source of the sulfate is atmospheric deposition, which annually ranges from 15 to 22 kg/ha in these watersheds (National Atmospheric Deposition Program 1987). Alkalinity declines of 50 to 70 ueq/L in these lakes were estimated by the acidification model of Wright and Henriksen (1983), suggesting that in the absence of acidic deposition, these lakes would have positive alkalinity and pH above 6. There was no consistent relation between trace metal concentration in water and lake acidity. We measured total rather than free ionic concentrations of metals, which have been reported to increase at low pH (Borg 1983; Schindler et al. 1980).

Concentrations of aluminum, copper, mercury, manganese, and selenium varied significantly among fish populations (Table 3). Stepwise multiple regression of fish metal burdens on lacustrine physicochemical factors indicated that chemical factors accounted for significant portions of the variance in metal concentrations in fish (Table 4). The metals accumulated by fish that were affected by lake acidity were mercury and manganese. Accumulation of mercury in brook trout increased at lower pH, and lake pH accounted for 71% of the variation in fish mercury concentration among lakes. The addition of specific conductance (a measure of ionic strength) to the regression increased to 83% of the proportion of variance accounted for. For manganese, the most important variables were manganese in lake water, which

Table 2. Major ion and trace metal concentrations in lake water.
Values are means of four samples (two samples per lake on two dates).

Lake	pH	Alk	Ca	Mg	Na	K	Cl	SO ₄	Al	Mn	Pb	Zn
		<-----µeq/l----->							<-----µg/l----->			
E. Chairback	5.18	-6	29	27	20	2	19	77	91	66	2	8
Ledge	5.43	4	60	16	15	4	13	99	286	31	<1	5
Mtn. Coburn	6.63	45	85	32	21	6	-	-	245	20	1	9
Mtn. Rangeley	5.80	13	53	28	14	4	15	93	45	30	<1	8
Solitude	4.95	-9	46	14	22	5	14	102	169	62	1	6
Speck	5.08	3	50	18	18	5	9	88	287	70	5	12

Table 3. Mean concentrations, $\mu\text{g/g}$ wet weight, of trace metals in age 1 fish. A sample consisted of three fish pooled. N is the number of pooled samples analyzed. In each column, means with the same superscript letter were not significantly different ($p < 0.05$; one way ANOVA, Duncan's New Multiple Range Test).

Lake	N	Metal				
		Al	Cu	Hg	Mn	Se
E. Chairback	1	3.25 ^{a,b}	0.54 ^a	0.049 ^{a,b}	11.2 ^a	0.320 ^a
Ledge	2	8.86 ^{b,c}	1.62 ^b	0.046 ^{a,b}	2.22 ^c	0.155 ^b
Mtn. Coburn	2	2.22 ^a	0.51 ^a	0.025 ^b	2.88 ^c	0.080 ^b
Mtn. Rangeley	1	6.05 ^{a,b}	0.47 ^a	0.060 ^{a,b}	2.36 ^c	0.160 ^b
Solitude	2	14.73 ^c	1.27 ^b	0.130 ^c	7.34 ^b	0.105 ^b
Speck	2	4.89 ^{a,b}	0.48 ^a	0.085 ^a	6.85 ^b	0.205 ^{a,b}

accounted for 74% of the variance in manganese in fish, and pH, which increased the variance explained to 89%. For the remaining three metals, magnesium in water was the most important variable for aluminum in fish, zinc in water for copper in fish, and sulfate in water for selenium in fish. Water concentration of aluminum was the second most important variable for both copper and selenium in fish.

Acidity can influence trace metal uptake by fish through several mechanisms. For mercury, the form most readily accumulated by fish is methylmercury. The uptake is not increased by low pH (Rodgers et al. 1987), but bacterial methylathion of mercury in the water column is enhanced at reduced pH (Xun et al. 1987). This increased methylathion would result in increased concentrations of methylmercury in lake water at reduced pH and could account for the increased concentration of mercury in fish from acidic lakes. Increased concentrations of mercury have been reported in fish from soft water lakes (Rodgers and Beamish 1983; Scheider et al. 1979), which may account for the importance of specific conductance in the regression model. Ionic strength of water may affect fish mercury concentration because reduced concentration of ions in water, especially divalent cations, increases the permeability of gill membranes (Franzin and McFarlane 1980; McFarlane and Franzin 1980; Part et al. 1985). Certain metals, including manganese, become more soluble as pH decreases, and the free ionic species predominates at pH < 6 (Campbell and Stokes 1985). These factors would make manganese more available for uptake across the gill surface by fish inhabiting acidic lakes.

Magnesium concentration in water probably affects trace metal content of fish by increasing membrane permeability, as discussed above. Winner and

Table 4. Results of stepwise multiple regression analysis of fish tissue trace metal concentrations as dependent variables and lake physical and chemical factors as independent variables. The best one and two variable models are given for metals that varied significantly among lakes.

Metal	Number of Variables	Model	r ²	p
Al	1	3.18 - 1.85 log Mg	0.74	0.0015
	2	4.60 - 2.15 log Mg - 0.46 log Al	0.87	0.0002
Cu	1	1.24 - 1.55 log Zn	0.81	0.0004
	2	1.85 - 1.23 log Zn - 0.68 log Mg	0.94	0.0001
Hg	1	0.78 - 0.37 pH	0.71	0.0022
	2	-2.28 - 0.39 pH + 2.50 log cond.	0.83	0.0019
Mn	1	-1.05 + 1.05 log Mn	0.74	0.0013
	2	-4.89 + 2.07 log Mn + 0.40 pH	0.89	0.0005
Se	1	7.66 - 4.31 log SO ₄	0.63	0.0061
	2	9.89 - 5.06 log SO ₄ - 0.58 log Mg	0.77	0.0056

Gauss (1986) found that increased concentration of calcium or magnesium reduced the bioaccumulation of copper, cadmium, and zinc by Daphnia sp. Part et al. (1985) reported that calcium and magnesium in water reduced the transfer of cadmium from water into perfused fish gills, probably by changing the permeability of the gill epithelium. Conversely, water hardness and alkalinity had no effect on the uptake of copper by rainbow trout, salmo gairdneri (Lauren and McDonald 1986). The effect of zinc or sulfate concentration in water on trace metal uptake by fish is unknown.

Gills of fish reared under control conditions appeared normal, as described by Laurent and Dunel (1980), and free of lesions when examined by SEM (Figure 1A). Chloride cells were present in both primary and secondary lamellar epithelium and were distinguished by a denser surface pattern of shorter microridges and microvilli (Figure 1B). Exposure to low pH alone for up to 60 days post-hatch resulted in little change in gill morphology. At pH 4.5, the lowest pH tested, there was some apparent swelling of epithelial cells along the primary lamellae and increased amounts of mucus produced (Figure 2A). Exposure to aluminum concentrations of ≥ 75 ug/L in the absence of humic acid produced serious alterations in gill structure. At 75 ug/L, secondary lamellae did not develop normally, and large areas of the filament were devoid of them (Figure 2B). These present were concentrated at the distal end of the filaments, and appeared small and stubby. Exposure to

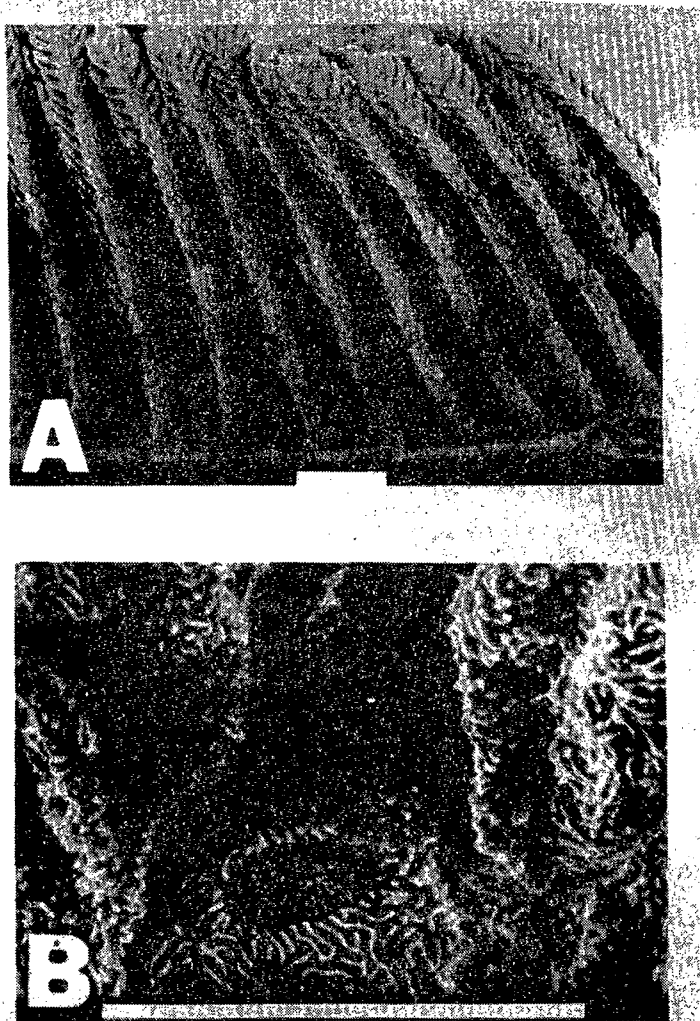


Figure 1. Scanning electron micrographs of normal gills of post-swim up Atlantic salmon fry exposed to pH 7.2 water without aluminum or humic acid. A: Gill filaments or primary lamellae extending from gill arch. Bar = 100 microns. B: Chloride cell on primary lamellar epithelium. Bar = 10 microns.

150 ug/L caused epithelial proliferation, especially of chloride cells, leading to fusion of adjacent primary lamellae (Figure 2C). Exposure to 300 ug/L caused a similar, but more severe effect (Figure 2D). At the highest concentration, individual filaments were barely distinguishable.

Alterations in morphology similar to those produced in fry during the 1986 experiments were also seen in fish from the 1987 experiments that were exposed to 240 ug/L aluminum in the absence of humic acid. Individual gill filaments were recognizable, but many sections were devoid of secondary lamellae (Figure 3A). Apical crypts were observed in chloride cells. Gill structure was normal in fish exposed to humic acid in the absence of aluminum (Figure 3B). In water containing 10 mg/L humic acid exposure to total alumi-

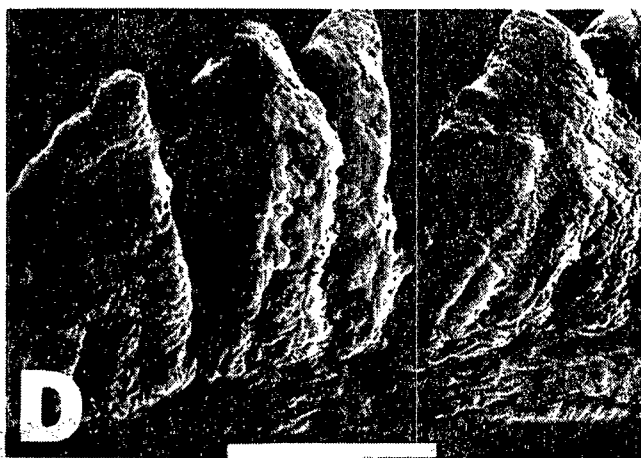
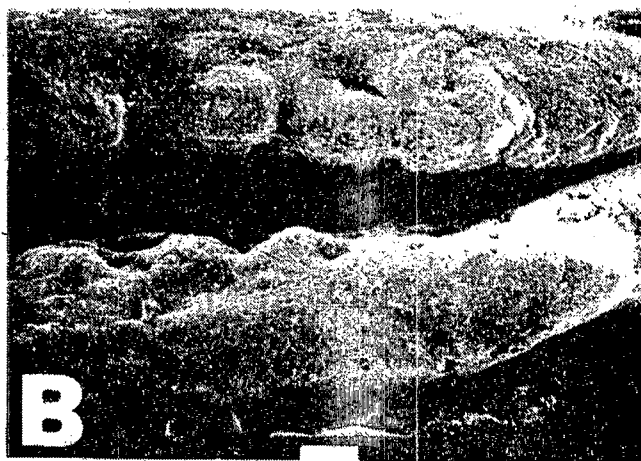
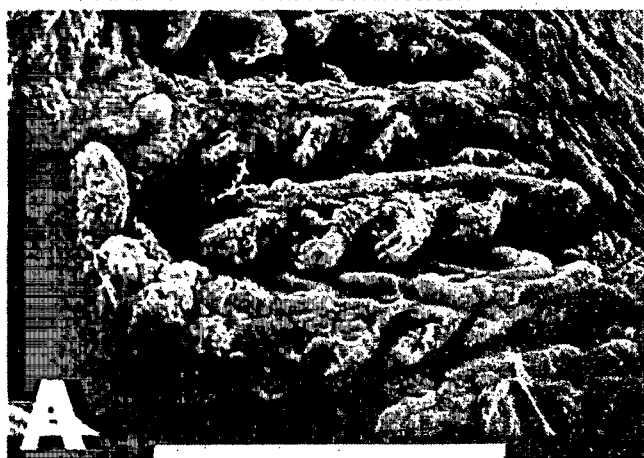


Figure 2. Scanning electron micrographs of gills of 60 day old Atlantic salmon fry exposed to low pH and aluminum without humic acid (all bars = 100 microns). A: pH 4.5, no aluminum. B: pH 5.5, 75 ug/L aluminum. C: pH 5.5, 150 ug/L aluminum. D: pH 5.5, 300 ug/L aluminum.

num concentrations as high as 2160 ug/L--nearly 10 times more aluminum than was necessary to produce striking morphological alterations in the absence of humic acid--produced no visible morphological effects (Figure 3C). Exposure to 3600 ug/L total aluminum in water containing 10 mg/L humic acid produced lesions identical to those produced by lower aluminum levels in the absence of humic acid (Figure 3D)--loss of secondary lamellae, epithelial hyperplasia, and development of apical crypts on chloride cells.

At lower concentrations of humic acid (5 mg/L), lower concentrations of aluminum caused morphological effects. Exposure to 78 ug/L total aluminum produced slight but noticeable alterations (Figure 3E). Secondary lamellae

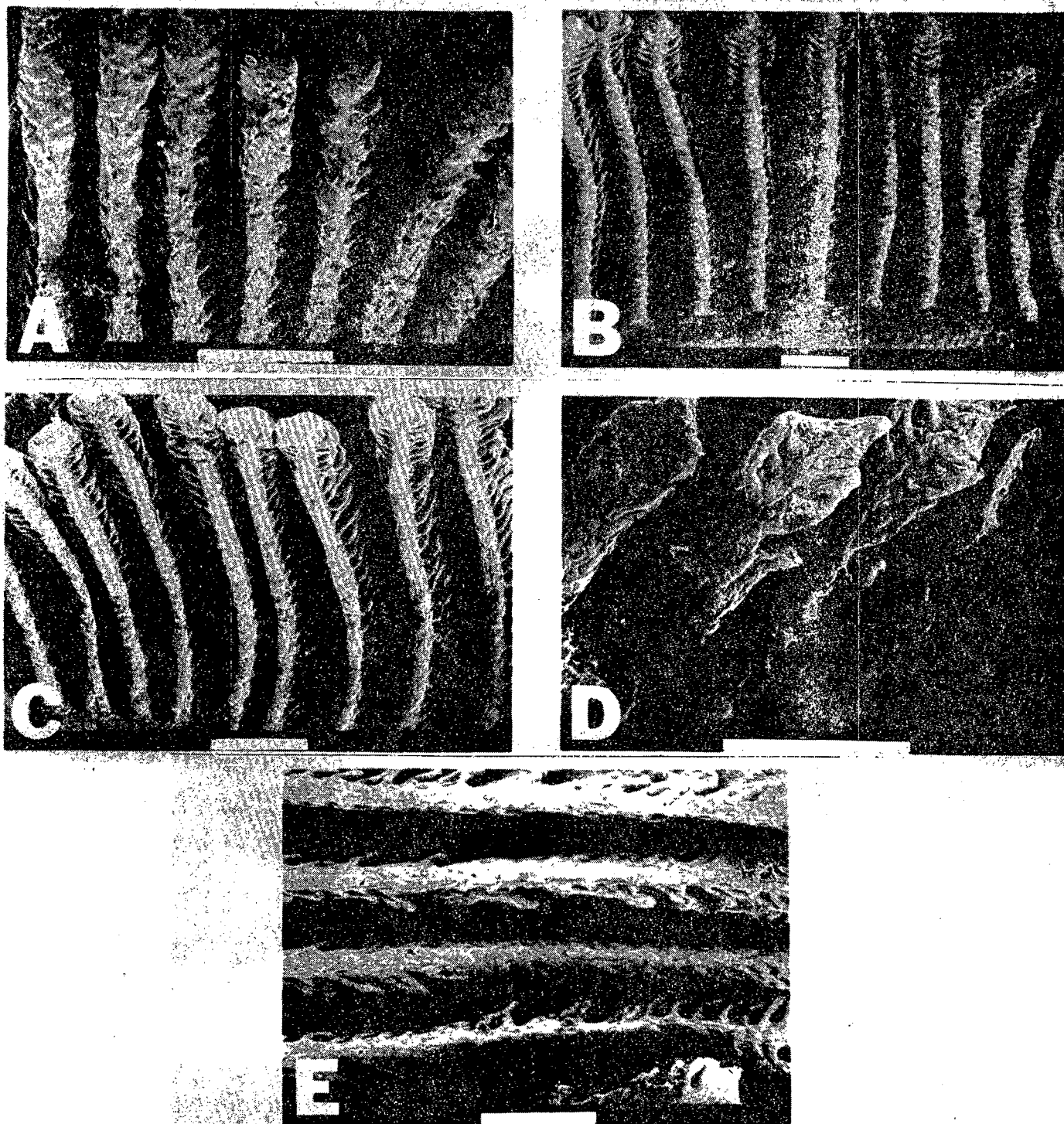


Figure 3. Scanning electron micrographs of gills of post-swim up Atlantic salmon fry exposed to low pH and aluminum with and without humic acid (all scale bars = 100 microns). A: pH 5.7, 240 ug/L aluminum, no humic acid. B: pH 5.7, no aluminum, 10 mg/L humic acid. C: pH 5.7, 2160 ug/L aluminum, 10 mg/L humic acid. D: pH 5.7, 3600 ug/L aluminum, 10 mg/L humic acid. E: pH 5.7, 780 ug/L aluminum, 5 mg/L humic acid.

were fused at the distal ends of the primary amellae, giving the ends of the filaments a clubbed look.

Apical crypts of chloride cells, normally present after seawater acclimation, were observed in fish exposed to pH 4.5 in the absence of aluminum (Figure 4A). A similar effect was previously reported by Leino and McCormick (1984). Exposure to aluminum at concentrations above about 150 ug/L at pH 5.5 also caused the development of apical crypts in the absence of humic acid. Pores of larger diameter were also observed in these aluminum-exposed fish (Figure 4B). In cross section, these were found to be lined with chloride cells (Jagoe et al. 1987). Humic acid (10 mg/L) prevented the development of apical crypts at aluminum concentrations up to 2160 ug/L (Figure 4C), but apical crypts were numerous in fish exposed to 3600 ug/L aluminum (Figure 4D). Some apical crypts were also observed after exposure to 780 ug/L aluminum in water containing 5 mg/L humic acid.

It seems likely that only free ionic hydroxy aluminum produces the morphological abnormalities. At high humic acid and low aluminum levels, virtually all of the aluminum is probably chelated to organic ligands; consequently the hydroxy aluminum fraction is low and damage is prevented. As the aluminum content of the water increases, the humic acid binding sites become saturated and abnormalities again appear as the hydroxy aluminum concentration increases. The observation that gill damage begins to appear at higher total aluminum levels with increasing humic acid concentration is consistent with this idea. Our attempts to confirm this hypothesis by analytically fractionating aluminum into chelated and ionic forms failed, possibly because of the high concentrations of organic acids or aluminum, or both.

The relatively greater morphological alteration observed in the younger Atlantic salmon (1986 study) supports the belief that young fish are the less dependant on gill respiration (El-Fiky et al. 1987). A similar degree of gill abnormality would kill an older fish that depended on gill respiration, whereas younger fish can survive, at least until they come to rely more on gill respiration. Chloride cell alterations observed in this study are consistent with increased (or attempts to increase) ionic transport activity in the gill. It appears that some aluminum finds its way into chloride cells (C. H. Jagoe, unpublished data; Youson and Neville 1987), which may affect chloride cell function to some degree. If each chloride cell is functioning less well, the only possible strategy open to the individual fish may be to form more cells, leading to epithelial hyperplasia and the observed abnormalities.

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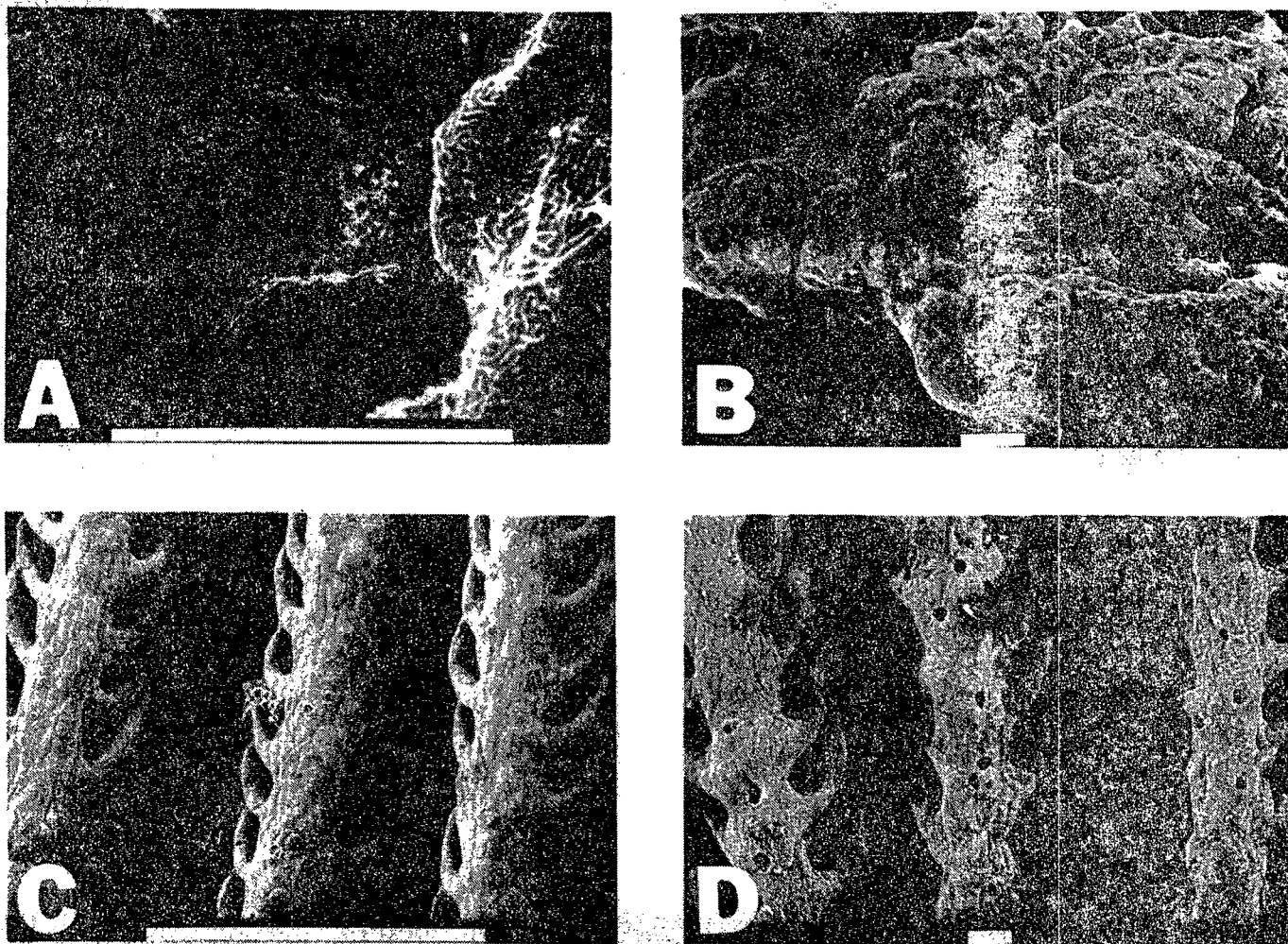


Figure 4. Scanning electron micrographs of gill epithelial surface of Atlantic salmon fry exposed to various levels of pH, aluminum and humic acid. A: pH 4.5, no aluminum, no humic acid (bar = 10 microns). B: pH 5.5, 150 ug/L aluminum, no humic acid (bar = 10 microns). C: pH 5.7, 2160 ug/L aluminum, 10 mg/L humic acid (bar = 100 microns). D: pH 5.7, 3600 ug/L aluminum, 10 mg/L humic acid (bar = 10 microns).

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BUFFER CAPACITY OF FRESHWATER ECOSYSTEMS FOR HEAVY METALS
AND HYDROBIOLOGICAL PARAMETERS DETERMINING IT

by

A.M. Nikanorov¹, A.V. Zhulidov¹, N.A. Dubova¹,
V.F. Gekov¹, I.Y. Kamov¹

ABSTRACT

Relationships between seasonal and yearly dynamics of phytoplankton biomass with the background concentration of copper in the river Usman are examined. The investigation seeks to directly estimate the degree and character of hydrobiota influence on the chemical composition of freshwater systems because developments in this area are of special importance for understanding the buffer capacity of freshwater systems for heavy metals.

ECOSYSTEM BUFFER CAPACITY

The problem of determination of freshwater ecosystem buffer capacity, which is the parameter allowing one to estimate the dose of a pollutant entering an aquatic ecosystem that does not seriously disturb the natural mode of functioning of the whole ecosystem, is one of the most urgent problems in modern water chemistry and ecology (Izrael et al. 1985, Parker et al. 1982, Izrael 1984, Konemann 1984). (This formulation is preliminary because it includes elements of uncertainty in relation to the options "seriously" and "functioning.")

