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INTERACTIONS OF BIOGEOCHEMICAL CYCLES IN AQUEOUS ECOSYSTEMS

Part 7

Proceedings of a workshop arranged by the Scientific Committee on Problems of the Environment (SCOPE) and the United Nations Environment Programme (UNEP) at Listvyanka/Irkutsk, USSR, September 2-8, 1988

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(Editors)

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Cover (front): Eastward view across the southern part of Lake Baikal with the research vessel Balchash (photo by S. Kempe).

Cover (back): Photograph of B.J. Dybowskii (1835-1930), the first scientist to explore Lake Baikal

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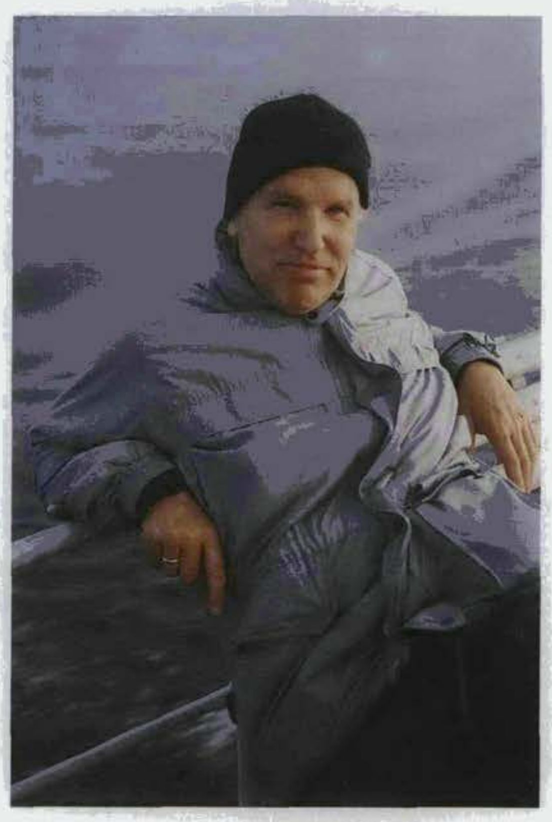

Egon T. Degens aboard the R/V Dybowskii on Lake Baikal, September 5th, 1988. This trip was Degens' last voyage. He died February 19th, 1989 (Photo by S. Kempe).

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The SCOPE/UNEP International program of Studies on the Biogeochemical Cycles has four principal subjects: Nitrogen with its focal point at the Swedish Academy of Sciences, Phosphorus (University of Saskatchewan), Carbon (University of Hamburg), and Sulphur (USSR Academy of Sciences). The four centers are undertaking the major task of studying the complex interactions between the cycles of these substances. The purpose is to demonstrate the resulting overall limits, which govern our lives and the future of mankind.

The emerging climate changes caused by the greenhouse effect make it increasingly clear that our Earth is an integrated system. But environmental systems can be stretched by mankind's actions to limits at which changes in them can occur rapidly and perhaps irreversibly. It is possible that some of nature's thresholds are already being crossed.

The best predictions now available on the climate change indicate potentially severe economic and social implications for present and future generations. These could - if not properly managed by international action - worsen international tensions and increase the risk of conflicts among and within nations. It is imperative that the world community act now against these present and future threats. National interests must be subordinated for the common good to protect the rights of all the living elements of the planet.

It is essential that the scientific understanding on which to base the policies to cope with climate change be rapidly established. Sufficient knowledge must be generated to move the center of action from the research laboratories to the decision-makers' desks. Only then can we make the complex choices essential in charting a wise and safe course to the future of our one Earth.

The Lake Baikal workshop (1988) was held under the joint auspices of the Hamburg University Carbon Study Unit and the Sulphur Study Unit of the USSR Academy of Sciences. The workshop addressed the role of interactions of biogeochemical cycles in aqueous ecosystems. Reports on studies carried out in lakes of various types and different climates and ecology provided a wealth of information and mapped the future steps towards making these studies globally comprehensive, and, hopefully, leading to the elaboration of the policies.

Lake Baikal which contains a fifth of the Earth's freshwater reserves was a most appropriate venue for a workshop on the interactions of biogeochemical cycles. It is among the cleanest of all lakes in the world and it is two million years old. Thus, it is an invaluable laboratory for the creation of indigenous species and its sediments are archive of the world's climatic history. The workshop indeed drew further international attention to this unique body of fresh water. Such scientific environmental interaction - true to the concept of the global commons - is inspiring to all who work for the indivisible global environment.

Nairobi, January 1989

MUSTAFA K. TOLBA
Executive Director
UNEP

Foreword

The main objective of the SCOPE "Biogeochemical Cycles" program is to generalize data on the quantitative assessment of reservoirs and fluxes of elements in different ecosystems and globally. As a rule during working group sessions new factual materials are discussed that characterize processes of a single element cycle, e.g., carbon, sulfur, nitrogen or phosphorus. Yet chemical and biological processes of element cycles in actual natural ecosystems are closely connected and interacted. For example, green plant photosynthesis is the vital process both in carbon and oxygen cycling, while during bacterial photosynthesis and microbial sulfate reduction the carbon cycle is closely interlaced with that of sulfur. Taking into account the importance of exchanging data on cycle interaction, SCOPE organized at least two workshops on the problem, in 1979 in Stockholm (Sweden) and in 1981 in Örsundsboro (Sweden). Proceedings of the meetings, published in two SCOPE Reports entitled "Some Perspectives of Major Biogeochemical Cycles" (SCOPE Report 17, 1981) and "The Major Biogeochemical Cycles and Their Interactions" (SCOPE Report 21, 1983), include reviews dealing with the interaction of element cycles in different ecosystems and globally.

A workshop on the interaction of sulfur and carbon cycles in intercontinental water bodies and marginal seas continued this work. It was held September 2-6, 1988, in Listvyanka, a village on the Lake Baikal. The workshop was organized on the initiative of the SCOPE Carbon and Sulfur units, the Institutes of Biophysics and Limnology of the USSR Academy of Sciences, Siberian Branch, with an active participation of the Center for International Projects of the USSR State Committee for the Environment Protection.

Experts from 15 countries as well as UNEP and SCOPE representatives participated in the workshop. A large group of scientists from the Siberian Branch of the USSR Academy of Sciences took part in the meeting for the first time. It was on their initiative that the workshop discussed and unanimously supported a Declaration on the necessity of creating an International Ecological Center on the Baikal with the aim to organize a complex interdisciplinary study of the Earth's largest freshwater lake.

We hope that all the participants of the Baikal workshop will keep in their memory the beauty of this unique lake, and, as stated in the Declaration, will propagate in their countries the idea of a joint study of the Baikal.

In conclusion I'd like to express sincere gratitude to all the participants of the workshop for their intensive and cooperative work and to thank the Siberian scientists for their hospitality and competent organization of the meeting and excursions over the Baikal.

Moscow, December 1988 M. IVANOV, Russian Academy of Sciences

Welcoming Address

"Leis' das Glöckchen ertönt, so verschwiegen." This old Russian folksong with its tender sound may stand for the serene beauty of Lake Baikal but at the same time it is an urgent call - an invitation to all of us to become guardians of the global environment.

It is not purely fortuitous that our workshop on "Interactions of Biogeochemical Cycles in the Aqueous Ecosystem" is held near the shores of this Siberian Lake. Our decision to come here has to do with Lake Baikal's exceptional personality, namely its size, its water quality, its special location, its old age, and last but not least its unique ecology. Indeed, Lake Baikal is the world's largest and deepest freshwater body, contains the cleanest water by all standards, resides in the heart of Siberia, is a few million year old rift lake, and provides shelter to almost 2,000 biological species found here and nowhere else on Earth. Truly a kind of Galapagos, holding information on causes, speed and direction of the evolution of aquatic life.

That a group of 90 biogeochemists from the SCOPE and UNEP community has come for a week to Lake Baikal as guests of the Limnological Institute of the USSR Academy of Sciences, Siberian Branch, is part of the celebrations held this year in the Soviet Union on the occasion of the 125th birthday of Vladimir Ivanovitsch Vernadskij (1863-1945), the foremost biogeochemist ever.

V.I. Vernadskij was the first to recognize life as the "Lord of the Planet Earth" and founded the field of biogeochemistry. In his book "The Living Substance in the Earth's Crust and its Geochemical Role" which he started to write in 1916, he saw organisms as the main driving force in the cycling of living and universal matter ever since life took command of crustal and environmental evolution. More than a thousand references and written in all European languages give credit to Vernadskij's linguistic skills; by the way, this is in striking contrast to many works written in English today. He even envisioned the influence of human activities in restructuring Planet Earth, and by introducing the "Noosphere", that is the sphere of the mind, he provided a new dimension to the environmental sciences.

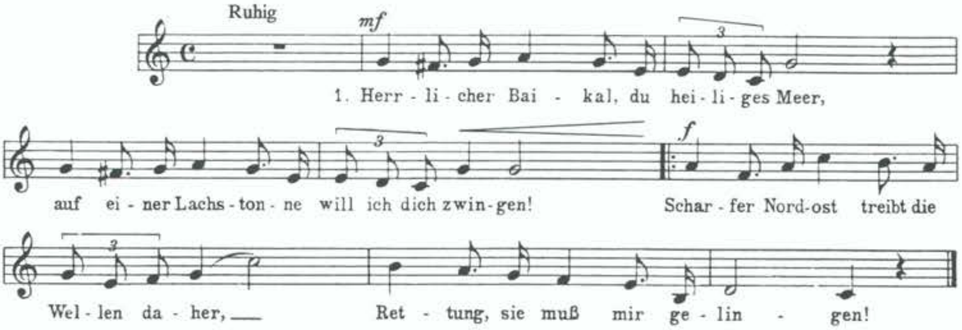
As a token of appreciation to this genial man on whose shoulders we all stand, we shall discuss the interactions of biogeochemical elements and in particular those between carbon and sulfur. His work will be our standard of reference and of quality which we will try to approach but in all probability shall never reach.

"Magnificent Baikal, you hallowed sea......" this old Russian popular song standing for freedom and against czarist tyranny may also provide hope to nature to eventually overcome human oppression by the growing environmental consciousness of people.

Listvyanka, September 1988

EGON T. DEGENS
SCOPE/UNEP International Carbon Unit

Herrlicher Baikal

Russisches Volkslied

Jahrelang schleppt' ich die Kette am Bein,
fern in Sibiriens östlichen Bergen,
bis ein Kam'rad es mir flüsterte ein :
"Schlag doch ein Schnippchen den Schergen!"

Glücklich entkam ich. Bei Tag und bei Nacht
hieß es, durch Steppen und Wälder nun traben.
Städte umging ich, das Bauernvolk bracht'
Brot mir und andere Gaben.

Herrlicher Baikal, du heiliges Meer !
In meiner Tonne setz' rasch ich hinüber.
Spann' meinen Kittel als Segel fürquer :
Treib mich, Nordost, schnell hinüber!

Lake Baikal

A Proposal for the Establishment of an International Center for Freshwater Ecology

at Listvyanka, Irkutsk Region, Russia

Background

Lake Baikal is the world's largest lake and contains a fifth of the earth's freshwater reserves. It owes its existence to large scale rifting processes which started 30-35 million years ago. Judged by high seismicity and related geological evidence, rifting is still ongoing. During the initial stage lasting up to about the Early Pliocene, the rate of subsidence was low and Lake Baikal was shallow. Since Middle Pliocene, subsidence rates increased substantially. The lake in roughly its present shape and configuration came into existence about 2 million years ago.

By all possible standards, Lake Baikal is the deepest and is among the cleanest lakes on earth. Of the 1,700 species of animals and plants populating the lake, circa 1,000 species are endemic in nature. This characteristic is shared by the large East African Rift Lakes (Malawi, Tanganyika and Kivu), the origin of which dates back to the Early Miocene.

Because of their unique geological settings and special ecology, rift lakes have attracted the curiosity of scientists for more than a century, but due to cumbersome logistics, concerted research activities by multidisciplinary teams from different nations were more the exception than the rule.

Growing awareness of human interference in the regular course of nature has given new impetus for studying these still pristine habitats. Moreover, general circumstances have recently become favorable so that the idea of creating an *International Center for Freshwater Ecology* at the shores of Lake Baikal has a good chance of realization. The *International Center* should become part of the Institute of Limnology founded at Listvyanka in 1932. The Limnological Institute belongs to the Russian Academy of Sciences, Siberian Branch, and the newly established *International Center* would consequently be under the auspices of that Academy.

The idea of the project has recently been voiced in an article (Nature, 1988), and has been discussed at length during an International SCOPE/UNEP Workshop on the "*Interactions of Biogeochemical Cycles in Aqueous Ecosystems*" (Listvyanka, 2-8 September, 1988). The project has been unanimously endorsed by the 90 participants from 20 nations and a *Statement* was signed by representatives of the Russian Academy of Sciences, the United Nations Environment Programme (UNEP), the Scientific Committee on Problems of the Environment (SCOPE), and the Director of the Limnological Institute, Russian Academy of Sciences, Siberian

To foster the idea further, a research team from the University of Milwaukee has been granted permission to execute a joint Russian/US study on Lake Baikal; the expedition was successfully carried out in August/September, 1988. Moreover, a new expedition on Lake Baikal is planned for summer 1989 by the Limnological Institute, this time in association with the University of Hamburg, FRG. This research cruise will involve a multidisciplinary study by means of seismics, sediment coring, water chemistry and sediment trap work.

At Irkutsk, contacts have been made with government authorities and the project has received favorable considerations. Since the *International Center* will be open to the international scientific community, colleagues were approached worldwide to promote the idea of the *International Center for Freshwater Ecology* in their respective countries. In Germany, the Federal Ministry of Research and Technology and the Ministry of Environmental Affairs were briefed on the forthcoming Soviet-German expedition on Lake Baikal, and on the project advanced by the Russian Academy of Sciences, Siberian Branch, to launch an *International Center for Freshwater Ecology* at the shores of Lake Baikal.

Activities at the Center

In 1988, the world's leading institute of marine ecology, the *Marine Biological Laboratory* Woods Hole, Massachusetts, USA, is celebrating its centennial. This Laboratory has served as the scientific "Mecca" for the international biological community ever since its foundation. We envision that the Lake Baikal Center would develop along similar lines as the Marine Biological Laboratory at Woods Hole did in the past, except that emphasis rests on freshwater ecosystem analysis. However, the principal research and teaching objectives will be identical. One of the plans is to bring together leading scientists from everywhere for research on arctic lakes and rivers and here especially on Lake Baikal. Emphasis will be placed on graduate programs for students and young scientists in order to advance environmental understanding among future generations of scientists. Legislative action has already been taken by the Russian State Council Decree on the Protection of the Lake Baikal Ecosystem.

The list of subjects to be explored cover a wide range and some pertinent ones are listed below (without ranking):

- monitoring, assessing and managing large lake ecosystems
- understanding biogeochemical cycling of elements
- elucidating mode of origin of endemic species in lakes establishing rates of evolution of endemic species by means of genetic mapping, comparative biology, and fossil record
- studying inflow (Selenga River) and outflow (Angara River) waters for natural and man-made chemical species

- checking on deleterious effects to the environment caused by industrial waste, for instance from cellulose plants
- modelling the physics and chemistry of Lake Baikal system
- make an intercomparison of origin, evolution and environmental quality of major rift lakes (Baikal, Tanganyika, Malawi), glacial lakes (Great Lakes of North America, Ladoga, Onega), volcanic lakes (Kivu, Van, Issyk Kul) and others.

Infra-Structure

The town of Listvyanka is less than two hours by car from Irkutsk airport. Present facilities at the Limnological Institute include :

(i) a small laboratory (500 m^2),
(ii) offices and seminar rooms (1,000 m^2),
(iii) a fleet of five research vessels, and
(iv) a hotel and a guest house with accommodations for up to 100 people.

The new *International Center* will be in the immediate vicinity of the Limnological Institute where sufficient and appropriate building ground is available. The *International Center* should have the following main and auxiliary facilities:

(i) all-purpose laboratory and office building (5,000 m^2),
(ii) computer center (1,000 m^2),
(iii) library (1,000 m^2),
(iv) modern port facilities, e.g., for deep-water submersibles,
(v) nearshore monitoring stations for water sampling, biological observations, sediment coring etc.,
(vi) platform for sediment coring when Baikal is frozen,
(vii) appropriate guest house facilities to accommodate visiting researchers and their families,
(viii) cultural center (cinema, swimming pool, sport facilities, conference rooms),
(ix) kindergarten and schools (teaching in Russian and English), and
(x) medical facilities.

Planning Phase

A conference, to which 10 to 15 internationally renowned scientists will be invited by the Russian Academy of Sciences, Siberian Branch, is expected to define critical issues involved in establishing an Ecological Center. Institutional policies should be defined in terms of private versus state versus international foundation, size and responsibilities of Board of Directors, research priorities, etc. Special emphasis should be given as to "how to finance" such an ambitious project and what national or international organizations could be approached as donors and sponsors.

It is proposed that immediately action be started to contact scientists willing to serve as advisors in the initial planning stage which lasts for perhaps one year (1989). Construction of buildings and set-up of research facilities should be accomplished in three years' time, so that the *International Center for Freshwater Ecology* could start its full-time research and educational activities by the year 1993.

Statement

The International SCOPE/UNEP Carbon and Sulfur Units held their 7th meeting on "*Interactions of Biogeochemical Cycles in Aqueous Ecosystems*" from September 2 - 8, 1988 at the Limnological Institute of the Siberian Branch of the Russian Academy of Sciences at Listvyanka on the shores of Lake Baikal. This international meeting was attended by 90 experts in the field of biogeochemistry.

During the meeting, participants had the opportunity to acquaint themselves with the proposal advanced by the Siberian Branch of the Russian Academy of Sciences of establishing an *International Center for Freshwater Ecology* at Listvyanka. The participants share the concern and intention of the Academy in protecting Lake Baikal and of creating the Center and bringing together experts from different disciplines and nations under the umbrella of the proposed Ecological Center. The participants wholeheartedly endorse the Academy's efforts and will propagate this idea in their respective countries and inform decision-makers.

Lake Baikal, containing almost one-fourth of the world's fresh water reserves is one of our most precious natural heritages. Its study is of interest not only locally to the Soviet Union but to all mankind. The proposed interdisciplinary work at the Center and the exchange of ideas and experiences among the international scientific community will open a new chapter in international cooperation in the field of environmental sciences.

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This statement was delivered to Chairman Nozhikov, Governor of the Irkutsk Region.

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GROUP 1 REPORT

Rivers and Estuaries

Chairmen: J.-M. MARTIN, V. V. GORDEEV
Rapporteurs: V. SUBRAMANIAN, V. ARTEMYEV

Working Group 1 discussed the recommendations of the Texel Workshop in the light of updating information available now as well as lectures given by the members of the group.

Along with this we discussed our priorities with respect to River and Estuarian Programs of SCOPE. Accordingly the working groups identify the major gaps in the knowledge regarding rivers and estuaries and make the following recommendations:

I. Major Gaps

I. 1. Fluxes: Our Knowledge About Fluxes Can Be Grouped as -

(i) Relatively better known - *DOC, DON, DP, DS*;

(ii) not well known - POC and hence TOC;

(iii) characterization and fluxes of individual components of DOC (such as lignin, amino acid) are not known;

(iv) essential trace metals such as Fe, Mn, Cu etc. - their total concentration and speciation both in dissolved and particulate form need to be known in detail;

(v) effect of natural (catastrophic events such as floods), or man-made (dams, diversion of channels) impact on fluxes;

(vi) diverse sources of C, N and other elements, i.e., natural vs. anthropogenic, riverine vs. atmospheric and their relative contribution to global fluxes;

(vii) present flux rates need to accommodate newly available data from the USSR and other regions for which data are available.

Processes:

(i) certain microbiological processes such as heterotrophic systems need to be studied better to understand nutrient cycling in micro-ecosystems;

(ii) photo-chemical reactions involving trace metals and organics can adversely affect C-availability. We do not know to what extent such processes affect primary production;

(iii) interaction at several interfaces such as air-water, water-sediment, sediment-pore water need to be studied to understand C-cycling processes (working groups 4 and 5 are dealing with this issue);

(iv) possible equilibrium/exchange between DOC and POC is not well known and kinetics of all the processes in micro-systems need to be understood for elemental cycling;

(v) particle interactions such as solid-solid (flocculation), organics-inorganics may regulate C-availability and hence biological activity in estuaries;

(vi) effect of human activities on the fluxes and processes need to be better understood.

II. Recommended Approaches

In order to close the gap in our knowledge both with respect to fluxes and processes mentioned above, we propose the following approaches -

(i) **Analytical**: Flux calculations and processes evaluation depend largely on methods used to analyze C and other elements; more recent methods of C analysis if extended to all river and estuarine systems, may significantly enhance present state of knowledge on C transport in estuarine and thus marine environments. Analysis of colloids and complex species of trace elements require investigation in the light of C-cycle. Stable isotope techniques may also help in flux determinations and processes studies.

(ii) **Experimental**: In the C-cycle, experiments on essential trace elements and nutrient studies should complement field data. Laboratory scale studies, simulation models of estuaries (large scale - Rhode Island model or small scale - China model) and tracer techniques can promote understanding of estuarine systems.

(iii) **Small Rivers and Estuaries:** They are ideal for detailed process investigations outlined earlier. Both analytical and experimental models can then become viable to interpret elemental transfer within a small system.

(iv) **Large Rivers:** Fluxes are best estimated in large systems globally and efforts to fill-up the existing gaps should be made in this regard. Available data on large rivers such as Yenisei (USSR), Ganges (India, Bangladesh) may be integrated in flux estimations.

(v) **Type-Systems:** River and estuarine systems need to be studied from diverse type-areas reflecting geology, climate, physiographic regions, pristine and at various levels of human impact, and flood and draught prone areas. Our present knowledge on most of these controlling factors is inadequate.

(vi) **Models:** All flux calculations and controlling factors need to be evaluated with respect to an appropriate modeling.

GROUP 2 REPORT

Natural Lakes and Reservoirs

Chairmen: E. CALLENDER, N. PECHURKIN
Rapporteurs: R. HOWARTH, Y. KUSNER

Recommendations and Conclusions

It has become generally accepted that lakes and reservoirs are not a significant term in global the global budgets of biogeochemical elements. The rationale for studying natural lakes and reservoirs consists of at least the following points:

- They are essential to humans from the view of water supply, agriculture, recreation, and power generation.
- The results of human activities is having an increasingly adverse effect on lakes.
- Sulfur emission is one important anthropogenic effect.
- Acid rain is a serious problem in some classes of lakes.
- Furthermore, subtle effects of sulfur additions affect other classes of lakes.
- Lakes are an excellent environment to record changes in global biogeochemical cycles and climate.
- Lakes are excellent sites to study processes that are important in other aquatic environments (marine).
- Lakes are significant habitats for biological diversity (preserve endemic species - Lake Baikal, Australian Salt Lakes, East African Rift Lakes).

Biogeochemical cycles of C, N, P, S, and trace elements are strongly interconnected and should not be studied in isolation.

Interactions between Sulfur and Carbon:

The effects of acid sulfate precipitation on lakes of low buffering capacity are now well known, and it is clearly established that quite a number of lakes have been adversely affected. However, sulfur additions to lakes can have consequences well beyond those due to acidity, and even large numbers of lakes can thus be affected in relatively subtle ways. In Figure 1, we outline some of these other effects of sulfur on lakes, emphasizing some direct and indirect effects on carbon cycling.

Effect of Increased Sulfate on H_2S Toxicity:

Sulfate reduction in lakes is generally limited by sulfate concentrations. Thus, if sulfate concentrations are increased, sulfate reduction rates will increase, and the potential for hydrogen sulfide to occur in the water column also increases. Hydrogen sulfide is toxic to a variety of oganisms, and in lakes where physical conditions allow this sulfide to accumulate in the water column, consequences can be severe.

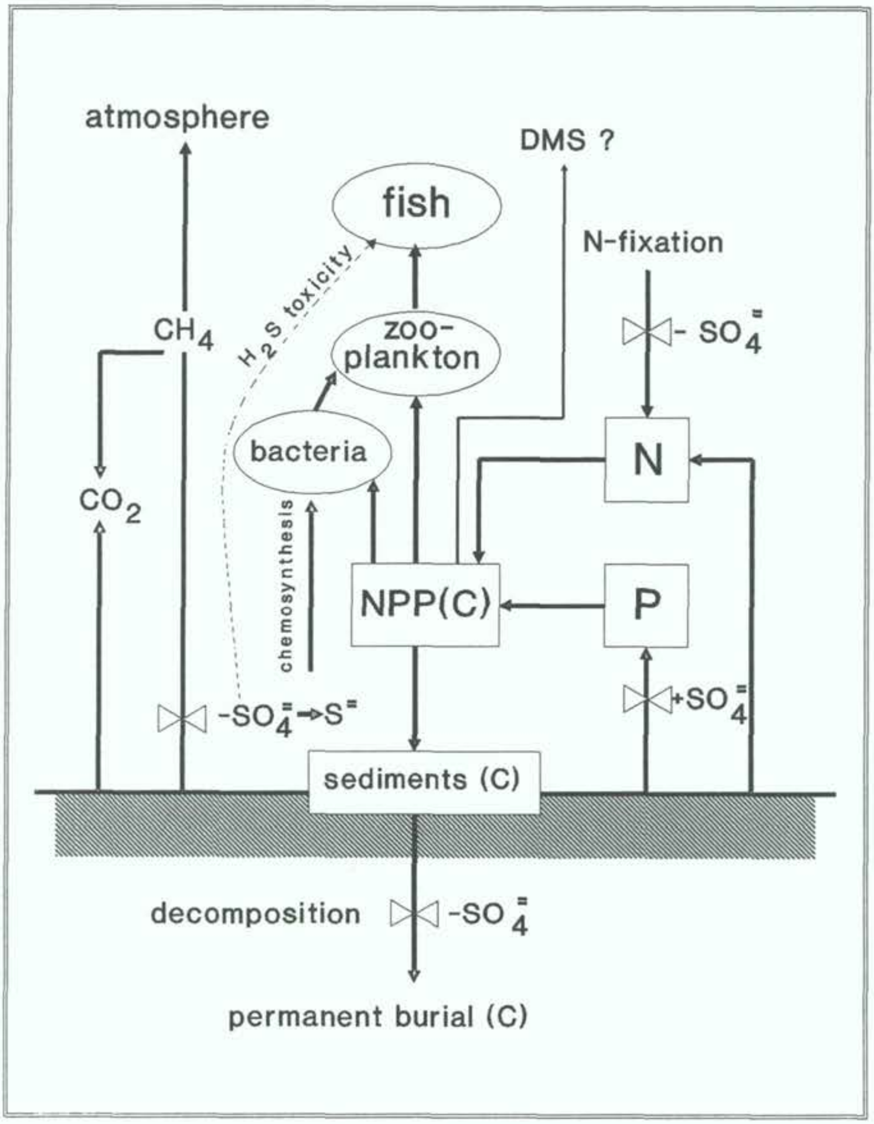

Fig. 1: Interactions of the sulfur and carbon cycles.

Effect of Increased Sulfate on Phosphorus Cycling:

Primary production in most lakes is limited by phosphorus availability, and so any change in phosphorus cycling will change primary production. Increased sulfate concentration may increase the release of phosphorus from lake sediments perhaps by reducing the amount of sorptive iron oxides and hydroxides in the surface sediments. Thus, increased sulfate inputs may cause further eutrophication.

Effect of Increased Sulfate on Nitrogen Fixation:

Nitrogen fixation can also be affected by increased sulfate concentrations, at least if concentrations are increased sufficiently. This is because sulfate inhibits the uptake of molybdenum by microorganisms, and molybdenum is required for nitrogen fixation. By increasing phosphorus availability while decreasing nitrogen fixation, an effect of higher sulfate concentrations may be to alter nutrient limitation from phosphorus to nitrogen.

Effect of Increased Sulfate on Carbon Burial:

The extent of anaerobic organic carbon degradation in sediments appears to be greater when sulfate serves as an electron acceptor (sulfate reduction) than when decomposition proceeds through methanogenesis. This is perhaps one reason why the organic carbon content of the sediments of Lake Baikal (where sulfate concentrations are relatively low) is high in relation to comparable marine ecosystems (where sulfate is much higher). Consequently, increasing sulfate concentrations in lakes may reduce the burial of organic carbon in sediments.

Effect of Increased Sulfate on Chemosynthesis and Anoxic Photosynthesis:

Chemosynthetic production and photosynthesis by anaerobic bacteria using sulfide as an electron donor are significant sources of organic matter production in some lakes. Since:

- these processes are dependent upon a supply of sulfide,
- the supply of sulfide increases with increased sulfate reduction, and
- sulfate reduction increases with higher sulfate concentrations,

we expect the productions by anoxic photosynthesis and by chemosynthetic bacteria to increase as sulfate inputs into lakes increase.

Effect of Increased Sulfate on Methane Flux to the Atmosphere:

The flux of methane from lake sediments is the difference between the rate of methane formation and methane oxidation. Increasing the sulfate concentration will both lower the rate of methane formation and increase the rate of anoxic methane oxidation. Thus, increasing sulfate concentration should greatly reduce the flux of methane from sediments. We recommend studies of the interaction of sulfur and carbon in a variety of lacustrine environments. We need to focus future research on interconnections that are not well understood (Fig. 2). While we recognize that there may be effects of the carbon cycle (mass) on the sulfur cycle, the strong effects of sulfur on carbon suggest that we concentrate our limited resources on these interactions.

The physical, chemical, and biological characteristics of a lake can greatly influence the relative importance of particular interactions between the sulfur and carbon cycles. We have tried to emphasize this by preparing a matrix of the effect lake-type factors on the interaction between sulfur and carbon (Fig. 2). In this matrix, a "+" sign indicates that whether or not increasing sulfate affects the particular C-S interaction as a function of the lake type. A "-" sign indicates that the lake type does not influence the effect of increasing sulfate concentration on the C-S interaction. Three "+'s" indicate a strong interaction, whereas question marks

PROCESS / FACTOR	sediment decomposition (carbon burial)	sediment P-release	nitrogen fixation	sulfide toxicity	methane flux (production, oxydation)	chemosynthesis	bacterial photosynthesis
1. Physical							
depth	+	+	+	+	+	+ ?	+++
stratification	+	+	+	++	+	+	+
turbulence	+	+ ?	+	+	+	+	+
residence time	+	+	+	+	+	+	+
cold vs. warm	?	–	+	+	?	+	+
natural vs. man-made	?	+	–	–	–	–	–
2. Chemical							
salinity (hydrochemistry)	+ ?	+ ?	–	+	+ or –	+	+
buffering cap.	– ?	– ?	–	++	–	+	+
mineralogical composition	+++	+++	–	+	–	+	+
3. Biological							
productivity gradient	+	–	+	+	+	+	+
community structure	–	–	–	+	–	+	+

+ = effects
– = no effect

Fig 2: The effects of lake type factors on the interaction between sulfur and carbon.

indicate uncertainty as to a possible interaction. The matrix represents concensus of the working group members but is only a preliminary attempt. In fact, there is still a great deal of uncertainty concerning many of the element interactions in lakes and the influence of lake characteristics on these interactions.

As a final note, strong interaction of sulfate with the carbon cycle is related to the mineralogical composition of a sediment.

GROUP 3 REPORT

Carbon and Sulfur Cycles in Seas Marginal to Continents

Chairmen: S. Naidu, A. Lisitsyn
Rapporteurs: R. Oremland, Y. Sorokin

I. Main Statements

This working group addressed questions of C and S cycles in regions of the oceans contingent on continental margins ("marginal seas"). These regions are exemplified by the Black, Baltic and Mediterranean seas, but excluded from our definition were seas such as the Caspian.

The group considered factors influencing C and S budgets in marginal seas. These factors encompass sources, fluxes and fate of these elements. With regard to sources, marginal seas receive C and S inputs from allochthonous and autochthonous means. Major allochthonous inputs include:

- terrestrial runoff,
- marine,
- air/sea exchange,
- hydrothermal and seep sources,
- postdepositional sources.

With regard to autochthonous, sources include:

- primary phytoplankton production,
- secondary production by higher food chain organisms and bacteria,
- chemoautotrophic production,
- benthic production (primary and secondary) including rooted plants and attached algae.

Primary production in the marginal seas can be evaluated as corresponding to mesotrophic- eutrophic levels. Under natural conditions it varies within 0.3-1 gm^2/a, being composed of phytoplankton production - phytobenthos production in relations 10:1 - 100:1. Main gaps in knowledge are caused by underestimations caused by the use of ^{14}C-method, missing of seasonal maxima, especially end winter early spring temperate seas, and scarce coverage of areas by stations. Total input of marginal seas into the global production is large and can be evaluated as 25-30%.

Modern anthropogenic input of nutrients creates the tendency of substantially enhancing primary production in marginal seas, especially in coastal areas for several times.

Furthermore, benthonic and microbial activities are correspondingly higher than in open ocean sediments. Sediment mineralization of organic carbon drives the S cycle via sulfate-reduction as well as by sulfate-linked methane oxidation.

Stable carbon isotopes ($\delta^{13}C$) in organic matter from many coastal/shelf sediments indicate that organic matter of terrestrial origin is deposited nearshore. Further, isotopic data and organic carbon contents of suspended matter and bottom deposits in estuaries and coastal seas indicate a large loss (in the order of 50-75%) of organic matter of terrestrial (fluvial) origin. It is not clear yet as to what extent the $\delta^{13}C$ of organic matter is influenced during consumption or alteration of organic matter. As a consequence the residue will be heavier and a contribution of organic matter with an originally isotopic light composition is marked. It is therefore recommended to study the transformation of organic matter in estuaries and coastal seas during consumption and degradation of organic matter using isotope techniques.

The group recognized several ways in which humans impact upon the C-S cycles in marginal seas:

- direct discharge of organic matter.,
- eutrophicaton developments by input of nutrients,

- destruction of natural ecosystems by activities such as chemical pollution, stimulation of H_2S production, mechanical construction, dredging and trawling,
- deforestation and irrigation practices disrupting normal terrestrial drainage.

II. Recommendations

The panel recognizes the need:

1. To acquire better spatial coverage of processes relating to the cycle of S-C in marginal seas. Although some areas are particularly well-studied (e.g., Black Sea, Mediterranean, etc.) a large group of marginal seas remain so far unstudied (e.g., Okhotsk Sea, high-latitude ice-stressed regions).
2. To intercalibrate the diversity of methods employed to estimate primary productivity, sediment/POC flux and microbial mineralization reactions. This is especially important for biological radio isotope tracer investigations.
3. To make comparative studies of the C/S cycles between pristine and polluted ecosystems in order to get an insight into the impact of human activities.
4. To pay particular attention to tropical marginal seas because of the fragile nature of coral reefs under threatened existence from deliberate human destruction.
5. To supplement field studies with laboratory investigations in order to substantiate the findings of the former.
6. To make comparative studies of marginal seas having different climatic regimes. This will achieve a better understanding of the role marginal seas play in the global environment.
7. To take an interdisciplinary approach to marginal seas investigations.

GROUP 4 REPORT

Air - Water - Life Interfaces

Chairmen: W. JAESCHKE, V. M. GORLENKO
Rapporteurs: V. ITTEKKOT, M. GLADYSHEV

Introduction

The group discussed the biogeochemical cycling of elements in the atmosphere and in aquatic ecosystems on land especially at the air-water-life interfaces. Emphasis was placed on the disturbance of the natural cycles by anthropogenic activities on the one hand and on the modulating influence of the biota on the other. Sulfur was treated as the reference element.

Consideration of Pathways Between Sources and Receptors

Anthropogenic emissions of sulfur containing gases lead to increasing concentrations of SO_2 and sulfate in the atmosphere even in remote areas. The atmospheric sulfur burden is brought back to the earth's surface by dry and wet deposition. Besides their deposition on vegetation and soil, sulfur compounds are also deposited on the surfaces of aquatic systems. The flux of anthropogenic atmospheric S into water bodies can be investigated by using sulfur isotopes provided that the industrial sulfur sources are isotopically different from the isotopic composition in environmental receptors. Sulfur isotope data have been mainly used for qualitative interpretation. However, with more effort this technique could also be used quantitatively.

Sulfur Isotopes Have Been Used to Demonstrate:

- An increase in sulfate concentration in small water bodies due to SO_2 dry fall out and sulfate deposition which originate from industrial sources;
- a link between the concentration of dissolved organic sulfur and the proportion of anthropogenic sulfate in small water bodies;
- the acquisition of sulfur by emergent plants from both the atmosphere and sediments; hence the decay of plants provides an indirect pathway for atmospheric S to enter the water body; and
- that sulfur isotope data for sediments and nearby soil horizons provide a comparison of fluxes to the soil with fluxes to the air-water interface and further downward movement through the water column to sediments.

Processes at the Air-Water Interface

The physical structure of the air-water interface is complex and still awaits clarification. However, with respect to its influence on mass exchange between air and water, existing informations from various laboratory and ield experiments allow an empirical description of the exchange flux, it is the product of: (i) the difference between bulk concentration in air and water respectively, (ii) C, and (iii) a coefficient K which has the dimension of a velocity. Generally, K depends on the structure of both the air and water boundary layer. Moreover, in most cases only one of the layers is controlling the flux. The flux of gases with large Henry coefficient meaning low solubility (O_2, N_2, CO_2, SO_2 DMS etc.) are controlled by the water layer. In contrast, gases with small Henry coefficients or large solubility (water vapor) are rate-controlled by the air layer.

Both the air- and water-controlled transfer velocities depend on the wind speed above the water surface. Comparison of experimental K-values, determined at the same physical conditions, show that K depends on D^{α} where D is the molecular diffusion coefficient and α a coefficient between 0.5 and 1.

A special situation is met for reactive substances if their reaction time is short compared to the time needed for the molecule to cross the boundary. Such reactions may be purely chemical or result from the interaction with special living communities and from organic films often found at the air-water interface.

Water Column Processes

Important regions in which reduced sulfur compounds are produced are the water bodies of marshlands, lagoons, lakes and intertidal areas. These water bodies range in salinity from freshwater to brackish-marine to highly saline and in depth from a few millimeters to several hundred meters.

The upper layer of these bodies is represented by an oxygenic photosynthetic zone which is the primary source of organic matter. Below this follows an oxic zone where organic matter becomes reoxidized by oxygen-respiring organisms. Where organic production exceeds oxidation, an anoxic zone develops. The interface between the oxic and anoxic zones is termed the chemocline. In lakes, this zonation can be stabilized by temperature, and a chemical stratification may result.

Within the sediment of the anoxic zone bacterial sulfate reduction may develop depending on the supply of sulfate and metabolizable organic matter. This process is the principal source of sulfide in the natural environment and in intertidal zones and sulfate-containing stratified lakes may be responsible for mineralizing up to 90% of the organic input.

The rate of sulfate reduction is controlled primarily by the rate of supply of organic matter and may reach 50 mg/l per day in shallow saline lakes.

In shallow water bodies and at acidic pH values, hydrogen sulfide may escape to the atmosphere but for other situations it is oxidized in the chemocline by cyanobacteria, green and purple photosynthetic bacteria and colorless chemosynthetic sulfur bacteria. This leads to a secondary zone of organic productivity, and localized matter or, in stratified lakes to a substrate, that acts as a biological filter preventing the loss of sulfide to the overlying zones. In the chemocline zone sulfide becomes oxidized to elemental sulfur which is subsequently re-reduced to sulfide in the anoxic zone by sulfate reducers.

Induced Emissions of Gases from Aquatic Systems

Recent field measurements have shown that reduced sulfur gases are released from the oxic zones of water bodies and wetlands. Emission of DMS (dominant species), DMDS, COS, H_2S and traces of CH_3SH were detected. The emission rate depends on temperature, sulfur concentrations, nature of the biological community and trophic status of the water.

In oceans, the DMS is commonly produced by a few algae species. The mechanisms of DMS formation in freshwater ecosystems are still unknown. The decomposition of organic matter has been suggested as a possible pathway. Therefore higher quantities of H_2S might also be released from these regions. Based on available data oceans appear to be the major source of DMS to the atmosphere. However in freshwater the decomposition of organic matter may contribute also to the release of H_2S and other sulfur gases in large quantities. This contribution may be further accelerated by continuing the input of anthropogenic sulfur compounds into the aquatic system.

Recommendations

The panel suggests a need for:

1. Further verification of source-receptor relationships with the help of stable isotope techniques and improved dispersion models;

2. improvement of the techniques for direct measurements of fluxes at the air-water interface;
3. investigation of the influence of living communities and surface films on gas exchange at the air-water interface;
4. better understanding of the mechanisms of the interaction of carbon and sulfur in the cycling of organic matter in freshwater systems;
5. a study of the role of vertically migrating aquatic organisms with respect to the gas-exchanges at the air-water interface; and
6. an examination of the possibility that biogenic emission of reduced sulfur gases might be enhanced by anthropogenic input of sulfur in aquatic ecosystems.

GROUP 5 REPORT

Interactions of Carbon and Sulfur at the Sediment-Water-Life Interface

Chairmen: W. S. REEBURGH, A. LEIN
Rapporteurs: R. B. COOK, V. A. GRINENKO

Statement of Problem

This group discussed biological and biogeochemical processes in the water column and sediments that influence the flux of particulate and dissolved material across the sediment-water interface. Processes in both marine and freshwater systems were considered. We attempted to integrate what is known on the individual carbon and sulfur cycles to provide a framework for the interaction of the carbon and sulfur cycles within the sediment-water environment.

The primary interaction of carbon and sulfur is during bacterial sulfate reduction. In this microbial reaction, organic matter is decomposed using sulfate as a terminal electron acceptor and hydrogen sulfide and bicarbonate are produced. Under certain conditions, the sulfide produced may react with organic matter to form an organic sulfide phase. This organic sulfur phase has been shown to be an important constituent of lacustrine sediments. In some environments, such as hydrothermal vents, primary productivity based on energy derived from sulfide chemosynthesis may be more important than sunlight-driven photosynthesis.

Recent work has suggested that reduction in anoxic environments may use methane as a substrate. In high sulfur systems, like Mono Lake, complete consumption of methane produced by methanogenic and fermenting bacteria may occur.

Indirect interactions of the carbon and sulfur cycles were also considered. One potentially important interaction in fresh water systems is the uncoupling of the well-known iron and phosphorus cycles by changes in sulfate. Increasing sulfate may cause an increase in the production of sulfide and iron sulfide compounds, via bacterial sulfate reduction. In this situation, iron may not be available to bind phosphate, thereby causing increased flux of phosphate to the water column with attendant effects on primary production.

Recommendations

Promising issues that should receive high priority for future research are summarized here for two categories: Methods Development and Processes Studies.

Methods Development

1. Improved methods are required to measure fluxes across the sediment-water interface. Efforts should be focussed on automated sensors coupled with data loggers.
2. Methods for examining the rates of opposing processes should be developed. For instance, net bacterial sulfate reduction is the sum of the sulfate reduction and sulfide oxidation. Separating net sulfate reduction into the two opposing processes may result in an improved understanding of factors controlling sulfur cycling in sediments. Similarly, methods for measuring methane oxidation and methane production could be improved.
3. Although stable C and S isotopes have been used as a tool in studies of the biogeochemistry of carbon and sulfur, increased use of these isotopes will provide additional evidence on processes and fluxes across the sediment-water interface as well as an overall constraint on the system. Isotope fractionation studies under controlled laboratory conditions should also be performed, so that data from processes and fluxes occurring in ecosystems can be properly interpreted.
4. Standard methods for measuring the various species of sulfur and carbon in sediments should be established, to ensure the comparability of values obtained by investigators. Furthermore, standard reference materials for the stable sulfur and carbon phases should be established and distributed to assure the quality of measurements.

Process Studies

1. Better temporal and spatial coverage of processes and fluxes should be acquired. Accurate budgets for the sediment and water column require such detailed spatial and temporal estimates of fluxes. Information on the variability of processes in space and time may lead to improved understanding of factors affecting these processes. Seasonal studies are essential for regional and global budgets.
2. Although much work has recently been performed 1on sulfur species, in the sediment subsequent to bacterial sulfate reduction, we still do not have a complete understanding of the factors controlling formation of these species. Additional work on the formation, stability and microbial mediation of organic and inorganic sulfur species plus hydrogen sulfide is required.

3. Interactions of the sulfur and carbon cycles with other element cycles require further attention. Examples are:

- Interactions of the S/Fe, S/N, and S/P cycles. Uncoupling of the Fe/P cycle may have direct effects on primary productivity.
- Biological and abiological reduction of elemental sulfur (S°).
- Sulfur reduction at low ($<30\mu$mol L^{-1}) sulfur concentrations, must be considered.

Decomposition and recycling of organic matter of the sediment-water interface. This zone is known to be the site of large changes but has defied careful study due to sampling problems. The recent development of microelectrodes and samples capable of high depth resolution provides tools for new investigations of this zone.

Modified systems, which also provide opportunities that should be pursued. Examples inlcude experimentally manipulated systems as well as systems modified by anthropogenic pollution.

GROUP 6 REPORT

Chairmen: D. McGINNIS, A. SHEVYRNOGOV
Rapporteurs: J. FISCHER, A. BOLSUNOVSKY

Introduction

Satellite images show qualitatively the global distribution of ocean, land surface and atmospheric properties. Besides the observations of distribution patterns, the quantitative retrieval of properties, such as chlorophyll and other water substance concentrations or land biomass, are needed to estimate local and global distribution and fluxes of carbon and sulfur. To accomplish this, algorithms are required to transform satellite observed radiances into estimates of these properties.

For the observation of ocean color the Coastal Zone Color Scanner (CZCS) was the only instrument in space, which successfully observed the chlorophyll distribution on a global scale. The accuracy of these estimates are within 30% for open ocean water. Up to now global maps of chlorophyll concentrations are available for 1979-1981. Processing of CZCS data for 1982-1985 is continuing.

Coastal waters, often containing several types of water substances, are more difficult to resolve in terms of chlorophyll concentrations. Even under the best conditions separation of the individual water substances, such as chlorophyll, suspended matter and yellow substance can only be achieved to within an accuracy of a factor of two.

Qualitative agreement between CZCS and shipboard measurements has been shown for large lakes, such as Lake Baikal. Since 1985 no system equal to CZCS is operating in space. However, for turbid waters such as those found in coastal regions, large rivers and lakes, the Cosmos and Landsat satellites can be used to study small scale phenomena. Because of the low radiometric and spectral resolution of the instruments on these satellites the estimates of water concentrations are less accurate.

Present technology permits the resolution of narrow spectral features, such as the sun-stimulated chlorophyll fluorescence. From shipboard and aircraft multispectral measurements with spectral resolution of 5 nm it is found that these measurements enhance the accuracy of the separation and estimation of different types of water substances.

Groundtruth or contact measurements are necessary for the evaluation and verification of new remote sensing techniques, as well as providing for detailed properties of the water substances substantial for ecological studies. Present fluorescence methods are widely used for phytoplankton chlorophyll estimation and its physiological state. Furthermore, the chlorophyll fluorescence induction has been used to separate different dominating phytoplankton species. With the help of luminescence measurements the spatial and temporal distributions of phytoplankton and dissolved organic matter are observed.

Recommendations

1. To consider the usefulness of results obtained from remote and contact optical methods for the thematic mapping of regional water surfaces.
2. To give attention to the possibility of using remote and contact measurements for the detection and estimation of anthropogenic influence on drainage areas.
3. To consider that intensive theoretical and experimental studies of primary and secondary hydro-optical patterns are necessary for adequate interpretation of remote sensing data.
4. To consider, as most important task, the necessity of employing three levels of measurements, namely, ship, aircraft and satellite, for water bodies having great ecological interest. These measurements are useful in the development of adequate and temporal calibration of satellite and contact measurements.
5. To consider the initiation of international complex experiments in the framework of SCOPE/UNEP activities for water bodies important for ecological investigations.
6. To consider as an important improvement in satellite observations the launch of a high resolution multispectral radiometer providing narrow band measurements in the spectral region of 400 to 800 nm for estimates of ocean color and atmospheric properties.

GROUP 7 REPORT

Modelling of Integrated Biogeochemical Cycles

Chairmen: N. S. ABROSOV, H. R. KROUSE
Rapporteurs: M. G. SADOVSKY, R. W. P. M. LAANE

There were no presentations in this working group concerning global cycling of either S or C, etc. nor cycling within an individual water body. Rather, modelling concepts were addressed in more general terms.

The term "modelling" is used in many ways. In general, it is a description of a real or hypothetical system. Models serve as a tool for solving specific problems. Therefore it is necessary to properly define the problem before chosing a model. There are two basic approaches.

1. Construct a model using a data base;
2. use a model to direct the data of acquisition.

Models may comprise statistics, budget calculations, dynamic simulation, etc. They may be physical, chemical, biological, economical, or any combination thereof e. g. an ecosystem model.

Models can be used to solve problems at different levels of complexity. There is considerable controversy as to the complexity required to solve a particular problem. In the interest of efficiency, one should start with the simplest approach that is consistent with the objectives. In the course of applying this model, an extension may be necessary.

Ideally, a model should be capable of prediction. However, it can also serve the useful purpose of integrating information from different disciplines and in turn provide direction to the individual disciplines. Therefore, it is important that there are continuous interactions between the constructor of the model and the researchers providing the inputs.

Most papers presented at this working group focussed on the mathematical aspects of modelling. Therefore, the discussion was directed more towards the appropriateness of specific equations and mathematical approaches rather than towards applications to S and C cycling. One presentation described computer modelling packages that were particularly accessible to resarchers not proficient in computing techniques.

Models more directly related to C and S cycling were presented in other working groups.

Recommendation

As models are tools for solving different problems, it is recommended that in future meetings concerning the cycling of elements, modellers should participate from the outset in other working groups.

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Lake Baikal Workshop - Objectives and Background

by
EGON T. DEGENS, Hamburg*)

With 2 Figures and 3 Tables

By definition, chemical elements essential for life are commonly referred to as biogeochemical elements. Since they may stem from the air, the water, the crust or the biological cell, biogeochemical cycling of elements involves all compartments of our Earth from a depth of 50 km (crust and upper mantle), to a height of 100 km (troposphere and stratosphere).

On the dry weight basis, bulk organic matter is composed of six major elements: carbon (47 %), oxygen (30 %), hydrogen (9 %), nitrogen (9 %), sulfur (1 %), and phosphorus (1 %). However, it would be ill-advised to study only the biogeochemical cycling of just these six major elements and not consider the large suite of metal ions that are of vital importance in sustaining life. Close to about 25 essential elements are structurally and functionally involved in cellular activities, and a deficiency in any one of them would be deleterious to life.

All chemical elements are part of the global cycling of matter, but their majority bears no affinity to life, except that many of them are toxic to organisms. Accordingly, the biological cell had to develop strategies to fend them off. The idea has been advanced that much of what we regard as the evolution of organisms can simply be viewed - in the sense of A. TOYNBEE - as the response of the cell to the challenge of a changing habitat (DEGENS, 1989).

In general, biogeochemical cycles describe the pathways along which organic and inorganic substances move and interact in the various compartments of our Earth. Globally combined they can be looked upon as a complex and dynamic network of flows of matter and forces in the air-water-earth-life system. To assess

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their operation principles requires a constant crossing of disciplinary bounds between physics, chemistry and the environmental sciences. A holistic approach seems to be mandatory, because only in this fashion can multifarious feedbacks and processes be duly considered.

This was actually a matter of course during the formative years of biogeochemistry. However, growing specialization has almost brought to a halt this prosperous - because reflective period of science. I doubt whether a Viktor Moritz Goldschmidt or a Linus Pauling could have come up with their schemes on the ionic radii of chemical elements - which they actually developed along different avenues - had they only considered a small specialized segment of the natural sciences. It was them, who first demonstrated that chemical elements have a logic and a liking or disliking to other elements, and that many elements feel more at home in the dead rather than in the living world.

Organizations too have fostered work in this arena of research; of special prominence are: The Scientific Committee on Problems of the Environment (SCOPE), and the United Nations Environment Programme (UNEP).

Fifteen years ago, SCOPE decided to give more emphasis to the biogeochemical cycling of elements. It all started in December 1975 at Örsundsbro, Sweden, with a workshop on "The Global Cycles of Nitrogen, Phosphorus and Sulfur" (SVENSSON & SÖDERLUND, 1976). In 1976 followed the establishment of the SCOPE International Nitrogen Unit at the Royal Swedish Academy of Sciences. The next moves came fast: Workshop on "The Global Carbon Cycle" in March 1977 at Ratzeburg, Germany (BOLIN et al., 1979); foundation of the SCOPE/UNEP International Carbon Unit at the University of Hamburg, Germany, in 1978; a year later establishment of the SCOPE/UNEP International Sulfur Unit at the Soviet Academy of Sciences. Since then, numerous workshops were held on regional and global aspects of the biogeochemical cycles of carbon, nitrogen, sulfur and phosphorus; attention has recently also been given to the metal ions. By now, the list of biogeochemical elements treated as part of SCOPE-UNEP programs encompasses practically all key elements of life.

The Baikal workshop is the first, where all biogeochemical elements are appraised with respect to their integrated feedbacks in what one perhaps may call a "biogeochemical supercycle". This time, our chief goal will be to look at the state of water in relation to the role biogeochemical elements play in this medium. Subsequent conferences are planned on the cycling of biogeochemical elements in air, soil, and solid earth. Thus, to prime the pump of our discussion, I will briefly summarize some pertinent data on water.

"Water is the best of all things !" This saying of Pindar (518-446 B.C.) has not lost its meaning over the ages. A grain seed properly stored for thousands of years in a pottery jar has a good chance to germinate once exposed to the humid soil. A bacterium, enclosed in a crystal of salt, is said to have come to life again after a few hundred million years of suspended animation. Some, however, suggested that the pickled bacterium is simply a modern contamination, but I see no reason why it could not have survived for all those years.

Water exists almost everywhere in our planetary system. Next to hydrogen and helium, water is probably one of the most ubiquitous single molecules around in outer space. Comets, meteorites, many moons of the outer planets and even Uranus, Neptune and Pluto are believed to carry substantial amounts of frozen water in different structural forms of ice (ice I to ice X). On Earth, water occurs not only at the surface in the form of water vapor in our atmosphere, or in snow flakes or rain drops, or in lakes, rivers and oceans, but it is found in virtually all rocks down to the Mohorovicic discontinuity and may possibly even be present in the upper mantle. In the crust, water can be fixed to various minerals or occurs as interstitial solution. In this context it is of note, that water at higher temperatures and pressures does not exist as H_2O but as hydronium hydroxide, $H_3O \cdot OH$. Living organisms are mainly water (ca. 80 %); actually, our eyes are essentially water, except for the 2 percent "contamination" of organic molecules and salt.

All appears to go back to Thales of Milet (ca. 640-546 B.P.) who declared that this Earth, its air, its sea, its mountains, its life, including its gods, are just different forms of water. I shall follow this proposition and will briefly inform on the amount of water held in the various terrestrial compartments involved in the hydrological cycle (Table 1).

The ocean has a volume of 1.37×10^9 km^3 which represents about 70 % of all waters contained in crust and hydrosphere. It has been found useful to express individual water layers in terms of sphere depth, that is the depth a given volume of water would yield if it were evenly spread as a layer around a smooth sphere having the surface area the size of our globe, i.e., 5.1×10^8 km^2 (DUXBURY, 1977). For comparison, the sphere depth of solid land currently above sea level would amount to 244 m.

Table 1

Distribution of the Earth's water by volume and sphere depth (after DUXBURY, 1977).

Type of reservoir	Volume (km^3)	Sphere depth (m)
Water vapor and condensate in the air	$\leq 2.0 \times 10^4$	circa 0.03
Organisms	1.6×10^5	0.3
Rivers and lakes	5.1×10^5	1
Groundwater	5.1×10^6	10
Glacial and other land ice	2.3×10^7	45
Crust (free + silicate-bound)	6.0×10^8	1,180
Sea	1.37×10^9	2,685

Sea water is turned over, molecule by molecule, in less than a thousand years and it will take about 5 to 10 million years to cycle one volume of ocean water through the crust. Hydrothermal waters discharged along mid-oceanic rifts have temperatures in the neighborhood of 300 °C and are further characterized by the abundance of certain metal ions, in particular iron, manganese, cobalt, zinc, calcium, and silicon.

Mean ocean depth is 3,800 m, and for percent ocean area between various depth zones see Figure 1. Distribution of water and land over the Earth is uneven as a glance at Figure 2 will reveal. Obviously the northern hemisphere is more continental than the southern hemisphere. All in all, land covers 29 % and the sea 71 % of the globe.

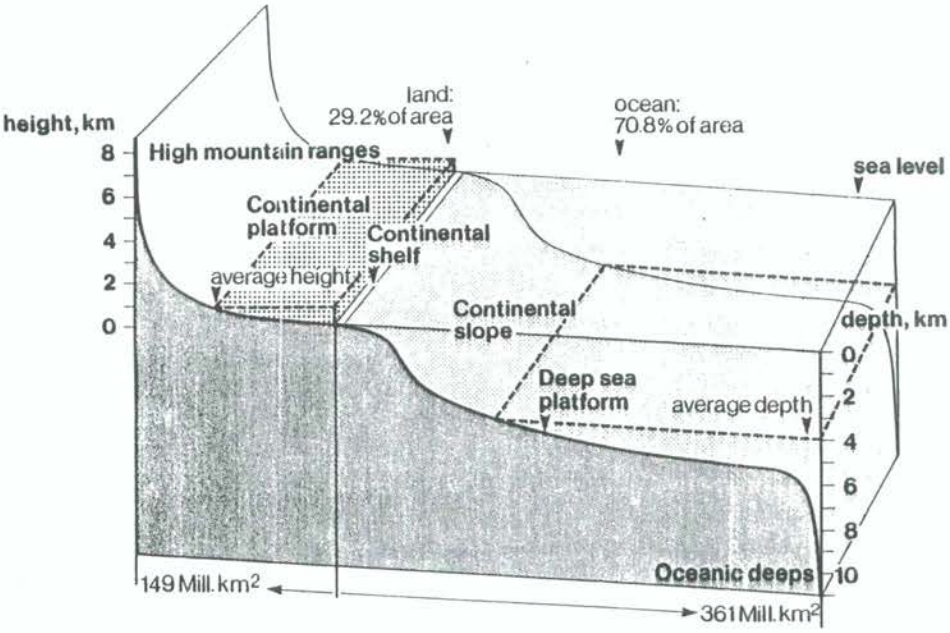

Fig. 1: Hypsometric diagram of the Earth's solid surface (KOSSINNA, 1921).

Waters on Earth exhibit different properties and come from a wide array of environments: hot to cold (-2 to 100 °C), acidic to alkaline (pH 1 to 11), fresh water to salty (< 100 ppm to 300 permil), deep to shallow, oxidizing to reducing, pristine to heavily polluted etc. Waters can occur in the free form, or be combined in solids, colloids or organic matter. It is the structure of water which changes in accordance with temperature and pressure, as well as type and amount of organic solutes, salts or solids present; so far no structural model on water exists which could explain water's polyfunctional characteristics (DEGENS, 1989).

Our workshop will focus on a rather important segment of the water cycle: rivers - lakes - estuaries. Especially lakes will stay in the limelight of our discussion,

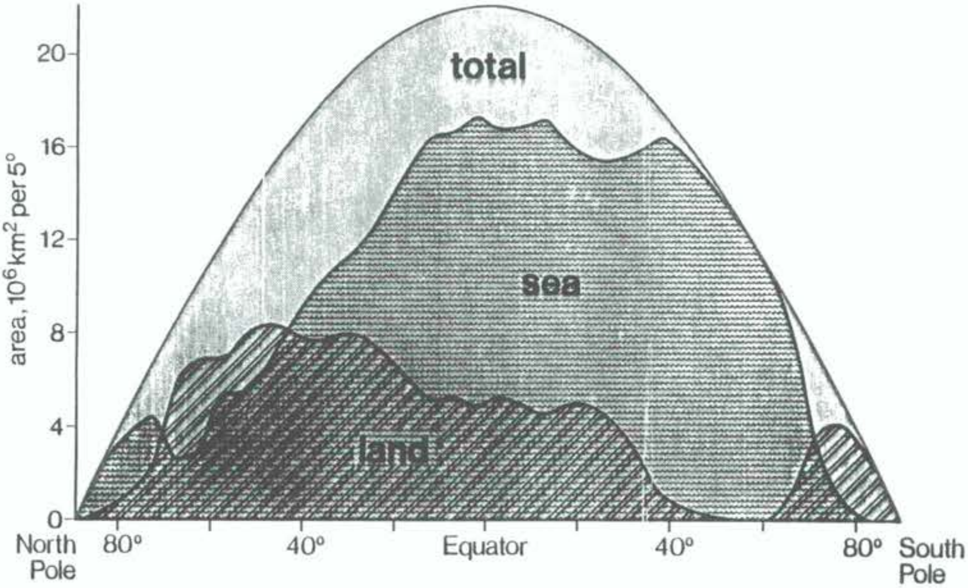

Fig. 2: Distribution of water and land over the Earth (BAUMGARTNER & REICHEL, 1975). Note the skewed distribution between northern and southern hemisphere.

because the topic rivers, as far as the cycling of carbon is concerned, has already been covered in previous workshops (DEGENS et al., 1991a), and the biogeochemistry of estuaries has been thoroughly treated at our previous workshop at Texel (DEGENS et al., 1991b).

In Tables 2 and 3 areal size and water volume of major lakes are depicted. Included is the Black Sea, which is located in an east-west intermontane depression between two alpine foldbelts. During the Quaternary ice ages, the Black Sea was a freshwater lake. The Caspian Sea has the same geological setting and was from time to time connected with the Black Sea via the Manych and Kura depressions. About two million years ago, the marine Akchagilian transgression had for the last time interconnected the Mediterranean, Black Sea, Caspian Sea and Lake Aral (PALUSKA & DEGENS, 1979). Lake Nicaragua is also a relic of the former ocean dating back to the time the Isthmus of Panama closed (Plio-Pleistocene boundary). All other lakes listed in Tables 2 and 3 have never been linked to world ocean. Baikal, Tanganyika, Malawi and Kivu are deep *rift lakes*, whereas the Great Lakes (Superior, Huron, Michigan, Erie, Ontario), the large Canadian lakes (Great Bear, Great Slave) and the North European lakes (Ladoga, Onega) are shallow and Holocene remnants of the last ice age and thus appropriately termed: *glacial lakes*. Lake Van in Eastern Anatolia is a product of volcanism, in that lava flows from the nearby Nemrut volcano dammed off part of the old Euphrates; subsequent subsidence above the emptied magma chamber during the past 50 to 100 thousand years produced a central basin having a water depth of more than 450 m. Lake Issyk Kul shares with Lake Van the high salt content (soda chemistry), water depth, and

Table 2

Area of major lakes in km^2.

Name of lake	Area (km^2)
Caspian Sea	423,300
Black Sea	423,000
Superior	82,382
Victoria	68,800
Aral	63,800
Huron	59,573
Michigan	57,994
Tanganyika	32,880
Baikal	31,500
Great Bear	31,068
Malawi	30,800
Great Slave	28,919
Erie	25,735
Winnipeg	24,331
Chad	11-22,000
Ontario	19,521
Ladoga	18,180
Balchasch	17,300
Eyre	8-15,000
Onega	9,549
Nicaragua	7,997

Table 3

Volume of major lakes in km^3.

Name of lake	Volume (km^3)
Black Sea	534,000
Caspian Sea	79,319
Baikal	23,000
Tanganyika	18,940
Superior	12,000
Malawi	8,400
Michigan	5,760
Huron	4,600
Winnipeg	3,110
Issyk Kul	1,732
Ontario	1,720
Ladoga	920
Van	607
Kivu	583
Erie	540
Manapouri	145

geological history. Lakes Chad and Eyre are Playa Lakes characteristic for arid to semi-arid climatic zones.

Lake Baikal contains close to one fourth of all fresh water reserves and is also the deepest lake on Earth. Jointly with Lakes Tanganyika and Malawi, it is an ecological refuge which deserves special attention.

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Isotope Data on the Nature of Riverine Sulfates

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With 1 Figure and 1 Table

Contents

Abstract

Data on sulfur and oxygen isotope composition of sulfates in different rivers are summarized. They are discussed with the objective of identifying natural sources and formation mechanisms of riverine sulfates.

Most of the river sulfates are mixtures of evaporite and secondary sulfates, the latter being produced during oxidation of sedimentary sulfides. Only a few rivers contained solely evaporite sulfate or secondary sulfates. In certain seasons, some rivers contain sulfates which had been transformed in at least one redox cycle. Sulfates of many rivers have apparently exchanged oxygen isotopes with water, indicating that they originate from deep horizons of sedimentary rocks.

The mean $\delta^{34}S$ and $\delta^{18}O$ values of riverine sulfates were found to be +8 and +7.5°/oo, respectively. This means that two thirds of riverine sulfate originate from evaporites and one third from oxidation of sulfide.

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1. Introduction

In the global sulfur cycle rivers are the main transport routes for the migration of sulfur from continents into the ocean. In order to understand the characteristics of this flux and its role in the sulfur cycle, one needs to evaluate the inputs from various sulfate sources. Isotopic data along with chemical analyses of water samples provide researchers with a unique tool for solving this problem. The isotopic compositions of sulfate-sulfur and sulfate-oxygen within in the main channel and in the tributaries of different rivers, make it possible to identify major sources of sulfur. Observations of seasonal changes can provide an insight into factors responsible for redistribution of input fluxes from these sources. In addition, investigation of the isotopic characteristics of major rivers on all continents allows an estimate of the mean $\delta^{34}S$ and $\delta^{18}O$ values of the total riverine sulfates drainage. These important geochemical parameters indicate the primary isotopic composition of oceanic sulfate, which may change under the influence of bacterial sulfate reduction, evaporite formation, and circulation of seawater through hot basalts.

Sulfates may enter rivers from several sources. For most non-industrial regions, the main sources are evaporites and sulfides from sedimentary rocks which are oxidized during interacting with oxygen-rich surface waters (RABINOVICH & GRINENKO, 1979; HITCHON & KROUSE, 1972). A small fraction of riverine sulfates originates from atmospheric sources which can be either natural or anthropogenic (STALLARD & EDMOND, 1981). It should also be remembered that over the last 50 years, rivers in developed regions have experienced a substantial influx of sulfates from industrial emissions, acid mine water drainage and in agricultural regions, sulfates in fertilizers have been washed off fields. Nowadays, the anthropogenic influx of sulfur is on the same scale as the natural one (IVANOV et al., 1983).

By a detailed analysis of the isotopic composition of different sulfur compounds, the flux of anthropogenic sulfur can be reliably evaluated on a regional basis (KROUSE, 1980; HOLT, 1975). However, there is still a considerable lack of isotopic data to estimate such fluxes on the global scale. This is the main purpose of the present study. Anthropogenic contributions cannot be properly evaluated unless natural sources of sulfate have been identified.

2. Sulfur and Oxygen Isotope Fractionation

Prior to considering the available data, the isotopic characteristics of sulfur compounds and fractionation of sulfur and oxygen isotopes are briefly discussed.

In marine evaporites, $\delta^{34}S$ values range over time from +10 to +29^{o}/oo, whereas contemporaneous sulfates have a fairly uniform sulfur isotopic composition. The mean value of $\delta^{34}S$ for sulfate sulfur in evaporites is +19.5^{o}/oo (MIGDISOV et al., 1983). Sedimentary sulfides have a wide variation in $\delta^{34}S$ and are usually depleted in the heavier ^{34}S in comparison to sulfate precursors. The estimated mean $\delta^{34}S$ value for sedimentary sulfides in platforms is -12.2°/oo, -5.7°/oo in geosynclines, and -8.7°/oo on continents (MIGDISOV et al., 1983). Total sulfur in geosynclines exhibits a lower $\delta^{34}S$ value (-3.5°/oo) as compared to the total sulfur in platforms (+1.4°/oo) due to a greater presence of evaporite layers on platforms. Sulfur in meteoric precipitation in non-industrial continental regions has a mean $\delta^{34}S$ close to +5°/oo, and in coastal regions, +13°/oo .

$\delta^{18}O$ values in evaporite sulfates range from +9 to +17°/oo (CLAYPOOL et al., 1980) and in rain water they vary from +3 to +21°/oo (HOLT et al., 1983).

The main process, causing changes in the isotopic composition of sulfate-sulfur in exogenous conditions, is bacterial sulfate reduction which results in an enrichment of the residual sulfate in the heavy isotope. However, as the sulfate content in most river waters is rather low, this process would not cause a pronounced fractionation of sulfur isotopes (HARRISON & THODE, 1958).

Oxidation of sulfide and elemental sulfur is not accompanied by a noticeable fractionation of sulfur isotopes. Therefore secondary sulfates inherit the isotopic composition of the primary sulfides (GRINENKO & GRINENKO, 1974).

Factors determining the isotopic composition of oxygen during sulfate production and bacterial sulfate reduction are somewhat more complex. The variation of $\delta^{18}O$ in sulfate depends not only on the intensity of bacterial reduction but also on the isotopic composition of oxygen in water in which the process takes place (MIZUTANI & RAFTER, 1973). Usually, with $\delta^{18}O$ of water more positive than -15°/oo, there will be accumulation of ^{18}O in the residual sulfate. However, the rate of change of $\delta^{34}S$ in sulfate will be several times greater than that of $\delta^{18}O$, provided there is a sufficiently high sulfate concentration.

The isotopic composition of oxygen in secondary sulfate, produced by oxidation of reduced sulfur compounds, is to a considerable degree governed by the environmental conditions. For example, bacterial oxidation of sulfur has been observed to produce only a slight difference between $\delta^{18}O$ in the sulfate formed and in the water, in which the oxidation took place (MIZUTANI & RAFTER, 1969). On the basis of laboratory experiments with Na_2S oxidized by O_2 bubbled through water, LLOYD (1967) concluded that two thirds of the total oxygen in secondary sulfate are controlled by water and one third by gaseous oxygen. To calculate the isotopic composition of secondary sulfate, he proposed the following formula:

$$\delta^{18}O\text{-}SO_4^{\ 2-} = 2/3(\delta^{18}O\text{-}H_2O - \alpha H_2O) + 1/3(\delta^{18}O\text{-}O_2 - \alpha O_2) \qquad (1)$$

where αH_2O and αO_2 are coefficients for kinetic isotopic effects of binding oxygen in sulfate, equal to 0 and 8.7°/oo, respectively. When finely ground pyrite suspensions were oxidized in water through which O_2 was bubbled, roughly equal amounts of sulfate oxygen originated from water and gaseous oxygen (SCHWARTZ & CORTECCI, 1974). The oxygen isotope composition of sulfate produced by bacterial oxidation reactions (TAYLOR & WHEELER, 1984; VAN EVERDINGEN & KROUSE, 1985). GOULD et al. (1990) have studied the $\delta^{18}O$ content of sulfate produced during the oxidation of four sulfide minerals by two environmental isolates of *Thiobacillus ferroxidans*. They concluded that the incorporation of oxygen from H_2O into the product SO_4^{2-} is primarily due to oxygen isotope exchange between H_2O and sulfur-containing reaction intermediates.

A comprehensive investigation of the isotope composition of natural sulfates was carried out by SHAKUR (1982) and appears in part in VAN EVERDINGEN et al. (1982, 1985). The incorporation of oxygen from H_2O into secondary sulfates was readily identified by negative $\delta^{18}O$ values (as low as - 10°/oo) particularly at higher latitudes.

Nowadays, it is an established fact that oxidation of reduced sulfur compounds in the atmosphere proceeds through formation of intermediate products including SO_2 which readily exchange oxygen atoms with water vapour, with the equilibrium constant depending on the temperature. Experiments on SO_2 oxidation to sulfate in the presence of water vapour have shown that, with the $\delta^{18}O$ value of vapour near -20°/oo, the value of $\delta^{18}O$ in the formed sulfate will be close to 0°/oo (HOLT et al., 1983). This value is probably a reasonable average for secondary sulfate formed in the atmosphere at intermediate latitudes. In meteoric precipitates, however, sulfate sulfur exhibits a somewhat higher $\delta^{18}O$ (+10°/oo, on the average). Although this is similar to the value for seawater sulfate in continental interior regions, it is likely due to the presence of sulfates formed during burning of fuel or roasting of sulfide-containing ores which are characterized by higher values of $\delta^{18}O$ (up to +40°/oo) (HOLT et al., 1982).

It should also be kept in mind, that when dissolved sulfate and water are in contact for long periods of time in regions of low pH and/or increased temperature, they undergo isotopic exchange which enriches the sulfate ^{18}O as compared to water. At 100 °C, this enrichment can be as high as 17°/oo . If we take into account the fact that stratal water that has undergone isotopic interchange with enclosing rock, may have $\delta^{18}O$ values of +8°/oo (HOEFS, 1980), then the $\delta^{18}O$ value of sulfates in thermal waters can be as high as +28°/oo .

3. Discussion and Conclusion

Several earlier investigations were concerned with the nature of the isotopic variations of river sulfate along the main channel. A general relationship has been demonstrated between $\delta^{34}S$ in riverine sulfates and $\delta^{34}S$ in sedimentary rock in the river basin (IVANOV et al., 1983). This relationship is even recognized in rivers of the USSR European region, which are characterized by substantial anthropogenic influence. In contrast, the effect of the enclosing rock on the isotopic composition of sulfate oxygen is not so pronounced. In the Amazon, $\delta^{34}S$ in dissolved sulfates differ only slightly from +7‰ both in 1976 and in 1977, whereas at the river mouth, $\delta^{18}O$ values dropped in 1976 from +8.2 to +3.0‰, and rose again to +11.7‰ in 1977. This temporal variation in oxygen isotopic composition was attributed to different intensities of redox processes during dry (1976) and rainy (1977) seasons (LONGINELLI & EDMOND, 1983).