Based on theoretical works (Ghilarov and Timonin 1972, Breymeyer 1979, Braginsky 1981, Trojan 1979 and 1984, Ravera 1984, Kimmerer 1984, Brown 1984, Kolasa and Biesiadka 1984, Remmert 1984, Barbault 1985, Rygg 1985, Stenseth 1985), one may assume that freshwater ecosystem buffer capacity in the above context is related to stability (homeostatis) of these ecosystems and, in particular, to species diversity, trophic levels and size structure of populations. In practice however, only species composition of some communities or trophic levels but not ecosystems on the whole is usually known rather well. Within the limits of individual trophic levels, stability is probably determined by interspecific competition (Murdoch et al. 1984, Thorp and Gothran 1984, Reice 1985). Thus, different trophic levels, as communities,

¹Hydrochemical Institute, Rostov-on-Don, USSR.

may reach equilibrium with habitat independently of each other (Brey Mayer 1979, Matsunaga et al. 1984).

It also turns out that there is a positive regression between freshwater ecosystem area and species diversity of hydrobiota and the structure of macrophyte cenosis (Bronmark 1985). Besides, in a number of cases when determining the structure and stability of communities, the leading species or complex of abundant species (Burkovsky and Azovsky 1985) included in the composition of biogeocenotic nucleus are very important. Variation in species composition of ecosystems mostly occurs unevenly, changing trends of many important biological processes (Futuyma 1973, Zhirmunsky et al. 1981).

Other difficulties involve the necessity of analysis of the processes influencing population dynamics and processes of interaction between community components (competition, predation, etc.), the need for information about the ecosystem informative structure, the difficulties in determination of taxonomic affiliation of a number of groups of invertebrates and lower plants, and also the poor knowledge of homeostasis mechanisms (and even individual organisms) comparing to the most important pollutants (Trojan 1979 and 1984, Nikanorov et al. 1982, Peterfi et al. 1983, Smalls and Cannon 1983, Nikanorov and Zhulidov 1984, Kimmerer 1984, Smith and Kallf 1985, Maksimov et al. 1985, Barbault 1985). The above problems do not allow one to quantify buffer capacity through species diversity even in general now, although we think that the prospects of such an approach are rather good. Wood (1983) showed, however, that the influence of metals upon phytoplankton is in close correlation with parameters characterizing complexation ability and does not depend on the composition and structure of a community.

It does not seem possible at present to consider the option "buffer capacity" and to compare it with the stability concept mainly because of the terminological uncertainty of this term (Futuyma 1973, Feodorov 1975, Solntzeva 1982, Nazarov 1983, Sergeev 1984). In conformation with dynamic systems in general, stability may be defined as an ability of a moving system to deviate slightly from some track at perturbations. If we consider perturbation as variation in primary condition of the system and deviation as a measure for differentiating between perturbed motion (functioning) and unperturbed motion, we come to the option of uniform and orbital stability according to Lyapunov. If the tracks still possess some properties of unperturbed tracks, we come to stability according to either Lagrange or Poisson. Thus, in an attempt to formulate the option "stability," it is necessary to understand which type of non-sensitivity is of greatest interest or which responses to perturbation are equivalent (or not equivalent).

The option "stability" developed in physico-mathematical fields of natural science may be used also for ecological system (Kindlmann and Leps 1985). In this case, however, one should keep in mind that, in the selection of parameters and variables on the basis of which the concept of stability is considered, the subsystem of a certain ecosystem must be relatively autonomic so that we can neglect the effect of the variables not used. Besides, time and space scales within the limit of which the concept of stability is considered must be logically correlated with the selected type of equivalence of ecosystem responses on perturbation. The option "ecosystem stability"

makes no sense if these facts are not taken into account. It should be specially indicated that arbitrary assumptions result from the fact that the concept of stability turns out to be inapplicable to real ecosystems due to the following reasons (Kindlmann and Leps 1985, Nunney 1985).

- It is assumed that the system in normal conditions is in equilibrium which is not true.
- System stability without information on the size of the field is investigated.
- Perturbations of permanent character in ecosystems are not taken into account.

Owing to the above reasons, the option of stability in ecology and geography is of non-formalized character (Futuyma 1973, Armand 1983, Preobrazhensky 1983, Svetlosanov 1983, Ulrich 1984, Gurtz and Wallace 1984, Noon et al. 1985). We must keep in mind that heavy metals (for instance, lead in concentrations up to 64 ppb when its background concentration in water is 0.1-0.6 ppb) stimulates reproduction of some invertebrates (Berglind et al. 1985).

Taking into account the above, the authors attempted to estimate buffer capacity through the interaction of the most important parameters determining behavior of pollutants (heavy metals, in particular) in freshwater ecosystems (Izrael et al. 1985). Parameters conditionally attributed to hydrobiological factors are discussed below.

Laboratory investigations indicated that hydrobiota (shell-fish, in particular) affect the forms of occurrence of extremely toxic heavy metals in natural waters (Nikanorov et al. 1985). Because laboratory results can be transferred to the processes occurring within natural ecosystems to quite a limited degree, however, continuous natural investigations at the river Usman in the Voronezh Biosphere Reserve were carried out. The reserve was chosen for long-term investigations because of the specificity of the problems of investigation carried out. Besides, Voronezh Reserve is located in a natural zone that is convenient for such investigations--forest-steppe characterized by optimal conditions for development of all biological components of an ecosystem. It is also important that there are laboratories in the Reserve providing short-term initial processing of the information. The area scheme, hydrographic network, and water regime of the river Usman are presented in the work of Nikanorov et al. (1985).

Because all the trophic groups of hydrobiota cannot be covered by long-term field investigations, it was decided to bend every effort to phytoplankton producers, often determining a whole number of the most important hydrochemical and hydrobiological parameters. Copper was used for this complex of investigations. Selection of copper for modeling purposes was related to the high biological activity of the element and its distinct ability to form complexes with dissolved organic matter (Brown and Rattigan 1979, Sposito 1981, Giesy 1983, Giesy et al. 1983, Borgmann and Ralph 1983 and 1984, Reddy and Rao 1983, Cairns et al. 1984, Winner 1984 and 1985, Borgmann and Charlton 1984, Rygg 1985, Blaylock et al. 1985).

The object of our investigations was to study relationships between seasonal and yearly dynamics of phytoplankton biomass in model biological current of the Usman with the background concentration of dissolved copper in its water.

The information on seasonal and yearly dynamics of phytoplankton biomass and dissolved copper concentration in the Usman is presented in Figures 1 and 2 and Table 1.

The information presented (in Figures 1 and 2) proves that seasonal dynamics of phytoplankton biomass in the Usman may reflect the following regularity--growth of biomass from winter to summer (autumn) and decrease by winter. Seasonal dynamics of dissolved copper concentration in the Usman is characterized, however, by an inverse relationship: copper concentration in water is maximum in winter and minimum in summer (autumn).

Quantification of the relationship between dissolved copper concentration and phytoplankton biomass is realized by processing of the results of natural investigations with mathematical statistics. To adequately describe the phenomenon studied, however, it is necessary to determine the form of the relationship between the variables studied. The form of the relationship

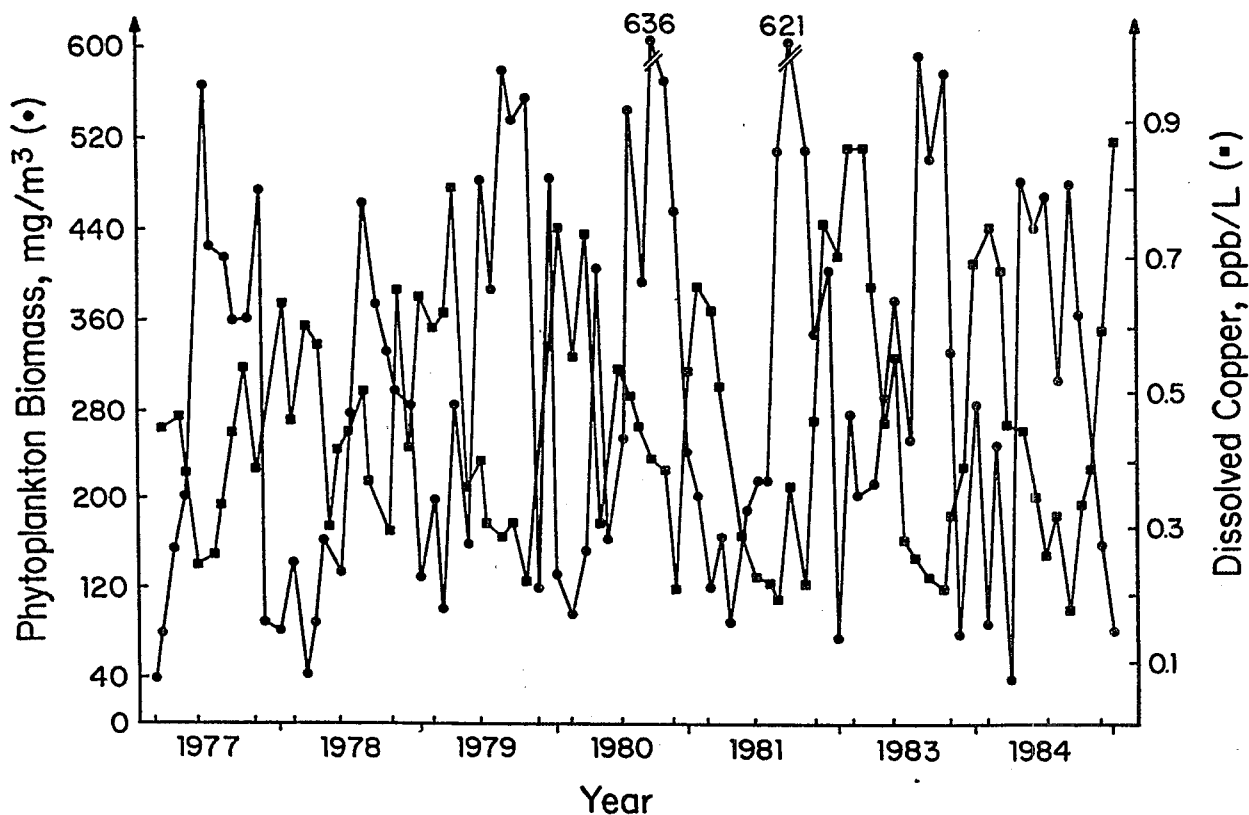


Figure 1. Monthly average of many-year variability of phytoplankton biomass and dissolved copper in the Usman River in the Voronezh Biosphere Reserve.

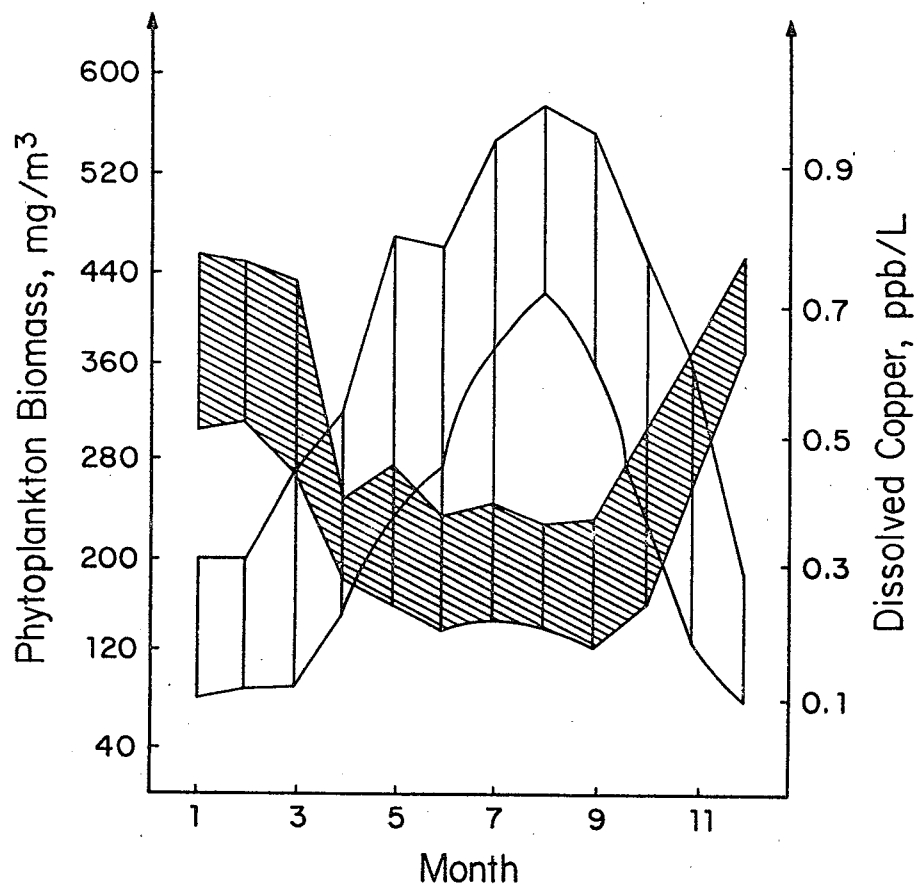


Figure 2. Confidence interval of 95% precision for many-year average of phytoplankton biomass and dissolved copper concentration in the Usman water (1977-1981, 1983, 1984).

depends on the character of the process studied and is determined by investigation of physico-chemical and biological regularities. Then, parameters of the constraint equation are quantified on the basis of statistical processing of field results.

We may assume that copper (M) entering a stream consists of five components:

- M_B - is copper left in water in dissolved form
- M_O - is copper sorbed and accumulated by phytoplankton (by all hydrobiota in more general case)
- M_{Δ} - is copper that moved to bottom sediments in the process of sedimentation of suspended organic and mineral material
- $M_{a\Delta}$ - is dissolved copper sorbed at the surface of bottom sediments directly from water

TABLE 1. AVERAGE CHANGE OF DISSOLVED COPPER CONTENT AND PHYTOPLANKTON BIOMASS IN THE USMAN, 1977-1981 AND 1983-1984

Month	Dissolved copper, ppb/L	Phytoplankton biomass, mg/L ³
January	0.637 \pm 0.12	139.8 \pm 59.7
February	0.636 \pm 0.107	143.7 \pm 55.1
March	0.593 \pm 0.129	184.8 \pm 96.3
April	0.536 \pm 0.056	238.5 \pm 87.3
May	0.386 \pm 0.098	357.4 \pm 117.7
June	0.319 \pm 0.079	371.1 \pm 91.2
July	0.332 \pm 0.084	471.9 \pm 77
August	0.316 \pm 0.007	504.4 \pm 79.1
September	0.307 \pm 0.091	472.9 \pm 82.4
October	0.401 \pm 0.123	341.7 \pm 103.4
November	0.545 \pm 0.106	252.9 \pm 114.4
December	0.706 \pm 0.058	144.0 \pm 58.2

- M_{aB} - is copper adsorbed by suspended solids and contained in them.

In this case, the many-year relationship between dissolved copper content and phytoplankton biomass is considered. So, the processes determining copper behavior in water may be neglected.

On the whole, the copper material balance equation may be written:

$$M = M_B + M_{a\Delta} + M_{aB} + M_0 + M_{\Delta} \quad (1)$$

As for quantity of copper adsorbed by bottom sediments, it is proportional to metal concentration in river water - C_{MB} .

$$M_{a\Delta} = \alpha' C_{MB} = \alpha' \frac{M_B}{v} \quad \text{or} \quad (2)$$

$$\frac{M_{a\Delta}}{v} = \frac{\alpha'}{v} \cdot \frac{M_B}{v} = \alpha \frac{M_B}{v}$$

so we finally obtain:

$$M_{a\Delta} = \alpha M_B \quad (3)$$

As a first approximation, the quantity of metal absorbed at suspension is proportional to suspension quantity and metal concentration in water. Taking into account physico-geographic and geological features of the Voronezh Reserve area and specific features of the Usman, however, suspension content in river water may be taken as a value slightly varying during a year. (Although in the flood period, suspension content increases.) Equality determining quantity of copper absorbed at suspended solids in unit water volume is written as:

$$\frac{M_{aB}}{v} = \gamma \frac{M_B}{v} \quad \text{or} \quad M_{aB} = \gamma M_B \quad (4)$$

where γ is a proportionality factor.

Hydrobiota accumulation ability in relation to dissolved metals is usually expressed by the accumulation factor, K_H , (Nikanorov et al. 1985). The accumulation factor is assumed to be the ratio between the metal concentration in the tissue of species studied (per unit dry weight) and the content of the same metal in similar water volume taken from the hydrobiota habitat. Thus, copper content in phytoplankton with regard for accumulation factors may be written as:

$$M_\delta = K_H M_B C_\psi \quad (5)$$

where C_ψ is phytoplankton mass in unit water volume.

The quantity of copper moved to bottom sediments with dead phytoplankton is estimated as:

$$M_\Delta = K_H M_B \beta C_\delta \quad (6)$$

where β is the mortality factor.

With regard for Equations 3 through 6, Expression (1) may be written as:

$$M = M_B + \alpha M_B + \gamma M_B + K_H M_B C_\phi + K_H M_B \beta C_\phi \quad (7)$$

or

$$M = M_B [I + \alpha + \gamma + K_H(I + \beta) C_\phi]$$

Using copper concentration per unit water volume and introducing the terms:

$$M_M = \frac{M}{v} ; C_{MB} = \frac{M_B}{v} ; a = I + \alpha + \gamma ; B = K_H(I + \beta) \quad (8)$$

we get the equation relating dissolved copper concentration to phytoplankton biomass in a unit water volume:

$$C_{MB} = \frac{C_M}{a + B \cdot C_\phi} \quad (9)$$

or for convenience of statistic processing dividing

$$C_{MB} = \frac{I}{A + B C_\phi} \quad (10)$$

where

$$A = \frac{a}{C_M} ; B = \frac{B}{C_M}$$

Introducing a new variable $Y = \frac{I}{C_{MB}}$, we get a straight line equation

$$Y = A + B \cdot C_\phi \quad (11)$$

With regard for considerable natural daily variability of C_{MB} and C_ϕ values (see above), estimation of the statistical relationship was conducted between averaged values.

For averaging all data, the array was divided into 12 groups according to the months of all years of investigations. Average values for C_{MB} and C_ϕ (Table 1) were estimated for each group. Figure 2 shows many-year average variations in C_{MB} and C_ϕ , which quantitatively proves the form of constraint Equation 10. Values of equation parameters (Equation 10) were determined by least-squares technique on the basis of table data (Equation 11).

Thus, we have

$$C_{MB} = \frac{I}{0.94 + 0.00477 C_{\psi}} \quad (12)$$

The correlation factor between many-year average values based on the months is 0.91.

Relationship 12 is shown in Figure 3. The off-side point (shown as a cross in Figure 3) corresponds to April, the period of the Usman ice cover break and flood when the content of suspension in the river and, hence, the content of copper sorbed on this suspension is increasing. Because the portion of copper sorbed on suspension may be considerable, this stimulates disturbance of Relationship 10 obtained if the inorganic suspension concentration during a year is uniform.

We must note that, in case you are looking for Relationship 11 based on direct measurement of C_{MB} and C_{ψ} values in the samples taken on the same day (total number of such pairs is 107), the regression relation of these parameters is poor (correlation factor approaches 0.2). This result reflects the general fact of relationship distortion with inaccurately present regressors (Davies and Hutton 1975). In our case, the interfering factors in the process of determination of interrelationships between processes are considerable non-uniformity of dissolved copper distribution and, in particular, phytoplankton in space and time and, hence, poor representativeness of some samples.

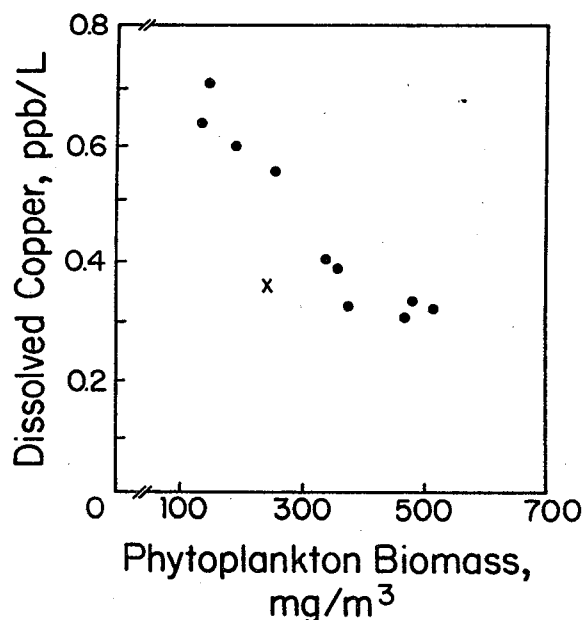


Figure 3. Many-year-average relationship between dissolved copper concentration and phytoplankton biomass in the Usman River (Voronezh Biosphere Reserve).

Mainly due to the impact of these factors, variability of dissolved copper concentration and phytoplankton biomass in the Usman water samples taken simultaneously reaches 4-fold (December 29, 1980) and 41-fold (August 29, 1984), correspondingly, and it may be even more in the samples taken at intervals of several hours or days. Thus, averaging is levelling the natural variability of the studied processes considerably. Averaging is conducted in such a manner that the efficient noise suppression would be combined with insignificant distortion of basic processes. Taking into account the above said, it is clear why the correlation is found between alga biomass and concentration of chemicals in the environment and, in particular, nutrients (Jones et al. 1984, Misztal et al. 1984).

Based on the data presented in the monograph of A.M. Nikanorov et al. (1985), one may judge the accumulation ability of hydrobiota in relation to chemical elements. Because of the methodological problems related to sampling and analysis of ultrasmall samples of phytoplankton, it was impossible to study specific peculiarities of the factors of chemical element accumulation by phytoplankton in the Usman. There are no reasons, however, to assume that accumulation ability of plankton micro-algae would be different from that of freshwater invertebrates.

Kinetics of metal absorption usually consists of two stages: the light one when fixation of ions on the surface of cells occurs with high pH during photosynthesis and the dark one characterized by ion transport to the cells with low pH due to increase of local carbonic acid concentration with respiration (Morel 1985). In this case, the rate of metal absorption by phytoplankton intensity of metal concentration decreases in water. Increase of metal concentration in bottom sediments and alga biomass growth are interrelated (Jackson 1987, Menarques and Lanza 1983, Hellmann 1983, Hamilton-Taylor et al. 1984, Falkner et al. 1984, Morel 1985, Izrael et al. 1985), fluctuating within 24 hours.

Metal concentration in phytoplankton cells depends not only on the concentration of metals in natural environment (Parker et al. 1982, Menarques and Lanza 1983, Jones et al. 1984, Les and Walker 1984, Vymazal 1984), but on the luminance, pH at the interface membrane-medium, balance constants, rate of diffusion (accumulation) through cell membranes, physiological condition, and taxonomic affiliation of algae (Briand et al. 1978, Stary et al. 1983, Falkner et al. 1984, Skowronski 1984, Flatau et al. 1984, Goreonova et al. 1984). Laboratory investigation showed that the rate of phosphorus consumption by phytoplankton depends on the size of the cells but not on the taxonomic affiliation (Smith and Kallf 1985). This affiliation, however, is disputed (Sommer and Kilham 1985) and so needs additional investigation.

Taking into account the above, we understand daily variability, intensity of metal accumulation by phytoplankton and, hence, daily variability in the concentration of dissolved metals in water. The last is exposed to serious influence of hydrophysical features of water bodies and streams, nonuniformity of microecological conditions within the water column (both vertical and horizontal), errors due to sampling and analysis of dissolved forms of metals, and other factors. All these parameters automatically determine daily variability of phytoplankton biomass distribution as well. Summariz-

ing the above, we may conclude that the content of chemical elements in freshwater ecosystems is directly related to the general value of hydrobiota biomass and its seasonal dynamics within these ecosystem (Figures 3 and 4).

The relationship between variation in biomass and season of the year for phytoplankton is also true for zooplankton and periphyton (Dreu 1976, Pork and Lokk 1979, Boynton et al. 1983, Izrael et al. 1985) and probably may be considered as general for all hydrobiota.

Speaking of seasonal variability of hydrobiota biomass in freshwater ecosystems and its role in water chemical composition formation in freshwater ecosystems, we note that some representatives of hydrobiota, and, in particular, bivalve mollusks, possess similar geochemical function owing to considerably varying filtration in different seasons. The most active filtration and intensity of feeding is registered in summer months but in autumn, winter, and early spring filtration rate decreases sharply up to full stop (Alimov 1981). Filtration intensity of bivalve mollusks increases with their weight and size (Alimov 1981).

Discussing the problem of hydrobiota influence upon freshwater ecosystem chemical composition, we note that the degree of this influence is related to the intensity of metabolism. Hydrobiota metabolic rate is determined, however, not only by seasonal variations in ambient temperature but by the peculiarities of their life cycles and, in particular, the rate of physiological and reproduction activity (Alimov 1981).

Speaking of hydrobiota metabolic rate, we must note that numerous investigations proved close relationships between the rate and intensity of exchange and the size of freshwater organisms. In most cases, the metabolic rate in animals increases but its intensity decreases if their weight is increasing. Summarizing investigations on this problem and quantification of relationship between metabolic rate and size of the freshwater bivalve mollusks were carried out by A.F. Alimov. The results of measurement of the metabolic rate of bivalve mollusks indicate that these animals do not possess either generic or specific character of exchange and metabolic rate is a function of their weight. We may assume that there are no significant differences in metabolic rate (Alimov 1981) between the animals of the same size that belong to different families Bivalvia. This phenomenon is not analyzed from the point of view of deep understanding of hydrobiota role (in particular, Bivalvia) in formation of freshwater ecosystem chemical composition. Taking into account the role of animals in ecosystem functioning (in particular, earth biogeocenoses), we may be more sure of the importance of the above phenomenon for the processes of formation of water chemical composition in water bodies and streams.

The investigation conducted is actually an attempt to directly estimate the degree and character of hydrobiota influence on the chemical composition of freshwater ecosystems, because investigations in this direction are of special importance for development of buffer capacity of freshwater ecosystems for heavy metals. While carrying out the above investigations, however, the facts indirectly proving hydrobiota influence upon metal content in freshwater ecosystems were revealed. Only this phenomenon, anyway, can satisfac-

torily explain disparity between historical dynamics of lead and mercury in freshwater invertebrate tissue and the relatively stable level of metals in bottom sediments of the Usman (Nikanorov and Zhulidov 1984, Nikanorov et al. 1982, 1983, 1985).