The influence of anthropogenic sulfur on isotopic characteristics of riverine sulfates was documented in the Arno River, Italy (LONGINELLI & CORTECCI, 1970). While upstream $\delta^{34}S$ and $\delta^{18}O$ values of sulfates were -4‰ and +3‰, respectively, they increased in going downstream to +8.0 and +8.5‰, respectively. The enrichment in ^{34}S and ^{18}O were attributed by the authors to bacterial reduction processes, but this notion does not agree with substantial increase in the dissolved sulfate content. It is more reasonable to suppose that these variations reflect inputs of sulfates washed off fields as well as industrial and municipal wastes.

Isotopic data for dissolved sulfates in major rivers of the Soviet Union and the Amazon at different times of the year are shown in Figure 1 and Table 1 (RABINOVICH & GRINENKO, 1979; LONGINELLI & EDMOND, 1983; GRINENKO et al., 1986). The top right-hand corner of Figures 1 features a sulfate field for evaporites.

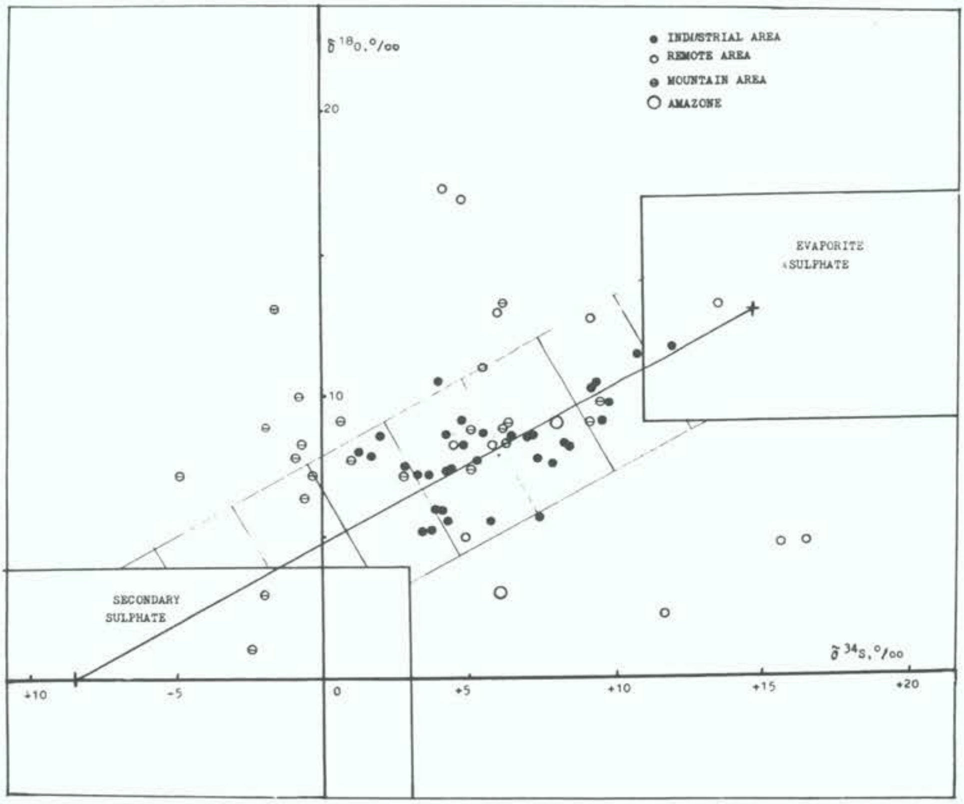

Fig. 1: Variations of oxygen and sulfur isotopic composition in riverine sulfates of different areas. Indicated are the fields of evaporite sulfates, secondary sulfates and zone of combined sulfates.

Table 1

Isotopic data for sulfate in rivers

Basin	River	Sulfate flux TgS/a	Date	$\delta^{34}S$	$\delta^{18}O$
Baltic Sea	W.Dvina	0.1	03.71	9.2	9.6
"	"	0.1	08.72	11.4	10.7
"	Nieman	0.1	01.72	11.4	1.1
"	"	0.1	03.72	4.2	1.6
Azov Sea	Don	0.9	03.65	8.6	4.2
"	"	0.9	06.67	7.9	1.7
"	"	0.9	08.69	8.6	5.5
"	"	0.9	07.70	8.5	6.4
"	"	0.9	11.72	7.4	4.4
"	Kuban	0.2	11.69	6.4	-0.6
"	"	0.2	02.70	8.3	-0.7
"	"	0.2	02.70	7.8	-0.8
"	"	0.2	09.70	7.1	2.8
Black Sea	Danube	1.9	05.71	8.0	1.3
"	"	1.9	03.75	5.9	4.1
"	Dniester	0.1	05.69	5.2	3.8
"	"	0.1	07.69	7.6	5.3
"	"	0.1	09.69	7.2	3.7
"	"	0.1	07.70	8.1	8.4
"	"	0.1	01.71	7.5	2.9
"	"	0.1	02.71	5.5	4.3
"	"	0.1	02.71	10.5	4.0
"	Dnepr	0.6	05.69	8.2	4.8
"	"	0.6	08.69	7.2	4.2
"	"	0.6	01.71	7.0	9.6
"	"	0.6	08.71	8.6	2.0
"	Rioni	0.1	01.69	1.0	-2.4
"	"	0.1	09.69	2.9	-2.0
"	"	0.1	02.70	13.2	6.2
"	"	0.1	01.71	9.7	9.5
Mediterranean	Arno	-	09.68	8.2	8.0
"	"	-	02.69	8.4	2.8
Caspian Sea	Kura	1.0	05.69	7.2	-0.3
"	"	1.0	08.69	9.1	0.7
"	"	1.0	03.70	7.3	-4.8
"	"	1.0	09.70	7.7	1.0
"	"	1.0	03.71	7.7	0.9
"	"	1.0	03.72	13.1	-1.6

Basin	River	Sulfate flux TgS/a	Date	$\delta^{34}S$	$\delta^{18}O$
"	"	1.0	05.72	8.9	-1.8
"	Terek	0.3	04.69	7.4	5.2
"	"	0.3	08.69	8.8	5.1
"	"	0.3	06.70	8.8	6.2
"	"	0.3	04.71	8.2	6.3
"	"	0.3	10.71	9.0	9.2
"	Volga	4.1	05.69	9.0	6.4
"	"	4.1	08.71	7.7	7.3
"	Ural	0.1	07.69	3.8	2.9
"	"	0.1	08.69	4.2	3.5
"	"	0.1	12.69	7.2	3.3
"	"	0.1	09.70	9.2	4.8
"	"	0.1	02.72	5.9	4.1
"	"	0.1	05.72	5.1	3.4
Aral Sea	Syr Daria	1.3	07.69	6.6	9.9
"	"	1.3	09.69	7.5	7.8
"	"	1.3	02.70	8.3	8.2
"	"	1.3	01.71	9.7	9.8
"	"	1.3	09.71	5.6	7.4
"	"	1.3	12.71	9.2	10.5
"	Amu Daria	2.5	05.69	10.4	9.4
"	"	2.5	07.69	9.1	9.0
"	"	2.5	03.70	9.1	9.6
"	"	2.5	06.72	11.7	12.0
Arctic	Yenisei	1.8	03.73	4.7	16.6
"	"	1.8	10.73	8.2	5.8
"	"	1.8	03.74	4.7	15.8
"	"	1.8	07.74	5.0	4.9
"	Ob	1.3	08.69	8.2	4.5
"	"	1.3	07.71	11.0	5.5
"	"	1.3	04.73	16.9	4.9
"	"	1.3	02.74	7.4	11.6
"	N. Dvina	1.2	04.69	12.9	6.8
"	"	1.2	03.70	12.6	9.2
"	"	1.2	04.72	13.2	13.6
"	Pechora	0.5	04.69	8.5	7.2
"	"	0.5	10.69	2.2	11.8
"	"	0.5	06.72	7.6	12.2
"	"	0.5	04.73	17.2	3.2
Atlantic	Amazon	18.0	07.76	2.8	7.6
"	"	18.0	06.77	11.7	8.1
Pacific	Amur	1.0	04.74	9.1	10.6

Shown below are isotopic characteristics of sulfates produced by bacterial reduction followed by hydrogen sulfide oxidation. In the bottom left corner, one can see the field of isotopic characteristics for secondary sulfates formed through oxidation of sedimentary sulfides. The straight line indicates the mixing line for the mean $\delta^{34}S$ and $\delta^{18}O$ in evaporites and secondary sulfates. It should be borne in mind that for individual rivers, the combined sulfates will fall within a broad strip (dashed in Fig. 1) rather than on a line, because isotopic composition of sulfide- and sulfate-sulfur contained in the river basin rock can exhibit considerable variation. In addition, the $\delta^{18}O$ content of H_2O may vary by a few permil over the course of a long river which in turn causes variations in the $\delta^{18}O$ value of SO_4^{2-} produced from sulfide oxidation.

Most of the analyzed samples, including those from rivers in industrially developed areas, constitute a mixture of evaporite and secondary sulfates. A very small number of samples comprise solely secondary sulfates or evaporite sulfates. Sulfates in a few isolated samples, have passed through at least one redox cycle. Many data fall above the sulfate mixture strip in Figure 1. An increased ^{18}O content in such sulfates shows that they have been involved in isotopic oxygen exchange with water. Since the rate of such an exchange is only significant at higher temperatures, it may be assumed that water containing such sulfates comes from considerable depths. One can argue, of course, that a part of these sulfates represents thermally oxidized anthropogenic sulfur. This alternative, however, is contradicted by the fact that most samples are from rivers in non-industrial and mountainous regions.

Anthropogenic sulfates in the Arno River, Italy, as well as in rivers flowing through industrial regions of the USSR do not show appreciable differences from sulfates in rivers in non-industrial regions. It appears that sampling in the river mouths constitutes the average of contributions from all anthropogenic sources, which are in turn close to the mean values for natural sources. More direct evidence on the inflow of anthropogenic sulfur can be obtained by monitoring individual regions (KROUSE, 1980).

The weighted average of $\delta^{34}S$ in dissolved sulfate in USSR rivers was earlier estimated at +9.2°/oo, which indicates that two thirds of total sulfate come from evaporites and one third are secondary sulfates (RABINOVICH & GRINENKO, 1979). For sulfates in the Amazon, the mean $\delta^{34}S$ value is close to +7°/oo (LONGINELLI & EDMOND, 1983). It is interesting that 60 % of the discharged riverine sulfates is from Permian evaporites, the sulfates from other evaporites constituting only an insignificant fraction, and 5 % of the sulfate originates from meteoric precipitation (STALLARD & EDMOND, 1981). The contribution of secondary sulfates does not exceed one third. For rivers in non-industrial regions, these proportions of evaporite and secondary sulfate sulfur seem typical.

The amounts of sulfate discharged by the Amazon and rivers in the Soviet Union are quite comparable. Therefore, in the absence of data from other major river systems of the world, one can tentatively adopt +8°/oo for the mean $\delta^{34}S$ in the overall river discharge into the ocean. A similar estimate yields a $\delta^{18}O$ value close to

+7°/oo. These values of the mean isotopic composition of riverine sulfates could be incorporated in model calculations of the global sulfur cycle.

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Mineralogy of the Clay-Sized Suspended Load from Headwater Tributaries of the Paraná River: Bermejo, Pilcomayo, and Paraguay Rivers

by
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With 7 Figures and 1 Table

Contents

Abstract

The clay-size fraction in suspended sediment samples from the Bermejo, the Pilcomayo, and the Paraguay rivers - headwater tributaries in the Paraná drainage system - was studied in order to establish the clay mineralogy signature of each basin, identifying clay sources and transport paths. The northernmost Andean tributaries (upper Bermejo and Pilcomayo) supply an illite-rich, fine-grained fraction, while the Bermejo southern headwaters (San Francisco River) mainly deliver a smectite-rich

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mineral assemblage. The tropical environment dominant in the Paraguay headwaters is the source of a predominantly kaolinite and smectite fine-grained mineral suite.

The Bermejo, which accounts for 5% of the Paraná drainage area, supplies over 50% of its suspended load and is a major controlling factor for the clay-size mineralogy exported by the Paraná to the continental platform. Its clay-size fraction follows a relative abundance of illite > smectite > chlorite > kaolinite, similar to the one delivered to the Paraná by the entire Paraguay River subsystem. This work is an integral part of a larger study which seeks to contribute to the knowledge on the sources of sediments to the SW Atlantic.

1. Introduction

The mineralogical analysis of the fine fraction (less than 2 μ equivalent spherical diameter) of river sediments has been an extensively used methodology to assist in the evaluation of weathering processes and to identify sources of sediments in river systems as well as in marine and lacustrine sedimentary deposits.

Noteworthy examples are the studies of BISCAYE (1965), GIBBS (1967), GRIFFIN et al. (1968), REYNOLDS (1971), NORTON (1974), EISMA et al. (1978), and IRION & ZÖLLNER (1990), among many others.

The SCOPE/UNEP Project "Transport of Carbon and Minerals in Major World Rivers", an integral part of SCOPE's "Global Cycles of Biogeochemical Elements" research, provided the framework to gather abundant information on a world-wide basis. EMEIS & STOFFERS (1982), IRION (1983), KONTA (1983), EMEIS (1985), KONTA (1985), NAIDU et al. (1985), MOWATT & NAIDU (1987), and KONTA (1988), have reported mineralogical data collected in many of the major world rivers.

This paper reports clay-size mineralogical data collected in the Bermejo, the Pilcomayo, and the Paraguay rivers, identifying possible sources of sediments in their headwaters. The first two rivers are the only Andean tributaries in the Paraná system, one of the large rivers in the world and a likely significant source - through the Rio de la Plata - of the sediments accumulated in the SW Atlantic continental shelf, continental rise, and in the Argentine Basin (KLAUS & LEDBETTER, 1988). Moreover, the Bermejo River provides - on a yearly basis - a dominant fraction of the sediment load of the Paraná. The Paraguay River has its headwaters in the tropical Mato Grosso (Brazil) and drains the Gran Pantanal, a swampy depression about 250 km wide.

The mineralogy of the Paraná fine fraction was first investigated by DEPETRIS & GRIFFIN (1968), and the apparent relationship between the mineralogical variability and the hydrological regime was pointed out by CASCANTE et al. (1985). Additional information can be found in the papers published under the auspices of the SCOPE/UNEP project developed to study the transport of carbon and minerals in major world rivers and which have been listed above. The mineralogical nature of the fine inorganic phases supplied by Andean tributaries of the Paraná, however, has not been evaluated so far.

This work is an integral part of an overview leading to update the knowledge on the nature of the sediments transported by the Paraná system to the sea, identifying sources and paths.

2. The Bermejo, the Pilcomayo, and the Paraguay Rivers

The Bermejo River (SOLDANO, 1947) - the name reflecting the reddish-brown coloration of its waters - has its headwaters between 21° and 25°S and between 64° and 66°W (Fig. 1), limited by several mountain ranges (e.g., S. Victoria, Chani, Tarija) between Argentina and Bolivia. The drainage basin covers an area of 0.13 x 10^6 km^2 (about 5% of the drainage area of the Paraná) and the annual discharge exceeds 10 km^3 (2.5 l/s/km^2), with high waters during January-March (the southern summer) partially supplied by meltwater. Mean precipitation reaches 540 mm/a. The upper reaches exhibit steep slopes, ca. 1.1 m/km.

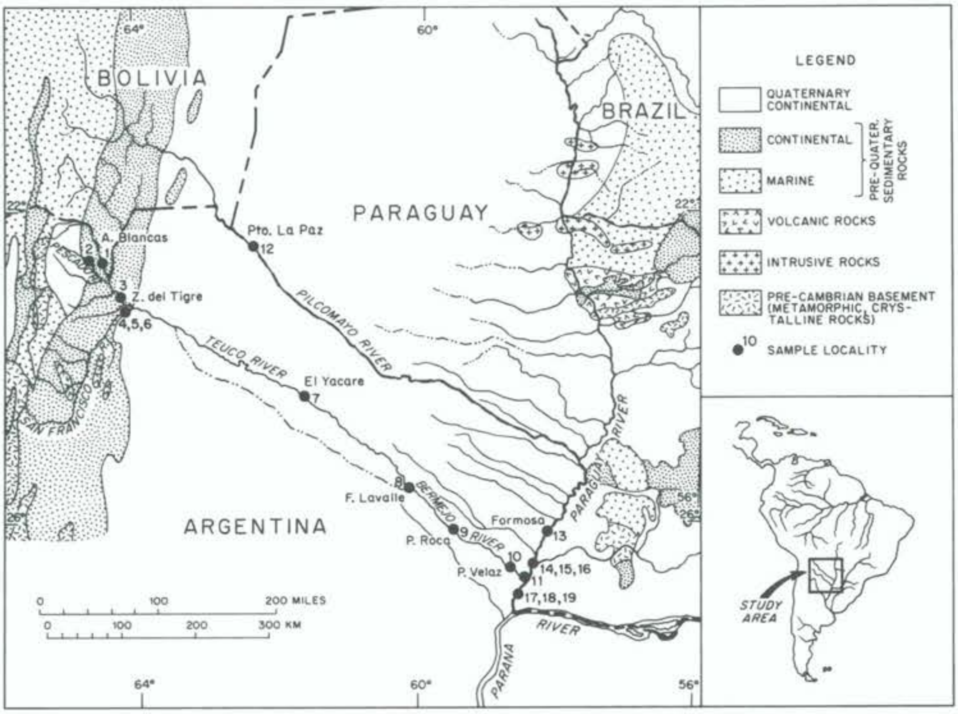

Figure 1: Map of the Bermejo, Pilcomayo, and Paraguay rivers, tributaries of the Paraná River. The numbers indicate samples referred to in Table 1: 1) Upper Bermejo; 2) Pescado River; 3) Bermejo River (Zanja del Tigre); 4, 5, and 6) San Francisco River; 7) Teuco River; 8) Bermejo River (F. Lavalle); 9) Bermejo River (Pte. Roca); 10) Bermejo River (Pto. Velaz); 11) Bermejo River (mouth); 12) Pilcomayo River (La Paz); 13) Paraguay River (Formosa); 14, 15, and 16) Paraguay River (Upstream Bermejo mouth); 17, 18, and 19) Paraguay River (Downstream Bermejo mouth).

Like the Bermejo, the Pilcomayo River - its northern neighbor - flows to the East towards the Paraguay River (Fig. 1). Its active headwaters lie between 19° and 22°S, in the Andean ranges of de los Frailes and Chacaya, roughly comprising 45% of its total drainage basin (ca. 0.126 x 10^6 km^2). Its mean annual discharge is about 5.4 km^3 (1.3 l/s km^2), fed by an annual precipitation of ca. 700 mm (SOLDANO, 1947).

The Paraguay River has headwaters in Campos dos Parecys (14°-20° S), in the central region of Mato Grosso (Brazil). Its upper catchments are close to Amazon tributaries (e.g., Tapajoz, Guapore/Madeira). The total drainage is ca. 1.1 x 10^6 km^2 of which over 76% is accounted for by the Paraguay proper, and the remaining 24% by the above described tributaries, the Bermejo and the Pilcomayo rivers. The mean annual precipitation exceeds 1,300 mm/a which results in a specific discharge of 7 l/s/km^2 in the active basin. The Paraguay delivers about 4.5 x 10^3 m^3/s of water to the middle course of the Paraná.

The Andean headwater geology (Fig. 1) is largely dominated by Prequaternary sedimentary rocks of continental (folded Tertiary, Upper Cretaceous, Triassic, Permian, and Upper Carboniferous) and marine (Lower Devonian, Silurian, and Ordovician/Cambrian) origin. Clearly, this predominance of sedimentary rocks, coupled to steep relief and a scarce vegetation cover, are the factors which determine the high sediment yield observed in the Bermejo. Volcanic (Quaternary andesites/basalts, Upper Triassic basaltic flows), and the Precambrian crystalline basement complex are also present in smaller proportions. The lower courses are totally covered by Quaternary (continental) sediments.

The upper Paraguay drainage basin touches the Brazilian Shield; marine Prequaternary sediments as well as intrusive and volcanic (basic) rocks are common (Fig. 1).

3. Sediment Transport

SOLDANO (1947) has reported a sediment mass transport rate of 61 x 10^6 Tg/a (ca. 470 Tg/km^2/a) for the Bermejo River, a load which seems to be provided in even proportions by the upper Bermejo and the San Francisco River. Most of this load is reportedly transported between December and February, the high water period. More recently, DRAGO & AMSLER (1981) assigned to the Bermejo a mean sediment concentration of about 6,500 mg/l, which is in relative agreement with the one that can be calculated from the figures reported by SOLDANO (1947). At any rate, the Bermejo exhibits a very large erosion rate and contributes a significant proportion of the sediment load transported by the Paraná on its middle reach. DRAGO & AMSLER (1981) have calculated that about 50% of the suspended load measured in the middle Paraná River, is supplied by the Bermejo. This mass of particulate suspended matter eventually finds its way into the SW Atlantic, thus probably contributing to high deposition rates in the continental shelf and rise.

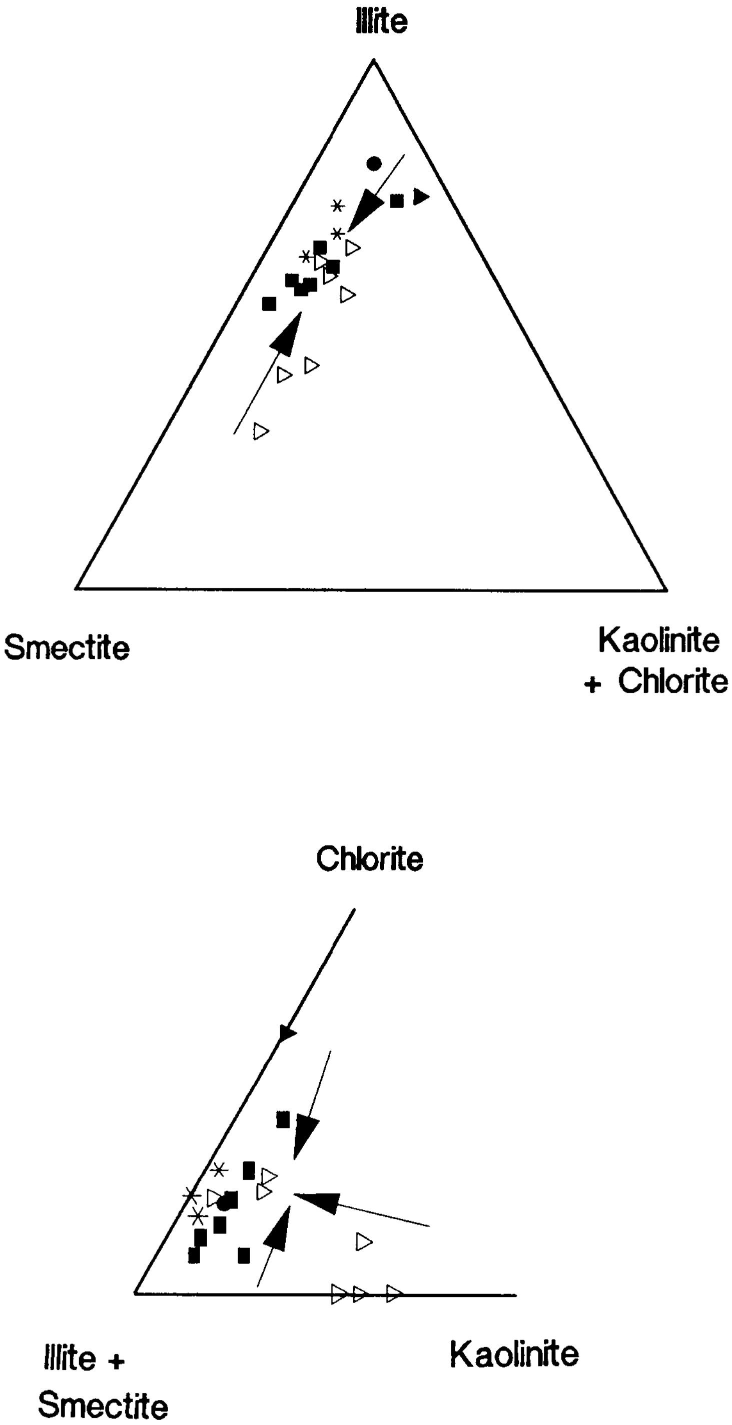

Figure 2: Diagrams showing the clay-size mineralogy and evolutionary paths (arrows) towards the Paraguay River mouth. Black dot, Pilcomayo River; black triangle Pescado River; star, San Francisco River; black square, Bermejo River; white triangle, Paraguay River.

TABLE 1

Clay-size Mineralogy Determined in the Bermejo, Pilcomayo and Paraguay Rivers.

Sample	Smectite	Illite	Kaolinite	Chlorite	Halloys.	Cryst. smect.	Cryst. chlor.	Mixed-layer type	Comments
1	10	73	3	13	-	0.61	g	I/S, Ch/S	Trioct.
2	5	75	-	20	-	0.64	g		
3	35	56	6	3	pr.	0.58	p	K/S,I/S	Ca or Mg
4	20	73	1	6	pr.	0.86	f		Ca/Mg
5	23	68	1	8	-	0.86	f		Ca/Mg
6	31	63	-	7	-	0.81	p		
7	26	61	3	9	-	0.73	g		Ca/Mg, Na
8	27	63	3	5	pr.	0.63	g	I/S	Ca/Mg
9	35	59	2	4	-	0.68	f	I/S	Ca/Mg
10	33	57	3	7	pr.	0.78	f	I/S, K/S	Na, Ca/Mg
11	41	54	2	3	pr.	0.67	p	I/S	Trioct.
12	10	81	3	7	-	0.70	g	I/Ch, K/S	Ca/Mg
13	55	30	15	-	pr.	0.46		I/S, K/S	
14	40	43	14	4	-	0.35			Ca/Mg
15	27	55	18	-	-	0.52		I/S	Ca/Mg
16	45	40	15	-	-			K/S?	Ca/Mg
17	30	64	5	8	-	0.55	f	I/S, Ch/S, K/S	Ca/Mg
18	22	65	5	8	pr.	0.75	g	I/S, K/S?	Ca/Mg
19	30	64	2	7	-	0.56	f	I/S	Ca/Mg

pr.= present, g= good, f= fair, p= poor
I/S= illite/smectite, I/Ch= illite/chlorite, K/S= kaolinite/smectite
Note: the comments are referred to the composition of smectites.

Little information is available on the sediment transport rates of the Pilcomayo River. Although one would expect a sediment exporting capacity similar to the one described above for the Bermejo, it does not seem to be the case: the Paraguay River has a concentration of suspended solids of 90 mg/l (DRAGO & AMSLER, 1981) before joining the Bermejo and after receiving the sediment load supplied by the Pilcomayo (Fig. 1). This river forms a large sedimentary deposit, a unique example of a major South American active alluvial fan. The system is filling up the lower portion of the channel with very fine sediment and is flooding the surrounding plain with relatively sediment-free water (IRIONDO, 1990). This mechanism is surely responsible for the reduced sediment- exporting capacity alluded above.

4. Clay-Size Mineralogy

A set of suspended sediment samples from the Bermejo, the Pilcomayo, and the Paraguay rivers were subjected to standard procedures to separate the fine fraction (less than 2 μ) by centrifugation. The resulting material was then analyzed by X-ray diffraction (BISCAYE, 1965; MOORE & REYNOLDS, 1989), and by scanning electron microscopy (SEM) (SMART & TOVEY, 1981; WELTON, 1984). The semi-quantitative mineral composition is given in Table 1. The samples exhibit a wide mineralogical variability not only in the major clay mineral species but also in their crystallinity and in the minerals present in trace amounts. The mineralogical signature of the analyzed samples has been plotted in Figure 2, where the evolutionary paths from the headwaters to the outflow in the Paraguay River is clearly depicted. Obviously, each mineral suite reflects the dominant geology in each tributary as the variability portrays the wide spectrum of geological composition present in the drainage basin.

The northernmost headwater tributaries (samples 1 and 2 in Fig. 1 and diffractogram *a* in Fig. 3) supply an illitic and chloritic mineral suite, surely supplied by continental/marine beds. The good crystallinity of chlorite reflects a relatively undegraded state and suggests the proximity of its source.

Further downstream, the fine fraction examined in the upper Bermejo (sample 3 and diffractogram *b* in Fig. 3), although still dominantly illitic, shifts its clay-size relative composition to a more smectitic type. Kaolinite becomes relatively more abundant, and halloysite as well as a kaolinite/smectite regular mixed-layer appear in trace proportions. This mineral suite suggests the increased relative significance of volcanic-sedimentary sources.

The southern tributary, the San Francisco River, exhibits a somewhat diverse mineral signature. Samples 4, 5, and 6 are dominantly micaceous with subordinate proportions of smectitic minerals. It is striking here the small proportion of kaolinite, the absence of mixed-layering, and the poor to fair crystallinity of chlorite. This association points towards igneous acid to basic rocks as possible sources. The crystallinities of these smectites (see diffractogram *c* in Fig. 3) are the highest of the examined sample set (Table 1), also indicating a fresh source of largely undegraded minerals.

The samples located downstream after the joining of the upper Bermejo and the San Francisco rivers (samples 7, 8, 9, and 10) show a rather uniform composition as the river flows towards its mouth. Most smectites are of the Ca/Mg kind and the mixed-layers are of the illite/smectite type. Traces of halloysite have been detected in some samples (8 and 10), and it is interesting to point out the good to fair natures of chlorite crystallinity, closer in appearance to those determined in the northern, upper Bermejo. The sample from Zanja del Tigre (see diffractogram *d* in Fig. 3) showed evidence of a rare kaolinite/smectite (R1) mixed-layer which is currently being studied (BERTOLINO, MURRAY & DEPETRIS, in preparation).

The Pilcomayo River (sample 12, diffractogram *e* in Fig. 3) delivers a clay-size mineral suite amply dominated by illite with subordinate proportions of Ca/Mg smectites, chlorite, and kaolinite. The crystallinity of chlorite is good, showing the diffractograms evidence of irregular mixed-layering of this latter mineral with illite. There are traces of kaolinite/smectite mixed-layers.

The samples from the Paraguay -upstream from the mouth of the Bermejo- clearly indicate that the Pilcomayo has little influence on the clay-size mineralogy of the Paraguay. The largely illitic mineralogy is diluted by Ca/Mg smectites and kaolinite which, moreover, seem to be the main fine weathering products of the marine beds, volcanic and intrusive rocks, outcropping in the upper Paraguay drainage basin. Chlorites are practically absent, and there are indications of illite/smectite and kaolinite/smectite mixed-layering (*f* in Fig. 3).

After receiving the Bermejo, the clay-size mineral fraction of the Paraguay becomes proportionally more illitic and chloritic, and less kaolinitic and smectitic.

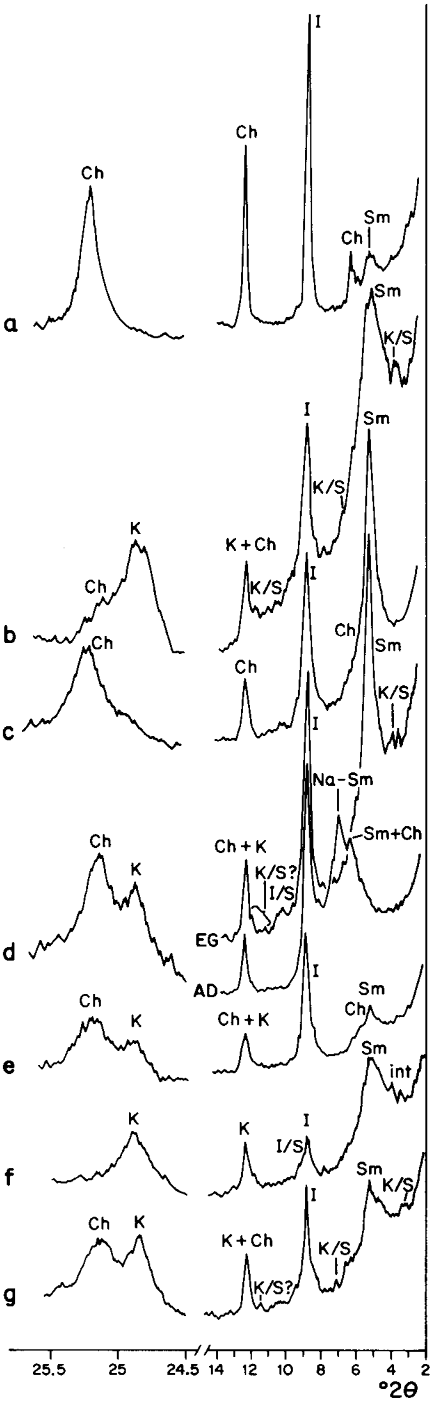

Figure 3: Selected X-ray diffractograms from suspended sediment samples (clay-size fraction). a) Pescado River, sample 2; b) Bermejo River, sample 3; c) S. Francisco River, sample 6; d) Bermejo River, sample 10; e) Pilcomayo River, sample 12; f) Paraguay River, sample 13; g) Paraguay River, sample 17. I= illite; Sm= smectite; K= kaolinite; Ch= chlorite; I/S= illite/smectite mixed-layer; K/S= kaolinite/smectite mixed-layer; AD= air-dried; EG= ethylenglycol solvated.

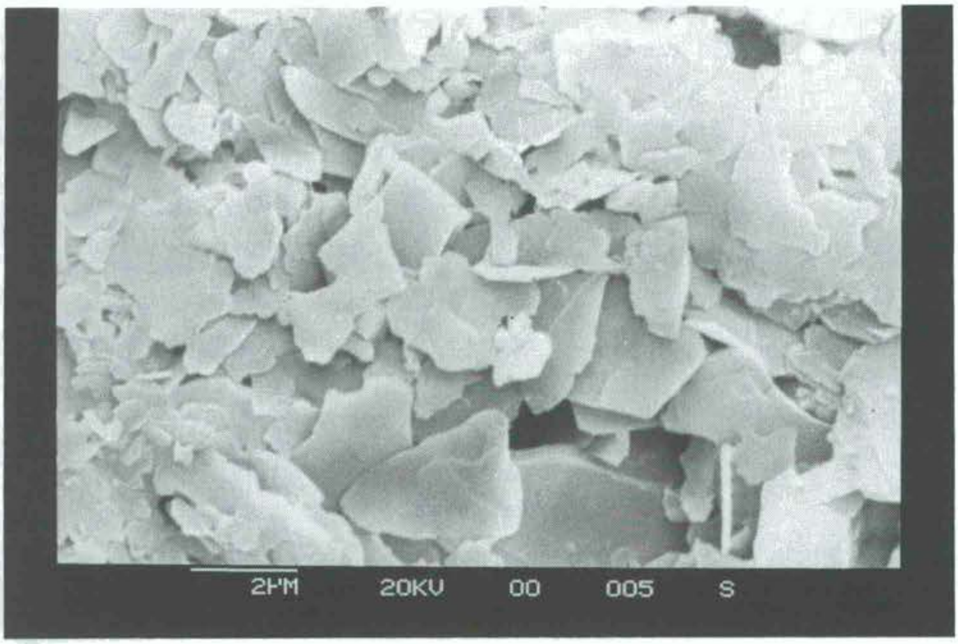

Figure 4: Pescado River (sample 2), upper Bermejo drainage basin. Illitic and chloritic irregulary-shaped crystals, with rounded (alteration) and sharply broken (transport) edges, as well as well-preserved crystals (center-right). Some edges appear expanded (alteration?). The picture suggests a mixture of fresh and altered material.

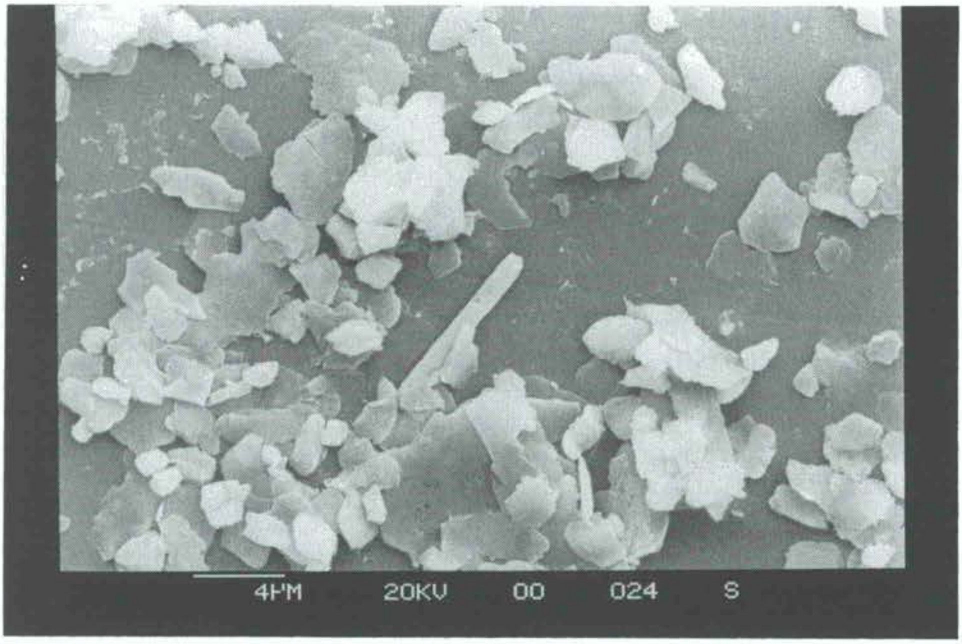

Figure 5: Upper Bermejo River (sample 3). Coarse-size clay, showing irregularly-shaped crystals; some surfaces show cracks and fractures as evidence of chemical alteration. There are crystals with curved edges, probably due to expansion (mixed-layering?).

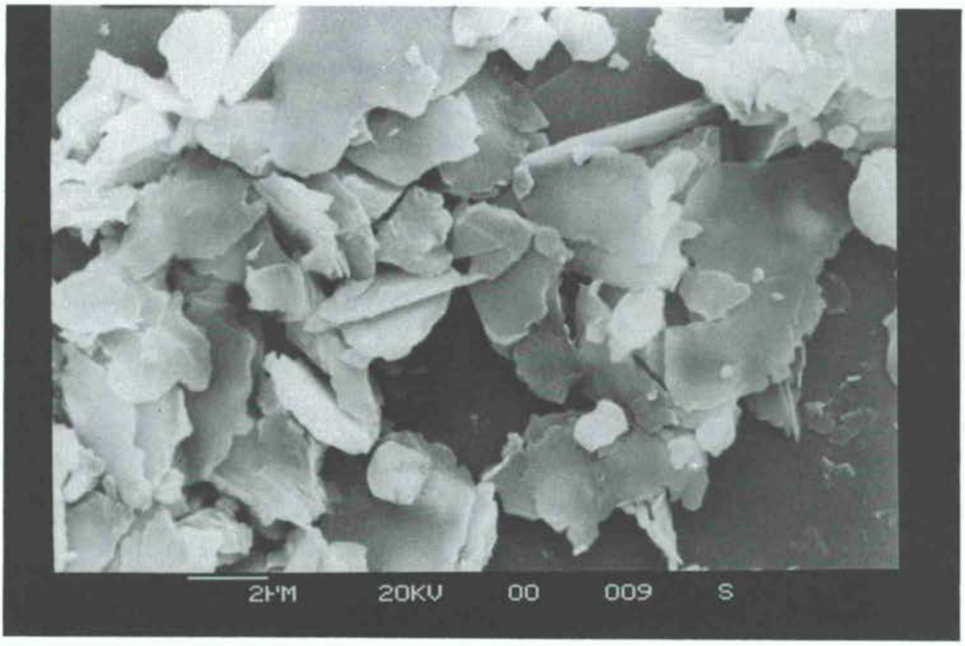

Figure 6: San Francisco River (sample 4). Mostly illites and chlorites, although some "books" are seen in the upper-left corner. Irregulary-shaped edges indicate the effect of chemical alteration and transport by water. A halloysite "tube" is also seen (center-left).

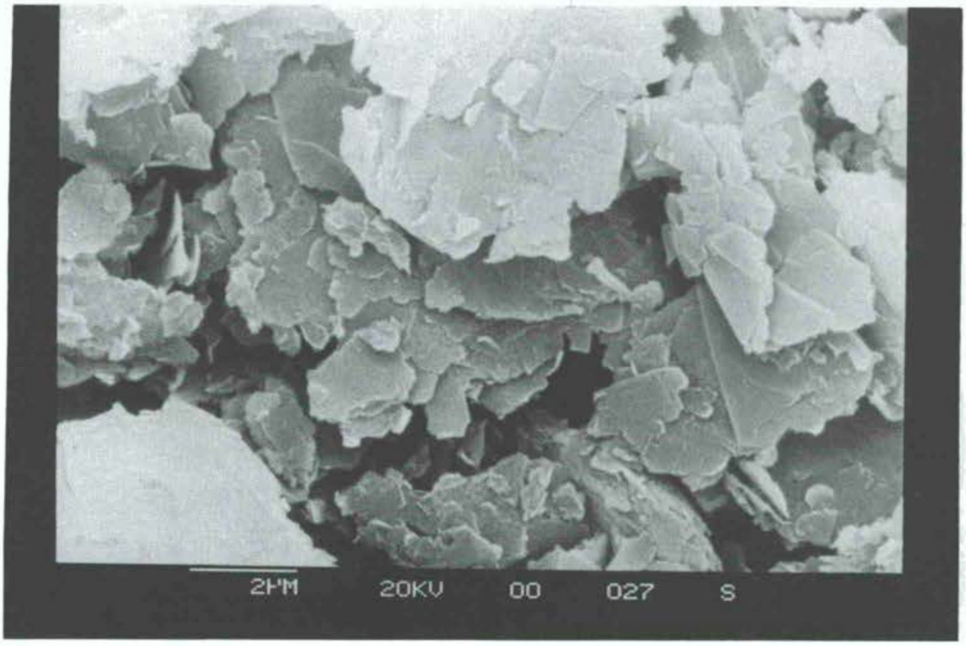

Figure 7: Paraguay River (sample 13). Coarse-size clay with broken straight and angular edges. Bent-over structures ("folders") are typical of micas (right).

There is evidence of illite/smectite as well as other types of mixed-layering (*g* in Fig. 3).

The observation of the samples by SEM allowed the identification of features typical of alteration, such as a) irregularly-shaped crystal edges as a result of dissolution; b) expanded edges in illitic flakes which could indicate a partial "opening" of illite layers in the initial stages of weathering, forming illite/smectite mixed-layers; and c) evidence of corrosion in (00l). SEM also allowed the observation of fissures and abrasion surfaces as well as broken and abraided "tubes" of halloysite like those identified by SALTER (1988) as a result of physical transport by groundwater. The selected SEM micrographs (Figs 4, 5, 6, and 7) illustrate some of the mentioned aspects.

5. Concluding Remarks

The X-ray diffractograms obtained utilizing oriented preparations of the suspended crystalline fraction of the two major Andean tributaries of the Paraná River, the Bermejo and Pilcomayo rivers, and the Paraguay, show that each basin produces its own clay-size signature determined by the geology, the climate, and the relief.

The northern tributary branch in the upper Bermejo basin (Pescado and upper Bermejo) delivers a suite of illite > > chlorite > smectite > kaolinite. The same fraction in the southern branch (San Francisco River), on the other hand, contains illite > smectite > chlorite > kaolinite. A similar relative abundance is observed at the mouth of the Bermejo.

The fine fraction composition of the Pilcomayo seems closer to the one observed in the upper Bermejo basin: illite > > smectite ≥ chlorite > kaolinite.

The tropical environment, through the upper Paraguay River, mostly supplies smectite and kaolinite and exhibits - before receiving the Bermejo - a relative abundance of clay minerals which follows the sequence illite ≥ smectite > kaolinite.

Finally, the Paraguay basin contributes to the Paraná basin a clay-size mineral suite which has a relative abundance of illite > smectite > chlorite > kaolinite. This composition is close, as could be anticipated, to the one determined for the middle and lower Paraná (e.g., DEPETRIS & GRIFFIN, 1968). The resemblance of the clay mineralogy from the Paraná River suspended load to the one determined for the bottom sediments of the SW Atlantic will be considered in a future work, now in preparation.

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First Assessment of Sediment Transportation and Deposition in Lakes and Rivers of the Changjiang Basin

by

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With 1 Figure and 7 Tables

Contents

Abstract

The Changjiang drainage basin has a total area of 1.83 x 10^6 km^2. Of this an estimated 0.6 x 10^6 km^2 is affected by severe erosion. The total load of sediments mobilized is in the order of 2.2 x 10^9 t of which 1.4 x 10^9 t are delivered from the upper part of the basin. Most of this material is deposited in alluvial fans and inland delta fans along the river valleys. In the lower Changjiang sections (below the Xicheng Station) sediment input amounts to 0.63 x 10^9 t from upstream sources and 0.83 x 10^9 t from regional erosion. Of this material 0.89 x 10^9 t are deposited in the river and in adjacent lakes. This leads to an aggradation of the river beds, which

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causes meandering. The lake sizes and water storage capacities are diminished which increases the chances of catastrophic floods.

In the estuary 0.46 x 10^9 t of sediment settle and only 0.05 x 10^9 t of particulate material reaches the ocean, i.e., 3.2 % of the material mobilized in the basin. An estimated total of 13 x 10^6 t of organic carbon is eroded in the basin. Part of this is oxidized or deposited locally in alluvial fans. It is calculated that 1 x 10^6 t stay in the middle and lower reaches of the Changjiang, 1 x 10^6 t are deposited in lakes and 2.6 x 10^6 t settle in the estuary. Only 0.27 x 10^6 t reach the ocean eventually.

1. The Physical Setting of the Changjiang River and its Basin

The Changjiang River is the largest Chinese river, its length amounts to 6,300 km and it passes through twelve provinces and one city (i.e., the provinces Qinghai, Xizang, Sizhaun, Yunnan, Guizhou, Gansu, Sanxi, Hubei, Hunan, Jiangxi, Anhui, Jiangsu, Zhajing, and the city of Shanghai). The drainage basin measures 1.83 x 10^6 km^2, equivalent to 18.75 % of the area of China.

The river originates southwest of the Goladuandong snow mountain in the Tangula Range, Qinghai Province, at an altitude of 6,543 m. Three river sections can be discerned, (i) the upstream reach down to Xicheng, (ii) the middle reach from Xicheng to Hukow (the outlet of the Poyang Lake), and (iii) the lower reach from Hukow to the river mouth (Table 1). The estuary itself stretches inland up to the city of Zhujing.

Table 1

Sections and drainage areas of the Changjiang River.

Section	Basin area (x10^6 km^2)		Length of river (km)	
Upper reach	1	55.0 %	3,400	53.7 %
Middle reach	0.68	37.6 %	938	14.8 %
Lower reach	0.122	6.8 %	1,992	31.5 %
Total	1.8	100.0 %	6,330	100.0 %

Topographically the western part of the basin is characterized by plateaus and mountains and the eastern part is mainly occupied by hills and plains. Mountains and plateaus comprise 65.6 % of the total basin area. Only 10 % of the basin area is occupied by plains.

As to the climate, most of the catchment basin is situated within the range of the southeast monsoon. The precipitation amounts to 1,000 mm/a on average and total discharge of the Changjiang River is 960 km^3/a. By discharge it is the fourth largest river on Earth after the Amazon, the Zaire and the Orinoco. The Changjiang has over 700 tributaries of which 19 have drainage basins > 10,000 km^2 and 8 have basins > 80,000 km^2. The Yalongjiang, Mingjiang, Jalingjiang, Hanshi rivers as well as the outlets of the Dongting and Poyang Lakes have drainage basins over 100,000 km^2 in area. The total surface area covered by water in the Changjiang Basin amounts to 66,700 km^2 or 3.6 % of the total basin area. 37,300 km^2 of this belongs to the rivers. The 703 lakes account for 18,384 km^2, while the rest is furnished by reservoirs (7,300 km^2) and lakes and ponds with areas $<$ 1 km^2 (4,500 km^2).

2. Sediment Source and Sediment Distribution in the Changjiang Basin

The severe destruction of the vegetation has caused a large increase in soil erosion. Soil is therefore the major source of particulate matter in the river. The statistical inventory of the Changjiang Basin shows that 37 % of its area or 562,000 km^2 are affected by severe erosion. On average, these areas lose 3 mm of topsoil per year (Table 2). Apart from surface erosion, channel erosion and land slides are important. According to the investigation of the Chendou Institute of Geography, about 200,000 collapses and land slides occurred in the upstream region recently, more than 10,000 of these were of a large scale.

Table 2

Sediments mobilized by erosion and their distribution.

Region	Erosion area (km^2)		Amount of sediment (x 10^{6}t)	
Jingshajiang River	135,400	38.4 %	466	33.3 %
Jalingjiang River	92,600	26.3 %	380	27.1 %
Mingjiang River	4,900	14.0 %	190	13.8 %
Area along the trunk Changjiang River in East Sizhaun Province			179	12.8 %
Other areas in upper reach			182	13.0 %
Middle and lower reach	210,000		825	
Total	562,000		2,230	

Most of the sediment mobilized by erosion is deposited in upstream reaches and only a small fraction is transported down to the middle and lower reaches of the Changjiang River. In granitic regions 40% of the mobilized material is carried out of the region, while areas with shales export 25 % of the initially mobilized matter. This causes a rapid aggradation of the beds of upstream tributaries.

3. Deposition of Sediments in the Changjiang Basin

3.1 Deposition in the River Plain

The sediment eroded in the upper reaches amounts to 1,405 x 10^6 t/a, of which only 522 x 10^6 t/a reach the middle and lower reaches of the Changjiang River. Recently this figure increased to 634 x 10^6 t/a because of the intensification of erosion. In case of the Jingshajiang Basin, the upper part of the Changjiang Basin, it is known that only 14 % or 100 x 10^6 t/a of the mobilized material reaches the Changjiang, while 86 % or 650 x 10^6 t/a is deposited upstream.

Deposition occurs either as alluvial fans located where the tributaries leave the mountains and enter the plain, or as accretion of the river bed itself. For example, the Xiajiang River, a tributary of the Jingshajiang River, has accreted by 3-5 m within 30 years, while the Wuchi section of the Beilongjiang River accreted by 3.32 m from 1957 to 1984. In general, aggradation amounted to 7-10 cm per year in certain river sections.

As a result of the siltation, the navigable stretches have been shortened in many rivers, e.g., in the Province of Sizhaun by 286 km and in the Hebei Province by 340 km.

The situation in the middle and lower reaches of the Changjiang is different from that upstream. Here the sediment, mobilized by erosion in the Hangjiang, Dongting and Poyang basins amounts to 825 x 10^6 t/a, of which only a small part reaches the Changjiang River (Fig. 1).

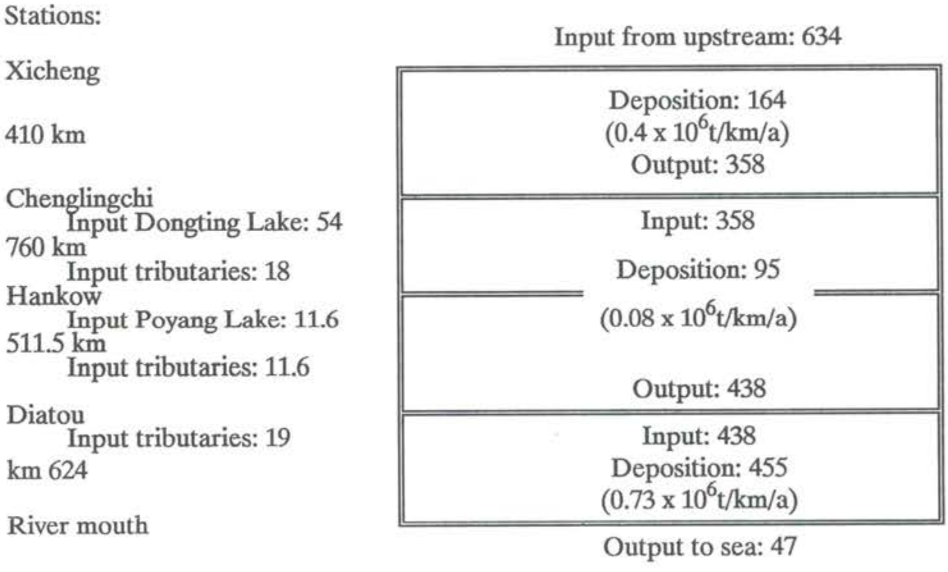

Fig. 1: Scheme of sources and sinks of sediments along the middle and lower reach of the Changjiang River (numbers if not noted otherwise are in 10^6t/a).

Figure 1 gives a summary of the estimated sediment fluxes in and out of the lower sections of the Changjiang River. At the Xicheng Station in the middle reach of the river, 634 x 10^6 t of sediment pass annually, but only 483 x 10^6 t are monitored at the station of Diatou. The difference plus the sediment input from tributaries is deposited in between. Most of this deposition occurs in the 410 km long stretch below Xicheng (164 x 10^6 t/a or 25-30 % of the total load). Calculated as loss per kilometer we find a deposition rate of 0.4 x 10^6 t/km in this stretch, while between Chenglingchi and Diatou only 0.08 x 10^6t/km are deposited. In the section below Xicheng the channel bed rose by 3-5 cm per year and the river bed presently is 8 m higher than the surrounding plain. The wandering stream is increasingly unstable and the danger of a dam-break and a catastrophic flood increases daily.

Serious siltation is also going on below Diatou in the lowermost 600 km of the river. 0.6 % of the amount transported past the Diatou Station is deposited amounting to 0.73 x 10^6 t/km/a. Only 9.4 % of the Diatou load or 47 x 10^6 t/a reach the sea. This deposition causes the rapid growth of sand bars and of beaches in the estuaries and decreases the width of the channel rapidly. It is estimated that the Changjiang delta expanded by 7,500 km^2 within 2,000 years.

At Yangshow City the width of the river measured 9 km, 1,000 years ago, compared to merely 2.3 km at present. Harbors along both sides of the river are seriously threatened. The port of Zhenjing is endangered by a fast growing sand bar outside its entrance and by siltation of its basins. As a consequence the shipping channel has to be dredged. In 1981, 1.4 x 10^6 m^3 of material were removed, while in 1982, this amount increased to 2.0 x 10^6 m^3. The shipping channel from Nanjing to Zhenjing shoaled due to siltation and passage has become difficult for ships over 10,000 t. Constant dredging has therefore become a necessity. Control of erosion in upstream areas would, to my opinion, be a more effective engineering strategy than dredging in order to keep channels and harbors open.

3.2 Deposition in Lakes and Reservoirs

90 % of the lakes with a size > 1 km^2 are situated in the middle and lower reach of the Changjiang River (Table 3). The upstream lakes occupy depressions along tectonic rifts. Alluvial fans and fan deltas are developed along the shores of these lakes. Little sediment reaches their centers, where the accumulation rate is quite small. For example, in the Dianchi Lake, one of the largest lakes in the Changjiang upstream area (298 km^2, mean depth 3.9 m), the accumulation rate amounts to only 0.34 mm/a.

Table 3

The distribution of lakes in the Changjiang Basin.

Region	Number of lakes	Surface area of lakes	
		(km^2)	%
Upstream area	79	1,995	10.8 %
Middle reach	438	10,753	58.5 %
Lower reach	186	5,636	30.7 %
Total	703	18,384	100.0 %

In contrast, the lakes of the lower Changjiang Basin are situated mostly on the alluvial plain of the Changjiang, where tributaries enter from the side. They form effective traps for upstream sediment input. For example, the tributary basin of the Poyang Lake is 162,000 km^2, of which 34,000 km^2 are affected by erosion, which mobilizes 100 x 10^6 t of sediment annually. 22.8 x 10^6 t or 15-20 % of this reach the lake, but only 11.6 x 10^6 t leave the lake, the difference is deposited.

In total, 170 x 10^6 t of sediments are trapped by the five largest lakes in the middle and lower Changjiang section (Table 4). Most of this amount is caught by the Dongting Lake (150 x 10^6 t or 88.6 % of total lake deposition).

Table 4

Annual average of sediment deposited in the five largest freshwater lakes.

Lake	Sediment input (x 10^6t)	Sediment output (x 10^6t)	Accumulation volume (x 10^6t)	Average sedimentation rate(t/km^2)
Dongting Lake	206	54.00	150.0	56,484
Poyang Lake	22.8	11.60	11.2	2,862
Hongze	17.50	10.30	7.2	3,900
Cao Lake	12.2	0.44	0.78	1,036
Tai Lake	0.44	0.10	0.34	145
Total	24.8	76.44	171.52	

The sediment accumulation rate has recently been assessed in these lakes by the use of the ^{210}Pb method (Table 5). The rates measured are different from the hydrologically estimated values: they are higher in case of Caohu and Thai lakes and lower in case of the Dongting and Poyang lakes (compare Tables 4 and 5).

Table 5

Sedimentation rates in lakes as measured by the ^{210}Pb method.

Lake	Accumulation Rate (mm/a)	Flux Rate (t/km^2/a)
Dongting Lake	25	18,750
Poyang Lake	2.0-2.5	1,875
Tai Lake	1.2-1.6	1,000
Cao Lake	1.65	1,238

Siltation also causes the lakes to shrink in area. Dongting Lake, for example, measured 4,350 km^2 in 1950, it was the largest lake in China at that time. In 1983, its area was reduced to 2,691 km^2. Similarly, Poyang Lake decreased in size by 1,185 km^2 between 1950 and 1985. In the Gianghan Plain in 1950 a total of 1141 lakes with a total area of 8,330 km^2 were counted, of which today only 570 lakes with a surface of 2,370 km^2 remain because of siltation and land reclamation. As a consequence, the storage capability for floods is reduced tremendously. Lake Poyang, for example, lost 5 km^3 of its volume within 30 years due to siltation.

Reservoirs are also threatened by siltation. In the Changjiang Basin we find 60 large, 400 medium and 20,000 small reservoirs totaling 7,300 km^2 in area. Because of siltation their volume is reduced by 10 % annually. Reduction in storage capacity is especially pronounced in the upstream region, e.g., the Belzow reservoir in the upper part of the Jutingjiang River accumulated 74×10^6 m^3 of sediment within six years of operation and lost 65 % of its volume. The Gongtzoi hydroelectric station in the upper part of the Dadu River was silted up by 180×10^6 m^3 of sediment within 11 years losing 48.1 % of its storage capacity.

4. The Influence of Sedimentation in Lakes and Rivers on Environment and Resources

4.1 The Distribution and Deposition of Organic Carbon

A rough calculation shows that in the Changjiang Basin annually 13×10^6 t of organic carbon are lost from the soils due to erosion (Table 6). 50 % of this is probably lost to the atmosphere by oxidation. Similar oxidation losses from eroded soil have been reported from the Amazon and elsewhere.

Table 6

Transportation and deposition of organic carbon in the Changjiang Basin (in 10^6 t/a).

1. Organic carbon from erosional area:	13.00	
2. Transportation to the East China Sea:	0.27	2 %
3. Deposition in estuaries and delta areas:	2.64	20.3%
4. Deposition in lakes:	0.99	7.6 %
5. Deposition, middle and lower reaches of Changjiang River:	1.07	8 %
6. Deposition in the upstream area and released:	0.85-0.90	65-70 %

The input of soil organic matter to lakes is important for their eutrophication. In Dianchi Lake, for example, 39 g $C/m^2/a$ are deposited (for deposition rates of other lakes see Table 7). Part of this is decomposed and released together with the

Table 7

Sedimentation rates of organic carbon in some lakes of the Changjiang Basin.

Lake	Area (km^2)	Sedimentation rate of organic carbon (g $C/m^2/a$)	Eutrophication level
Tai Lake	2,428	7-10	oligotrophic
Poyang Lake	3,914	16	oligotrophic
Caohu Lake	753	12	mesotrophic
Dianchi Lake	298	39	eutrophic

associated nutrients, to the water column. In Tai Lake, for example, 10-15 % of the organic carbon in the bottom sediments are, according to our investigations, liberated by wave action and by currents. This causes an organic matter content in the water of 4-8 mg/l and increases the concentrations of nutrients.

4.2 Deposition and Water Resources of Rivers and Lakes

The water resource of the Changjiang Basin is tremendous, totaling 960 km^3/a. The volume of water stored in lakes amounts to 74.3 km^3. This capacity is, however, quickly diminished by siltation and reclamation. According to certain, albeit incomplete statistical data, the total lake surface was reduced by 10,000 km^2 within the past 30 years and the storage capacity was diminished by 35 km^3. The siltation of river beds decreases water storage capacity also, an estimated 10 km^3 may have been lost this way. One may estimate that the reduction in storage capacity will claim another 2.5-3.0 km^3 due to siltation of lakes. This will increase the danger of floods and may bring disaster to the low lands surrounding, for example, Dongting Lake and Tai Lake, as well as to the Jianjiang section of the Changjiang Basin. This relation between siltation, water resources and environmental threats is straightforward. Measures to protect the storage capacity for water in the Changjiang Basin are badly needed. Otherwise the environment cannot be protected.

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Water and Porewater Chemistry of a Lake Baikal Central Basin Station

by

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With 5 Figures

Contents

Abstract

Water and sediment samples were taken at a station in the central basin of Lake Baikal in August 1989. Nutrient concentrations in the water column were extremely low in the upper 40 m and increased with depth. Particulate organic carbon, nitrogen and total phosphorus had a pronounced maximum around 40 m and decreased considerably together with oxygen at water depths >65 m. Calculation of oxygen consumption and reactive dissolved phosphate production shows that remineralization of a "Redfield" compound accounts for only 36 % of the oxygen consumption. Porewater nutrient profiles were highly variable at low concentrations

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presumably as a result of a low supply of biogenic precursor compounds and in the case of phosphate solid phase fixation by iron/manganese concretions.

1. Introduction

Lake Baikal is by volume the largest body of freshwater in the world containing about 20 % of the global freshwater reserves. Its depth (1,600 m) is unrivalled among large lakes. In spite of this the lake has not turned anoxic in the deeper layers in the course of its existence. The combination of rapid turnover and low supply of degradable organic matter to the deep Baikal may be responsible for this.

While a wealth of information can be found in the Russian literature only few publications have appeared in commonly accessible form, among those the comprehensive treatment on the biology of Lake Baikal by KOZHOV (1963). In the present communication data on the distribution of nutrients and particulate matter is given for a station in the central basin of Lake Baikal. In addition, nutrient porewater profiles from a sediment core from the same station will be presented.

2. Material and Methods

Water and sediment samples were obtained at station 24 ($z = 1676$ m) in the central basin of Lake Baikal in August 1989 (Fig. 1). This site has been chosen for a one-year sediment trap deployment and data presented here also serve as background information for this experiment.

Water samples were obtained by standard hydrocast procedures using 10 dm^3 Niskin bottles (General Oceanic). Oxygen was determined by Winkler titration. Nutrients were analyzed on unfiltered samples following GRASSHOFF et al. (1983). Samples for the analyses of particulate organic carbon (POC), nitrogen (PN) and total phosphorus (TPP) were filtered onto precombusted (450° C, overnight) GF/C filters after screening through a 250 μm sieve to remove larger zooplankton. After drying at 40° C filters were stored in polypropylene boxes in the dark. POC and PN were analyzed by high-temperature combustion using a Carlo Erba Elemental Analyzer. TPP samples were treated with peroxodisulfate (30 min, 110° C) and analyzed for liberated ortho-phosphate.

A sediment core (24b) obtained with a 100 x 8 cm i.d. gravity corer (MEISCHNER & RUMOHR, 1973) was used for porewater sampling. A second core (24a) was used for sedimentological sampling. Since this type of corer does not use a core catcher surface sediments remain virtually undisturbed. Core 24b was extruded and cut into 2 cm slices which were stored intermittently in PE bags at 4° C. Porewater was obtained by squeezing in a modified version of the apparatus originally described by HARTMANN (1965). 0.45 μm cellulose nitrate filters were employed. Samples for the analysis of reactive dissolved phosphate (RDP) were analyzed undiluted whereas ammonia (NH_4^+) and silicic acid ($Si(OH)_4$) samples

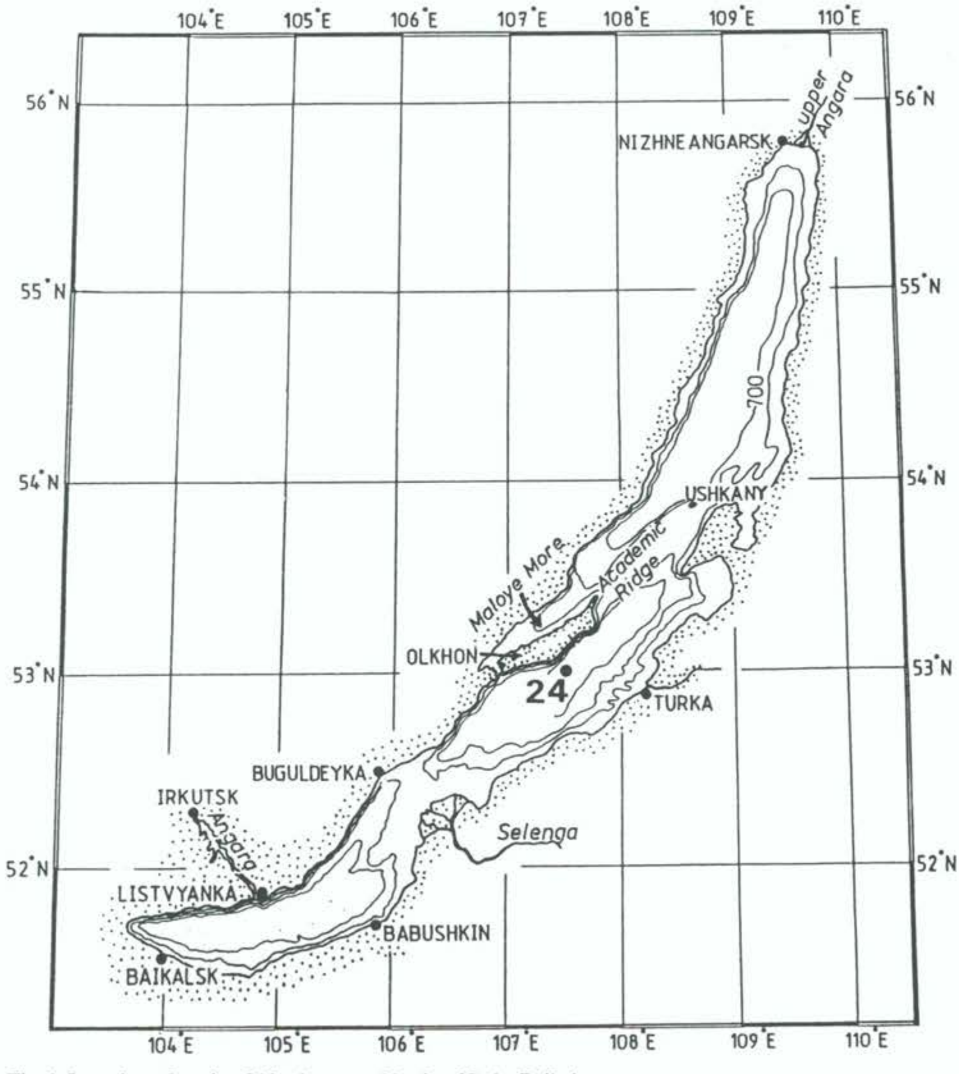

Fig. 1: Location of station 24 in the central basin of Lake Baikal.

were diluted 1:10 with double distilled water. Due to the small sample volumes only single determinations could be carried out. Triplicate analysis of a mixed porewater sample gave reproducibilities of ± 0.4 % (RDP), ± 2.4 % ($Si(OH)_4$) and ± 6.2 % (ammonia) for core 24b.

Water overlying the sediment in the core liner was siphoned off and analyzed for inorganic nutrients after settling of the resuspended material.

3. Results and Discussion

3.1 Water Column Chemistry

Conductivity showed extremely little variation over the depth profile with a value of 132 ±2 μS/cm. Oxygen was slightly elevated at the surface showing a minor decrease towards 10 m thereafter increasing to a maximum value at 30/40 m (Fig. 2). A more or less continuous decrease in deeper waters corresponds to an oxygen consumption of 34 μmol/m^3/m (65-800 m).

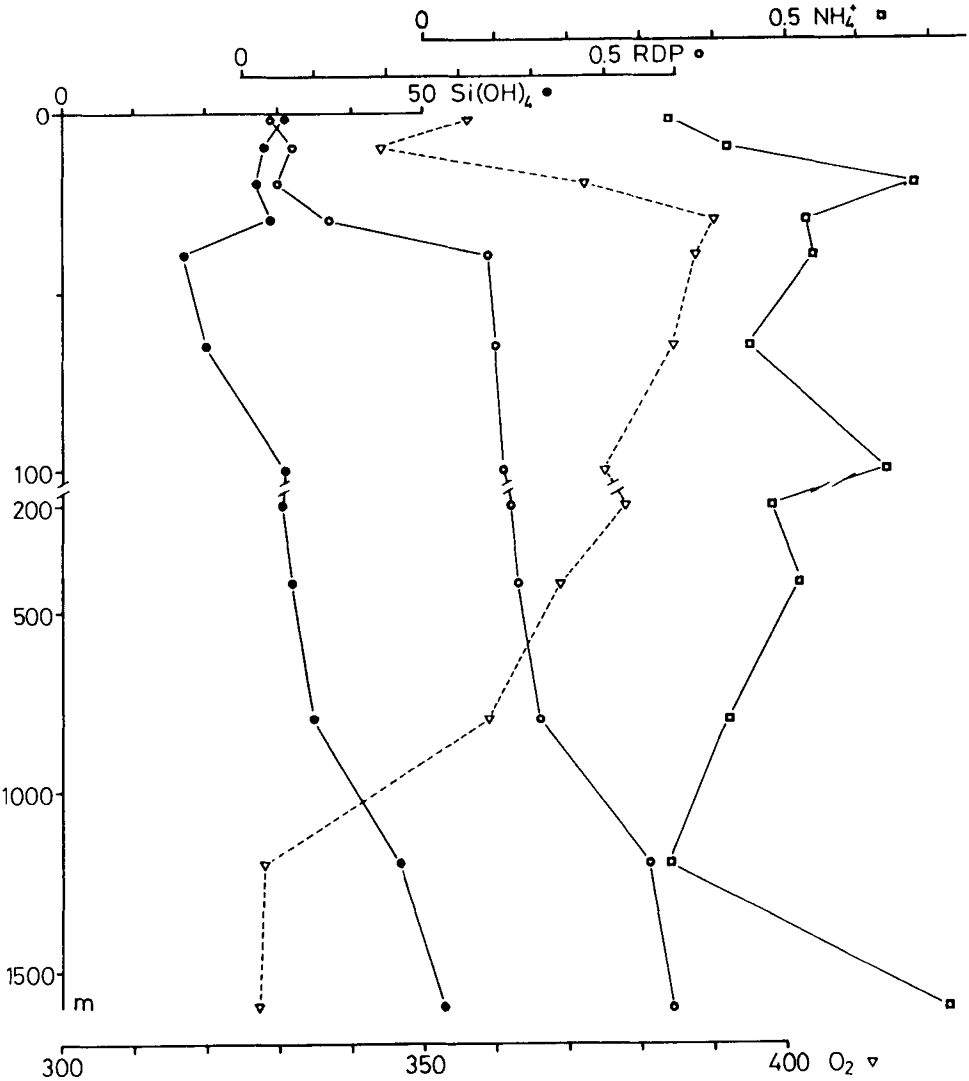

Fig. 2: Nutrient and oxygen profiles at station 24. Concentrations are given in μmol/dm^3.

Silicic acid varied little in the upper 30 m, decreased slightly in the 40 and 65 m samples and increased thereafter totalling 19 μmol/m^3/m (65-800 m). RDP had low concentrations in the upper water column and increased markedly in the 40 m sample followed by a minor increase (0.08 μmol/m^3/m; 65-800 m). The two lowermost samples were, as in the case of silicic acid, higher and did not follow the general trend. In combination with uniform oxygen concentrations at these depths this suggests the existence of a homogeneous layer of considerable thickness with rather uniform chemical features.

As expected ammonia concentrations were low (Fig. 2). Whether the maxima at 20, 100 and 1,600 m are the result of increased heterotrophic activity at these depths remains open.

Parameters characterizing the composition of particulate matter showed a pronounced covariation with depth (Fig. 3). Highest concentrations were found at the oxygen maximum around 30 m water depth. This suggests that here the highest phytoplankton concentration has to be expected. This is supported by visual inspection of the filters from this depth, which were vividly greenish-brown.