In characterizing hydrobiological parameters determining buffer capacity of freshwater ecosystems for heavy metals, we note that, from the conceptual point of view, the most important fact that should be taken into account is that the action of the given group of parameters is directed mainly to partial excretion of metals introduced to ecosystem from the biogeochemical cycle by way of their burial in bottom sediments in the process of sedimentogenesis (Jackson 1978, Parker et al. 1982, De Master and Nittroner 1983, Hamilton-Taylor et al. 1984). In this case, the measure of ecological efficiency of metal excretion from the biogeochemical cycle by way of their burial in bot-

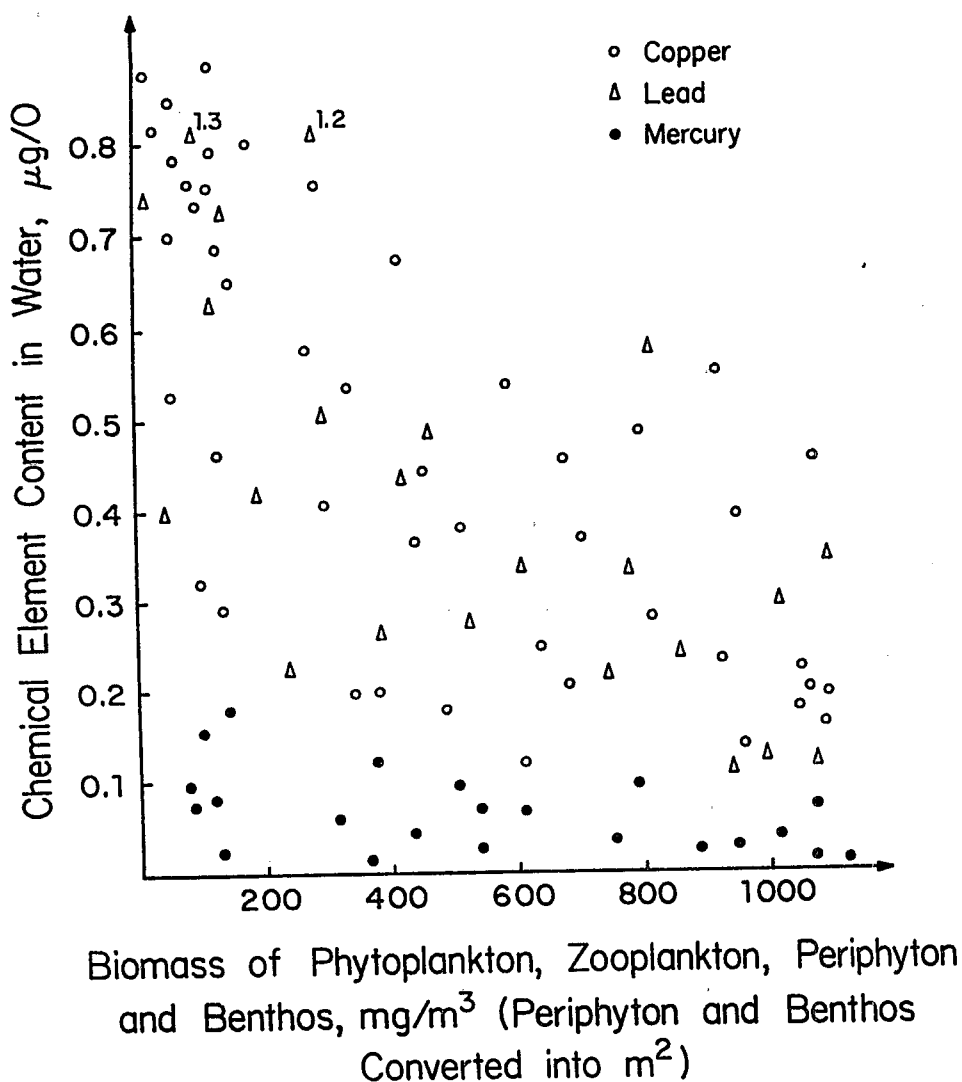


Figure 4. Chemical elements in freshwater ecosystems.

tom sediments and the ecological consequences of this process for living organisms will depend mainly on correlative rates of two processes--complexation of heavy metals introduced to ecosystem with dissolved organic matter and transformation of metals into less toxic forms under the influence of this process on one hand and accumulation of metals (and the most toxic forms among them) by hydrobiota on the other.

At present, there is no unambiguous information on the kinetics of these processes. It was provided, however, that in the process of cultivation of blue-greens Chroococcus paris in the water with concentration of heavy metals (Cd, Cu, Zn) from 2 ppm up to 90% of the total quantity of metals was sorbed by the cells within 1 minute and fixation was practically complete in 10 minutes (Les and Walker 1984). In this case, absorptivity of the cell at pH 7 was 53, 120, and 65 mg/g dry weight for cadmium, copper, and zinc, respectively (Les and Walker 1984).

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COMMUNITY RESPONSE OF AQUATIC ORGANISMS TO PESTICIDE STRESS

by

S.J. Lozano¹

INTRODUCTION

Problems in pollution studies often require the investigator to infer species-environmental relationships from community composition data and habitat measurements. Usually the data consist of abundance values for several species and measurements of natural habitat. For pollution studies, habitat measurements would include the water and/or sediment concentrations of a toxicant. When sufficient differences exist between sites (e.g., lake, river reach or experimental pond), it would be useful to use multivariate techniques to demonstrate multi-species relationships between habitats. Multivariate analysis techniques were used to describe the changes in the zooplankton communities along a toxicant gradient in a littoral enclosure study conducted in a small, 5-ha pond in northern Minnesota.

The research program (Brazner et al. 1987) was designed to produce new and improved procedures for determining primary and secondary ecological effects of pesticides on non-target biota in natural aquatic systems. Chlorpyrifos was chosen as a model pesticide for the study because of prior experience in testing the compound in the laboratory and in outdoor systems at the Environmental Research Laboratory-Duluth (Holcombe et al. 1982, Jarvinen and Tanner 1982, Eaton et al. 1984) and because of the availability of numerous laboratory and field studies using chlorpyrifos as a test chemical (Marshall and Roberts 1978).

The research design was to use 12 (5m x 10m) enclosures constructed on the north side of a 2-ha pond that has a diverse community of aquatic plants and animals. The littoral areas of the pond are well developed with cattails, pond grasses, and macrophytes growing in unconsolidated, highly organic sediments. An inert polyolefin film formed three walls of each enclosure with the fourth side (5m in length) being the shore of the pond. Average depth of the enclosures at the deepest end was 1.1m. Because the enclosures included natural shoreline, littoral zone and sediments, all

¹Center for Lake Superior Environmental Studies, University of Wisconsin-Superior, Superior, Wisconsin USA.

components of the habitat and food supply for endemic pond organisms were available. This allowed replication to be incorporated into the experimental design without seriously compromising the ecological integrity of the results.

Responses of all major trophic levels and the physical and chemical environment to a single application of chlorpyrifos were measured during the summer of 1986. Pre-treatment samples for characterizing biological, physical, and chemical conditions were collected 10 days prior to pesticide application. Post-treatment samples were collected periodically up to 405 days after application when chlorpyrifos was no longer measurable in the water column. Chlorpyrifos was applied to achieve the following average peak concentrations.

Treatment Group	Expected Concentrations (ug/L)	Number of Replicate Enclosures
Untreated	0.0	2
Low Concentration	0.5	2
Medium Concentration	5.0	4
High Concentration	20.0	4

The concentrations of chlorpyrifos were selected to encompass reported LC₅₀ values for a wide variety of organisms present in the pond and the prescribed application rates recommended for mosquito control.

EXPERIMENTAL

ENVIRONMENTAL CHEMISTRY

The water chemistry parameters of conductivity, pH, alkalinity, color, turbidity, dissolved organic carbon (DOC), dissolved nitrate, and dissolved phosphate were monitored weekly in each enclosure to reveal any dose-response relationship between pesticide application and the environmental chemistry of the enclosures. In addition, enclosures were monitored continuously for conductivity, pH, temperature, and dissolved oxygen (DO). Chlorpyrifos [0.0-diethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate] emulsifiable concentrate (22.4% active ingredient) was applied on June 16 at 10 a.m. A single application was made to each of the 10 treatment enclosures. Enclosure applications were spaced 15 min apart and the order of application was from low to high concentration. A composite water sample was collected from each enclosure at pre-determined times. Each enclosure was divided by volume into four equal quadrants. Samples from each treatment enclosure were collected at 1 day pre-treatment and at 1, 2, 4, 8 and 12 hours and 1, 2, 4, 8, 16, 32, 64, and 128 days after treatment.

INVERTEBRATE STUDIES

Inverted funnel traps were used to sample zooplankton to determine abundance and composition. This sampler, designed for use in littoral areas (Whiteside and Williams 1975), is placed on the substrate where it collects organisms as they move out of the vegetation at night. Samples are relatively free of detritus and are easily counted.

The sampler consists of a plexiglass plate to which three glass funnels are attached. The funnel mouths are placed on the substrate and the organisms move up through the funnels into collection bottles centered around the stem of each funnel. Samplers were placed at sunset in four selected locations in the deeper zones of each enclosure, and retrieved early the following morning. Samplers were preserved in 5% formalin. In the laboratory, zooplankton were concentrated through a 80- μ screen and identified as to genus or species using a compound microscope.

MULTIVARIATE DATA ANALYSIS

For our analysis, we used the complete \log_{10} zooplankton counts per square meter from Day 4 and the preliminary count data from Day 4 to Day 404. Stepwise discriminant analysis was employed to examine the effects of chlorpyrifos on the zooplankton community on Day 4. Discriminant analysis was done through the computer programs available in Statistical Package for the Social Sciences (Nie et al. 1970). Detrended correspondence analysis (Hill and Gaugh 1980) was used to analyze the long term effects from Day 4 to Day 404. Detrended correspondence analysis has been used in numerous field studies and has the distinct advantage of producing axes that correspond to approximate standard deviation units of zooplankton species counts. On the axes, 100 units are equivalent to one average standard deviation, which is close to one half-change for many species replacements along an environmental gradient (Hill and Gaugh 1980).

RESULTS AND DISCUSSION

Analysis of pre-treatment samples revealed that the microinvertebrate community in early June was dominated by cladocerans and copepods. The percentage of total abundance per square meter was 48 percent for cladocerans and 28 percent for copepods. Rotifer populations, at 22 percent of total abundance in pre-treatment samples, were also at their highest in June based on preliminary results from pre-treatment to Day 128.

Pre-treatment percent similarity between reference versus low, medium and high treatment populations was measured by Renkonen's Index (Renkonen 1938) for microinvertebrate funnel trap data. Percent similarities of species abundance in the treatment enclosures relative to the control enclosures was high, ranging from 81% for the low treatment enclosure to 88% for the medium and high treatment enclosures. After pesticide application, there was an overall decline in abundance of species within the different treatment enclosures.

The microinvertebrate community was reduced at all three treatment levels, with 30 of 35 taxa declining when compared to reference populations (Table 1). Total abundance of the treated populations was reduced by at least 60% as compared to reference populations. Cladocerans and ostracod populations from treated enclosures (Table 1) were smaller (75 percent to 99 percent reduction) than the reference populations with almost complete mortality at the medium and high treatment application rates. There was little or no statistically significant impacts on copepod and rotifer populations.

Discriminant analysis was used to define those zooplankton species that contributed to the differences between treatment levels in zooplankton communities. The individual variables used in the analysis are listed along with the relevant standardized function coefficients in Table 2. All three discriminant functions were significant, although the first two functions explained 93 percent of the total variation. The effects of chlorpyrifos on zooplankton community responses were clearly demonstrated in the Day 4 samples (Figure 1). There was no overlap between treatment groups classification.

It appears that the first discriminant function separates treated enclosures from the control zooplankton communities. The second discriminant function separates the three treatment groups (low to high). There appeared to be no pattern to the order that a zooplankton taxa was selected for entering the discriminant analysis. Cyclopyris (ostracod), Mytilina (rotifer), Copepodite (copepod) and Alona (cladoceran) were the first four species that were included in the discriminant analysis. Most cladocerans and the one species of ostracods (sensitive species to chlorpyrifos) were correlated, however, with the first discriminant function, whereas rotifers and copepods were correlated with the second discriminant function (both groups were not sensitive to chlorpyrifos). These results correspond to the analysis of variance results (Table 1) discussed above.

Sayler et al. (1983) used a discriminant analysis to evaluate the significance of synthetic oil on the functional activity of sediment microbial communities. Effects of the synthetic oil on the microbial community responses were evident 1 month after treatment. In this study, the microinvertebrate community began recovery after 3 months.

To show the long term effects of chlorpyrifos in the enclosure studies, a detrended correspondence analysis was employed (Hill and Gauch 1980). The sample points, corresponding to control or treated enclosures, were used to describe the community trajectories (vectors) in species space. Like all ordination techniques, detrended correspondence analysis is a data reduction technique, reducing n-species space onto three or four axes. The goal of the analysis is to arrange the individual species in a manner that discloses their fundamental relationships, i.e., species abundance is used to reveal the relationship between zooplankton communities and the habitat, in this case the four treatment level groups (control, low, medium, high).

The results of the ordination are shown in Figures 2-4 for each treatment comparison. By Day 64, the low treatment zooplankton community had returned to the control cluster (Figure 2). For the medium and high treatment groups, there was some evidence of recovery by Day 405, more than 1 year

TABLE 1. ESTIMATED MICROINVERTEBRATE ABUNDANCE GIVEN AS GEOMETRIC MEANS OF ORGANISM NUMBERS PER SQUARE METER, TREATED AND CONTROL (UNTREATED) ENCLOSURES, 1986 LITTORAL ENCLOSURE STUDY.

Taxa	Control (+ 2S.E.)	Low	Medium	High
Cladocerans				
<u>Chydorus</u>	762.0 (1783 - 325)	5.9 *	1.3 *	0.8 *
<u>Pleuroxus</u>	35.2 (85 - 14)	0.3 *	0.2 *	0.0 *
<u>Simocephalus</u>	32.0 (77 - 13)	1.5 *	0.1 *	0.0 *
<u>Alona</u>	39.1 (61 - 25)	8.6 *	0.2 *	0.0 *
<u>Ceriodaphnia</u>	41.0 (57 - 29)	0.1 *	0.0 *	0.0 *
Copepoda				
<u>Acanthocyclops</u>	137.7 (360 - 52)	19.8	4.5 *	1.5 *
<u>Mesocyclops</u>	76.4 (203 - 28)	10.3	30.7	18.7
<u>Eucyclops</u>	32.7 (128 - 8)	14.4	12.9	11.8
Nauplii	504.8 (1026 - 248)	103.4	185.9	140.1
Copepodites	407.0 (1362 - 121)	54.1	75.0	51.3 *
Harpacticoid	103.7 (189 - 57)	12.6	90.4	77.8
Unknown sp.	0.8 (3 - 0)	0.3	1.6	1.0
Ostracoda				
<u>Cyclocypris</u>	116.9 (191 - 71)	28.7 *	16.7 *	3.8 *
Rotifera				
<u>Brachionus</u>	37.8 (97 - 14)	15.2	38.1	25.4
<u>Platytas</u>	54.8 (146 - 20)	1.9	11.5	14.0
<u>Monostyla</u>	67.8 (173 - 26)	6.3 *	19.1	9.1 *
<u>Polyarthra</u>	4.0 (10 - 1)	1.7	18.2	8.7
<u>Trichocerca</u>	101.5 (248 - 41)	28.4	69.6	25.7
<u>Keratella</u>	3.0 (11 - 0)	3.7	17.1	10.2
<u>Testudinella</u>	31.8 (65 - 15)	6.5	25.8	19.7
<u>Notholca</u>	133.6 (392 - 45)	45.1	42.2	50.3
<u>Lecane</u>	4.3 (8 - 2)	0.5	1.1	2.0
<u>Asplanchna</u>	5.7 (10 - 3)	0.0	1.4	1.9
<u>Euchalnis</u>	73.5 (289 - 18)	8.2	23.2	15.7
<u>Trichotria</u>	12.8 (27 - 6)	8.8	6.2	10.4
<u>Ploesoma</u>	4.2 (16 - 1)	3.5	3.2	2.0
<u>Mytilina</u>	17.5 (39 - 8)	7.1	8.0	2.8
Unknown sp.	29.4 (88 - 9)	32.7	35.4	16.8
Other Invertebrates				
Amoeba	28.3 (43 - 18)	95.8	52.5	74.2
Planaria	140.8 (387 - 51)	4.4	138.9	63.5
Nematode	9.8 (13 - 7)	0.8	5.4	1.5 *
<u>Hydracarina</u>	9.4 (17 - 5)	19.0	17.3	8.7

*Tukey's Studentized Range Test, $p \leq 0.05$.

after pesticide application (Figures 3 and 4). The recovery rates for the low treatment was comparable to the microbial communities reported by Sayler et al. (1983). The enclosure walls were not removed until 450 days after treatment, thereby eliminating the possibility of zooplankton colonization from untreated to treated littoral zones. The slower recovery rates in the medium and high treatment groups for the zooplankton community may have been more rapid if the enclosure walls had been removed. As stated earlier, the species that were most important in the ordination analysis were sensitive

TABLE 2. ZOOPLANKTON VARIABLES UTILIZED BY STEPWISE DISCRIMINANT ANALYSIS TO DISCRIMINATE BETWEEN EXPERIMENTAL ENCLOSURES AFTER CHLOPYRIFOS TREATMENT.

Discriminating variable	Discriminant function coefficient		
	Function 1	Function 2	Function 3
Cladocerans	0.60	-0.16	0.19
<u>Chydorus sphaericus</u>	-0.55	-0.66	-0.11
<u>Pleuroxus</u>	0.64	0.02	-0.36
<u>Sida crystallina</u>	-0.09	-0.14	1.08
<u>Alona costata</u>	1.06	0.83	-0.09
<u>Ceriodaphnia</u>			
Copepoda			
<u>Acanthocyclops</u>	-0.84	-0.64	-0.26
Nauplii	-0.52	-2.22	-1.25
Copepodites	0.81	1.72	0.34
Ostracoda			
<u>Cyclocypris</u>	0.11	-1.28	-0.33
Rotifera			
<u>Platytas</u>	-0.61	1.03	-0.68
<u>Monostyla</u>	-0.08	-0.43	-0.68
<u>Notholca</u>	1.12	1.56	0.89
<u>Lecane</u>	0.44	0.68	0.65
<u>Trichotria</u>	0.44	0.68	0.65
<u>Ploesoma</u>	0.55	1.26	-0.01
<u>Mytilina</u>	-0.05	-0.49	0.23
Other Invertebrates			
Amoeba	-1.24	-0.52	0.72
Planaria	0.48	0.33	-0.53
Eigenvalues	28	13	3
Percent Variation			
Explained	64	29	7
Wilk's Lambda	0.001*	0.018*	0.245*

*p \leq 0.05, Chi Squared Test

species including cladocerans, amphipods and ostracods. Species that were important for determining the second axis were rotifers, copepods and two species of cladocerans. Under the constraints of our experimental design, we have found that recovery for zooplankton species from a littoral zone of a pond is negatively correlated with the concentration of chlorpyrifos.

In summary, the two methods of multivariate analysis have successfully demonstrated the relationship between zooplankton community and habitat. Recovery can be demonstrated for different pesticide treatment levels and a correspondence between zooplankton populations and habitat was established.

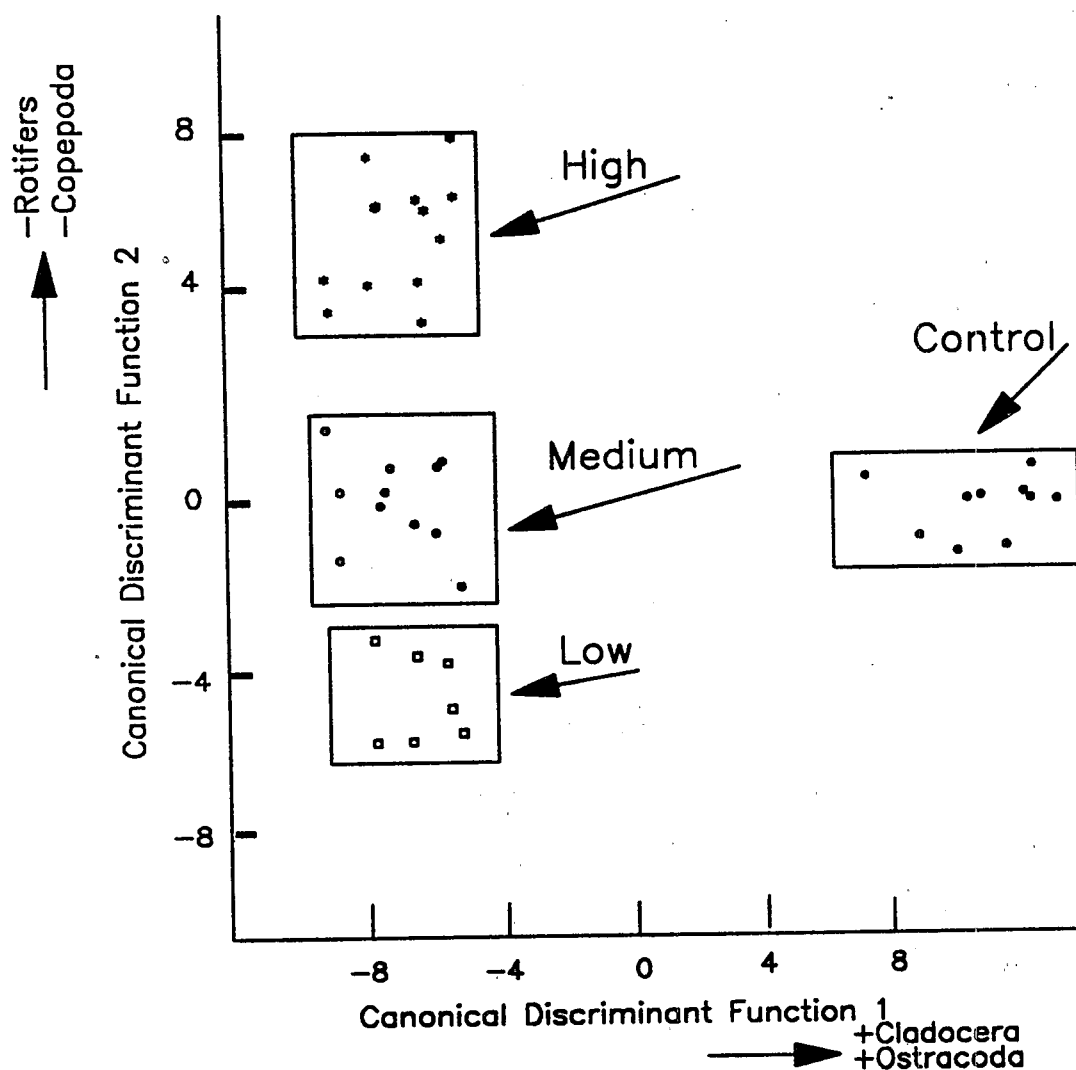


Figure 1. Littoral enclosures, zooplankton discriminant scores from Day 4. Discriminant analysis for 44 species of zooplankton at four treatment levels of chlorpyrifos, 1986 littoral enclosure study.

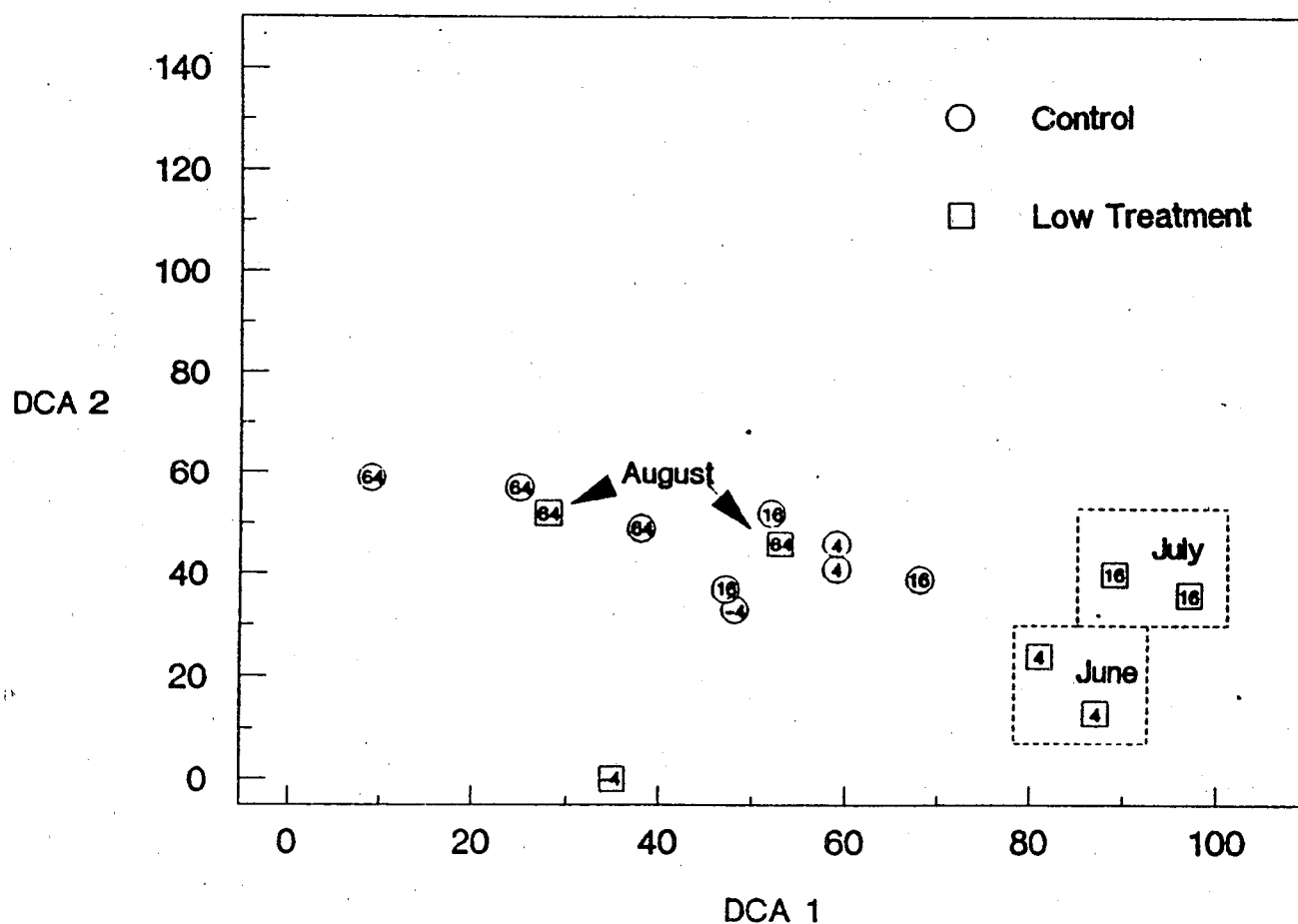


Figure 2. Detrended correspondence analysis--zooplankton. Distribution of samples on first and second detrended correspondence ordination axes. Codes within circles (control enclosures) and squares (treatment enclosures) are days relative to chlorpyrifos treatment. Low enclosures are boxed to emphasize the temporal succession of the treated zooplankton community.

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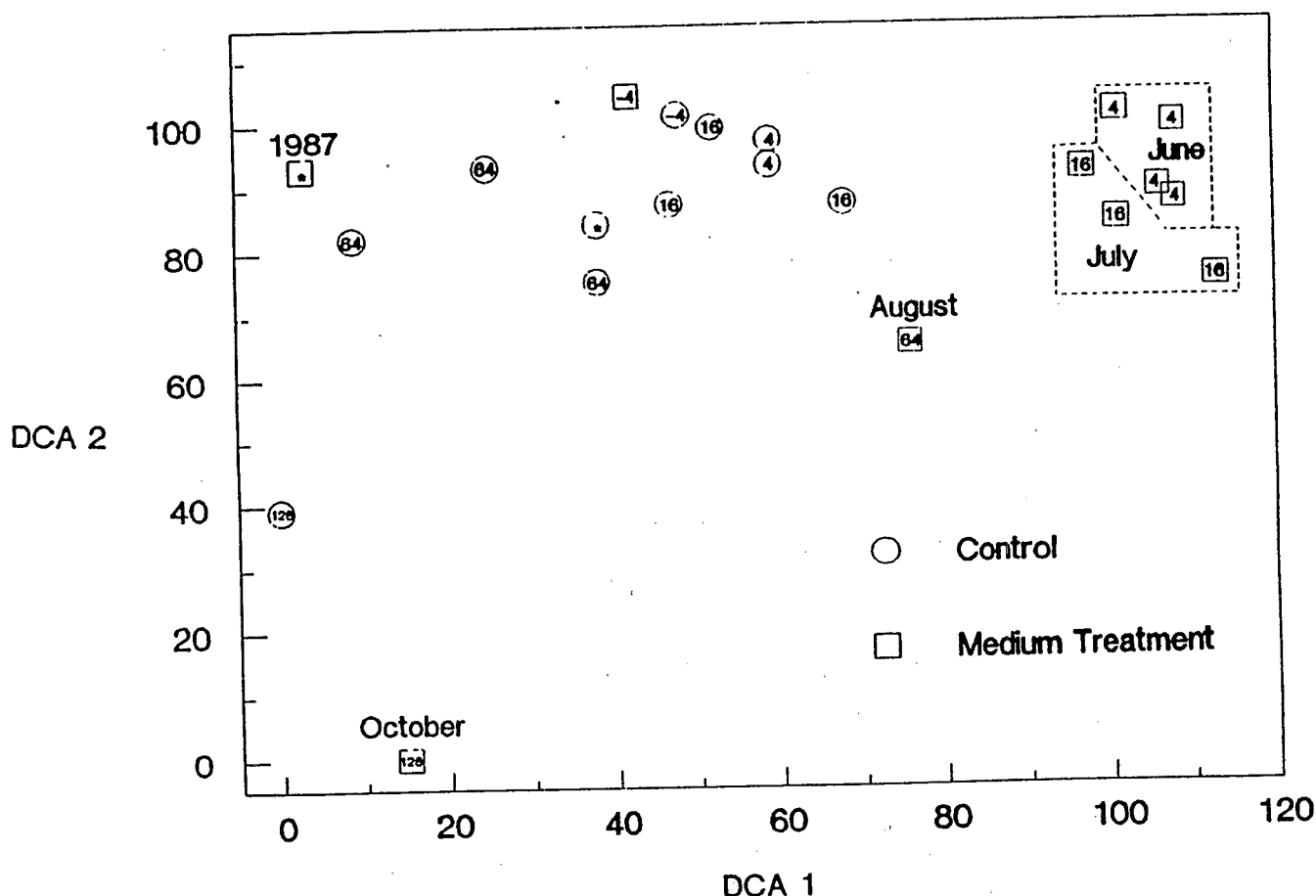


Figure 3. Detrended correspondence analysis--zooplankton. Distribution of samples on first and second detrended correspondence ordination axes. Codes within circles (control enclosures) and squares (treatment enclosures) are days relative to chlorpyrifos treatment. Medium enclosures are boxed to emphasize the temporal succession of the treated zooplankton community.

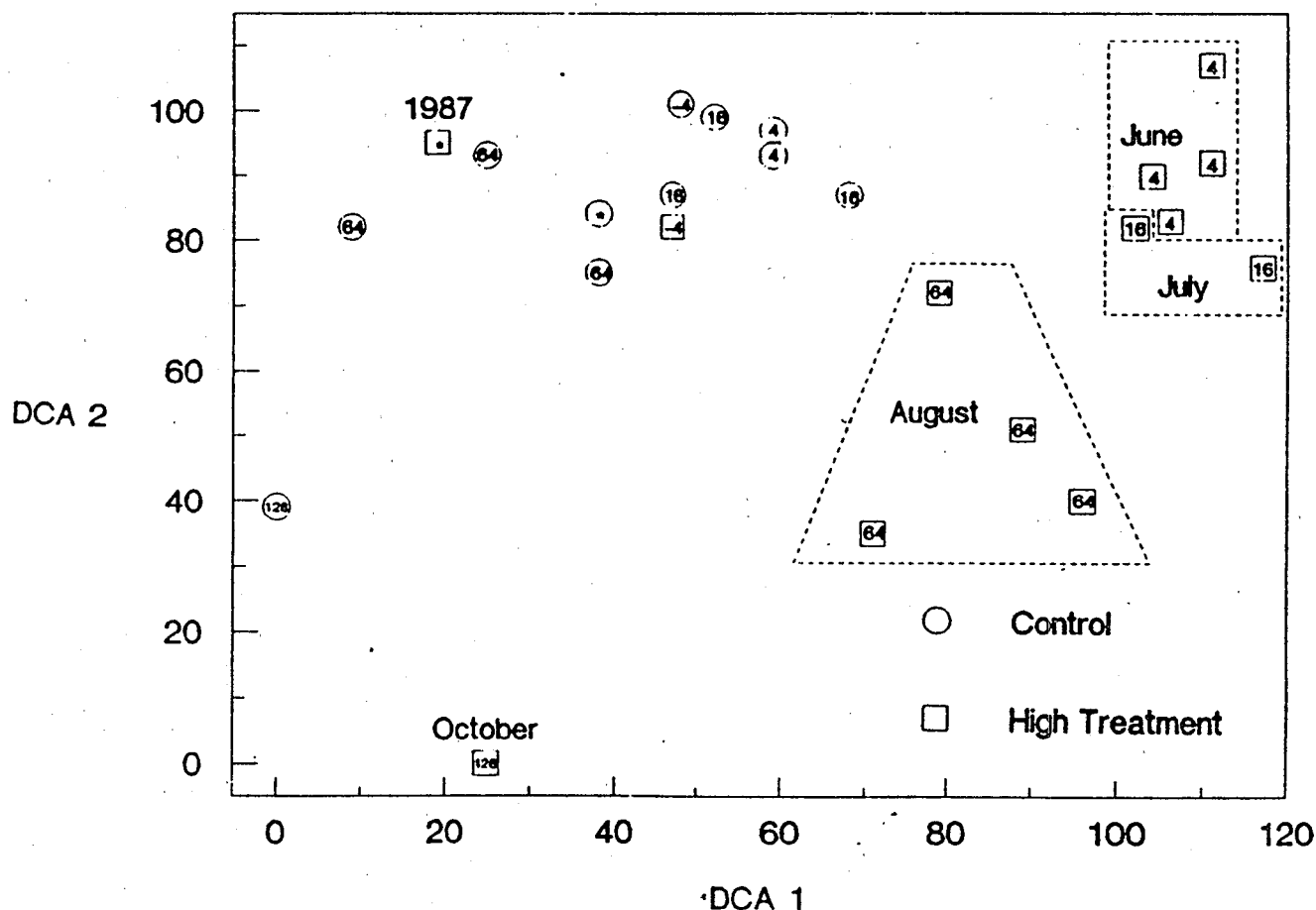


Figure 4. Detrended correspondence analysis--zooplankton. Distribution of samples on first and second detrended correspondence ordination axes. Codes within circles (control enclosures) and squares (treatment enclosures) are days relative to chlorpyrifos treatment. High enclosures are boxed to emphasize the temporal succession of the treated zooplankton community.

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THEORETICAL AND METHODOLOGICAL ASPECTS
OF MODELING LACUSTRINE ECOSYSTEMS

by

A.A. Matveyev¹, A.M. Nikanorov¹, Yu. A. Dombrovskiy², and V.V. Selytin²

ABSTRACT

Selection of a particular mathematical model for simulating an environmental ecosystem is largely a subjective process. This paper examines some means of reducing this subjectivity by identifying methods that facilitate an a priori evaluation of the required area, the dimensions, and the degree of detail desired.

INTRODUCTION

A broad range of ecosystem water models is utilized at the present time, from the simplest inlet-outlet models that include empirically selected relationships to cumbersome models that have dozens and even hundreds of variable simulation systems. Models also are differentiated according to degree of localization, from those that describe individual bays and shore areas to models depicting the entire water body.

In selecting a particular mathematical method for describing a system and obtaining the desired degree of model resolution, the researcher is guided by the purpose of the modeling effort, the available data, and the technical capabilities of each model. To a large part, such a choice is largely subjective. The purpose of this work is to examine some of the means of reducing this subjectivity by identifying methods that facilitate an a priori evaluation of the required area, the dimensions, and degree of detail. Also discussed are some standardized quantitative analysis processes for ecosystems such as Lake Baikal and Lake Sevan.

PRIMARY WATER ECOSYSTEM MODEL AND MODIFICATIONS

The primary orientation in a mathematically modeled ecosystem for water bodies utilizes the following model

¹Hydrochemical Institute, Rostov-on-Don, USSR.

²Mechanics and Applied Mathematics Research Institute, Rostov State University, Rostov-on-Don, USSR.

$$\frac{Dy}{Dt} = \text{div } D\text{grad}y - v\text{grad}y - K(y), \quad (1)$$

$$\text{div}V = 0 \quad (2)$$

$$y(0) = y_0 \quad (3)$$

$$vy - D\text{grad}y|_r = q, \quad (4)$$

where:

$y \in R_+^N$ - ecosystem condition vector

D - dispersion matrix

v - transport velocity vector field

$K(y)$ - kinetic operator

y_0 - initial condition vector

q - substance flow over boundary surface G

As a result of the commonality of physical principles that lie at the system's basis, most of the existing models of spatially distributed systems may be directly derived from Equations 1 through 4. The construction of the models is generally differentiated by:

- o space-and-time aggregation, and consequently by mathematical formalism (partially derived equations, ordinary differential equations, and difference equations)
- o dimensions and degree of non-linear concrete understanding of the kinetic member $K(y)$
- o ability to define the vector field V (calculation with the aid of a special hydrodynamic model or formation on the basis of full-scale survey data)

This model analysis primarily relies on two modifications of the original model (Equations 1 through 4), which are shown in abbreviated form below.

CHAMBER (COMPARTMENTAL) MODEL

If a water body is divided into M fixed spaces (chambers) and a new condition vector is introduced

$$y \in R_+^{N \times M}$$

where Y_r is the reserve or concentration of the i -component in the K -chamber, and

$$K = \text{entier}\left(\frac{r-1}{N}\right) + 1, \quad (5)$$

$$i = r - N(K-1) \quad (6)$$

Then Equations 1 through 4 may be shown as

$$y_r = \sum_{e \in M(K)} (P'_{Ke} - P'_{eK}) + \sum_{j \in N(t)} (P''_{ij} - P''_{ji}), \quad r = \overline{1, NxM} \quad (7)$$

where:

$M(k)$ - the number of chambers that border with K -chamber

P''_{ij} - substance flow from j to i component of the ecosystem during the course of the biotic cycle

$N(i)$ - number of components interacting with i -component

Here P_r depends on the dimensions of the chambers and parameters D and V , the overall advective and diffusion overflow of substance from chamber C into chamber K in a unit of time.

We should note that the first total (Eq. 7) also includes interchange flows with external mediums P_{0e} and P_{e0} , i.e., it takes into account the boundary condition (Eq. 4); whereas the second total, which represents the kinetic member, was derived on the basis of the additive principle of biotic flows. Equation 7 may be written in a matrix form:

$$y = (F - F_0)y + u, \quad (8)$$

$$p = Fy, \quad (9)$$

where:

$F(frs)$, $F_0 = \text{diag}(ff^0)$ - non-negating matrix dimensions $(NxM) \times (NxM)$

P - production vector ($P_r = \sum_e P'_{re} + \sum_j P''_{rj}$)

u - intake vector

The apparent correlation

$$\sum_r frs \leq f_s^0, \quad S = \overline{1, NxM} \quad (10)$$

ensures that solutions 8 and 9 are positive.

In stationary conditions

$$\bar{y} = (F_0 - F)^{-1} u = wu \quad (11)$$

Knowing matrix W makes it possible to calculate the contributions of any inflow U collected in K-chamber:

$$\alpha_{KS} = \frac{W_{KS} U_S}{\bar{y}} = \frac{W_{KS} U_S}{\sum_s W_{KS} U_S} \quad (12)$$

Calculation of the relative discharge α_{KS} of the three rivers that flow into Lake Baikal: Selenga ($S = 15$), Barguzin ($S = 26$), and Upper Angara ($S = 42$) was conducted with the aid of a chamber water exchange model ($M = 45$) and showed that the most significant contribution to the levels of concentration in all areas of the lake comes from Selenga. The values of relative depositions $\alpha_{k,15}$ range from 0.69-0.80 (hydrocarbons), 0.28-0.42 (phenols), 0.46-0.65 (zinc, lead). The values of relative depositions $\alpha_{k,42}$ are sufficiently low and consist of 0.11-0.20 for hydrocarbons, 0.10-0.31 for phenols, and 0.08-0.21 for zinc and lead.

DISCRETE MODEL (DYNAMIC BALANCE METHOD)

Given a certain characteristic time interval τ and going from derivatives to differences, one may get the discrete analysis of Equations 8 and 9. The production-balance modification of the difference model has the clearest physical meaning, which may be formally constructed by implicit approximation as

$$P_\tau = \int_t^{t+\tau} F y d\tau \approx \tau F y^{t+\tau} \quad (13)$$

Then, it can be easily shown that Equations 8 and 9 become

$$y^{t+\tau} - B(y^t + P_\tau + U^t), \quad (14)$$

$$P_\tau = A(y^t + P_\tau + U^t),$$

$$B = (I + \tau F_0)^{-1}, \quad A = \tau F B, \quad (15)$$

$$I = (\delta_{rs}), U^t = \int_t^{t+\tau} u(\tau) d\tau.$$

System 14 and 15 characterize the dynamic balance method. Let's note that the stationary condition matrix W is now expressed through A, B:

$$W = B[I - (A+B)]^{-1} \quad (16)$$

OVERALL SUBSTANCE DISTRIBUTION FEATURES FOR THE ENTIRE LAKE BODY

Let us represent the water body in the form of a unidimensional system that takes in a flow of non-conservative impurities. Then the distribution of y concentration along a certain characteristic x axis is described by Equation 17

$$y_t = Dy_{xx} - vy_x - Ky, \quad (17)$$

whose stationary solution has the following appearance

$$y = C_1 \exp(\lambda_1 x) + C_2 \exp(\lambda_2 x), \quad (18)$$

$$\text{where } \lambda_{1,2} = \frac{v}{2D} \pm \sqrt{\frac{v^2}{4D^2} + \frac{K}{D}},$$

and C_1, C_2 are determined by boundary conditions.

Let L represent the typical water body dimension, one determined by the distance between inlet and outlet. Assuming that $\lambda_1 < 0, \lambda_2 > 0$ and taking into account that function $y(x)$ must be a monotonous reduction, we get the apparent disparity

$$C_1 |\lambda_1| \exp(\lambda_1 L) < C_2 \lambda_2 \exp(\lambda_2 L) > 0 \quad (19)$$

Let us find a condition in which distribution (Eq. 18) is close to being equal, i.e., $y(0)$ and $y(L)$ are sufficiently close. Keeping in mind (Eq. 19) and $\lambda_2 > |\lambda_1|$ it is not difficult to establish that the criterion we seek can be shown by the expression

$$\mu = |\lambda_1| \cdot L \ll 1 \quad (20)$$

Let us introduce the following parameters:

$\tau_k = 1/K$ - time constant for "removing" impurities

$\tau_v = L/v = V/\Delta V$ - time of conditional water change (V - lake volume,
v - flow volume)

$\tau_D = L^2/D$ - diffusion time

$$a = \frac{\tau_v}{\tau_k}, \quad b = \sqrt{\frac{\tau_D}{\tau_k}}$$

Then Eq. 20 is written:

$$\mu = \frac{\tau_b}{\frac{1}{2} \tau_k \sqrt{(\frac{1}{2} \tau_k)^2 + \frac{\tau_k \tau_b^2}{\tau_D}}} \ll 1 \quad (21)$$

Apparently what follows in the evaluation is

$$\frac{ab}{a+b} < \mu < \min(a, b) \quad (22)$$

Inequalities (Eq. 20 and 22) make it possible to conduct a preliminary analysis of the model. If $\min(a, b) \ll 1$, then the distribution has a generally non-local character. If $\min(a, b) \gg 1$, then the affecting zone is significantly smaller than lake volume V.

The correlation $\frac{a}{b} = \frac{\tau_v}{\tau_k \tau_D} > 1$ shows that turbulent exchange has a predominant role in the substance dispersion mechanism, and when $\frac{a}{b} < 1$

the migration process is dominant. It should be noted that use of all three parameters for judging the nature of substance dispersion in the lake is justified only in the case when the water body is viewed as being homogeneous (absence of stagnant areas, extreme narrowing, etc.). When this is not the case, appropriate corrections should be made for similar evaluations.

Let us apply the given schematic for analyzing the distribution of some substances in Baikal. Let us evaluate τ_v , τ_D , τ_k

$$\tau_v = \frac{V_6}{\Delta V_6} = \frac{23000 \text{ km}^3}{60 \text{ km}^3/202} \approx 400 \text{ yrs.}$$

The width of Lake Baikal ($L = 40$ km) may be taken as the characteristic dimensions because the principal migration occurs along the axis of the Selenga River Delta/Angara source. For such an area, the turbulent diffusion coefficient is on the order of

$$D = 10^4 \frac{\text{cm}^2}{\text{c}} \quad \text{Then } \tau_D = \frac{L^2}{D} = 50 \text{ years.}$$

The calculated rates for removing substances (Table 1) are on the order of 5×10^{-3} L/year or $\tau_K = 200$ years. Thus, $a = 2$, $B = 0.5$ and $\mu \in (0.4, 0.5)$.

TABLE 1. EXTERNAL BALANCE OF CERTAIN SUBSTANCES IN LAKE BAIKAL

Balance element substance	Influx of U, tons/year	Run-off from Angara, tons per year	ΔU tons per year	Overall amounts in lake, \bar{Y} thousands per year	Estimates of removal rates, \bar{K} , L/year
Phenols	310	79	231	80.5	2.9×10^{-3}
Hydrocarbons	19306	7551	11755	2576	4.6×10^{-3}
Zinc	513	138	375	52.9	7.1×10^{-3}
Lead	44	24	20	9.2	2.2×10^{-3}

From this we can conclude that the determining mechanism for dispersing quasiconservative substances in Baikal is the turbulent exchange, and the distribution of these substances has a certain inequality

$$(y(L)/y(0)) \sim e^{-\mu} \approx 0.6$$

Let us note that for the more labile impurities, although they are removed slowly from the ecosystem (i.e., $\tau_K = 2$ year), $a = 200$, $B = 5$, $\mu = 5$, $y_B' / y_0 \sim e^{-5} \approx 0.007$, which explains the localized effect of the affecting zones of some of the sources, having a relatively high level of concentration. (Another cause of localization may be dilution by purer sources.)

COMPARING COMPLETE DISPERSION AND MIGRATION MODELS

When time correlation τ_D , τ_V , τ_K is such that $\frac{a}{b} \gg 1$ and $B \ll 1$,

then the water body may be considered to be completely intermixed and instead of Eq. 17, a chamber model is used.

$$y = \frac{1}{\tau_v} (y^0 - y) - \frac{1}{\tau_k} y, \quad (23)$$

where y^0 is the substance concentration upon intake.

When $\frac{a}{b} \ll 1$, then the diffusion is relatively low and Eq. 17 becomes a migration equation.

$$y_t = -y\tau - \frac{1}{\tau_k} y, \quad (24)$$

where: $\tau = x/v$, $\tau \in [D, \tau_v]$

Equations 23 and 24, which describe the finite conditions, are much simpler than the original (Eq. 17). These equations considerably facilitate the modeling of the hydrochemical process. In addition there is an absence of diffusion parameter τ_D , the assessment of which is always problematic.

Should the diffusion model (Eq. 17) be replaced by one of the approximate schematics (Eq. 23 or 24), it is necessary to know the magnitude of error. Let us mark y_1 for solution 23 and y_2 for solution 24 (Figure 1) where

$$y_1 = \frac{y^0}{1 + \tau_v/\tau_k}, \quad (25)$$

$$y_2 = y^0 \exp(-\tau/\tau_k). \quad (26)$$

Apparently the maximum error reading of Delta y

$$\Delta y \leq \max \{ |y - y_1|, |y - y_2| \} < |y_2 - y_1| \quad (27a)$$

may be large when replacement of model 17 is inadequate, causing big, relative errors with the increase of

$$a = \tau_v/\tau_k$$

In solving practical problems, it is often sufficient to evaluate only the average concentration for a given volume. The error rate of such an evaluation will be found when Eq. 17 is replaced by Eq. 23 or Eq. 24, i.e., conforming to indeterminate conditions of parameter τ_D .

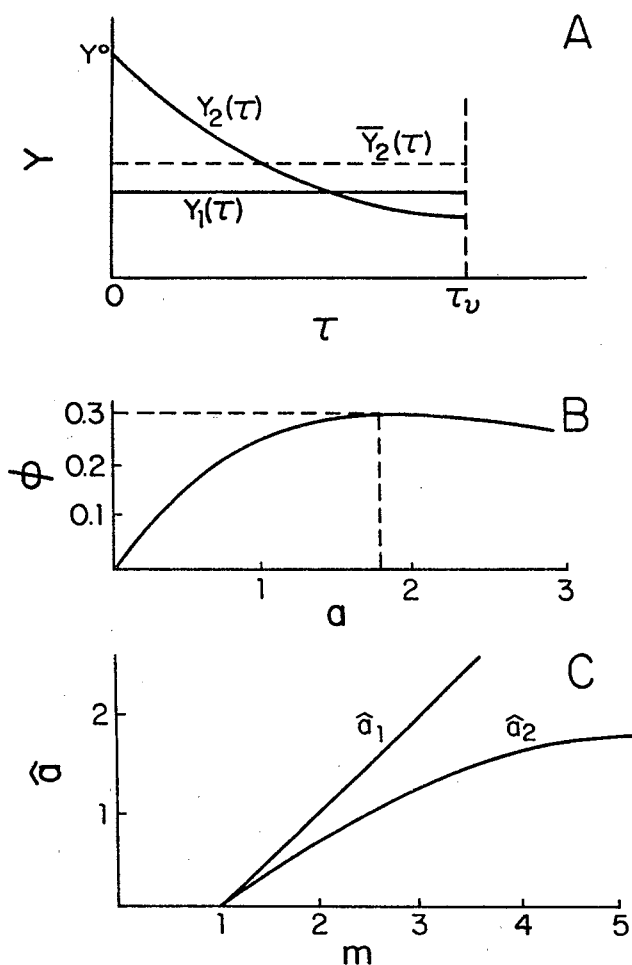


Figure 1. Comparison of complete interblending and removal rates--(A) distribution of concentrations with complete interblending (Y_1) and removal (Y_2), (B) averaging error with an undetermined diffusion coefficient, and (C) identification of kinetic parameter on the basis of the complete interblending model (a_1) and removal (a_2).

$$\bar{y}_2 = \frac{1}{\tau_b} \int_0^{\tau_b} y_2(\tau) d\tau = y^0 \frac{1 - \exp(-\tau_b/\tau_k)}{\tau_v/\tau_k} \quad (27b)$$

Thus, since $y_2 > y_1$, then to get the relative accuracy of δ_y , the following disparity is written

$$\delta \bar{y} < \frac{y_2 - y_1}{y_1} = \frac{1 - \exp(-a) - a \exp(-a)}{\tau_v / \tau_k} . \quad (28)$$

It can be easily established that (a) when $a = 1.8$ reaches the maximum value $\mu_m = 0.3$ (Figure 1). Consequently, what we have is an equilibrium evaluation of the relative error rate $\delta y < 30\%$, whose actual magnitude, as a rule, is substantially less.

Low sensitivity of \bar{y} to parameter τ_D explains the ability to model the distribution of substances in the water bodies, by operating only with the diffusion coefficient order D.

ERRORS IN EVALUATING THE KINETIC PARAMETER

Errors During Replacement of Model

The speed with which the substance is transformed is the key parameter of any autopurification model; however, its magnitude is rarely known in advance. In addition, when this parameter is being evaluated, it is necessary to back away from some other concrete model. This leads to specific errors when the established coefficient is substituted in another model. Let us demonstrate this.