The highest variation in concentrations of elements in the particulate matter was found in the 30 to 65 m samples. Here, TPP decreased at a lower rate than POC/PON. This is also evident in the C/P and C/N ratios (Fig. 4). While the uppermost samples had high values suggesting the presence of highly degraded organic material, the C/N values in the 30 and 40 m samples suggest the presence of a healthy phytoplankton community. This is evidently not the case for the C/P ratios. The exact value or rather the range of values for a Redfield compound is presently discussed. Nevertheless, the 40 m value of 154 is certainly not representative of healthy plankton. This, together with the relatively high RDP value at this depth,

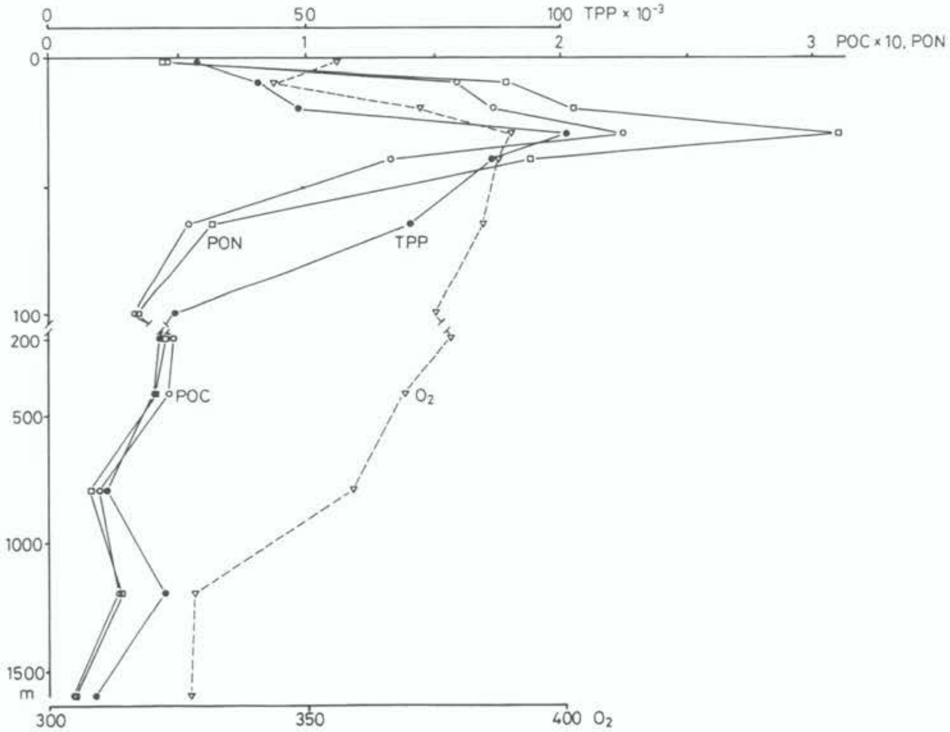

Fig. 3: Distribution of POC, PN, TPP and oxygen at station 24. Concentrations in µmol/dm^3.

indicates that the population was not fully developed at the time of sampling. Indeed, the data summarized by KOZHOV (1963) show that autumn plankton blooms usually start to develop in mid-September.

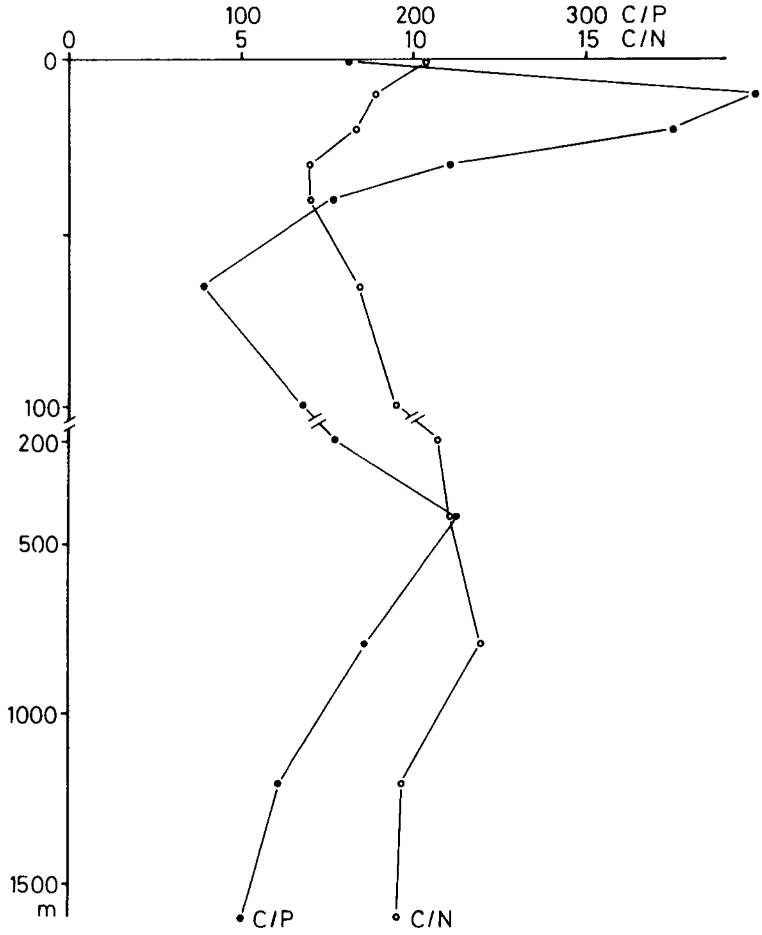

Fig. 4: Particulate C/N and C/P molar ratios for station 24 samples.

The data at hand cannot explain why a C/P ratio <100 was found at 65 m. Differences in the plankton assemblages might be the reason for this phenomenon. This is supported by $Si(OH)_4$/RDP ratios which had their minimum values in the 40 and 65 m samples (50 and 59, respectively) compared to values >240 in the upper water column and 85 ± 2 at depths >100 m.

These results suggest that nutrient concentrations in the upper water column are strongly controlled by phytoplankton activity. Without knowing nitrate values it is, however, not possible to decide whether RDP is a productivity limiting nutrient. However, older Russian data suggest that RDP and $Si(OH)_4$ are never completely depleted and that nitrate might be the productivity limiting factor (KOZHOV, 1963).

Furthermore, the differences in $Si(OH)_4$/RDP ratios together with the data of the particulate matter indicate that various phytoplankton assemblages are present within the euphotic zone.

3.2 Porewater Chemistry

The sediment at station 24 is characterized by alternating layers of diatomaceous ooze and silty clay/clayey silt of variable thickness. In addition, iron and manganese concretions were found at the surface and at a depth of about 23 cm (K. ANTON & E. KARABANOV, pers. comm., 1989). As in the case of the solid phase, inorganic components dissolved in the interstitial waters also show a high degree of variability (Fig. 5).

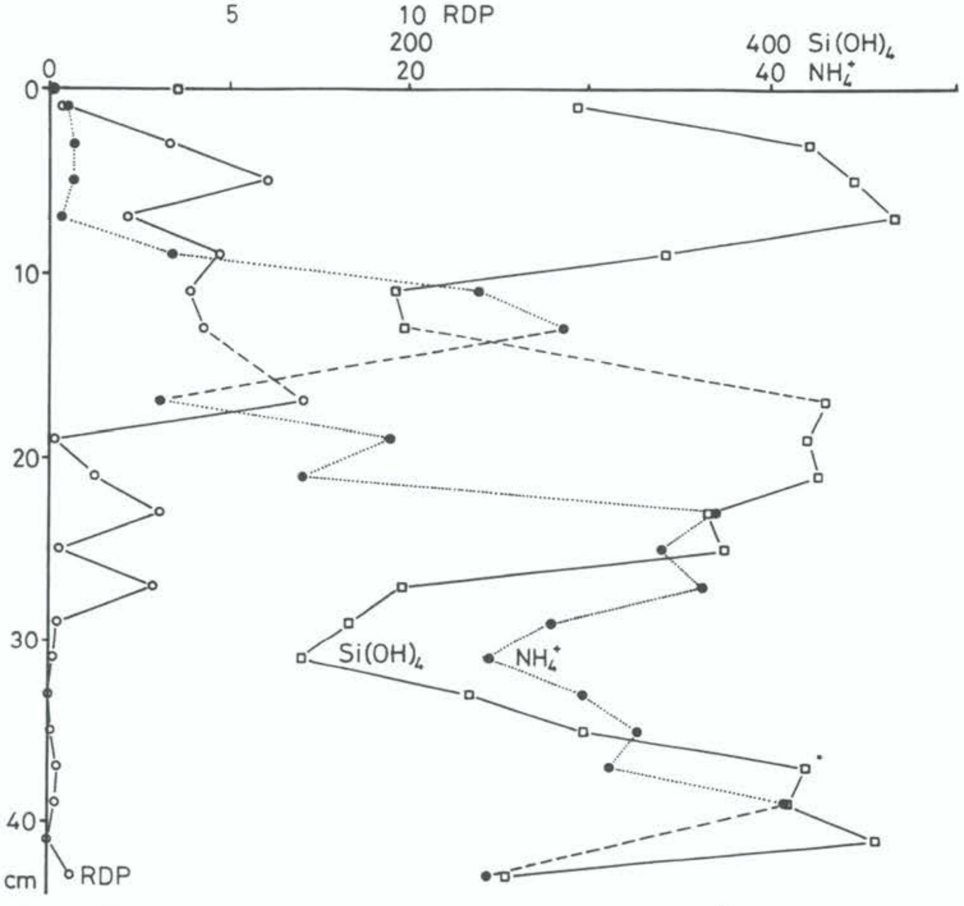

Fig. 5: Porewater profiles for inorganic nutrients. Concentrations in $\mu mol/dm^3$. Missing sample intervals are indicated by a dashed line. Sample points at $z = 0$ cm correspond to overlying water.

Elevated RDP concentrations were observed in the upper 16 cm only, thereafter concentrations decreased to extremely low values. Ammonia showed maxima at 10-14, 22-28, and 38-40 cm. Compared with the overlying water, both

RDP and ammonia were not particularly enriched in the top 2 cm. Silicic acid showed broad maxima centered at 7, 19, and 30 cm. These maxima do not completely coincide with diatomaceous ooze layers. However, it should be borne in mind that sedimentological description and porewater analyses were carried out on two separate cores. Our cores from Lake Baikal show that sediments display a high local variability, even in deep water. Thus, the discrepancy between visual inspection and chemical analysis might well be the result of patchy sediment distribution. Chemical and micropaleontological analysis of the solid phase of core 24b should give more information about the control of the concentrations of porewater constituents.

Compared to other lacustrine or marine sediments RDP and ammonia concentrations are extremely low in Lake Baikal porewaters. This suggests that the sinking particulate organic material is heavily depleted with regard to N and P. This is not in contradiction to the observed decrease of the C/N and C/P ratios in the water column suspended material with depth since the vertical flux is maintained by relatively rare, large, fast sinking aggregates. Furthermore, benthic heterotrophic production apparently is not extensive and cannot reconstitute organic matter with a "Redfield" signal as is commonly found in deep oceanic surficial sediments (SUESS & MÜLLER, 1980). This is supported by the observations of KOZHOV (1963), who reported the almost complete absence of benthic organisms in deep water sediments of Lake Baikal.

As solid phase analyses of other Lake Baikal sediment samples indicate, manganese and especially iron concretions are highly enriched in phosphorus (GRANINA et al., 1991). The higher porewater RDP concentrations in the upper 8 cm might well be the result of partial redissolution of amorphous iron phosphates.

Although porosity and density data of dried sediment are as yet not available for core 24b, a rough estimate suggests that porewater fluxes into the overlying water are negligible for ammonia and RDP, whereas silicic acid flux would be around 110 $\mu mol/m^2/d$ (calculated for $z = 7$ cm, Fig. 5).

4. Conclusions

The relatively low nutrient concentrations in Baikal deep waters might be the result of two independent phenomena: (i) rapid turnover of the entire water column and (ii) low supply of particles from which these compounds can be liberated. The distribution of particulate compounds suggests that biogenic material produced in the euphotic zone does not reach greater water depths in the form of finely dispersed material. This does not exclude the possibility of particle transfer by fecal pellets or strings produced by zooplankton, mainly *Epischura* sp. and *Macrobectopus* sp. However, the data of VOTINTSEV et al. (1975; cited in DEGENS & ITTEKKOT, 1983) indicate that only about 3 % of the total primary production will reach deep water sediments pointing to a highly efficient recycling system within the upper water layers.

On the other hand, the establishment of a system of strong convection currents with the onset of winter cooling should lead to a decrease in nutrient concentrations and a concurrent increase in oxygen in deeper waters finally resulting in homogeneous distributions. The data at hand suggest that mixing time might not be sufficient to reach this. Furthermore, convective mixing does not extend to depths >300 m (KOZHOV, 1963). Whether increased heat flow from the bottom as a result of the occurrence of hydrothermally active faults (GOLUBEV, 1986) can explain the apparently rapid overturn of the entire water column has to remain the subject of further study.

5. Acknowledgements

This work was supported financially by the Bundesminister für Forschung und Technologie through grant MFG 0081 6. The help of L. Granina, S. Karabanov and K. Anton with the sampling is gratefully acknowledged as is expert technical assistance of R. Kopp during cruise preparations and analysis of particulate compounds.

Note added in proof:

WEISS et al. (1991) have shown from freon measurements that deep waters of Lake Baikal are ventilated by convection from the upper water column with a mean turnover time of eight years as a result of the combined effects of temperature and pressure on water density (the "thermobaric" effect), Model calculations by these authors suggest that 27 g C/m^2/a or about 20 % of the total primary production is exported from the eutrophic zone. This value is considerably higher than the 11 g C/m^2/a obtained from the empirical flux-depth relation given by BETZER et al. (1984). On the other hand, the value derived from VOTSINTSEV et al. (loc. cit.; 3.6 g/m^2/a) agrees fairly well with the 3.3 g C/m^2/a calculated with the BETZER et al., equation for a water depth of 1500 m. This would suggest that heterotrophic degradation of organic material sinking out of the euphotic zone takes place mainly at intermediate water depths.

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The Role of Purple and Green Bacteria in the Carbon and Sulfur Cycles in Stratified Lakes

by
V.M. GORLENKO, Moscow*)

With 2 Tables

Contents

Abstract

Under favorable light conditions purple and green sulfur bacteria play an important role for H_2S oxidation and make a considerable contribution to the primary production of stratified lakes containing sulfide. In detail, the rates of carbon and sulfur cycling depend on lake type.

1. Introduction

Purple and green bacteria can grow photolithoautotrophically using sulfide as H-donor and CO_2 as carbon source (PFENNIG, 1967, 1978; KONDRATIEVA & GORLENKO, 1978). Some species of these microorganisms can switch from the phototrophic to dark aerobic or even anaerobic chemotrophic metabolism (KRASILNIKOVA et al., 1977; KAMPF & PFENNIG, 1980). However, the extensive and abundant occurrence of purple and green bacteria in natural habitats is due to their

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capacity to use sulfide for photosynthesis. This physiological characteristic permits phototrophic bacteria to occupy a separate ecological niche in water bodies which contain a photic sulfide zone. These are: stratified meromictic, dimictic and monomictic lakes and also holomictic basins with high sulfide production. Green or purple sulfur bacteria usually predominate due to their high tolerance to sulfide and higher growth rates under the photoautotrophic conditions compared to non-sulfur purple bacteria and cyanobacteria.

In the H_2S containing water body phototrophic bacteria play a special role for the carbon and sulfur cycles (PFENNIG, 1978; BIEBL & PFENNIG, 1978; GORLENKO et al., 1983). H_2S, CH_4, H_2, CO_2 and organic acids are formed in bottom waters or in the surface layer of silty sediment as a result of anaerobic dissimilation of organic matter. In sulfate-rich basins sulfate reduction predominates over methane fermentation, H_2S and CO_2 being major gaseous products of respirative activity (CAPENBERG, 1975). Phototrophic purple and green sulfur bacteria develop at the upper border of the anaerobic zone and are the primary consumers of H_2S. In the course of bacterial photosynthesis H_2S is oxidized to S^o and SO_4^{2-} thereby completing the sulfur cycle. Thus phototrophic bacteria can drive the sulfur and carbon sub-cycles within anaerobic environments.

2. Results

In the water of stratified lakes sulfide oxidation takes place in the narrow chemocline, in which the daily rhythm provides the conditions for the development of both aerobic or microaerophylic and anaerobic microorganisms utilizing sulfide (GORLENKO et al., 1983). Intensity of development as well as the type of biogeochemical process mediated by phototrophic bacteria depend upon the type of the basin and the physico-chemical conditions of the individual habitat. The kind of the H_2S oxidation product depends, to a great extent, on the species composition of the phototrophic bacteria and the kind of sulfur compounds present.

The depth of the H_2S boundary shows daily variations caused by the changes of light intensity. Its level is lowest at noon when the photosynthetic activity of microorganisms is at the maximum, and it is highest before dawn when photosynthesis is yet impossible.

Dim light penetrating to the chemocline maintains photosynthesis of phototrophic bacteria but is practically of no effect for eucaryotic algae. The better adaptation to low light intensities presumably lets various species of green sulfur bacteria predominate over purple bacteria in most stratified lakes (BIEBL & PFENNIG, 1978). Thus light is one of the most important factors for the intensity of development and species composition of phototrophic bacteria. But H_2S supply rate is also decisive for the activity of phototrophic bacteria (see Tables 1 and 2).

Table 1

Contribution of phototrophic bacteria to photosynthetic production of the meromictic lakes studied.

Type of lake		Lake name	Photosynthesis of bacteria C. [mg/m^3/day]	Production of photosynthetic bacteria C. [mg/m^3/day]	Production of C. [mg/m^2/day]	% of production of photosysnthetic bacteria
low SO_4^{2-} freshwater	OT	Gekh-Gel	20	58	333	15
	---------	Maral-Gel	60	90	42	70
	MT	Kononjer	80	180	60	75
----	--------- MT	Mishinjer	325	195	175	52
Fe^{2+}-rich -----		Kuznechikha	95	70	600	14
	ET	The Nekrasov Bay	224	140	228	38
high SO_4^{2-} freshwater	MT	Belovod	170	836	1.450	13
		Sakovo	315	190	320	37
		Tcherniy Kichier	65	41	550	7.2
	ET	Bolshoy Kichier	65	15	550	2.7
salinous	MT	Mogilnoye	485	224	301	43
	---------	Pomyaretskoye	325	224	205	52
		Repnoye	149	219	1.407	14
	ET	Veysovo	309	213	938	19

Note: ET = eutrophic; MT = mesotrophic; OT = oligotrophic

Table 2

Characteristics of sulfur cycling processes in the meromictic lakes studied.

Type of lake		Lake name	Content [mg/l]		Rate of sulfate reduction [mg/l/day]		Production of H_2S [mg/m^3/day]		Oxidized H_2S [mg/m^2/day]	
			SO_4^{2-}	H_2S	in water	in silt	in water	in silt		
low SO_4^{2-}	ET	Gekh-Gel	20	3.8	0.012	-.-	106	-.-	82	(328)
	---------	Maral-Gel	20	2.5	-.-	-.-	-.-	-.-	127	(508)
freshwater	MT	Kononjer	41	2.5	0.0008	5.2	7	500	210	(840)
fresh-	ET	Mishinjer	38	0.8	-.-	2.1	-.-	225	275	(1.100)
Fe^{2+}-rich -----		Kuznechikha	36	16	0.017	3.6	113	350	99	(396)
water	MT	The Nekrasov Bay	-.-	3	-.-	-.-	-.-	-.-	197	(788)
freshwater	MT	Belovod	730	15	0.071	-.-	500	-.-	474	(1.896)
		Sakovo	710	11	0.0018	4.5	9	500	268	(1.072)
	---------	Tcherniy Kichier	120	65	0.016	13.3	130	780	58	(232)
high SO_4^{2-}	ET	Bolshoy Kichier	60	17	0.006	6.18	130	130	20	(80)
	MT	Mogilnoye	2.000	176	0.1	10.8	200	320	316	(1.268)
sali-		Pomyaretskoye	900	340	0.34	28.4	500	1.840	300	(1.206)
nous	---------	Repnoye	2.000	119	0.12	15.6	104	650	309	(1.239)
	ET	Veysovo	36.000	790	0.08	19.2	500	2.200	316	(1.268)

Note: Data calculated for complete H_2S oxidation up to SO_4^{2-}, are given in brackets.
Out of brackets: if H_2S is oxidized only up to S°.
ET = eutrophic; MT = mesotrophic

H_2S production in stratified lakes is performed by sulfate-reducing bacteria. Measurements made with $^{35}SO_4^{2-}$ have shown that bacterial sulfate reduction is not very intensive in the water column of the hypolimnion, amounting to only 0.01-0.1 mg H_2S/l/d. The highest sulfate reduction rate was recorded directly below the bacterial plate in the chemocline. This is due to the rich supply of organic matter produced by phototrophic bacteria. At greater depth, H_2S production rate decreases and increases once more at the bottom where rapidly sinking fresh organic matter is accumulated. In the surface layer of bottom sediments H_2S production increases abruptly amounting to 1-10 mg H_2S/l/d.

The intensity of sulfate reduction and extent of development of phototrophic bacteria varies in different lakes. The highest sulfate reduction rate was recorded in salty meromictic lakes enriched with sulfates (0.9-2.0 g SO_4^{2-}/l). These may be lakes of marine or continental origin (GORLENKO, 1979). In the bottom sediments of these lakes daily H_2S production reaches 15.6 to 28.4 mg/l, which accounts for about 80 % of the total H_2S production in the lake. In the bottom region of salty meromictic lakes up to 790 mg/l H_2S is accumulated. One cubic meter of chemocline water of saline lakes may contain from 26 to 162×10^3 mg H_2S. These amounts are sufficient to maintain photosynthesis of the phototrophic bacterial population for 12-120 days.

Daily photosynthesis intensity may reach 485 mg C/l. Phototrophic bacteria production in these lakes is about 220 g C/m^2/day, which makes 15-52 % of total phototrophic production, including algae.

Phototrophic bacteria are capable to oxidize up to half of the H_2S produced in the water body of highly trophic lakes, such as Veisovo and Pomyaretskoye lakes (GORLENKO, 1979). The remaining amounts of sulfide are accumulated in bottom sediments or oxidized chemosynthetically or chemically.

Among freshwater meromictic lakes the development of phototrophic bacteria is most intensive in those enriched with sulfate for example in gypsum karst areas (GORLENKO et al., 1983). Overall water mineralization of the monimolimnion in these lakes is 0.7-2 g/l, sulfate amount is from 100 to 730 mg/l, sulfide concentration at the bottom may reach 60 and even 150 mg/l. Sulfur cycle intensity in such lakes depends upon sulfate concentration and trophic level.

H_2S production in eutrophic lakes varies from 9 to 130 mg H_2S/m^2/d, and in sediments from 130 to 780 mg H_2S/m^2/day. At the time of their most intensive development phototrophic bacteria suffer from sulfide deficiency, and hence sulfate but not elemental sulfur is normally the H_2S oxidation product of the dominating green bacteria.

Production of phototrophic bacteria in sulfate-containing poorly mineralized lakes varies from 150 to 300 g C/m^2/day. Green and purple bacteria contribution to photosynthetic production is 27-60 %. Compared to salt-water meromictic lakes, meromictic fresh water and sulfate-rich lakes sulfur conversion rates can therefore be high, but elemental sulfur is of no importance for the sulfur turnover.

Bacterial photosynthesis rates were the lowest in meromictic oligotrophic lakes poor in sulfate. It may be exemplified by the Azerbaidjanian mountain lakes Gek-Gel and Maral-Gel (GORLENKO et al., 1983). Because of the low sulfate content in these lakes (20 mg/l), there is only 2-4 mg/l of sulfide in the hypolimnion and in the bottom region it is completely bound as FeS, since about 20 mg Fe^{2+}/l was found near the bottom.

In Gek-Gel Lake the chemocline is situated between 25 and 30 m of depth. Phototrophic bacteria produce 58 mg C/m^2/day, and hence oxidize about 82-328 mg sulfide/day. It follows that in Gek-Gel Lake phototrophic bacteria have an additional source of electrons owing to syntrophism with sulfur reducing bacteria. Bacterial photosynthesis constitutes up to 70 % of total photosynthesis of algae and bacteria.

Thus oligotrophic lakes are distinguished by the low intensity of the sulfur cycle. H_2S production is limited by sulfates and organic matter. Sulfur is not formed via H_2S oxidation.

In lakes enriched with Fe^{2+} the sulfur cycle is fundamentally different. In some lakes protected from wind Fe^{2+} is accumulated in the hypolimnion and meromixis takes place due to the development of ferrobacteria. This kind of meromictic lakes is illustrated by the Kuznechiha and Oha-Lampa lakes (GORLENKO et al., 1980). In the bottom region of Kuznechiha Lake Fe^{2+} concentration amounts to 150 mg/l, while the surface content is only 40 mg/l, and sulfide amounts to 15 mg/l at most. No free H_2S is present, all sulfide of the mixing zone of the monimolimnion is bound to gradually settling FeS. Contribution of photosynthesizing bacteria to primary production was small, 70 mg C/m^2/day, and consequently within this time they were bound to oxidize from 99 to 396 mg H_2S. As a result of sulfate reduction only 113 mg H_2S /m^2/day was produced in the whole water column. As the possibility of H_2S diffusion from lower strata must be ruled out, it is obvious that green bacteria in the Kuznechiha Lake could perform photosynthesis only on account of sulfide produced in the chemocline. Conceivably, green sulfur bacteria are supplied with sulfide by sulfur reducing bacteria similar to *Campylobacter* sp. and *Desulfuromonas acetoxidans* (PFENNIG & BIEBL, 1976; WOLFE & PFENNIG, 1977). In lakes enriched with Fe salts the sulfur cycle is therefore confined to the chemocline and the contribution of phototrophic bacteria to total photosynthetic production may reach 14-38 %.

A peculiar feature of Fe^{2+}-rich lakes is that the sulfide produced in the monimolimnion is buried in the sediments and removed from further sulfur turnover.

Higher iron content was also recorded in dimictic lakes situated in marshy areas, such as small lakes of Karelia and some lakes of Estonia (DUBININA, 1977; DUBININA & KUZNETSOV, 1976; GORLENKO & LOKK, 1979). Localization of sulfur cycling in these lakes is similar to that in the meromictic lakes discussed above.

3. Conclusion

Purple and green sulfur bacteria production in stratified lakes of different types constitutes 13-75% of total primary production (see Table 1).

Contribution of phototrophic bacteria to general productivity depends on the trophic level of the lake. Contribution of purple and green bacteria to the photosynthetic production of the lake was the highest in oligotrophic and mesotrophic lakes. In highly trophic lakes absolute values of bacterial photosynthesis are large, whereas its contribution to synthesis of organic matter is usually not high.

Carbon cycle reactions mediated by purple and green bacteria are closely connected with those of the sulfur cycle (see Table 2).

In most of the lakes studied, green sulfur bacteria predominated. It was shown (PFENNIG, 1975) that at relatively high sulfide concentration these phototrophs generally oxidize sulfide to elemental sulfur. But if H_2S content in the medium is not high, then its complete oxidation to sulfate occurs. In lakes with a low gradient in H_2S concentration phototrophic bacteria suffer from deficiency of H_2S as H-donor. In these conditions microorganisms oxidize sulfides to sulfates, and in case of very low H_2S concentrations, switch on to syntrophic growth with sulfur reducing bacteria.

Thus under favorable light conditions phototrophic bacteria occupy a predominant position for H_2S consumption and make a considerable contribution to the primary production of stratified lakes containing sulfide.

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Peculiarities of Bacterial Hydrogen Sulfide Formation in the Curonian Bay and Drukshiai Lake (Lithuania)

by

A.A. KUCHINSKENE, Vilnius*)

With 2 Figures and 3 Tables

Contents

Abstract

The intensity of bacterial hydrogen sulfide formation (sulfate and sulfur reduction) due to anthropogenic pollution was investigated both in the northern part of the Curonian Bay and in the Drukshiai Reservoir, which cools an atomic power station (APS).

Sediments of the Curonian Bay were sampled at six stations (from 3.5 to 8 m water depth) in summer 1985 and 1987. The intensity of sulfate reduction increased 1.5 times from 1985 to 1987 and amounted to more than 1 mg S^{2-}/dm^3 per day in the most polluted area. The most intensive sulfur reduction, 3.95 mg S^{2-}/dm^3 per day, was recorded in 1987 in the top two centimeter of bottom sediments at the station near the ferry terminal (8 m water depth). A tendency toward an increase of the number of sulfate reducing bacteria was also observed in the bottom sediments of the bay.

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The investigations of the Drukshiai Lake were conducted seasonally at six stations in 1982-1983 (during the construction of the APS) and in 1984-1987 (during the first years of its functioning). The comparison of the two periods manifests the intensification of the sulfate reduction process in the entire lake, being most pronounced near the warm water outlet. Here the process increased from 0.03 up to 0.20 mg S^{2-}/dm^3 per day, and the content of acid-soluble sulfides rose from 41.3 to 124.0 mg/dm^3. The most intensive sulfur reduction was observed 1987 also near the warm water outlet and reached up to 1.21 mg S^{2-}/dm^3 per day in the top two centimeter of bottom sediments.

1. Introduction

Microbiological reduction of sulfate and sulfur is the main source of hydrogen sulfide (H_2S). Being strictly anaerobic, sulfate and sulfur reducing bacteria gain energy for their life processes during electron transfer from organic substrates to sulfate or sulfur, reducing them to H_2S. Water pollution by organic substances as well as warming greatly intensify the processes of bacterial hydrogen sulfide formation, thus significantly influencing hydrochemical and biological regimes in bottom waters and bottom sediments (EVANS, 1972; POWELL et al., 1979; GERLACH, 1981; SOROKIN, 1982; IVANOV, 1983). In this paper data on bacterial hydrogen sulfide formation resulting from anthropogenic pollution in Curonian Bay and Drukshiai Lake are presented.

2. Materials and Methods

Study sites: The Curonian Bay is located in the western part of the central segment of the Baltic Sea, joining the latter by a narrow strait at the Lithuanian port Klaipeda (Fig. 1). The area of the bay is 1,610 km^2, the mean depth is 3.7 m. Its water is of the bicarbonate-calcium type with a medium mineralization (220-300 mg/l) (JANKEVICHUS & BARANAUSKENE, 1978). The northern part of the bay was deepened for the ferry to Germany, and that negatively influenced the biota of the ecosystem. At Klaipeda the bay is polluted by industrial wastes of a pulp and paper mill and by the sewage water of the city.

Drukshiai Lake is the water-basin used for cooling the atomic power station (APS) in the north-east of the Lithuanian SSR (Fig. 2). Its area is 44.8 km^2, and its maximum and average depth is 32 m, and 8 m, respectively. The construction of the APS started in 1979. The lake water is of bicarbonate-calcium type with a mineralization of 221.8-241.5 mg/l and a slightly alkaline pH in the epilimnion (BUNIKIS, 1982). Up to 75 % of the bottom sediments are represented by the highly mineralized carbonate mud. In the southern, shallow part of the lake the mud is enriched with organic substances. The first energy block of the APS was put into operation in the beginning of 1984. Since then the whole area near the warm water

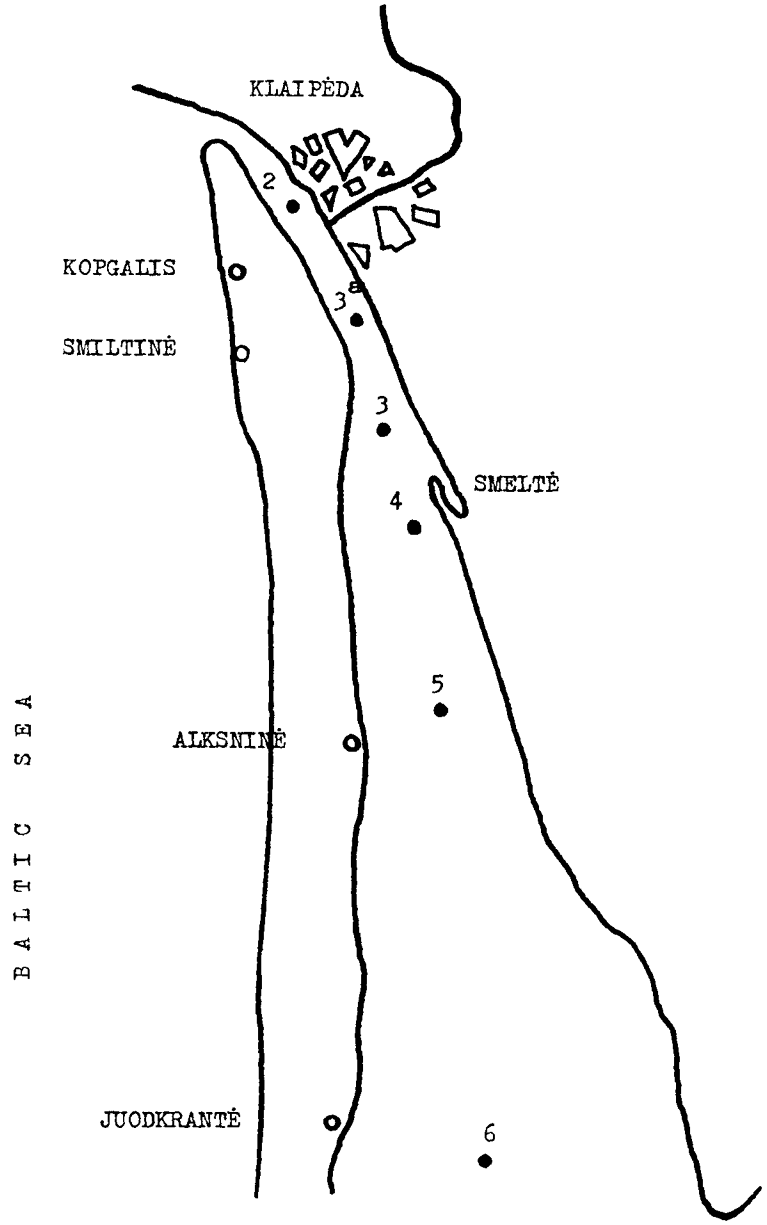

Fig. 1: Locations of stations in the Curonian Bay. (st. 2 - 6.0 m; st. 3a - 6.0 m; st. 3 - 6.0 m; st. 4 - 8.0 m; st. 5 - 3.5 m; st. 6 - 3.5 m).

outlet is no longer covered with ice in winter. The water temperature is never below 10° C in winter and in summer it rises sometimes to 30° C. The sulfate concentration in the water increased from 6-10 to 14 mg/l.

Sampling and analytical methods: Bottom sediment samples were collected into sterile glass tubes using an Ekman-Bergy type instrument. The concentration of

Fig. 2: Locations of stations in Lake Drukshiai. (st. 1 - 32.0 m: st. 2 - 31.0 m; st. 3 - 9.0 m; st. 4 - 6.0-7.0 m; st. 5 - 10.0-11.0 m; st. 6 - 4.0 m; APS = Atomic Power Station).

sulfates was measured by colorimetric methods (ALIOKIN et al., 1973; TAKATAKAI, 1974). Elemental sulfur and acid soluble sulfides in bottom sediments were analyzed by the methods of VOLKOV & ZHABINA (1980). Sulfate reduction rate was measured (in situ) in 20 ml glass tubes, which were pushed 0-2 cm and 2-5 cm deep into the sediment, so that the sediment layer filled the tube beneath the plunger completely. The intensity of the process was measured in duplicate or triplicate glass-tubes using the $Na_2{}^{35}SO_4$ tracer technique (IVANOV, 1965; IVANOV et al., 1976; SOROKIN, 1982). Sulfur reduction rates were measured in bottom sediments at the depths 0-2, 2-5 and 5-8 cm with elemental ^{35}S using a similar tracer technique. Elemental ^{35}S was prepared by acidifying $Na_2{}^{35}S_2O_3$ solution by the method of ROY & TRUDINGER (1970).

Sulfate reducing bacteria were counted on various media: Postgate "C" (POSTGATE, 1965) with lactate as a carbon source, media proposed by WIDDEL & PFENNIG (1981) with acetate .and propionate as carbon sources. Sulfur reducing bacteria were counted on the medium proposed by PFENNIG & BIEBL (1976), acetate, glucose, and casein hydrolyzates being the carbon sources.

3. Results and Discussion

The annual increase of the anthropogenic pollution of Curonian Bay is evidenced not only by the intensification of sulfate reduction, but also by the increase of the fecal pollution index. The number of the *Escherichia coli* bacteria is sometimes 2×10^6 cells per liter at stations examined near Klaipeda.

The number of sulfate reducing bacteria in the bottom sediments of the Curonian Bay, when determined in the medium with lactate, increased from 10^3-10^5 cells/ml in 1985 to 10^5-10^7 in 1987. In 1987 up to 10^2 cells/ml of sulfate reducing bacteria mainly of the *Desulfovibrio* genus were observed in the near bottom water of the most polluted area of the bay near Klaipeda. The number of sulfate reducing bacteria developing in different media - with acetate, propionate, lactate - was similar and amounted to 10^3-10^5 cells/ml in 1985.

In 1987, in the most polluted area of the northern part of the bay the mean number of sulfur reducing bacteria was 10^4 cells/ml. In the medium with acetate, bacteria with the morphology of *Desulfuromonas acetoxidans* and *Campylobacter* sp. prevailed. In the medium with casein hydrolizate, bacteria similar to *Campylobacter* sp. developed. In the medium with glucose, large, thread-like bacteria dominated.

The intensity of sulfate reduction processes in the bottom sediments of the most polluted area of the bay near the pulp and paper mill (station 3a, Fig. 1) and near the ferry pier (station 3, Fig. 1) exceeded 1 mg S^{2-}/dm^3 per day (see Table 1).

Table 1

Sulfate reduction rate in the upper 2 cm of sediments in the northern part of the Curonian Bay.

Station depth	Sulfides mg/dm³		S^{2-}, SO_4^{2-} mg/dm³		Sulfate reduction $mgS^{2-}/dm^3/day$	
m	1985	1987	1985	1987	1985	1987
6.0	-	125.1	-	48.0	-	0.47
6.0	304.8	736.0	44.8	91.2	1.09	1.80
8.0	912.8	818.4	44.8	50.0	1.33	1.60
6.0	-	217.6	-	51.0	-	0.74
3.5	212.8	150.6	32.0	42.0	0.34	0.63
3.5	24.8	40.0	25.6	39.0	0.13	0.37

Along with the increasing number of sulfate reducing bacteria, the intensity of sulfate reduction grew 1.5 times in 1987 in comparison with 1985. A marked accumulation of acid-soluble sulfides was also observed. Their concentration in sediments in some cases reached 900 mg/dm³. To the south of Klaipeda, where the influence of sewage waters is less, the sulfate reduction rate was lower, but still 1.9-2.8 times higher in 1987 than in 1985. This indicates the tendency toward eutrophication in this region and the expanse of pollution to the outer regions of the bay. In 1987 we observed an oxygen deficit in bottom waters at some stations where the process of hydrogen sulfide production was most intensive.

In 1987, we investigated the intensity of sulfur reduction in the northern part of the bay (see Table 2). The most intensive sulfur reduction was observed near the ferry pier (station depth 8 m) in the top 2 cm bottom sediments and was 3.6 times higher than hydrogen sulfide production due to sulfate reduction. At other stations the intensities of sulfur- and sulfate reduction processes were similar. Sulfur reduction was usually less pronounced in the lower sediment layers (2-5 and 5-8 cm). The data obtained show that the sulfur reduction process is important in biogenic hydrogen sulfide formation and in some cases is more intensive than sulfate reduction.

Table 2

Elemental sulfur content and sulfur reduction rate in the bottom sediments in the northern part of the Curonian Bay.

Station depth, m	Sediment layer, cm	S° mg/dm^3	Sulfur reduction mg S^{2-}/dm^3/day
6.0	0-2	608	1.34
	2-5	256	0.64
	5-8	272	0.69
8.0	0-2	1232	3.95
	2-5	1184	3.08
	5-8	1120	2.00
6.0	0-2	240	1.00
	2-5	208	0.70

Another anthropogenic influence - "temperature pollution" is experienced by Drukshiai Lake. In the period 1979-1984, while the APS was being constructed, pollution due to sewage waters was local. The most intensive sulfate reduction was observed in the deep water zone (stations 1 and 2 in Fig. 2, 32 and 31 m depths, respectively), where notable stratification with oxygen deficit at the bottom was observed in mid summer, as well as in the shallow bay (station 6, Fig. 2) due to the high content of allochthonous organic substance. At the other stations of the lake, sulfate reduction in the upper (0-2 cm) layer of bottom sediments was considerably lower than at the stations mentioned above. In 1983 we observed a considerable intensification of sulfate reduction during summer time (up to 0.65 mg S^{2-}/dm^3 per day) in the construction area of the water intake channel (station 2, Fig. 2) and up to 0.73 mg S^{2-}/dm^3 per day in the shallow bay, which was obviously caused by the pollution of those areas during the construction of the APS.

The number of sulfate reducing bacteria in bottom sediments increased 10-20 times during the first years of operation of the APS. Their number in the medium with lactate was 10^3-10^5 cells/ml. In the media with acetate and propionate the number of sulfate reducing bacteria was by 1-2 orders lower, reflecting obviously the organic substance composition in sediments.

No considerable seasonal changes in the composition of predominant genera and species of sulfate reducing bacteria were registered. In the medium with lactate, the bacteria of *Desulfotomaculum* gen. and *Desulfovibrio* sp. prevailed. Among acetate-using sulfate reducing bacteria, *Desulfotomaculum acetoxidans* and *Desulfobacter* sp. dominated. In the medium with propionate, lemon-shaped cells similar to *Desulfobulbus propionicus* prevailed.

The number of sulfur reducing bacteria in the lake sediments was 10^3-10^5 cells/ml (refer to Table 3). Bacteria of *Desulfuromonas acetoxidans* and *Campylobacter* sp. prevailed.

Table 3

Elementary sulfur content, sulfur reduction and number of sulfur reducing bacteria in bottom sediments in Druksiai Lake in 1987.

Location	Station depth	sample depth	S° mg/dm³		Sulfur reduction mgS²⁻/dm³/d		S-red. bacteria cells/ml S° + acetate	
	m	cm	May	July	May	July	May	July
1	32	0-2	25.6	120.0	0.01	0.07	10^3	10^4
		2-5	21.6	112.0	0.01	0.08	10^3	10^3
		5-8	16.0	104.0	0.01	0.06	10^3	10^3
2	31	0-2	520.0	632.4	0.27	0.49	10^3	10^5
		2-5	360.0	568.0	0.25	0.45	10^4	10^4
		5-8	320.0	416.0	0.19	0.33	10^4	10^4
4	6	0-2	272.0	288.0	0.30	1.21	10^3	10^4
		2-5	280.0	280.0	0.49	1.09	10^3	10^3
		5-8	184.0	224.0	0.18	0.67	10^3	10^3

In comparison with the period before the APS became operational, the first years of its operation marked the intensification of sulfate reduction processes in the bottom sediments of the lake, which was most pronounced in the warm water outlet zone (station 4, Fig. 2), where the process increased from 0.03 to 0.20 mg S^{2-}/dm^3 per day. With the intensification of the sulfate reduction process, the content of sulfides in the sediments increased, and gradually they accumulated even in the shallow water zones of the lake. The content of acid-soluble sulfides in the zone influenced by heat increased from 41.3 up to 124.0 mg/dm^3.

In 1987, the intensity of sulfur reduction in the deep water and in the warm water outlet zone was studied (refer to Table 3). The highest sulfur reduction was observed in sediments near the warm water outlet (station 4) and near the intake channel (station 2) (station depths 6 and 31 m, correspondingly). The process was more intensive in summer: in the upper layers of bottom sediments at the stations mentioned above, sulfur reduction was respectively 2 and 6 times higher than sulfate reduction.

In general, the sulfate and sulfur reduction intensities in the lake are comparable, thus indicating that hydrogen sulfide in the upper sediment layers is produced via both bacterial dissimilatory processes.

Our studies evidence that the anthropogenic impact, produced during the APS construction, and "temperature pollution", exhibited since the beginning of APS operation, no doubt influence the biota of the lake. The warming leads to more intensive development of macrophytes, the resulting increase of the organic substance content and enhancement of the sulfate reduction process in turn may cause anaerobic conditions and fish death.

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Seasonal Variations of Cellulose Decomposition Rates in Bottom Sediments of Freshwater Lakes

by
B.B. NAMSARAEV & M.V. IVANOV, Moscow*)

With 2 Figures and 1 Table

Contents

Abstract

The rate of cellulose decomposition and the numbers of cellulose-decomposing microorganisms were studied in silt sediments of a fresh water lake in a forest area from April to November, 1983. The activity of cellulose-decomposing microorganisms depends on the water temperature and on the availability of cellulose. Two maxima of cellulose decomposition were observed, one in April-May, caused by the spring water warming and the high supply of cellulose from the late autumn leaf litter, and the second in August and September, caused by the input of considerable amounts of cellulose from fallen leaves and herbs.

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1. Introduction

Accumulation of the hard-to-decompose leaf litter and phytoplankton fraction is observed in sediments of water bodies. A considerable quantity of this organic matter is cellulose, the major cellular polymer of plants and of many algae species (IMSHENETSKIY, 1953). In silt sediments of fresh water lakes it constitutes up to 12% of the organic matter (KUZNETSOV, 1973). Various species of microorganisms, including anaerobic cellulose-decomposing bacteria, participate in the remineralization of cellulose (IMSHENETSKIY, 1953; NAMSARAEV, 1984). Their number amounts to 10^3 cells/g of wet mud, abruptly decreasing vertically in the sediment.

According to GOMAN (1973), KUZNETSOV (1973), and HOENIGER (1985) up to 1.5 % of cellulose is decomposed in silt sediments per day. A certain dependence of the process rate on seasons has been reported. In Lake Baikal, for example, the cellulose decomposition rate in bottom sediments was by 2-3 orders lower during winter than in summer (GOMAN, 1973).

We studied cellulose decomposition rates, cellulose bacteria numbers and their metabolism in bottom sediments of a forest lake during the period lasting from early spring to late autumn in order to understand seasonal dynamics of this important remineralization process in detail.

2. Materials and Methods

Microbiological studies were performed from April to November, 1983, in the shallow Sionskoye Lake, located in the Prioksky Reserve of the Moscow Region. The Lake is located in a mixed forest area. Its shores are covered by a dense vegetation. The northern shore, where a small river flows in, is marshy, the other shores are sandy.

The upper layers of the bottom sediments consist of black-colored silts with abundant residues of roots, leaves and stems. An insignificant admixture of sand was observed. The content of sand increases with the depth of sediments.

During the investigation period the water level in the lake varied. The greatest overflow was observed in April, when the lake area measured 7 ha. During summer the water level gradually fell, and the lake area in August-September shrank to 2-3ha.

Bottom sediment samples were taken with a stratometer. The methods for counting cellulose bacteria cell number, measuring cellulose decomposition rate as well as analyzing for metabolites and cellulose contents were described earlier (NAMSARAEV & IVANOV, 1982; NAMSARAEV, 1984). Values of pH and Eh were measured with an Ionometer 102.

3. Results

In the beginning of April the temperature of the water and the upper silt layers was 8°C, in the middle of May it rose up to 20°C (Fig. 1). The highest temperature of 25°C was registered in July. In August the decrease of temperature was observed, and during the autumn months its value fell to 2°C.

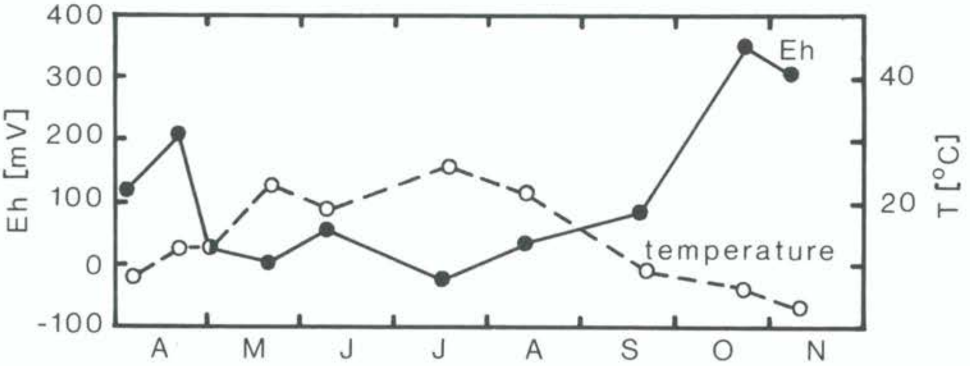

Fig. 1: Variations of the redox values (1) and temperature (2) in the top sediment layer (0-3 cm) of Sionskoye Lake, April-November 1987.

pH values in the silts varied from 6.2-6.4 during spring months, rose to 6.7 in July, and decreased gradually to 6.0-6.1 in autumn. Eh values noticeably decreased in spring, and rose sharply up to 350 mV in autumn (Fig. 1).

During the early spring warm-up of the lake, the cell numbers of all cellulose-decomposing bacteria increased in the sediments, those of anaerobic decomposers even by a factor of 100, reaching a maximum value of 105 in May (Fig. 2). The numbers stayed at this level until cold weather set in autumn. Considerable variations in aerobic and spore-forming anaerobic bacteria numbers were observed (Fig. 2). The first maximum in the number of aerobic bacteria was registered in April-May, and a second one in July-August.

At the end of April, when the temperature rose to 12°C, the maximal decomposition rate, i.e. 0.0090 mg of cellulose/g of wet silt/day, was observed. During the summer months a noticeable decrease of the rate to 0.0047-0.0052 mg/g/day was observed. Later on, in August-September, the decomposition rate rose to 0.0088-0.0071 mg/g/day. In late autumn, the process rates decreased sharply connected with a water temperature decrease to 2-6°C.

The cellulose content in the sediments was considerably lower in summer than in spring and autumn. Using uniformly labelled ^{14}C-cellulose, we studied the variations of the concentrations of cellulose metabolites. During the microbial decomposition of cellulose a considerable amount of CO_2, constituting 2.4-11.9 % of the cellulose carbon, is formed (Table 1). The variations in CO_2 production correlate

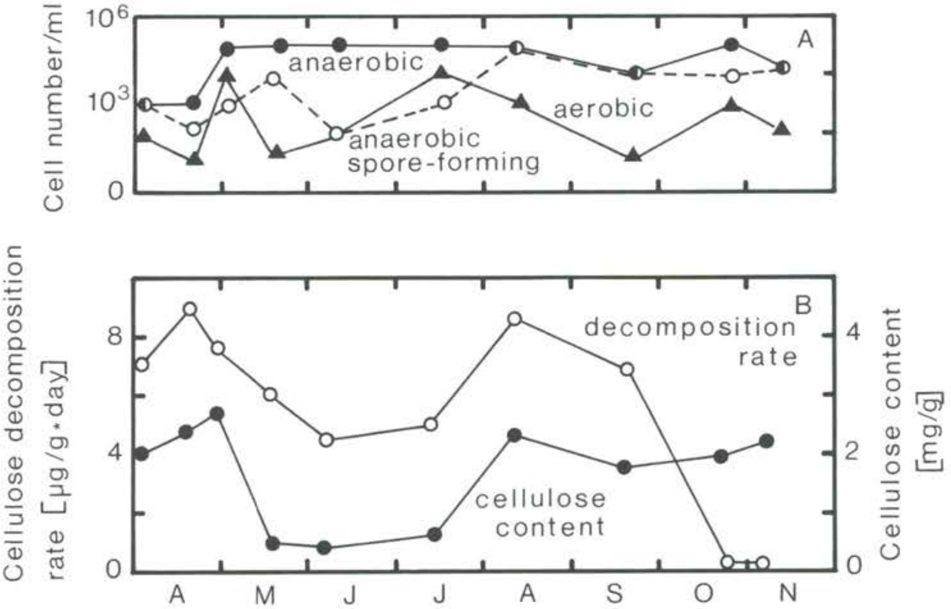

Fig. 2: Temporal variations in the number of aerobic, anaerobic and anaerobic spore-forming cellulose-decomposing microorganisms (A), cellulose decomposition rate and cellulose content (B) in the surface layer (0-3 cm) of bottom sediments of Sionskoye Lake in April-November, 1987. Depth of sampling is 0.1-0.5 m. Mean values of 3 determinations are shown.

Table 1

Cellulose metabolites formation rates in bottom sediments of Sionskoye Lake (μg C/g/day).

Dates of sampling	April 5	April 22	May 4	June 7	July 15	August 12	September 19
Metabolites:							
CO_2	308.2	488.3	426.8	194.8	199.2	585.5	313.3
Formiate	0	0	60.9	0	33.8	84.7	0
Acetate	123.1	235.6	223.3	115.0	161.5	317.2	156.1
Propionate	22.0	59.5	0	20.4	59.5	11.1	1.9
Butyrate	66.5	0	0	20.1	50.2	10.6	0
Valeriate	42.5	60.2	13.5	45.4	0	42.3	0
Cellobiose	18.5	0	10.5	55.2	0	45.8	0
Glucose	88.2	60.5	54.0	0	77.6	108.4	90.5
Lactate	15.2	121.0	80.4	24.3	0	16.8	21.5
Succinate	0	45.4	0	0	13.0	0	0
Methane	0	0	0.06	0	0.45	0.19	0
Cellulose decomposition rate	3,168	3,968	3,388	2,046	2,292	3,889	3,124

with the changes of the cellulose decomposition rate. Two distinct maxima of CO_2 formation were observed: in April and in August, corresponding to the highest rates of cellulose decomposition. The formation of acetate, reaching up to 0.32 mg C/kg/day, was also related to cellulose decomposition. Other volatile fatty acids - formic, propionic, butyric and valeric - were also detected as decomposition products. In some samples lactate and succinate were found. Glucose and cellobiose - cellulose decomposition intermediates - were also present among the labelled products. In samples collected in May, July and August the formation of volatile hydrocarbonic gaseous products was noted. The rate of the process was 0.000027-0.00045 mg C/kg/day.

4. Discussion

The observed variations in the activity of cellulose-decomposing microorganisms in bottom sediments of a fresh water forest lake show that temperature and cellulose availability are the controlling factors of cellulose decomposition. The first maximum in the rate of cellulose decomposition observed at the end of April - beginning of May is caused by the rise in water and sediment temperature and by an abundant supply of cellulose. During spring, night frosts can cause the formation of ice crystals in plant cells triggering their disruption and cellulose, contained in cell walls, becomes available for cellulose-decomposing microorganisms. During summer a gradual decrease of bacterial cellulose decomposition is observed caused by a decrease in the cellulose content of sediments. In August, with the new cellulose supply to the sediments from leaf litter, a noticeable increase of bacterial decomposition is observed which remains at the same level throughout September. The input of a large cellulose supply in August 1979 is confirmed by the data on phytomass in the shore zone of Sionskoye Lake. In this period *Pharagmites communis purum* grew rapidly, yielding 3.45 kg dry weight/m^2. It was accompanied by an abundance of algal cells undergoing decomposition in the silty sediments; 94-96 % of the algae were cellulose-containing diatomic and *Trachelomonas* cells.

The cell numbers of cellulose bacteria also depended on the temperature regime of the lake. During the spring warm-up of the lake the bacteria numbers of all 3 groups (aerobic, anaerobic and spore-formers) increased. Then the number of anaerobes remained at a constant level until the begin of autumn frosts, while the number of the other groups fluctuated noticeably during the period of observation. In all the samples the content of aerobes was lower than that of anaerobes. Obviously the environmental conditions of the lake sediments are more favorable for anaerobes which is testified by rather low Eh values in the silt. The results of the analyses of cellulose metabolites, among which the products of anaerobic cellulose decomposition were detected, substantiate this conclusion.

The seasonal variations in the number of anaerobic cellulose-decomposing bacteria have been studied earlier in sediments of Lake Baikal (GOMAN, 1973). An increase in the number of these microorganisms and in the rate of decomposition was observed in summer too. In summer 0.4-0.8 % of cellulose is decomposed per day, but only 0.003-0.02 % in winter. Up to 0.5 % of cellulose is decomposed during summer in the silts of Canadian lakes (HOENIGER, 1985). These data show that in summer months cellulose bacteria become noticeably more active. The processes of lignocellulose destruction were studied with radioisotope methods in Foolic Lake (Alaska) and in freshwater marshes in Georgia, USA, by FEDERALE & VESTEL (1980) and BENNER et al. (1984). There only up to 0.1 % of the cellulose fraction of lignocellulose was decomposed per day which is considerably lower than the decomposition rates in Sionskoye Lake sediments studied by us, where up to 0.26-1.5 % of cellulose was decomposed per day. Maximum rates up to 1.28-1.5 %/day were observed at the end of May - beginning of June. Obviously, the differences in decomposition rates can be explained by considering differences in substrates - cellulose or lignocellulose - and in the physicochemical conditions of the studied lakes and marshes.

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The Relation between Phytoplankton Content and Primary Production in the Krasnoyarsk Reservoir

by

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With 5 Figures

Contents

Abstract

Data on the seasonal dynamics of phytoplankton, chlorophyll and the primary production/destruction ratio in the Krasnoyarsk reservoir in 1978 and 1985-1987 are presented. A comparative assessment of the relationship between hydrological and hydrobiological properties and the primary production/destruction ratio is offered.

1. Investigation Areas and Methods

This investigation aimed at studying the seasonal dynamics and interrelations of phytoplankton, chlorophyll and primary production in the Krasnoyarsk Reservoir.

In 1978 investigations were carried out in the lower part of the reservoir, at the Schetinkinsky reach, and in 1985-1987 in the upper part of the reservoir, in the Syda Bay of the Krasnoyarsk reservoir. In these areas the seasonal dynamics of species composition of phytoplankton, the time of changes of phytoplankton community succession, the physiological state of algae in different seasons were investigated and compared.

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Chlorophyll and pheophytin were determined according to LORENZ (In: TOPACHEVSKY, 1975), the number and biomass of algae were measured by standard methods in Fucks-Rosenthal and Najotte chambers. Primary production was evaluated using the oxygen modification of the flask method (KUZNETSOV & ROMANENKO, 1963). Flasks were incubated at depths: 0, 0.25 T, 0.5 T, 1.0 T, 2.0 T, and 2.5 T where T is the value of visibility of a standard white disk of conventional transparence. Samples for chlorophyll and phytoplankton determinations were taken from the same horizons. All parameters were measured at ten day intervals.

Fig. 1: Seasonal variations of the temperature of the water surface layer in the Krasnoyarsk reservoir.

During the investigations temperature of the water surface layer in the reservoir varied from 17.2 to 25.7°C in 1978 and 1985, from 15.0 to 29.0°C in 1986 and from 13.8 to 23.3°C in 1987 (Fig. 1). The lowest temperature values were observed in June and late August to early September.

2. Results and Discussion

Diatoms dominated the phytoplankton in the reservoir in the first half of summer (late June), a situation which did not vary considerably during a number of years irrespective of the observation site.

In 1978 the dominant species in the spring-summer phytoplankton were *Asterionella formosa*, *Melosira granulata*, *Fragilaria crotonensis*. In 1985 *A. formosa* contributed in the period of mass development as much as 94 % to the total biomass and 100 % of the diatoms; in 1986 *A. formosa* was also dominant in the spring-summer plankton.

In 1987 the temperature was lower than in the previous years, which affected the development of the algal community. In June plankton showed a rather high species number (15-20 species), which gradually decreased and only by June 10 *A. formosa* became dominant in the plankton. The shift from the spring-summer to summer-autumn type of plankton occurred in the second half of July. During the shift the amount of diatoms in plankton decreased and the amount of blue-green algae increased. At the same time the number of algal species also increased. While in the period of mass development of diatoms only 3-4 algal species were present in plankton, their number rose to 15-20 during the shift. Green and peridinic algae were responsible for the increase in the species number.

In 1978 the summer-autumn community consisted mainly of *Aphanizomenon flos-aquae* with a small contribution of *Anabaena sp.* and *Microcystis aeruginosa*. The algal community included also *Cyclotella comta*.

In 1985, in August, *Asterionella formosa* was replaced by *Fragilaria crotonensis*. Domination of *A. flos-aquae* in plankton was observed by mid-August.

The summer of 1986 was noted for higher temperatures of the surface layer. In July the temperature of water during the day rose to 29.0°C which apparently inhibited the development of plankton, and blue-green algae appeared in late July with the domination of *Anabaena sp.* and *Microcystis aeruginosa*. The biomass of phytoplankton was equally represented by blue-green algae and diatoms, *Fragilaria crotonensis* dominating among the latter. In the same period up to 25 algal species were concurrently present in plankton. The majority of species belonged to blue-green algae (class of volvoxia). Beginning with the second half of August the biomass of blue-green algae decreased by an order of magnitude as compared with diatoms and this situation remained till late August - early September. During several days in the first decade of September the surge of blue-green algae development was observed and by the end of the first third of September the total amount of algae began to decrease. Mass development of *Aphanizomenon flos-aquae* in plankton was not observed in 1986.

As noted above, the thermal regime of 1987 differed from the previous years by lower temperatures throughout the vegetation season. Therefore *A. formosa* was dominant in plankton till the end of the second third of July. Development of blue-green algae was very rapid. *A. flos-aquae* was present both as individual filaments and as bundles. In terms of biomass the presence of other groups of algae was unimportant in this period, though the number of species varied, reaching 12-17.

In 1978 the biomass of diatomic algae amounted to 3.3 g/m^3. Even when blue-green algae accounted for 90 % of the biomass, their amount was lower than in the

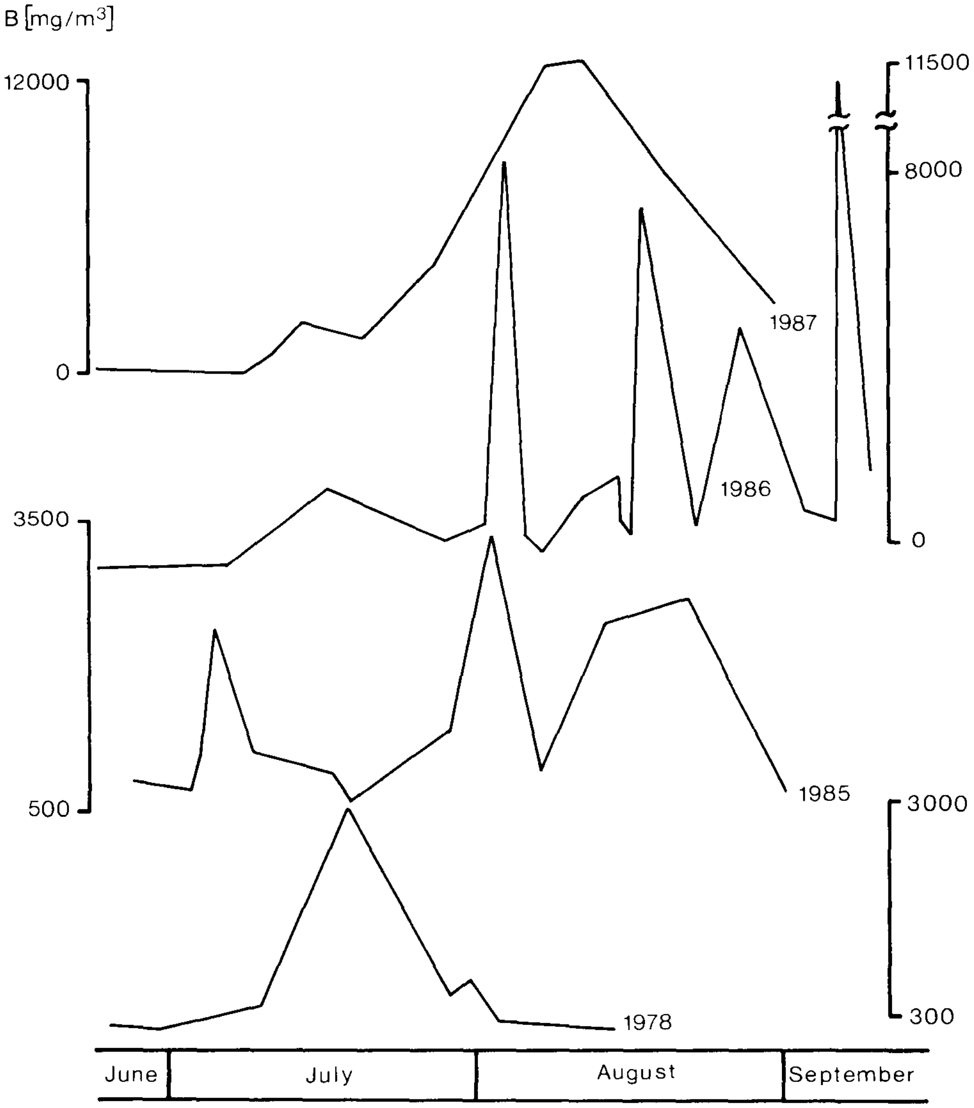

Fig. 2: Seasonal variations of phytoplankton biomass in the Krasnoyarsk reservoir.

spring-summer plankton. In 1985 the biomass of diatomic algae in the period of their maximum development was comparable with the biomass of blue-green algae (2.5 g/m^3 and 3.5 g/m^3, respectively). In 1981-1987 the biomass of diatoms differed from that of blue-green algae by a factor of 4-5 (1.6-2.0 g/m^3 and 8.8-11.0 g/m^3, respectively) (Fig. 2). Thus with the aging of the reservoir the development of plankton showed an increase in the biomass of blue-green algae.

The amount of chlorophyll, as well as the biomass, fluctuated considerably during the season of development (Fig. 3).

As can be seen from the data, the concentration of chlorophyll and the biomass of phytoplankton are rather closely interrelated. However, the use of chlorophyll concentration as an indicator of biomass is limited both by the accuracy of the

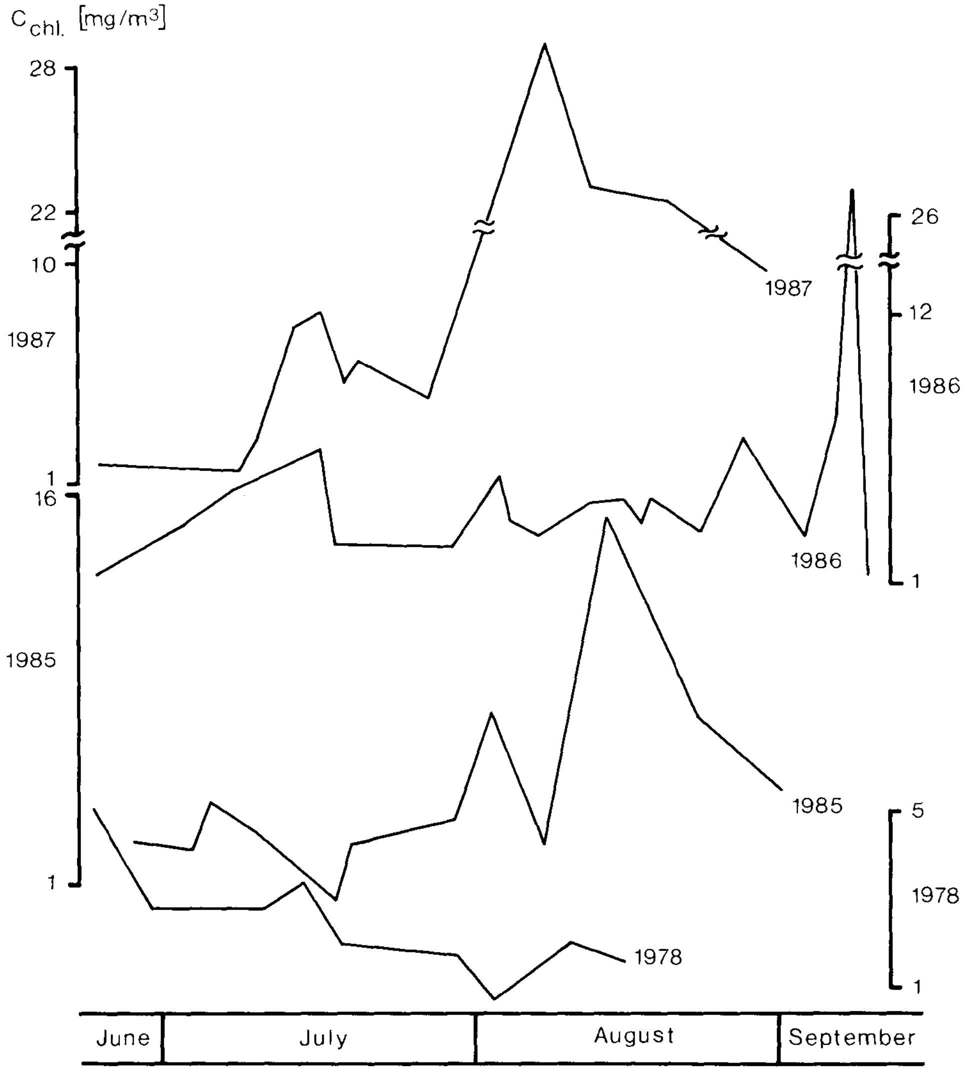

Fig. 3: Seasonal variations of chlorophyll in the Krasnoyarsk reservoir.

method used for chlorophyll determination and by the fact that the chlorophyll content of phytoplankton varies widely depending on a number of factors. It is known that different groups of algae can contain varying amounts of chlorophyll per unit of biomass, leading to differences in the relationship between these parameters. Besides, the degree of relationship also depends on the age of algae, i.e. their physiological state (PYRINA & ELIZAROVA, 1975; TRIFONOVA, 1979; SHCHUR & SID'KO, 1983).

The chlorophyll content per phytoplankton biomass unit (ß value) in the Krasnoyarsk reservoir considerably fluctuated during the season (Fig. 4). In 1978 the maximum levels of ß were observed in June (0.58-0.80 %) when diatomic algae were dominant in plankton and their biomass was as high as 90-100 % of the total biomass. In this period the percentage of pheophytin was 20-40 % of total chlorophyll. Owing to the higher temperature of the surface layer and increased insolation the diatomic cenosis ages. The amount of derivatives in plankton increases (up to 90 %), while the amount of total and "pure" chlorophyll decreases and ß decreases also. We observed the decrease of the ß value in the period of species composition change in all the years under investigation (Fig. 4). In 1986 plankton shift involved several groups of algae: the spring diatoms were replaced by blue-greens with the domination of *Anabaena sp.* and *Microcystis aeruginosa*. In mid-August, along with these species of blue-green algae, the diatomic *F. crotonensis* started to develop becoming dominant in plankton (about 80 % of the total biomass) till the end of the second third of August. At this time the ß value was 0.06 %. The amount of pheophytin in this period was about 75 % of the total amount of chlorophyll. With the development of the second peak of blue-green algae (*M. aeruginosa*) in September, the ß value rose to 1.0. Apparently, the observed shift in phytoplankton in 1986, especially in the autumn-summer plankton, was determined to a greater extent by the meteorological conditions, i.e. by frequent strong winds which stirred the water and caused blue-green algae to descend to greater depths. After replacement of one dominant group of algae by another the ß value rose.

VINBERG et al. (1961) reported that the concentration of phytoplankton chlorophyll fluctuates rather widely; the lower the phytoplankton biomass, the higher the chlorophyll content of algal cells and the higher the amount of oxygen produced by algae. Thus, the changes in primary production during the season are interrelated with the ß value as can be seen in Figure 4. Low values corresponded to low values of the ratio between primary production and destruction of organic matter (A/R). In 1978 this ratio was negative (-1.07). During the shift in the species composition of phytoplankton, an intensive process of degradation of organic matter takes place, i.e. an increase in oxygen consumption and an increase in destruction level is observed. Besides, in this period, as noted above, the species number in plankton increases, which also leads to a decrease in the ß value. In the initial period of both diatomic and blue-green algae development an increase in the ß value is observed (0.8 in 1978; 0.4-0.6 in 1985, 1987 and 4.0 in 1986 for diatoms; 0.5 in 1978; 0.6-0.8 in 1985; 1.0 in

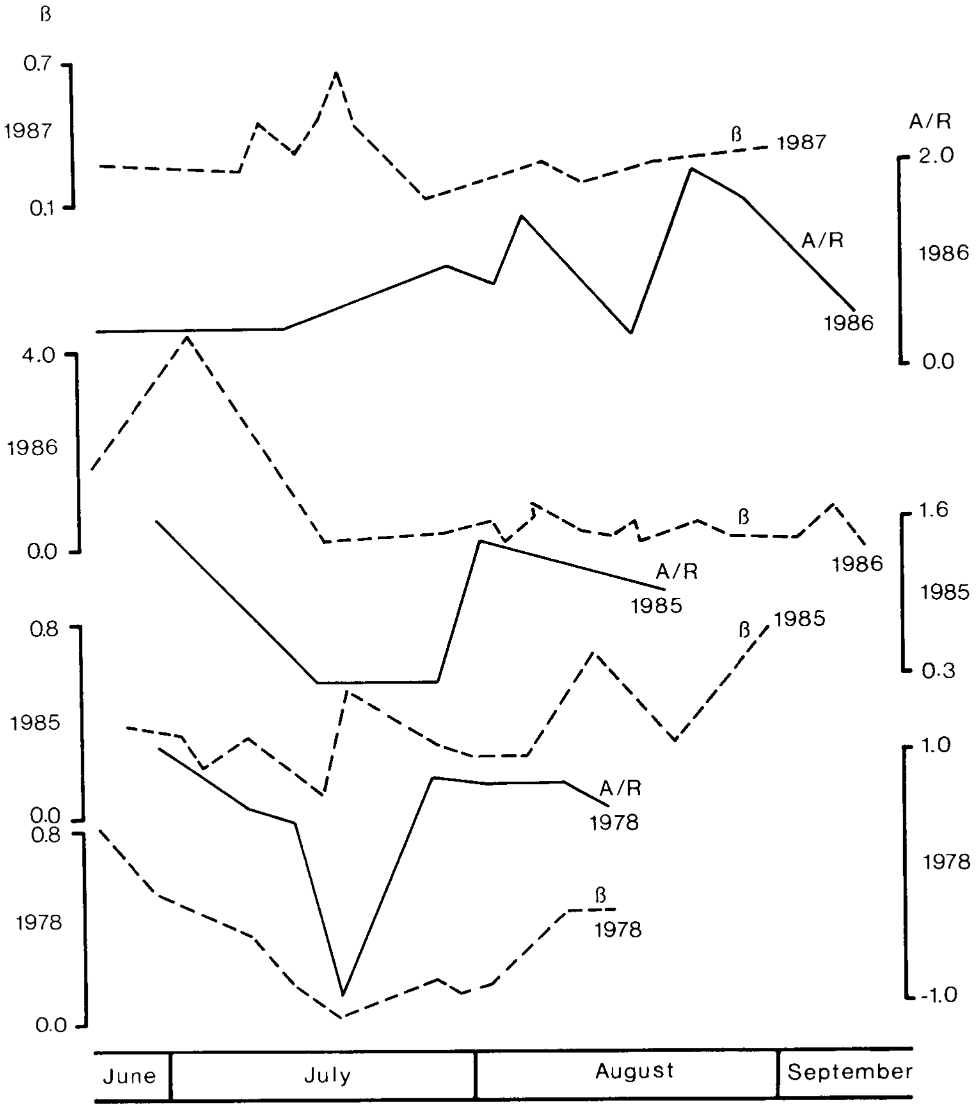

Fig. 4: Seasonal variations of ß values and production/destruction ratios in the Krasnoyarsk reservoir.