The simplest method to evaluate coefficient K is by the expression

$$\hat{K} = \frac{U_1 - U_2}{\bar{Y}} , \quad (29)$$

where V_1, V_2 are the substance flows, inlet and outlet, respectively, and Y is the amount of the substance in the lake.

When the dimensions of the water body are significant, however, the determination of Y requires the accumulation of a great amount of data, and the selection of an effective averaging method.

Another method to evaluate K (or $\hat{a} = \hat{K}\tau_v$) is to use models 25 and 26. Accordingly (Model 25)

$$\hat{a}_1 = m - 1 , \quad (30)$$

where $m = y^0/y$, and consequently (Model 26)

$$\hat{u}_2 = e n m \quad (31)$$

The derived values of \hat{a}_1, \hat{a}_2 are marginal for the \hat{a} value that is sought:

$$\hat{a}_2 < \hat{a} < \hat{a}_1$$

We can easily see in Figure 1 that, as m increases, (\hat{a}_2, \hat{a}_1) grows rather quickly and the quality of the evaluation worsens. In particular, when $m = 3$, the relative error reading for determining K may get to 80%:

$$\delta_u < \frac{m-1-\text{en } m}{\text{en } m} . \quad (32)$$

The high sensitivity of the parameter that has been identified (the solution of an inverse problem) to the type of model is formally explained by the weak sensitivity of the direct problem solution (average concentration \bar{y}) to parameter a .

Non-stationary Error

Beginning from a certain moment in time t_0 , let the concentration of the substance in the water body increase at the inlet point, for example, according to the demonstrative law:

$$y_0(t) = \begin{cases} y_0 & , t < t_0 \\ y_0 e^{r(t-t_0)} & , t \geq t_0 \end{cases} \quad (33)$$

Then the evaluation of K according to formulas 30 and 31 will result in the appearance of additional dynamic errors. Let us examine the transfer equation Eq. 24 first. The nonstationary solution at the outlet point has the form

$$y_{\partial \text{ blx}}(t) = e^{-k\tau_b} y^0(t-\tau_b) = y_0 e^{-(k-r)\tau_b + r(t-t_0)}, \quad t \geq \tau_b + t_0 \quad (34)$$

from which we derive

$$\hat{\hat{K}}_2 = \frac{1}{\tau_b} \ln[y^0(t)/y_{\partial \text{ blx}}(t)] = \begin{cases} \hat{K}_2, & t < t_0 \\ K_2 + r \frac{t-t_0}{\tau_b}, & t_0 \leq t < t_0 + \tau_b, \\ \hat{K}_2 + r, & t \geq \tau_b + t_0 \end{cases} \quad (35)$$

Thus, as could be expected, with a positive trend $r > 0$ the evaluation of the kinetic parameter is too low and too high when it is negative. It may be shown that the evaluation of the complete intermixing model (Eq. 23) has an identical characteristic:

$$\hat{\hat{K}}_1 = \begin{cases} \hat{K}_1, t < t_0, \\ \frac{\hat{K}_1 + r - \frac{r}{1 + \tau_b \hat{K}_1} \psi(t)}{1 + \frac{r \tau_b}{1 + \tau_b \hat{K}_1} \psi(t)}, t > t_0 \end{cases} \quad (36)$$

where $\psi(t) = \exp[-(\frac{1}{\tau_v} + \hat{K}_1 + r)(t - t_0)]$ When $t \rightarrow \infty \hat{\hat{K}}_1 \rightarrow K_1 + r$.

STRUCTURE OF THE BIOTIC CYCLE

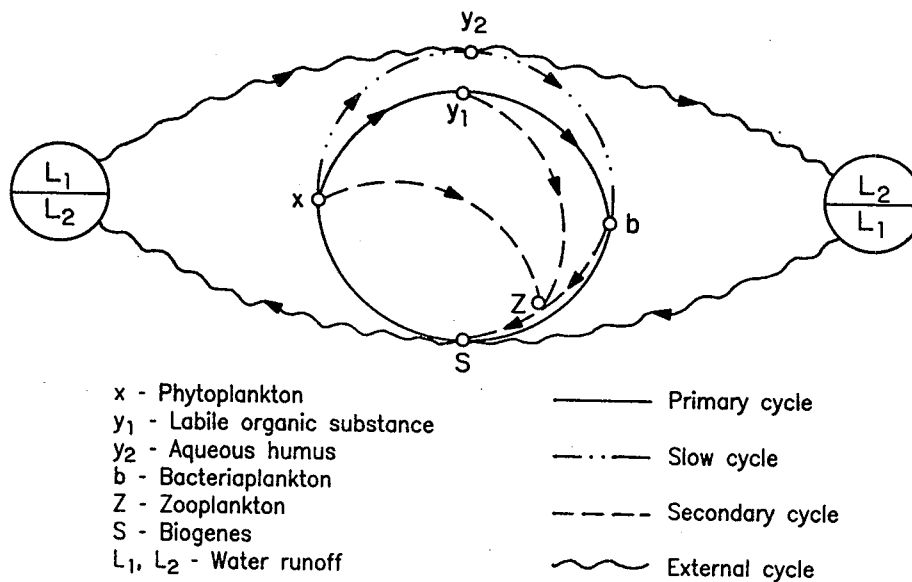
The design of the ecosystem's kinetic operator, describing the interaction and transformation of its individual components during the biotic cycle, is an informal process. Here we should take into account both general mechanisms that are endemic to lacustrine bodies, as well as their specific features that at times play a decisive role in the model's synthesis.

The most important moment is the selection of the vector of the ecosystem's state. Naturally, this selection, to a large degree, is determined by the purpose of the study and the area of its implementation, and is unavoidably tied to aggregation of the elements of the ecosystem. Also taken into account is any information that is necessary for identification and verification.

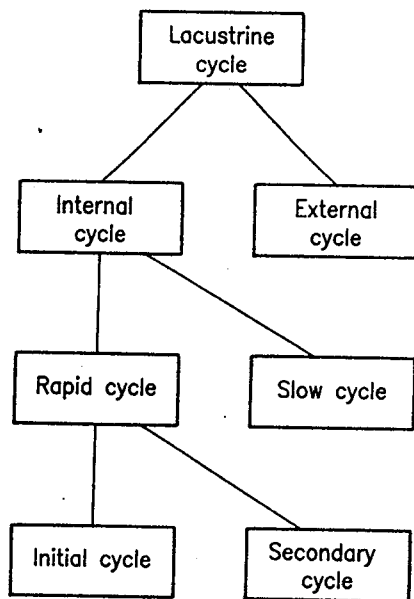
A quantitative method for resolving the question of the aggregation of the variables and the selection of an optimal (meaning, the least redundant) condition vector is closely tied, however, to the analysis of the substance flow structure and energy in the ecosystem. A partial understanding of these flows is derived from the biotic types of the lacustrine ecosystems, for which a methodology and a means of plotting them was developed by G.G. Vinberg. Moving from energy to real aspects and adding the organic and mineral components, as well as the exchange flows occurring with the environment, we get the complete picture that characterizes the biotic cycle of biogenic elements. All these aspects serve as the foundation for developing the mathematical models of ecosystems. The nitrogen cycle dynamic model in the pelagic layer of Lake Baikal, one which relied on an expanded biotic picture, was plotted and studied earlier.

Analysis of the flow structure will be conducted on the basis of an aggregated functional diagram of the pelagic layer (Figure 2a), one that reflects the principal stages of substance and energy transformation. This diagram includes three links in the biotic chain:

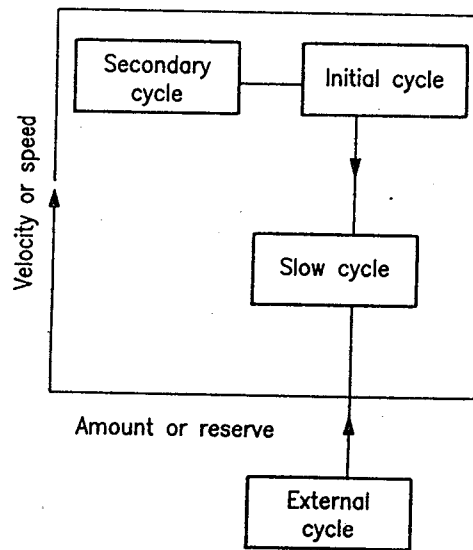
X - initial producers, autotrophs (phytoplankton on the top)



A



B



C

Figure 2. Structure of the lacustrine biotic cycle--(A) aggregated functional schematic, (B) decomposition diagram for small parameters, and (C) macrostructure.

B - heterotrophs, reducers (bacterioplankton, simple forms)

L - heterotrophs, consumers (zooplankton, fish, as well as hydrochemical components)

S - mineral forms of biogenes (assimilated by phytoplankton)

y_1 - dissolved labile organic substance

y_2 - aqueous humus

Notation of the two organic substance fractions is due to their different roles in the hydrochemical and hydrobiologic activity because aqueous humus is significantly different from labile fractions both in composition and speed of mineralization.

Marking $W = (x, y_1, y_2, B, L, S)$ as the vector of the condition of the ecosystem, $P = (P_{ij})$ the matrix of substance flows between individual components, U_1, U_2 the vectors of inlet and outlet flows, the following dynamic form is written

$$\dot{W} = (P - P^T)e + U_1 - U_2 \quad (37)$$

Averaging Eq. 37 over a particular characteristic period of time (for example, one year), and omitting members on the right side of the equation that provide a significantly smaller contribution to the algebraic totals in comparison with other members of the same sign, we come to the reduced model

$$\dot{W} = (\tilde{P} - \tilde{P}^T)e + \tilde{U}_1 - \tilde{U}_2 \quad (38)$$

After examining the biotic composition of the lakes, which was derived during the International Biologic Program, as well as relying on the generalizing works of G.G. Vinberg, I.B. Ivanova, A.F. Alimova, and B.A. Skopintsev, it is possible to conclude that there is regular transfer from Eq. 37 to Eq. 38. Therefore, the original system (Eq. 37) is divided into three subsystems: initial cycle (x, y_1, B, S), slow cycle (y_2), and a secondary cycle (L), which together with the external cycle that is created by flows U_1 and U_2 forms the macrostructure of the lacustrine cycler (Figure 2c).

The same result may be achieved by a somewhat different means, by comparing the internal and external flows:

$$\min(A, R) \gg \max(\sum U_{1i}, \sum U_{2i}), \quad (39)$$

where A is the primary products (assimilation), R is the overall destruction. Splitting the internal cycle on the basis of the speed of transformation into fast and slow cycles, we have

$$C \gg K_2, \quad (40)$$

where:

$C = \min(A, R)/q$ the speed of the rapid cycle

$q = x + y_1 + B + L + S$ the amount of substance in the rapid cycle

K_2 = rate of mineralization of the aqueous humus y_2 ; thus stressing the basic (initial subsystem in the rapid cycle, having a mass of $q_1 = x + y_1 + b + S$, and a secondary subsystem (L) that includes the higher trophic levels:

$$q_1 \gg L. \quad (41)$$

This procedure is shown in diagram form on Figure 2b.

Conditions 39 through 41 have a non-rigid form and are done for a broad range of lacustrine body types. The specifics of the ecosystem, as applicable to this analysis scheme, are reflected in concrete values of flows A, R, U_1 , U_2 (as the degree of flowage in the lake rises, the roles of U_1 , U_2 is increased); coefficient values K_2 and C (C is reduced from 10-20 L/year for shallow well intermixing and well heated lakes to 0.1 to 1 L/year for deep oligotrophic lakes); correlation of labile (q) and hard-to-acidify (y_2) substances (in dystrophic water bodies the share of y_2 is high and can reach 50% higher); composition and concrete proportions of q_1 and L (in deep water bodies due to the relative thinness of the production layer, the basic part of q_1 , consists of mineral substances. For Baikal, the variable (and consequently the initial cycle) should include a cymatoa, "rachok epishchura," a member of the microzooplankton family, because of its significant contribution to the overall destruction picture (25% R), which compares with breathing of bacteria (62% R).

In addition to the theoretical aspects, the cross-linking of the biotic cycle is of interest as a base for constructing reduced models, which are at the base of theoretical and analytical studies.

REDUCED MODELS OF SUBSTANCE CYCLES IN THE ECOSYSTEMS OF LAKE BAIKAL AND LAKE SEVAN

The existence of the macrostructure of biotic flows, which was examined in the previous section, makes it possible to carry out reductions of the original system. To describe the space-and-time dynamics of phytoplankton and biogenic elements, it is possible to utilize the initial cycle model.

$$\begin{aligned}
\dot{x} &= ps(x) - Ex, \\
\dot{y} &= Ex - Ky, \\
\dot{s} &= Ky - p(s)x,
\end{aligned}
\tag{42}$$

where:

$y = y_1 + B$, the aggregate of detritus bacteria

$p(S)$ - the rate of initial assimilation

K - the rate of mineralization

E - the die-off rate of the phytoplankton

Below we will examine another reduced model, one which makes it possible to examine some changing trends in the hydrochemical activity and the primary products as a result of the changes in the volume and composition of the substances that enter Lake Baikal.

Let us mark $q_1 = x + y_1 + B + S$ as the amount of limiting biogenesis taking part in the initial cycle. Apparently, the variable q_1 belongs in the slow category. The slow cycle model has the form

$$\begin{aligned}
\dot{q}_1 &= (1-\eta)Q^0b - vq_1 + K_2y_2 - \$A - \rho A, \\
\dot{y}_2 &= \eta Q^0b - vy - \$A - K_2y_2,
\end{aligned}
\tag{43}$$

where:

$A = cq_1$, the primary products

Q^0 - the total concentration of the limiting biogenesis in the inflow

v - flow velocity

ρ - the amount of primary products that is removed from the cycle as a result of sedimentation and burial

η - amount of aqueous humus in Q^0

$\$$ - amount of aqueous humus in A

K_2 - rate of aqueous humus mineralization y_2

Let us find the stationary solution of system (43);

$$\bar{q}_1 = Q^0 \frac{1-\eta+\delta}{(1+\delta)(1+\lambda+\mu)-\lambda\delta}, \quad (44)$$

$$\bar{y}_2 = Q^0 \frac{\eta-\eta_1\lambda+\mu}{(1+\delta)(1+\lambda+\mu)-\lambda\delta}, \quad (45)$$

where: $\delta = \frac{K_2}{v}$, $\lambda = \rho c/v$, $\mu = \xi c/v$.

The average content of biogenetic material in the water body is:

$$\bar{Q} - \bar{q}_1 + y_2 = Q^0 \frac{1+\delta+\mu+\eta\lambda}{1+\delta+\lambda+\delta\mu+\mu}. \quad (46)$$

Formulas 44 through 46 show that, like separate components q_1 , q_2 , the overall amount of Q depends not only on the inflow of concentrations Q^0 , but also on the composition of the inflow.

Since the primary product is proportional to q_1 , then based on Eq. 44, it follows that

$$A|_{\eta=1} : A|_{\eta=0} = \frac{\delta}{1+\delta} \quad (47)$$

Thus, with sufficiently low correlation of $\delta = K_2/v$, the reduction of the amount of allochthonous organic substances (in the form of aqueous humus) in the inflow leads to a proportional increase in the primary products of the water body. Let us also note that in accordance to the concept shown in model 43, when predicting the content of aqueous humus and the productivity of the water body, differentiation on the basis of biologic (labile and stable) aspects rather than the chemical (mineral and organic substances) is more important.

For forecasts using model 43, it is necessary to know the dimensionless parameters η , λ , δ , μ , as well as value Q^0 .

As a rule, only the most superficial a priori evaluations of the model coefficients are available, and these are adjusted also by modeling. Let us show another sufficiently general evaluation method. Let $W \in M$ be the vector of indicators that are directly measured with some accuracy, where $W \in R_+^m$ - is the area, whose dimensions are determined with a potential accuracy W , and $\Theta \in \Theta_0$ - the vector of unknown parameters, where $\Theta_0 \subset R_+^n$ - the location of initial evaluations. If $F(\Theta) = W$ - the equation system that ties in the parameters and observations, as for example Eq. 44 and Eq. 45, then the narrowing of initial mass Θ_0 is given by the expression

$$F^{-4}(M_1) = \Theta \Theta_0 \quad (48)$$

where $\omega_1 = \omega \cap \omega_0$, $\omega_0 = F(u_0)$.

The location ω is usually represented by an m-dimensional parallelepiped, and, if reliable evaluations are absent, θ_0 should quite naturally be taken as positive.

Based on the available published material by K.K. Votintsev, I.V. Glazunova, L.A. Vykristyuk, Ye. N. Tarasova, V.T. Bogdanova, and A.I. Mesheryakova of the USSR Academy of Sciences Limnological Institute, as well as on evaluations of the composition and rate of destruction of the organic material by B.A. Skopintsev, we took the following areas of ω and θ_0 for nitrogen and phosphorus:

$$\omega: \left\{ \begin{array}{l} 350 \frac{M_{\Gamma N}}{M^3} < Q_N^0 < 450 \frac{M_{\Gamma N}}{M^3}, \\ 30 \frac{M_{\Gamma P}}{M^3} < Q_P^0 < 40 \frac{M_{\Gamma P}}{M^3}, \\ 160 \frac{M_{\Gamma N}}{M^3} < Q_N < 190 \frac{M_{\Gamma N}}{M^3}, \\ 14 \frac{M_{\Gamma P}}{M^3} < Q_P < 18 \frac{M_{\Gamma P}}{M^3}, \\ 90 \frac{M_{\Gamma N}}{M^3} < q_{1N} < 110 \frac{M_{\Gamma N}}{M^3}, \\ 10 \frac{M_{\Gamma P}}{M^3} < q_{1P} < 14 \frac{M_{\Gamma P}}{M^3}, \\ 56 \frac{M_{\Gamma N}}{M^3} < y_{2N} < 87 \frac{M_{\Gamma N}}{M^3}, \\ 3 \frac{M_{\Gamma P}}{M^3} < y_{2P} < 5 \frac{M_{\Gamma P}}{M^3}, \\ 20 < y_{2N}/y_{2P} < 28, \\ 8 < q_{in}/q_{1P} < 12, \\ 0.1 < Q/Q^0 < 0.4, \end{array} \right. \quad (49)$$

$$\theta_0: \begin{cases} 0.3 < \eta < 0.8, \\ 0.2 < \lambda < 2, \\ 0 < \gamma < 10, \\ 0 < \mu < 8, \end{cases} \quad (50)$$

Evaluation of y_{2n} , y_{2p} was carried out for Nopn, Popn at large depths; Q_N^0 , Q_P^0 were calculated on the basis of the total influx of nitrogen and phosphorus with the surface runoff and from the atmosphere. To evaluate λ , calculations done by L.A. Vykristyuk and K.K. Votintsev for the Copn flow that ends up in the bottom deposits were utilized. In addition, it was assumed that the utilized hydrochemical information pertains to the quasi-stationary activity of Baikal. In accordance with algorithm 48, a congruent central evaluation with dimensionless parameters was found

$$\eta = 0.5 \quad \lambda = 1.5 \quad \gamma = 6 \quad \mu = 2,$$

which corresponds to the values

$$Q_N^0 = 395 \text{ mg/m}^3, Q_N = 179 \text{ mg/m}^3, q_{1N} = 102 \text{ mg/m}^3, y_{2N} = 77 \text{ mg/m}^3$$

$$Q_P^0 = 36 \text{ mg/m}^3, Q_P = 15.3 \text{ mg/m}^3, q_{1P} = 11 \text{ mg/m}^3, y_{2P} = 4.3 \text{ mg/m}^3$$

*[Note: m-gamma in formula above should be read as mg].

The correlation $q_{1N}/q_{1P} = 9.2$ indicates adequate balancing of that part of nitrogen and phosphorous that actively participates in the cycle.

In comparison with other large lakes, the retention coefficient is relatively low

$$R = \frac{\lambda(1-\eta)+\gamma\mu}{1+\lambda+\gamma\mu+\mu+\gamma} = 1 - Q/Q^0 \approx 0.6 \quad (51)$$

which attests to the need for stricter limitations on the influx of biogenic materials from the runoff.

Thus, since parameter δ is sufficiently large, then changes of η do not seriously affect the primary products. The basic factor in its increase is played by Q^0 .

A similar mode (Eq. 43) for slow variables was utilized to reconstruct and predict the trophic state of Lake Sevan, whose natural activity has been disrupted by dropping water levels between the 1930s and 1970s. This resulted in a substantial increase of primary products and worsening of oxygen

conditions in the hypolimnion. Because biogenic exchange with the bottom bed plays a rather significant role in Lake Sevan, whose average depth after the drawdown is only 31 meters, variables that include the amounts of nitrogen and phosphorus in the active bottom layer were added to the model.

Figure 3 shows the model reconstruction results of the period when draw-down occurred, as well as predicted estimates of primary products with reduced outflows from the lake and influx from river runoffs. An important result of the model analysis was the conclusion that one of the main reasons for the increase in primary products (PP) is the too rapid drawdown of the water level (up to 1 meter per year), which the ecosystem was unable to handle. At the present time, it has been noted that there has been a downward trend in primary products, one that is minimized by an increased flow of nitrogen and phosphorus from the runoff. Taking into account this factor, the model demonstrates the stabilization of the primary products of the lake at a level that is more than two times in excess of allowable levels (Figure 3).

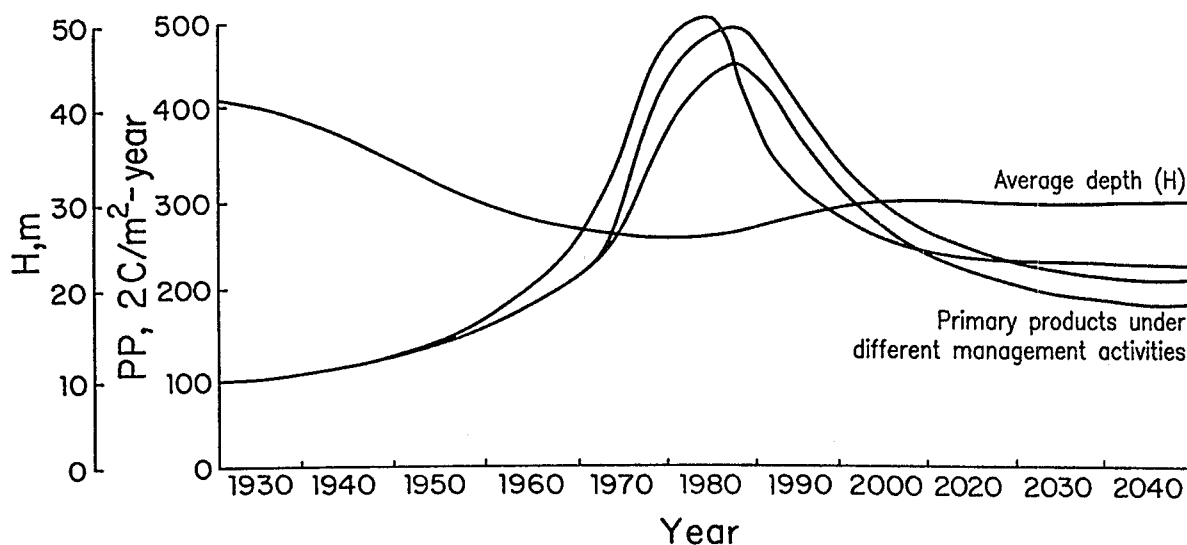


Figure 3. Primary products dynamics of Lake Sevan under various external effects.

ASSESSMENT OF RISKS OF TOXIC POLLUTANTS TO AQUATIC ORGANISMS
AND ECOSYSTEMS USING A SEQUENTIAL MODELING APPROACH

by

R.A. Park¹, J.J. Anderson², G.L. Swartzman²,
R. Morison³, and J.M. Emlen⁴

ABSTRACT

A sequential modeling strategy is presented in which increasingly complex fate and effects simulation models of aquatic ecosystems are used to assess the environmental risks of chemical exposure. The strategy is based on the assumption that complex models better represent the natural systems, thereby decreasing analysis uncertainty.

INTRODUCTION

A major challenge for environmental protection is the assessment of risks to the quality of terrestrial and aquatic ecosystems from exposure to pesticides and industrial chemicals. The premanufacture chemical review program of the U.S. Toxic Substances Control Act, for example, specifically calls for the predictive assessment of environmental risk (USEPA 1979); yet that program allows only 90 days for the analysis. Mount (1979) has stated that risk assessment should relate to site-specific properties of ecosystems and to differences in organisms, water chemistry, and sediments. Mathematical models have long been recognized as one means of quickly translating theory, laboratory findings, and mesocosm results to field conditions, thus providing a rationale for risk assessment.

Many models have been proposed to aid in risk assessment. In Figure 1 representative models are arrayed along three axes on the basis of their spatial, biological, and chemical complexity. To the left of the diagram

¹Holcomb Research Institute, Butler University, Indianapolis, IN, USA;

²Center for Quantitative Studies, University of Washington, Seattle, WA, USA;

³Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, DC, USA;

⁴Environmental Research Laboratory, U.S. Environmental Protection Agency, Corvallis, OR, USA (Current Address: National Fisheries Research Center, U.S. Fish and Wildlife Service, Seattle, WA).

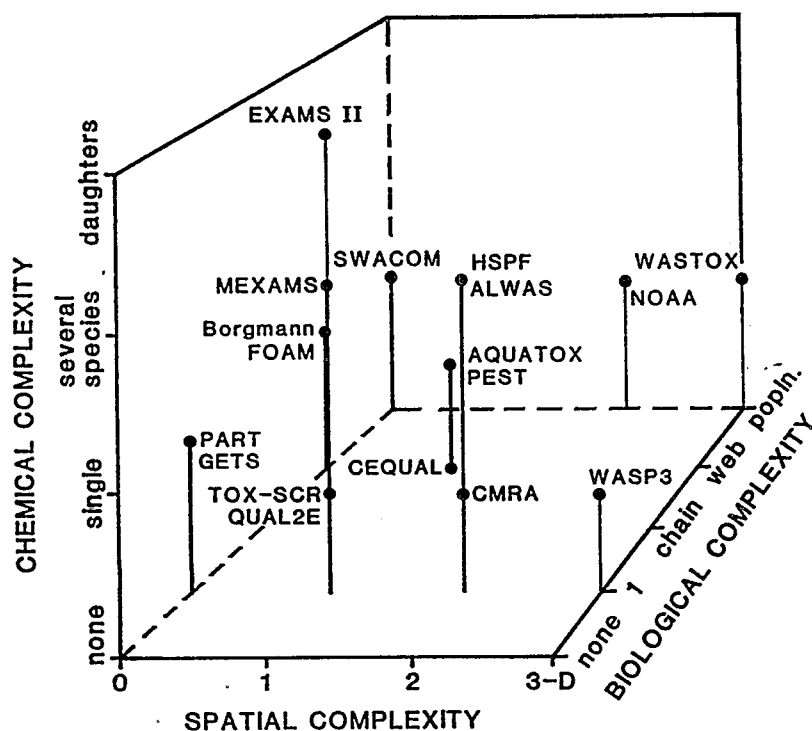


Figure 1. Representative models of varying levels of complexity useful for risk assessment.

are the traditional screening models, exhibiting low spatial complexity and varying levels of chemical and biological complexity. To the right of the diagram are models of greater spatial complexity, exhibiting the level of detail appropriate for application to specific sites. Generally there is a tradeoff between increasing chemical complexity and increasing spatial complexity. The NOAA and WASTOX models are the most demanding of data and computational power, they have both spatial and biological complexity and owe their existence to the intensive field efforts and large datasets that have been amassed for the Great Lakes. Such complex models are not appropriate for routine risk assessment.

Recognizing that the U.S. Environmental Protection Agency must evaluate large numbers of chemicals each year based on minimal amounts of data, our goal has been to develop a fast and judicious procedure capable of separating chemicals that can either be accepted or rejected in the initial phase of the analysis from those that need additional study with more sophisticated tools. The resulting sequential modeling strategy, based on existing and new models and designed to assist in decision making, is an important contribution to environmental risk assessment.

OVERVIEW

Based on personal experience and the deliberations of two workshops, we have developed a multi-tiered strategy for applying simulation models to

assess the probable fate and effects of chemicals. The strategy recognizes that models of increasing complexity require more effort to apply, but provide superior representations of ecosystemic buffering of potentially harmful chemicals, thereby decreasing uncertainty in the risk assessment.

As shown in Figure 2, fate and effects models of increasing complexity are used for those chemicals that can neither be accepted nor rejected on the basis of respectively conservative and liberal assumptions used in multiple executions of simpler models.

MODELING STEADY-STATE, SHORT-TERM EXPOSURE

In its simplest form, exposure can be represented as steady-state partitioning of a chemical among environmental phases. Partitioning models can consider transfers among air, water, and soil compartments; in fact, these elegant models account for simultaneous transfers, preserve mass balance, and yet are parsimonious. For this reason, partitioning models have enjoyed a great deal of popularity as evaluative tools in risk assessment. In their simplest form, they utilize partition coefficients to predict the distribution of a chemical.

Efficient computation of both equilibrium and nonequilibrium partitioning is facilitated using the chemical engineering concept of fugacity, an approach advocated by Mackay and colleagues (Mackay 1979, Mackay and Paterson 1981, Mackay et al. 1983, 1986, Neely and Mackay 1982). Fugacity is the "escaping tendency" of a chemical from a particular phase; if equilibrium is assumed, a single fugacity is computed for all phases.

Equilibrium fugacity is represented in the PART model (Park, in prep.), implemented in the Lotus 1-2-3 spreadsheet program. Missing parameters are estimated using established quantitative structural activity relationships. The model has been verified by comparison with Mackay's results. Field validation was performed using data on parathion, which was applied to give 0.05 ppm initial concentration in Israeli fish ponds (Perry and Gasith 1978); the predictions seem to be consistent with observations (Figure 3).

The simulation represents steady-state conditions 7.32 days after initial dosing, the time computed for fish to reach equilibrium. We propose to use this model to compute the environmental exposures for both the first- and second-tier effects models (Figure 2).

MODELING SINGLE-SPECIES COHORT EFFECTS

Dose-response toxicity models provide the basis for all ecosystemic risk assessments. The challenge is to incorporate dose response into a methodology that includes natural fluctuations in viability and mortality. The newly developed HEALTH model (Anderson, in review) assumes that, at the beginning of a life stage, an organism has an initial level of health that can increase or decrease over time as the organism encounters beneficial and deleterious

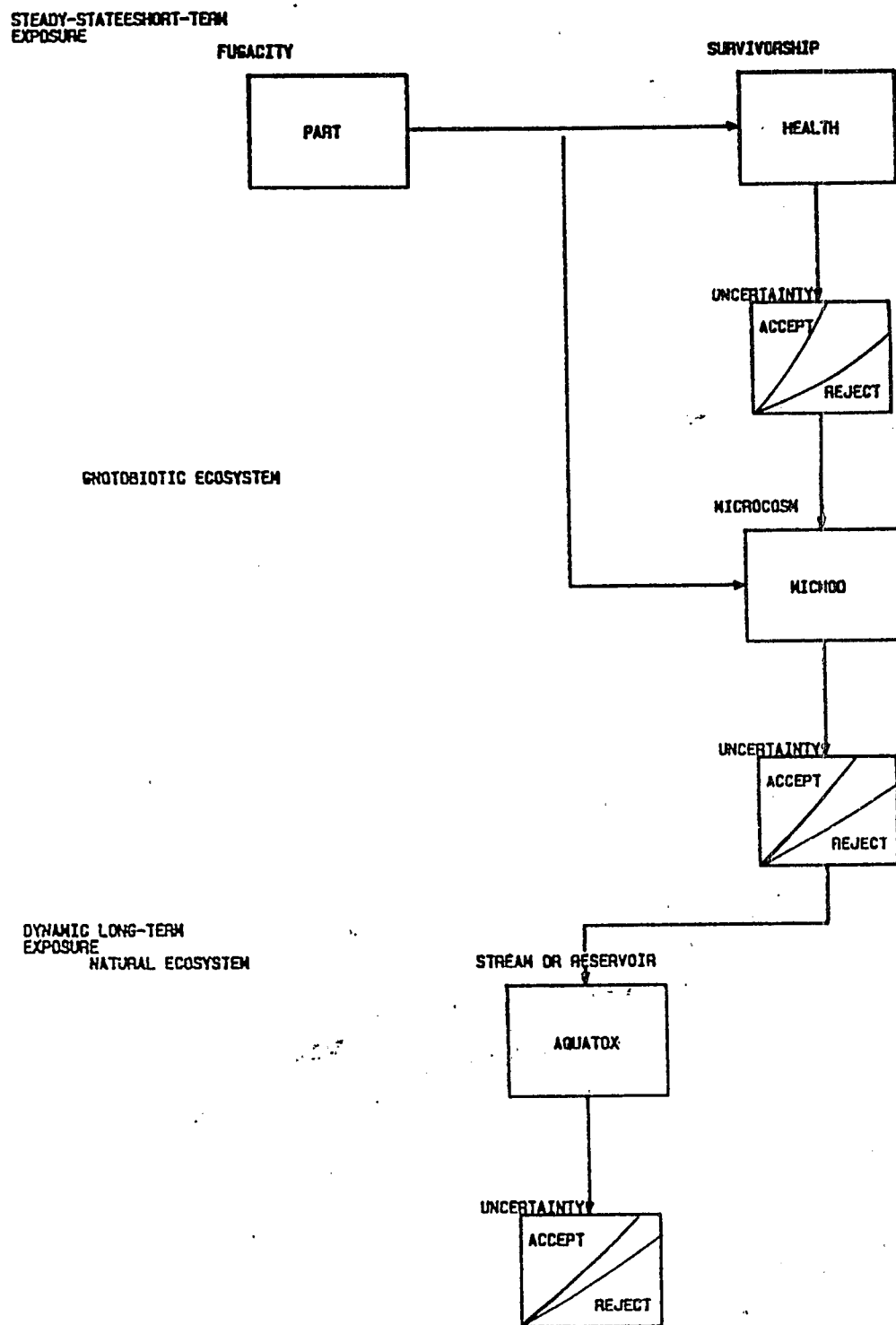


Figure 2. A sequential strategy for using models and evaluating uncertainty in risk assessment of chemicals potentially harmful to the environment.

events. The two parameters of the model, initial health and rate of health loss, can be estimated using as few as three points on a survivorship curve (Figure 4). Health changes include damages to biochemical systems when they are "hit" by toxic substances (cf. Clayson et al. 1985).

The dynamics of health are modeled as a continuous form of the "gambler's ruin" process, using a random walk with drift in which the organism eventually loses when health becomes zero and mortality occurs (Figure 5). Because a broad range of environmental conditions is implicit in the survivorship curves that form the basis for the model, and because parameter estimation incorporates large sources of error, this model generates a large region of uncertainty that may require further analysis.

EVALUATING MODEL UNCERTAINTY

Many problems are associated with the communication of risk assessments (Slovic et al. 1982), especially because of the complexities and uncertainties inherent in risk data. Fundamental differences in approaching uncertainty by scientists and regulators result in underevaluation of scientific uncertainty with regard to risk (Gawiaak and Byrd 1987).

PART Screen 1

A1: [W8] 'PART Ver 2.1 - Fugacity Model (R.A. Park, Holcomb Research Inst.) **MENU**

Notes Compute Modify Save Quit PPMGraph Graph% Output

Use arrow keys and [Enter] to select choice, [Alt] A to return to menu

	A	B	C	D	E	F	G	H
1	PART Ver 2.1 - Fugacity Model (R.A. Park, Holcomb Research Inst.)							
2	Parathion	Dor, Israel fish ponds, equil. on day						7.32
3	Analyst RAP	Notes: example		Computed on 11-Oct-87				
4	Mol. wt.	291.17	Sol. =	24.00	mg/l	Vapor P. =	2.30E-05	mm Hg
5	Mol. vol	302.60	Kow =	6.46E+03		LC50 =	NA	(est.)
6	Kpsed =	56.32	Kpsoil =	6.45E+01	(contains		2.00 % organic carbon)	
7	Kbiota =	444.01	Henry =	6.10E-06	m3atm/mol	FUGACITY =	4.61E-10	
8	Init. conc. (ppm)=		0.05	Total Moles (g) =		1.72E-04		
9								
10	COMP.	CONC.	VOLUME	Z	VOL.* Z	MOLES	%	PPM
11		g/g	m3_mol/m3atm	mol/atm	mol			ugmol/g
12	Air	1.19E-03	1.0E+01	4.00E+01	4.00E+02	1.85E-07	0.11	0.00
13	Water	1.00E+00	1.0E+00	1.64E+05	1.64E+05	7.56E-05	44.04	0.02
14	S.sed	2.00E-06	1.0E+00	1.85E+01	1.85E+01	8.52E-09	0.00	1.24
15	Sed.	2.00E+00	1.0E-02	1.85E+07	1.85E+05	8.52E-05	49.61	1.24
16	Biota	2.84E-05	1.0E+00	2.07E+03	2.07E+03	9.54E-07	0.56	9.78
17	Soil	2.00E+00	1.0E-03	2.11E+07	2.11E+04	9.75E-06	5.68	1.42
18	Pure	3.30E-03	1.0E-03	8.40E-10	8.40E-13	3.88E-22	0.00	0.00
19								
20					3.72E+05	1.72E-04	100.00	
11-Oct-87 10:00 AM								

CMD

Figure 3. PART Screen 1.

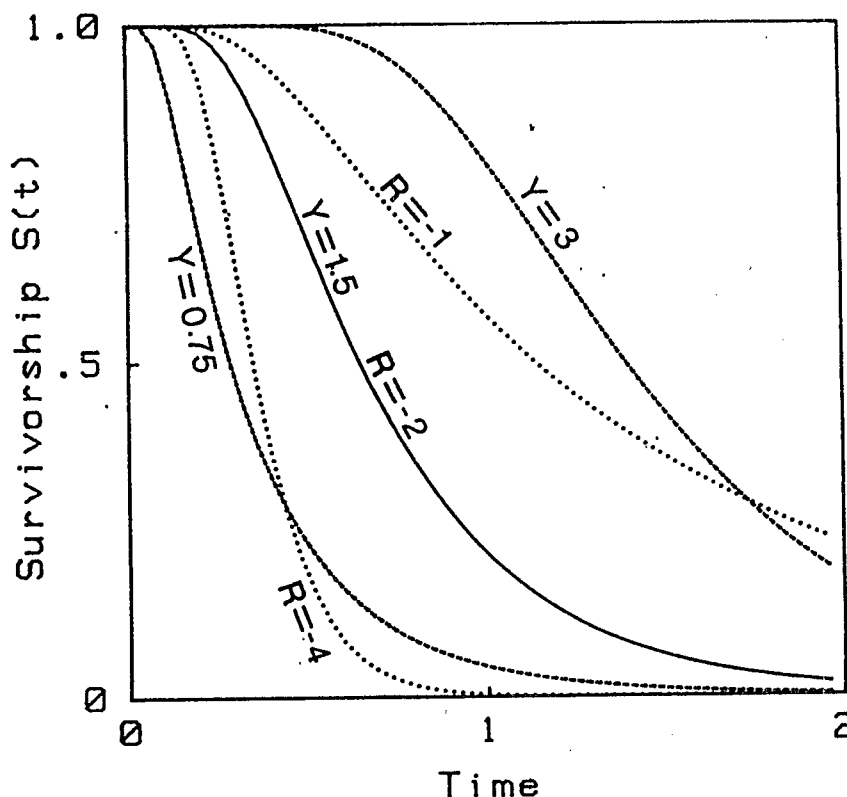


Figure 4. Change in survivorship curves with organism age as initial health, Y , and rate of change of health, R , are varied (Anderson, in review).

A graphical representation of model uncertainty should help break down communications barriers between scientists and regulators. A particular model is run with at least two and possibly many combinations of assumptions, including the most conservative and least conservative options, which are represented by two curves in the graph (Figure 6). The area between the curves is the region of uncertainty due to model accuracy; biological, environmental, and chemical variability; and lack of adequate data on the chemical of interest. If the likely environmental concentration for a chemical falls within the region of uncertainty, further analysis is indicated, either with or without additional data on the chemical.

MODELING REPLICABLE ECOSYSTEMIC EFFECTS

If a more detailed analysis is indicated, MICMOD (Swartzman and Rose 1984) may be used. It represents a gnotobiotic ecosystem containing nitrogen, phosphorus, eight phytoplankton groups, and five zooplankton groups (Taub and Crow 1980); it has the advantage of having been well validated against the results of replicable microcosm experiments. It can be used to evaluate both direct

and indirect effects of a toxic chemical on zooplankton; the direct effects are through toxicity, and the indirect effects are through changes in phytoplankton biomass that serves as food for the zooplankton. The model, however, does not represent the complex degradation pathways and buffering capacity of a natural ecosystem, so that the region of uncertainty may still be too great (Figure 2).

MODELING NATURAL ECOSYSTEMIC FATE AND EFFECTS

No truly appropriate ecosystem effects model exists for aquatic systems at this time (cf. Bartell et al. 1982, 1983, Barnthouse et al. 1982, O'Neill et al. 1983, Borgmann 1985, Barnthouse and Suter 1986, Bartell 1987). The AQUATOX model, currently under development by the senior author, is one response to an obvious need for toxic effects models. The model uses ecosystem bioenergetic algorithms from the CLEANER (Park et al. 1980, 1986) and LAKETRACE (Park 1985) models, transport and degradation algorithms from the PART and PEST (Park et al. 1980, 1981, 1982) models, and toxicokinetic algorithms from the FGETS model (Barber et al. 1986, Suarez et al. 1987). Dose-response formulations are still being developed.

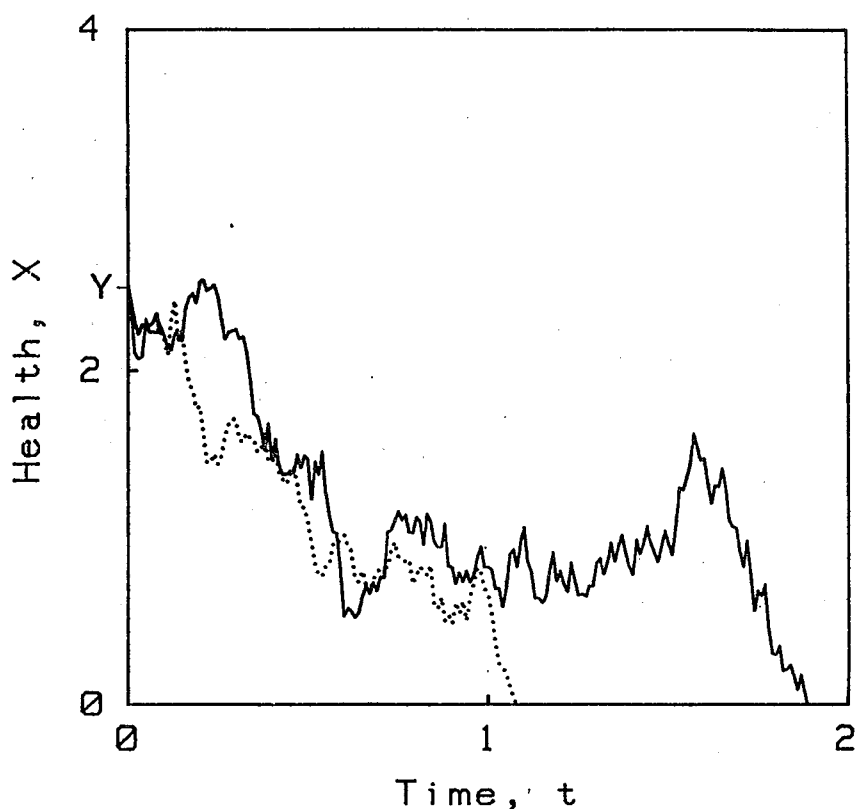


Figure 5. Two random walks of health over time; mortality occurs when health goes to zero. Differences in paths are due to random fluctuations (Anderson, in review).

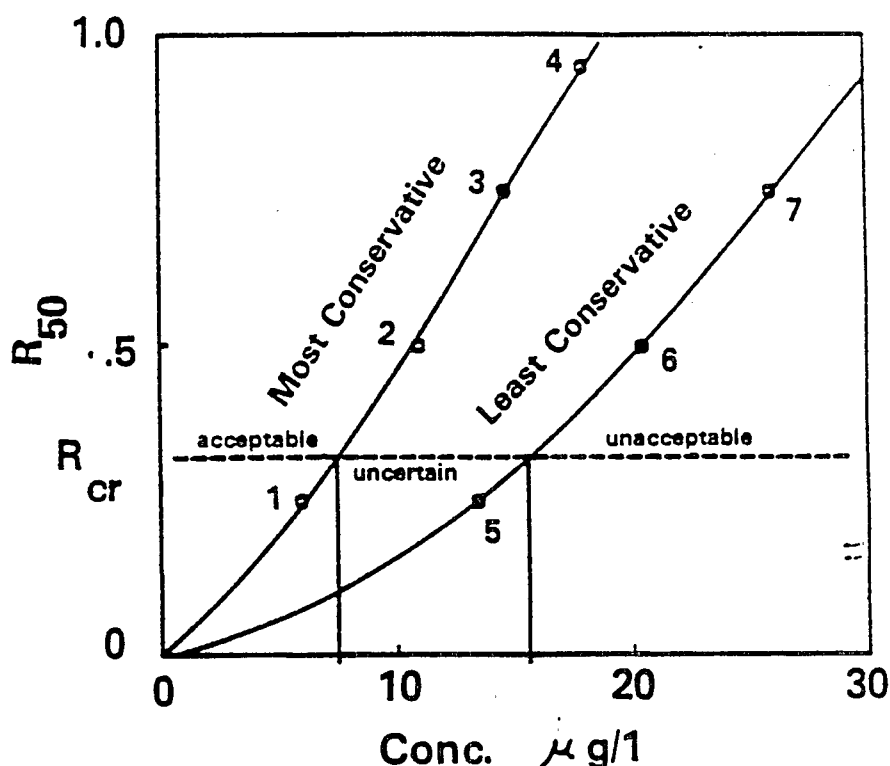


Figure 6. Tripartite decision graph showing median population reduction dose-response curves generated by the most and least conservative implementations of a model (Morison and Anderson 1987).

The model (Figure 7) represents an ecosystem with nitrogen (nitrate and ammonia), phosphate, oxygen, two groups of algae, generalized zoobenthos-zooplankton, two groups of fish, and detritus in a stream or reservoir. It is designed to evaluate both direct and indirect toxicological effects on typical aquatic ecosystems at risk from intentional and unintentional applications of chemicals; default site conditions are provided. The model is implemented on a microcomputer and takes full advantage of that user-friendly computing environment. Pull-down menus (Figure 8) are used to pick options, including full-screen editing of chemical and biological characteristics (Figure 9) and site conditions. Simulation results are summarized in tabular and graphical form (Figure 10).

SUMMARY

In summary, a sequential modeling strategy has been developed in which increasingly complex fate and effects simulation models of aquatic ecosystems are used to assess the environmental risks of a chemical. The strategy is based on the assumption that the more complex models better represent the natural buffering of biotic systems against deleterious chemicals, thereby decreasing the uncertainty in the analysis. A graphical representation of

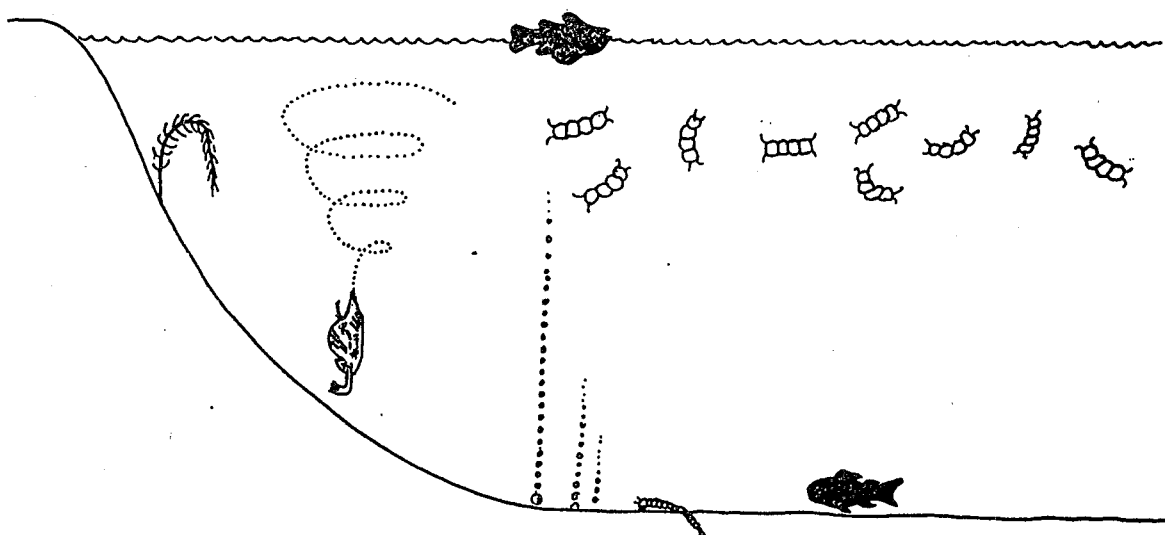


Figure 7. The AQUATOX model for simulating the fate and both direct and indirect effects of toxic chemicals on aquatic ecosystems.

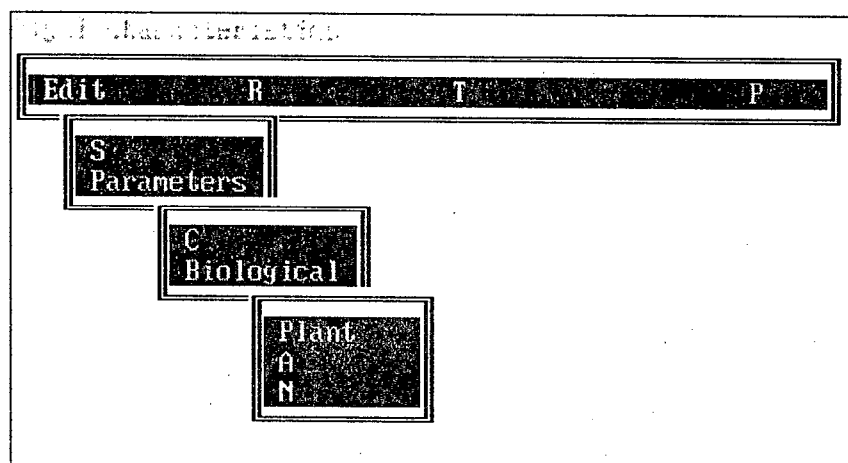


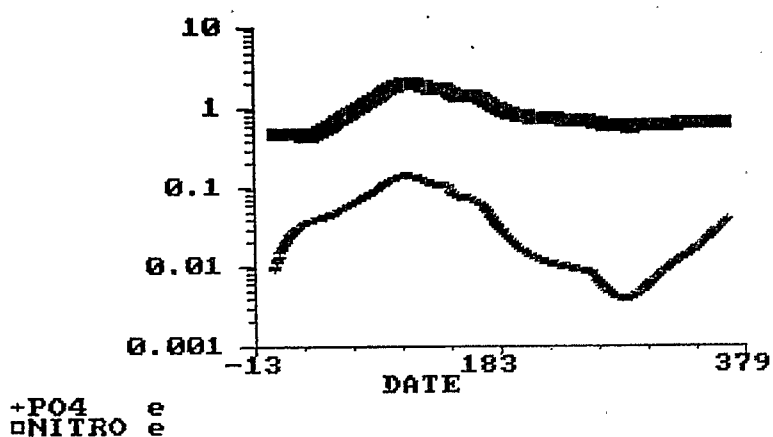
Figure 8. An example of a pull-down menu in AQUATOX.

uncertainty is used to convey the results of the analyses to decision makers, indicating that, at a particular stage in the sequence, a chemical may be accepted for licensing, rejected, or subjected to the next stage of analysis.

ACKNOWLEDGMENTS

Research supported in part by the U.S. Fish and Wildlife Service (Cooperative Agreement 14-16-0009-87-954) and by the U.S. Environmental Protection Agency (Contract 7B1037NAEX).