1986 and 0.35 in 1987 for blue-green algae). At the same time the production/destruction ratio in 1978 and 1985 was about 1.0. The variations of production/destruction ratio in 1986 differed from that of the previous years. While in 1978 and 1985 the seasonal variations showed a single peak distribution pattern, in 1986 several peaks were observed during the season. Such distribution of the production/destruction ratio is caused by the replacement of several algal species during the season: diatoms were replaced by blue-greens which were later replaced by diatoms and a new surge of blue-green algae at the end of the vegetation season.

The observed relation between the ß value and the production/destruction ratio depends on the variations of the surface layer temperature and the intensity of solar radiation; the decrease in biological parameters was observed against the background of an increase in hydrological parameters. At the same time the change in the species composition of plankton was observed.

In summary, a direct relationship exists between the ß value and the production/destruction ratio (Fig. 5).

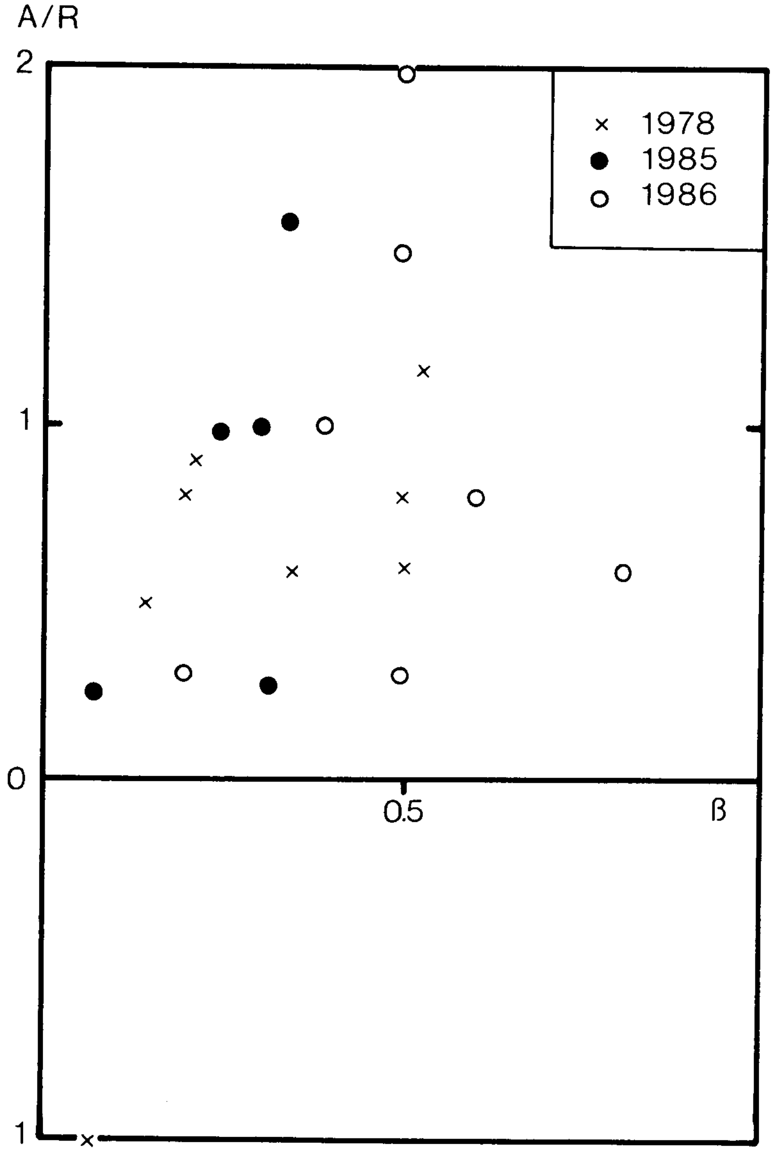

Fig. 5: Production/destruction ratios plotted versus ß values in the Krasnoyarsk reservoir in 1978 and 1985-1987.

3. Conclusions

1. The spring-summer community of phytoplankton in the Krasnoyarsk reservoir is represented by several diatom species: *Asterionella formosa*, *Melosira granulata*, *Fragilaria crotonensis* in 1978, which in the process of development of the reservoir are replaced by one dominant species *A. formosa* (in 1985-1987).

In July-August, during the period of highest water temperatures and the lowest flow rate of the reservoir, a surge of blue-green algae development is observed (*A. flos-aquae* in 1978, 1985 and 1987, and *M. aeruginosa* and *Anabaena sp.*, in 1986). The biomass values of these algae increase with the age of the reservoir from 1.0 g/m^3 in 1978 to 8.0-12 g/m^3 in 1985-1987.

2. The primary production of the Krasnoyarsk reservoir during the vegetation season is interrelated with the ß value and pheophytin percentage of the total chlorophyll. At the time of the shift in species composition the ß value sharply falls (to 0.06-0.08) and the production/destruction ratio decreases. At the same time pheophytin in the euphotic zones rises to 90 % of total chlorophyll.

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Biogeochemical Processes in Impoundments and their Impact on Water Quality

by

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With 1 Figure and 5 Tables

Contents

Abstract

The biogeochemistry of the small reservoir Talovaya Balka (Voronezh Region, Byelorussia) was studied. The high nutrient input to the lake led to the proliferation of blue-green algae causing an increase in pH of up to 9.2-9.7 in the epilimnion. In bottom sediments processes of sulfate reduction (at a rate of 23.9 mg S/dm^3/day) and methane formation (1.27 mmol CH$_4$/dm^3/day) take place.

Anaerobic transformation of organic matter in bottom sediments generates a concentration gradient at the sediment-water interface, as well as diffusion of phosphates, hydrogen sulfide, ammonium, bicarbonate, and methane from sediments

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to the overlying water. The flux from the sediments is an additional source of nitrogen and phosphorus compounds maintaining a high photosynthetic activity in the water.

1. Introduction

In arid and semiarid regions small reservoirs commonly serve to regulate local watersheds. They are a major water source for industry, irrigation, and communities and play therefore an important role in man's life. Because of their small sizes, their aquatic ecosystems, however, can hardly stand man's impact. Even a one-time input of a small quantity of fertilizers or waste waters may trigger biological activity. In turn, this causes rapid changes in important water characteristics, such as pH, alkalinity, and of the concentrations of oxygen, nitrate, phosphate, hydrogen sulfide, etc.

2. Object and Methods

The object of study, Talovaya Balka, is an impoundment (volume: $2x10^6$ m^3; maximum depth: 8-9 m) located in the Voronezh Region, USSR. It was first filled in 1950; at present, the level is stable due to local runoff, derived from melting snow mainly.

Water samples were obtained with Ruttner's bathometer from the deepest part of the reservoir near the dam. Sediment samples were collected with a sectional gravity sampler. Porewaters were squeezed from the sediment under 5 atm pressure immediately after recovery. Alkalinity, pH, and the concentrations of oxygen and hydrogen sulfide were also measured immediately after recovery according to accepted methods (RESNIKOV et al., 1970). The contents of nitrates, phosphates, ammonium, and sulfates were determined spectrophotometrically. Prior to this, nitrates were reduced to nitrites in a copper-cadmium column. Nitrites were detected with Griss' reagent (WOOD et al., 1967). The ammonium concentration was measured with Nessler's reagent. The phosphate content was determined via phosphorus-molybdenum complex formation after phosphomolybdic acid reduction with ascorbic acid (NIKULINA, 1965).

The intensity of production-destruction processes in the water was determined from a change in oxygen content in light and dark glass bottles (ROMANENKO & KUZNETSOV, 1974). The intensity of microbiological production of methane and reduced forms of sulfur were determined with the radioactive labeling according to accepted methods (IVANOV et al., 1976; LAURINAVICHUS & BELYAEV, 1978). Radioactivity was measured on a Beckman Liquid Scintillation Counter LO-1000. The content of reduced forms of sulfur was measured according to the methods by VOLKOV & ZHABINA (1980). Methane was determined by the "head space" method with an inner standard. The gas was analyzed on a Pue Unicam gas chromatograph with a flame-ionization detector.

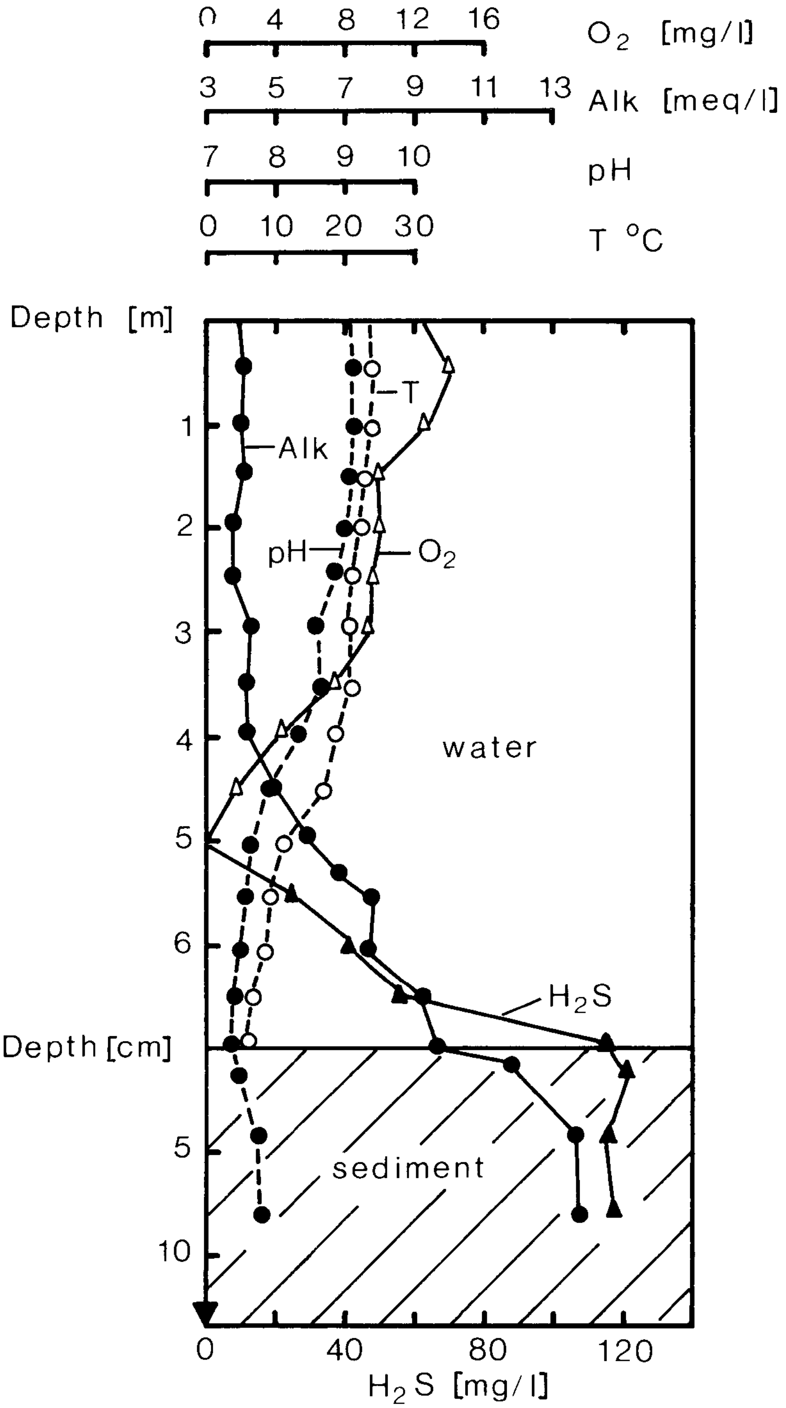

Fig. 1: Impoundment Talovaya Balka, July 1987. Vertical distribution of hydrochemical characteristics.

3. Results

3.1 Water

During the 38-year existence of the Talovaya Balka impoundment its water composition changed notably. Mineralization has increased, the concentrations of sulfate and chloride have become higher, and the sodium/calcium ratio has increased (see Table 1). At present the impoundment is stratified during summer (Fig. 1). Within the top layer of the water column (0-1 m) pH reaches 9.2-9.7 as a result of active photosynthesis. At the end of July the organic matter production yields 2.46 g $C_{org}/m^2/day$. Dissolved oxygen disappears at a depth of 5 m; instead, from 5.5 m downwards hydrogen sulfide appears, its concentrations increase up to 110 mg/l at the bottom (Fig. 1). The content of nitrates is low throughout the whole water profile (see Table 2). The concentrations of ammonium, phosphate and methane increase with depth (see Table 2).

Table 1

Ionic composition of water and porewater in mmol/l.

Sampling date	Ca^{2+}	Mg^{2+}	Na^+	K^+	CO_3^{2-}	HCO_3^-	SO_4^{2-}	Cl^-	TDS
and place					mmol/l				mg/l
1951[*] July	0.9	0.4	0.5	-	-	2.6	0.2	0.1	176
1976 April	0.8	0.6	1.9	-	-	2.5	0.7	0.4	256
1980 August	1.0	1.2	3.7	-	-	2.7	1.5	1.8	333
1986 August	1.4	1.1	4.0	0.2	0.3	4.7	1.8	1.3	670
1987 July *Water:*									
top layer	1.7	0.3	3.5	0.2	0.2	3.9	2.2	1.9	450
5.5 m deep	2.0	0.2	5.2	0.2	0.1	3.5	2.0	2.9	600
7 m deep	1.8	0.3	7.0	0.2	-	7.0	1.2	2.4	850
1987 July *Porewater:*									
0-2 cm	1.8	0.4	6.1	0.3	-	8.7	0.8	2.4	950
2-5 cm	2.3	0.2	7.0	0.3	-	10.5	0.9	2.2	825
5-10 cm	1.8	0.3	7.0	0.3	-	10.6	0.9	2.4	825

(TDS = Total Dissolved Solids)

[*] Data from ANTIPOV-KARATAEV & KADER (1953)

3.2 Bottom Sediments

Sediments of the reservoir are black, pelitic, carbonate-free silts smelling of hydrogen sulfide. Within the sediment column, acid-dissolvable sulfide sulfur varies from 1.30 to 2.46 g/dm^3. The quantities of Cr^{2+}-reducible elemental sulfur and pyrite sulfur increase with sediment depth (see Table 3). In parallel, an almost linear decrease of methane concentration takes place (see Table 2).

Table 2

Nutrient content (mmol/l) in water and porewater (July 1987).

Sampling place	pH	HCO_3^-	SO_4^{2-}	$H_2PO_4^-$	HPO_4^{2-}	HS^-	NH_4^+	CH_4
Water:								
top layer	9.2	3.90	2.20	-	0.01	-	0.05	-
5.5 m deep	7.6	3.52	2.05	0.01	0.02	0.47	0.22	0.01
7 m deep	7.6	7.00	1.20	0.02	0.04	3.33	0.66	0.03
Porewater :								
0-2 cm	7.4	8.70	0.80	0.03	0.05	3.64	0.79	0.03
2-5 cm	7.6	10.50	0.90	0.02	0.05	3.48	0.87	0.29
5-10 cm	7.7	10.60	0.90	0.02	0.03	3.48	0.74	0.26

3.3 Porewater

The mineralization of porewaters is higher than that of the water column (see Table 1). Compared to the near-bottom water, the sulfate content is lower in the porewater and the alkalinity, ammonium and phosphate concentrations are higher. Porewaters contain reduced sulfur compounds ($H_2S + HS^-$) (see Table 2), but the nitrate concentration is as low as in the water column; nitrites were not found.

Table 3

Sediment characteristics.

Depth cm	Water content %	Eh mV	$S_{H2S} + FeS$ g/dm^3	$S_{FeS2} + S°$ g/dm^3	S-R* mgS/dm^3/d
0-2	77.7	-253	1.30	0.32	23.9
2-5	77.4	-218	2.46	0.32	-
5-10	76.3	-193	1.62	0.31	9.0
10-15	73.4	-178	2.10	0.65	9.0
15-20	67.3	-178	2.35	1.00	1.8
20-25	67.7	-	1.77	1.27	0.5
25-30	69.3	-	1.89	1.27	-

* S-R = sulfate reduction rate

3.4 Intensity of Bacterial Processes

The highest rate of bacterial sulfate reduction (23.9 mg S/dm^3/day) was registered within the top layer of sediments (see Table 3). There bacterial methane production as a result of CO_2 reduction with hydrogen reaches its maximum value of 2.40 ml CH_4/dm^3/day as well. In the lowest layers bacterial sulfate reduction drops down to 0.5 mg S/dm^3/day.

4. Discussion

Photosynthesis is the main process taking place in the water column. Its activity depends to a considerable extent on the input of biogenic elements. With low nutrient input, phytoplankton develops poorly. The resulting low primary production of organic matter, low oxygen consumption, and high water transparency indicate the oligotrophic character of the impoundment. With substantial nutrient input, particularly in summer, phytoplankton grows rapidly, oxygen is often absent from the bottom water, transparency is low, and the sediments are rich in organic matter and reduced forms of iron and other metals. All this manifests eutrophication of the impoundment (KUZNETSOV, 1974).

Due to photosynthesis, the components of the carbonate system change in concentration according to:

$$H_2CO_3 <--> H^+ + HCO_3^- <--> 2H^+ + CO_3^{2-} \qquad (1)$$

$$nHCO_3^- + nH_2O --> (CH_2O)n + nO_2 + nOH^- \qquad (2)$$

$$nCO_3^{2-} + 2nH_2O --> (CH_2O)n + nO_2 + 2nOH^- \qquad (3)$$

The change of the carbonate ion concentration causes alteration of pH and alkalinity. At pH > 7.5, typical for the majority of impoundments in the central and southern parts of the USSR, organic compound synthesis, as follows from (2) and (3), is accompanied by alkalization of the water (SAVENKO, 1981).

In areas of active photosynthesis (see Table 2), high concentrations of CO_3^{2-} causing high pH values render water unusable for irrigation purposes (KOVDA, 1968). Photosynthetic processes also provoke a decrease of total dissolved inorganic carbon (DIC = HCO_3^- plus CO_3^{2-}) in the water. This carbon is transferred with sinking organic particles to the deeper water column and to the sediment where its destruction increases DIC again. Liberation of free CO_2 decreases the pH. Presence of sulfide in porewater and the overlying water contributes to alkalinity (Fig. 1). In the studied porewater dissolved sulfide ($H_2S + HS^-$) comprises from 9.5 to 25.2 % of total alkalinity (Fig. 1).

Since in sediments the redox potential is low, sulfate reduction becomes the main respirative process causing accumulation of a large amount of reduced iron compounds in sediments. Accumulation of hydrogen sulfide and hydrosulfide in porewater indicates that reactive iron has been exhausted in the sediment (VOLKOV, 1984; Ostroumov et al., 1961). High concentrations of hydrogen sulfide and hydrosulfide in porewater provoke their diffusion to the near bottom water and formation of the hydrogen sulfide layer in the water.

Mineralization of organic matter in the course of sulfate reduction causes a release of bicarbonate, ammonium, and phosphate:

$$\begin{aligned}&(CH_2O)aC\,(NH_3)aN\,(H_3PO_4)aP + 1/2aCSO_4^{2-} = \\ &aCHCO_3^- + aNNH_3 + aPH_3PO_4 + 1/2aCH_2S \qquad (4)\end{aligned}$$

where aC, aN, and aP are stoichiometric coefficients depending on the type of organic matter (Richards, 1965). In further calculations the values aC, aN, aP are taken to be equal to 106, 16, and 1, respectively, as typical for phytoplankton organic matter (Redfield et al., 1963).

It is noteworthy that in the sediments the anaerobic situation is beneficial for dissolution of phosphate compounds, and the concentration gradient provokes their diffusion to the overlying water where they can be reused by photosynthetic organisms.

Methane production ranks second among anaerobic processes. According to Kelly-Robertson (1979), intensity of methane production depends on the amount of primary production and in some cases can indicate the trophic level of the water body. The high gradient of methane at the sediment-water interface sustains methane diffusion into the overlying water where methane, after being oxidized, takes part in transformations of the carbonate system.

5. Estimates of Mass Exchange

Diffusion fluxes across the sediment-water interface were calculated according to Fick's model. The rates of sulfate reduction and methane production were measured, while the rates of bicarbonate, nitrate, and phosphate release in the course of organic matter destruction were calculated from the stoichiometric formula by Richards & Redfield cited above (see Table 4).

Table 4

Nutrient fluxes across the sediment-water interface.

	HCO_3^-	SO_4^{2-}	$H_2PO_4^-$	HPO_4^{2-}	HS^-	NH_4^+	CH_4
Diffusion[*] coefficients in 10^{-6} cm^2/sec	6.66	6.14	4.78	4.11	11.26	11.76	9.62
Fluxes 10^2 mmol/m^2/day	-312	+146	-1.67	-1.89	-145	-54	-43

[*] Diffusion coefficients from Li & Gregory (1974) were recalculated according to the equation by Stoks & Einstein for 5° C.

A comparison of Fick's model for diffusion flux with the model of multicomponent diffusion by LASAGA (1979) allowed to estimate the relative errors of the former. As seen from Table 5, the errors are rather large. We thought it was due to the fact that the main requirement for the use of multicomponent models, i.e. the requirement of electroneutrality, was not met (i.e., [Σanions] > [Σcations] (see Table 1). Then we introduced a conditional cation with a charge equal to the difference between the charges of anions and cations and calculated errors for conditional diffusion coefficients varying from 5×10^{-6} to 20×10^{-6} cm^2/sec (see Table 5). As seen from Table 5, for coefficients 10×10^{-6}, and 15×10^{-6} cm^2/sec the errors in flux calculation according to Fick's model never exceed 15 %, which is quite acceptable.

Table 5

Errors in calculation (in %) of fluxes through the sediment-water interface according to Fick's model as compared to a multicomponent diffusion model, %.

For diffusion coefficients in 10^{-6} cm^2/sec	HCO_3^-	SO_4^{2-}	$H_2PO_4^-$	HPO_4^{2-}	HS^-	NH_4^+
Without regard of electroneutrality						
	-35.6	+17.0	-10.1	-50.1	-151.6	+17.6
With regard of electroneutrality						
5	+18.2	+10.8	-5.7	-24.3	-54.8	+11.1
10	-6.0	+4.2	-2.0	-7.7	-15.0	+4.4
15	+3.0	-2.5	+1.1	+3.8	+6.6	-2.5
20	+9.9	-9.4	+3.7	+12.3	+20.2	-9.8

6. Conclusion

It has been shown that an intensive photosynthetic activity of microorganisms and algae in the top layer of the studied impoundment causes a pH increase up to the values toxic for irrigated plants. In the lower layers oxygen is consumed as a result of organic matter destruction almost completely and water DIC increases.

Destruction of organic matter in the sediments of the studied reservoir yield carbon dioxide, hydrogen sulfide, methane, nitrogen and phosphorus compounds, which diffuse to the overlaying water. Ammonium and phosphate inputs to the water maintain a high photosynthetic activity.

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A Small Simulation System for Modeling the Carbon Cycle in the Krasnoyarsk Reservoir

by
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With 10 Figures

Contents

Abstract

We propose to adopt an originally biophysical approach for developing water quality prediction models for a model of the Sydinski Bay of the Krasnoyarsk reservoir. This approach is based on a theoretical and experimental analysis of laboratory model ecosystems. We also give an outline of the Small Simulation System, intended for simulation experiments with models of aquatic ecosystems. An analysis of hydrobiological and hydrological predictions for some variants of the model shows that on average the simulation results are in qualitative, and for some

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components, in quantitative agreement with observation data throughout the season. We also compare theoretical and experimental estimates of the type and strength of intrapopulational relations effective in the bacterioplankton component of natural ecosystems.

1. Introduction

Water quality prediction and forecasting the state of aquatic ecosystems becomes a vital problem given an increasing shortage of fresh water.

In this paper, we consider a non-conventional approach to water quality modelling, based on biophysical theoretical and experimental research. Several steps have to be taken. First, the laws that govern the organization, stability, and controls of "ideal" laboratory ecosystems must be investigated. Second, the means to determine chemical and other density-dependent factors (autostabilization phenomena) must be identified which, third, suggest field experiments to determine the limiting factors in the natural ecosystems (based on autostabilization). Fourth, experiments with identified chemical factors and some other hydrobionts to measure kinetic parameters must be carried out and, fifth, the ecosystem model must be synthesized, incorporating the obtained kinetic characteristics. Sixth, the model must be verified on basis of the existing evidence (i.e., relating it to a similar water body) and seventh computations of the forecast and overall cost estimates of ecological implications of the project must be conducted.

2. Results and Discussion

2.1 Laws of an Ideal Community

An ideal community is an array of populations the density dynamics of which are governed exclusively by environmental chemical factors, which, in turn, might be influenced by the actual population numbers. Some of these factors may originate outside the system or may be supplied from within. A sufficient degree of environmental homogeneity is also assumed.

In order to obtain the general conditions relating the number of coexisting species in the community to the number of density-dependent chemical factors in the environment, we consider a mixed culture with no predation. It is convenient to start with a theoretical analysis of interacting populations (i.e., bacterial) with a model of DEGERMENDGI (1981) describing the density dynamics of m species in an open system of the chemostat type (DEGERMENDGI et al., 1979). We assume the SGR (specific growth rate) for each species to be dependent on or controlled by a few (n) medium factors which, in turn, are controlled by the actual densities of these species.

We arrive at the following system of differential equations,

$$X_i = [g_i(A_1,,A_n) - D] * X_i;\ i = 1,,m; \qquad (1)$$

$$A_j = D^*(A_{j0} - A_j) + \sum_{k=1}^{m} a_{jk}{}^*f_{kj}{}^*(A_1,,A_n) * X_k;\ j = 1,,n;$$

where $g_i(A_1,,A_n)$ is the SGR for the ith species, D is the flow rate, A_{j0} and A_j are, respectively, the input and medium concentrations of the jth growth-influencing factor (some of A_{j0} can be zero). The term $a_{jk}f_{kj}(A_1,,A_n)X_k$ stands for the production or utilization rate of the jth substance by the kth species.

It is obviously very difficult to suggest any "versatile" form of g_i as a function of $A_1,,A_n$. However, using the form of the system of equations (1), it can be shown that the number of species in steady-state coexistence will not possibly exceed the number of independent growth-controlling factors, determined by the densities, X_i, of these species (i.e., $m <= n$). In the following, this "ecological theorem" for mixed cultures will be called the principal statement or the extension of the Gauß principle.

Autostabilization of density-dependent chemical factors. The essence of this phenomenon consists in the lack of dependence of the steady-state (mean) level of concentration of the growth-limiting factors in the ecosystem upon the input rates of these factors. Theoretically, this result follows from an analysis of the relationships for the steady-state concentrations $\underline{A}_j$ in equation system (1) assuming an equal number of species and factors, i.e., $m = n$.

$$\underline{A}_j = r_j(D) = f(A_{j0});\ j = 1,,n$$
$$\underline{X}_i = \phi_i(A_{10},,A_{n0});\ i = 1,,m$$

In other words, there is a correlation between population biomasses and input concentrations of the limitants and no correlation with the background level of the limiting factors. Hence, no correlation should be observed between the limited-population biomass and the background limitant concentration.

2.2 Prediction Models

The above results have been used as a basis to develop water quality prediction models for the part of the Krasnoyarsk reservoir which suffers most from algal bloom, the Sydinski Bay. The work was conducted within the scientific project "Clean Yenisei".

Field evidence (Fig. 1) provided the information about the kinetics of the system. In 1984, the dynamics of PO_4^{3-} and the net algal biomass in the bay were monitored at station No. 1 (Fig. 2). Phosphorus was selected because it is a possible limiting factor for productivity. We have made an attempt to test the theoretical results discussed above which imply the absence of a correlation between the background level of the limiting factor with the amount of biomass present under limiting conditions.

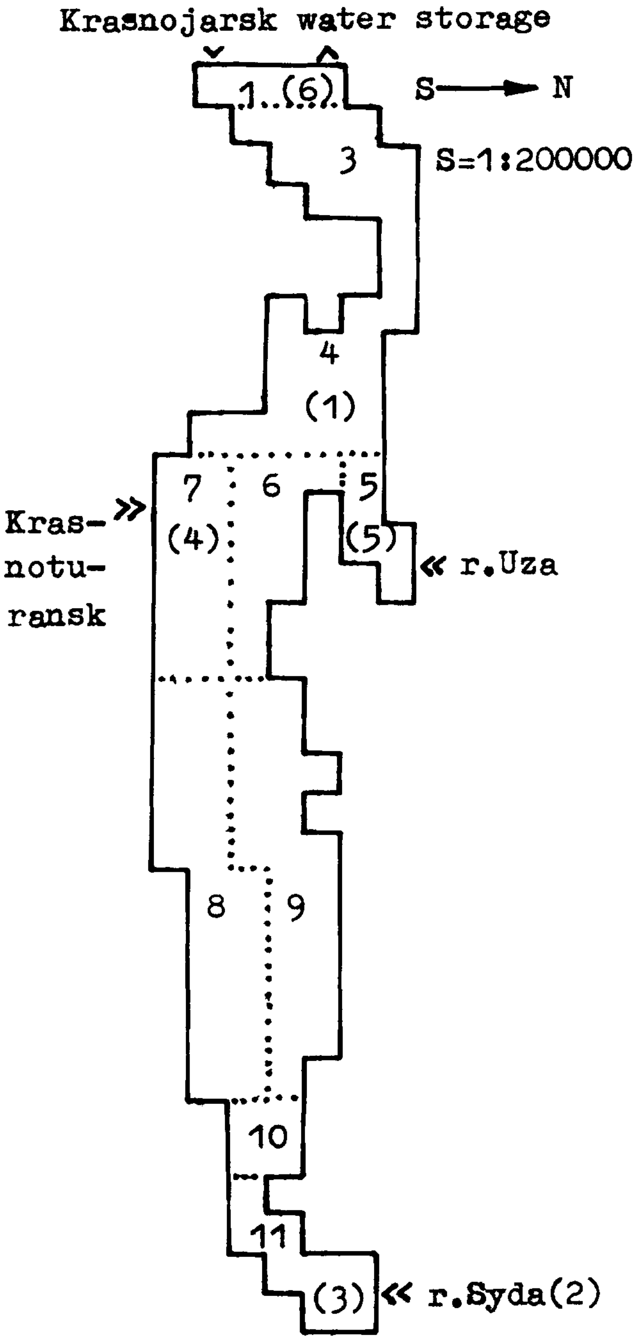


Fig. 1: Map of compartment boundaries (...), compartment numbers and field station numbers (bracketed) in Sydinsky Bay (30.07.1985).

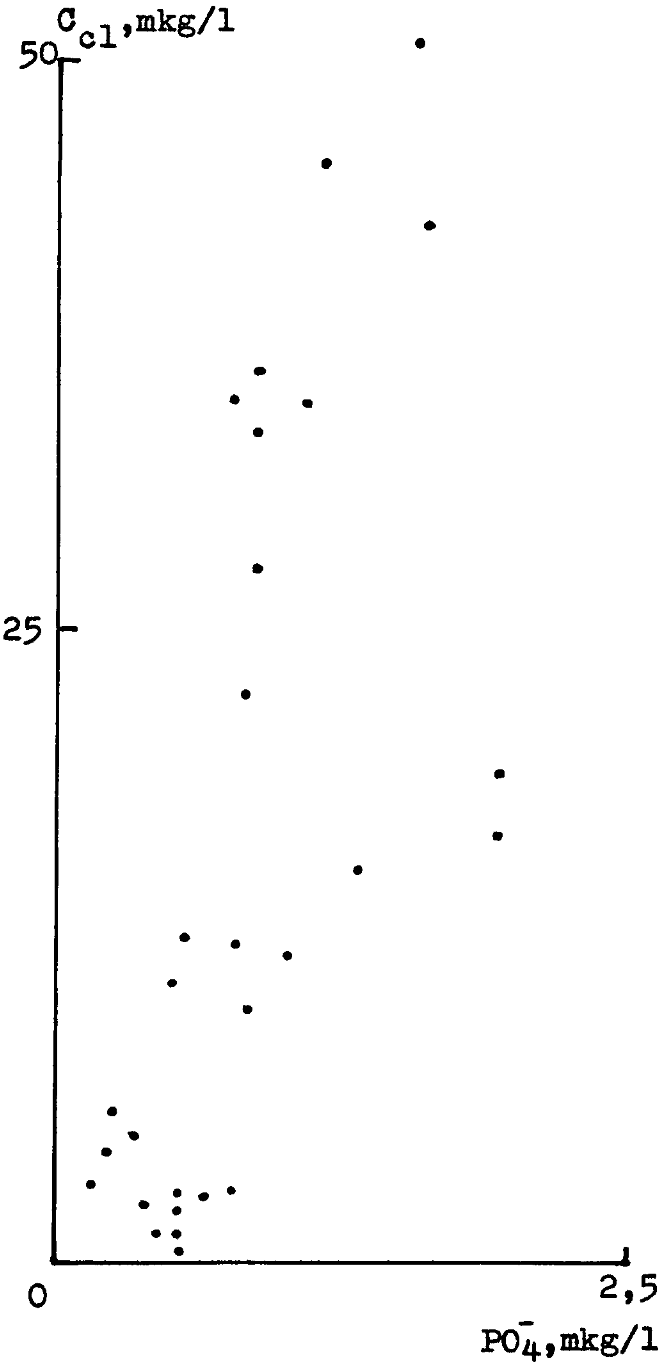


Fig. 2: Observed distribution of concentrations of chlorophyll a, C_{cl}, and phosphorus, 24.08.1984 to 29.08.1984, in the Sydinsky Bay (station No. 1).

The biological results obtained are shown in Figure 2. Actually, instead of the algal biomass, the concentration of the chlorophyll *a*, C_{ch}, was measured which, over short periods, is directly related to the biomass. The value of C_{ch} can be translated into the equivalent amount of phosphorus, C_p, which sustained the algae growth and the formation of the associated quantity of chlorophyll. According to KISELEV (1969), $C_p \approx 0.325\ C_{ch}$. Then, the range of variation in the phosphorus input concentration, δC_{p0}, can, corresponding to the observed chlorophyll content variation ($\delta C_{ch} \approx 50$ μg/l, Fig. 2), be estimated to amount to $\delta C_{p0} \approx 16$ μg/l. The variation range of the phosphorus background concentration can be approximately estimated from Figure 2 to 1.6 μg/l, i.e. one-tenth of the input concentration. This fact provides a serious basis for an experimental test of the limiting action of phosphorus, and this was done during the 1985 field work season. We obtained the SGR for blue-green algae (*Aphanizomenon flos-aquae*) as a function of the PO_4^{3-} concentration, P: gBGA($GBGA_{max}$,P). Similarly, the following kinetic curves have been obtained: gB(GB_{max},DOM) which is the SGR of aggregated bacterioplankton versus dissolved organic matter, and $GB_{max}(t^o)$. The characteristics for diatomaceous algae, gDA and also GBGAmax(E,t^o) (E is illumination and t^o is temperature) have been taken from TILMAN (1986).

In addition to SGR as a function of limitants, given the particular features of ecosystem models of type (1), one can both theoretically and experimentally estimate the "strength" and the "type" of the intra- and interpopulation interactions. As a criterion one can use the nature of the "acceptor" population growth acceleration in response to the fluctuation of the biomass level of the "donor" species (DEGERMENDGI & ADAMOVICH, 1984). In practice, for example, as an estimate of the influence exerted by bacteria upon themselves, this quantity, B_{bb}, (b --> b at $\delta X_b = 1\ g/m^3$) can be calculated from the relationship:

$$B_{bb} = \ln \frac{X_f^{e} * X_i^{c}}{X_f^{c} * X_i^{e}} / [(\delta t)^2 (X_i^e - X_i^c)]$$

where the subscript i denotes the initial time and f the final time, and the superscript symbolize either the experiment, e, or the control, c. According to the data of 01.09.1986 from station No.1, $B_{bb} \approx -(0.072 \pm 0.021)\ h^{-2}$. The same quantity can be estimated theoretically and collated with the experimental value, which would allow to test the adequacy of accounting for interpopulation interactions.

Using field data about ecosystem components plus experimental data, the ecosystem model was formulated (similar to (1)) and is shown as a block diagram in Figure 3.

The ecological model was incorporated in a specially designed simulation prediction system suitable for personal computers. The system features the following principal units: a hydrological unit (implementing gravitational, wind and residual currents), the water body morphology unit, the ecological unit, etc.

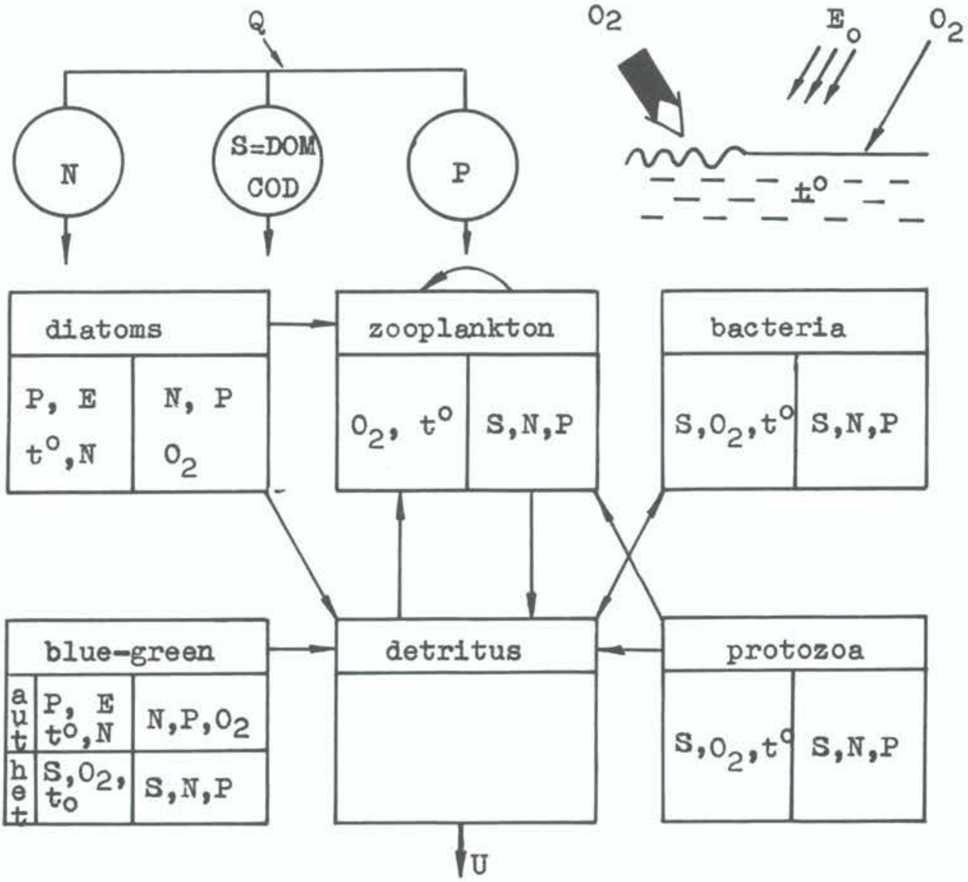


Fig. 3: Block-diagram for the Sydinsky Bay ecosystem model. In the boxes: left - elements utilized and growth conditions; right - produced substances. Limiting trophical relations indicated by arrows. O is the matter flow, N is nitrogen, S is DOM, P is phosphorus, O_2 is oxygen, t^o is temperature, U is the sedimentation rate; auto stands for autotrophic growth component, and het. - for the heterotrophic component.

The SSPS (small simulation prediction system) is intended to be used in mathematical simulation experiments of aquatic ecosystems (lakes, water reservoirs, bays, rivers).

A sequential computation flowchart is implemented. First the hydrological parameters are calculated by the Eulermethod. Then, after hydrological mixing, the ecological parameters of the ecosystem are computed.

The model is quite versatile. To adjust it to a new water body, one has to specify the bathymetric map, to identify surface compartments, to set the appropriate input series (either retrospective or predicted ones), and to describe the corresponding hydrometeorological conditions (winds, precipitation, evaporation, solar radiation, water temperature, etc.).

The ecological unit of the model (ECOS) describes the ecosystem processes for different water layers and is designed using results of special experimental tests and published data as well as hypotheses pertinent to the problem.

The input (time) series unit (ISU) provides information about the known external parameters for the given ecosystem (ISU is a local data bank of spatial and temporal characteristics).

Multivariant calculations taking into account hydrological, meteorological and other information relating to the model (Fig. 3) have been carried out for the following ecosystem structures (denoted by 1, 2, 8 in Fig. 5):

1. hydrological model alone, biological processes are "frozen";
2. bacterioplankton is limited by the available organic matter, no other components;
3. the following components are present: diatomaceous and blue-green algae, bacteria, protozoa, organic matter, phosphorus, nitrogen, no zooplankton and no transformations;
4. equal to experiment 3 but with transformations;
5. like experiment 3, except that gDA is increased and zooplankton is introduced (3);
6. like experiment 5, but with transformations;
7. like experiment 6, except that gDA is increased further still;
8. similar to experiment 3, but also including zooplankton cannibalism as well as transformations, gDA is somewhat smaller.

Component dynamics due to hydrological processes. Figures 4 to 9 show calculations for the eight variants along with the observation data (+).

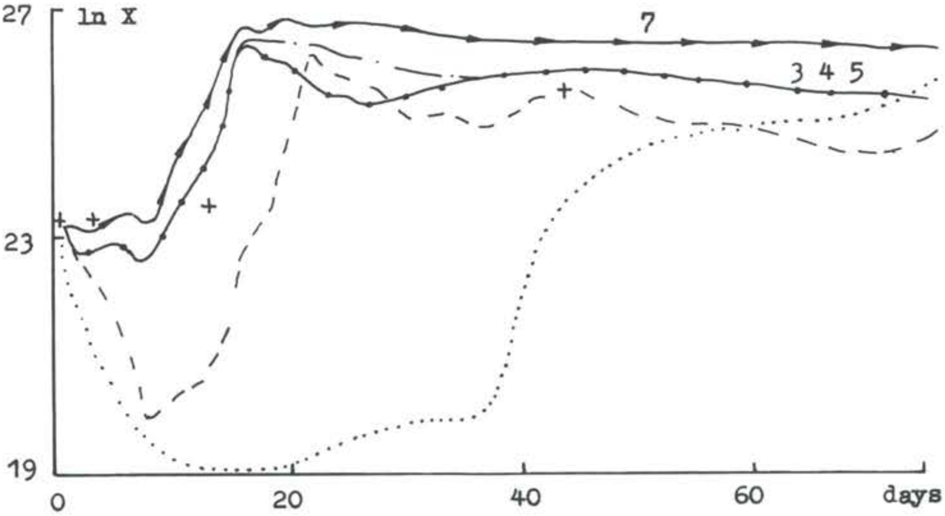


Fig. 4: Bacterial dynamics, compartment No. 1.

Throughout the seasons, but excluding the bloom period, the hydrological calculations (variant No. 1) turn out to be qualitatively, and for some compartments and components also quantitatively, close to the observations. This is particularly true for compartments No. 5 and No. 11 which are strongly affected by tributary rivers (Figs. 5 and 6) which create continuous-flow conditions (especially so for compartment No. 11).

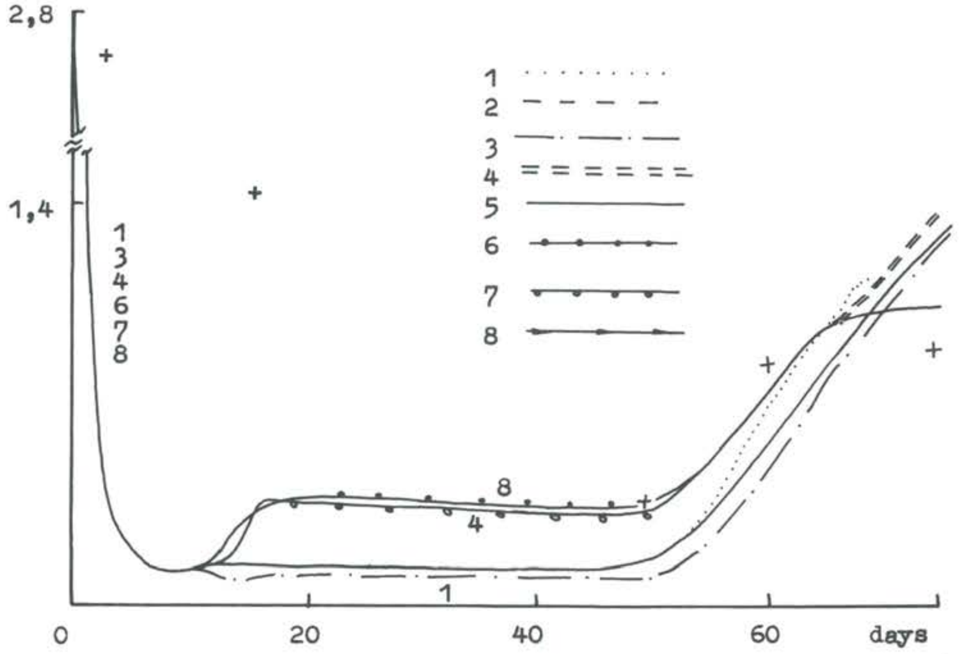


Fig. 5: Dynamics of the total mineral nitrogen (here and in the following all components in g/m^3); compartment No. 11.

The dynamics of aggregated bacterioplankton, B, and COD. The dynamics of B are related to the variations of input of the growth-limiting organics into the compartments. Wherever this inflow declines, bacterioplankton dies back and the density of B decreases (especially in compartments 4 and 7 which lack strong substrate inflow). An important implication of this result is that the inflow of allochthonous organic matter cannot by itself adequately explain the observed B dynamics, and the formation of additional autochthonous matter has to be assumed. This was the reason to advance to more complex ecosystem models.

The dynamics of the ecosystem with the turnover taken into account. In this and the next calculation variants we shall discuss only the dynamics of some specific biological components of the ecosystem because, and this we have to admit, the dynamic of hydrochemical components (COD, total mineral nitrogen and phosphorus) does not show much change in various ecosystem variants.

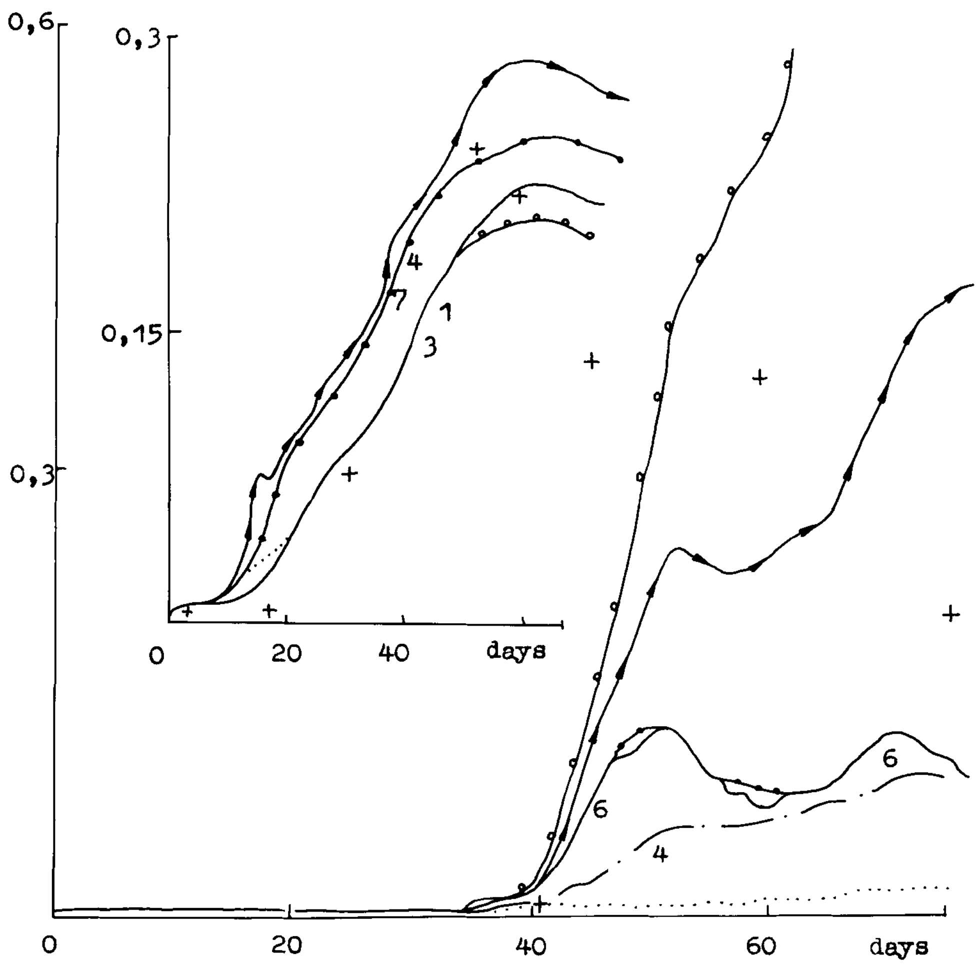


Fig. 6: Dynamics of phosphorus, compartment No. 11.

Fig. 7: Blue-green algae dynamics, compartment No. 11; for variants 5 to 8 the scale is increased by a factor of 10.

Diatoms. The obtained DA dynamics are quantitatively quite close to the experiment in the flow-through regions (Fig. 8) and qualitatively for compartment No. 7, with the calculation according to variant 8 (with the zooplankton cannibalism). In the absence of the pressure of zooplankton, the number of DA rises to very high levels. It follows that the zooplankton growth kinetics and the nutrient ranges are bound to play an important part in the DA "blooming" kinetics (particularly so in the fall).

The blue-green algae. The calculated BGA dynamics (Fig. 7) resemble observations less than in the case of DA, although the autumn explosion phase is reasonably well predicted in variants 7 and 8 (increased SGR of DA or cannibalism, bringing down the numbers of zooplankton). We are as yet unable to adequately reproduce the fall-off phase in BGA numbers because of the obvious lack of information about the real mechanisms of this process.

Bacterioplankton. The calculated dynamics of the seasonal change of the feedback coefficients B_{bb} for several ecosystem type variants, which take into account the dynamics of COD, temperature, etc., is presented in Figure 10. We can see intraseasonal peaks in the size of the negative feedback in the B control (B_{bb} up to -0.005 h^{-2}). If the COD level, a limiting factor of B, were as actually observed, then B_{bb} would be = -0.004 h^{-2} (see the beginning and the end of the season in Fig. 10). The natural level of B_{bb} is of the order of -0.07 h^{-2}, i.e. some 20 to 200 times larger than obtained theoretically. The sign of the feedback (i.e., negative) coincides with the prediction. Therefore, the natural "amount" of feedback in the B regulation is

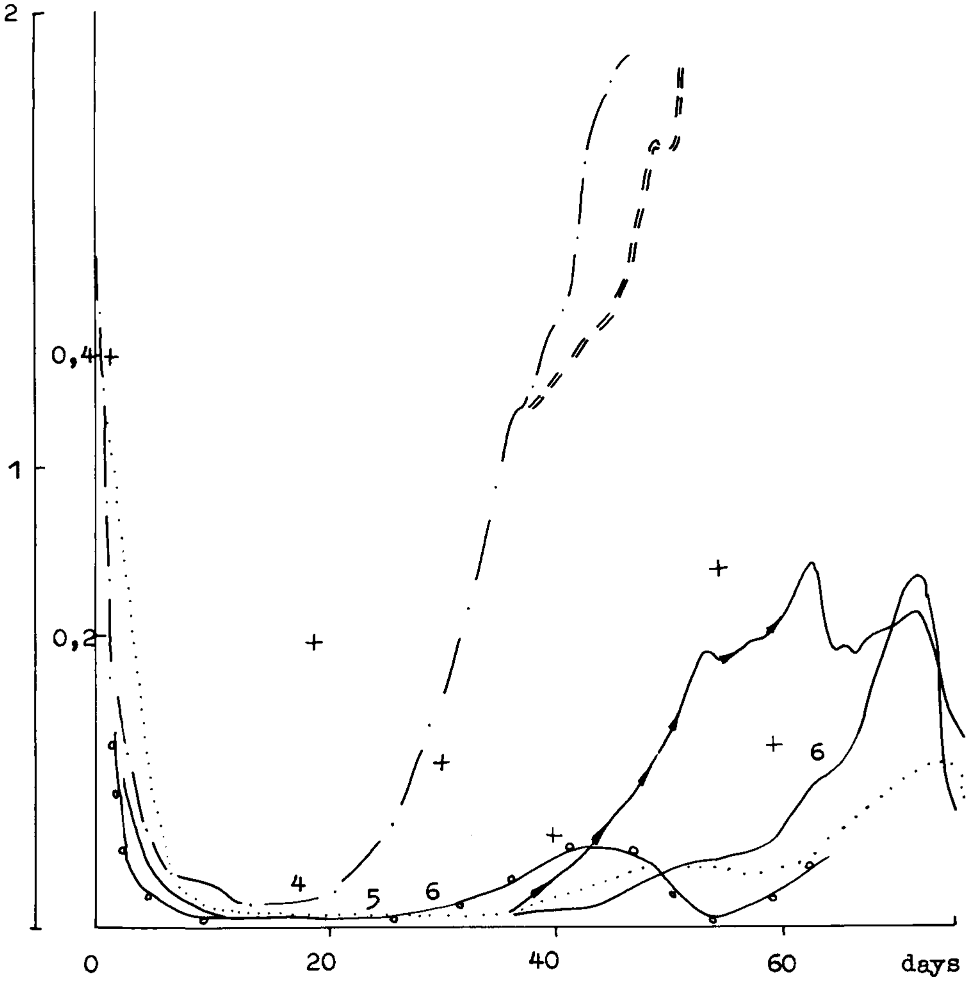
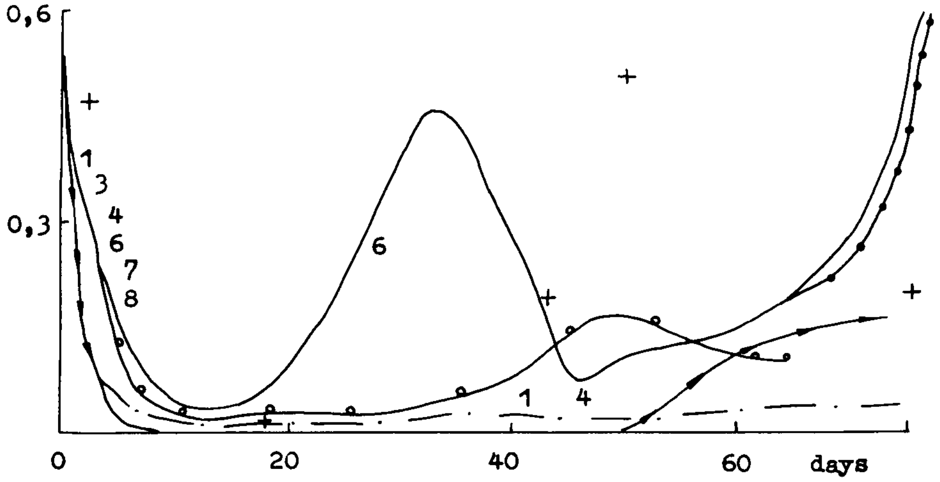


Fig. 8: Dynamics of diatoms, compartment No. 11; data and calculation variants plotted on the right scale (in g/m^3).



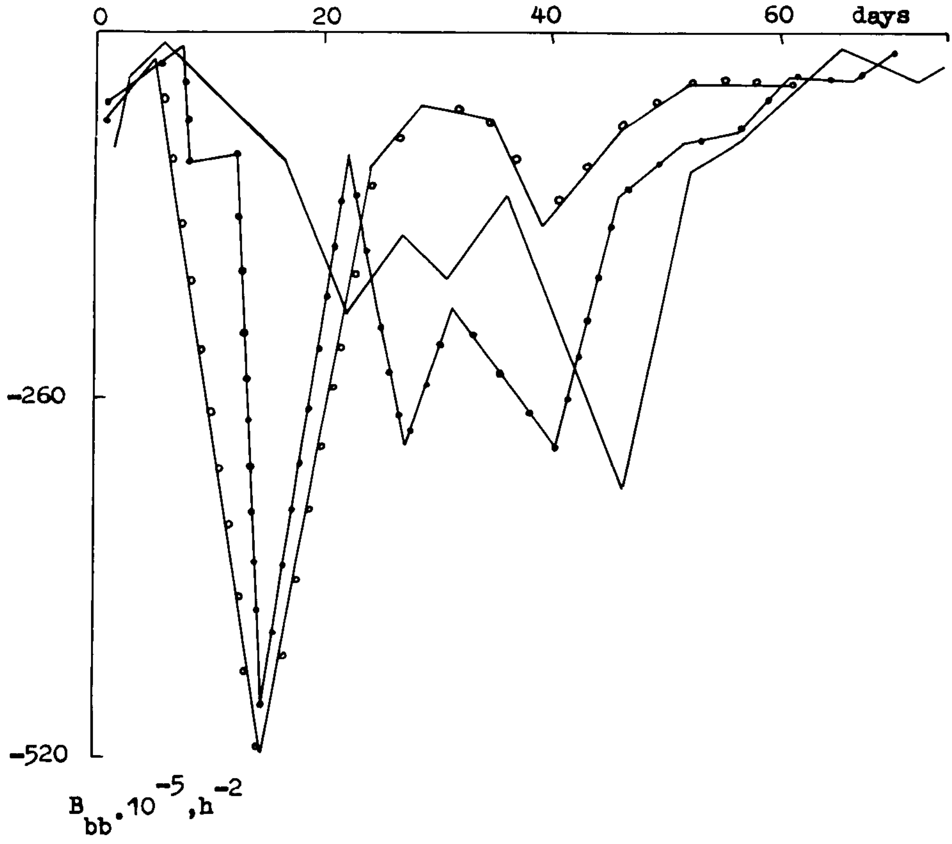


Fig. 9: Dynamics of aggregated zooplankton, compartment No. 11.

Fig. 10: Calculated seasonal dynamics of the feedback coefficient in bacterial control, B_{bb}, obtained with $\delta X_B = 1$ g/m^3, compartment No. 11.

substantially larger than in the theory. There are several hypothesis that could explain this discrepancy. The proposed parameters B_{ij} are an essentially new criterion to test model validity and to obtain new knowledge about the nature of intraecosystem relations (B_{bb} is just one of such parameters).

3. Conclusion

1. A non-conventional approach is proposed for developing prediction models for water quality. This approach is based on a theoretical and experimental analysis of laboratory ecosystems and "idealization" of some hydrophysical parameters (ideal mixing, thermostabilization).

2. The analysis of stable laboratory communities has led to the following conclusions: (a) the number of coexisting species is not greater than the number of environmental factors (an extension of the Gauß principle); (b) spatial heterogeneity plays only a very small part in species coexistence even under the conditions of weak exchange flows; (c) the importance of the autostabilization effect. These principles were made the basis of the ecosystem model for the Sydinsky Bay of the Krasnoyarsk reservoir.

3. Multivariant calculations of the ecosystem dynamics were in reasonable agreement with the field observation data. For the first time the theoretical and experimental estimates can be compared as to type and strength of natural intrapopulation relations in the aggregated bacterioplankton component. In conclusion, the obtained model adequacy is by no means less accurate than in more conventional approaches.

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Anthropogenic Effects upon the Inner Water Bodies and the Preservation of Endemic Forms

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Contents

Abstract

The reaction of the biota on anthropogenic impacts can occur on three levels, that of the organism, that of populations and that of ecosystems. The type of the reaction depends upon intensity and duration of the contaminant release. The phenomenon of the endemism dynamics can serve as an indicator of the changes in ecosystem conditions and of the anthropogenic pressure on biotic turnover. Endemic species win under steady-state conditions, while under anthropogenic pressure and in the case of environmental shifts they lose to the species capable of fast adaptation. The knowledge of population kinetics of a given ecosystem as well as a good monitoring system are required for the evaluation and prognostication of the ecosystem development at each trophic level.

1. Three Types of Biota Response to Anthropogenic Impact

Biota can, upon an anthropogenic disturbance, react on the levels of the organism, of populations and ecosystems.

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The organism level is the most susceptible and the most rapidly reacting. It is characterized by changes of the organism behavior and physiology within the limits of the genetically governed reaction norm. At this level the action of the toxic substances can be overcome if the flow of the contaminant is relatively low. Typical examples of physiological changes include the modification of the susceptible elements, like replacement of metabolic routes by those less susceptible to a given inhibitor, permeability decrease of the membranes, the inhibitor inactivation etc. Physiological adaptations represent a substantial component of the total biota adaptation mechanism.

A long-term contamination effect activates the protection mechanisms at the next level: that of specific populations.

In populations with high multiplication rates and short duration of generations, rapid changes can occur in favor of mutant forms more resistant to the contaminant. Many examples of rapid changes (in the order of a few days or even a few hours) are known for microbial populations both for laboratory conditions and in the natural environment. Perhaps, the universal propagation of antibiotics-resistant populations of pathogenic microorganisms (PECHURKIN, 1978; FRANKLIN & SNOW, 1984) can serve as the most vivid demonstration of changes of this type. The populations of organisms with long development cycles and retarded changes of the generations (one micro-evolutionary transition usually requires 30-50 generations) are more characteristic for the replacement of susceptible species by previous, closely related and more resistant versions capable of performing the same metabolic functions.

The replacement of the species is usually associated with a change in the number of links of the trophic chain, and therefore, one can talk about the third level of response of the living systems to contamination, i.e. the ecosystem level. Unfortunately, even in this case one does not have to go far for examples. The breakdown of the trophic chains during the eutrophication of lakes, and the development of decomposition chains with the predominance of blue-green algae and heterotrophic bacteria become a common picture characterizing unfavorable results of anthropogenic effects.

2. Endemism Dynamics as an Indicator of Ecosystem Changes under Anthropogenic Impact

Preservation of Siberian endemic species, particularly in Lake Baikal and in its district, is a most urgent problem. It has become especially acute in the last few years due to the growing anthropogenic effect upon local ecosystems. But the quantitative aspects of endemism were studied rather poorly, so far. A high degree of adaptation to certain ecological conditions, which very often fluctuate only slightly, is considered to be one of the main characteristics of endemic species. For example, under conditions of limited growth the endemic species is capable of exploiting the limiting substrate (food) down to lower concentrations than its competitors in a given habitat. This capability gives the endemic species appreciable advantages both in evolutionary and ecological aspects in a population of competing organisms.

However, the long-term adaptation to steady-state conditions narrows the borders of the range of tolerable conditions and raises the vulnerability of the species to changes in the environmental parameters. This narrowing of tolerable conditions is characteristic for all types of specializations.

In contrast to highly adapted specialists the "generalists" are capable of existing over a wide spectrum of ecological conditions. This permits them to displace specialists under changing ecological conditions including those caused by human activity.

When analyzing the responses of Lake Baikal ecosystems to anthropogenic impact, results of this impact are detected at all hierarchic levels. The behavior responses of fish to toxic substances can serve as one of the most sensitive indicators of Baikal water contamination (NOVITSKY, 1981). Under experimental conditions Baikal endemic fish (omul, goby) display an avoidance response to toxic substances (phenols, copper sulfate, paper and pulp industry effluents) at concentrations dozens and hundreds of times below that of avoidance concentrations for other Siberian fish (roach, minnow). The concentration of the pollutants disturbing feeding behavior in endemic and general Siberian populations has appreciably shifted; for phenol by a factor of 10, for copper sulfate by a factor of 100. A high susceptibility of endemic organisms to pollutants should also affect their migratory routes in Lake Baikal and thus result in population and ecosystem changes.

The development of the weed *Elodea canadensis* (ditch-moss, water-thyme) in a number of southern Baikal sites where it has not been detected previously (Bolshie Koty Bay) may be a first manifestation of population changes in local ecosystems of Lake Baikal. This water-weed is a typical generalist, it competes with the narrow specialist, the endemic *Draparnaldia*. In our experimental determinations of photosynthesis (using an electrode method) both in clear Baikal water as well as in Baikal water after the addition of industrial effluents, *Elodea canadensis* samples did not change their activity, whereas *Draparnaldia* samples changed their photosynthesis rate by 10-20 %.

The Lake Baikal biota responses to contamination at the ecosystem level are characterized by a proliferation of bacteria and fungi capable of utilizing discharges of the industrial effluents containing sulfates and cellulose.

3. Conclusions

The phenomenon of endemic species dynamics may serve as an indicator for changes in the conditions of an established ecosystem including the anthropogenic pressure on each link of the biotic cycle. But it is quite possible that this indicator will be noticed too late, after the change became irreversible.

However, if we do not only want to understand these phenomena, but also to make forecasts of the ecosystem development at every trophic level we must know quantitatively the growth and development kinetics of the populations representing a given ecosystem. From this point of view it is evident that Baikal endemic species are insufficiently studied. A sophisticated monitoring system is required in order to determine the specific kinetic constants of each link. Only then it may be possible to preserve the most valuable gene pool and phenotype complexes of endemic species which have evolved over time in the Baikal region.

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Environmental Impact of Man-Made Lakes on River Physico-Chemical Systems: Case Studies of Nigeria

by

OLASUMBO MARTINS & EMMANUEL A. OLOFIN*)

With 3 Figures and 2 Tables

Contents

Abstract

This article attempts to evaluate the effect of dams and reservoirs on river systems using case study examples of Nigeria. While taking an overview of reservoir distribution in the country, it becomes obvious that:

(i) 12.5% of Nigeria's land surface is covered by inland waters;

(ii) Kano State alone accounts for 31% of existing reservoirs in Nigeria;

(iii) Kano State and three others (Niger, Gongola and Sokoto) States possess close to 80% of total artificial dams and reservoirs.

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The above facts dictate the focal areas considered.

An assessment of post-dam changes is made with particular reference to major climatic zones: sudano-sahelian, tropical humid, savanna, and the humid (forest) zones - as well as the biological environment, in the country. Both positive and negative effects of dam/reservoir construction are discerned upstream and downstream of the regulated rivers.

The Kano and Chalawa channels are used as case studies to evaluate channel geometry on post-dam era, while the Kainji Lake is revisited in order to assess possible hydro-chemical speciation downstream of the lake with special consideration to more recent chemical data collected from the outflow station. Further, from the inception of the Jebba Dam, a quantification of total water volume exported through the Niger drainage basin is undertaken, taking cognizance of the installation, recently, of more dams within the basin. Only 127 km^3 of water is discharged through the Niger system in contrast to 200 km^3 usually presumed in most publications.

1. Introduction

River regulation may take several forms, principally dam construction, canalization and stream diversion. In Nigeria, regulation by dam construction is the most common and the only form that is widely discussed in the literature. The first attempt in the country at what may be considered the fore-runners of dams are low barrages in form of dykes and bunds in the Sokoto Basin about 1918, which was washed away in 1922 by floods (ADAMS, 1985) followed by another attempt in Kware, the same basin in 1925, which was also washed away in 1940. However, the first set of real dams occurred in the 1950's in the humid zone mainly for domestic water supplies to small towns. We would like to call these "municipal" dams. It is open to debate which was the very first municipal dam, but it is believed that the first one was constructed in 1954 at Erinle on one of the tributaries of River Oshun. By 1960 about 67 towns were supplied from reservoirs behind similar dams, mostly in the south-western part of the country (FANIRAN et al., 1977; AYOADE & OYEBANDE, 1978).

The first major (and so far the largest) construction work and one that is multi-purpose is the Kainji Dam on River Niger at Bussa, which was completed in 1967 and commissioned in 1968. From this point, dam construction moved to the sudano-sahelian zone, where the main objectives are irrigation and urban water supply. One of the first dams here is the Birni Kudu Dam (principally a municipal dam) commissioned in 1969, followed in quick succession by Karaye, Bagauda Tiga and other dams in the Kano Region.

In the late 1970's dam construction again returned to the humid south-western zone, where Ojirami Ero, Ikeregorge and Oyan are examples. In the Guinea zone, the Jebba and Shiroro were constructed. Today, the sudano-sahelian zone is littered with myriads of earthfilled reservoirs. A total of 22 operating dams exists and 13 others are being constructed or are in the design state.

In this paper two dams on the headstreams of the Hadejia River and on the Niger River are selected as cáse studies to discuss the environmental impacts of dams in the sudano-sahelian Guinea and rainforest ecological zones of Nigeria. The variables under discussion include the quantity, duration and regime of reservoir and stream water. A 'pre' and 'post' approach is pursued in order to isolate the effects of dam construction on these variables.

2. Case Studies

2.1 The Kano River and Chalawa River Basins

At least 22 dams are in operation in the Kano State (Table 1), a good number of which are located in the Kano and Chalawa basins (Fig. 1). Of these, the Tiga

Table 1
Inventory of man-made lakes in Kano State of Nigeria.

Location	Surface area of reservoir (km^2)	Total capacity (x 10^{6}m^3)	Rank	Catchment area (km^2)
1. Birnin Kudu	0.61	1.19	21	40
2. Bagauda	3.76	22.14	9	207
3. Karaye	1.98	17.22	12	80
4. Keffin Gana	1.8	n.a.	19	n.a.
5. Tiga Dam	178	1,968	1	6,641
6. Ibrahim Adamu	2.63	7.99	17	n.a.
7. Ruwan Kanya	2.50	n.a.	16	n.a.
8. Tomas	14.97	60.3	6	585
9. Mohammadu Ayuba	1.16	5.54	20	n.a.
10. Jakara	16.59	65.19	5	559
11. Gari	33.18	214	3	1,155
12. Kafin Chiri	8.42	31.12	7	225
13. Warwade	5.26	12.3	13	106
14. Tudun Wada	3.5	20.79	10	85
15. Watari	19.59	104.55	4	653
16. Guzuguzu	6.35	24.6	8	106
17. Magaga	3.72	19.68	11	119
18. Pada	4.09	12	14	62
19. Marashi	2.15	6.77	18	43
20. Kango	1.55	8.73	15	41
21. Rimin Gado	0.10	0.26	22	5
Subtotal:	313.91	2,602.37		10,712
22. Chalawa Gorge*	101.17	969	2	3,859
Grand Total:	415.08	3,571.37		14,571

* nearing completion n.a. = not available

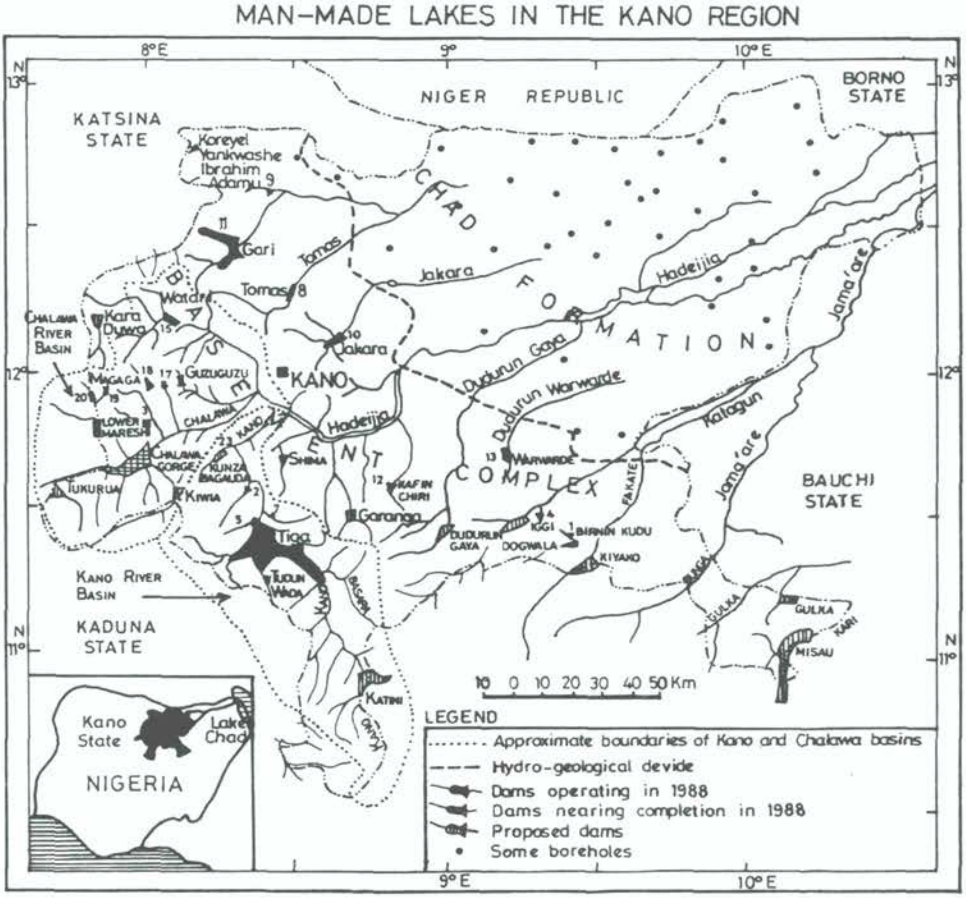

Fig. 1: Man-made lakes in the Kano region.