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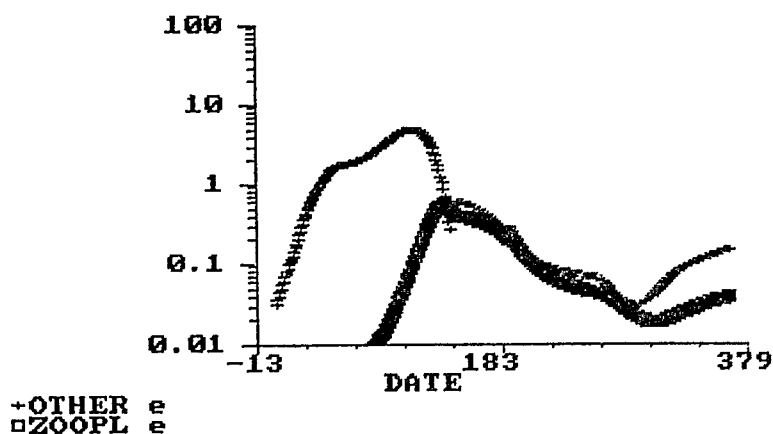


Figure 10. AQUATOX plots of annual patterns of concentration of key ecosystem components for default conditions without toxicological impacts.

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REMOTE MONITORING OF ECOLOGICAL CONDITION OF AQUATIC ECOSYSTEMS

by

A.A. Gittel'son¹ and A.M. Nikanorov¹

ABSTRACT

This work examines the development of scientific grounds for remote sensing of the factors determining buffer capacity of aquatic ecosystems for heavy metal pollution. These methods may be used in short-term biomonitoring of heavy metals in surface waters.

INTRODUCTION

One of the basic objectives of water chemistry and aquatic biology is to develop scientific grounds and methods of monitoring the ecological condition of aquatic ecosystems. Buffer capacity of a water body is probably an important factor for decision-making in this kind of monitoring. Ecosystem buffer capacity for heavy metals is determined by three basic parameters (Izrael et al. 1985, Nikanorov et al. 1985): sorption-accumulation capacity of hydrobiota, complexation capacity of dissolved organic matter (DOM), and deionization capacity of bottom sediments. Sorption of heavy metals by mineral suspension also is important. Ecological efficiency of removal of metals from the biogeochemical cycle is determined by metal complexation with DOM (i.e., their transformation into less toxic forms) (Prokofiev 1981, 1983), metal accumulation by hydrobiota, and burial in bottom sediments in the process of sedimentation.

Metal toxicity is proportional to the rate of a compound's accumulation in living cells (Izrael et al. 1985). Ionic forms of heavy metals possess maximum accumulation ability. The ability of DOM to form complexes with heavy metals is determined by many parameters of the environment, including mineralization (Lapin and Krasnyukov 1986). Ambient temperature and species composition are important factors of metal uptake by phytoplankton cells.

Thus, we may name the factors mainly determining buffer capacity of aquatic ecosystems for heavy metal pollution. They are hydrobiota biomass and its condition determined by chlorophyll-a, suspended minerals and dissolved organics concentrations, temperature, and water salinity. Measurement

¹Hydrochemical Institute, Goskomhydromet, USSR.

of these parameters with quick-screening methods would allow monitoring of the aquatic ecosystem's ecological condition at a higher level and decision-making in the actual time scale.

This work examines the development of scientific grounds for remote sensing of the factors determining buffer capacity of aquatic ecosystems for heavy metal pollution. These methods may be used as a basis for short-term biomonitoring of heavy metals in surface waters.

REMOTE SENSING OF CHLOROPHYLL-a IN PHYTOPLANKTON

We carried out a whole set of investigations of radiation characteristics of water bodies in the visual spectrum band and examined their hydrochemical and hydrobiological parameters. Radiation parameters, invariant in relation to remote sensing instruments, survey conditions, seasonal variations in species composition of phytoplankton, etc., are determined on the basis of this set. Radiation models of mesotrophic and eutrophic water bodies relating their spectral luminance factors to hydrobiological and hydrochemical parameters are developed.

The following set of instruments was developed.

1. Spectrometer with high spectral resolution for measuring luminances of upwelling radiation (B_{\uparrow}), sky in zenith (B_H), and irradiance (E_0) in the mode of continuous recording in the wave band from 430 to 750 nm (Gittelson et al. 1986a).

2. Quick-screening spectrometer measuring B_{\uparrow} , B_H , and E_0 values in nine spectral channels, 10 to 15 nm wide, in the band from 430 to 750 nm in less than a second.

3. Portable spectrophotometer for measuring of water attenuation factor in nine spectral channels, 15-nm wide (Gaivoronskii et al. 1983).

4. Nephelometer for measuring water scattering factors at 90° .

5. Spectrofluorimeter for measuring water fluorescence intensity (Gittelson et al. 1986a).

6. Instrument for registration of the data of measurement recording information for subsequent "unloading" to the computer.

Figure 1 presents spectral luminance factors typical of the studied water bodies--the rivers Don, Seversky Donetz, and Kuban, and the reservoirs Tsymlyanskoye, Kuibyshevskoye, Rybinskoye, Sea of Azov, Lake Balaton. Maximum luminance at the waves from 540 to 580 nm is mainly determined by light scattering by suspended solids. At the high concentrations of phytoplankton in the band 630 to 635 nm, we register minimum $\rho(\lambda)$ and maximum is registered at the waves 650 to 655 nm. At all C_{XA} concentrations, $\rho(\lambda)$ minimum is registered at 670 nm wave and maximum varies from 685 nm at low C_{XA} values to more than 700 nm is registered at $C_{XA} > 30 \text{ mg m}^{-3}$. All local $\rho(\lambda)$ dependency

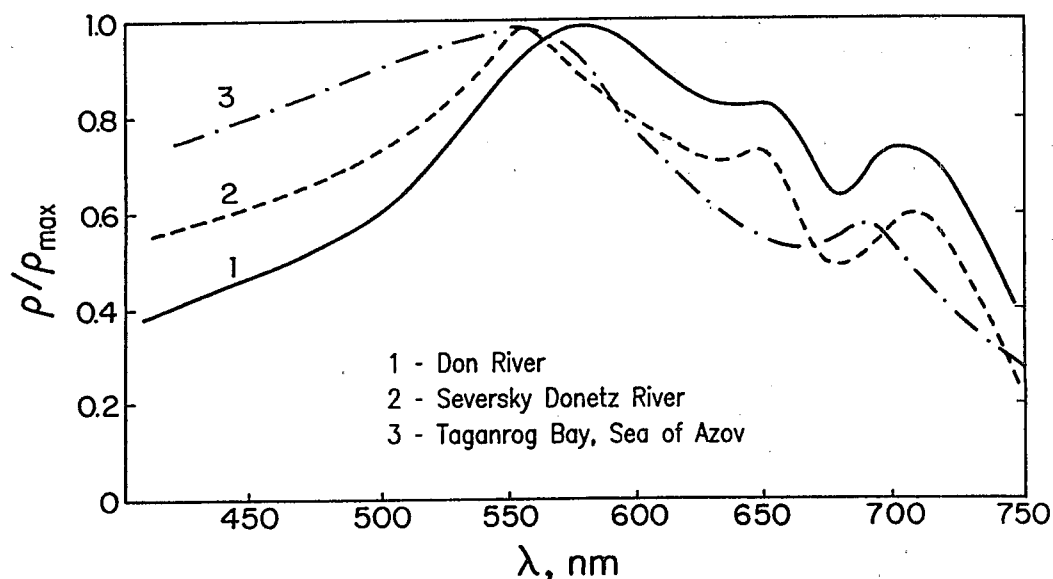


Figure 1. Typical relationships between spectral luminance factor (SLF) and wave length for different water bodies.

extremes are mainly related to spectral motion of the factors of light absorption by phytoplankton pigments. $\alpha(\lambda)$ minima of $\rho(\lambda)$ at 630 and 670 nm correspond to $\alpha(\lambda)$ maxima and maximum at 650 nm corresponds to minimum at $\alpha(\lambda)$. $\rho(\lambda)$ maximum at the wave length more than 685 nm may be determined by luminescence of phytoplankton pigments (Gordon 1979) and variation in the ratio between water absorption factors and phytoplankton pigments at high concentrations (Vasilov and Kopelevich 1982). Not excluding possible contribution of luminescence signal in water radiation at 680 nm, we must point out that the shift of maximum location to long wave band with $C_{x\lambda}$ increase proves the validity of the model (Vasilov and Kopelevich 1982).

Decoding features of optically active ingredients in spectrometric information must be the function of spectral luminance factor (SLF) at different waves such as color index, where one of $\rho(\lambda_1)$ values is as variable as possible with variation of C_K concentration and another one depends on C_K to minimum extent. However, both this value and $\rho(\lambda)$ should reflect the influence of survey conditions and apparatus function of the sensor as accurately as possible. Spectral motion of primary hydrooptical parameters is the most important factor in selection of decoding features. $\rho(\lambda)$ varies with C_K mainly due to variation in $\alpha(\lambda)$. In the short wave band of the spectrum, $\alpha(\lambda)$ is related to $\alpha_F(\lambda)$, $\alpha_{POB}(\lambda)$ and $\alpha_B(\lambda)$ and in the long wave band ($\alpha_{POB} \approx 0$) is related only to $\alpha_F(\lambda)$ and $\alpha_B(\lambda)$, $\alpha(670)$ increasing with $C_{x\lambda}$ growth and $\alpha(700)$ decreases. So, $\rho(675)$ may be the components of decoding $\rho(700)$ may be also.

Availability of the above $\rho(\lambda)$, $\alpha(\lambda)$ and $\sigma_{180}(\lambda)$ allowed us to try the following decoding features (Gittelsohn et al. 1986e, Kondratyev et al. 1987b).

$$\rho(700)/\rho(560); \quad \rho(550)/\rho(670);$$

$$\rho(700)/\rho(670); \quad \rho(700)/\int_{\lambda_{\min}}^{\lambda_{\max}} \rho(\lambda) \cdot d\lambda;$$

$$[\rho(700) - \rho(675)] / [\rho(700) + \rho(675)];$$

$$\rho(700)/\rho(520); \quad \rho(700)/\rho(620).$$

For the rivers Don and Seversky Donetz, C_{XA} relation to radiation parameter $\rho(100)/\rho(560)$ is the following (Figure 2).

$$C_{XA} = 67.67 [\rho(700)/\rho(560)]^{2.75}, \text{ mg m}^{-3} \quad (1)$$

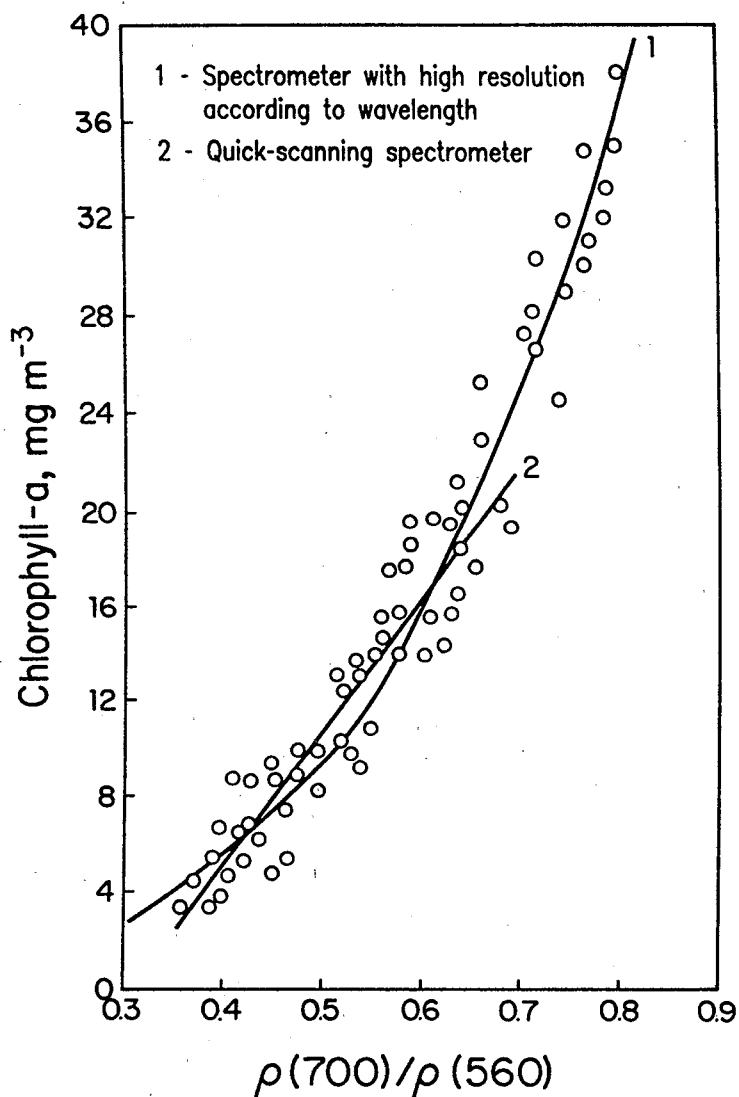


Figure 2. Relationships between chlorophyll-a concentration in phytoplankton and $\rho(700)/\rho(560)$ ratio for the river Don and Seversky Donetz based on the data.

where the number of stations is $n = 68$, correlation coefficient is $r = 0.962$, factor is $F = r^2(n-1)/(1-r^2) = 843$, standard error of δC_{XA} evaluation is not more than 2.43 mg m^{-3} . Suggested features were validated at Lake Balaton in a wider range of C_{XA} concentrations. If C_{XA} is 4.5 to 100 mg m^{-3} (Figure 3).

$$C_X = 122.85[\rho(700)/\rho(560)]^{2.3}, \text{ mg m}^{-3} \quad (2)$$

when $n = 103$, $r = 0.954$, $F = 2046$, $\delta C_{XA} = 2.8 \text{ mg m}^{-3}$. The rest of the features suggested are as efficient as the above ones.

Stability of models (1) and (2) was tried many times. Using equations (1) and (2), C_{XA} were estimated on the basis of remote surveys and values were compared with C_{XA}^{AH} determined analytically. For the rivers Don and Seversky Donetz and the sea of Azov, standard deviation of the initial and measured values does not exceed 3.2 mg m^{-3} and it does not exceed 2.3 mg m^{-3} (Figure 4) for Lake Balaton.

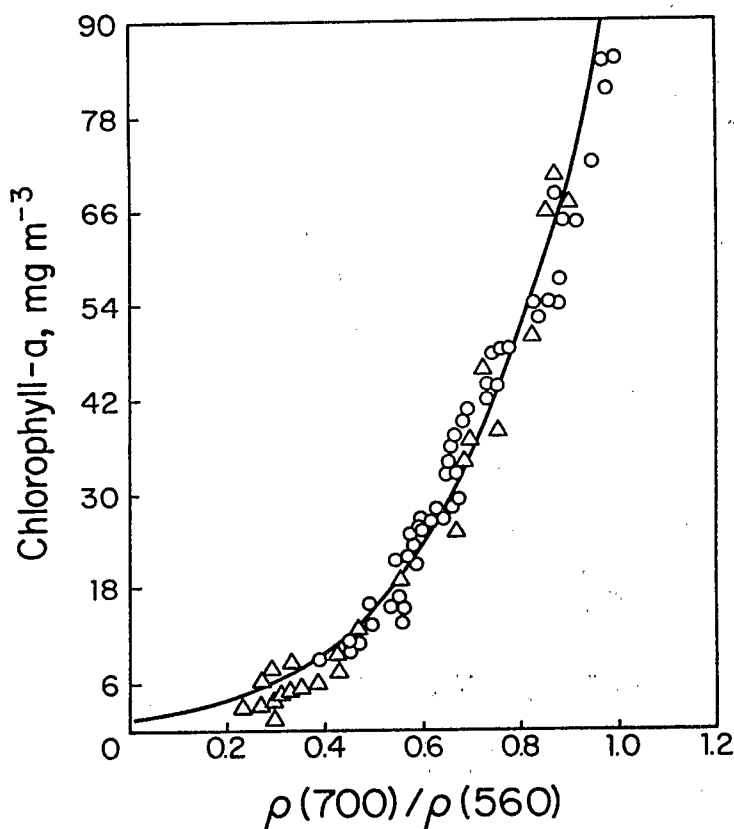


Figure 3. Relationships between chlorophyll-a concentration in phytoplankton and $\rho(700)/\rho(560)$ ratio for Lake Balaton.

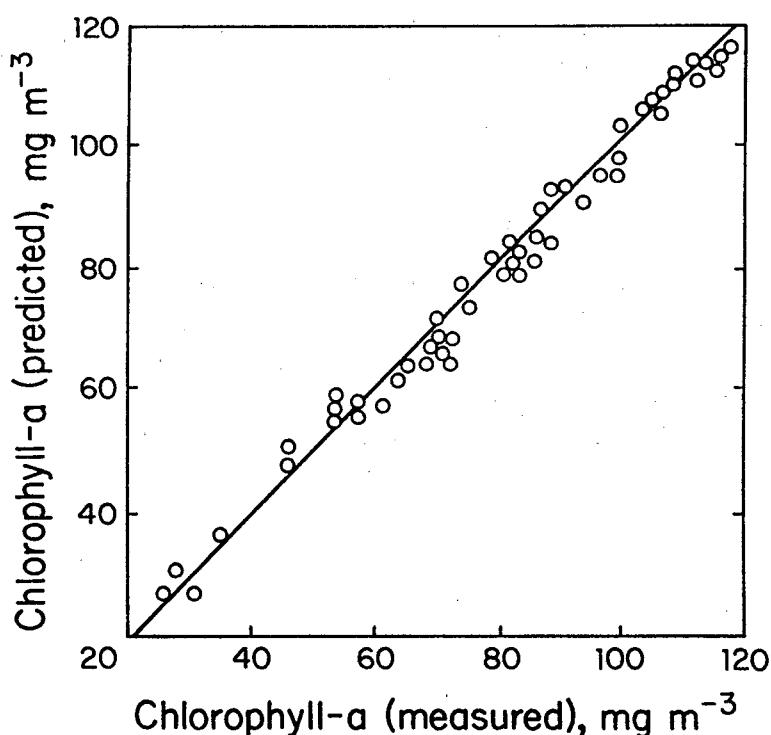


Figure 4. Comparison of chlorophyll-a concentration values predicted by radiation model of the type (1) - C_{λ}^{np} and analytically determined C_{λ}^{n3m} .

REMOTE SENSING OF SUSPENDED SOLID CONCENTRATION

Optical features of suspended solids are mainly determined according to scattering factors. The most serious variation of $\rho(\lambda)$ with C_{ss} variation is observed in the band 540 to 580 nm; ρ is minimum in this band. So, the selection of one of SLF making up the decoding feature is evident-- $\rho(560)$. The results of factor analysis of spectrometric data (Kondratyev et al. 1987a) show that in the wave band from 580 to 660 nm and from 500 to 520 nm spectral variables do not contribute greatly to the dispersion of three marked factors. This allows us to assume that the influence of SLF is unimportant in these wave bands to the final factor solution. This allows us to apply SLF in the above wave bands for valuation of C_{ss} in decoding features on the basis of spectrometric information. We evaluated a number of features and the following ones turned out to be the most efficient:

Regression equation of C_{ss} constraint with radiation parameters for the rivers Don and Seversky Donetz is the following

$$C_{ss} = 60.98 \{ [\rho(560) - \rho(520)] / [\rho(560) + \rho(520)] \}^{0.49} \quad (3)$$

where $n = 61$, $r = 0.93$, $F = 373$, $\sigma_{C_{ss}} = 3.2 \text{ g m}^{-3}$.

There are two reasons for rather serious errors of C_{chl} estimation. One of them is the variation of $\delta_{180}(\lambda)$ and $\rho(\lambda)$ in "referent" areas with C_{chl} variation, the other one is the variation in granulometric composition of particulate matter, which affects SLF seriously. In the process of remote sensing of surface water quality, we should probably use an approach for C_{chl} determination and a parameter functionally bound with C_{chl} by the average radius of the particles and by the law of their distribution according to their size. This integral parameter determining environment turbidity is rather closely bound to the factor determining upwelling radiation and possessing maximum loads in the wave band from 540 to 660 nm (Kondratyev et al. 1987a).

With considerable variation in the concentrations of particulate matter at the water surface in the process of chlorophyll-a concentration, determination of $\rho(620)$ and $\rho(520)$, which are in minimum dependency on C_{chl} and C_{XA} , is rather efficient.

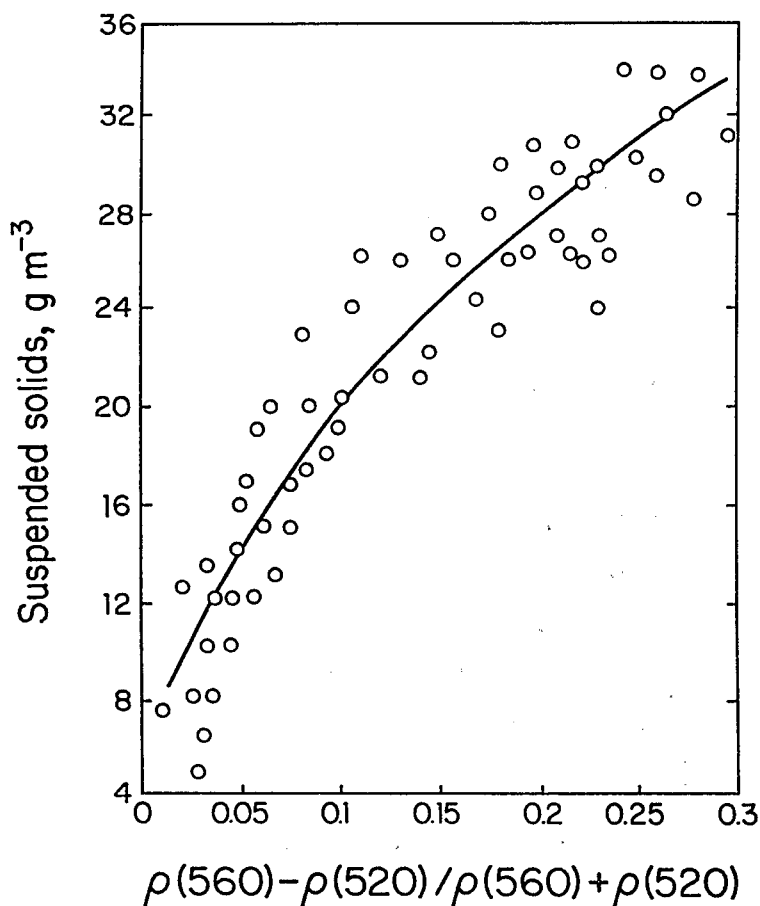


Figure 5. Relationships between suspended solids concentration and $[\rho(560) - \rho(520)] / [\rho(560) + \rho(520)]$ ratio for the rivers Don and Seversky Donetz.

Measurement of DOM concentration is carried out according to its luminescence in natural waters. Spectro-luminescent features of humic and fulvic acids are studied to understand the demands for the systems of induction of the signal of DOM fluorescence, its registration, and determination of decoding features of ingredients on the basis of the information obtained.

When observing at the wave $\lambda = 470$ nm, the maximum at the excitation spectrum of fulvic acids is marked at the waves 340-350 nm. When we have humic acids with $\lambda = 550$ nm, it is marked at the waves 460-470 nm. In the wave band from 400 to 450 nm, there is a plateau in the excitation spectrum; excitation intensity at this plateau is 0.7-0.8 of maximum (Figure 6).

Spectral features of fluorescence excitation when it is observed at the waves 470 and 550 nm allows one to estimate concentrations of fulvic and humic acids in solutions. With excitation at $\lambda_B = 350$ nm, fulvic acid (FA) fluorescence is maximum when $\lambda_H = 470$ nm, and humic acid (HA) fluorescence is

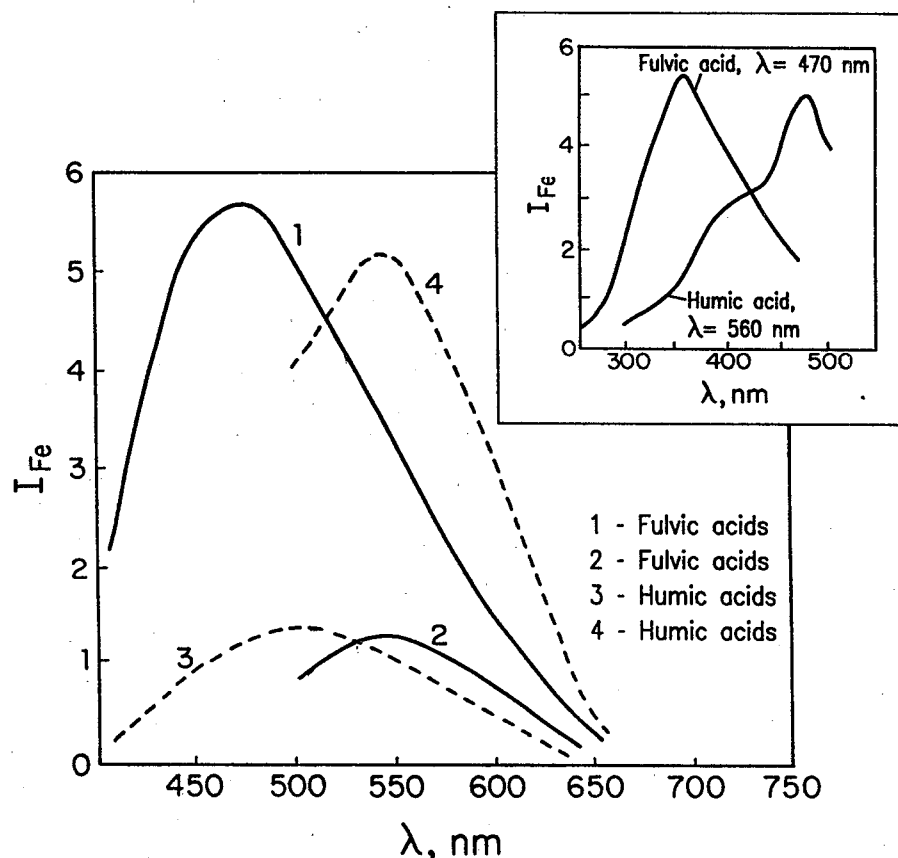


Figure 6. Fluorescence spectra of fulvic acids (1,2) and humic (3,4) with excitation at waves $\lambda=350$ nm (1,3) and $\lambda=470$ nm (2,4). Insertion presents fluorescence excitation spectra: 1 - of fulvic acids with $\lambda=470$ nm; 2 - of humic acids with $\lambda=560$ nm.

maximum when $\lambda_H = 500$ nm (its fluorescence intensity being much lower than that for FA). With excitation at $\lambda_B = 470$ nm, HA fluorescence intensity is 4 to 5 times higher than that for FA (Figure 6). Thus, with fluorescence excitation at the wave $\lambda_B = 350$ nm and observation at $\lambda_H = 470$ nm, it is possible to estimate FA concentration and at $\lambda_B = 470$ nm and $\lambda_H = 560$ nm, we may estimate HA concentration. It is reasonable to use iteration (taking into account contribution of HA fluorescence at $\lambda_H = 470$ nm and FA fluorescence at $\lambda_H = 560$ nm) to estimate their concentrations in mixed solutions.