Dam is the biggest and the most effective (OLOFIN, 1984). It is built at a point, where it controls about 91 % of the normal flow of River Kano. Together with the Bagauda Dam about 95 % of the normal flow of the river is controlled at the point of observation in Chiromawa. The reservoir behind the dam is the largest in the sudano-sahelian zone of the country containing 1970 x 10^6 m^3 at full capacity, with a surface area of 178.1 km^2 at that capacity. So far, the reservoir has achieved its full capacity only on three occasions: in the wet seasons of 1975, 1980 and 1988, while there was one occasion (1983/84 dry season), when the storage was as low as 40 % of the full capacity due to drought, evaporation, use, and excessive release (WRECA, pers. comm.). Apart from release into canals for irrigation, the management of Tiga Dam maintains perennial flow in the natural channel downstream of the dam.

On the other hand, the operating dams in the Chalawa River Basin to date (Sep 1988) are on the tributaries of Hadejia River and together control about 40 % of the normal flow of the river at the point of observation. The Chalawa Gorge Dam, now under construction on River Chalawa itself is expected to raise the control in the basin to about 90 %. Also, the management has not maintained regulated discharge in the channels downstream of the dams.

2.1.1 Downstream effects

Figure 2 illustrates the configuration of the discharge hydrographs of Kano and Chalawa rivers before and after dam construction. If we consider a mean monthly discharge less than 1 m^3/sec as dry, the Kano River before all dams (time t) was seasonal, dry for five months. It has changed to a perennial stream, however, at time t + 1 (after the major dams). Also, the variation between the seasons has been narrowed down from a pre-dam range of 0 to 164 m^3/sec to a post-dam range of 7.1 to 28.0 m^3/sec, while the mean annual discharge decreased from 37 to 13.2 m^3/sec, i.e.,

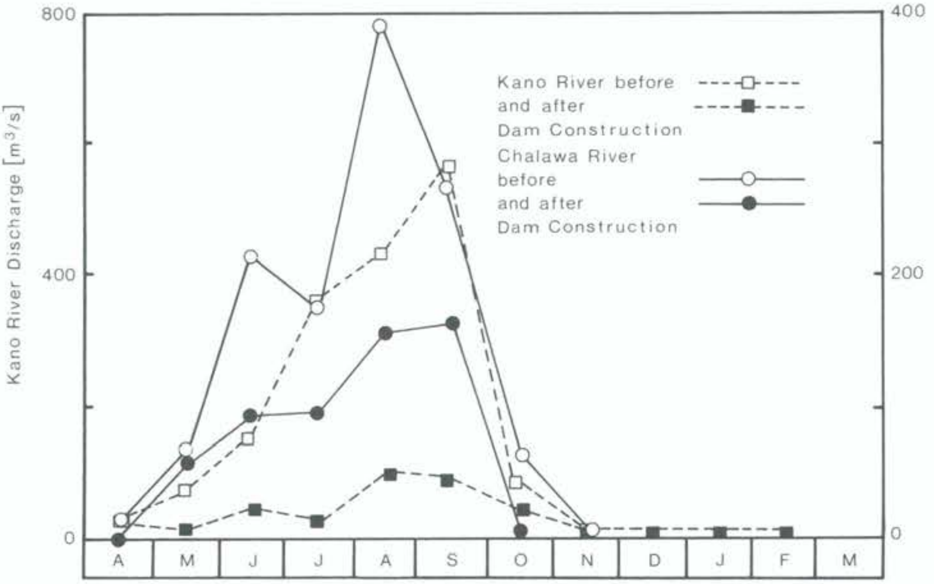

Fig. 2: Discharge hydrographs of Kano and Chalawa rivers before and after construction of dams.

$$Q_{t+1} = 0.36\, Q_t \qquad \text{Eq. 1}$$

where Q_{t+1} is mean discharge after the dams; and Q_t is mean discharge before the dams.

Actually, this relationship was only achieved after the Tiga Dam management was mandatorily made to maintain 15 m^3/sec in the channel. Before then in 1979 (five years after implementation), the relationship was (see OLOFIN, 1984):

$$Q_{t+1} = 0.26\, Q_t \qquad \text{Eq. 2}$$

But the most affected parameter is the average maximum flow in the wet months from June to September. This parameter measures the mean flood flow of the river during the most susceptible period of flooding. The mean flood flow (Q_f)

decreased from a pre-dam (time t) 383.3 m^3/sec in the post-dam (time t + 1) period, giving the following relationship:

$$Q_{ft+1} = 0.17\, Q_{ft} \qquad \text{Eq. 3}$$

Using the same threshold of a monthly mean discharge of 1 m^3/sec, it is observed that the Chalawa River remains seasonal after the major dams become operational since six months were dry in pre-dam period and the same months are still dry after.

The variation between the seasons only marginally narrowed from a pre-dam 0 to 83.0 m^3/sec to a post-dam 0 to 56.5 m^3/sec. The mean annual discharge has been reduced from 20.8 (pre-dam) to 11.1 (post-dam) to give the following relationship:

$$Q_t + 1 = 0.53\, Q_t \qquad \text{Eq. 4}$$

Also, the most affected parameter is the mean flood flow during the wet season where the post-dam average is only 48.8 % of the pre-dam value, i.e.,

$$Q_{ft} + 1 = 0.49\, Q_{ft} \qquad \text{Eq. 5}$$

However, the fact that the post-dam mean flood discharge is not significantly different from the pre-dam one in any of the months indicates that basic characteristics such as flash flow and concentration of flow in a few months are still largely unchanged.

The most important hydrological consequence of these changes in flow characteristics downstream of sudano-sahelian dams is that flooding in such locations is either completely eliminated or considerably ameliorated. In the case of the Kano River flooding has been completely eliminated (i.e., not counting the flooding in August 1988 consequent on the failure of the Bagauda Dam). The change in the mean flood flow of the Chalawa River has also been sufficient to eliminate flooding in the locations, even if the flash flow still encourages channel erosion and migration. Work on the Bakolori Dam in the Sokoto River Basin (ADAMS, 1985) has shown that the mean flood level decreased by about one meter in downstream areas. In the flattish terrain of Sokoto, or Chad Basin, a reduction of one meter implies thousands of hectares of pre-dam fadama (flood plain) land being left high and dry, as it has happened in Hadejia area downstream of Kano and Chalawa river basins. It should be stated that flood control, usually considered a positive environmental impact of dams, may be a negative effect if care is not taken, as shall be shown later.

2.1.2 Upstream effects

The effects of dams upstream, apart from the flooding of large tracts of land in the reservoir basins consequent on impoundment, are not as clear to see as those in downstream reaches. Consequently, not much is found in the literature on the effects on flow characteristics of rivers upstream of dams. In the sudano-sahelian zone inflowing rivers remain seasonal and the characteristic flash flow is unchanged. However, near the reservoirs the stage of inflowing rivers is affected, usually higher than the pre-dam height, and a drawdown zone is also created in the same way as the reservoir itself has its drawdown zone. Thus, in the drawdown zones the duration of flow is longer than the pre-dam one and the quantity of water stored is greater than the pre-dam discharge in such zones. These characteristics have been observed around Tiga and other dams in the Kano State.

Further, apart from the normal use of reservoir water, excessive evaporation, usually more than 2,000 mm per year in this zone, creates wide seasonal variations in the depth of the reservoir and the extent of its drawdown reaches. For example, OLOFIN (1985) has calculated that at full capacity 451.8 x 10^6 m^3 of water will be lost from the Tiga Lake each year through evaporation. Consequently, during the dry season following a poor wet season (such as 1983/84 and 1987/88) many small reservoirs usually dry up completely due largely to excessive evaporation. Lake Alou in Borno State and Gwarzo in Kano State are two examples. Conversely, overflowing and/or dam failure have also occurred in very wet years, such as the 1988 wet season.

2.2 The Niger Basin

2.2.1 Temporal shift of major ion distribution

Physical response of the Niger Valley up- and downstream of Kainji Dam has been discussed (IMEVBORE, 1975; MARTINS & NURUDEEN, 1988). Perhaps some of the most important geochemical responses are not only the 8 % net increase in annual TDS of the river (MARTINS, 1983), but also the concentration distribution of certain dissolved ions over the hydrological year.

Figure 3 depicts the distribution of bicarbonate, calcium, magnesium and sodium ions at an outflow station of Kainji Dam. While concentration of ions in

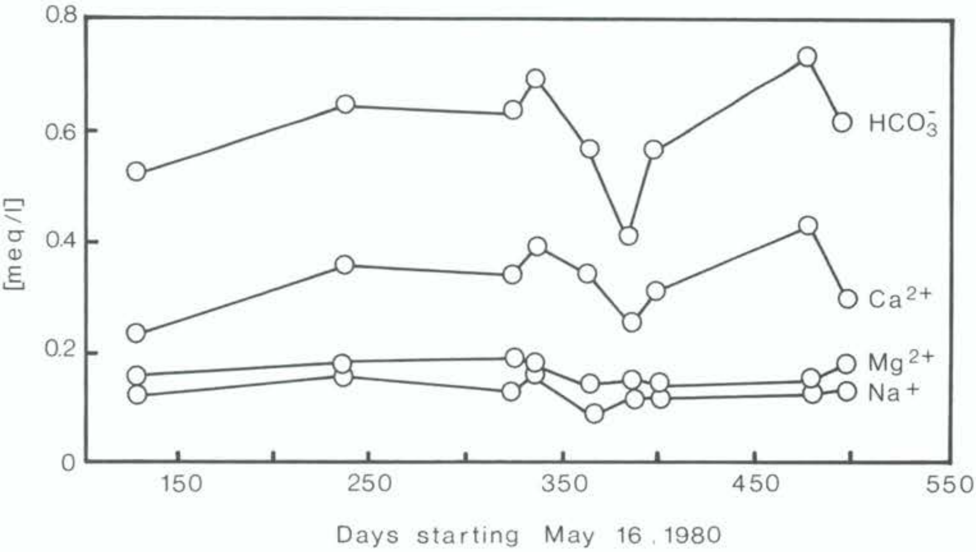

Fig. 3: Major ion distribution in the outflow station of Kainji Lake.

tributary river waters are being diluted throughout the wet season, May through October, bottom reservoir water, relatively richer in bicarbonate and calcium ions, are released at the outflow station. Total mixing of the low-ion precipitation water with the lake water seemed to be attained at the outflow station towards November, leading to an abrupt fall in dissolved ion concentration until December. This development was in contrast to what occurs further downstream (at Lokoja) where initial dilution of major ion concentrations was reported at the beginning of the wet season (MARTINS, 1983, 1988).

2.2.2 Decrease in discharge rate (1982-1987)

Table 2 shows water discharge through the Niger River system at Onitsha, between 1982 and 1987. The period under consideration covers the inception of one additional dam within the basin - the Jebba (on the Niger River). The hydropower dam is located about 600 km upstream of the delta and 80 km downstream of Kainji with a water surface area of around 300 km^2. The average annual discharge is 755 m^3/sec or 24 km^3. Its inflow (824 m^3/sec) is being controlled mainly by the Kainji Dam outflow (796 m^3/sec) - only 3.4 % of its annual average inflow is derived from local input - precipitation, tributary etc. Within the six-year period, an annual average of 127 km^3 of water is discharged through the river system. This is much lower than the discharge rate of 200 km^3 normally assumed for the Niger River Basin in most publications. The decrease in water volume may not necessarily be attributed to the Jebba Dam alone, but also to a row of minor dams constructed within the basin in the past six years (Shiroro Dam on Kaduna River, Kiri Dam on Benue River tributary, etc.).

Table 2
Water discharge through the Niger River system at Onitsha, 1982-1987
(all values are in m^3/sec).

Year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	Dec
1982	1721	1586	1129	1528	1759	2494	5499	8079	11,622	11,771	6567	3271
1983	2269	1702	1721	1795	1979	2865	4617	4914	9440	8238	1862	930
1984	-	-	-	-	966	2303	4776	7188	10,505	8314	3465	1416
1985	922	754	647	804	924	1758	4265	9950.5	14,793	13,173	2829	2035
1986	1293	994	895	1050	1114	1987	3121	-	11,337	12,216	3554	1910
1987	1282	964	1140	1383	1466	1875	3558	5656.5	11,677	12,179	5339	1347
Average:	1497	1200	1106	1312	1368	2214	4306	7158	11,562	10,982	3936	1818

3. Acknowledgements

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Guri Lake (Venezuela), a Blackwater Reservoir

by
JORGE PAOLINI, Caracas*)

With 6 Figures and 1 Table

Contents

Abstract

The Guri Lake, the largest blackwater reservoir of the world, was sampled at one station during the dry and rainy season. The lake water is extremely poor in electrolytes (conductivity 9.5 µS/cm; $TZ^+ < 90$ µeq/l) and acidic (pH 6.2). The predominant dissolved compounds are organic carbon and reactive silica. Their average concentrations amount to 4.42 mgC/l and 1.98 mgSi/l. The low alkalinity values (mean 83 µeq/l) indicate that the lake water is poorly buffered.

1. Introduction

The Guri Lake is the second man-made lake on the Lower Caroní River and the largest blackwater reservoir in the world. The dam was built for hydropower electricity generation and the total power output of the dam is 10,000 MW. This

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power output is the largest in the world for any individual dam site and the reservoir ranks seventh with respect to the volume of impounded water (135 km^3).

The Caroní River, below the Guri dam, has been sampled regularly since 1981 for the Transport of Carbon and Minerals in Major World Rivers SCOPE/UNEP Project, coordinated by the International Carbon Unit at Hamburg University (DEGENS, 1982).

In the present study, which is preliminary in nature, the Guri Lake was sampled at only one station. The station is located close to the dam, and was sampled at different depths and analyzed for dissolved oxygen, temperature and alkalinity, conductivity, turbidity, nutrients, and dissolved organic carbon in order to characterize its physico-chemical status during the dry and rainy season. The results presented here correspond to the final filling phase of the lake.

2. Hydrology

2.1 Caroní River Basin

The Caroní, the most important blackwater tributary of the Orinoco River, drains an area of 95,000 km^2 in the southeastern part of Venezuela. The river basin can be divided into two hydrographic basins. The Upper Caroní basin extending about 80,000 km^2 from its headwater in the border with Brazil to the confluence with the Paragua River. The lower basin, called the Lower Caroní, extends for 15,000 km^2, from the junction with the Paragua River until its mouth at the Orinoco. It has the largest hydroelectric potential of Venezuela (approximately 18,665,000 KW).

The climate in the watershed is tropical and is determined by the position and activity of the intertropical convergence zone (ITCZ) and the northeast trade winds. The mean annual precipitation in the watershed is estimated to 2,650 mm although its distribution in the watershed is irregular. In the Lower Caroní the rainfall is below 2,000 mm/a and in the Paragua basin, it exceeds 3,000 mm/a.

The mean annual air temperature in the basin is 22.9 °C. In the lowlands it can reach 27.6 °C compared to 11.5 °C around the tepui summits.

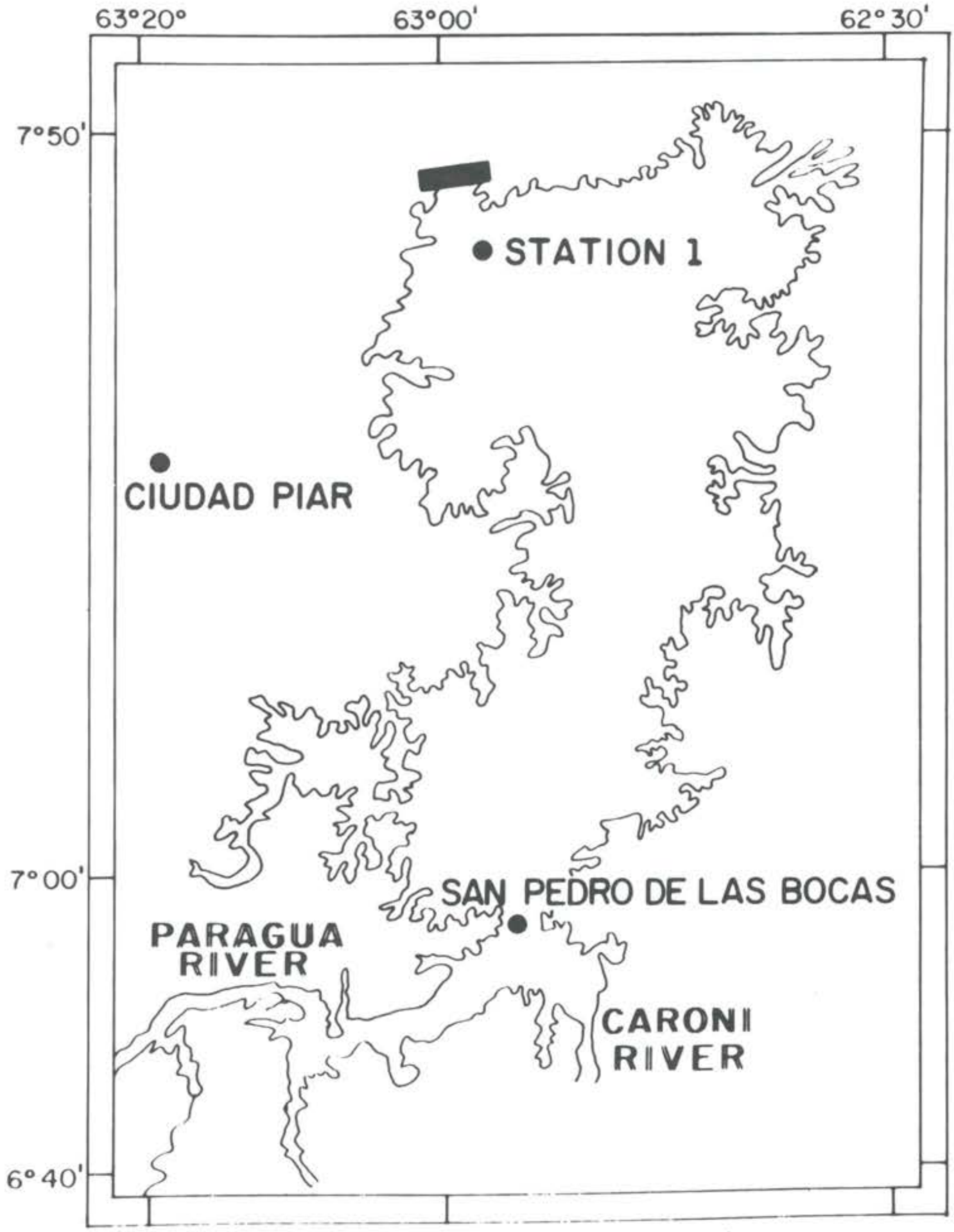
Approximately 60 % of the total area is covered by tropical forest (HUBER, 1986).

Three of the four geologic-tectonic provinces of the Venezuelan Guayana Shield are crossed by the Caroní and Paragua rivers: (a) the Imataca or Bolívar Province (granulite-amphibolite facies) in the lower basin; (b) the Pastora or Esequibo Province (greenstones) in the northern central basin and (c) the Roraima or Canaima Province (quartzites and conglomerates of the Precambrian Roraima group) in the central and upper basin (SCHUBERT et al., 1986).

The water chemistry of the Caroní River was the object of several recent studies (BRICEÑO et al., 1988; NEMETH et al., 1982; PAOLINI, 1986; PAOLINI et al., 1983, 1987). Riverine transport of total carbon - organic and inorganic - has been estimated to be 1.04×10^6 t C/a.

2.2 Guri Lake

The Guri Dam was built 100 km upstream of the confluence of the Caroní River with the Orinoco, near the town of Guri, in the Necuima Canyon. The



Map of Guri Lake, Venezuela

Fig. 1: Map of Guri Lake, Venezuela.

construction of the first stage began in 1963 and was completed in 1968. The normal operating height during the first construction stage was 215 m above sea level (a.s.l.), the total flooded area corresponding to this elevation was approximately 800 km^2 and the storage volume amounted to 17 km^3. The final construction stage was completed in late 1986 and the normal maximum operating height increased to 270 m a.s.l., the corresponding flooded area is 4,250 km^2 and the total volume 135 km^3.

The lake is fed by two major inflows, the rivers Caroní and Paragua. Both rivers join at San Pedro de Las Bocas (Fig. 1). The highest discharge values are registered during the months June to August and the lowest from January to April (see Fig. 2).

In 1972, limnological studies of the Guri Lake were started and were intensified in 1980 (Alvarez et al., 1986; Elosegui, 1979; Gonzalez, 1987; Lewis & Weibezahn, 1976; Ray et al., 1987).

All these studies point out that the water is dark in color, slightly acidic and poor in electrolytes. The thermal stratification period encompasses the months from June to December, while isothermal conditions prevail from January to the beginning of June (Alvarez et al., 1986; Gonzalez, 1987). According to the lake classification of Hutchinson (1957), the Guri Lake can be described as "warm - monomictic".

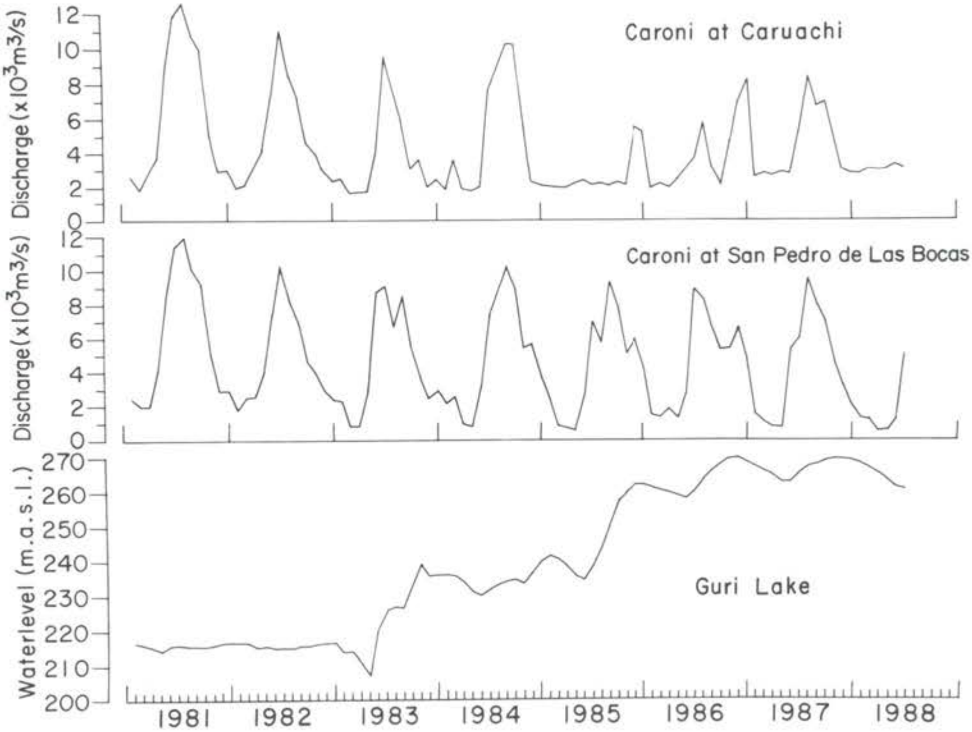


Fig. 2: Discharge of the Caroni below and above Guri Lake 1981-1988 in comparison with the water level of the Guri Lake.

The dissolved oxygen profiles are very similar to the temperature profiles and during the stratification an oxycline develops which coincides with the thermocline (ALVAREZ et al., 1986).

3. Materials and Methods

Figure 1 shows a map of Guri Lake including the sampling station used in this study. The water samples were taken in August 1985 (rainy season) and January 1986 (dry season). In August 1985 additional samples of the Paragua and Caroní Rivers were taken above their confluence at San Pedro de Las Bocas and below the dam (Caruachi).

Water samples were collected from selected depths using a 2.5 liter Van Dorn bottle. Temperature and dissolved oxygen were measured with a field thermistor YSI (model 57). Conductivity was measured by a WTW portable meter (model LF 56) and pH electrometrically by a WTW portable meter (model pH Digi 88). Transparency was measured with a Secchi disc. A turbidimeter Baush & Lomb (Mini Spec 20) was used for measuring the turbidity. Alkalinity, Ca, Mg, Na, K, Si and Cl and dissolved organic carbon (DOC) were determined following the chemical procedures described by MICHAELIS & ITTEKKOT (1982).

4. Results and Discussion

The Caroní discharge at San Pedro de Las Bocas (Guri inflow) and at Caruachi (Guri outflow) is shown together with the variation of the lake level in Figure 2 for the last eight years.

The rising of the water level for the final construction stage began in April 1983 and then stabilized at the 235 m level (on average) in 1984. In 1985 the reservoir filled most vigorously between May and November, when it reached the 262 m level. The subsequent drop in level was due to the dry season and after that it gradually rose to the operating level at 270 m in November 1986.

The discharge pattern for the Caroní River at the two stations (San Pedro de Las Bocas and Caruachi) was similar for the years 1981-1984. The major flood occurs from June to August with an average maximum discharge between 9,000 and 12,000 m^3/s. Since 1985, the Caroní River at Caruachi has shown the influence of the impoundment.

Figure 3 shows the temperature and dissolved oxygen profiles for the two sampling dates. It is clear that the lake is isothermal during January and is stratified in August. These results agree with those reported previously by ALVAREZ et al. (1986) and GONZALEZ (1987). The dissolved oxygen curve in August shows an oxycline that follows the temperature curve for the same month and that indicates a resistance to oxygen penetration to lower depths. In January, the dissolved oxygen curve follows the temperature curve until a depth of 40 m but after that depth it

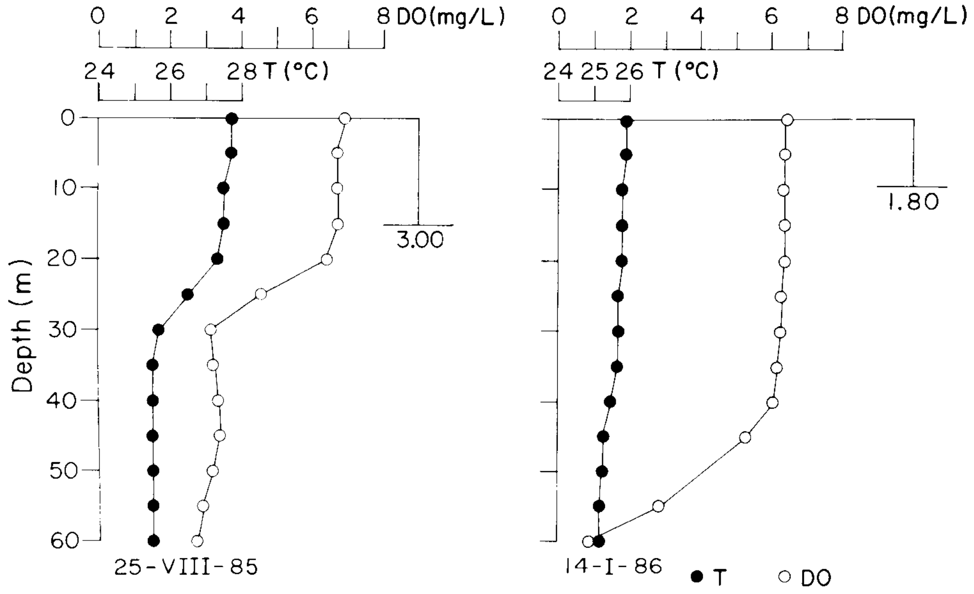


Fig. 3: Vertical profiles of dissolved oxygen (DO) and temperature for August, 1985 (left) and January, 1986 (right), Station 1, Guri Lake.

drops rapidly. This is probably due to consumption of O_2 resulting from the decomposition of organic matter.

The electrical conductivity is extremely low and varies between 8.6-10.5 μS/cm with a mean value of 9.5 μS/cm ($\sigma = 0.77$, $n = 19$). It decreases with depth in both months (Fig. 4). The pH is slightly acidic and its mean value was 6.16 ($\sigma = 0.39$, $n = 19$). Its decrease with depth is similar to the decrease in conductivity.

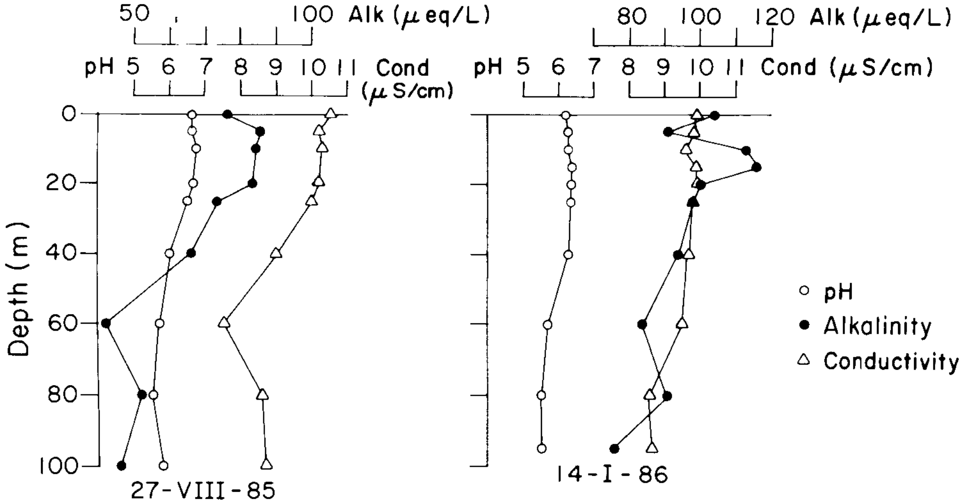


Fig. 4: Vertical profiles of alkalinity and conductivity for August, 1985 (left) and January, 1986 (right), Station 1, Guri Lake.

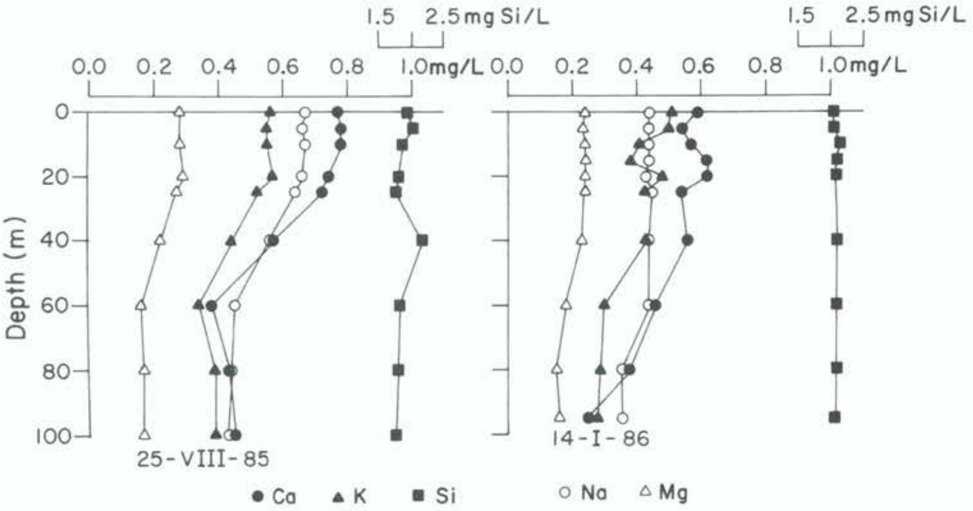


Fig. 5: Vertical profiles of dissolved silica and major cations for August, 1985 (left) and January, 1986 (right), Station 1, Guri Lake.

The four major cations (Ca, Mg, Na and K) and the alkalinity follow the same pattern as the conductivity and pH (Figs. 4 and 5). Also, these low concentrations are similar to the values found by PAOLINI (1986) and PAOLINI et al. (1987) for the Caroní River at Caruachi, a place located below the dam. Another peculiarity of the Guri is the very low content of calcium, which has also been reported from other South American rivers (FURCH et al., 1982; VEGAS et al., 1988).

As was pointed out previously, one of the most outstanding properties of the Guri water is its black color and this is reflected in the observed values of dissolved organic carbon (DOC) and color (Pt-Co Scale) (Fig. 6). The mean value of DOC

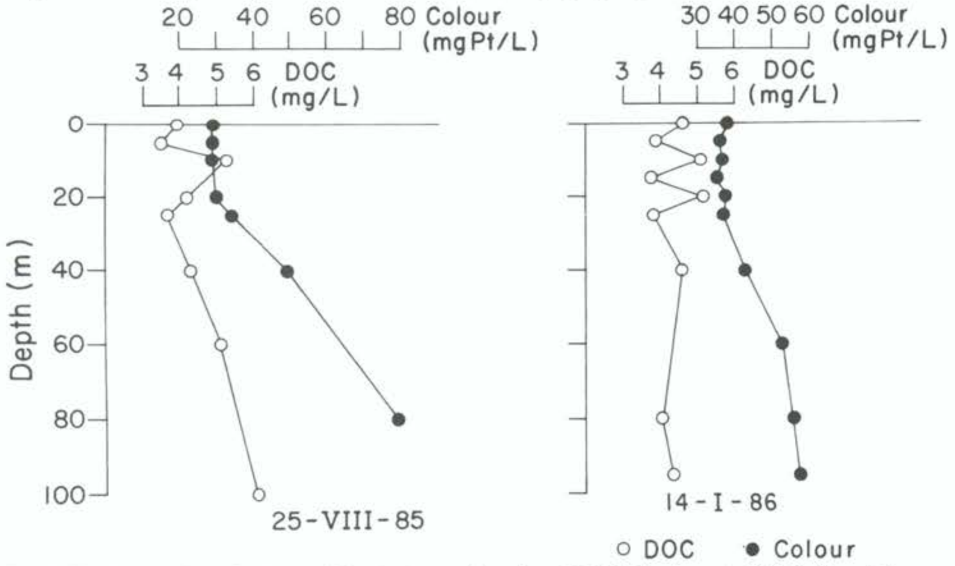


Fig. 6: Vertical profiles of color and dissolved organic carbon (DOC) for August, 1985 (left) and January, 1986 (right), Station 1, Guri Lake.

was 4.42 mg/l ($\sigma=0.70$, $n=17$) and is close to that reported by LEWIS & CANFIELD (1977) for the Guri Lake in July 1974 (5.0 mg/l) and lower than the values (5.87 mg/l) found by PAOLINI (1986) and PAOLINI et al. (1983, 1987) for the Caroní River downstream of the dam. This difference can be attributed to the fact that the water intake for the generators draws water from the hypolimnion and this water is richer in DOC than the surface water (see Fig. 6). The increase of DOC with depth can probably be related with the observed decrease of dissolved oxygen.

The concentration of reactive silica varies only slightly with depth (Fig. 5). Its mean value amounts to 1.98 mg/l ($\sigma=0.15$, $n=18$). This value is very close to the value reported by PAOLINI (1986) and PAOLINI et al. (1987) for the Caroní River of 2.30 mg Si/l.

The anion chloride shows a pattern similar to the reactive silica and its mean value is 0.47 mg/l ($\sigma=0.04$. $n=19$).

In Table 1 the physico-chemical properties of the waters of the Upper Caroní (San Pedro de Las Bocas, Paragua in La Paragua and Caroní in Arekuna) are compared with those of the Guri Lake and the Lower Caroní (Caruachi).

Table 1: Physico-chemical characteristics of the Caroní River

Sample	pH	Cond µS/cm	Turb NTU	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Si mg/l
San Pedro	5.75	5.35	8.0	0.18	0.12	0.40	0.28	1.14
Paragua	5.85	6.80	7.0	0.27	0.12	0.48	0.27	2.57
Caroní	5.72	5.30	8.0	0.25	0.10	0.32	0.28	0.97
Guri, Aug.	6.25	9.44	1.5	0.62	0.24	0.58	0.48	1.87
Guri, Jan.	6.09	9.55	1.2	0.51	0.22	0.42	0.40	2.08
Caruachi	6.05	9.10	2.8	0.51	0.19	0.49	0.42	2.26

Sample	Alk µeq/l	Hardness µeq/l	Cl mg/l	DOC mg/l	Color mgPt/l
San Pedro	37	35	0.45	5.64	72
Paragua	53	42	0.46	4.73	58
Caroní	32	25	0.49	5.30	66
Guri, Aug.	67	67	0.46	4.50	40
Guri, Jan.	97	64	0.48	4.35	43
Caruachi	55	-	0.50	-	61

The data in this table show that the Upper Caroni is slightly more acidic and has a higher concentration of DOC and suspended matter (according to the turbidity) than the Guri Lake. On the other hand, the Upper Caroni carries lower concentrations of cations and has a lower conductivity than the Guri Lake. Particularly Ca (factor 2), Mg and K increase in concentration in the lake and below the dam. Using the chloride concentration as reference we can conclude that evaporation is a negligible process in explaining these increases in concentrations. Another possible source of cations could be release from decomposing organic matter. Since DOC increases with depth in the lake, rates of DOC decomposition must be low. The difference in concentration of DOC between the Upper Caroní and the lake is about 1 mg/l. It is known that the concentration of major cations in organic matter is mostly below 1%. Therefore release from DOC cannot explain the increase by a factor of two for calcium. Other sources need to be considered (for example, groundwater inputs and leaching from submerged building material, such as the concrete of the dam itself). More research is needed to understand this increase in concentration of the major cations.

5. Conclusions

The Guri Lake, formed by the impoundment of the Caroní River, is an oligotrophic ecosystem. The predominant compounds in the Caroní watershed are the dissolved organic carbon and reactive silica. Among the major cations the order of abundance is Na > Ca > Mg > K for the Upper Caroni and Ca > Na > Mg > K for the Guri Lake and Lower Caroní. Further research is needed to explain these changes.

The observed water chemistry within the Caroní basin corresponds to rivers which drain the deeply weathered rocks of the Guayana Shield.

6. Acknowledgements

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Nitrogen Forms in the Amazon River Basin and Estuary

by

V.V. GORDEEV, V.A. KONNOV & YU.V. KONNOVA, MOSCOW*)

With 5 Figures and 3 Tables

Contents

Abstract

During the first Soviet oceanographic expedition to the Amazon River (9th cruise of R/V PROFESSOR SHTOKMAN) samples of water and suspended matter were collected along the main and lower course of the Amazon River, from major tributaries (Madeira, Rio Negro, Trombetas, etc.), and in the estuary.

The samples were analyzed for concentrations of different nitrogen compounds (NO_2^-, NO_3^-, $N_{org.dis.}$, $N_{org.par.}$) and various hydrochemical parameters. It was found that all three types of waters (white, clear, and black) have a similar distribution pattern of N forms (arranged in the order of increasing concentrations: NO_2^-, NH_4^+, NO_3^-, $N_{org.par.}$, $N_{org.dis.}$). Also the O_2 content showed a linear regression with NO_3^- in all three water types.

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In the Amazon estuary NO_3^- and NH_4^+ are almost completely consumed by a diatom plankton bloom in the so-called green waters which have salinities above 14 ⁰/oo. At the same time biogenic suspended matter is enriched with organic nitrogen.

1. Introduction

Transport of biogenic elements, including nitrogen, by major rivers has been largely unknown until recently (MEYBECK, 1982; GORDEEV, 1983).

In the Amazon River and its estuary nitrogen compounds have now been studied by several researchers (WILLIAMS, 1968; SCHMIDT, 1972; GIBBS, 1972; WISSMAR et al., 1981; EDMOND et al., 1981; STALLARD & EDMOND, 1983; FURCH, 1984; RICHEY, 1982; RICHEY et al., 1985; FERREIRA et al., 1988). A comprehensive geological and biogeochemical research program of the Amazon basin was also carried out in March-April of 1983 by the Soviet oceanological expedition on board of the R/V PROFESSOR SHTOKMAN (GORDEEV, 1984; GORDEEV et al., 1985).

The present article analyzes data of dissolved and particulate N in the Amazon waters, in some of its tributaries, and in the estuary.

2. Samples and Analytical Procedures

The locations of the sampling stations in the Amazon basin and estuary are shown in Figure 1. Surface water samples were collected in polyethylene tanks. Subsurface samples were taken with clean 10 l bathometers attached to a polyethylene coated rope. Water was filtered under vacuum through the WHATMAN GF/C glass fibre filters (1 µm pore-size). The filtered water (50-100 ml) was acidified by hydrochloric acid to pH = 1-2 and stored in glass flasks with hermetic stoppers in a freezer.

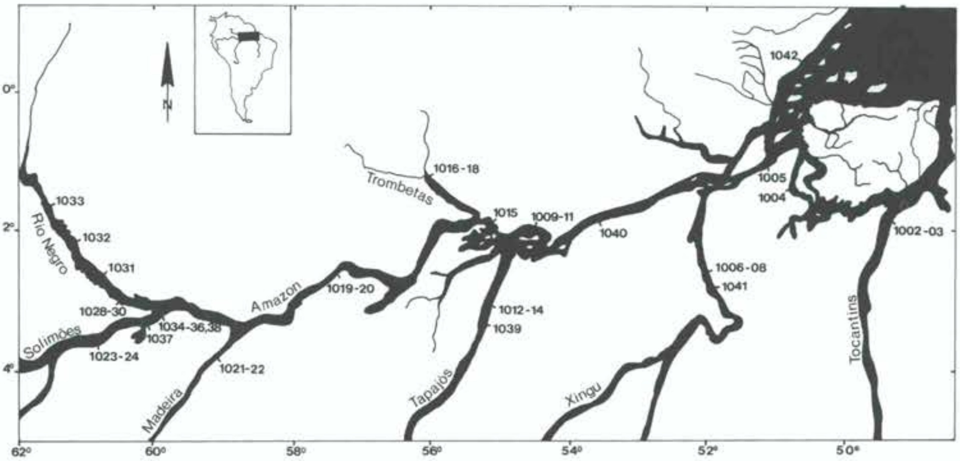

Fig. 1a. Sampling stations of the 9th cruise of R/V PROFESSOR SHTOKMAN in the Amazon river basin.

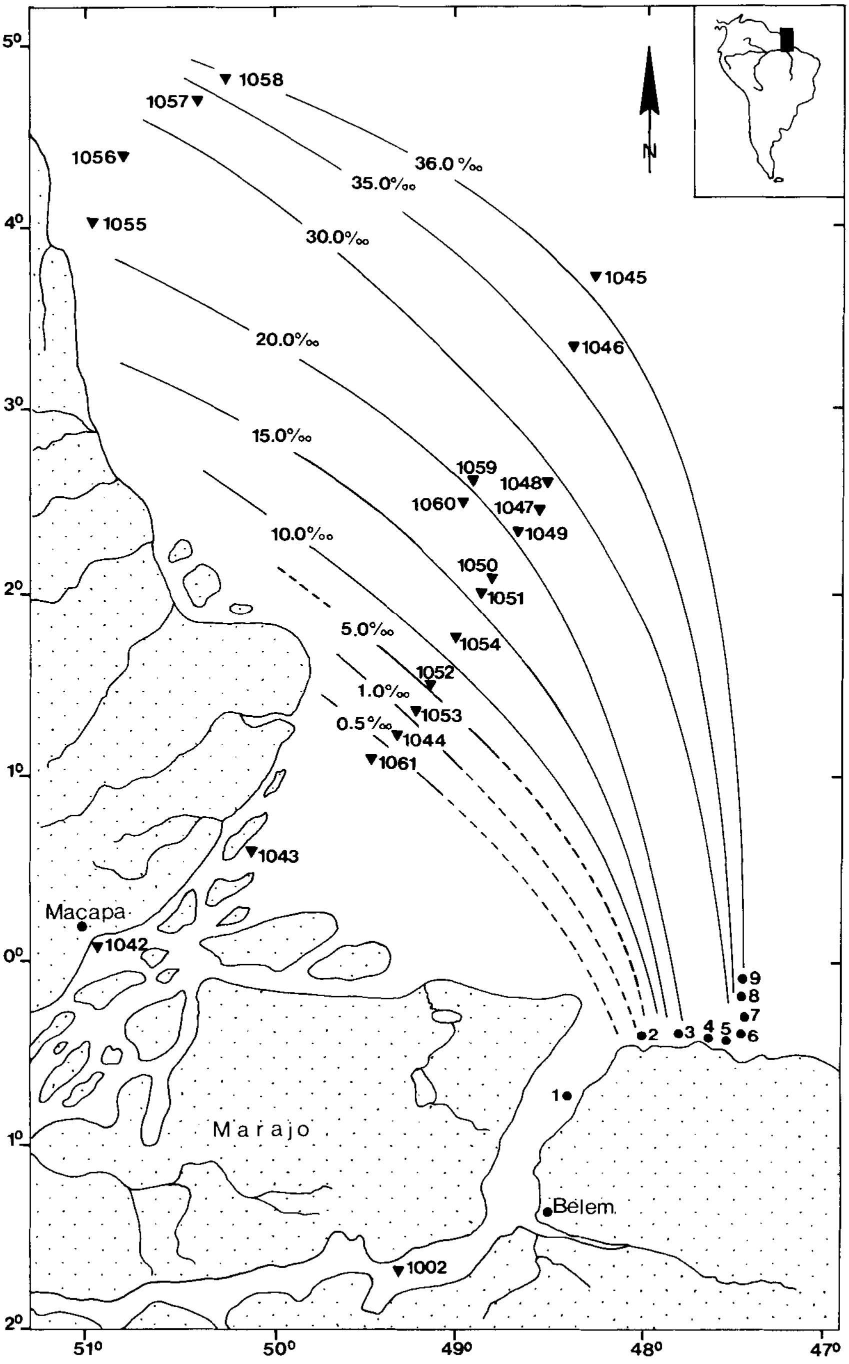

Fig. 1b: Stations of the 9th cruise of R/V PROFESSOR SHTOKMAN within the mixing zone of Amazon and Atlantic waters. Triangles indicate stations. Dots mark surface samples collected during the cruise. Salinity distribution according to YU.M. GUSEV.

Nitrogen compounds were determined using colorimetric methods: nitrite - by the denitrogenation reaction; ammonium - by the phenolhypochloride method; nitrate - after reduction to nitrite in a copper-cadmium column. The N content in organic compounds was determined with potassium persulfate oxidation first in the alkaline and afterwards in the acidic media.

3. Results and Discussion

3.1 Amazon Basin

The Amazon basin data of dissolved inorganic nitrogen (NO_2^-, NO_3^-, NH_4^+), dissolved organic nitrogen ($N_{org.dis.}$), total dissolved nitrogen ($N_{tot.dis.} = NO_2^- + NO_3^- + NH_4^+ + N_{org.dis.}$), and particulate organic nitrogen ($N_{org.par.}$) are presented in Table 1 and Figure 2. For comparison, the table contains data on the dissolved and particulate organic carbon published earlier (ARTEMYEV, 1988; ARTEMYEV & DANYUSHEVSKAYA, 1988).

As shown in Table 1 and Figure 2, all three types of the Amazon waters (white, clear, and black) have a similar pattern with regard to the distribution of nitrogen compounds - concentrations increase from NO_2^- to $N_{org.dis.}$ in the following order: NO_2^- --> NH_4^+ --> NO_3^- - -> $N_{org.par.}$ --> $N_{org.dis.}$. This is in contrast to the average of the global river runoff, where, according to MEYBECK (1982), particulate organic nitrogen ($N_{org.par.}$) prevails.

Nitrite: NO_2^- was found to be below the limit of detection in nearly all water samples from the Amazon River and its tributaries (i.e., $< 0.1\ \mu M$).

Ammonium: Concentrations of ammonium (NH_4^+) were higher than reported by other authors (Table 2), except for the data of MEYBECK for the Amazon, Solimoes, and Rio Negro. These exceptionally high values were probably due to transformation of part of the organic N into NH_4-N during sample storage in the acid medium for three months prior to the analyses. This was especially the case for the Tocantins and Xingu water samples with high concentrations of $N_{org.dis.}$. Nevertheless, NH_4^+ is only of secondary importance in all types of Amazon waters.

Nitrate: NO_3^- appears to be the most frequently found form of dissolved inorganic nitrogen. According to our estimates the nitrate content in the Amazon River during high water period corresponds to the global mean (7.1 μM). The clear and black waters of the Amazon tributaries contain 1.5-2.0 times less nitrate.

Dissolved organic nitrogen: $N_{org.dis.}$ is the dominant form of the dissolved nitrogen. Its content in the white waters of the Amazon and Madeira amounts to 65 % of the $N_{tot.dis.}$, while its content in clear and, particularly, in black waters is still higher: 73 % and 83 %, respectively.

Total dissolved nitrogen: The $N_{tot.dis.}$ content of the three types of the Amazon waters is almost identical to the global average (26.8 μM). The clear waters of the Tocantins and, particularly, of the Xingu are characterized by great fluctuations of $N_{org.dis.}$ concentrations (Fig. 2).

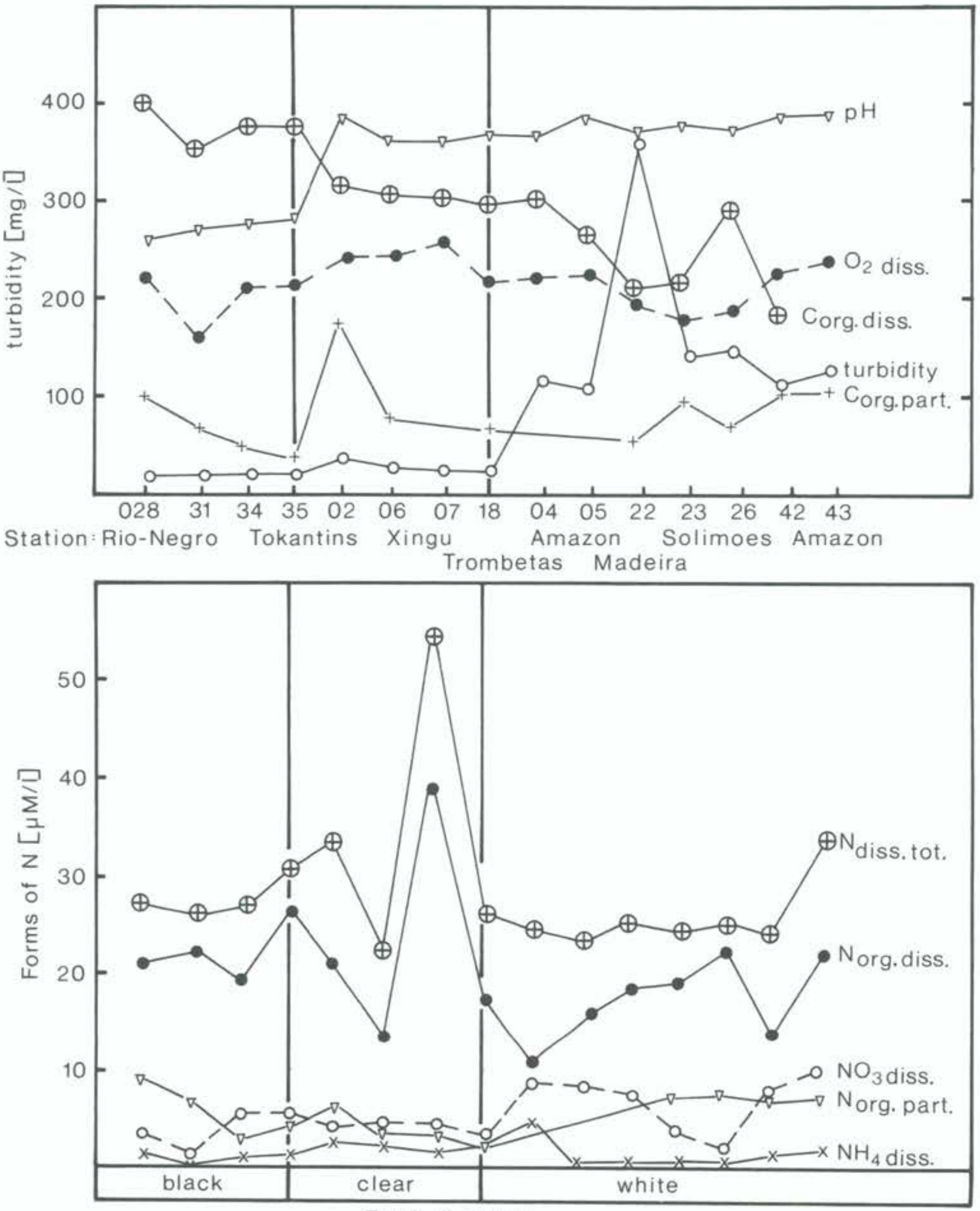

Fig. 2: Distribution of turbidity, pH, dissolved oxygen, dissolved and particulate forms of the organic carbon and nitrogen in three types of Amazon waters.

Particulate organic nitrogen: $N_{org.par.}$ content in the Amazon River amounts to 20-40 % of total nitrogen ($N_{tot.dis.}$ + $N_{org.par.}$), thus being considerably less than that of the global river average (60 %). The ratio ($N_{org.par.}$/$N_{org.dis.}$) was always less than 1 for all three types of waters.

Table 1

Forms of the nitrogen and organic carbon in waters of the Amazon River

Station	Total	Sample	TSM	pH	O2	Dissolved forms						Particulate forms				
river	Depth	Depth				NO_2^-	NO_3^-	NH_4^+	N_{org}	N_{tot}	C_{org}	N_{org}	N_{org}	C_{org}	C_{org}	C/N
	m	m	mg/l		ml/l	µM/l	µM/l	µM/l	µM/l	µM/l	mg/l	µM/l	%	mg/l	%	ratio
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
White waters:																
1004	22	0	86.7	7.09	4.12	0.20	9.4	3.2	11.8	24.6	4.9	-	-	-	-	-
Amazon		10	127.4	7.01	4.08	0	9.0	6.4	8.8	24.3	6.6	-	-	-	-	-
1005	13	0	79.6	7.42	4.31	0	7.8	0.4	15.7	23.9	5.7	-	-	-	-	-
Amazon		10	88.8	7.35	4.30	0	8.5	1.8	15.8	26.1	4.6	-	-	-	-	-
1009	11	0	124.4	7.50	4.01	-	-	-	-	-	5.3	5.3	0.06	2.2	1.8	30
Amazon		10	134.7	7.25	3.86	-	-	-	-	-	6.0	7.9	0.08	3.1	2.3	29
1020	43	40	149.7	7.04	3.52	-	-	-	-	-	3.8	7.7	0.07	1.6	1.0	14
Amazon																
1022	11	0	295.2	7.00	3.54	0	7.8	1.1	17.4	26.3	3.7	-	-	2.0	0.7	-
Madeira		10	439.3	6.80	3.31	0	7.4	0.5	20.2	28.1	4.0	-	-	-	-	-
1023	13	0	126.0	7.20	-	0	7.1	2.5	20.2	29.8	5.0	-	-	2.1	1.6	-
Solimoes		12	116.5	7.20	3.22	0	0.6	1.0	18.6	20.2	5.0	7.1	0.085	2.0	1.7	20
1024	23	0	127.8	6.90	2.88	-	-	-	-	-	5.7	5.5	0.06	1.1	0.8	18
Solimoes		20	126.4	6.90	2.81	-	-	-	-	-	6.5	6.2	0.07	1.6	1.3	23
1025	13	0	98.6	7.05	3.09	-	-	-	-	-	5.2	7.7	0.11	0.8	0.9	8
Amazon		10	124.9	7.02	3.04	-	-	-	-	-	4.6	8.8	0.10	1.4	1.1	11
1026	54	0	135.9	7.05	3.44	0	2.2	0.4	23.5	26.1	5.6	5.3	0.05	1.5	1.1	21
Amazon		40	154.5	7.02	3.13	-	-	-	-	-	5.2	7.7	0.07	0.9	0.6	8
1027	29	0	74.3	6.90	4.02	-	-	-	-	-	5.9	7.3	0.14	-	-	-
Amazon		25	127.2	6.80	3.64	-	-	-	-	-	4.5	9.5	0.10	1.6	1.3	13
1042	34	0	94.9	7.32	4.28	0	8.2	2.4	13.6	24.2	3.4	-	-	-	-	-
Amazon		20	105.6	7.27	4.33	-	-	-	-	-	4.5	7.1	0.09	2.0	1.9	20
1043	20	0	112.5	7.40	4.54	0	11.0	2.8	23.2	37.0	-	6.8	0.08	2.0	1.9	22
Amazon		15	106.9	7.36	4.59	-	-	-	-	-	-	7.8	0.10	2.2	2.0	20
Clear waters:																
1002	30	0	26.8	7.45	4.92	0	3.4	10.8	29.4	43.6	7.9	6.5	0.34	3.2	11.9	35
Tokantins		25	24.2	7.45	4.75	0	5.8	4.6	14.5	24.9	4.2	-	-	-	-	-
1003	13	0	25.2	7.35	4.92	-	-	-	-	-	5.2	1.8	0.10	2.4	9.4	94
Tokantins		10	29.7	7.32	4.58	-	-	-	-	-	6.2	7.7	0.36	2.3	7.6	21
1006	16	0	8.6	7.14	4.95	0	4.7	3.8	11.7	20.2	5.7	4.0	0.65	1.2	13.9	21
Xingu		15	10.4	6.80	4.67	0	5.0	3.6	14.8	23.4	6.0	-	-	-	-	-
1007	27	0	9.2	7.15	5.17	0	5.0	-	55.0	5.7	-	-	-	-	-	
Xingu		13	8.0	6.70	4.74	0	4.0	5.2	29.0	38.2	6.1	-	-	-	-	-
		23	7.0	6.77	4.45	0	4.9	0.8	22.1	27.8	5.4	-	-	-	-	-
1008	30	20	7.8	6.65	4.49	-	-	-	-	-	5.4	2.3	0.41	0.3	16.6	10
Xingu																
1018	13	7	10.1	7.10	4.01	0	2.6	3.8	18.2	25.5	5.6	-	-	1.0	9.3	-
Trombetas																
Black waters:																
1028	23	0	5.1	5.08	4.38	0	4.6	2.9	26.4	33.9	7.7	5.4	1.6	1.3	25.5	16
Rio Negro		20	6.3	4.80	4.30	0	3.1	1.3	18.7	23.1	7.7	13.3	3.0	2.3	36.5	12
1029	37	0	5.7	5.20	3.28	-	-	-	-	-	7.7	7.3	1.8	1.4	24.9	14
Rio Negro		12	5.0	5.18	4.00	-	-	-	-	-	7.5	5.2	1.5	0.8	15.2	10
		30	8.8	4.90	4.02	-	-	-	-	-	8.1	6.6	1.05	1.7	19.3	19
1030	14	0	5.4	5.30	4.11	-	-	-	-	-	7.5	3.9	1.0	0.8	14.2	14
Rio Negro		15	4.3	5.19	3.53	-	-	-	-	-	6.2	3.9	1.3	0.6	14.6	12
1031	9	0	4.9	5.25	-	0	2.1	0.8	18.4	21.3	7.1	6.2	1.8	1.0	20.5	11
Rio Negro		6	3.7	5.18	2.97	0	0.8	1.5	28.3	30.6	6.6	8.6	3.2	-	-	-
1032	9	0	4.6	5.20	4.13	-	-	-	-	-	9.1	5.6	1.7	1.5	31.5	19
Rio Negro		7	4.4	4.90	3.27	-	-	-	-	-	11.5	4.4	1.4	1.1	25.2	18
1033	14	0	4.4	5.05	3.85	-	-	-	-	-	8.7	5.0	1.6	1.1	25.7	16
Rio Negro	14	12	5.4	4.90	3.56	-	-	-	-	-	8.8	6.0	1.5	1.0	18.9	12
1034	30	1	5.0	5.34	4.23	0	5.8	1.5	22.9	30.2	7.1	1.9	0.53	0.4	8.8	17
Rio Negro		15	5.5	5.37	4.06	-	-	-	-	-	6.9	3.3	0.84	1.0	18.2	22
		25	5.9	5.45	3.93	0	5.4	2.8	16.6	24.8	7.5	3.0	0.71	0.8	13.9	20
1035	40	0	4.8	5.30	4.19	0	5.5	2.9	29.5	31.6	7.2	-	-	-	-	-
Rio Negro		33	9.8	6.00	3.95	0	5.4	0.8	27.0	32.0	7.4	4.1	0.61	0.4	4.1	7

The absolute $N_{org.par.}$ concentrations varied insignificantly (about 3-8 µg-at/l). The percentage of organic nitrogen in the particles of white, clear, and black waters differed, however, greatly - they amounted, on average, to 0.08 %, 0.45 %, and 1.8 %, respectively (the global average is 0.12 %). The Rio Negro waters have an extremely high content of $N_{org.par.}$ (up to 3.2 %) which is most likely caused by the input of nitrogen compounds from soil.

Table 2

Comparison of literature data on nitrogen and organic carbon forms in waters of the Amazon River.

River	Time	Dissolved forms				Particulate forms							References
		NO_2^- µM/l	NO_3^- µM/l	NH_4^+ µM/l	N_{org} µM/l	N_{tot} µM/l	C_{org} mg/l	N_{org} µM/l	N_{org} %	C_{org} mg/l	C_{org} %	C/N	
1	2	3	4	5	6	7	8	9	10	11	12	13	14
Amazon	63/64	0.05	3	-	-	20	4.5	-	-	-	-	-	GIBBS (1972)
Solimoes	Sep.	0.1	10	-	9.3	19.4	2.03	7.5	-	0.9	-	8.5	WILLIAMS (1968)
Amazon	1967	0.05	9.6	-	10	19.7	3.5	6.2	-	1.12	-	13	
Rio Negro		0.17	3.9	-	10.3	14.3	5.9	9.0	-	1.49	-	12	
Amazon		0.15	8.5	-	-	-	-	-	-	-	-	-	EDMOND et al. (1981)
Amazon	May-Jun.	0-0.13	4.0-14.7	0.1-1.4	-	-	2.7 -4.8	-	-	-	-	-	STALLARD & EDMOND (1983)
Madeira		0.07	8.4	0.4	-	-	-	-	-	-	-	-	
Trombetas		0.02	3.1-4.3	0.2	-	-	7.8	-	-	-	-	-	
Tapajós		0.03-0.08	1.5-2.5	0.3	-	-	-	-	-	-	-	-	
Xingu		0.03-0.11	0.8-2.6	-	-	-	-	-	-	-	-	-	
Rio Negro		0.12	1.7-5.3	1.0	-	-	6.4	-	-	-	-	-	
Solimoes		0.13	3.4	-	-	43	-	-	-	-	-	-	FURCH (1984)
Tapajós		0.10	0.3	-	-	23.9	-	-	-	-	-	-	
Rio Negro		0.05	2.6	-	-	28.1	-	-	-	-	-	-	
Amazon	1982/83	-	5-25	1-2	9-45	-	-	17.5 -34.6	-	-	-	-	RICHEY et al. (1985)
White waters: Amazon, Madeira													
	Mar-Apr.	<0.1	7.2	2.0	17.2	26.5	5.0	7.2	0.08	1.8	1.4	18	This study
Clear waters: Tokantins, Xingu, Trombetas													
		<0.1	4.4	4.5	24.3	33.2	5.8	4.5	0.37	1.7	11.5	22	
Black waters:													
Rio Negro		<0.1	4.1	1.8	23.5	29.4	7.8	5.5	1.5	1.1	19.8	16	
Solimoes*		0.07	3.6	(2.8)	10.7	(17.1)	2.0	-	-	-	-	-	MEYBECK (1982)
Amazon*		0.07	2.8	(2.5)	14.3	19.6	5.0	-	-	(5.0)	-	-	
Rio Negro*		0.07	1.8	(1.8)	21.4	(25)	6.3	-	-	2.06	-	-	
		0.07	7.1	1.1	18.6	26.8	5.75	40	0.12	4.8	1.0	8.3	

* Author's estimates from other authors'data

C/N ratio: The C/N ratio in the particulate riverine material, according to MEYBECK (1982), is rather constant (within the range from 8 to 10) and correlates with the similar ratio found in the surface soil layers serving as the major source of the particulate organic matter.

In the waters of the Amazon basin the C/N ratios are, however, somewhat different (Table 1): they were 21.8, 18.4 and 14.9 in clear, white and black waters, respectively. Higher values may be caused by a higher fraction of terrestrial plant residues which have an N content lower than that of phytoplankton. The mean C/N ratio in the terrestrial grasses is, for example, 35.7 compared to 15.6 in higher aquatic plants (GLAZOVSKAYA & DOBROWOLSKAYA, 1984).

In the lower section of the Madeira FERREIRA et al. (1988) found a direct dependence between the concentration of nitrate and that of dissolved oxygen. As an explanation the authors suggested that organic matter is oxidized in the flood plain lakes (várzea) both aerobically and anaerobically. In the former case oxygen is consumed and in the latter case nitrate is reduced (denitrification) resulting in the production of NH_4^+ and N_2.

During the Soviet expedition this dependence was also observed in the three types of the Amazon waters. It should be noted that the straight lines representing different types of waters in Figure 3 are separate lines. Different rates of the organic

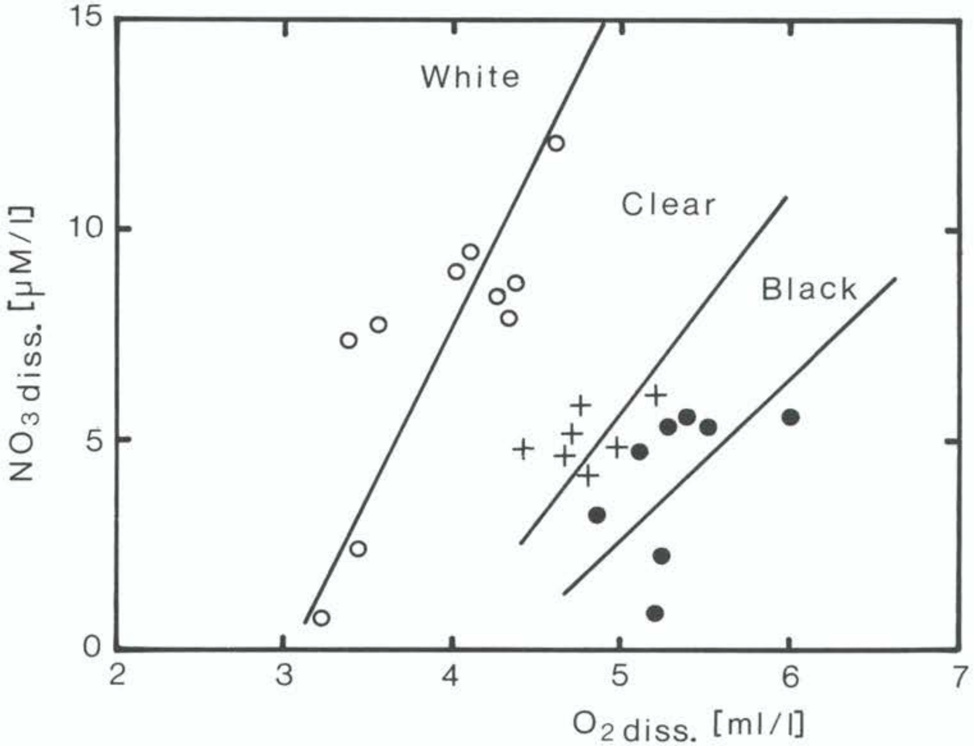

Fig. 3: Relation between nitrates and the dissolved oxygen contents in three types of Amazon waters.

carbon oxidation in different water types are probably due to different composition of organic matter and changes in the environmental conditions. It is noteworthy that, in March-April 1983, we never observed 100 % oxygen saturation in Amazon waters (white waters - 62 - 93 %; clear waters - 82- 92 %; black waters - 58-79 %).

3.2 Amazon Estuary

The Amazon River is characterized by a tremendous water discharge amounting to ca. 200,000 m^3/sec (NORDIN & MEADE, 1985) with the maximum mean monthly values exceeding three times the minimum values. The sediment transport to the ocean is also enormous (1.1-1.3x10^9 t/a) (MEADE et al., 1985) making the Amazon River second only to the Ganges-Brahmaputra (1.67x10^9 t/a).

Dispersal of the river water in the Atlantic ocean is determined by two major factors: (i) the intense Guyana Current flowing north-westward across the continental slope and external shelf; and (ii) powerful tides along the Brazilian coast. Among other factors one should mention permanent passats, bottom relief, and, in particular, shallow river mouth bars.

In April-June 1971 the river flow in the surface layer and near the pycnocline was directed across the shelf in the vicinity of the river mouth but diverted northward further out, followed the shelf and mixed with the Guyana Current (GIBBS, 1982).

The bottom current near the river mouth was directed toward the coast. This implies a moderate circulation independent of tides. The maximal current velocity near the river mouth is 1.8 m/sec decreasing north-westward to 0.4 m/sec at 4° N.

In order to study the tidal impact on variability of water parameters a 24-hour anchorage was made at station 1044 (Fig. 1). During the observation period the tidal was syzygial with the water level difference of about 3.5 m.

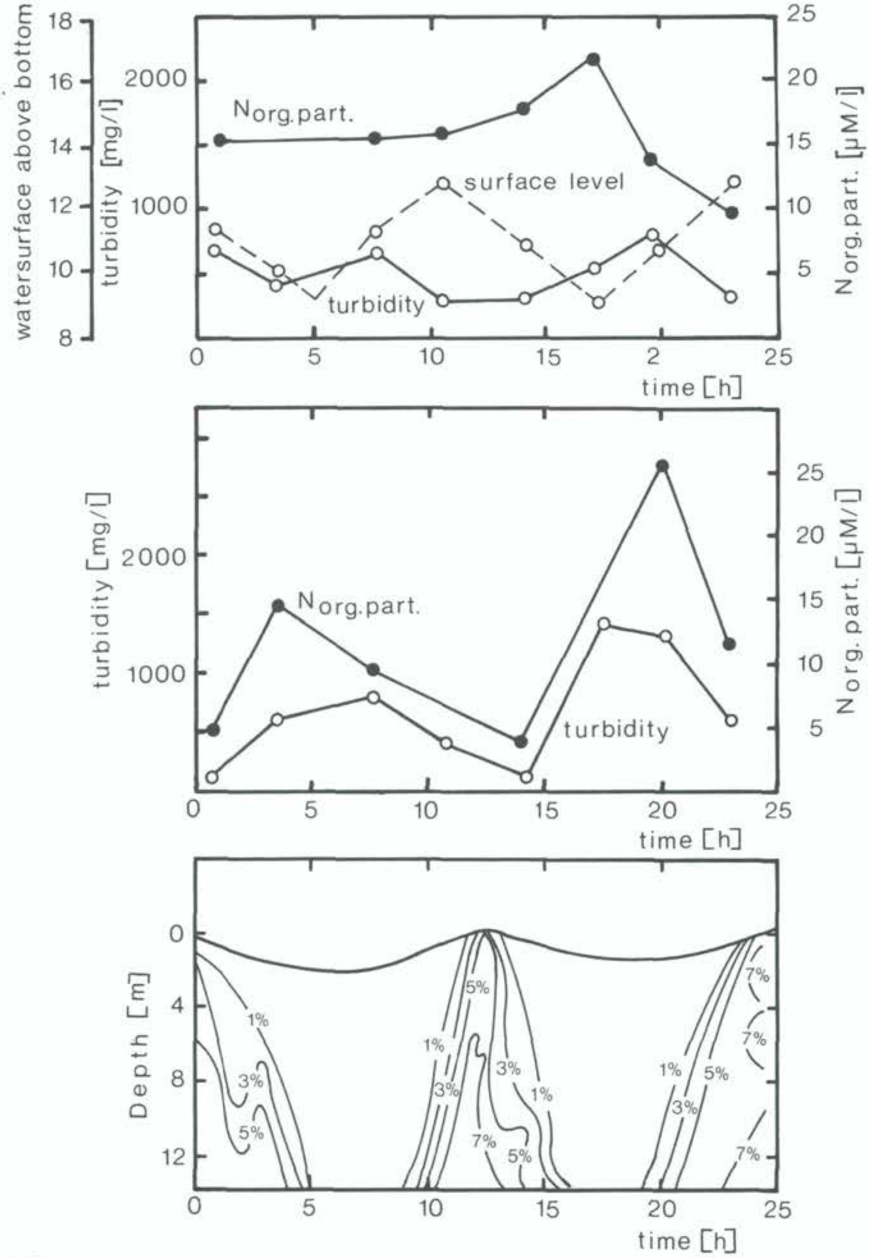

Fig. 4: Temporal variations of turbidity and particulate organic nitrogen in surface waters (a), turbidity and particulate organic nitrogen 1 m above the bottom (b), and salinity (c) at st. 1044.

Figure 4 shows changes in water level, salinity, concentration of suspended matter and $N_{org.par.}$ at the surface and at 1 m above the bottom. Most of the time river waters dominated throughout the water column (S < 1 ^{o}/oo). Only at high tide brackish waters (6-7 ^{o}/oo salinity) were present and remained for 1.5 hours at the surface. Intense water movements disturbed the bottom sediments and suspended matter concentration increased by more than one order of magnitude at the bottom (2 - 3 times at the surface) reaching extremely high values (up to 4,000 mg/l).

The $N_{org.par.}$ concentration in the surface layer does not correlate with the suspended matter concentration. From 10 to 17 hours the $N_{org.par.}$ increases from 16 to 24 μg-at/l while the suspended matter concentration varies insignificantly. This is probably due to growth of phytoplankton that has a higher N content ($N_{org.par.}$ content in the suspended matter increases twofold - from 0.03 to 0.06 %). In near-bottom waters with the totally suppressed photosynthesis the changes of $N_{org.par.}$ concentration correlate with the changes in concentration of suspended matter.

The Amazon estuary was previously classified into three zones according to water color and salinity: brown waters - the zone of terrigenous material; green waters - the zone of biogenic material; and blue waters - the oceanic zone (SHOLKOVITZ & PRICE, 1980). Optical studies carried out during the 9th cruise of R/V PROFESSOR SHTOKMAN provided data for a 4-zone classification: brown-yellow, yellow, green and blue waters (MONIN & KOPELEVICH, 1983). The boundaries between brown-yellow and yellow waters (boundary 1) and between yellow and green waters (boundary 2) represent fronts where salinity and other characteristics change rapidly, while the boundary between green and blue waters (boundary 3) is less pronounced.

The first two zones are characterized by an extremely high turbidity and are separated by a jump in salinity of about 5-6^{o}/oo. The change from the yellow to the green waters occurs at the salinity of about 14^{o}/oo and corresponds to the end of the river mouth bar and the beginning of a considerable increase in depth. The suspended matter concentration here drops to 3-10 mg/l. The clearing of the water and nutrient inflow favor an increase in productivity. According to our data (MONIN & GORDEEV, 1988) there was a sharp increase in the diatoms development in 1983 near stations 1047-1049 and the width of the growth belt was about 20 km. This correlates with EDMOND's et al. (1981) estimates although the salinity during our observations was 17-22 ^{o}/oo instead of 7-15 ^{o}/oo in their work.

Table 3 and Figure 5 illustrate the distribution patterns of different N forms versus salinity along the Amazon River profile from the mouth toward the ocean .

Nitrate: The maximum content is observed at 3-5 ^{o}/oo salinity (up to 13.8 μg-at/l) which significantly exceeds its concentration at zero salinity (8-9 μg-at/l) (Fig. 5a). The maximum nitrate content coincides with a slight but significant minimum of dissolved oxygen. At a salinity of 10 ^{o}/oo the NO_3^- concentration rapidly drops and remains at a low level (1-2 μg-at/l and less, i.e., down to 0.2) until the open ocean water is reached. A sharp decrease in nitrate concentration is observed in parallel

Table 3

Forms of nitrogen and organic carbon in waters of the Amazon estuary.

Station	Total Depth	Sample Depth	TSM	Sal.	pH	O_2	Dissolved forms						Particulate forms				
							NO_2^-	NO_3^-	NH_4^+	N_{org}	N_{tot}	C_{org}	N_{org}	N_{org}	C_{org}	C_{org}	C/N
	m	m	mg/l	permil		ml/l	μM/l	μM/l	μM/l	μM/l	μM/l	mg/l	μM/l	%	mg/l	%	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1044-1	12	0	735	0.44	7.85	4.87	0	13.2	1.6	14.2	29.0	3.4	16.0	0.03	4.5	0.61	20
		8	165	4.19	7.57	4.37	0	14.0	-	33.8	-	5.5	5.7	0.05	1.25	0.75	15
1044-2	12	8	510	1.50	7.55	4.70	0	13.0	3.5	28.5	45.0	5.9	14.3	0.04	3.7	0.72	18
1044-3	11	0	584	0.07	7.50	5.44	0	11.4	4.0	16.5	31.9	-	16.0	0.04	3.9	0.67	17
		8	698	0.07	7.74	5.16	0	12.2	-	10.4	-	-	-	-	7.9	1.1	-
1044-4	12	0	361	0.83	7.80	5.07	0	7.2	4.0	28.6	39.8	3.3	16.8	0.065	1.9	0.52	8
before front		0	199	5.96	7.63	4.37	0	13.8	-	8.2	-	2.9	-	-	-	-	-
after front		8	356	6.20	7.90	-	0	10.2	7.0	12.0	29.2	4.0	-	-	2.1	0.59	-
1044-5	10	0	450	0.61	7.77	5.01	0	2.7	8.0	23.0	33.7	1.8	18.6	0.06	4.1	0.91	15
	10	8	84	3.72	7.60	4.48	0	13.8	-	-	-	4.1	4.8	0.08	1.1	1.3	16
1044-6	9	0	474	0.05	7.84	5.20	0	12.6	2.8	-	-	4.6	21.6	0.06	6.0	1.3	21
		8	1068	0.06	7.70	5.10	0	0.4	2.2	9.4	12.0	5.4	-	-	7.4	0.89	-
1044-7	10	0	722	0.07	7.90	5.26	0	8.6	4.0	19.2	31.8	-	14.6	0.03	12.8	1.8	60
		8	1074	0.32	7.70	5.05	0	12.0	3.8	-	-	-	26.8	0.03	3.1	0.29	10
1044-8	12	0	293	1.26	7.85	4.91	0	12.6	3.5	20.9	37.0	4.2	10.2	0.05	2.0	0.68	14
before front	8	8	394	3.69	7.62	4.44	-	-	-	-	-	4.5	8.3	0.03	0.8	0.20	7
after front	0	-	-	-	-	0	11.8	5.4	24.0	41.2	4.2	9.0	-	1.7	-	-	
1045	1100	0	0.67	36.23	8.15	4.55	0	0.5	-	-	-	-	-	-	-	-	-
		400	0.85	36.74	7.83	3.00	-	-	-	-	-	-	0.72	1.2	0.08	9.4	8
		750	1.11	34.60	7.80	2.42	-	-	-	-	-	-	0.40	0.5	0.25	22.5	45
1047	43	0	1.3	22.18	8.15	4.96	0	0.4	0.4	24.6	25.4	2.4	5.0	5.3	1.1	84.6	16
		18	1.8	36.15	8.10	3.82	0	0.8	0.3	-	-	2.3	0.66	0.51	0.3	16.6	32
		40	1.3	36.24	8.12	3.76	0	0.8	1.1	13.0	14.9	1.7	1.4	1.5	0.4	30.7	20
1048	70	0	0.70	30.54	8.17	4.70	0	0.2	0.4	12.0	12.6	2.8	2.3	4.6	0.4	57.1	12
1049	27	0	2.1	17.49	8.15	5.86	0	1.1	5.6	22.8	29.5	4.1	5.9	3.9	1.4	66.6	17
		25	19.0	36.18	8.09	3.39	0	2.2	0.1	19.6	21.9	2.3	2.8	0.20	0.4	2.1	10
1050	14	0	4.0	10.63	8.06	4.96	0.1	8.6	3.4	16.8	28.9	3.3	1.1	0.38	0.7	17.5	46
		10	39.0	32.03	8.04	3.52	0.2	1.4	0.1	12.6	14.3	1.9	-	-	-	-	-
1052	10	0	138	9.79	7.76	4.47	0.1	5.3	5.6	13.4	24.4	3.1	4.6	0.04	1.2	0.87	19
1054-1	10	0	23.3	9.97	7.79	4.70	0.25	4.2	0.6	11.8	16.8	2.2	2.2	0.13	0.5	2.1	16
		8	165	23.09	7.95	3.60	-	-	-	-	-	3.5	2.7	0.02	0.7	0.42	19
1054-2	10	0	7.6	10.79	7.90	4.65	0.1	1.2	-	20.2	-	5.3	1.6	0.29	0.5	6.6	22
		8	19.1	18.52	7.97	4.18	0.25	2.7	0.9	5.8	9.6	2.5	-	-	0.75	3.9	-
1054-3	10	0	5.3	14.22	7.98	4.99	0	1.6	2.1	17.3	21.0	2.9	3.6	0.95	0.75	14.1	19
		8	17.0	29.11	8.02	3.48	0	1.4	1.8	14.6	17.8	2.0	-	-	0.3	1.8	-
1055-1	11	0	7.3	21.34	8.10	5.05	0	3.6	0.1	8.7	12.4	1.6	3.5	0.67	0.8	11.0	16
		8	112	34.83	8.04	2.79	0	1.0	2.4	9.0	12.4	1.4	-	-	-	-	-
1055-2		8	266	31.94	7.99	2.69	-	-	-	-	-	-	4.4	0.02	-	-	-
1056	64	0	0.70	25.62	8.20	5.18	0	1.4	2.5	-	-	2.1	2.1	4.2	-	-	-
		10	1.80	28.03	8.18	4.60	0	0.4	2.7	9.0	12.1	2.0	1.5	1.1	-	-	-
		40	1.77	36.36	8.10	3.94	0	1.0	0.2	18.0	19.2	2.3	0.78	0.61	-	-	-
1057	84	0	1.80	33.21	8.20	4.79	0	1.0	0.7	7.9	9.6	1.7	1.0	0.78	-	-	-
1060	38	0	3.8	19.68	8.15	7.06	0	0.1	2.6	16.2	18.9	2.6	-	-	-	-	-
		30	9.3	36.30	8.10	3.59	0	0.3	2.5	-	-	2.9	1.8	0.27	-	-	-

with an abrupt decrease in turbidity due to suspended matter precipitation (suspended matter concentration drops from 700-1,000 mg/l at a low salinity to 3-10 mg/l at 10 °/oo). As already mentioned, this stimulates high biological productivity.

Ammonium: NH_4^+ is distributed along the profile in a pattern similar to that of the nitrate (Fig. 5b). The reasons for the maximum content at the salinity of 3-5 °/oo are identical to those for the nitrate. It can be supposed that the growing ammonium concentration is partially due to the death of fresh water hydrobionts. Within the green waters the ammonium is partially consumed by plankton, partially dispersed and transformed into the more stable N forms.

Dissolved organic nitrogen: $N_{org.dis.}$ behavior depends on salinity in a different way than that of NO_3^--N and NH_4^+-N (Fig. 5b). A wide range of concentrations is

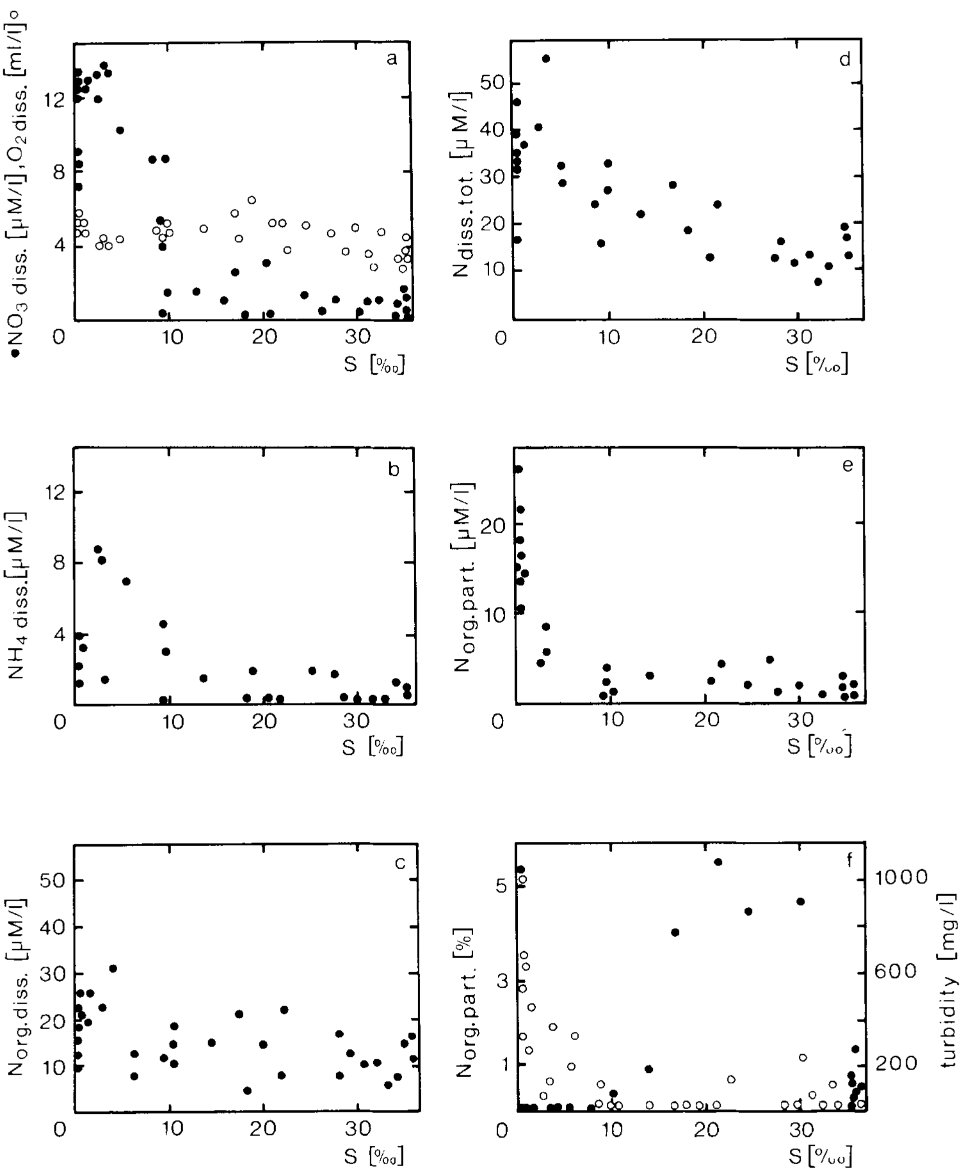

Fig. 5: Distribution of nitrogen forms in the Amazon estuary versus salinity: (a) NO$_3$, O$_2$; (b) NH$_4$; (c) N$_{org'dis.}$; (d) N$_{tot'dis.}$; (e) N$_{org.par.}$; (f) N$_{org'par.}$ (%), turbidity.

observed at all salinities. Against this background the N$_{org.dis.}$ content constantly decreases from 20-30 μg-at/l at low salinities to 10-15 μg-at/l at 30-36 ^{0}/oo. We can probably speak of a quasi-conservative behavior of the N$_{org.dis.}$ in the Amazon estuary.

The total dissolved nitrogen: The distribution of the sum of all forms of dissolved nitrogen is the superposition of the distributions of these forms (Fig. 5d). It is noteworthy that the maximum content is observed at a low salinity and that concentrations systematically decrease while the salinity increases.

Particulate organic nitrogen: The distributions of $N_{org.par.}$ if expressed in μg-at/l (Fig. 5e) or in percentage to dry matter of the suspended particles (Fig. 5f), differ along the profile. Expressed in μg-at per unit of volume the $N_{Org.par.}$ behaves similarly to the suspended matter distribution (Fig. 5f), i.e. it sharply drops (from 15-20 μg-at/l to 3-5 μg-at/l) during the salinity increase from 0 to 10 ^{o}/oo and decreases later more gradually to 1-3 μg-at/l and below. Expressed in %, the $N_{org.par.}$ is low and constant at < 10 ^{o}/oo (0.03-0.06 %) and jumps by two orders of magnitude (maximum up to 5.3 %) at salinities > 10 ^{o}/oo. Such a high suspended matter enrichment by nitrogen as well as a spread in values (almost tenfold) is due to the intense N assimilation by the planktonic organisms. It was shown (SHOLKOVITZ & PRICE, 1980) that phosphorus has a similar distribution pattern in the Amazon estuary.

4. Conclusion

Analysis of the concentration of main nitrogen forms (nitrite, nitrate, ammonium, dissolved organic nitrogen, total dissolved nitrogen, and particulate organic nitrogen) in the major water types of the Amazon basin (white, clear, and black waters) shows that their distributions follow a similar pattern. Nitrite concentrations are very low everywhere and the dissolved organic nitrogen dominates all other N-forms. High C/N ratios in the suspended matter (average values for different water types vary from 16 to 22) indicate an important contribution of terrigenous organic matter to the particulates in the Amazon River as already mentioned in the literature (WISSMAR et al., 1981). A direct linear dependence of the nitrate concentration with the dissolved oxygen can be explained by the organic matter reduction in várzea lakes at high water periods. The fact that the regression lines representing the NO_3^--$O_{2dis.}$ dependence do not coincide for different water types and show different slopes, testifies to variable intensity of organic matter reduction processes in white, clear, and black waters.

The behavior of the nitrogen forms in the Amazon estuary is particularly affected by an intense precipitation of the riverine suspended matter, by a complicated pattern of currents that was adequately described by the GIBBS three-layer model (GIBBS, 1982), as well as by a jump in the diatom productivity in the green water zone (at salinities > 14 ^{o}/oo).

The inflow of saline water near the bottom towards the river mouth favors the formation of nitrate and ammonium maxima at salinities of about 3-5 ^{o}/oo (the so-called biogenic trap). The salinity increase is accompanied by lower turbidity that favors a diatome bloom. An outburst of plankton productivity leads to an almost complete disappearance of nitrite and ammonium and a sharp relative enrichment of N in the suspended matter. A similar nitrate distribution was observed by EDMOND et al. (1981) in May-June 1976 with the only difference that a 20 km zone of high productivity was found within the salinity range of 7-15 $^{o}/oo$ while in 1983 it ranged from 17 to 22 $^{o}/oo$. Unlike nitrate and ammonium, the dissolved organic nitrogen behaves quasi-conservatively in the Amazon estuary. Although differences in the $N_{org.dis.}$ are considerable throughout the salinity range, it can be supposed that this N form is of low importance to the phytoplankton growth.

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Geochemistry of Sedimentation in Estuaries of Rivers from the Arid Climate Zone

by
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With 3 Tables

Contents

Abstract

Using the examples of the rivers in the basins of the Sea of Azov, Caspian Sea and Lake Aral (i.e., the Kuban, Volga, Don, Ural, etc.) the authors studied the regularities in the geochemistry of sedimentation in estuaries and coastal waters. It is shown that the climatic aridity influences ongoing estuarine processes: adsorption processes are intensified, aggregates form from organic matter and minerals, and chemogenic calcite dilutes metal concentrations in suspensions within the estuarine mixing zone. The geochemical differentiation is apparent in river deltas and becomes weaker in areas transitional to the sea.

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1. Introduction

Recently, investigations of estuarine processes have gained special importance. This is due to several reasons, primarily because transitional regions of the river-sea interface suffer from heavy technological impact but also because they represent effective geochemical barriers. The latter considerably affects precipitation of chemical elements and determines how elements enter the marine ecosystems. Of special interest in this context are the estuaries of the Sea of Azov, Caspian Sea and Lake Aral. Particulate and dissolved substances are transported to these estuaries by rivers which originate in the humid zone, but their deposition is governed by the conditions of an arid and semiarid climate. Thus large amounts of bicarbonate type fresh water are available in arid regions forming extensive mixing zones with the brackish waters of the inland seas.

2. Sediment Material Losses in Estuaries

It is well known (e.g., GORDEEV, 1983; KHRUSTALEV, 1986) that estuaries represent traps for terrigenous substances and prevent further transport of certain chemical elements. The following data characterize the estuarine losses of dissolved and particulate matter.

The Volga delta traps from 30.6 to 42 % of the metals transported by the riverine suspended matter. Additionally, from 23.6 to 39.6 % accumulate in the coastal area (up to 3 m isobath) (see Table 1). Only a small portion of the particulate matter is transported to the open Caspian Sea. Sedimentation in the outer estuaries of the North Caspian Sea is accompanied by a decrease in concentration of particulate elements due to preferential settling of the terrigenous fraction and a relative increase in the particulates derived from the "marine" environment. Concentration of dissolved metals also decreases but to a lesser extent than that of particulate forms. In the North Caspian Sea, which is actually the outer estuary of the Volga, Ural and Terek, we can therefore observe an intense separation of dissolved metals from their particulate form.

Investigations have shown that after passing through the transitional zones of the river-sea interface chemical elements change their properties. The data of KONOVALOV et al. (1968) and our own investigations in the river waters of the Volga, Ural and Terek (KHRUSTALEV, 1978) allow to discern two groups of elements: (i) Ba, Pb, Ti and (ii) Sn, Mn, V, Fe, Zn, Ni, Cu. The former group contains metals transported mainly in particulate form while the latter represents metals transported both in dissolved and particulate forms. In North Caspian waters the elements group somewhat similarly: (i) Ba, Pb, Fe, Mn, V are associated with particulates while (ii) Ni, Cu and Mo are predominantly dissolved. Fe, which easily forms oxide-hydroxide coatings in oxic seawater, changed, however, from the dissolved to the particulate form.

Table 1

Rate of deposition of elements with suspended matter in the Volga delta and in adjacent coastal waters.

Element 1	Mean delta 2	Depo. delta 3	Depo. delta 4	Mean coast 5	Depo. coast 6	Depo. coast 7	Mean SM 8	Disch. SM 9	Disch. SM 10
Fe	1.64	208.3	33.2	1.64	180.4	28.7	5.20	239.2	38.1
Ti	0.24	30.5	40.3	0.24	26.4	34.9	0.41	18.8	24.8
Mn	0.05	6.4	30.6	0.09	9.9	47.4	0.10	4.6	22.0
V	37	469.9	39.6	41	451.0	38.0	58	266.8	22.4
Ni	17	215.9	35.4	17	187.0	30.7	45	207.0	33.9
Cu	25	317.5	39.7	25	275.0	34.4	45	207.0	25.9
Pb	14	117.8	42.7	15	165.0	39.6	16	73.6	17.7
Ga	6	76.2	27.2	6	66.0	23.6	30	138.0	49.2
Mo	1	12.7	33.9	1.	11.0	29.3	3	13.8	36.8
Zn	37	469.9	39.1	37	407.0	33.8	71	326.6	27.1

Columns:

2: Mean elemental concentration in delta sediments (Fe, Ti and Mn in per cent, others in ppm).

3: Deposition in delta (in 10^3 t/a for Fe, Ti and Mn, and in t/a for the other elements).

4: Deposition in delta in % of total transport.

5: Mean elemental concentration in coastal sediments (Fe, Ti and Mn in per cent, others in ppm).

6: Deposition in coastal waters (in 10^3t/a for Fe, Ti and Mn, and in t/a for the other elements).

7: Deposition in coastal waters in % of total transport.

8: Mean elemental concentration in suspended matter (SM) (Fe, Ti and Mn in per cent, others in ppm).

9: Discharge of elements into the Caspian Sea by suspended matter (in 10^3 t/a for Fe, Ti and Mn, and in t/a for the other elements).

10: Discharge of elements into the Caspian Sea by suspended matter in % of total transport.

Similarly, high losses of particulate elements are also found in the Don River where in the coastal area from 28.3 to 69 % of the transported elements come to rest. In case of the Kuban River from 12 to 48 % of the total elements settle in the delta and from 20 to 35 % precipitate in the coastal area (see Table 2). These data show that different rivers vary with regard to the amounts of the terrestrial matter settled in the delta and in coastal waters.

Table 2

Rates of deposition of elements associated with suspended matter in the Kuban delta and in coastal waters under natural runoff, in t/a (using data on element concentrations in the suspended matter by LUBCHENKO & BELOVA, 1973).

Element 1	Transport into delta 2	Transport out of delta 3	Deposition in delta 4	Deposition in coastal reg. 5	Discharge to sea 6
Fe	300135	197960	102175	89250	108710
Ti	23555	15510	8045	6930	8580
Mn	3365	3136	230	1056	2079
Zr	1548	799	746	307	442
Zn	1077	926	151	414	512
V	660	484	175	216	268
Cr	586	428	158	191	237
Ni	316	249	67	131	138
Cu	182	160	22	71	88

Columns:

2: Transport (in t/a) above the delta (m1) determined by multiplying the suspended matter transport with the elemental concentrations of the suspended matter.

3: Discharge (in t/a) into coastal waters by the Kuban and Protoka distributaries (m2) determined by multiplying the suspended matter transport with the elemental concentrations of the suspended matter.

4: Deposition in the delta (m1-m2) calculated by taking the difference between the transport rates above the delta minus that at the river mouths of the Kuban and Protoka distributaries.

5: Deposition in coastal waters as estimated by multiplying the amount of accumulated terrigenous material with the mean concentration of the elements in bottom sediments (on a carbonate-free basis).

6: Discharge into the Sea of Azov estimated by difference between the discharge and deposition in the coastal water, and by multiplying the suspended matter discharge to the sea with its concentrations in elements.

3. Granulometric Differentiation

Deltas and transitional zones are also characterized by a significant granulometric differentiation of the alluvial material. Particularly, a relative enrichment of suspended pelitic particles occurs. As different minerals tend to form grains in different size fractions, the total elemental composition changes according to changes in the size distribution of suspended particulates. An example are Zr and

Ti, which occur in easily deposited aleuritic and gross-aleuritic particles (LUBCHENKO & BELOVA, 1973; GORDEEV, 1983). Ni, Cu, and Ga are, on the other hand, related with the fine-grained fraction and are lost only to a small extent in deltas and outer estuaries. This behavior is, for example, documented for the Saint Lawrence estuary (BEWERS & YEATS, 1977). There 89 % of $Fe_{par.}$ and 47 % of $Mn_{par.}$ settle in the estuaries, compared to only 11 % of $Cu_{par.}$.

4. Flocculation

Mixing of river water with seawater is accompanied by the formation of flocs. These consist mostly of organic matter. According to experimental data flocs are formed rapidly at a salinity of about 5 ^{o}/oo and at slower rates at salinities up to 30 ^{o}/oo (SHOLKOVITZ, 1976). Under the environmental conditions of the Sea of Azov, the Caspian Sea and Lake Aral the flocculation range is probably limited due to an intense consumption of organic matter by zooplankton. Significant flocculation in the mixing zones probably occurs outside the areas of mass growth of algae.

Floc sizes do not allow their gravitational settling because of the strong hydrodynamics. Flocculation should therefore favor enrichment of suspended matter rather than formation of bottom sediments. The real situation is, however, different. The humic matter is transported in the form of polyelectrolytes or negatively charged hydrophilic colloids and forms aggregates with the fine-grained minerals adsorbing certain elements dispersed in water. In the suspended matter one can observe under a microscope irregularly shaped aggregates composed of amorphous organic matter and clay-sized minerals. Thus flocs settling together with pelitic particles enrich bottom sediments with elements they have adsorbed.

5. Adsorption-Desorption Processes

Analysis of concentrations of chemical elements in water, suspended matter, and bottom sediments of the outer estuary indicate a wide range of sorption phenomena and the presence of two opposing processes, i.e., adsorption and desorption. The complex nature and dynamics of sorption processes can be illustrated by the system: Kuban River / river mouth / the Sea of Azov. The system is characterized by a rapid change of riverine to marine processes. Chemical elements can be subdivided into two groups according to changes in their concentrations. The first group includes Fe, Ni, V, Cu, and Mn with their relative content gradually decreasing 1.5-4 times while passing through the river mouth. For example, the $Ni_{par.}$ content in the spring of 1977 decreased from 27 to 17 ppm, from 80 to 23 ppm in summer, and from 38 to 21 ppm in autumn, probably due to desorption. At the salinity above 5^{o}/oo fluctuations in the elements content are usually insignificant (DEMINA et al., 1978; GORDEEV, 1983). The second group comprises Pb, Co, Cr and Zn. As a rule, their content varies insignificantly during the transition to the different sedimentation conditions (KHRUSTALEV, 1982). According to DEMINA et al. (1978)

the Fe, Mn, and Cu contents decrease exponentially with the decreasing salinity in the Kuban estuary, while the Zn content decreases insignificantly.

It is noteworthy that in the clayey silts of the coastal area and in suspended matter of the Kuban water Mn, Ni, and Cu concentrations usually coincide or are slightly lower than their concentrations in the bottom sediments. Therefore, the above-mentioned combination of the inconsistent trends in sorption processes exists in reality. The simultaneous existence of the two seemingly opposite, yet interrelated processes of desorption and adsorption indicates non-conservative behavior of chemical elements in the mixing zones. Increased macro- and microelement concentrations in bottom sediments as compared with suspended matter is due to (i) adsorption to clayey minerals in the mixing zone, (ii) differentiation of mineralogical composition of a fine-grained fraction and (iii) flocculation. It is probable that such minerals as kaolinite, chlorite and hydromica in new environmental conditions intensely adsorb Fe, Cu, Mn, Ni, and other elements. They therefore lose their negative charge, become neutral, form aggregates and consequently precipitate enriching the bottom sediments with certain compounds.

In the Taganrog Bay, which receives the waters of the Don, chemical elements of suspended matter divide also into two groups. The first group includes V, Ni, and Cu which decrease in content seawards. In spring, at the beginning of flooding, the maximum contents are localized within limited areas near the Don river mouth. In summer and autumn the areas expand. The external boundaries coincide with the 6-7 $^{o}/oo$ isohaline. Lowered V, Ni, and Cu contents in suspended matter of the mixing zone cannot be explained by desorption alone. Newly formed calcite may play an important role for diluting concentrations of metals. The second group includes Co, Cr, and Pb, their concentrations in the suspended matter also tend to decrease although not so obviously and not throughout the year.

Adsorption and desorption effects can be evaluated only approximately due to the lack of laboratory experiments which could simulate different environmental conditions and estuarine processes. Often changing sedimentation conditions (within the nine years of observations from 1970-1979 not a single situation was repeated) render very different elemental distributions and statistics of the long-term data base allow only a rough assessment of sorption processes. Investigations have shown that desorption dominates in the years with low discharge and adsorption in years with high discharge. This highlights a unique self regulation of marine ecosystems.

Distribution of particulate and dissolved elements in the mixing zones of the Volga, Ural, and Terek supports the concept that sorption actively participates in the geochemistry of sedimentation. Estuaries have a lower content of most elements in the suspended matter and a higher content of some dissolved elements when compared to rivers. Typically higher contents are found for Fe, V, Cu, Mo, and Ni in coastal waters in front of the river. Now a question arises: what factors cause these high contents in the transition zones of the Volga, Ural, and Terek in spite of the intense consumption of elements by phyto- and zooplankton? Part of the answer may have been given by STRAHOV (1976): "real geochemical mobility of an element is determined not only by the ratio between its dissolved and particulate forms but also by its distribution in the granulometric fractions of suspended matter. Low content of the dissolved form of an element is probably compensated by its subcolloidal fraction in the suspended form that should enhance its migration ability". When exposed to different hydrochemical and hydrobiological conditions, the elements adsorbed to colloids desorb in the estuary. Beyond this zone the content of microelements both in the suspended matter and in solution is lower than that in river water.

Unlike the situation described above for the outer estuary we have not observed any significant loss of dissolved elements in the deltas of the Volga, Don, and Kuban despite a weaker runoff. While passing through the Kuban delta chemical elements even increase in concentration. Fe, Cr, and Cu enrich 6x, 4x, and 3x, respectively in the Kuban between Krasnodar and Temryuk (see Table 3).

An only insignificant downstream increase in concentrations of elements is found in the Volga and Don river mouths particularly during the warm season.

Table 3

Changes in concentrations and discharge of dissolved elements in the Kuban River during transport in the delta (using data by LUBCHENKO & BELOVA, 1973).

Element 1	Dissol. μg/l 2	Dissol. μg/l 3	Transport t/a 4	Transport t/a 5	Difference t/a 6
Fe	82.00	13.00	746.20	139.20	+607.00
Mn	13.00	4.00	118.30	46.40	+71.90
Zn	3.60	3.10	32.76	35.96	-3.20
V	1.60	0.64	14.56	7.42	+7.14
Cu	0.80	0.24	7.28	2.78	+4.50
Ni	0.40	0.24	3.64	2.78	+0.86
Co	0.14	0.12	1.27	1.39	-0.12

Columns:

2: Concentration, in μg/l, at river mouth of the Kuban River (station Temryuk).
3: Concentration, in μg/l, above the delta (station Krasnodar).

4: Transport, in t/a, at river mouth of the Kuban River (station Temryuk).

5: Transport, in t/a above the delta (station Krasnodar).

6: Changes in the transport of dissolved elements, in t/a.

Total discharge of the Kuban River was 11.6 km^3/a of which 9.1 km^3/a reach the Sea of Azov. The element transport was estimated by multiplying the river runoff by the concentration of the various elements in the water.

The above data show that in an arid climate mobility of chemical elements increases gradually from the inner delta to the coastal water. This is accompanied by an increase of mineralization of river water.

6. Conclusion

A considerable geochemical differentiation occurs during the sediment transport through estuaries. Under arid climate conditions the separation process is very pronounced in the delta and less pronounced, though broad in scope, in the transition zones. Precipitation of particulate elements occurs mainly in deltas and is sometimes (for example in the Kuban delta) accompanied by their increased input to the dissolved form. Estuaries are traps for particulate and, less effectively, for dissolved elements. This causes changes in the migration pattern of elements beyond the estuaries. The role of dissolved forms increases especially for geochemically mobile elements, such as V, Cu, Mo, and Fe. In case of the Kuban the dissolved Mo dominates during its transport in the delta.

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Transformation of Organic Matter in the Amazon River Estuary

by
V.E. ARTEMYEV, Moscow *)

With 6 Figures

Contents

Abstract

The behavior of dissolved organic matter (DOM) and of particulate organic matter (POM) was investigated in the estuarine mixing zone of the Amazon. Samples were collected by the Soviet expedition aboard the R/V PROFESSOR SHTOKMAN in April 1983. Non-conservative behavior of OM was found in the low salinity zone of the estuary, it is largely determined by physico-chemical processes such as flocculation, adsorption and desorption. In the Amazon estuary biological production of OM by phytoplankton is evident at a large distance from the river mouth in the clear "green" waters.

1. Introduction

Several major factors determine changes in the concentration of DOM and POM in the mixing zones of estuaries: simple dilution, gravitational settling of

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particles, and physico-chemical and biological processes. Since the behavior of OM in the estuary is usually "non-conservative" and does not depend on simple dilution, the present article focuses on the physico-chemical and biological processes that influence the DOM and POM discharge of the Amazon.

Samples of water and suspended matter were collected on two profiles in the Amazon estuary during the Soviet expedition with the R/V "PROFESSOR SHTOKMAN" in April 1983 (Fig. 1). Sampling techniques and analytical procedures were described in ARTEMYEV & LAZAREVA (1986). In order to determine the behavior of OM in the Amazon estuary we compare the field measurements of

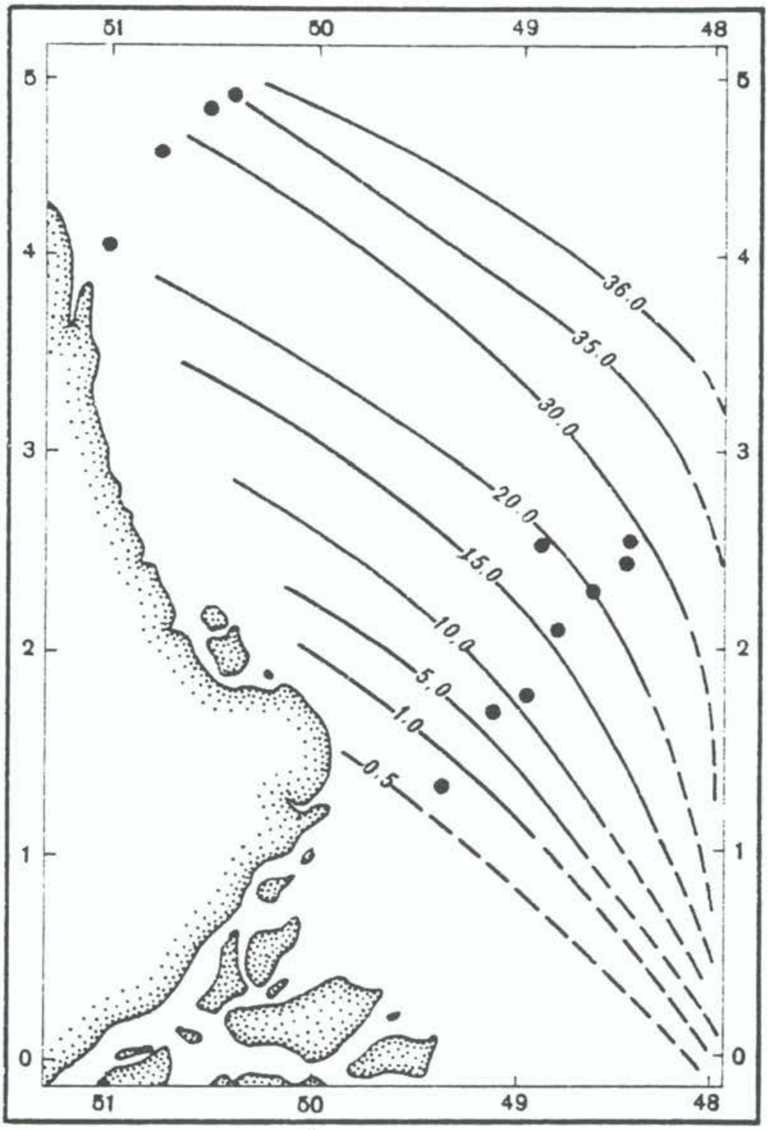

Fig. 1: Sampling stations and water salinity (^{o}/oo) in the Amazon River estuary.

dissolved and particulate organic carbon (DOC, POC) and their relation to salinity with experimental data gained by mixing river and seawater in the research vessel laboratory. The experiments were carried out according to the technique of SHOLKOVITZ (1976). The fresh water samples were collected near Obidos and the seawater samples were taken 200 miles offshore.

2. Results and Discussion

Field and experimental data are shown in Figure 2. In order to establish the dependence of DOC and POC concentrations on salinity, field data were normalized by calculating moving averages of three respectively five points (ARTEMYEV & SHAPIRO, 1987). It is clear from Figure 2 that DOC distribution with salinity does not correspond to simple conservative dilution. Statistical analysis shows that the simple dilution hypothesis is turned down in 95 % of the cases and therefore rules out "conservative" behavior of DOM in the Amazon River estuary.

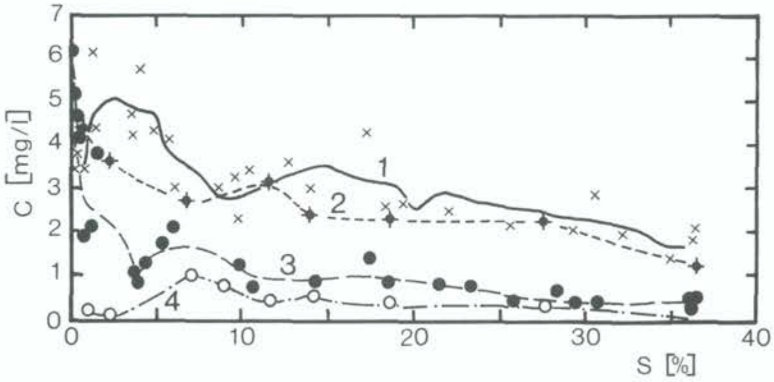

Fig. 2: Dissolved (C_D) and particulate (C_P) organic carbon in seawater of the Amazon River mouth and in mixed samples of river and ocean water with regard to salinity: 1 - C_D in natural conditions, 2 - C_D in experimental conditions (upon flocs filtration), 3 - C_P in natural conditions, 4 - C_P in flocs formed during the experiment.

Generally DOC and POC concentrations decrease towards the sea, but small increases in DOC are matched by small decreases in POC and vice versa.

To qualitatively assess the OM fluctuations for different endmember mixtures and to elucidate their nature a model was elaborated to take into account both advection and turbulent diffusion (ARTEMYEV & SHAPIRO, 1987). The data obtained were compared with the results of laboratory experiments. Figures 3 and 4 show the integral and differential "losses"[1] in the Amazon estuary. As is shown, different stages of water mixing are characterized by both higher and lower "losses" of DOM and POM. Lower losses manifest "input" or newly formed OM. Based on direction and intensity of OM concentration changes in the mixing zone, we have classified five types of waters (ARTEMYEV & LAZAREVA, 1986).

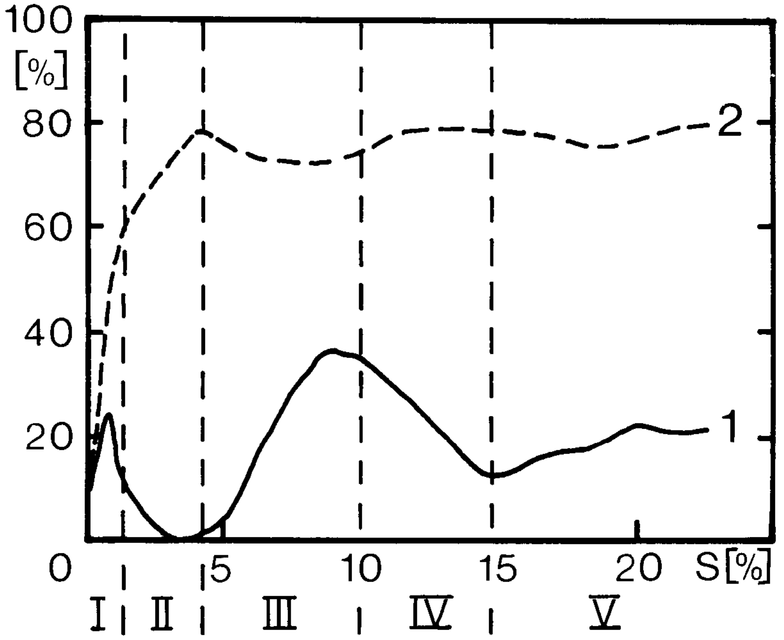

Fig. 3: Integral "losses" of the riverine DOM (1) and POM (2) in the mixing zone of the Amazon River and ocean waters. 1 - V: zones of DOM and POM (explained in the text) (ARTEMYEV & LAZAREVA, 1986).

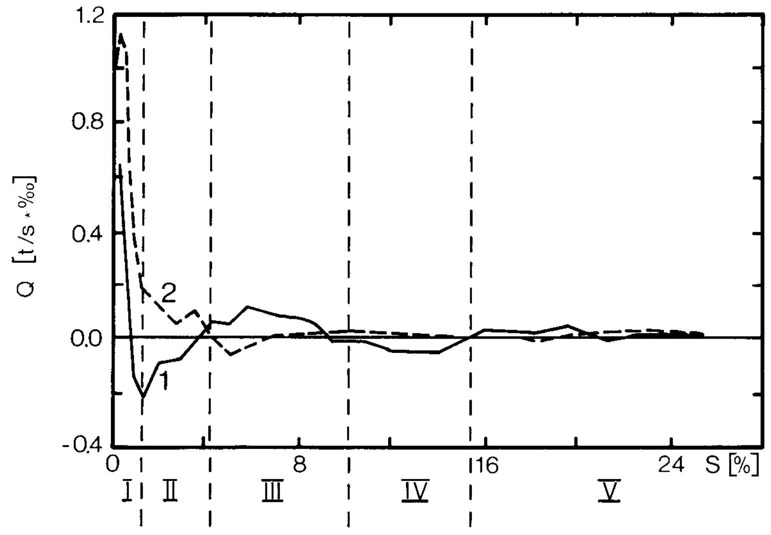

Fig. 4: Intensity of differential losses of DOM (1) and POM (2) in the mixing zone of the Amazon River and ocean waters. 1 - V: same as Figure 3.

Deviation from simple dilution of riverine OM can be caused by biological processes (primary OM production) or by physico-chemical processes (flocculation, adsorption, desorption) or by both. Let us now consider to what extent and at what stages of mixing these factors influence OM behavior in the Amazon estuary.

Aquatic primary productivity is known to depend on two factors: solar irradiation necessary for photosynthesis, and presence of nutrients in the photic layer. The amount of solar energy received by the water surface in the tropics is sufficiently high, yet light penetration depends both on quality and quantity of dissolved and particulate components which determine the optical characteristics of the water column[2] (KOPELEVICH, 1983).

The Amazon plume is divided offshore into four zones with different hydro-optical characteristics: they have brown-yellow, yellow, green, and blue waters (MONIN & KOPELEVICH, 1983). The first two zones (salinity < 12 ^{o}/oo) are characterized by high turbidity due to abundant suspended matter and intense resuspension of bottom sediments by strong turbulence.

Green water occurs 100 km offshore, it has a much lower concentration of suspended particles and a higher water transparency which favours phytoplankton growth. EDMOND et al. (1981) also found waters with a higher phytoplankton productivity in the Amazon estuary, although at a larger distance from the river mouth. High chlorophyll concentrations (over 200 mg/m^3) were also detected by the French CALIPSO expedition (May, 1983) in the clear (green) waters of the estuary in the 10-12 ^{o}/oo salinity range (Fig. 5). Phytoplankton was observed in these waters with a fluorometer sensitive at the chlorophyll-*a* absorption maximum (675-678 nm) (MONIN & KOPELEVICH, 1983). Figure 5 shows that the green water zone

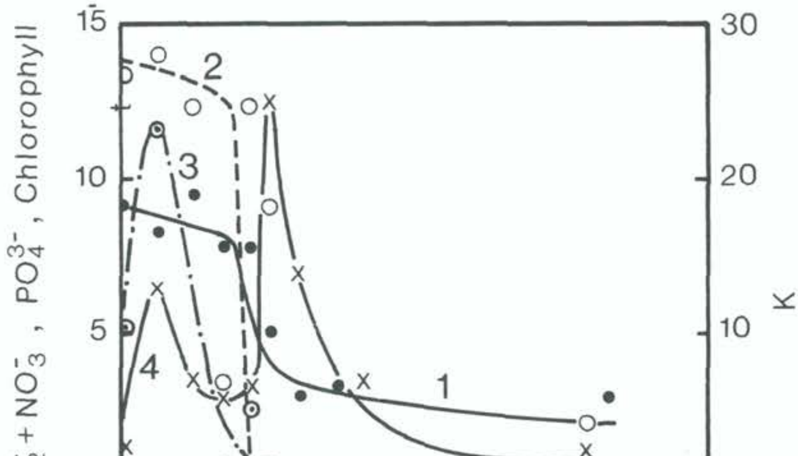

Fig. 5: Changes in phosphate concentration (1), accumulated nitrates and nitrites (2), hydrooptical characteristics (3) and chlorophyll (4) along the profile river-ocean in the Amazon River estuary in May 1983 (MONIN et al., 1986).

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[1] A conventional term denoting the OM transformations caused by physical, chemical and biological processes (V.A.).

[2] Light reduction, absorption and dispersion coefficients.

corresponds to the maximum of chlorophyll-*a* concentration (at salinities 10-15 $^{0}/oo$). It starts where the k coefficient of vertical light reduction sharply drops and water becomes transparent for sunlight. The higher DOC content in these waters is probably due to phytoplankton growth (Fig. 2). We also detected a maximum of chlorophyll-*a* at a salinity of 3-4 $^{0}/oo$. This does not result, however, from phytoplankton activity because the turbidity is too high in these brown-yellow waters. This maximum is probably caused by the resuspension of pigment-rich bottom sediments.

Because of the high turbulence and the associated turbidity in the inner estuary of the world's largest river, favorable conditions for phytoplankton growth are met only far offshore (EISMA, 1988). Figure 6 shows that the maximum primary productivity in the Amazon estuary is found in waters with a salinity of 10-15 $^{0}/oo$. while in the Zaire, Ems and Rhine estuaries it occurs at much higher salinities even more seawards.

The importance of physico-chemical processes in the mixing zone of river and ocean waters was emphasized by many authors (SHOLKOVITZ, 1976; EISMA, 1988; ARTEMYEV & LAZAREVA, 1986; ARTEMYEV & SHAPIRO, 1987). Figure 2 shows that the mixing experiments satisfactorily correlate with the results of the field observations (DOC and POC correlation coefficients are 0.7 and 0.8, respectively). Floc formation and removal of DOM occurs both in the mixing experiments and under natural conditions. The investigations show that this process is most effective in the upper zones of the Amazon estuary at low salinities.

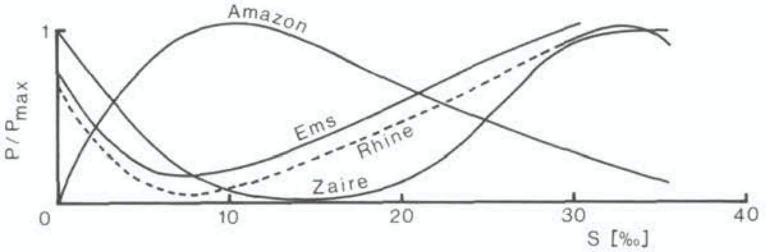

Fig. 6: Distribution of the primary productivity in relation to salinity in the estuaries of the Amazon, Zaire, Ems and Rhine rivers (EISMA, 1988).

3. Conclusion

The comparative study of factors affecting the OM behavior in the Amazon estuary shows that physico-chemical processes (flocculation, adsorption, desorption) are mainly responsible for changes in the DOM and POM ratio during the intense water mixing in the Amazon River estuary. Biological processes on the other hand, i.e., primary production, become important for OM concentrations and transformations far offshore in clear waters with high transparency.

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The Hydrogen Sulfide Balance in the Black Sea

by

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With 1 Figure and 8 Tables

Contents

Abstract

Experimental data on sulfate reduction rates in sediments and in water of the Black Sea, obtained by radio-isotope measurements (^{35}S method), are reviewed. The annual hydrogen sulfide production in shallow (aerobic) and in deep water (anaerobic) zones has been quantitatively evaluated and the total hydrogen sulfide balance was calculated. Two ecosystems which suffer most from anthropogenic impacts are recognized: the water/sediment interface in the shelf zone and the O_2/H_2S interface in the water column of the Black Sea.

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1. Introduction

The H_2S in the Black Sea is generated by the bacterial sulfate reduction both in the water column and in the Holocene sediments (i.e. those less than 7,300 years old). The quantitative aspects of sources and sinks of H_2S have, however, been a subject of scientific dispute for a long time.

A number of scientists both from the Soviet Union and from other countries presented calculations of the sulfur balance in the Black Sea based on the experimental data of SOROKIN (1962). He was the first to use the radioisotope method to determine the rate of H_2S formation in the water column and in sediments of the Black Sea. Later, several short-comings were discovered in the analytical procedures. For instance, radioisotopes were introduced into prepared silt suspensions instead of into natural silt monoliths. Besides, only acid-soluble sulfides were analyzed to determine labelled sulfur incorporation while all reduced sulfur forms should have been monitored (IVANOV, 1979).

In recent years, the ecological situation of the Black Sea has drastically changed. A rise of H_2S containing waters and the mass mortalities of benthic animals in the northwestern shelf in summer were reported (MUSIY et al., 1987; ZAITSEV, 1983).

Thus, a quantitative evaluation of the H_2S production both in shallow and deep waters of the Black Sea is needed in order to determine the areas subjected most to anthropogenic stress. We have carried out four biogeochemical cruises to different parts of the Black Sea (Fig. 1).

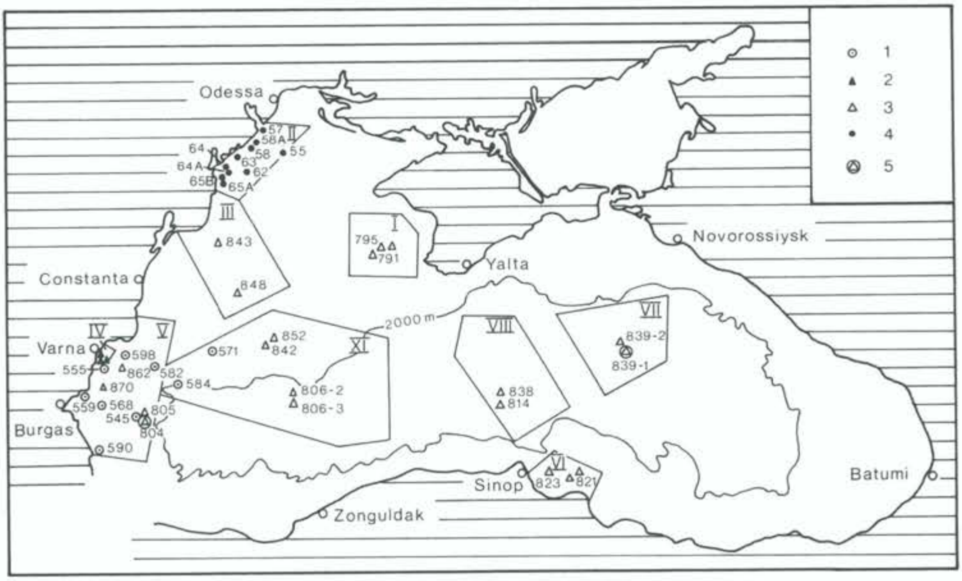

Fig. 1: Map of sampling locations. Polygons: I - the Kalamitsky; II - the north-western; III - the Danubian; IY - near Varna; Y - the Bulgarian; YI - the Anatolian. Sample stations: 1 - Cruise 5 of the R/V PROFESSOR SHTOKMAN, December 1980; 2 - diving sampling near Varna, October 1983; 3 - Cruise 8 of R/V VITYAZ, November-December 1984; 4 - R/V MIKLUKHO-MAKLAI, August 1987; 5 - water-column sampling stations during the 8th cruise of R/V VITYAZ.

2. Material and Methods

We review the results of the investigation of deep water sediments collected at 14 stations (Table 1) and shelf sediments collected at 21 stations (Table 2). Also the deep water column was analyzed (Fig. 1) vertically at 22 standard horizons (Table 3).

Table 1

Rate of sulfate reduction (S-R), H_2S production in Holocene sediments (past 7,300 years), and rate of H_2S burying in deep-water sediments in the Black Sea.

St. Nr. Depth m	Sed. layer cm	Thickness (H) cm	Water content (B) %	S-R µgS/kg/d (I)	H_2S prod. g/m²/a (P)	ΣS_{H2S} in sediment % (P')	ΣS_{H2S} in sediment g/m² (P')	Burial rate gS/m²/a
1	2	3	4	5	6	7	8	9
				0-500 m in depth				
580	5-10	8	79	49.7	9.0	1.168	255.1	
193	15-20	27	74	41.6	20.5	1.123	1,025.0	
	60-80	70	71	4.0	4.6	0.065	171.5	
	150-170	75	68	4.4	5.0	0.042	131.0	
	200-220	65	79	1.6	2.3	0.117	207.6	
	290-310	60	80	0.1	0.1	0.061	95.2	
Sum		**305**			**41.5**		**1,885.4**	**0.27**
821	0-4	6	65	29.0	2.3	1.032	273.0	
433	8-12	8	60	22.0	2.1	1.047	416.0	
	16-18	5	60	18.0	1.7	1.021	260.0	
	20-30	19	60	31.0	7.0	1.023	988.0	
	55-70	32	55	17.6	6.0	1.027	1,872.0	
	90-100	65	55	49.0	33.6	1.024	3,802.5	
	190-200	100	50	6.5	6.2	1.003	6,500.0	
	290-300	115	45	8.7	8.6	1.008	8,222.5	
	420-430	70	45	6.7	4.0	1.012	5,005.0	
Sum		**420**			**71.5**		**27,339.0**	**3.9**
Average for depth 200-500 m					**56.5**			**2.1**
				500-1,000 m in depth				
791	0-4	5	72	57.9	4.9	0.187	34.0	
602	6-10	5	69	8.4	0.6	1.065	214.6	
	11-13	6	62	24.6	1.8	1.037	307.4	
	17-21	5	62	24.6	1.5	0.823	203.3	
	23-26	5	67	27.1	1.9	0.812	174.2	
Sum					**10.7**		**933.5**	**0.13**
601	0-2	2	77	52.5	2.2	2.106	126.0	
1065	2-5	6	78	11.0	1.4	2.389	410.0	
	10-15	15	71	2.4	0.6	1.402	793.0	
	30-100	77	50	0.2	0.15	1.300	6,506.5	
Sum		**100**			**4.35**		**7,835.5**	**1.10**
Average for depth 500-1,000 m					**7.5**			**0.62**

Depth 1,000-2,000 m

842	0-1	6.5	80	24.9	3.8	2.000	338.0	
1400	12-15	13.5	80	76.7	24.6	1.100	386.0	
	25-32	16.0	80	56.4	21.4	1.112	457.6	
	40-50	14.0	82	31.8	11.7	1.220	400.0	
	50-72	22.0	84	6.1	4.0	0.910	416.4	
Sum		**72**			**65.5**		**1,998**	**0.30**
852	0-3	5	85	25.2	4.0	1.590	155.0	
1450	7-10	7	75	52.7	7.0	1.340	305.0	
	15-20	9	72	17.6	2.7	1.328	436.0	
	22-30	10	80	3.0	0.7	2.749	715.0	
	32-38	8	85	17.2	4.3	1.782	278.0	
	40-45	7	87	5.4	1.4	0.968	114.5	
	48-52	11	85	19.5	6.8	1.160	249.0	
	62-68	11	62	31.7	4.3	0.800	434.7	
Sum		**68**			**31.2**		**2,687.2**	**0.40**
805	0-3	4.0	81	27.4	2.7	2.270	224.3	
1450	5-10	7.5	42	12.7	0.8	2.270	1,284.0	
	13-15	3.5	42	0.6	0.02	1.050	277.1	
	15-25	15.0	76	19.4	5.7	1.040	486.7	
	35-45	19.0	75	11.2	4.0	0.760	469.3	
	54-65	27.0	70	18.2	7.8	1.200	1,263.6	
	88-97	21.0	50	15.8	3.1	1.100	1,501.5	
Sum		**97.0**			**24.12**		**5,506.5**	**0.80**
571	2-5	5	76	20.0	2.0	1.048	163.5	
1450	10-15	13	50	8.6	1.0	2.896	2,450.5	
	25-80	60	50	9.4	5.3	2.192	8,541.0	
Sum		**78**			**8.3**		**11,155.0**	**1.6**
Average for depth 1,000-2,000 m					**24.9**			**0.79**

Depth more than 2,000 m. Western halistaz and middle part of sea.

806	0-5	5	80	19.3	2.3	1.41	183.3	
2141	5-7	6	77	58.7	7.2	0.75	134.6	
	15-20	15	73	7.0	1.8	1.10	579.1	
	32-36	17	78	27.2	10.0	3.00	1,458.6	
	50-60	25	86	26.6	22.5	1.20	546.0	
	75-85	17	80	11.6	4.7	2.60	1,149.2	
Sum		**85**			**48.5**		**4,050.7**	**0.6**
814	0-5	7.5	62	23.4	2.2	1.04	370.5	
2180	10-15	12.5	60	30.9	4.6	1.12	650.0	
	25-30	30.0	50	20.0	5.7	1.00	1,950.0	
	70-76	26.0	50	34.3	8.5	1.05	1,690.0	
Sum		**76**			**21.0**		**4,660.4**	**0.7**
584	2-5	5.5	78	56.2	6.7	0.461	72.5	
2200	10-15	24.5	78	0.4	0.2	0.344	241.0	
	50-70	38.0	75	30.3	21.8	0.551	680.5	
	70-90	20.0	31	1.8	0.3	0.480	358.1	
Sum		**90**			**29.0**		**1,352.1**	**0.2**
Average for regions of western halistaz					**32.8**			**0.49**

				Eastern halistaz				
839 2160	0-2	3.5	76	20.3	1.4	1.80	196.6	
	5-10	11.5	75	4.8	1.0	1.70	635.4	
	20-25	20.0	57	4.2	0.9	1.00	1,118.0	
	45-50	21.0	54	1.0	0.2	1.00	1,256.0	
	62-69	16.0	52	8.7	1.4	1.14	1,138.0	
	75-85	39.0	36	4.2	1.2	0.90	2,920.0	
	140-150	39.0	46	1.3	0.4	1.24	3,395.0	
Sum		**150**			**6.5**		**10,659**	**1.5**

P = (I * H * V * 1000 * 365)/(100-B) where V is the weight of wet sediment (1.3 g/cm^3) and B is the water content (%), and

P' = [ΣS_{H2S} * H * V(100-B)]/(1000 * 7,300) where ΣS_{H2S} is the total content of all reduced sulfur compounds (%).

Table 2

Rate of sulfate reduction (S-R'), H_2S production in Holocene sediments and rate of H_2S burial in shallow-water sediments (0-200 m) in the Black Sea.

St. No. Depth m	Sed. layer cm	Thickness cm (H)	Water content % (B)	S-R rate µgS/kg/d (I)	H_2S production g/m^2/a (P)	ΣS_{H2S} in sediments (reservoir) %	g S/m^2 (P')	Burial rate gS/m^2/a
1	2	3	4	5	6	7	8	9
				Polygon near Varna				
5/26	0-1	3.5	57.0	470	18.5	0.06	-	-
	7-10	6.5	50.4	3,220	198.6	0.11		
Sum		**10**			**217.1**			
6/16	0-1	1	66.0	177	2.4	0.044		
	1-3	4	71.2	4,940	323.3	0.048		
	7-12	7	66.7	2,360	237.5	0.720		
Sum		**12**			**563.2**			
7/17	0-1	1	67.2	140	2.0	0.090		
	1-3	8	70.0	9,680	1,224.8	0.104		
	15-20	11	70.0	10,070	1,752.0	0.145		
Sum		**20**			**2,978.9**			

*North-western shelf polygon**

55/18	0-1	1	-	60,000	711.7	0.0041	
63/11	0-1	1	-	28,000	332.1	-	
65A/20	0-1	1	-	34,200	403.3	0.0027	
57/	0-1	1	35.8	242,700	2,879.0	0.2532	
11	1-2	1	38.0	427,000	4,052.2	0.2445	
65B/	0-0.5	1	47.1	236,400	2,804.3	0.2727	
11	1-3	2	50.6	97,800	185.6	0.3236	
	3-5	4.5	44.8	94,000	4,001.4	0.3341	
	10-12	6.5	50.3	54,400	335.6	0.2125	
	16-18	4.0	46.1	102,200	3,879.5	0.2151	
64A/	0-0.5	1	36.1	47,600	564.7	0.8991	
16	0.5-1.5	4	47.6	314,300	1,193.1	0.3323	
	9-11	6	51.2	286,400	1,630.7	0.2703	
65/11	2-3	3	42.3	241,900	2,525.2	0.1858	

Bulgarian polygon (rate of sediment accumulation: 100-50 cm/1,000 years)

559/	5-10	25	42.1	204.3	57.6	0.095	184.7	
26	40-60	130	34.0	37.1	67.3	0.099	1,104.2	
	250-270	140	28.2	7.2	17.0	0.300	3,931.2	
	320-350	55	26.2	0.2	0.2	0.065	343.9	
Sum		**350**			**142.1**		**5,564**	**1.59**
555/	2-5	4	35.0	243.9	19.8	0.046	23.3	
22	7-10	19	31.8	172.3	22.8	0.063	105.8	
	40-60	45	31.1	123.2	38.1	0.030	121.1	
	80-100	47	27.0	39.5	12.1	0.384	1,712.8	
	135-160	43	23.8	6.2	1.7	0.538	2,285.6	
Sum		**160**			**94.5**		**4,248.6**	**1.2**
598/	0-1	1.5	71.1	3,022.0	74.2	1.214	68.6	
55	2-5	3.5	42.5	55.8	1.6	0.498	129.1	
	5-10	25	43.0	9.2	1.9	0.836	1,548.6	
	50-70	105	39.5	10.8	8.9			
	200-220	85	37.9	5.4	3.5			
Sum		**220**			**90.1**			
590/	0-1	2.0	58.2	2,303.8	52.8	0.194	20.7	
59	2-5	6.5	56.3	1,428.2	100.0	0.337	126.4	
	10-15	77.5	54.7	705.8	564.2	0.291	1,328.3	
	160-180	95.0	43.9	528.7	425.6	0.525	3,631.0	
Sum		**180.0**			**$1,141.8^{x}$**		**5,040.0**	**1.44**
568/	0-2	3.5	63.1	380.3	17.1	0.087	8.13	
86	5-10	11.5	51.9	85.3	97.0	0.129	93.3	
	20-40	50.0	51.5	48.8	24.1	0.625	1,970.3	
	90-110	95.0	50.5	0.7	6.3	0.831	5,080	
Sum		**230.0**			**144.5**		**7,151.8**	**2.0**
862/	0-3	5.5	45.0	799.2	37.9	0.1	39.3	
61	8-10	9.5	37.5	25.8	1.9	0.5	385.9	
	20-25	10.0	40.7	16.0	1.3	1.3	578.2	
Sum		**25.0**			**41.1^{x}**		**1,003.4**	**2.0**

870-2	0-5	5.0	58.0	632.0	35.7	0.0915	24.6	
/57	5-10	10.0	56.8	379.2	41.6	0.5171	292.0	
	20-25	20.0	54.2	380.0	78.7	0.1009	119.1	
	45-53	31.5	51.7	30.6	9.5	0.2200	435.1	
	80-90	53.5	50.0	17.8	9.0	0.3692	1,252.0	
	150-160	40.0	45.9	104.9	36.8	0.4	1,125.3	
Sum		**160.0**			**211.3**		**4,594.3**	**1.3**
Total for Bulgarian shelf for 3,500 years								
The Kalamitsky polygon (rate of sediment accumulation: 5 cm/1,000 years)								
795/	0-1.5	1.5	63.2	605.5	11.7			
150	1.5-6	6.0	63.0	40.0	3.1	0.289	165.0	
	6-11	5.0	60.0	17.2	1.0			
	11-25	21.5	58.4	23.0	5.6	0.455	4,000.0	
	40-50	17.5	54.5	13.9	4.0	1.302	2,118.0	
Sum		**50.0**			**25.4**		**6,283**	**0.9**
The Dunaysky polygon (rate of sediment accumulation: 10 cm/1,000 years)								
843/	0-2	2.5		651.0	19.3			
52	3-5	10.0		810.0	96.1			
	20-25	12.5		75.0	8.9			
848/118	0-5	12.5		128.9	19.1			
	20-25	12.5		22.9	2.7			
The Anatolian polygon (rate of sediment accumulation: 33 cm/1,000 years)								
823/108	0-5	7.5		447.9	39.8			
	10-20	12.5		9.0	1.3			
	20-25	7.5		7.6	0.5			
	30-40	42.5		7.0	2.8			
	100-110	40.0		3.0	1.1			

* rate of sediment accumulation is not measured;

x values not included in calculation of mean value

Sediment monoliths for the experiments were obtained from dredges and tube corers by subsampling the recovered sediment with tipless glass syringes. Water samples were carefully drained into glass vessels from Niskin water samplers. Radioisotope experiments were carried out on board at in-situ temperature. Incubations lasted from 24 to 72 hours. The amount of ^{35}S tracer transferred from sulfate was determined in all major reduced compounds: in acid-soluble, elemental and pyrite sulfur.

The methods applied were described in detail in IVANOV et al. (1984), VAINSHTEIN et al. (1985) and LEIN et al. (1986) which also provide a lithological description of the sediments and their geochemical characteristics.

Table 3

Rate of bacterial sulfate reduction and H_2S production in the water column of the hydrogen sulfide zone of the Black Sea.

Station/	Interval	Thickness	Sulfate reduction rate		H_2S production
Depth, m	m	m	*μg S/kg/d	mg $S/m^3/a$	$gS/m^2/a$
			Eastern halistaz		
839/	150	10	1.52	554.8	5.55
2160	160	15	1.58	576.7	8.65
	180	20	4.21	1,536.6	30.73
	200	35	1.62	591.3	20.70
	250	-	tr**	tr	tr
	300	-	tr	tr	tr
	500	-	tr	tr	tr
	760	-	tr	tr	tr
	1,500	-	tr	tr	tr
	2,160	10	1.12	409.0	4.09
Sum					**90.41**
			Western slope		
804/	100	15	1.00	365.0	5.48
1,620	130	30	1.50	547.5	16.43
	160	-	tr	tr	tr
	170	10	1.56	569.4	5.69
	180	-	tr	tr	tr
	190	10	1.56	569.4	5.69
	200	-	tr	tr	tr
	300	10	1.10	401.5	4.02
	500	-	tr	tr	tr
	1,000	-	tr	tr	tr
	1,400	-	tr	tr	tr
	1,620	10	1.12	409.0	4.09
Sum					**41.4**
Mean value for water column for both areas					**65.9**

* 1 μg S/kg = 1 mg S/m^3

** tr(ace) = i.e. less than the sensitivity of the method (< 0.002 μg S/kg/day)

3. Results and Discussion

3.1 Hydrogen Sulfide Production in Sediments of the Deep Black Sea

The sediments obtained at sites 839, 806, 584 and 838 are typical with respect to their composition and accumulation rates for the entire basin more than 2000 meters deep (Table 1).

High intensity of sulfate reduction was observed in the sediments of the western basin (st. 584). In the sediments of the eastern basin the rate of sulfate reduction was lower and decreased by one order below the transition from Unit 1 (the modern coccolith ooze) to Unit 2 (the sapropel) (Table 1).

The total content of reduced sulfur compounds (ΣS_{H2S}) changes negligibly throughout the deep water column. In sediments, the mean content of reduced sulfur forms comprise 1 % of the dry sediment weight.

The rate of sulfate reduction was measured in sediments obtained along a slope section (200-500 m, 500-1000 m and 1000-2000 m). Rates and ΣS_{H2S} fluctuate within the same limits as in the basin sediments.

The daily rates of sulfate reduction (μg S/kg of silt/day) can also be expressed as H_2S production per square meter of sediment surface (Table 1). The areas of sediments in the anaerobic zone of the Black Sea are given with their different accumulation rates in Table 4. These data allow to calculate the annual H_2S production (Table 1 and 4). It was discovered that those sediments of the western basin (> 2000 m deep) with sedimentation rates exceeding 5 cm/1000 years, produced five times more H_2S than the sediments of the eastern basin with a much larger sedimentation rate equal to 30 cm/1000 years. The highest H_2S production was observed in the sediments of the western slope sediments at depths of 1400-1500 m with a sedimentation rate of 5 cm/1000 years. At lower depths, H_2S production in sediments (sedimentation rate of 30 cm/1000 years) is the same as in sediments of the eastern basin. At the foot of the Bulgarian and Anatolian slopes, H_2S production in the sediments amounts to 56.5 $g/m^2/a$ but the total surface area of these sediments is insignificant (Table 4).

For further calculations of the H_2S balance it is essential to know which portion of the produced H_2S is buried in the sediments and which is transferred into the water column. The total annual H_2S production varies from 6.5 to 56.5 g/m^2, while only 0.5-2 g/m^2 are buried annually in sediments (Table 4). Calculations of the sulfur flux from sediments into near-bottom water, based on radioisotope results, showed that 95 % of the total annually produced H_2S enters the water body.

3.2 Hydrogen Sulfide Production in the Water Column of the Deep Black Sea

The rate of the bacterial sulfate reduction was determined in the water column of the eastern basin (st. 839) and at the western slope (depth of 1620 m, st. 804). In the water column of the western basin bacterial sulfate reduction was observed only within the interval from 150 to 200 m, i.e. in the 50 m thick layer marking the transition between the aerobic and anaerobic zones (Table 3). In the water column at the western slope the distribution of sulfate reduction rates was more complicated. Between 100 and 300 m of depth three horizons (10 m thick each) were found which had a sulfate reduction rate below the limit of detection (< 0.02 μg S/kg/day). Total water column H_2S production of this region was two times lower than in the eastern

Table 4

Hydrogen sulfide burial in sediments and H_2S flux from sediments into water column into the hydrogen sulfide zone of the Black Sea at depths more than 200 m for the past 7,300 years.

Station nos.	Depth	Area*	H_2S** production	H_2S flux into sediments		H_2S flux from sediments		H_2S flux in sediments in % of
	m	10^3 km^2	g/m^2/a	g/m^2/a	10^3t/a	g/m^2/a	10^3t/a	H_2Sprod.
			Eastern halistaz					
839/	2,160	57.6	6.5	1.52	87.6	5.48	288	23.4
			Western halistaz					
806,584,814/	2,141-2,200	46.0	32.8	0.49	22.5	32.31	1,490	1.5
			Western slope					
805,842,571,852/	1,400-1,450	36.0	24.9	0.79	22.5	24.00	864	3.2
601, 791	602-1,065	38.0	7.5	0.62	23.6	6.90	264	8.3
580, 821	200-433	3.6	56.5	2.10	7.6	54.4	207	3.7
Total of studied area		**181.2**	**18.0**	**0.9**	**164**		**3,113**	**5.0**
Total of entire area		**306.3**			**276**		**5,251**	**5.0**
Total H_2S production in sediments							**5.53 x 10^6 t S/a**	

* areas are given with due account of sediment accumulation rate

** average data from Table 1 for sediments with equal sediment accumulation rate

basin. The average sulfate reduction amounted to 65.5 mg S/m^2/a (Tables 3 and 5) and the H_2S production is calculated to be 20.2x10^6 t/a (Table 5).

3.3 Total Hydrogen Sulfide Production in the Deep Black Sea

According to the data of Table 5, 25.7x10^6 t of H_2S are formed annually in sediments and in the water column. The estimate of the H_2S production reported by AIZATULIN & SKOPINTSEV (1974) and presented in the same table for comparison amounts to 7.22x10^6 t/a. Calculations of these authors are based on the sulfate reduction data of SOROKIN (1962). On the other hand SKOPINTSEV (1975) used the experimental data of SOROKIN (1971) on H_2S oxidation and calculated that 75x10^6 t H_2S are oxidized annually (Table 6). Hence the oxidation of H_2S would exceed the

Table 5

H_2S production in water and in sediments of the hydrogen sulfide zone (area 306.3 x 10^3 km^2).