On the basis of spectral features identified with a lidar-spectroanalyzer, possibilities for remote sensing of HA and FA concentrations were studied. Investigations were carried out in a laboratory at the distances of sensing from 2 to 5 meters. Solutions were put into quartz glass tubes that were 0.15 diameter and 0.3 m long. Power of laser exciting radiation was from 100 to 300 kW at $\lambda = 347$ nm when generating impulse at 30 to 35 nm. FA fluorescence maximum was registered with a lidar receiver in the wave band 447 ± 10 nm and 540 ± 10 nm for HA (Figure 7). Fluorescence spectral features identified with laser excitation allow one to estimate concentrations of DOM with one excitation - 347 nm. Intensity of reverse radiation at the waves 447 and 540 nm influences concentrations of HA and FA in two-component solutions. Relationships of fluorescent parameter (ratio between fluorescence signal at certain wave lengths to the signal of water Raman scattering) indicate that this parameter is a measure of HA and FA concentration in a solution (Figure 7).

We estimated fluorescence section of both components of organic matter attributed to mean mass molecule. Calculation of fluorescence section σ_φ is conducted with the following formula.

$$\sigma_\varphi = \psi_0 \frac{\sigma_{kp} \cdot n_{H_2O}}{n_\varphi} \quad (4)$$

where σ_{kp} is Raman scattering section, M^2/strad ; n_{H_2O} is concentration of water molecules; n_φ is concentration of FA and HA molecules; $\psi_0 = I_\varphi/I_{kp}$ is fluorescent parameter; I_φ , I_{kp} are intensities of the signal of fluorescence and Raman scattering, respectively. Fluorescence parameter was determined at low (0.1-0.5 ppm) concentrations of organic matter. In this case, the relative contribution of fluorescence to the signal of Raman scattering is rather unimportant.

For HA with mean molecular mass 35000 a.n. $\sigma_{rk} = (1.2 \pm 0.5) \cdot 10^{-23} \text{ m}^2/\text{strad}$; for FA with mean molecular mass 1000 a.n. $\sigma_{rk} = (1.5 \pm 0.5) \cdot 10^{-25} \text{ m}^2/\text{strad}$. For such complex multicomponent substances as HA and FA, the fluorescence section may vary considerably depending on the relation between molecules with different mass in a solution because efficiency of FA and HA fluorescence is mainly determined by this factor.

The sensitivity threshold of the method as well as its error depends on the conditions of measurement and in particular, probing depth, hydrooptical

features of the environment, etc. In our experiments, the sensitivity threshold of the method was less than 5 ppb at the probing depth of 0.25 m. It is evident that, at greater depths of probing, the sensitivity threshold of the method will be much lower.

Application of the method of fluorescence parameter at inland surface waters is often complicated due to rather high values of water attenuation factor and problems connected to the evaluation of fluorescence contribution of different organic substances to the signal at the frequency of water Raman scattering. So, surface waters need a completely different method of evaluation of hydrooptical parameters of the environment and of evaluation of fluorescent signal in remote laser probing. It may be used on the SLF measurement with lidar-spectroanalyzer in the intervals between laser impulses. SLF equals the ratio between luminescences of radiations upwelling from water and downwelling upon it. SLF provides information on absorbing and scattering features of aquatic environment. Using decoding features of optically active ingredients defined for inland surface waters (Gittelsohn et al. 1986e, Kondrat-

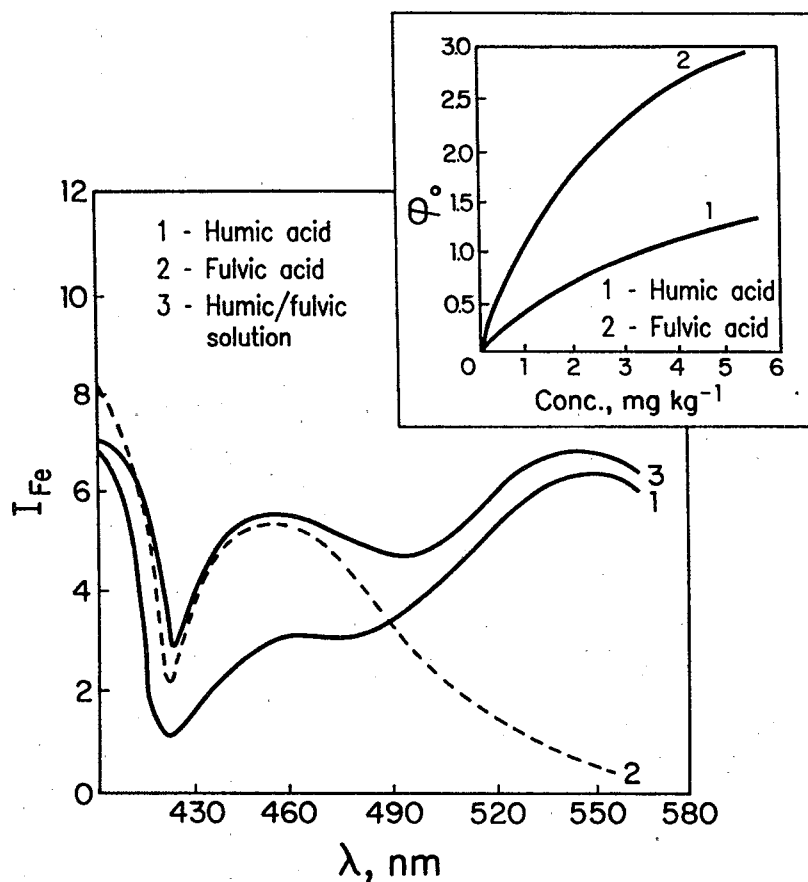


Figure 7. Fluorescence spectra obtained on lidar-spectroanalyzer for humic acid, fulvic acid, and a combined solution. Insertion presents relationship between $\phi_0 = I_\phi / I_{kp}$.

yev et al. 1987b) on spectrometric information and evaluating fluorescence signal registered by lidar on SLF functional at different wave lengths, it is possible to take into account the influence of absorbing and scattering features of the environment upon the intensity of fluorescent signal registered by lidar (Gittelsohn et al. 1986c). This allows one to increase the field of application of laser spectroscopy considerably and to apply it for remote sensing of organic matter concentration in surface waters. Testing of the method suggested on a number of water bodies proved its validity.

REMOTE SENSING OF WATER SALINITY AND TEMPERATURE

The relationship between SHF radiation of water bodies and their physico-chemical parameters (PCP) is the basis for the SHF radiation method of water salinity and temperature estimation. Luminance temperature is the measure of self-radiation. The relationship between the luminance temperature of water and its PCP is studied under laboratory and field conditions. Laboratory-measuring the SHF-radiometric complex included radiometers with wave lengths 2.25, 3.0, 7.77, 18, and 30 c and fluctuation sensitivity at least 0.3 K. All the field measurements were conducted with the help of the airplane AN-2. Antenna systems of this airborne complex provided relations between airplane flight altitude, H, and the side of resolution element at the area $D=0.7 H$. Some results of the experiments and calculations are presented in Figures 8 and 9. Field experiments cover the measurements of PCP of water bodies with salinity from 0 to 400 g kg⁻¹.

The investigations provided stable functional relationship between self-radiation field intensity and water salinity, which allows remote sensing (Gittelsohn et al. 1986b), Gittelsohn et al. 1986d, Gittelsohn et al 1987). Important spectral features in radiation-salinity and radiation temperature relationships are detected that are the basis for actual solution of an incorrect inverse problem--a determination of PCP of water bodies according to their SHF self-radiation and development of the procedure for remote measurement of PCP.

According to modeling options and experimental information, radiation features of water bodies in the SHF band depend on water salinity and temperature and on the condition of the water surface as well. The degree of influence of different parameters upon radiation features however, is quite different according to the spectrum. This peculiarity determines possibilities for remote sensing of hydrophysical parameters and evaluation of their origin and intensity on the basis of the data of SHF radiation intensity measurement (luminance temperature T_{λ}) in certain fragments of the spectrum solving a system of radiation-hydrophysical equations (Gittelsohn et al. 1986d).

$$F_{\lambda i}(Q_{\lambda}, \dots, Q_j, \dots, Q_n) = T_{\lambda i} \quad (5)$$

$$i = 1, 2, \dots, m \quad m \geq n$$

Because the relationship among T_{λ} and water temperature and salinity is non-linear (Figures 8 and 9), Equation 5 is non-linear in the general case. If the absolute values of temperature, salinity, and other parameters Q_j are

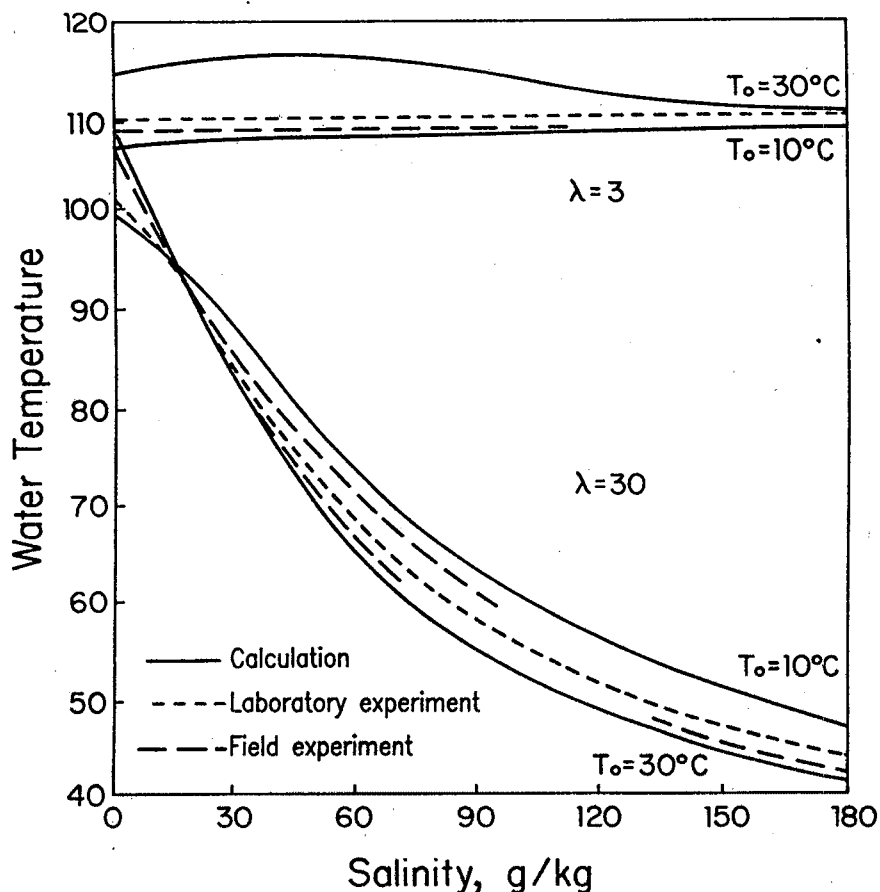


Figure 8. Relationship between water luminance temperature in SHF band and its salinity with different thermodynamic temperature values.

not the features identified but their ΔQ_j variations linearized and presented as:

$$\sum_{j=1}^n a_{ij} \Delta Q_j = \Delta T_{\lambda i} \quad i=1,2,3,\dots,m \quad (6)$$

where $\Delta T_{\lambda i}$ is variation in luminance temperature at the fragments of spectrum λ_i , related to variations in PCP of a water body. $a_{ij} = \Delta T_{\lambda i} / \Delta Q_j$ are coefficients describing radiation field sensitivity at the wave length λ ; to variations of Q_j parameter (within the limits of linear relationship $\Delta T_{\lambda i}(\Delta Q_j)$). In centimetric and decimetric wave bands, the rate $\partial T_{\lambda} / \partial T_0$ strongly depends on water surface temperature. The area of wave lengths from 5 to 8 c where emissivity does not depend seriously on water PCP and is about 0.5 K/°C is the exception. The influence of salinity of water bodies is especially strong in decimetric area of the spectrum (Figure 8) where the rate of radiation-salinity relationship varies from 0.5 to 1 K/°/‰.

Possibilities of remote sensing of physico-chemical parameters in water bodies according to their SHF-self-radiation are tested in laboratory and field conditions in a wide spectrum of variations in water salinity (from 0 to 400 g kg⁻¹) and temperature (from 5° to 27°C).

Determination of the exact characteristics of the method in the field is rather a serious problem. Due to high variability of PCP of water bodies and pilot plots in time and space, joint experiments with simultaneous contact and noncontact measurements of PCP are presented.

Joint simultaneous measurements of geophysical parameters with quick-screening contact and remote methods allowed us to estimate exact characteristics of the method in a wide range of PCP variation.

In the result of validation, testing, and metrological evaluation of the method, its metrological and technological-economic parameters were defined:

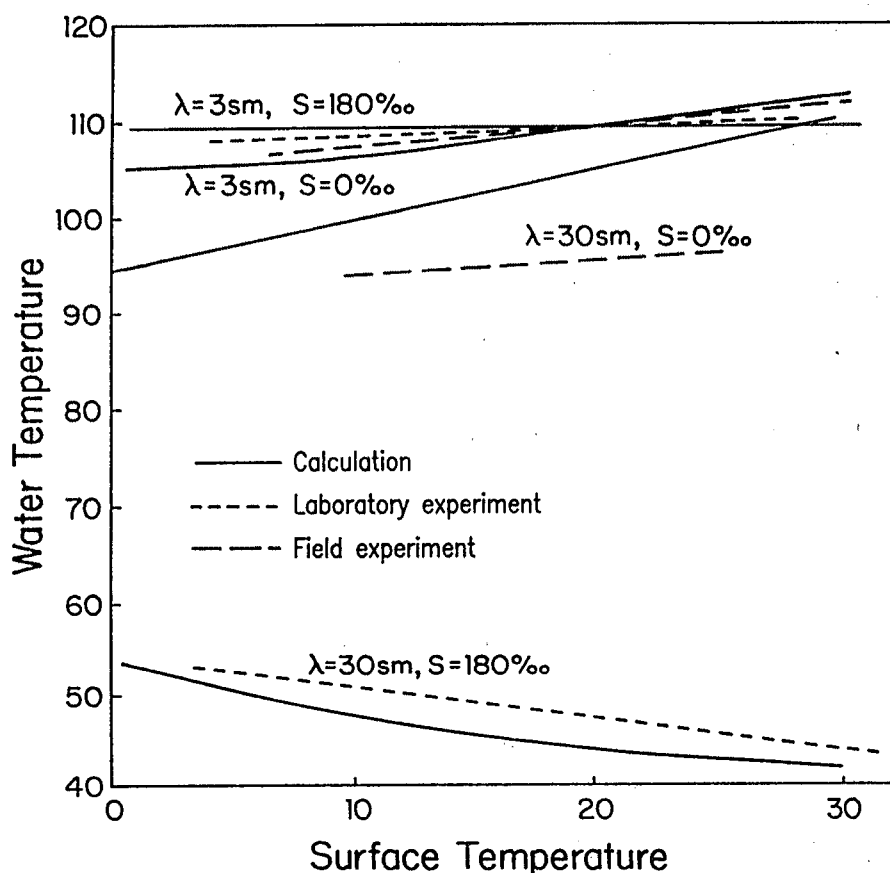


Figure 9. Spectral relationship between sensitivity of SHF radiation intensity and variations in thermodynamic temperature of water surface: $S=0^\circ/\infty$; $S=20^\circ/\infty$; $S=40^\circ/\infty$; $1-T_0=30^\circ\text{C}$; $2-T_0=20^\circ\text{C}$; $3-T_0=10^\circ\text{C}$; $1-T_0=0^\circ\text{C}$.

- Response threshold according to salinity from 0.2 g kg^{-1} for HCl to 2 g kg^{-1} for NaCl;
- Salinity estimation range--from the value corresponding to response threshold to 400 g kg^{-1} .
- Resolution according to salinity with radiometer time constant $\tau = 1 \text{ s}$ is 1 g kg^{-1} ;
- Determination error of area-averaged salinity with radiometer time constant $\tau = 1 \text{ s}$ with confidence 0.95 is 2 g kg^{-1} ;
- Resolution according to water surface temperature with radiometer time constant 1 s is 0.6°C .
- Determination error of area-averaged water surface temperature is not higher than 2°C with confidence level 0.95 in temperature variation range from 0 to 35°C .

Spatial resolution is 0.7 of the flight altitude. Capacity of hydrochemical survey of the pilot plot with 1 km distance between the routes is $162 \text{ km}^2/\text{hour}$. The results of hydrochemical survey are presented in 1 hour as the charts of salinity and water temperature variations.

Figure 10 presents comparison of water salinity data measured with contact methods and remote sensing using SHF-radiometric complex. Figure 11 presents comparison of contact and remote sensing data on thermodynamic temperature of water bodies.

CONCLUSION

The investigations created the necessary prerequisites for development and application of noncontact methods of chlorophyll-a concentration estimation in phytoplankton with standard error not more than 2.3 mg m^{-3} , suspended soils concentration with standard error less than 3.5 ppb, concentrations of humic and fulvic acids with the error less than 5 ppb, water salinity with the error about 0.5 g kg^{-1} and temperature--less than 0.6°C . Validation of these methods with short-term control of aquatic ecosystems allows us to conclude that their application further improves monitoring of water bodies, provides short-term determination of buffer capacity, and allows decision making in real-time.

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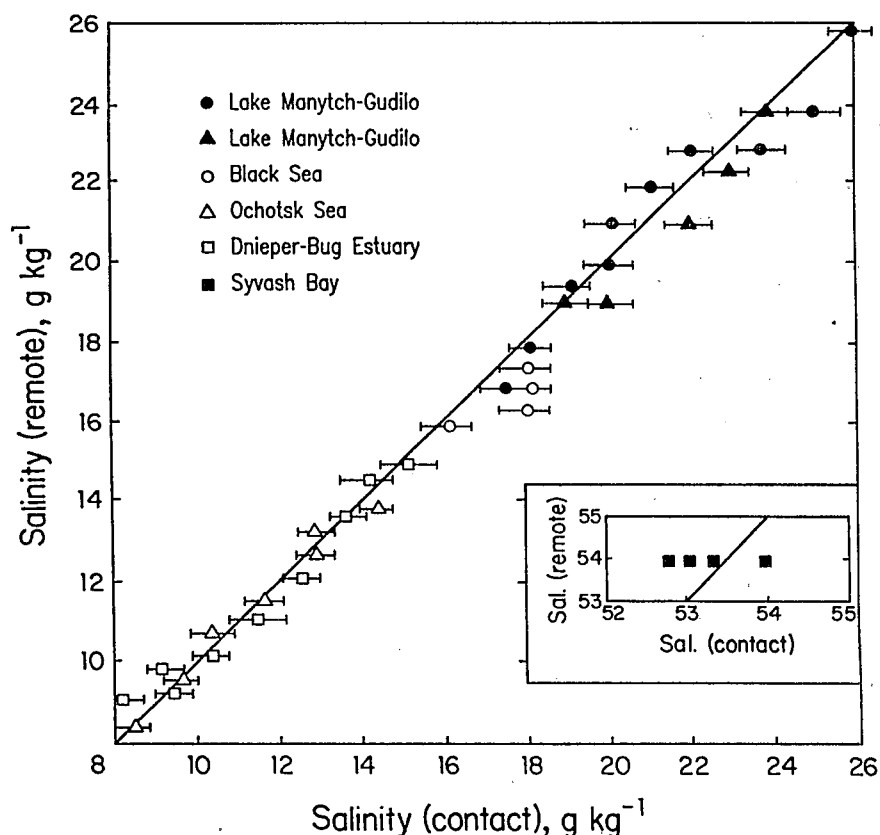


Figure 10. Comparison of results of water salinity measurements with contact (M_{cont}) and SHF radiation (M_{dist}) methods.

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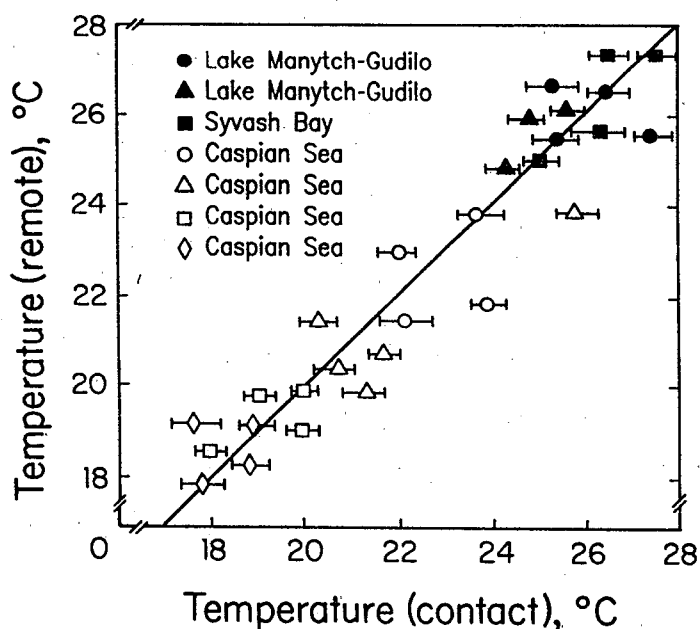
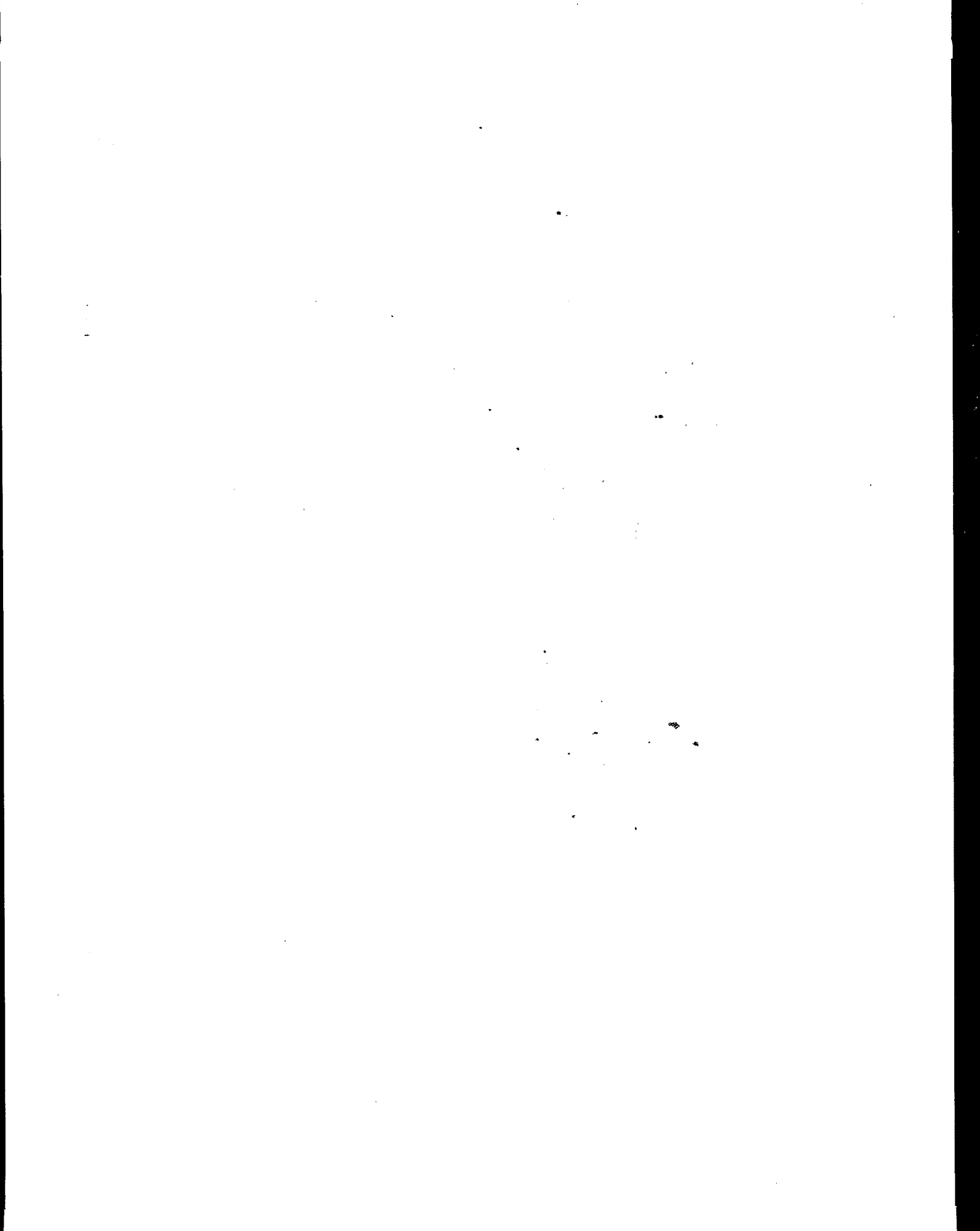


Figure 11. Comparison of results of thermodynamic water temperature measurements with contact (T_{cont}) and SHF-radiometric (T_{dist}) methods.

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