Zone	Average rate of H_2S production mg $S/m^2/d$	g $S/m^2/a$	Total H_2S production 10^6 t S/a	References
Water column	35.0	13.0	3.62	SOROKIN (1962), SKOPINTSEV (1975)
	178.0	65.9	20.20	This study
Sediments	32.9	12.0	3.60	SOROKIN (1962)
(7,300 years)	46.5	18.0	5.50	This work
Total	78.5	25.0	7.2	SOROKIN (1971), AYZATULLIN & SKOPINTSEV (1974)
	224.5	83.9	25.7	This study

H_2S production by 10 times. Taking into consideration the rate of upwelling that mixes H_2S into the aerobic zone, AIZATULIN and SKOPINTSEV (1974) reduced the estimate of total H_2S oxidation to 26-36x10^6 t/a. Nevertheless even this estimate is more than three times larger than the apparent H_2S production (Table 5). Our estimate, however, of the H_2S production (25.7x10^6 t/a; Tables 5 and 6) is close to the lower limit of the H_2S oxidation estimated above.

We also attempted to calculate the oxidation rate of H_2S in the water column. The total amount of H_2S produced throughout the Holocene, i.e. in the last 7300 years, should have been 188x10^9 t (Table 6), assuming that the H_2S production was close to that observed today. The presently existing H_2S reservoir in the Black Sea amounts to 5.27x10^9 t (based on a great number of direct measurements). Subtracting the H_2S reservoir from the total H_2S produced during the Holocene, we obtain an H_2S oxidation rate of 25x10^6 t/a and a specific oxidation rate of 81.8 $g/m^2/a$ (Table 6) which is very similar to our average H_2S production rate of 83.9 $g/m^2/a$ (Table 5). This close coincidence suggests that our balance may be correct since H_2S oxidation should not exceed H_2S production.

The supply of solid forms of sulfur from the water column to deep water sediments amounts to 1.2-1.6 g/m^2 (pyrite and elemental sulfur; TAMBIEV & ZHABINA, 1988). If these values are reliable, then the sulfur flux from water to sediments approximately balances the H_2S flux from sediments to water.

In conclusion, the H_2S reservoir in the Black Sea is caused by the bacterial sulfate reduction in the water column itself. Reduction occurs in the layer between

Table 6

Balance of hydrogen sulfide in the deep-water zone of the Black Sea (1 = H_2S mass in primary reservoir of the past 7,300 years; 2 = reserves in the modern sea).

H_2S flux	1	2	H_2S oxidation rate		References
10^6 t/a	H_2S mass 10^9 t	H_2S mass 10^9 t	10^6 t/ 7300 years	10^6 t/a	
26-75	-	3.7-5.27	-	26-76	SKOPINTSEV (1975)
25.7	188	5.27*	25.0	-	This work

* samples of water from tight batometers (BREWER & SPENCER, 1974)

the oxygen and hydrogen sulfide zones where the input of sinking phytoplankton is largest.

3.4 Hydrogen Sulfide Production in Sediments of the Shallow-Water Zone

In the shallow-water zone, H_2S is produced only in sediments. They differ from the deep-water sediments by their variable granulometric and chemical composition and by highly variable sedimentation rates. This circumstance complicates balance calculations. We therefore determined the rates of sulfate reduction in sediments of six sampling areas (polygons) which represent a large range of lithological types of shelf sediments (Table 2).

Sand and shell sediments, which cover 60 % of the Black Sea shelf (STRAKHOV, 1976), are represented by the sediments of the Kalamitsky polygon (Table 2). Alevrytic and clayey-alevrytic sediments occupy nearly 40 % of the shelf area. Typical sections of these sediments were examined on the Bulgarian shelf between 16 to 86 m depth (10 sites) and also in the Danube and Anatolian polygons.

The sulfate reduction rates in the upper layer of shelf sediments (0-5 cm) vary from 0.2 to 3.0 mg/kg of wet silt/day (Table 2). Shallow-water estuarine pelitic sediments of the northwestern shelf are the exception, here the rate of sulfate-reduction varies from 60 to 427 mg/kg/day (Table 2) in the upper 5 cm of sediments. There is another interesting peculiarity of the modern northwestern shelf sediments, an inversion in the distribution of the total reduced sulfur compounds in vertical sections as compared to the normally expected increase in diagenetic sulfur from the surface downwards. At site 64a, the content of the reduced sulfur is three times higher in the layer 0-1.5 cm than in deeper horizons (Table 2).

These data suggest an increase of bacterial sulfate reduction in sediments of certain northwestern Black Sea shelf areas during the last decade.

Annual H_2S production in coarse-grained sediments of the Kalamitsky polygon amounts to 25.4 g/m^2. If we assume that the same production is characteristic for sandy and shelly Holocene sediments of the entire shelf, then the H_2S production amounts to 1.72×10^6 t/a (Table 7). 4.5 % of this are buried in the sediments.

In fine-grained and alevrytic-clayey sediments 136.5 g $H_2S/m^2/a$ are formed. Considering the areas which these sediments cover, an H_2S production of 6.17×10^6 t/a can be calculated (Table 7). According to these estimates 7.89×10^6 t/a of H_2S are

Table 7

Balance of sulfur in the aerobic zone of the Black Sea (0-200 m shelf).

Shelf areas	Kalamitsky	Bulgarian, Dunaysky, Anatolian	Total shelf
Lithology	shelly sands; small admixture of pelytic clays	alvryte pelitic-alevryte, alevryte-pelitic sediments	
Sedimentation rate*, cm/1000 a	5	50	113***
Area**, $10^3 km^2$	67.8	45.2	
H_2S production, $g/m^2/a$	25.4	136.5	
H_2S burial in sediments:			
in $g/m^2/a$	0.95	1.60	
per area in $10^3 t/a$	64.4	72.3	136.7
H_2S flux from sediments:			
in $g/m^2/a$	24.4	135.0	
pre area in $10^3 t/a$	1654	6102	7756
Total H_2S production in $10^3 t/a$	1720	6170	7890

*Rates of sediments were calculated by lithological characteristics of vertical sediment section

**Areas were calculated from the lithological map of modern sediments (STRAKHOV, 1976)

***SKOPINTSEV (1975)

produced in shelf sediments of the Black Sea, 97 % of which enter near-bottom waters.

4. Conclusions

The presented data suggest that 33.4x10^6 t of H_2S is produced annually in the Black Sea (Table 8). The H_2S input from sediments to the water column amounts to 13x10^6 t/a; of which 5.25x10^6 t/a are contributed by deep water sediments (Table 8). This flux is partly balanced by the downward flux of solid reduced sulfur forms.

In shelf sediments, which cover less than 1/3 of the total Black Sea area, H_2S production is larger than in deep water sediments. 97 % of this production (7.89x10^6 t/a) is transferred from the sediments into near-bottom and oxygen-containing waters.

Oxygen consumption during oxidation of 135 g of $H_2S/m^2/a$ derived from sediments (Table 7) amounts to approximately 180 g/m^2/a. Total oxygen production during photosynthesis is calculated from primary production estimates of SOROKIN (1982) of 300 g C/m^2/a to be 800 g/m^2/a. Hence, 20-25 % of the oxygen formed by photosynthesis is consumed by the oxidation of H_2S produced in the sediments.

In the sediments of the Black Sea 0.42x10^6 t of H_2S are buried annually (Table 8). This value is 2.4 times smaller than our previous estimate of 1x10^6 t/a; the calculation was made using the data bank on the reduced sulfur content of sediments (LEIN & IVANOV, 1983). The difference in these two evaluations is not essential for the total H_2S balance in the Black Sea, since the flux of reduced sulfur from sediments to water (13x10^6 t/a) exceeds the quantity of sulfur buried in the sediments by two orders (Table 8).

Table 8

Total H_2S production in the Black Sea.

Zone		Total H_2S production 10^6 t S/a	Burial in sediments 10^6 t S/a	Flux from sediments 10^6 t S/a
Water column	Shallow water (< 200 m)	-	-	-
	deep water (200-2,200 m)	20.20	-	-
Sediments	shallow water	7.89	0.14	7.75
	deep water	5.53	0.28	5.25
Total		33.92	0.42	13.00

Thus more than half of the total annual H_2S production in the Black Sea occurs in the water column, or, to be more precise, in the 50 m thick layer at the O_2/H_2S interface.

The pollution of the sea by anthropogenic organic compounds and nutrients may trigger massive development of plankton. This may cause an increase of the H_2S production in the water column which, in turn, may result in the ascent of the O_2/H_2S interface of the Black Sea.

In shallow waters sulfate reduction can only take place in sediments. The H_2S production in shelf sediments amounts to 7.89×10^6 t/a. Of this only 3 % are buried in sediments and 97 % are transferred as H_2S to near-bottom waters. Input of anthropogenic substances may already have increased the H_2S production in the northwestern shelf where the rate of sulfate reduction reaches 60 mg/kg/day, i.e., 1-2 orders of magnitude higher than the average. Summer outbursts of H_2S have already resulted in mass mortality of benthos.

Thus, two ecosystems in the Black Sea are subjected to anthropogenic stress: the shallow-water zone at the sediment/water interface and the deep-water zone at the O_2/H_2S interface. Further pollution by organic compounds and mineral nutrients may lead to the death of this unique water body.

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Geochemical Activity of Sulfate-Reducing Bacteria In Coastal Shallow Sediments of the Sea of Japan, Okhotsk, Carribean and Black Seas

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With 1 Figure and 3 Tables

Contents

Abstract

The sulfate reduction rates were investigated in coastal shallow sediments from the Sea of Japan, the northwestern shelf of the Black Sea, the Okhotsk Sea and the Carribean Sea, as well as in mangroves of the Batabano Gulf (Carribean Sea, Cuba) and for algal-bacterial mats of Crater Bay (Okhotsk Sea, Kuril Islands). The sulfate reduction rate was estimated with $^{35}SO_4^{2-}$ as the total formation of the acid-volatile sulfide compounds, pyrite, thiosulfate, and a fraction of the elemental sulfur plus part of organic sulfur. Intensity of sulfate reduction varied from 9.0 to 768 $\mu M\ SO_4^{2-}/m^2/day$ in mud samples and from 9.2 to 245 $\mu M\ SO_4^{2-}/m^2/day$ in mangrove and mat

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samples. A decreased sulfate reduction rate is accompanied by a higher percentage of the sulfide in pyrite. In Batabano Bay mangrove sediments thiosulfate contained 40.6 - 98 % of the total reduced ^{35}S. Isotopic composition of the sulfur in sulfates, monosulfide and pyrite was determined. Monosulfide and pyrite were enriched in ^{32}S, having $\delta^{34}S$ values equal to $-23.04^{o}/oo$ and $-15.83^{o}/oo$ respectively. Sulfate was depleted in ^{32}S, its $\delta^{34}S$ varying from $+21.46$ to $53.81^{o}/oo$. The intensity of bacterial sulfate reduction was directly correlated with the C_{org} content in sediments.

1. Introduction

Sulfate-reducing bacteria play a major role for the anaerobic destruction of organic substance in marine sediments. Together with other anaerobic biogeochemical processes the bacterial sulfate reduction participates in the early diagenetic transformations of mineral compounds in marine sediments.

High transport rates of a variety of different organic substances create anaerobic conditions in the coastal marine sediments due to a consortment of aerobic microorganisms. Besides they supply energy substrates for the anaerobes - including the sulfate-reducing bacteria - in a form of metabolic end products. Hence a high content of organic matter in coastal sediments causes high rates of bacterial sulfate reduction. Recent investigations have shown that from 50 to 90 % of the global sulfate reduction occurs in coastal, shelf and continental slope sediments (JÖRGENSEN, 1983; IVANOV et al., 1989; VOLKOV & ROZANOV, 1983). In various types of coastal sediments the organic matter is formed in the immediate vicinity of the reduced sediment. This occurs in sediments related to bacterial mats, mangroves and salt marshes. A high sulfate reduction rate in these systems is due to a high content of labile organic matter.

Numerous papers have appeared recently discussing the sulfate reduction processes in sediments of different coastal ecosystems - shelfs, salt marshes and bacterial mats related to shallow sediments. Research data were generalized in a review by SKYRING (1987). Yet numerous coastal ecosystems (e.g., mangrove sediments) remain to be studied. It should be noted that when determining sulfate reduction rates in experiments with a radioactive tracer, most researchers concentrate on the acid-soluble forms and pay no attention to other reduced sulfur compounds which comprise a larger part of the products of sulfate reduction. This results in underestimating the intensity of sulfate reduction processes.

2. Investigation Sites and Methods

We have studied bacterial sulfate reduction in shallow coastal sediments of the marginal Sea of Japan, the northwestern shelf of the inner Black Sea, the island zones of the Okhotsk Sea (the Kuril Islands) and the Carribean Sea (Cuba) as well as the mangrove sediments in the Batabano Gulf (Cuba) and algal-bacterial mats of the Crater Bay (the Kuril Islands).

The sulfate reduction rate was determined radiometrically with $Na_2{}^{35}SO_4$. The intensity of the process was calculated as a total formation of acid-soluble sulfur compounds, pyrite, thiosulfate and a fraction of elemental sulfur plus a part of the organic sulfur. The acid-soluble sulfides were extracted by acidifying the samples with hydrochloric acid, pyrite was extracted after reduction with $CrCl_2$, elemental sulfur plus partial organic sulfur was extracted with acetone, and thiosulfate in pore water was determined by a thin-layer chromatography (KARNACHUK et al., 1990). All sulfur forms were isolated for a quantitative analysis from one sample, a part of the extracted compounds was used for the isotope analysis. The isotope content of sulfur compounds was determined by mass-spectrometry.

3. Sulfate Reduction Rates in Studied Sediments

High rates of bacterial sulfate reduction were observed in shallow water sediments (Table 1). Sulfate reduction rate in sediments of the Sea of Japan varied from 24.3 to 768 μM SO_4^{2-}/m^2 per 24 h, in the northwestern shelf of the Black Sea from 86.1 to 323 μM SO_4^{2-}/m^2 per 24 h. High rates were also observed in the upper 1 cm-thick layer of the algal-bacterial mats in the Crater Bay (the Okhotsk Sea) varying from 23.8 to 245 μM SO_4^{2-}/m^2 per 24 h, and in the upper mangrove horizons of the Batabano Gulf (the Carribean Sea) from 9.2 to 88.6 μM SO_4^{2-}/m^2 per 24 h. In the silty sediments of the Crater Bay and Batabano Gulf the sulfate reduction rate was 9.0-43.9 and 3.4-216 μM SO_4^{2-}/m^2 per 24 h, respectively. The observed rates were of the same order of magnitude as those previously registered in litoral marshes of the Great Sippiwisset (HOWARTH & TEAL, 1979; HOWARTH & MERKEL, 1984), and Sapelo Island (SKYRING et al., 1979; KING, 1983; HOWARTH & GIBLIN, 1983; HOWES et al., 1984), shallow water sediments of Limfjorden (HOWARTH & JÖRGENSEN, 1984), litorals of San Francisco Bay (OREMLAND & SILVERMAN, 1979), and cyanobacterial mats of the Spencer Gulf (SKYRING et al., 1983).

4. Rates of Reduced Sulfur Compounds Formation

The hydrogen sulfide formed in bottom sediments as a result of sulfate reduction can be subjected within a short period to different chemical transformations. As a result, the sediments accumulate pyrite, elemental and organic sulfur, thiosulfate and possibly other reduced sulfur forms (VOLKOV & ROZANOV, 1983). When measuring the sulfate reduction rate by a radioisotope method in Pacific (IVANOV et al., 1976) and Indian Ocean sediments (IVANOV et al., 1980b) the greatest amount of tracer was normally observed in the pyrite sulfur. Similar results were obtained when studying sediments in the Baltic Sea (LEIN et al., 1982) and the Caspian Sea (IVANOV et al., 1980a). Noticeable amounts of the labeled pyrite were

Table 1

Sulfate reduction intensity (I_{SR}) in sediments under study.

Station	Sediment type	Water depth m	Sediment depth cm	Temp. t°C	Eh mV	I_{SR} mM SO_4^{2-} $/m^2$/day
1	2	3	4	5	6	7
Sea of Japan, Trinity Bay, September						
1	mud	16.0	7.0	16.0	66	622.6
2	"	23.0	8.0	15.0	58	191.3
3	"	20.0	9.0	15.0	-42	360.9
4	"	7.0	7.0	16.0	4	268.1
5	"	1.0	9.0	17.0	-28	227.4
Vostok Gulf, September-October						
1	mud	9.0	12.0	14.0	51	24.3
2	"	26.0	12.0	14.0	63	610.2
3	"	14.0	10.0	14.0	53	768.6
Black Sea, north-western shelf, Dniester polygon, August						
58A	shell debris	15.8	1.0	-	-	86.1
57	mud	11.0	4.0	13.5	-	323.4
Danube polygon						
65B	mud	11.0	8.5	-	-	188.6
64A	"	16.0	5.5	7.3	-	313.3
Okhotsk Sea, the Kuril; Islands Crater Bay, August-September						
5	algo-bacterial mats	5.0	0.5	10.0	-172	65.2
13	"	5.0	1.0	10.0	-167	244.9
19	"	0.5	0.5	20.0	-197	23.8
3	mud	6.0	3.0	10.0	-93	23.0
7	"	15.0	2.0	6.0	160	9.0
10	"	15.0	6.0	4.0	-86	43.9
16	sand	0.5	3.0	10.0	320	2.1
Caribbean Sea, Cuba; Batabano Gulf, June						
4	mangrove	0.2	1.0	31.0	-47	88.6
12	"	0.2	2.0	30.0	50	9.2
3	mud	3.5	3.0	31.0	-47	216.0
5	"	9.0	2.0	31.0	50	59.6
6	"	7.0	2.0	30.0	50	3.4
9	"	5.5	2.0	32.0	-20	13.7
14	"	7.0	2.0	30.0	60	113.7

observed in experiments on sulfate reduction in salt marshes sediments (HOWARTH & TEAL, 1979; HOWARTH & GIBLIN, 1983; HOWARTH & MARINO, 1984; HOWARTH & MERKEL, 1984).

Our experiments with labeled sulfate - with the objective to determine the sulfate reduction rate - in the Batabano Gulf showed that after an incubation of 4 hours 59.8 % of reduced sulfur was contained in pyrite, and after a 7-hour incubation 93 % of ^{35}S was observed in pyrite. Samples of coastal sediments from the Sea of Japan contained up to 96.5 % of the tracer in pyrite.

SKYRING & LUPTON (1984) showed that in the sediments of Hamelin Pool (Shark Bay/Australia) low sulfate reduction rates were accompanied by higher tracer accumulation in pyrite. A similar dependence was usually observed in our samples. 0.1 % of the recovered tracer was registered in pyrite of algal-bacterial mats of the Crater Bay thus evidencing high sulfate reduction rates.

In silts rates were one order of magnitude lower. Up to 20 % of the total reduced sulfur was observed in pyrite. About 92.5 % of the tracer was detected in pyrite of the sandy sediments with low sulfate reduction intensity (Table 2).

Table 2

^{35}S incorporation into reduced sulfur formed under sulfate reduction (in percent of the total process intensity) in the Crater Bay sediments (Kuril Islands).

St. No.	Sediment type	Sample depth cm	I_{SR} mgS/kg /day	^{35}S incorporation in reduced S compounds $H_2S + HS^-$ %	S_{pyr} %	$S^\circ + S_{org}$ %	$S_2O_3^{2-}$ %
1	2	3	4	5	6	7	8
5	mats	0-0.5	417.2	95.5	0.2	0.2	4.1
13	"	0-1	783.7	96.8	0.3	0.1	2.8
19	"	0-0.5	158.5	94.6	0.5	0.6	4.3
3	"	0-1	16.2	98.3	1.7	0	0
7	mud	0-2	14.4	72.4	17.4	10.2	-
10	"	2-8	23.4	20.2	20.0	59.8	-
16	sand	0-3	2.2	3.8	92.5	3.7	0

In the coastal silts of the Sea of Japan an increase of sulfate reduction rate was accompanied by a higher content of the reduced ^{35}S in the acid-soluble fraction and a lower formation rate of pyrite and other acid-insoluble sulfur compounds (Fig. 1).

A noticeable tracer content was registered in the $S^\circ + S_{org}$ fraction of samples under study. During a 6-hour incubation of the Batabano Gulf sediment sample

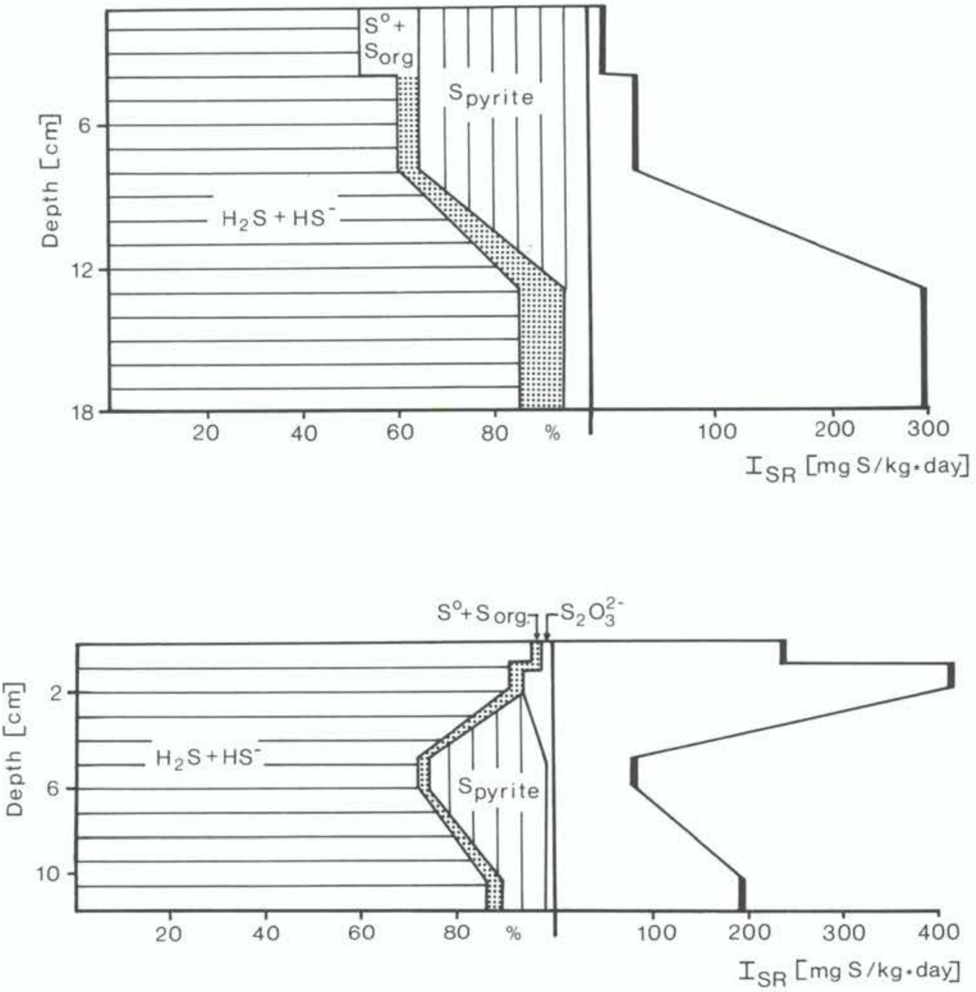

Fig. 1: Tracer distribution in the reduced sulfur compounds (in the total sulfate reduction rate) and sulfate reduction rate in silt columns of coastal sediments in the Sea of Japan (A) and Black Sea (B).

44.3 % of the tracer was reduced and accumulated in the above fraction. In the Crater Bay sediments the major tracer sulfur was observed in the intermediate form of the oxidation process - the elemental sulfur. This is possibly due to a parallel process of a partial oxidation of the hydrogen sulfide by the oxidized iron. Pyrite is intensely formed in the sample sediments (Table 2). The rate of the tracer inclusion into the $S^o + S_{org}$ fraction in the Sea of Japan coastal sediments decreases with sediment depth (Fig. 1). On the one hand, this is due to a switch from oxidation to reduction in the lower horizons; on the other hand, this may be caused by an increase of the rate of sulfate reduction with sediment depth.

We have shown the possibility of thiosulfate accumulation as a result of bacterial reduction of sulfates. The thiosulfate may originate from different processes. Firstly, thiosulfate can accumulate as an intermediate product of sulfate reduction. Secondly, hydrogen sulfide produced as a result of sulfate reduction can be oxidized to thiosulfate. In any case, ignoring thiosulfate in the sulfate reduction balance in experiments with radioactive sulfate may lead to underestimating the calculated sulfate reduction capacities. In most samples of the Batabano sediments and sediments related to algal-bacterial mats in the Crater Bay the thiosulfate contained a minor content of the total reduced sulfur. However, in some samples of the Batabano Bay including the mangrove samples thiosulfate contained 98.0 and 40.6 %, respectively, of the total reduced sulfur. In the coastal sediments of the Sea of Japan we checked only the upper horizons of the sediment column for thiosulfate formation. No tracer was registered in the thiosulfate, yet in one sample of the Troitza Bay the thiosulfate in the upper horizon contained 31.6 % of the total reduced sulfur. It should be noted that the method implied for detection of all sulfur reduced forms in single samples requires that the thiosulfate should be determined prior to extraction of hydrogen sulfide because acidification of the sample enhances the chemical oxidation of thiosulfate to elemental sulfur.

5. Reduced Sulfur Compounds Content

The activity of sulfate-reducing bacteria in marine sediments is also characterized by the distribution of reduced sulfur forms. We have studied the reduced sulfur content in the sediments of the northwestern Black Sea shelf (Table 3). The S-H_2S distribution in the Black Sea was investigated by OSTROUMOV et al. (1961). No reduced sulfur compounds were found in the silty sediments. Nowadays, appearance of the hydrogen sulfide in this sea area is due to a sharp increase in sulfate reduction rates registered in the tracer experiments. In turn, the activity of the sulfate-reducing bacteria may be caused by increased input of organic matter and nutrients transported by rivers. Intense reduction processes accompanied by the authigenic mineral formation of sulfides were observed in the shelf sediments of the oxygen zone of the western (Bulgarian) sector of the Black Sea (VAINSHTEIN et al., 1985). The content of reduced sulfur compounds (0.20 to 0.90 % of sediment dry weight) was lower at high sulfate reduction rates in comparison with the data on shelf zones in the ocean and inland seas obtained by other authors (VOLKOV & ROZANOV, 1983). This is mostly due to losses of the hydrogen sulfide and its derivatives under the active hydrodynamic conditions of the marine shelf zone (H_2S oxidation, transport to the near bottom layer, etc.). The ratio between the various reduced sulfur forms was practically constant, pyrite dominated (Table 3). As is known, this distribution pattern is a result of the high sulfate reduction rates and is not related to the sediment location (VOLKOV & ROZANOV, 1983).

6. Isotopic Composition of Sulfur Compounds

Another indirect geochemical criterion of the bacterial sulfate reduction is the isotopic composition of sulfur compounds. Laboratory experiments with pure

Table 3

Sulfate reduction intensity (I_{SR}), content and isotope composition of sulfur compounds in the Black Sea north-west shelf.

St. No.	Sample depth cm	I_{SR} mgS/kg /day	ΣS_{H2S} in % of dry weight	Red. S in % of ΣS_{H2S}			$S\text{-}SO_4^{2-}$ mg/l pore wat.	$\delta^{34}S$ °/oo S_m	$\delta^{34}S$ °/oo S_{pyr}	$\delta^{34}S$ °/oo SO_4^{2-}
				S_m	S_{pyr}	$S^\circ + S_{org}$				
1	2	3	4	5	6	7	8	9	10	11
Dnestrovsky polygon										
57	0-1	242.7	0.2532	17.0	69.4	13.6	459.3	-10.14	-11.54	25.32
	1-2	427.0	0.2445	2.2	79.1	18.7	394.5	-0.25	-14.25	24.30
	5-6	85.4	0.3860	8.6	82.1	9.3	-	-	-14.98	-
	10-11	199.6	0.2022	0.0	88.2	11.8	-	-11.49	-11.88	-
Danube mouth										
65B	0-0.5	236.4	0.2727	15.9	75.1	9.0	253.3	-9.46	-	31.56
	1-3	97.8	0.3236	39.3	48.0	12.7	101.6	-18.73	-	52.05
	3-5	94.0	0.3341	26.0	67.9	6.1	108.2	-19.90	-6.24	48.97
	10-12	54.4	0.2126	26.7	66.1	7.2	101.1	-23.04	-6.83	49.55
	16-18	102.2	0.2151	27.2	64.6	8.2	111.5	-22.81	-7.22	53.81
Dunaysky polygon										
64A	0-0.5	47.6	0.8991	37.9	56.2	5.9	-	-	-4.44	21.46
	0.5-1.5	314.3	0.3323	12.2	80.0	7.8	351.6	-	-7.04	29.79
	4-6	45.8	0.1971	20.1	58.3	21.6	309.3	-12.94	-	33.30
	9-11	286.4	0.2703	19.3	71.4	9.3	312.1	-	-15.83	32.64

cultures of the sulfate-reducing bacteria grown on lactate have shown that the low sulfate reduction rate is accompanied by the maximum fractionation of sulfur isotopes and enrichment of the reduced compounds with ^{32}S and oxidized compounds with ^{34}S. On the opposite, a minimal isotope fractionation is observed at a high reduction rate (THODE et al., 1951; GRINENKO & GRINENKO, 1974; KROUSE & MCCREADY, 1979).

We have established certain regularities in the Black Sea sediments in relation with the bacterial sulfate reduction. Pore water sulfate was enriched by heavy isotopes and $\delta^{34}S$ varied from +21.46 to 53.81°/oo. The monosulfide lightened to $\delta^{34}S$ equal -15.83°/oo (Table 3). A relatively heavy isotope content of reduced sulfur compounds is due to maximal (up to 427 mg S_{red}/kg per 24 h) rates of sulfate reduction.

7. Impact of Organic Matter Content in Sediments on Sulfate Reduction Rate

The content of organic matter is an important factor influencing sulfate reduction in marine sediments. Two organic matter fractions are present in marine sediments - easily utilizable and hard-to-access for microorganisms. The ratio of these fractions in total organic matter varies in different types of coastal sediments (WESTRICH & BERNER, 1984). SKYRING et al. (1983) and COHEN et al. (1980) showed that photosynthetic products of cyanobacterial mats consist almost totally of the easily-oxidized organic compounds. Hence the residual organic matter content in sediments, characterized by the C_{org} index does not properly reflect its initial content. Nevertheless, we can observe a correlation between the sulfate reduction rate and C_{org} content in the sediment. All sediments with a high sulfate reduction rate had a higher organic carbon content as compared with the mean values for marine sediments. For example, C_{org} in coastal sediments in the Sea of Japan amounts to 2.4 % (of total sediment dry weight), to 5.3 % in the Batabano Bay and to 5.9 % in the Crater Bay.

The highest sulfate reduction rates were registered in sediments of the areas polluted by organic matter from anthropogenic sources. In the coastal areas of the Troitza Bay (Sea of Japan) high sulfate reduction rates were observed in sediments within the navigable channel (577 μM SO_4^{2-}/m^2/day) and in sediments of the Vostok Bay within the area polluted by effluents of an agar plant (767 μM SO_4^{2-}/m^2/day).

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Biogeochemical Differentiation of Ocean Matter and Biogenic Substance Matrices

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With 2 Figures and 2 Tables

Contents

Abstract

The transport of chemical elements from the oceanic surface layer to the sediments is intimately associated with the biogenic production of paticulate matter. Dissolved macro- and microelements are extracted from seawater by biological activity, enriched and settled with sinking pellets and macroflocs. Organic matter, opal and calcium carbonate serve as matrixes for many elements which can only reenter the elemental cycles when the encasing matrix is decomposed or dissolved.

1. Introduction

Accumulation of chemical elements by marine organisms has usually been discussed for the elemental level. Organisms, however, bind elements into complex

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organic molecules (proteins, lipids, carbohydrates), or deposit them into minerals composing shells (carbonates, silica, etc.) or other parts of the organism. The differentiation on the isotope level is also of considerable importance, i.e. isotopic fractionation occurs in organisms and is particularly pronounced in case of the major components of organic matter (O, H, C, S, etc.).

Biogeochemical differentiation in seawater implies that organisms bind dissolved elements and compounds, resulting in their consequent concentration in shells and skeletal material. The differentiation is accompanied by the separation of the physiologically essential elements from others, causing the pronounced enrichment of the former (thousand and hundred thousand times higher than their content in the water) and changing the ratios between element concentrations. At the same time a wide range of metallorganic compounds can for example be formed. The biogeochemical differentiation encompasses separation of initially dissolved elements, formation of new associations and their enrichment in accordance with the physiology of species or biocenoses.

All elements in the ocean participate in more or less closed biogeochemical cycles. According to the law of the biological turnover of elements (PERELMAN, 1979), the latter successively enter the organisms (become organized) or leave them (become desorganized, mineralize). It should be noted that in different environments each element cycle shows different time scales. The turnover is also characterized by its capacity (maximum amount of element bound to living matter), and its rate (maximum amount of the living matter composed or decomposed per time unit).

2. Biogeochemical Differentiation on the Molecular Level

Biogeochemical differentiation on the molecular level implies the formation of new compounds (molecules) by phytoplankton from elemental or molecular precursors contained in seawater and their consequent transformation in the food chain. These compounds belong predominantly to a) organic compounds; b) carbonates, and c) opal. Each group is functionally connected with certain macro- and microelements. Binding and unbinding of these elements during photosynthesis and respiration proceed in different ways.

2.1 Biodifferentiation with Organic Matter Molecules (OM-matrix)

Organic matter (OM) usually contains relative constant proportions of C, P, N, H, O, S, and several microelements. C_{org} amounts to 40-60 % of the total OM content. During OM decomposition the ratio between the matrix elements can change.

While the OM sinks from the warm surface layer towards the sediments major components, i.e., proteins, carbohydrates and lipids, decrease in concentration. This decrease is accompanied by an increase in the relative content of humic and fulvic acids consisting of fragments of proteins and carbohydrates. The rate of geochemical decomposition is proportional to the energy stored in the OM; in the water column, where 92-99 % of OM is decomposed, this rate is therefore 10-30 times larger than during the diagenesis of OM in the sediments (in the ocean in general).

The C_{org} flux at depth can be measured by sediment traps. These data, in connection with measured primary production, allow to establish depth depending rates of decomposition. According to SUESS (1980) decomposition follows the equation:

$$C_{flux} = C_{prod} \times 5.9 \times X^{-0.616}$$

where:

C_{prod} - is the primary production of carbon;

C_{flux} - is the carbon flux at the depth X.

This relation suggests that the vertical flux of OM is a function of the primary production, and hence its latitudinal, circumcontinental and vertical zoning.

To conclude, the specific relations between elements in the OM differ from those existing in the environment and comprise the first stage of the biochemical differentiation. The second stage is the decomposition during the settling of pellets and macroflocs and in the consequent transformations in the bottom sediments.

2.2 Biodifferentiation with Opal Molecules (SiO_2 amorphous-matrix)

Above, we have considered the biodifferentiation of C_{org}, i.e., the cell content and the soft tissues of organisms. Silica experiences a similar differentiation during composition and decomposition of skeletal material (shells) of diatoms, radiolaria, silicoflagellates and silica sponges. Silica is also found in minor quantities in soft tissues.

The dissolved silica concentration in the ocean varies from traces to average values of 1.2-3.6 mg/l (maximum 20-27 mg/l, Bering Sea). Silica concentration in the suspended matter of the surface layer (calculated from several hundred determinations by the author) varies from below 1 % (of the dry suspended matter) to 50-80 %. The average content of amorphous silica in diatoms is 43 % (average C_{org} content is 18.7 %). The silica content in the suspended matter of the Southern Ocean matter was 11.45 % while the C_{org} content was 8.67 (LISITZIN, 1964).

The ratio of Si_{amorph} to C_{org} in diatoms amounts to 2.3. Since the total primary production of diatoms amounts to 20 billion tons the diatoms bind 20 x 2.3 = 46 billion tons of silica.

The silica of shells is related to certain macro- and microelements (BORDOVSKY, 1964). Similar to OM we can speak of the SiO_2 -matrix or opal-matrix. During its decomposition some elements are transferred to the near-bottom and pore waters. This release occurs at different rates.

2.3 Biodifferentiation with Calcium Carbonate Molecules ($CaCO_3$- matrix)

Calcium is contained in shells, skeletons and soft tissues of marine organisms. Its role is more important than that of silica because total $CaCO_3$ discharge from continents is three times larger than that of silica and amounts to 1.36 billion tons per year according to recent estimates (LISITZIN, 1978). It should be noted that, while silica is bound mostly by organisms of the first step in the food chain (phytoplankton), the calcium carbonate is bound also by organisms of the second (and successive) steps in the food chain.

The carbonate material of shells is related to several microelements and, judging from a few estimates, this relationship is regular and enables us to speak of a $CaCO_3$-matrix.

Figure 1 shows a relationship between the primary production and absolute masses of C_{org}, opal and $CaCO_3$ and the terrigenous matter captured from suspension by biofiltration. Absolute masses have been estimated for a sediment layer representing the last 0.7 million years. It follows from the diagrams that sediment formation near the surface of oceans and seas, far from continental sources of sedimentary matter (river mouths), has a decisive impact on absolute masses of elements in bottom sediments including the absolute masses of terrigenous components. The biogenic components are generated via primary productivity at the expense of dissolved matter and are then settled with pellets and macroflocs. Also terrigenous components are extracted from the water by filtration and subsequent packaging into pellets or by macrofloc formation. Both mechanisms depend on the primary production capacity which in turn determines the capacity of zooplankton

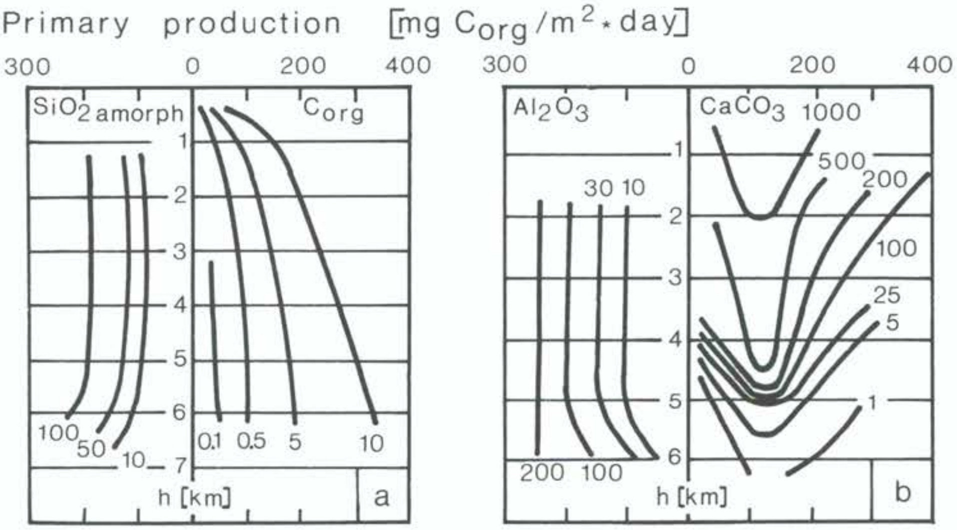

Fig. 1: Nomograms showing absolute masses of amorphous silica, C_{org}(a), terrigenous material (in terms of Al_2O_3), and $CaCO_3$ (b) in bottom sediments in relation to primary production and sea depth. The sediment layer represents the last 0.7 million years (BOGDANOV et al., 1983).

filtration and of excretion of organic mucus. Terrigenous material in the pelagic beyond the continental slopes is heavily impacted by biogenic processes. Individual terrigenous particles can settle only where the role of biota is insufficient. Terrigenous material is characterized by its exceptionally resistant geochemical matrix that can hardly be decomposed in the water column nor in bottom sediments.

3. Biodifferentiation on the Molecular Level and Formation of Authigenic Minerals

The formation of biogenic minerals composed of macroelements - calcium and silicon - occurs on a broad scale in the ocean (LISITZIN, 1978), causing an enormous transport of $CaCO_3$ and opal to bottom sediments, i.e., 1.82 billion tons in total. Carbonates and opal form matrices.

Another important site of biogenic mineral formation was recently identified in the upper layer of sediment where organic matter is transformed by bacteria (IVANOV, 1979; IVANOV & LEIN, 1980; VOLKOV, 1979).

Biogeochemical differentiation on the molecular level results in the formation of OM consisting of 12 basic elements and numerous minor elements. Plankton can contain up to over 70 elements (Fig. 2), all bound in larger molecules.

The pathways of the macro- and microelements in the ocean from the moment they extracted until they are deposited are closely connected with the fate of the matrix they are bound to. They are chemically inactive until they are released when the matrix is destroyed (dissolved or decomposed). This marks a new stage in the transformation of the carrier-free element. New forms of an element are adapted to

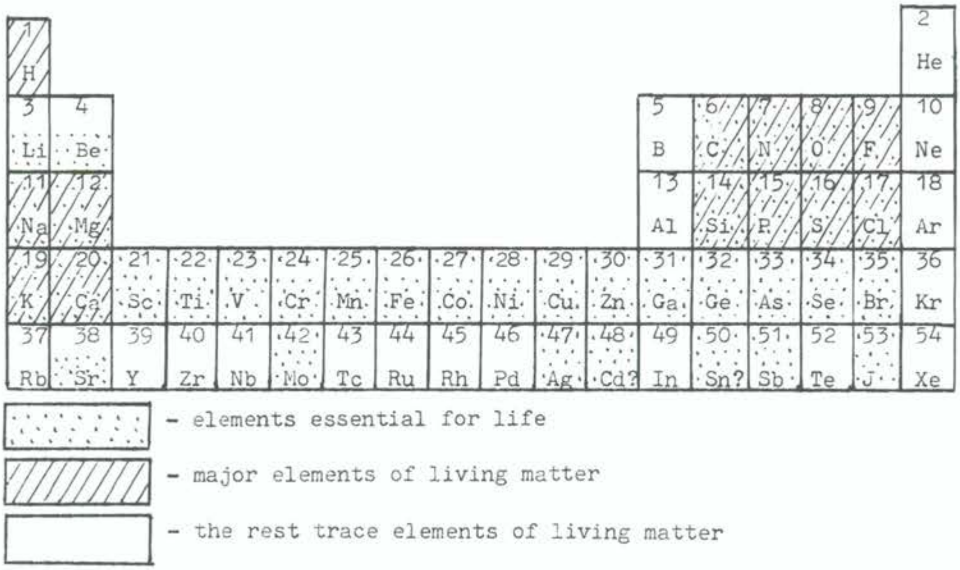

Fig. 2: Elements essential for life (as of 1981); 12 major elements shown with oblique hatching make up 99 % of the living matter. (MERTZ, 1981, with contributions of the author.)

the modified physico-chemical environment or involved into a new biological cycle. Elements from terrigenous matrices are not involved into the cycle.

4. Biodifferentiation on the Elemental Level

After the dissolved elements are transformed by the biota into suspended matter they become encased double, i.e. in cells and shells that constitute organisms, and in the pellets produced by biofiltration. Element transfer into the water is possible, first, when the pellet surface is destroyed and, secondly, when the carrier (matrix) is destroyed. Elements are locked within matrices, they can be transported together with them and exist for a long time under conditions that are chemically and physically unsuitable for release as individual atoms. Formation of new minerals is possible only after an element is released from the matrix.

The following regularities in the biodifferentiation on the elemental level exist (VINOGRADOV, 1944; PATIN, 1979; MOROZOV, 1975):

1) Micro- and macroelement content in seawater and in the newly-formed suspended matter (plankton) decreases with an the increase in atomic number.

2) Elements with the atomic number below 30 show a correlation (0.60-0.77) between the accumulation coefficient and atomic number.

3) Element enrichment by plankton correlates with the ion potential (a relation between the valence and the ion radius) at the 95 per cent level of probability.

4) Organisms are mostly composed of elements with atomic numbers < 20. Twelve of them are classified as basic elements. Skeletons are formed of salts with solubilities not less than 10^{-3} (Ca, Si, Mg, Al, Fe, etc.).

5) Ions are transported through cell membranes in the form of chelates.

6) Total number of elements used by organisms is over 70. The ability of organisms to concentrate chemical elements is determined by the accumulation coefficient (C_a) - a ratio between the element's content in the organism and its content in seawater.

Elements can be classified into four groups:

- elements not concentrated by marine organisms, i.e. Na, (Mg), Ra, (F), Cl (abundant in seawater);
- elements accumulated to a lesser degree by marine organisms ($\lg C_a < 2$), i.e. K, Rb, Cs, Ca, Sr, Ba, B, Mo, W, F, Br, J;
- elements strongly enriched by marine organisms ($\lg C_a = 2\text{-}4$), i.e. Al, C, Cu, Ag, Au, Zn, Cd, Hg, Ca, Si, Ti, Sn, V, As, Sb, S, Se, Cr, Mn, (J), Fe, Co, Ni;
- elements intensively concentrated by individual or certain groups of organisms ($\lg C_a > 4$), i.e. Al, C, (Sn), Ni, P, Mn, Fe, Co.

7) Data presented in Table 1 indicate that suspended matter consisting of organic residues has accumulation coefficients 1-3 orders of magnitude higher than that of the initial plankton. This implies that the specific surface of suspended matter exceeds that of the plankton organisms (Table 2) since sorption capacity of the dead OM is extremely high. Apart from the elements captured

Table 1

Accumulation coefficients of elements (wet weight).

Suspended matter	10^4-10^6
Bottom sediments	10^4-10^6
Plankton (total)	10^3-10^5
Zoobenthos (soft tissues)	10^3-10^5
Phytobenthos	10^2-10^4
Fish (soft tissues)	10^2-10^4

Table 2

Specific surface of suspended matter and organisms (sorption capacity) in cm^2/g^*.

Ocean suspended matter	100,000 - 3,000,000
Red deep-sea clay and diatomic sediments	250,000 - 1,490,000
Bacteria	35,000
Algae	2,000
Zooplankton	600
Crustaceans, benthos	50
Fish	2
Mammals	0.05

* per m^2 of ocean 1-10 kg of suspended matter are found

- total ocean surface is over 361 x 10^6 km^2

and stored within cells, dead plankton also accumulates numerous elements adsorbed to the surface.

8) As long as elements are bound in matrices (OM, $CaCO_3$ and SiO_2-amorphous) their physico-chemical properties are not manifested; they become reactive again only when released from the matrix.

Data on accumulation coefficients suggest that enrichment of element-hydrolyzates by marine organisms is more effective than enrichment of other micro- and macroelements. Physico-chemical adsorption seems to be the dominant process, apart from biological mechanisms responsible for the selectivity of accumulation.

Hydrobionts accumulate (concentrate) only those elements present in seawater vital for their normal activity. For this they have to spent energy. From a geochemical view point these organisms function as a biogeochemical barrier detaining and accumulating certain elements, primarily those of low environmental concentrations.

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Indirect Effects of Sulfur on the Carbon Cycle of Aquatic Ecosystems: Molybdenum Availability, Planktonic Nitrogen Fixation and Nitrogen Limitation

by
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Contents

Abstract

Primary production in temperate-zone lakes is often controlled by phosphorus, while nitrogen is frequently more limiting in temperate-zone estuaries. One reason for this difference is a difference in the extent to which nitrogen fixation makes up relative deficits in nitrogen. In freshwater lakes, N-fixing, planktonic cyanobacteria frequently bloom and make up temporary deficits in N availability. In contrast, N-fixing cyanobacteria rarely occur in the plankton of temperate estuaries, even though the waters of these estuaries are often very depleted in N relative to P.

Why are N-fixing cyanobacteria rare in the plankton of estuaries and coastal marine ecosystems? One reason may be the low availability of molybdenum, a metal usually considered to be required for nitrogen fixation. The biological availability of

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molybdenum is not simply a function of molybdenum concentration since sulfate can inhibit the assimilation of molybdate, the thermodynamically stable form of molybdenum in oxic waters. This inhibition may be particularly great in seawater since sulfate concentrations are so high. Thus, sulfate can exert an indirect effect on nitrogen and carbon cycling through regulating molybdenum uptake and nitrogen fixation.

Short-term bioassay experiments to test these hypotheses have yielded conflicting results. On the other hand, the hypotheses are strongly supported by observational data collected in saline lakes. The molybdenum availability, as predicted from sulfate and molybdenum concentration data, is the best predictor of the abundance of N-fixing cyanobacteria in these lakes.

1. Introduction

The direct interactions between the carbon and sulphur cycles in aquatic ecosystems are well studied and well appreciated. Sulfate reduction is a dominant process in marine sediments, accounting for 25% to 90% of the organic carbon degradation in near-shore sediments (JORGENSEN, 1982; HOWARTH, 1984; LEIN, 1983). In lakes, acidity from both sulfuric and nitric acids in acid precipitation can have profound effects on the structure and function of the ecosystem (SCHINDLER et al., 1985). Sulfate reduction in lakes can partially ameliorate these effects by generating alkalinity and consuming acidity (COOK et al., 1986; SCHINDLER et al., 1985).

The sulphur cycle also can affect carbon cycling indirectly through influencing the cycles of other elements such as nitrogen and phosphorus, but these interactions are less well known than are the direct C-S interactions. In this paper, I summarize the effect of sulfate on nitrogen fixation and on nitrogen limitation of net primary production in aquatic ecosystems. I argue that N fixation is regulated in part by Mo availability, and Mo availability in turn is controlled by the relative concentrations of sulfate and Mo since sulfate can inhibit molybdate assimilation. These interactions are explored in more detail elsewhere (HOWARTH & MARINO, 1988; HOWARTH, 1988; MARINO et al., 1990). Another indirect effect of S on C cycling in aquatic ecosystems, is the effect of S on P cycling.

2. Nitrogen Limitation in Aquatic Ecosystems

Ecologists have long been intrigued by the apparent paradox that net primary production is so often limited by P in lakes and by N in estuaries and coastal marine ecosystems. Recently, it has become apparent that not all lakes are P limited (for example, see LEVINE & LEWIS, 1987) and probably not all estuaries are N limited (SMITH, 1984; HOWARTH, 1988). Nonetheless, one is struck by the contrast between a large class of lakes (such as those of the Canadian Shield and of the northeastern United States) which generally are P limited (SCHINDLER, 1977) and a large class of estuaries (such as those along the Atlantic coast of North America from New York to Nova Scotia) which generally are N limited (HOWARTH, 1988).

One major reason for the difference in nutrient limitation between temperate estuaries and temperate lakes is a difference in the extent to which N fixation makes up relative deficits in N (HOWARTH et al., 1988; HOWARTH, 1988). In mesotrophic and eutrophic freshwater lakes, N-fixing, planktonic cyanobacteria frequently bloom when the ratio of N to P in nutrient inputs is below the Redfield ratio of 16:1 (SCHINDLER, 1977; FLETT et al., 1980; HOWARTH & MARINO, 1988). The resulting N fixation increases N concentrations sufficiently that the lakes can remain P limited (SCHINDLER, 1977; HOWARTH, 1988). In contrast, N-fixing cyanobacteria rarely occur in the plankton of temperate estuaries (CARPENTER, 1971; SMAYDA, 1973; HOWARTH & MARINO, 1988), even though the waters of these estuaries are often very depleted in N relative to P (HOWARTH & COLE, 1985; HOWARTH, 1988). Two exceptions to this pattern, the Baltic Sea and the Harvey-Peel estuarine system in Australia, are discussed in section 5, below.

In mesotrophic and eutrophic ecosystems, cyanobacterial benthic N fixation is severely limited by insufficient light and is generally not important in the N economy (HOWARTH et al., 1988). However, in oligotrophic lakes and estuaries, N fixation by benthic cyanobacteria can be an important source of N to these ecosystems (LOEB & REUTER, 1981; REUTER et al., 1986; ALLNUT et al., 1981; SMITH, 1984; HOWARTH et al., 1988). There appears to be little difference between benthic N fixation in freshwater and marine systems, unlike the case for planktonic fixation (HOWARTH et al., 1988); reasons for this are discussed in section 5, below.

N fixation also can be mediated by heterotrophic bacteria. However, heterotrophic N fixation in the water column is seldom found to contribute significantly to the N economy of aquatic ecosystems (STEWART, 1969; PEARL et al., 1981; GOLDMAN & HORNE, 1983). Heterotrophic N fixation in the sediments of both lakes and estuaries occurs widely yet rarely contributes more than 1-2% of the total N inputs to these ecosystems (HOWARTH et al., 1988).

3. Trace-Metal Controls on Nitrogen Fixation by Planktonic Cyanobacteria

Fe and Mo are both generally thought to be necessary components of nitrogenase and therefore required for N fixation (FOGG & WOLFE, 1954; SHAH et al., 1984; but see discussion on V in section 6, below). Both Fe and Mo are probably less available in seawater than in most freshwaters, perhaps in part explaining the lower rates of N fixation in marine ecosystems (HOWARTH & MARINO, 1988). For Fe, supporting information comes from the finding that iron additions can increase rates of N fixation in freshwaters even when Fe concentrations are already high

(WURTSBAUGH & HORNE, 1983) and from knowledge that Fe concentrations are much lower in seawater than in freshwaters (see HOWARTH & MARINO, 1988, synthesizing data from GORDON et al., 1982; COLLIER & EDMOND, 1984; SHARP et al., 1984; and MOREL & HUDSON, 1985).

In contrast to Fe, Mo concentrations are actually higher in seawater than in most freshwaters (HOWARTH & COLE, 1985; HOWARTH & MARINO, 1988). However, the biological availability of Mo is not simply a function of Mo concentration since sulfate can inhibit the assimilation of molybdate, the thermodynamically stable form of Mo in oxic waters (HOWARTH & COLE, 1985; COLE et al., 1986; HOWARTH & MARINO, 1988). The inhibitory effect of sulfate on molybdate assimilation is a result of the striking similarities in stereochemistries of these two anions (HOWARTH & COLE, 1985).

Sulfate concentrations in most natural waters are 10,000-fold to 1,000,000-fold greater than Mo concentrations, whereas the demand for S by N-fixing cyanobacteria probably exceeds the demand for Mo by only a few hundred-fold (HOWARTH & MARINO, 1988). Consequently, cyanobacteria face a severe problem in assimilating molybdate in the presence of such greater quantities of sulfate. They may have enzyme systems capable of the needed discrimination between sulfate and molybdate, but presumably such discrimination bears an energetic cost, as seems likely for discrimination between toxic and essential cationic trace metals (MOREL & HUDSON, 1985).

Since both sulfate concentrations and the ratio of sulfate to Mo are so much greater in seawater than in freshwaters, the biological availability of Mo in seawater is presumably much less than in freshwaters (HOWARTH & COLE, 1985; HOWARTH & MARINO, 1988). That Mo availability in seawater is in fact low is indicated by the low Mo concentrations in marine seston and by the extremely low ratio of particulate to dissolved Mo in seawater (HOWARTH & MARINO, 1988). Thus, even though dissolved Mo concentrations are higher in seawater than in freshwaters, the Mo content of seston is lower in seawater; typical Mo concentrations in marine seston are 4 nmol/g dry weight, or values very similar to those found in Mo-deficient crops (MANHEIM & LANDERGREN, 1978). Freshwater seston has Mo concentrations which are 10- to 40-fold greater (BERTINE, 1970; DUMONT, 1972).

The ratio of particulate to dissolved Mo in freshwaters is typically near 1:1 (BERTINE, 1970; DUMONT, 1972). However, the ratio is in the range of 1:0.001 to 1:0.000035 in seawater (HOWARTH & MARINO, 1988). For cationic metals in either lakes or seawater, the ratio of particulate to dissolved metal is usually near or above 1:1, and from this MOREL & HUDSON (1985) infer that the biological availability of most cationic metals is high. For Mo, it would appear that the biological availability is much greater in freshwaters than in seawater (HOWARTH & MARINO, 1988).

4. Evidence Relating Molybdenum to Nitrogen Fixation

Clearly sulfate concentrations can affect Mo availability, but is Mo truly important in regulating N fixation in natural waters? Our initial attempt to answer this question was a short-term bioassay experiment. We added molybdate to Baltic Sea water and increased rates of N fixation, and we decreased N fixation through the addition of sulfate (HOWARTH & COLE, 1985). However, such short-term bioassay experiments have not consistently supported a relationship between Mo availability and N fixation in saline waters. For instance, WURTSBAUGH (1988) found that Mo additions stimulated N fixation in water samples from a freshwater lake, East Canyon Reservoir, but not in saline water samples from the Great Salt Lake. Also PEARL et al. (1987) failed to find any stimulatory effect from adding Mo to seawater taken from the coast of North Carolina.

The confusion generated by such experiments leads me to accept the arguments of SMITH (1984) and of HECKY & KILHAM (1988) that such short-term bioassays are inappropriate tools for addressing ecosystem-scale questions (see also discussion in HOWARTH, 1988). This may be particularly true for experiments with N fixation by cyanobacteria, which are notoriously prone to bottle effects. Rather, we need longer-term experiments at the scale of the ecosystem or ecosystem-scale observations.

Such observations have recently been made in a set of 13 saline lakes in Alberta, Canada (MARINO et al., 1990). In a study of the relationship between abundance of N-fixing cyanobacteria and various chemical parameters such as P, Fe, sulfate, and Mo, in these saline lakes, the best (and only statistically significant) predictor of the abundance of N-fixing cyanobacteria was the ratio of sulfate to Mo (MARINO et al., 1990). These results strongly suggest not only that sulfate affects Mo availability but that Mo availability controls N-fixing organisms in these saline lakes.

5. Molybdenum Speciation and Reduced Molybdenum

Molybdate is the thermodynamically stable form of Mo at neutral pH under oxic conditions, but reduced Mo compounds would be expected to occur in reducing environments (BERTINE, 1970; MANHEIM & LANDERGREN, 1978; HOWARTH & MARINO, 1988). Unlike molybdate, these reduced Mo compounds bear no stereochemical resemblance to sulfate, and sulfate should not in any way affect their biological assimilation (HOWARTH & COLE, 1985; HOWARTH & MARINO, 1988). Thus, Mo is probably much more available in reducing environments than in oxic water. This may be one of the reasons that N-fixing, benthic cyanobacteria are so abundant in both marine and freshwater ecosystems whenever light penetrates to the bottom; the sediments may supply reduced Mo (HOWARTH & MARINO, 1988; HOWARTH, 1988). This may also explain why planktonic, N-fixing cyanobacteria are so abundant in the Harvey-Peel estuarine system in Australia (HOWARTH & MARINO, 1988); the Harvey-Peel system averages only 1 meter in depth and frequently has low oxygen concentrations (LUKATELICH & MCCOMB, 1986).

We have speculated that reduced Mo compounds such as Mo(IV) and Mo(V) cations may be present to some extent even in oxic waters (HOWARTH & MARINO, 1988), perhaps formed through photoreduction in surface films or perhaps persisting after diffusing from reduced sediments. Unfortunately, virtually nothing is known about the kinetics of oxidation or reduction of Mo compounds (HUGHES, 1981). However, Mo(V) complexes strongly with various organic ligands (HUGHES, 1981). It seems plausible that such chelation might slow the oxidation of reduced Mo compounds back to molybdate, particularly in organic-rich waters (HOWARTH & MARINO, 1988). This may account for the unusually high abundances of planktonic, N-fixing cyanobacteria in the Baltic Sea since it is thought that the initiation of blooms of these organisms in the Baltic is associated with organic-rich waters (HOWARTH & MARINO, 1988).

6. Vanadium and Iron-Core Nitrogenases

Recent work (BISHOP et al., 1986; ROBSON et al., 1986; DILWORTH et al., 1987; CAMMACK, 1988) has found that, contrary to earlier beliefs, Mo is not absolutely required for N fixation and that V can substitute for Mo in some organisms. There may even be a nitrogenase which uses Fe as its core metal rather than Mo or V (CAMMACK, 1988). To date, only work on V and Fe-core nitrogenases in pure-cultured organisms have been published, and the implications of these findings for rates of N fixation in nature are virtually unexplored. Some preliminary, unpublished work in the Soviet Union has found no evidence for activity by V-based or Fe-core nitrogenases in a variety of lakes (A.I. SARALOV, pers. comm.). The very low activity of the V-based nitrogenase in pure cultures (BISHOP et al., 1986) also suggests it may be rather unimportant in natural ecosystems (HOWARTH & MARINO, 1988). In any event, our saline-lake study indicates that sulfate and Mo are major regulators of N fixation in such ecosystems (MARINO et al., 1990).

7. Conclusions

Sulfate inhibits the assimilation of molybdate by cyanobacteria. As a result, Mo availability is frequently lower in natural waters than might be expected, particularly in seawater where sulfate concentrations are very high. Consequently, sulfate partially regulates rates of N fixation. N-limited ecosystems are more likely when the sulfate/molybdenum ratio in a water body is high.

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Controls on Sulfur Cycling in Small Lakes

by
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With 5 Figures and 2 Tables

Contents

Abstract

The factors controlling the sulfur cycle in small lakes, with particular regard to sulfur accumulation in lake sediments, are reviewed for several northern temperate lakes in North America. The primary means of sediment S accumulation is through bacterial sulfate reduction coupled with reaction of product sulfide with either iron or organic matter. Accumulation of S by sedimentation of organic sulfur originating from algae may be important for lakes with high primary productivity, for lakes with low concentrations of SO_4^{2-}, or for lakes with extremely low rates of SO_4^{2-} reduction.

1. Introduction

Over the past 10 to 15 years a number of studies have been conducted on the biogeochemistry of sulfur in lakes. These studies have shown that (i) the sulfur cycle in small lakes has been affected by increased atmospheric deposition (RUDD et al.,

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1986a; NRIAGU & SOON, 1985; FRY, 1986), with attendant effects on the acid-base chemistry of lakes (LANDERS et al., 1988; BRAKKE et al., 1988); (ii) under certain conditions SO_4^{2-} reactions, particularly bacterial sulfate reduction, can counteract acidification by producing alkalinity (COOK et al., 1986); (iii) historical changes in lake water SO_4^{2-} concentrations may be recorded in sediments (MITCHELL et al., 1988).

The purpose of this paper is to examine the biogeochemical processes that remove SO_4^{2-} from the water column of small lakes. Because the primary reactions that sulfur undergoes are closely linked to organic carbon and may produce inorganic carbon (SCHINDLER, 1985), this paper will also discuss the interactions of the carbon and sulfur cycles. Data will be presented from several northern temperate lakes located in North America.

A schematic diagram of the sulfur cycle in small lakes is presented in Figure 1. In the water column, SO_4^{2-} is taken up by plankton in a variety of chemical forms, including ester sulfate and carbon-bonded sulfur (DAVID & MITCHELL, 1985). These forms of organic sulfur may be decomposed in the water column or settle out of the water column and undergo diagenesis in the sediment. Lakewater SO_4^{2-} is conveyed by diffusion and bioturbation to the oxic and anoxic portions of the sediment, where it may undergo reactions, the most important of which is bacterial sulfate reduction forming hydrogen sulfide. Hydrogen sulfide thereby produced may either diffuse to oxic zones, where it is eventually oxidized back to SO_4^{2-}, or react to form metal sulfides. Recent work using stable sulfur isotopes (NRIAGU & SOON, 1985) and

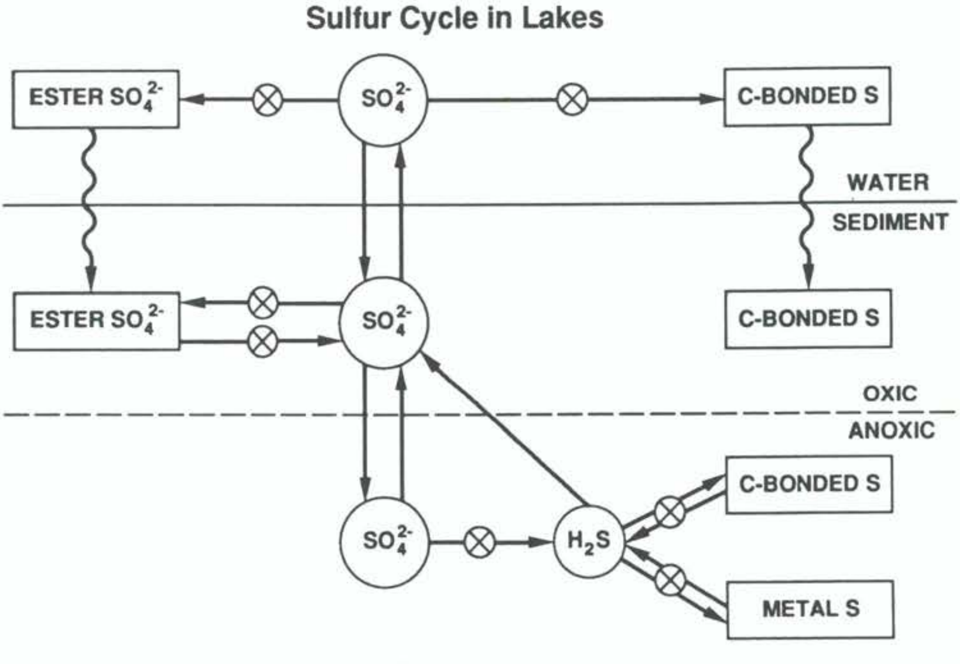

Fig. 1: Schematic diagram of the sulfur cycle in small lakes.

radiosulfur (RUDD et al., 1986a; LANDERS & MITCHELL, 1988) showed that the sulfides produced may react with organic matter to form organic sulfur compounds. The factors controlling which reaction path the hydrogen sulfide follows are not understood (NRIAGU & SOON, 1985; RUDD et al., 1986a; CARIGNAN & TESSIER, 1988). Because of the many mobile forms of sulfur, the total amount of sulfur in a particular chronohorizon is the sum of historical and contemporary sedimentation and diagenesis, thereby confounding paleolimnological interpretation (HOLDREN et al., 1984; CARIGNAN & TESSIER, 1988).

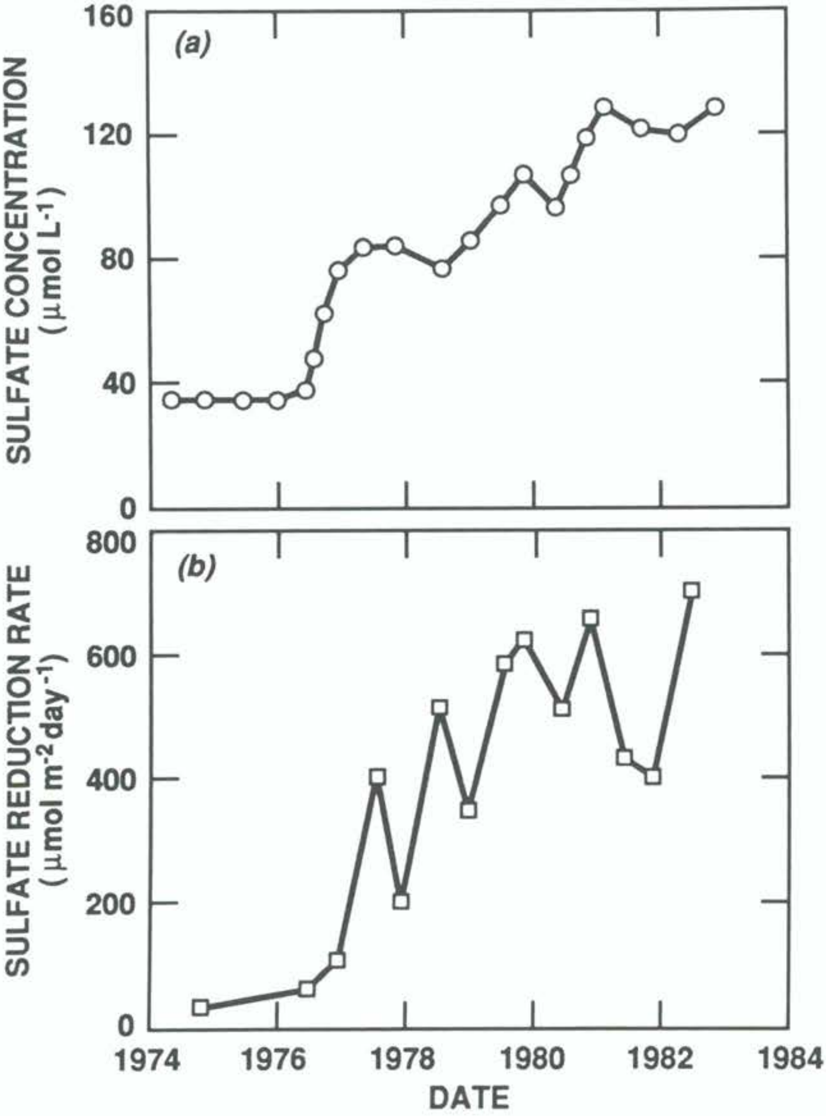

Fig. 2: Lakewater SO_4^{2-} concentration and areal rates of bacterial sulfate reduction in the anoxic hypolimnion of Lake 223 in the Experimental Lakes Area of northwestern Ontario (data from COOK & SCHINDLER, 1983, and COOK et al., 1986).

2. Reactions of Sulfur

Rates of bacterial sulfate reduction in the sediments are a function of both SO_4^{2-} concentrations (COOK & SCHINDLER, 1983; KELLY & RUDD, 1984; LOVELY & KLUG, 1986) and, rarely, organic carbon supply (RUDD et al., 1986a). Retention of the reduced sulfur (S(-II)) in the sediments as an iron sulfide depends on the supply of reducible iron to the sediments (RUDD et al., 1986a; HERLIHY et al., 1987; CARIGNAN & TESSIER, 1988); retention as organic sulfur compounds depends on unknown factors but has been shown to occur as a result of bacterial sulfate reduction (NRIAGU & SOON, 1985; RUDD et al., 1986a).

In Lake 223 (Experimental Lakes Area, northwestern Ontario, Canada), experimental additions of sulfuric acid caused lakewater SO_4^{2-} concentrations to increase three-fold, causing bacterial SO_4^{2-} reduction rates to increase both in the anoxic hypolimnion and in the sediments throughout the lake (Fig. 2; COOK & SCHINDLER, 1983; COOK et al., 1986). Similar findings on the relationship between SO_4^{2-} concentrations and SO_4^{2-} reduction rates have been reported in limnocorrals (PERRY et al., 1985; SCHIFF & ANDERSON, 1987) and in another whole-lake experiment (RUDD, pers. comm.). Prior to the experimental acid additions in Lake 223, organic matter decomposition in littoral sediments and in the hypolimnion occurred by three main processes: oxic decomposition, bacterial sulfate reduction, and methanogenesis (Fig. 3). With the SO_4^{2-} additions, bacterial SO_4^{2-} reduction was likely stimulated at the expense of methanogenesis, because the energy yield is greater for bacterial SO_4^{2-} reduction than that for methanogenesis (LOVELY & KLUG, 1986). As Lake 223 was acidified, a change occurred, not in the total amount of organic matter that decomposed, but in the way in which it decomposed (COOK, 1981; KELLY et al., 1982, 1984). The reduced sulfur was effectively retained by profundal sediments, primarily in an acid-volatile sulfur form (COOK, 1981). As a consequence of the increased rate of SO_4^{2-} reduction, the concentration of total sulfur and the rate of sulfur accumulation in the profundal sediments of Lake 223 also increased (Fig. 4).

The supply of organic matter to the sediments can have a dramatic effect on sulfur reactions and retention in lake sediments. The rate of bacterial SO_4^{2-} reduction at Lake 227, Experimental Lakes Area, was stimulated by experimental eutrophication. Nitrogen and phosphorus additions, which were made to stimulate cultural eutrophication, caused primary production rates and concentrations of chlorophyll *a* to increase (FEE, 1979; SCHINDLER et al., 1987). The sedimentation rates increased from 45 $g/m^2/a$ (KIPPHUT, 1978) to 210 $g/m^2/a$ (ANDERSON et al., 1987) as a result of the fertilization. Anoxic conditions in the water column increased and extended throughout the hypolimnion (COOK, 1984). These changes led to an increase in the transport of SO_4^{2-} to the sites of bacterial sulfate reduction and an increase in rates of bacterial sulfate reduction. The accumulation of total sulfur in the sediments increased from 9 to 20 $mmol/m^2/a$ (Fig. 4) as a consequence of both

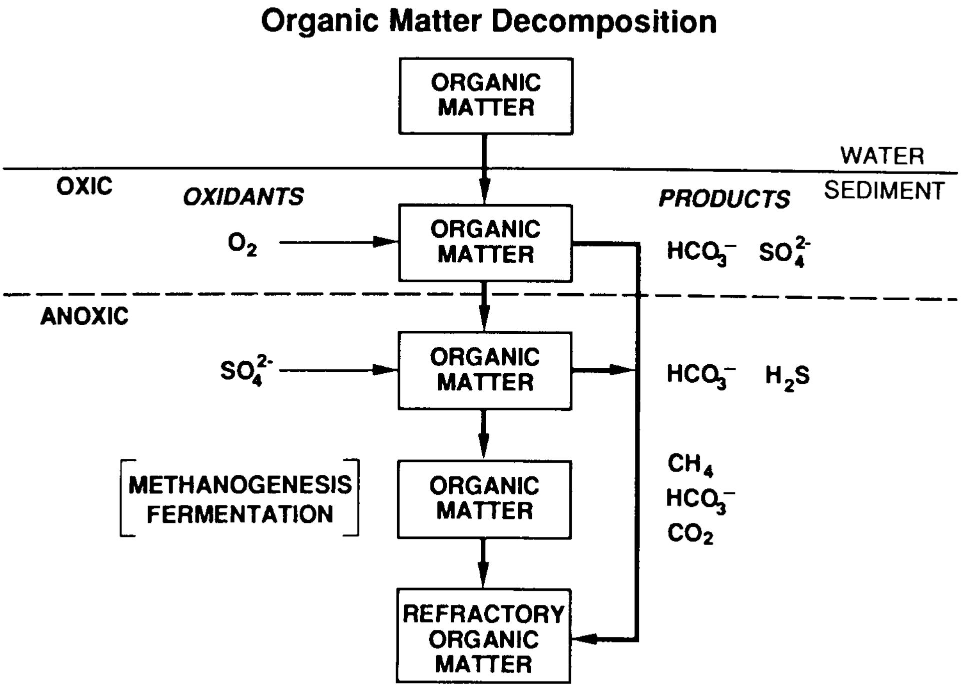

Fig. 3: Schematic diagram of the primary reactions that decompose organic matter in lakes (based on a figure from MARTENS & JANNASCH, 1983).

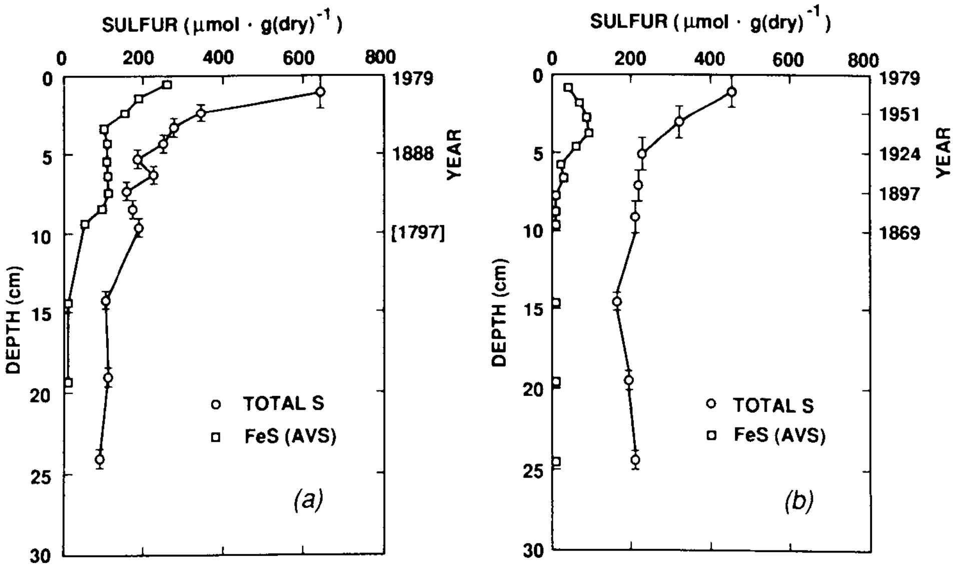

Fig. 4: Total sulfur profile in the sediments of (a) Lake 223 and (b) Lake 227 (source: COOK, 1981).

increased SO_4^{2-} reduction and S(-II) retention and an increased sedimentation of organic sulfur derived from algae. Although complete analyses for sulfur species were not made, acid volatile sulfur and authigenic pyrite were among the forms accumulating (COOK, 1984).

A low rate of organic carbon supply may also limit bacterial SO_4^{2-} reduction. At McNearney Lake (northern Michigan, U.S.A.) the supply of organic matter to the sediments apparently causes the rate of bacterial SO_4^{2-} reduction to be low (FRY, 1990). The lake is naturally acidic, apparently for the past several thousand years, and is ultra oligotrophic, having very low levels of chlorophyll a and low rates of bulk sedimentation (COOK et al., 1990). The lakewater concentration of SO_4^{2-} in McNearney Lake is 75 μmol/l. The small concentration of sulfur in the sediments has remained relatively constant over the past few hundred years (Fig. 5) and exhibits no changes at the time of increases in the anthropogenic polycyclic aromatic hydrocarbons or lead (COOK et al., 1990). Data on stable sulfur isotopes shows only a slight depletion of $\delta^{34}S$, indicating a small amount of bacterial SO_4^{2-} reduction and of sulfide retention (FRY, 1990). However, data on stable sulfur isotopes from other small oligotrophic lakes in which both high rates of bacterial SO_4^{2-} reduction and efficient retention of sulfides occur, indicate surface sediment depletions of 10-15 $^{o}/oo$ in comparison with downcore $\delta^{34}S$ values (FRY, 1986; NRIAGU & SOON, 1985). In McNearney Lake, because of the low rates at which organic matter is supplied to

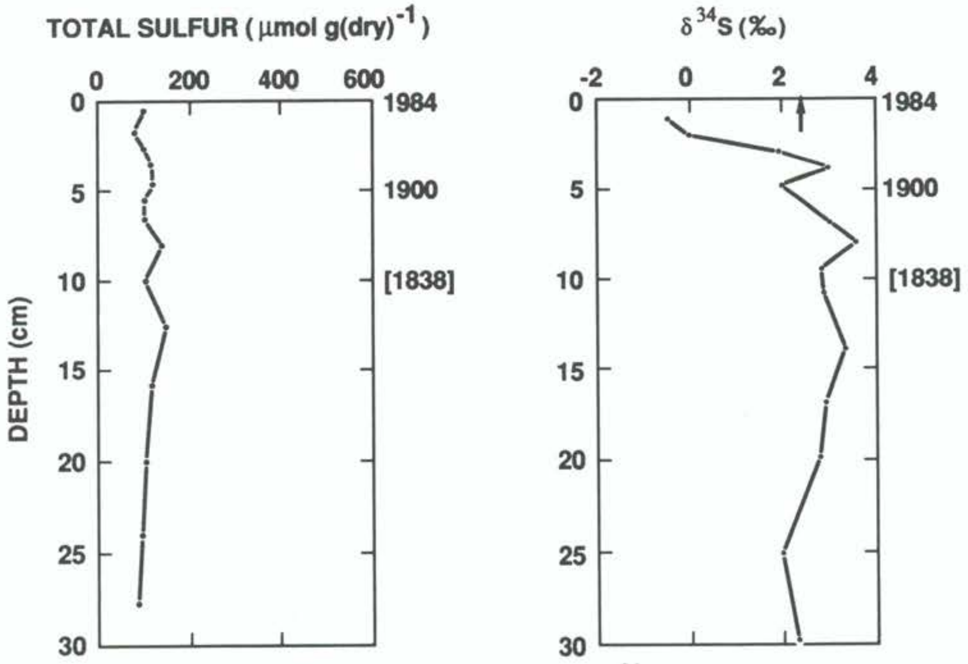

Fig. 5: Total sulfur profile and stable sulfur isotope content ($\delta^{34}S$) in McNearney Lake, Michigan (source: FRY, 1990). The anthropogenic Pb and polycyclic aromatic hydrocarbon rises occurred at 3-4 cm in this core (COOK et al., 1990).

the sediments, most of the organic matter is evidently oxidized aerobically at the sediment-water interface. Little of the organic matter in the anoxic portion of the sediments is apparently suitable for bacterial SO_4^{2-} reduction, despite high lakewater SO_4^{2-} concentrations. The sedimentary sulfur accumulating in McNearney Lake is derived from organic sulfur formed in the water column, along with some limited amounts of sulfur derived from bacterial SO_4^{2-} reduction. Other workers have observed that bacterial SO_4^{2-} reduction rates in certain lakes were low and attributed these rates to low supplies of organic carbon (DAVID & MITCHELL, 1985; RUDD et al., 1986b).

3. Whole-Lake Sulfur Budgets

Whole-lake sulfur budgets are presented in Table 1 for six lakes that have received detailed examination for the mechanism of sulfur removal. Three lakes in mid-continental North America (Lake 223, Lake 302N, and Lake 302S, all of which are located at the Experimental Lakes Area) have a large portion (>50 %) of the

Table 1

Whole-lake sulfur budgets for six lakes, showing the processes by which sulfur is retained (in mmol/m^2/a).

In-lake retention	Natural inputs	Acid inputs	Total inputs	Out-flow	Change in storage	Bact. SO_4^{2-} reduct.	S_{org} sedimen-tation
Lake 223[a)]	76	227	303	101	80	123	3
Lake 227[b)]	82	-	82	74	-	6	6
Lake 302S[c)]	83	151	234	64	65	94	<11
Lake 302N[c)]	116	-	116	58	12	45	<11
Little Rock Lake[d)]	21	-	21	11	-	6	9
South Lake[e)]	421	-	421	403	-	9	9

[a)] For the period 1976 through 1983. From COOK et al. (1986), except for the estimate of organic sulfur sedimentation which was estimated by COOK (1981), who used nitrogen to sulfur ratios.

[b)] For the period 1974-1975 and 1978-1979 (from COOK, 1981). Organic sulfur sedimentation was estimated by using nitrogen to sulfur ratios.

[c)] For the period 1981 through 1985. Organic sulfur sedimentation is an estimate of gross sedimentation; no estimates are available for decomposition at the sediment-water interface (RUDD, pers. comm.).

[d)] Estimated budget for reacidification conditions. Organic sulfur sedimentation is estimated by using carbon to sulfur ratios (from BAKER et al., 1989).

[e)] For the period 1981 through 1982 (from MITCHELL et al., 1985, and LANDERS & MITCHELL, 1988), except for SO_4^{2-} reduction rates, which were estimated for 1986 (OWEN & MITCHELL, 1989).

input sulfur removed. These lakes have relatively long water residence times, which allows more time for sediment reactions to affect lakewater concentrations and causes a greater loss of SO_4^{2-} from the water column (KELLY et al., 1987; BAKER & BREZONIK, 1988). Also, these three lakes have somewhat higher lakewater concentrations of SO_4^{2-}, which affect rates of bacterial SO_4^{2-} reduction, because of its first-order SO_4^{2-} dependence (LOVELY & KLUG, 1986).

A low percentage of retention of input sulfur may be due in part to short water residence times and to low concentrations SO_4^{2-}. South Lake (Adirondack region, New York, U.S.A.) has a short water residence time (0.5 years, OWEN & MITCHELL, 1989) and consequently does not have a large percentage of retention of sulfur input to the lake (BAKER & BREZONIK, 1988). South Lake, along with Little Rock Lake (northcentral Wisconsin, U.S.A.), Lake 227, and Lake 302N, also has concentrations of SO_4^{2-} near that at which methanogenesis may become energetically favored over bacterial SO_4^{2-} reduction (≈ 30 μmol/l; COOK, 1981; LOVELY & KLUG, 1986). Interestingly, although rates of bacterial SO_4^{2-} reduction in Lake 227 were quite high because of stimulation by eutrophication, the reduced sulfur was not sequestered efficiently by the sediments and thus remained in the hypolimnion as hydrogen sulfide, to be oxidized at fall and spring overturn (COOK, 1981).

Rates of organic S sedimentation were similar in each of the lakes, ranging from 3-11 mmol/m^2/a (Table 1). The rate of organic S sedimentation for Lake 302S is gross sedimentation, because estimates of recycling at the sediment-water interface were not made. BAKER et al. (1989) estimated that 50 % of the incident sulfur in Little Rock Lake was recycled at the sediment-water interface, and DAVID & MITCHELL (1985) estimated that 26 % of the incident sulfur was recycled in South Lake. Applying these recycling rates to the Lakes 302N and 302S would bring the net organic S sedimentation rates to 5-8 mmol/m^2/a; these rates are similar to those for the other lakes (Table 1).

4. Interactions of the Carbon and Sulfur Cycles in Small Lakes

The primary reactions that sulfur undergoes are closely linked to organic carbon production and decomposition. Without this link, the behavior of sulfur in small lakes would be conservative. Sulfur reactions, particularly bacterial sulfate reduction, also affect inorganic carbon concentrations by producing HCO_3^-.

Sulfur is a minor nutrient present in algae at a ratio of about 1 S atom to 100 carbon atoms. Under certain conditions (for example, short water residence times, low rates of bacterial SO_4^{2-} reduction, or small concentrations of SO_4^{2-}), organic sulfur sedimentation may be the primary means of sulfur removal from the water column. For lakes that have these characteristics, increases in lakewater SO_4^{2-} concentrations will not likely lead to increased algal uptake of sulfur and increased in-lake retention of sulfur, because the nutritional requirement for sulfur has not been affected. However, some limited evidence suggests that the concentration of organic S in algal protoplasm may increase slightly with increases in lakewater SO_4^{2-} (DATKO et al., 1978). Increases in nutrient inputs (e.g., N, P) to a lake may lead to an increased sedimentation of organic carbon and organic sulfur, even though the C:S ratio of the sedimenting material does not change. However, due to increases in decomposition which likely accompany increased productivity, the increased net sedimentation of organic sulfur will not be proportionally as large as the increase in primary productivity.

Sulfur and carbon also interact through microbially mediated decomposition of organic matter, with SO_4^{2-} as a terminal electron acceptor. This reaction is limited by SO_4^{2-} in lakes with SO_4^{2-} concentrations below 1-2 mmol/l (LOVELY & KLUG, 1986). Because SO_4^{2-} reduction is first order with respect to SO_4^{2-} at these concentrations, increases in SO_4^{2-} will cause increases in rates of SO_4^{2-} reduction. At low SO_4^{2-} concentrations (<20-40 μmol/l), methanogenic bacteria may predominate over bacteria that reduce SO_4^{2-}, and rates of bacterial SO_4^{2-} reduction have been observed to be low (LOVELY & KLUG, 1986). However, the factors determining the exact cutoff in SO_4^{2-} concentration between SO_4^{2-} reducers and methanogens is somewhat uncertain. Workers have reported SO_4^{2-} concentrations as low as 0.2-5 μmol/l in anoxic pore waters (COOK, 1981; HOLDREN et al., 1984; KELLY & RUDD, 1984; COOK et al., 1986, 1987; RUDD et al., 1986a).

Hydrogen sulfide produced by bacterial SO_4^{2-} reduction may react with organic matter to form organic sulfur compounds (NRIAGU & SOON, 1985; RUDD et al., 1986a). The exact conditions under which this reaction occurs and the factors controlling this reaction are not known. RUDD et al. (1986a) added $^{35}SO_4^{2-}$ to sediments in situ and observed that some of the tracer was lost from both the organic and inorganic sulfur pools through oxidation or isotopic exchange over an eight-month period. More tracer was lost from the inorganic sulfur pools, leaving the organic form the predominant phase. Studies in which SO_4^{2-} has been added to whole lakes (Fig. 4) or to intact sediments cores (R.W. HOWARTH, Cornell University, pers. comm.) revealed that inorganic sulfur was the phase that exhibited increases. In an examination of sulfur sediment accumulation in a lake in the Adirondacks (New York, U.S.A.), WHITE (Indiana University, Bloomington, Indiana, pers. comm.) showed that both inorganic and organic sulfur have increased, but inorganic sulfur has increased more during the past 100 years.

A product of bacterial SO_4^{2-} reduction is HCO_3^-, which represents another interaction between the sulfur and carbon cycles. This production of HCO_3^- can affect the alkalinity of lakes and can counteract the effects of atmospheric deposition (COOK et al., 1986; SCHINDLER et al., 1986). Increases in SO_4^{2-} deposition will cause increases in bacterial SO_4^{2-} reduction and increases in production of HCO_3^-, thereby providing a homeostatic mechanism for maintaining alkalinity concentrations and slowing the rate of acidification (COOK et al., 1986). The efficiency with which this homeostasis maintains alkalinity depends on the amount of SO_4^{2-} that is retained by the lake, which is a function of SO_4^{2-} concentration and hydraulic residence time,

Table 2

Rates of iron accumulation in lake sediments.

Site	Fe accumulation ($mmol/m^2/a$)	Reference
Little Rock Lake	12	Baker et al. (1989)
McNearney Lake	16	Cook et al. (1990)
Lake 223	20	Cook (1984)
Lake 227	25	Cook (1981)
Lake 96760	40	Carignan & Tessier (1988)
Big Moose Lake	200	White, Indiana University, Bloomington, Indiana (pers. comm.)

and the ability of the sediments to sequester reduced sulfur (S(-II)) in an inorganic or organic sulfur form. In the Lake 223 experiment, the sediments retained nearly all of the sulfur produced by bacterial SO_4^{2-} reduction, much of it as iron sulfides (Fig. 4; Cook et al., 1986). The efficiency of retention also appears to be high in the Lake 302S experiment (Rudd, pers. comm.). The rate of supply of iron to the sediments may eventually limit the ability of sediments to sequester sulfur (Schindler, 1985; Carignan & Tessier, 1988). For lakes in the mid-continent of North America, rates of iron sedimentation in lakes are comparable in magnitude to atmospheric deposition of sulfur, whereas in the Adirondack Mountains, in New York, rates of iron sedimentation are greater than atmospheric deposition by 5- to 10-fold (Table 2). Once the inventory and supply of iron are exhausted (Anderson & Schiff, 1987), the capacity for sulfur retention by reaction with iron is diminished, and, unless other reactions occur (e.g., incorporation into organic forms), hydrogen sulfide may build up to high concentrations and eventually be oxidized back to SO_4^{2-}, nullifying the gains in alkalinity.

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Measurements of Phytoplankton Primary Production in the Sea: Problems in Preparation of $NaH^{14}CO_3$ Solutions and in Filtrations of Samples

by
BO RIEMANN, Hϕrsholm*)

With 3 Figures

Contents

Abstract

Reliable determinations of phytoplankton primary production from measurements of ^{14}C uptake depend on a number of methodological conditions. Severe errors are introduced when dilutions of industrially produced ^{14}C solutions are used directly, since these solutions often (i) inhibit primary production, (ii) contain high non-volatile rest activities, and (iii) have wrong ampoule specifications. It is important to prepare ^{14}C solutions from distillation of $Ba^{14}CO_3$. Moreover, the specific activity of the working solutions should be measured or documented with a certificate of quality. In routine monitoring studies, it is better to measure primary production by acidifying and bubbling the samples instead of filtering samples onto membrane filters.

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1. Introduction

Almost 40% of the global primary production is produced in the oceans at a rate of about 50-100 g C/m²/a. Direct measurements of the productivity can be made by several methods, although the ^{14}C technique has been preferred since its introduction by STEEMANN NIELSEN in 1952.

A large number of reports have discussed precautions and limitations in the ^{14}C procedure, and it is a fair judgement that 30 years of research have not clarified what is really measured by the standard ^{14}C technique. Nevertheless, there is today no alternative analytical protocol for measuring primary production in the sea.

A theoretical diagram of transport of $^{14}CO_2$ in a marine food chain structure is demonstrated in Figure 1. A number of dissolved and particulate pools of carbon are

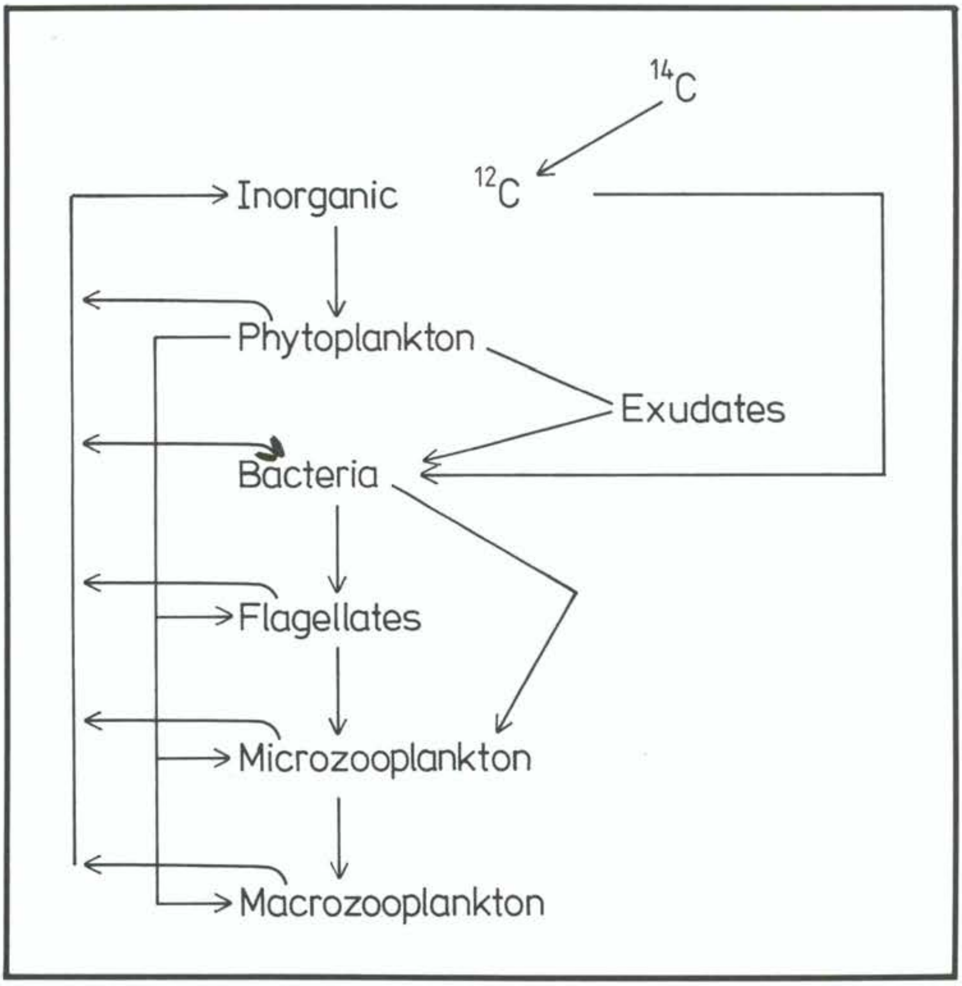

Fig. 1: An example of a marine food chain structure through which ^{14}C is transported and located in a number of dissolved and particulate phases.

present in water. The rate at which ^{14}C flows through these pools depends on several factors, but it is often a question of minutes before significant quantities of ^{14}C are found in all major pools (Fig. 1). The $^{14}CO_2$ assimilated by phytoplankton is transported up the food chain to zooplankton indirectly via bacteria or directly via grazing of ^{14}C-labeled algae.

In the standard ^{14}C procedure, natural water samples are passed through a filter and the ^{14}C activity on the filter is related directly to phytoplankton photoassimilation of $^{14}CO_2$. In some cases, re-assimilation of respired $^{14}CO_2$ is of less importance, but respiration at other trophic levels than algae can be quantitatively significant, as can losses of ^{14}C-labeled dissolved organic material released directly from the phytoplankton. The food chain described in Figure 1 is not general. A number of possible food chain scenarios can occur with varying importance of specific links. Nevertheless, all the links in the food chain mentioned in Figure 1 occur and can be important in the assimilation and the transport of $^{14}CO_2$.

Today, measurements of phytoplankton primary production are important in (i) monitoring global changes in the productivity of the oceans, (ii) determining effects of eutrophication in particular coastal marine areas and marginal seas, (iii) evaluating effects of toxic elements on natural populations of phytoplankton and on the general metabolism of organic matter in aquatic environments, and (iv) understanding overall production and decomposition of organic matter in aquatic systems.

It is the object of this report to discuss current methodological status of the ^{14}C technique, particularly emphasizing preparation of $NaH^{14}CO_3$ solutions and filtration versus acidification and bubbling procedures. Comprehensive reviews on the ^{14}C procedure are found in SHARP (1977), PETERSON (1980) and SφNDERGAARD & JENSEN (1986).

2. Preparation of $NaH^{14}CO_3$

The $^{14}CO_2$ solution used for measurements of phytoplankton primary production is often prepared from dilutions of industrially produced $NaH^{14}CO_3$ solutions (STRICKLAND & PARSONS, 1972) or from trapping $^{14}CO_2$ gas from $Ba^{14}CO_3$ using HCl (STEEMANN NIELSEN, 1977). Several authors have cautioned about the industrially produced ^{14}C bicarbonate because a number of artifacts are introduced in the measurements of primary production (WILLIAMS et al., 1973; NAIR, 1974; STEEMANN NIELSEN, 1977). Recently BRESTA et al. (1987) demonstrated that industrially produced ^{14}C bicarbonate solutions contained high non-volatile rest activities and had poor accuracy and dissatisfactory ampoule specifications. Moreover, BRESTA et al. (1987) found strong inhibitory effects of three out of four industrially produced ^{14}C solutions on the photosynthesis of cultures and natural populations of phytoplankton.

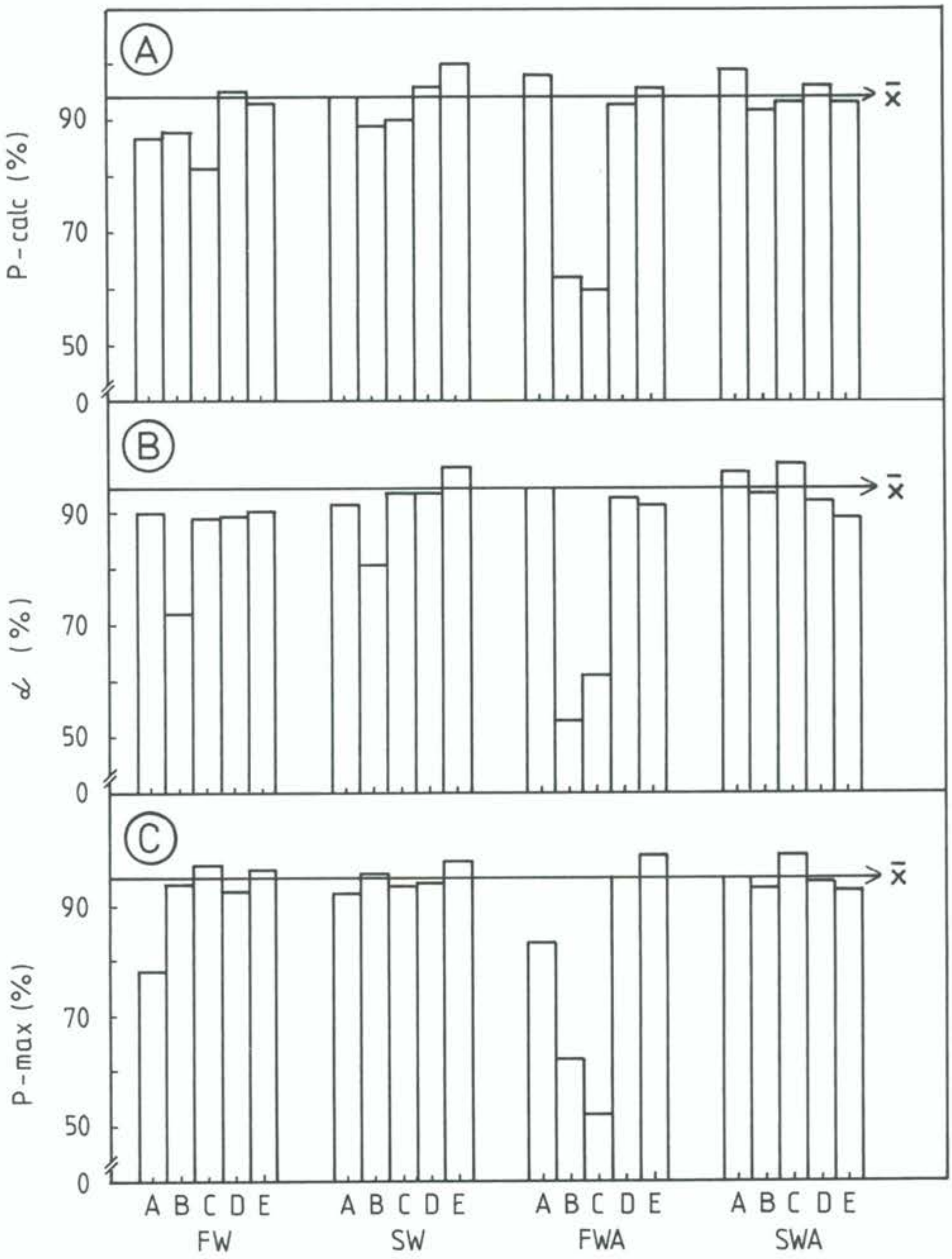

Fig. 2: Effects of using different ^{14}C-labeled CO_2 solutions from five different manufacturers (named A - E). On (A), the relative integrated rate of primary production per volume of inoculum (P-calc.); the slope (l) of the initial ascending part of the P-I curve, L expressed in relative units; (C) the relative maximal rate of primary production (P-max) per volume of inoculum; x = mean values. - FW = freshwater samples, SW = seawater samples, FWA = artificial freshwater medium inoculated with *Selenastrum capricornutum*, SWA = artificial seawater medium inoculated with *Phaeodactylum* sp. (redrawn from BRESTA et al., 1987).

Below, I briefly discuss the importance of (i) using ^{14}C solutions prepared by trapping $^{14}CO_2$ gas, released by adding HCl to $Ba^{14}CO_3$ in sodium hydroxide, and (ii) using ^{14}C solutions with a "Certificate of Quality".

First of all, inhibitory effects of industrially produced ^{14}C solutions have been reported to reduce estimates of primary production by up to 50 % (BRESTA et al., 1987). In the plots of Figure 2, three out of four industrially produced ^{14}C solutions revealed marked inhibitory effects on (i) the rate of particulate primary production, (ii) the initial slope of P versus I, and (iii) maximum rate of primary production. These effects include probably metal contaminations, since ^{14}C solutions can increase metal concentrations 6-fold compared with the ambient metal concentration in open ocean surface samples (FITZWATER et al., 1982).

Two of the batches studied gave 30-40 % inhibition in all three variables studied. Thus, primary production can be severely underestimated because of contaminated products.

Secondly, another matter of importance is that most of the industrially produced $^{14}CO_2$ solutions contain a high non-volatile rest activity (Fig. 3). Except for the solution prepared from $BaCO_3$ by distillation, non-volatile rest activity ranged from 13 to 194 dpm/µCi. Such levels of non-volatile rest activity make measurements of phytoplankton release of extracellular organic carbon unreliable. A number of

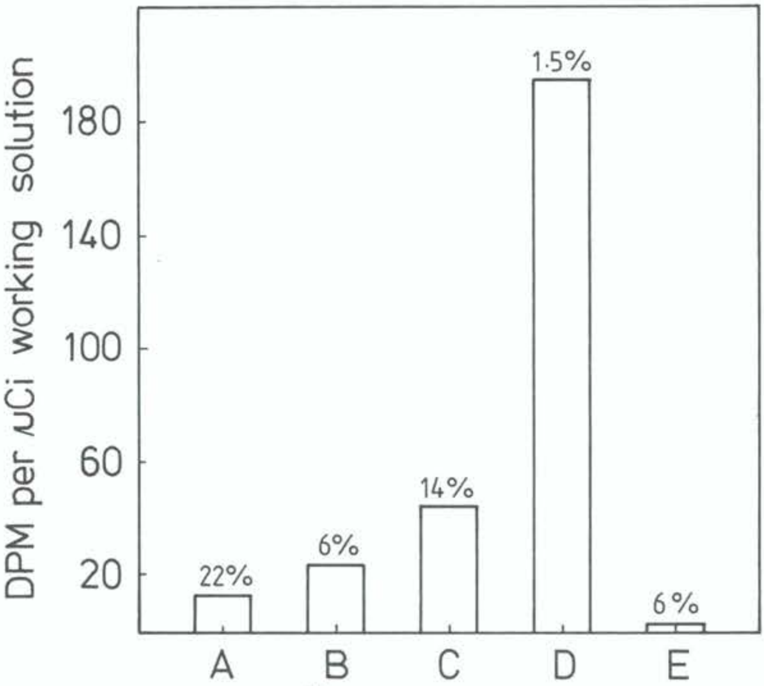

Fig. 3: Non-volatile rest activity in different ^{14}C-labeled CO_2 solutions from five different manufacturers (named A-E). The numbers in % indicate relative standard error of the mean (redrawn from BRESTA et al., 1987).

published results of release rates from phytoplankton are probably too high because of high non-volatile rest activities in the $^{14}CO_2$ solutions.

A final problem with the industrially produced $^{14}CO_2$ solutions is that ampoule specifications are often wrong. Since it is not a routine procedure to measure the specific activity of the added $NaH^{14}CO_3$, the calculated rates of primary production are based on the written specifications from the manufacturer. BRESTA et al. (1987) reported that some of the industrially produced $^{14}CO_2$ solutions differed by 18 % from the specific activity specified by the manufacturer, and that ampoules of the same batch varied by up to 27 %.

The overall conclusion is that $^{14}CO_2$ working solutions should not be prepared using dilutions of industrially produced ^{14}C-solutions. Instead, distillation of $Ba^{14}CO_3$ should be preferred (STEEMANN NIELSEN, 1977). Furthermore, careful control of specific activity and non-volatile rest activities should be carried out, if not explicitly specified by the manufacturer with a "Certificate of Quality".

3. Filtration Versus Acidification and Bubbling Procedures

In a recent intercomparison exercise carried out by ICES (1987), it was concluded that a major reason for observed variations in the measured ^{14}C incorporation into particular material between different laboratories was caused by differences in the filtration procedure.

In the standard ^{14}C procedure, samples are filtered onto membrane filters after incubation, and radioactivity measured from the filter is used to calculate primary production. If exudates have been released from the phytoplankton during incubation, primary production is then underestimated. Moreover, the vacuum pressure used for filtration may induce leakage of labeled organic material, which causes further underestimations of the primary production. These problems have been discussed continuously since the introduction of the ^{14}C technique (see SHARP, 1977; PETERSON, 1980, and references therein). Since leakage of organic materials from phytoplankton induced by filtration apparently depends on several factors, it is not appropriate to apply a fixed vacuum pressure when different environmental samples are examined. Species composition, physiological status as well as stress induced by various postincubation storage procedures are all factors influencing leakage from phytoplankton cells.

A possible way to circumvent the filtration step in the ^{14}C procedure is to acidify and bubble the sample. Thereby, inorganic $^{14}CO_2$ is removed and the rest activity in organic ^{14}C, present in particles or in dissolved forms, is assumed to have been produced by phytoplankton via photosynthesis. Results from this procedure introduced by SCHINDLER et al. (1972) have been compared with those from filtration methods and agreement between the two methods was reported by SCHINDLER et al. (1972) and THEODORSON & BJARNASON (1975). GÄCHTER et al. (1984) reported that the acidification and bubbling method gave 30 % higher values than their filtration procedure. Unfortunately, GÄCHTER et al. (1984) filtered their ^{14}C-labeled environmental samples onto 0.8 μm filters. Therefore, any labeled particles < 0.8 μm must have escaped their filtration results and only be included in the results from the acidification and bubbling method. SφNDERGAARD (1985) demonstrated that radioactivity in the size class < 1.0 > 0.2 μm averaged 26 % of the activity retained on a 1.0 μm filter from oligotrophic Lake Almind, and SφNDERGAARD (1985) suggested that this loss of radioactivity < 0.8 μm could explain the discrepancies observed by GÄCHTER et al. (1984).

The choice of method depends on the purpose of the experiment. In many basic research studies, it is necessary to separate the primary production into dissolved and particulate pools. A number of different techniques were recently reviewed by SφNDERGAARD & JENSEN (1986). The majority of these procedures are, however, not designed for large scale experiments and are not standard procedures. Therefore, in routine or large-scale monitoring studies, it is easier and more correct to measure "total primary production", for example, by means of the acidification and bubbling technique. Results from this technique do not include $^{14}CO_2$ lost by respiration of phytoplankton, bacteria or other microorganisms, but they do contain $^{14}CO_2$ released as extracellular organic carbon from phytoplankton or from cells stressed by filtration procedures.

The International Agency for ^{14}C Determination is currently studying a number of basic aspects of the acidification and bubbling procedure with special reference to the application of the technique as a general alternative to measure phytoplankton primary production in the sea.

4. Conclusions

The procedures used in preparation of $NaH^{14}CO_3$ working solutions, are critical to the reliability of the primary production measurements. Three major pitfalls have been described and remedies suggested. First, it is important to prepare $NaH^{14}CO_3$ from distillation of $Ba^{14}CO_3$ and not by dilution of industrially produced $NaH^{14}CO_3$ of high specific activity. Secondly, the specific activity of the working solutions should be measured, if it is not documented by the manufacturer with a "Certificate of Quality". Finally, acidification and bubbling methods can be used in routine and large-scale monitoring programs to avoid the loss of ^{14}C due to excretion or induced via filtration stress.

5. Acknowledgements

I wish to thank Kirsten Christoffersen for valuable suggestions and Kathleen Gail Jensen for comments and linguistic improvements.

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The Importance of Reduced Inorganic Sulfur to the Sulfur Cycle of Lakes

by
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With 3 Figures and 3 Tables

Contents

Abstract

It is generally believed that sulfate from acid deposition has stimulated bacterial sulfate reduction in lake sediments, and that a portion of the reduced sulfur is stored in sediments. However, the factors controlling both the forms and the amounts of sulfur retained are not well understood. We have found that reduced inorganic sulfur (pyrite + FeS + elemental sulfur) makes up a substantial portion of the total sediment sulfur in many lakes in North America that receive sulfuric acid

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deposition. In an experiment where sulfate was added to the overlying water of sediment microcosms from one lake, we observed significant increases in the inorganic, but not the organic forms of sulfur in sediments. Our data indicates that some lakes are storing sulfides produced by sulfate reduction primarily in inorganic forms rather than as carbon bonded sulfur. Since a large percentage of the total iron in the sediments of some of these lakes is in the form of ferrous sulfides, iron availability may now be limiting sulfide storage in regions where iron inputs to sediments are low.

1. Introduction

Sulfate, rather than carbon, usually limits dissimilatory sulfate reduction in lakes (Kelly & Rudd, 1984; Smith & Klug, 1981; Carignan, 1985; Herlihy & Mills, 1985). Therefore the historical increase in sulfate loading due to acid deposition (Husar, 1986) should have increased sulfate reduction rates in lake sediments. This increase in sulfate reduction rates has been demonstrated experimentally by additions of sulfuric acid to whole lakes and experimental enclosures (Cook & Schindler, 1983; Kelly & Rudd, 1984; Schiff & Anderson, 1987).

Sulfate reduction may be important in ameliorating the effects of acid deposition because each equivalent of sulfate reduced generates an equivalent of alkalinity. However, for this alkalinity gain to persist the reduced sulfur must be buried permanently, or lost as reduced sulfur, because acid is generated when sulfides are oxidized.

Both iron and organic matter are potentially important sinks for sulfides in lake sediments (Cook, 1981; Nriagu & Soon, 1985; Rudd et al., 1986), but their relative reactivities and potentials for oxidation are understood poorly. Rudd et al. (1986) found that organic sulfur was a major end product of sulfate reduction in lakes of the Adirondack Mountain Region, but that iron sulfides were dominant in several Norwegian lakes. It has been suggested that very high sulfate loading (Nriagu & Soon, 1985) or low sediment pH (Rudd et al., 1986) may increase the storage of sulfides in iron sulfide minerals rather than in organic matter. These conditions would not be typical of most lakes.

In this paper we present data on the forms of sulfur and iron in sediments from six lakes in the northeastern United States, as well as the results of laboratory studies, to determine whether inorganic reduced sulfur is an important sink for sulfides produced by bacterial sulfate reduction. Data from these lakes are compared to previous studies where both total and inorganic reduced forms of sulfur were measured.

2. Forms of Sulfur in Sediments

2.1 Total Sulfur in Lake Sediments

We examined the amounts and forms of sulfur in six New England lakes, where sulfate concentration in the overlying water and organic carbon concentrations in the sediments varied (Table 1). All these lakes currently receive acid deposition. The three Cape Cod ponds are all within 15 km of the ocean and also receive sulfate from sea salt. Total sulfur concentrations in sediments (measured using a LECO SC-32 sulfur analyzer) varied over more than an order of magnitude, ranging from a low of 0.1% in Lakes of the Clouds to a high of 1.1% in Miles Pond (Fig. 1). Two of the three New Hampshire lakes (Mirror & Cone) showed a clear enrichment of S in

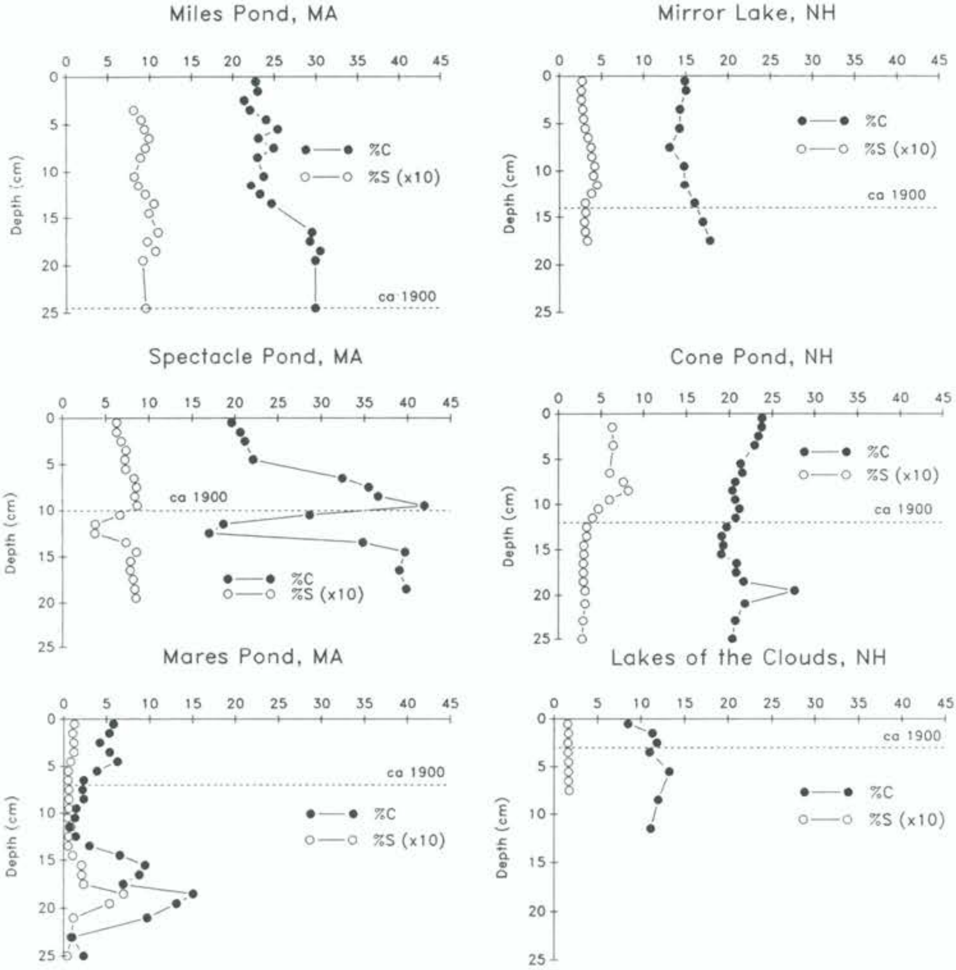

Fig. 1: Profiles of carbon and sulfur in sediment cores from six New England lakes. Sulfur concentrations have been expanded 10 times to show details of the profiles. Characteristics of the six lakes are given in Table 1. The approximate depth in the sediment which corresponds to 1900 is shown by the dashed line. Cores were dated using lead profiles (GIBLIN et al., 1989).

Table 1. Sediment and water column data from six New England lakes (Giblin et al., submitted). Contemporary sulfur accumulation rates (C) represent the average calculated from the sediment interval 1900-1984. Pre-industrial (P) rates represent the average of the remainder of the cores (usually 50-100 years) and are calculated assuming constant sedimentation rates. The percentage of the total sulfur which is present in reduced inorganic forms (RIS) for each interval is shown. The percentage of the total iron in the sediments which was present as pyrite (FeS_2) and iron monosulfides (FeS) is indicated for both contemporary and pre-industrial intervals.

Lake	$SO_4^=$ in overlying water µM	Water depth where core taken M	Average carbon in sediments %		S accumulation rate m moles/m^2/yr	Amount of S accumulating as RIS %	% of Fe present as FeS + FES_2
CAPE COD, USA							
Miles	45	5	23	C	80	48	39
				P	72^a	40	49
Spectacle	77	5	30	C	41	23	58
				P	27^b	12	56
Mares	50	11	4	C	22	50	9
				P	27^{b,c}	65	46
NEW HAMPSHIRE, USA							
Mirror	60	8	15	C	25	52	10
				P	18	26	9
Cone	70	8	18	C	34	33	85
				P	21	16	15
Lakes of the Clouds	30	2.5	11	C	5	8	4
				P	5	5	2

[a] Bottom of core - estimated date 1900; [b] Large changes in bulk density in the core. Constant sedimentation rates unlikely; [c] Average of 7-14 cm only.

sediments deposited since 1900 when compared to older sediments (Table 1). Similar sulfur enrichments have been reported in recent sediments taken from lakes in both New England and the Midwestern United States, Canada, and Great Britain (Table 2 and NORTON et al., 1988). In contrast, sediments taken from the oligotrophic high elevation Lake of the Clouds did not show a clear pattern of sulfur enrichment in recent sediments. KIMBALL et al. (1989) report that mean sulfate concentrations in cloudwater on Mt. Washington were not significantly different between the late 1930's and 1980's. This lake may not have experienced a significant increase in limnetic sulfate concentrations in the last fifty years. There was also no clear pattern in the Cape Cod ponds. These lakes may have also experienced large changes in the sedimentation rates, as evidenced by large changes in the carbon concentration of the sediments. This would make it difficult to discern any changes in total sulfur caused by acid deposition.

2.2 Reduced Inorganic Sulfur

Possible forms of reduced inorganic sulfur (RIS) stored in sediments include all iron monosulfides, pyrite (FeS_2), and elemental sulfur. The chromium reduction method (ZHABINA & VOLKOV, 1978) was developed for the analysis of the sum of all reduced inorganic sulfur. There has been discussion in the literature concerning the true nature of the chromium reducible sulfur (CRS) fraction. Although tests on sulfur containing amino acids (WIEDER et al., 1985; CANFIELD et al., 1986), yeast (HOWARTH & JORGENSEN, 1984;), egg albumin (CANFIELD et al., 1986) and methylene chloride extracted marine muds (MORSE & CORNWELL, 1987) showed that these forms of organic sulfur were not liberated by this procedure, BROWN (1986) has suggested that organic sulfur may be released from humic material by the technique.

We found chromium reducible sulfur (CRS) concentrations in these lake sediments ranged from 5 to 200 μmol-S/g dry weight (Fig. 2). All lakes, except for Mares Pond, had higher concentrations of CRS in sediments deposited after 1900 when compared to older sediments (Fig. 2). The percentage of total sulfur in recent sediments which could be recovered by chromium reduction ranged from 8 to 50% (Table 1). The percentage of total sulfur which was recovered as CRS was lower in older sediments in all lakes except Mares Pond. Other investigators working on lakes in the Adirondack region of New York, the Midwestern United States, and Quebec, Canada, have also reported that CRS is enriched in recent sediments and have

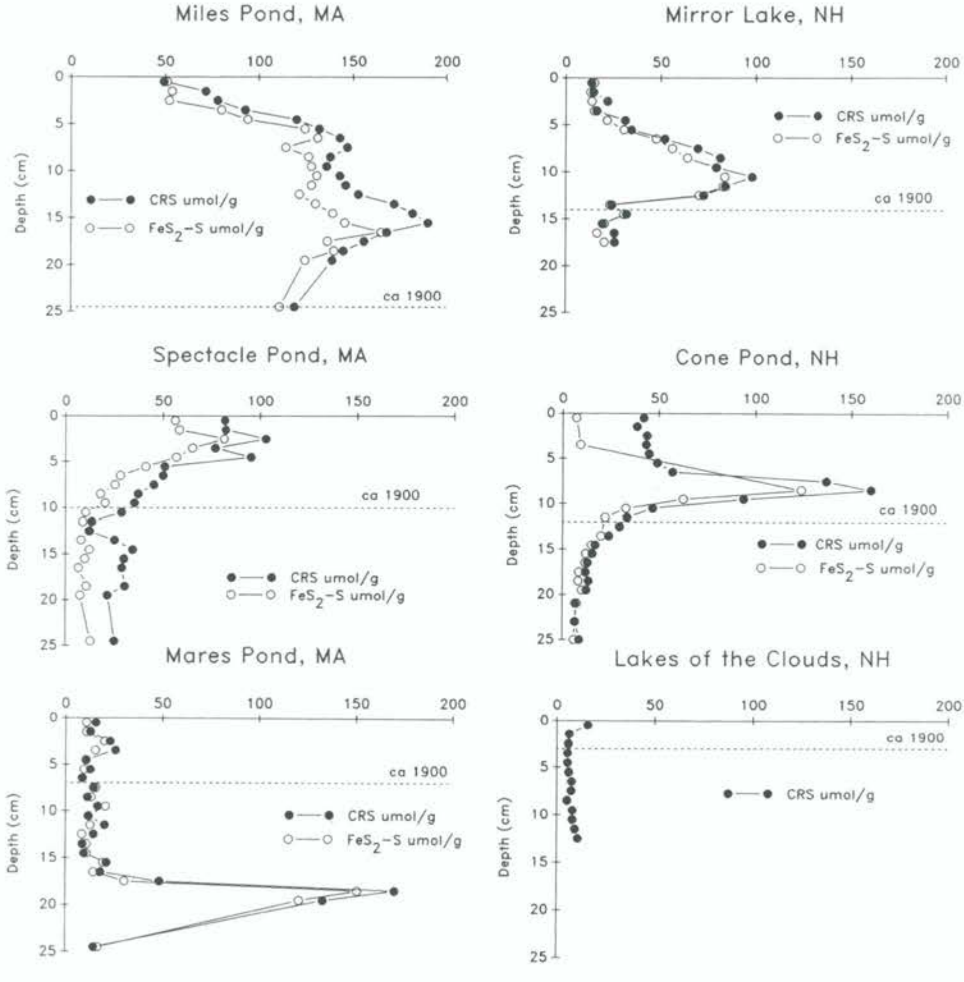

Fig. 2: Profiles of chromium reducible sulfur (CRS) and pyritic sulfur in the same sediment cores shown in Fig. 1.

reported that CRS may make up a major portion of the total sediment sulfur (Table 2).

To further characterize the nature of inorganic reduced sulfur in lake sediments, we independently measured elemental sulfur (as described in TROELSEN & JORGENSEN, 1982) and pyrite (FeS_2, using the technique of LORD, 1982). In lakes where elemental sulfur was measured separately, it was a minor fraction of the total sulfur with concentrations never exceeding 10 µmol/g dry weight in the sediment. Other investigators have also reported that elemental sulfur makes up only a small

Table 2. Sediment and water column data from other studies where information on both sulfur accumulation rates and reduced inorganic sulfur concentrations was available. Contemporary (c) sulfur accumulation rates represent the average for the last 85-100 years. Pre-industrial (p) rates represent averages from sediments deposited before 1900. The percentage of the total sulfur which is present as reduced inorganic sulfur (RIS) is shown for each interval. In some cases pyrite (FeS_2) or iron monosulfides (FeS) were measured separately. In other cases only the sum of RIS was reported. When specific information on the form of RIS was not available, range was calculated for the minimum and maximum amount of iron present as ferrous sulfides.

Lake	$SO_4^=$ in overlying water µM	Water depth where core taken M	Average carbon in sediments %		S accumulation rate m moles/m^2/yr	Amount of S accumulating as RIS %	% of Fe present as FeS + FeS_2
SOUTHWESTERN QUEBEC[1]							
10636	71	22	20	C	31	63	22-43
				P	16	50	
78042	82	22.5	18	C	43	79	30-61
				P	9	1	
79269	63	11.5	21.4	C	18	59	32-64
				P	10	0	
79245	75	12	22	C	17	44	23-45
				P	8	13	
96760	94	9.8	14	C	29	75	16-32
				P	13	48	
77978	73	10	23	C	10	16	13-25
				P	6	9	
ENGLISH LAKES DISTRICT[2]							
Blelham Tarn	121	14	12	C	108	48	~12
				P	46	38	~3
ENGLISH LAKES DISTRICT[2] (cont'd)							
Windermer	79	35	8	C	16	28	~2
				P	8	8	~1
Ennerdale Water	51	42	6	C	12	22	~1
				P	8	22	<1
NEW YORK, USA							
South Lake[3]	55	20	18	C	24	52	
				P	12	21	
Big Moose[4]	60	24	20	C	47	25	5-11
				P	19	ND	
WISCONSIN, USA							
Little Rock[5]	25	9	-	C	30	38	
				P	23	19	

[1] Carignan and Tessier 1988; [2] Sediment sulfur data from Davidson et al. (1985). Calculation made using the bulk densities in Pennington (1981). Lake sulfate concentrations from Sutcliffe et al. (1982). Total Fe from Pennington (1981) and MacKereth (1966); [3] Owen and Mitchell, in press; [4] White et al., submitted; [5] Brezonik et al. 1987.

portion of the total sulfur pool (SMITH & KLUG, 1981; NRIAGU, 1968; OWEN & MITCHELL, 1989; NRIAGU & SOON, 1985), except in lakes which receive very high sulfate loadings (HERLIHY et al., 1988; NRIAGU & SOON, 1985).

We found that pyrite was the major constituent of CRS at nearly every depth in the sediment in the five lakes we examined (Fig. 2). CRS was too low in Lake of the Clouds to allow us to make this comparison. Pyrite made up 75-100 % of the CRS in sediments where the CRS exceeded 100 μmol/gdw. In sediments with lower chromium reducible sulfur values, pyrite made up greater than 50 % of the total sulfur in all but a few samples (Fig. 2). FeS was measured separately on only a few samples but in all cases it accounted for the remaining chromium reducible sulfur. Therefore, we believe that the chromium reduction technique is specific for reduced inorganic sulfur (RIS) and not extracting organic sulfur from these lake sediments.

DAVIDSON et al. (1985) separately measured both pyrite and FeS in sediments from lakes of different trophic status. He concluded that pyrite was a major portion of the RIS in oligotrophic lakes with a low turnover of organic carbon or seasonal anoxia. FeS dominated the RIS pool in more productive lakes. COOK (1981) found that most of the sulfide accumulated in sediments of an experimentally acidified lake was in the form of acid volatile sulfides (H_2S + FeS). HERLIHY et al. (1988) reported that pyrite was not a major end product of sulfate reduction in a lake receiving large quantities of sulfate and iron from acid mine drainage. The fairly low (30-80 μM) limnic sulfate concentrations of our study lakes and their oligotrophic to mesotrophic character may have favored the formation of pyrite over FeS.

3. Storage of Sulfides Produced from Sulfate Reduction

3.1 Organic vs. Inorganic Forms

Several investigators incubating lake sediments with $^{35}SO_4$ reported that the most important long term end product of sulfate reduction was organic-S (RUDD et al., 1986; LANDERS & MITCHELL, 1988). In a sulfate enriched lake in the Sudbury region of Canada, stable sulfur isotope analyses indicated that organic sulfur was forming via dissimilatory sulfate reduction (NRIAGU & SOON, 1985). Organic sulfur has also been identified as an important endproduct of sulfate reduction in freshwater bogs (WIEDER et al., 1987; BROWN, 1986; BAYLEY et al., 1986).

There is growing evidence, however, that in many lakes a substantial amount of the sulfide produced from sulfate reduction is stored in reduced inorganic forms. In six New England lakes, we found that the incorporation of organic S in sediments has changed very little in response to sulfate loading while RIS storage has increased in most lakes (Table 1). For lakes in Quebec, CARIGNAN & TESSIER (1988) found that a greater percentage of the total sediment sulfur was in the form of RIS in recently deposited sediments, when compared to sediments deposited more than 100 years ago (Table 2). They concluded that nearly all the anthropogenically derived excess sulfur present in sediments of these lakes is accumulating as inorganic rather than as organic forms. A number of other authors have also found that a large percentage of the total sediment sulfur is in the form of reduced inorganic sulfur and that RIS accumulation has increased in lakes receiving acid deposition (Table 2). Reduced inorganic sulfur, rather than organic sulfur, was the major form in which sulfides were retained in sediments in an experimentally acidified lake (COOK, 1981).

Much of RUDD et al.'s (1986) radiotracer work was done in shallow sediments with low organic carbon contents, and this may account in part for the difference in findings. In studies where cores from several depths were analyzed, cores from deeper water usually had higher concentrations of RIS (GIBLIN et al., 1989; CARIGNAN & TESSIER, 1988; BREZONIK et al., 1987). Because organic sulfur can form during bacterial oxidation of pyrite (LUTHER et al., 1986), we tested whether the dissolved oxygen concentration of the overlying water influences the final form in which sulfides are stored in sediments. We incubated intact cores, half of which the water column was kept oxic, while the other half were kept anoxic. Sulfate concentrations in the overlying water were maintained between 1 and 2mM. After 110 days we compared the amount and forms of sulfur in the sediments. Sulfur increased in both treatments, but the increase in sulfur was greater under anoxic conditions (Fig. 3). In both cases the increase in sulfur was due to the accumulation of RIS (Table 3). Organic sulfur concentrations decreased slightly, probably from

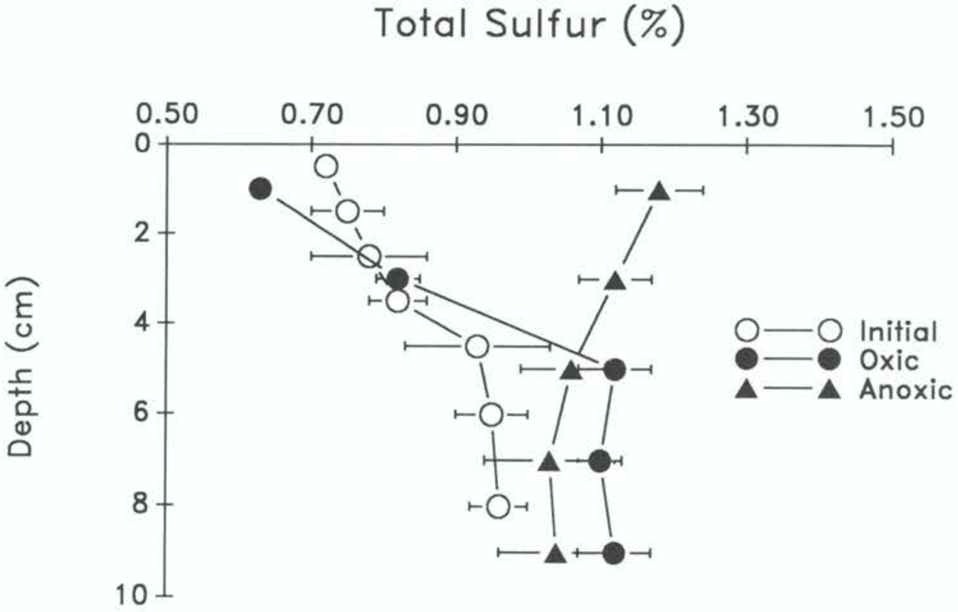

Fig. 3: Total sulfur profiles in initial (n = 2) cores taken from Miles Pond, and intact cores incubated for 110 days with elevated sulfate concentrations in the overlying water. Sulfate concentrations were maintained between 1 and 2 mM. The water column of half the cores was kept oxic (n = 3) while in the other half of the cores, the water column was kept anoxic (n = 3).

organic matter mineralization. Therefore, at least in this case, dissolved oxygen concentration was not a factor in determining whether sulfides were stored in organic or inorganic forms.

A number of other factors, such as pH or organic matter quality, could influence whether sulfides are stored primarily in organic or inorganic forms in lake sediments (RUDD et al., 1986). Further investigations are necessary to determine what factors control the form in which sulfides are stored in lake sediments. However, the importance of RIS formation to the sulfur cycling of a wide variety of lakes has been demonstrated.

Table 3. Solid forms of sulfur in initial cores taken from Miles Pond and cores incubated for 110 days with 1-2 mM sulfate in the overlying water. Cores were incubated with either an oxic or an anoxic water column. Total sulfur was corrected for the contribution of porewater sulfate. Organic sulfur was calculated as the difference between chromium reducible sulfur (CRS) and total sulfur. ($\bar{x} \pm$ SE; n=2 all treatments)

	Total Sulfur		
Depth cm	Initial µmol/gdw	Oxic µmol/gdw	Anoxic µmol/gdw
0-2	229 ± 16	174 ± 9	362 ± 26
2-4	250 ± 15	247 ± 14	349 ± 25
4-6	293 ± 30	345 ± 21	363 ± 41
6-8	299 ± 38	342 ± 14	303 ± 15
Total mass to 8 cm µmol/cm²	100.2	105.6	126.8
	Organic Sulfur		
Depth cm	Initial µmol/gdw	Oxic µmol/gdw	Anoxic µmol/gdw
0-2	131 ± 5	106 ± 8	113 ± 14
2-4	131 ± 16	105 ± 2	93 ± 17
4-6	131 ± 27	98 ± 1	122 ± 25
6-8	107 ± 7	110 ± 4	98 ± 15
Total mass to 8 cm µmol/cm²	46.1	38.7	39.2
	CRS		
Depth cm	Initial µmol/gdw	Oxic µmol/gdw	Anoxic µmol/gdw
0-2	99 ± 2	68 ± 3	267 ± 18
2-4	118 ± 6	144 ± 17	272 ± 29
4-6	162 ± 25	261 ± 4	215 ± 17
6-8	192 ± 22	233 ± 13	205 ± 2
Total mass to 8 cm µmol/cm²	54.1	68.6	87.9
	%CRS		
	Initial	Oxic	Anoxic
0-8 cm	54	65	69

3.2 Importance of Iron to Reduced Inorganic Sulfur Storage

It has been suggested that the iron concentration in sediments is an important factor controlling reduced sulfur storage in lakes (SCHINDLER, 1985; CARIGNAN & TESSIER, 1988). We examined the distribution of reduced and oxidized iron in New England lake sediments to determine if iron availability limits sulfur storage. We found that a considerable portion of the iron in lakes with highly organic sediments, such as Miles, Cone, and Spectacle Ponds, was in the form of ferrous sulfides (Table 1). These findings are similar to CARIGNAN & TESSIER'S (1988), who found that iron sulfide formation may be limited by available iron in eight Ontario lakes (Table 2). In contrast, much less of the total iron in Mirror Lake and Lake of the Clouds was present as ferrous sulfides (Table 1). Iron also is abundant in sediments of lakes in the English Lake district and in the Adirondacks (Table 2). It appears that RIS storage, and therefore alkalinity generation from sulfate reduction, may already be limited by iron availability in some lakes but that the importance of iron varies regionally.

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Drought and Flood Frequency in the Changjiang River Basin During the Past 1,020 Years

by
ZHANG YI-GANG, Wuxi*)

With 1 Figure and 2 Tables

Contents

Abstract

The historical records of droughts and floods in the Changjiang River Basin (961 A.D. to 1980 A.D.) were evaluated. The record can be divided into three cycles. The third cycle should end within the next 50 years. It is, however, masked by the increasing impact of anthropogenic activities.

1. Introduction

The sediment and carbon transports of a river are greatly affected by climate. The study of climate history, especially the history of droughts and floods, could help to understand the secular variation of riverine transport. A short-term history of a major river basin may reflect the influences of short-term local factors, whereas its long-term history may reveal the impact of long-term regional and global factors.

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Thanks to the long historical records and files of many counties along the Changjiang River, it is possible to reconstruct the history of droughts and floods for the entire Changjiang River Basin. For its upper and middle reaches data are available for the period 961 A.D. to 1980 A.D. and for the lower reaches from 1470 A.D. to 1975 A.D. The upper reaches from the source of the Changjiang down to Yichang drain an area of about 1 x 10^6 km^2; the middle reaches have a drainage area of about 500,000 km^2 and the lower reaches from Wuhan down to the river mouth drain an area of about 300,000 km^2. This paper explores temporal trends in the history of droughts and flood in the Changjiang River Basin (CHEN HAILONG, 1987; ZHU KEZHENG, 1973).

2. Frequency of Droughts and Floods

The frequency of drought and flood years is listed in Table 1 for the investigated time spans. There were 137 drought years and 127 flood years during the 1,020 years of record of the upper and middle reaches of the Changjiang River, i.e., one drought year in every seven years and one flood year in every eight years, on average. For the lower reaches, the frequency is higher, as there are 80 drought years and 104 flood years in 505 years, averaging to one drought year in every six years and one flood year in every five years. The lower reaches are more susceptible to

Table 1

Frequency of drought and flood years of Changjiang River Basin during the past 1,020 years.

Century	Upper and middle reaches		Lower reaches	
	Droughts	Flood	Droughts	Floods
10	2	2		
11	8	3		
12	15	9		
13	9	5		
14	4	8		
15	30	11	3	5
16	16	10	15	19
17	15	12	19	19
18	3	17	12	21
19	14	36	9	21
20	21	14	22	19
Total:	137	127	80	104
Statistical years:	961-1980		1470-1975	

flooding. In view of the fact that there are more data and details for the upper and middle reaches, the following discussion will be concentrated on these reaches.

The drought and flood years are not equally distributed throughout time. In some periods, droughts and floods appeared to be more frequent than in others. For example, there were 19 drought years in the later half of the 15th century. Particularly in the 20 years from 1481 to 1500 nine drought years occurred. Likewise, 21 flood years occurred in the early half of the 19th century, including 14 flood years from 1831 to 1850. On the other hand, the earlier half of the 11th century had only one flood year, and no flood year was recorded for the later half of the 14th century.

In addition to a single drought or flood year, there were periods with continued droughts and floods lasting from two to four years (Table 2). It is possible to divide the over 1000 year long record into three cycles. The first cycle lasted from the 11th century to the 14th century and shows a relatively low frequency of droughts and floods. It features only 10 anomalous periods lasting 24 years in total. The second cycle lasted from the 14th century to the 18th century and marks a period of frequent droughts and floods. Here the 15th century is most prominent when 14 anomalous periods lasting 34 years in total occurred. The 15th century was the most severe drought period on history, and the extensive and frequent migrations of people recorded in history may be linked to the anomalous climate.

Table 2
Anomalous drought and flood periods for the upper and middle reaches of the Changjiang River in the past 10 centuries.

Century	Continued drought period	Alternating drought and flood period	Continued flood period	Summation of anomalous years
11	1057-1058, 1073-1075, 1136-1137	1056-1058	-	10
12	1182-1183	1170-1171, 1190-1194	-	8
13	1201-1202, 1253-1254, 1299-1300	-	-	6
14	-	-	-	0 -
			1st cycle:	*24 years total*
15	1426-1427, 1440-1441, 1445-1448, 1455-1456, 1458-1459, 1467-1468, 1482-1484, 1487-1488, 1494-1495	1437-1438, 1458-1460, 1467-1470, 1472-1473, 1478-1479	-	34
16	1508-1509, 1522-1523, 1538-1539, 1544-1545, 1588-1590	1537-1539	-	14
17	1641-1643, 1659-1660, 1689-1690	1607-1609	1612-1614	13
			2nd cycle:	*61 years total*
18	-	1785-1786	-	2
19	1811-1812, 1819-1820	1826-1828, 1830-1835, 1843-1847, 1877-1878, 1883-1885	1838-1841, 1844-1849, 1851-1853, 1869-1870, 1889-1890	42
20	1928-1929, 1940-1942, 1959-1961, 1971-1972	1924-1926, 1935-1938, 1944-1945, 1953-1954	1937-1938, 1948-1949	25
			3rd cycle:	*69 years total*

The third cycle, lasting from the 19th century until now, is characterized by intensified floods and an increasing frequency of anomalous years. The 19th century was the most severe flood period in terms of total flood years, duration of a single continued flood period and flood frequency. In the 19th century, not only the upper and middle reaches of the Changjiang and the entire Changjiang River Basin experienced serious floods, but also all of China suffered frequent inundations. There were 335 incidents of inundation in China from 1794 to 1903, including nine periods of very serious inundation, each of which caused the death of more than ten thousand Chinese. For the 20th century, both droughts and floods are frequent and the number of drought years ranks second only after the 15th century.

3. Time Trends

The three cycles mentioned above can be perceived intuitively on Figure 1, where the numbers of drought and flood years per decade are plotted. The transitions from the first to the second cycle and from the second to the third cycle occurred in the late 14th and the early 18th century. It seems that each cycle lasts for about 350 years. The second cycle peaked during the 80's of the 15th century and the third cycle culminated during the 40's of the 19th century. It is interesting to note that the Huanghe River (Yellow River) changed its estuary from the Bohai Gulf to the Yellow Sea in 1495 and then back to the Bohai Gulf in 1855 after 360 years. These catastrophic changes of the Huanghe River occurred shortly after the two culminations in drought and flood frequency of the Changjiang River. This consistency may be incidental or may be caused by regional or global climate changes. The main factor controlling these cycles is not known. Astronomical causes may be the most likely factors to control such cycles.

Figure 1 suggests that droughts and floods appear to become more and more frequent throughout the record. This fact is probably closely related with increasing anthropogenic activities particularly for the last 100 years. Although the third cycle tends to be dominated by floods, droughts surpass floods in the last 100 years,

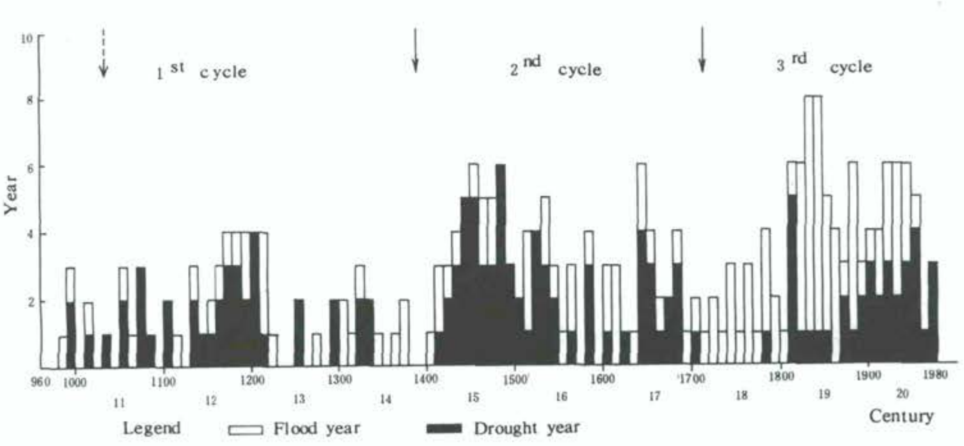

Fig. 1: Frequency of drought and flood years in each decade of the past ten centuries in the upper and middle reaches of the Changjiang River.

especially in the last 40 years. Owing to extensive deforestation, the percentage of forest in Sichuan Province decreased from 20 % in the 50's to 13 % in the 80's. The erosion of soil has been greatly intensified and reaches 2.4×10^9 tons for the entire river basin in the last 36 years which, in turn, has brought about an increasing sedimentation in the lakes of the middle reaches. The averaged annual deposition of suspended solids in these lakes grew to more than 250×10^6 t. In addition, land reclamation accelerates the decrease in lake size. Dongting Lake shrank by 50 % between 1949 (4,350 km^2) and 1980 (2,740 km^2). Consequently, the fish production of Dongting Lake declined from 30,700 t in the 50's to 16,100 t in the 70's. In addition, the lake area of the lower reaches is shrinking too. For example, Poyang Lake occupied an area of about 6,000 km^2 during the Tang dynasty (618-917 A.D.), and diminished to 5,050 km^2 in 1949 and then to 3,960 km^2 in 1980. Lake area of the entire drainage area of Changjiang River decreased from about 25,000 km^2 in the 50's to 15,600 km^2 in the 80's. The same trend is visible throughout all of China, where the lake area decreased by 11 % during the last 30 years. Both the intensified deforestation and the increasing shrinkage of lakes have caused the climate to become dryer and dryer (TU CHANGWANG, 1961).

It appears that the next 50 years could mark the end of the third cycle. Naturally, droughts and floods would tend to be less in terms of frequency and intensity. However, the increasing anthropogenic activities are offsetting the natural trend (Fig. 1).

4. Conclusions

1. The drought and flood history of the last 1,020 years of the Changjiang River Basin comprises three cycles, each of which lasted about 350 years or so, probably controlled by astronomical factors.

2. The frequency of droughts and floods in each cycle is higher than in the previous cycle, indicating the impact of anthropogenic activities.

3. It is obvious that the impact of anthropogenic activities including extensive deforestation and increasing reclamation has greatly intensified during the last 100 years.

4. For the next 50 years, one may expect the end of the third cycle. However, the increasing anthropogenic activities are offsetting the naturally decreasing trend in the reoccurrence of droughts and floods.

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Oceanographic Observations During the 1986 Damming of Russell Fjord by the Hubbard Glacier+)

by

WILLIAM S. REEBURGH & DAVID L. NEBERT, Fairbanks*)

With 9 Figures

Contents

Abstract

Russell Fjord, lcoated at the head of Yakutat Bay on the southcentral coast of Alaska, was dammed by the advancing Hubbard Glacier in May, 1986. Freshwater from snowmelt and runoff accumulated behind the glacier dam in Russell Fjord, resulting in a water level rise of some 25 m during the summer. The glacier dam failed on October 7, and the accumulated water (estimated to be some 5 km^3) discharged into Yakutat Bay. Tides were evident in Russell Fjord about 26 hours

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following the outbreak. This report presents a water level record obtained with a pressure recorder deployed shortly after the damming was reported, as well as results from a series of hydrographic stations that were occupied in September, 1985, about three weeks before the glacier dam failed.

1. Introduction

Russell Fjord has a glacial origin and continues to be influenced by glaciers. Reports of early explorers (summarized in TARR & MARTIN, 1914), the presence of submarine moraines (REEBURGH et al., 1976), differences in vegetation succession on fjord walls (RUSSELL, 1893) and oral histories from native residents (DE LAGUNA, 1972) indicate that the fjord has either been filled with glaciers or dammed several times in the recent past. These events are summarized in MAYO (1988a, b).

Hydrographic and bathymetric studies were performed in anticipation of such a damming event in 1973 (REEBURGH et al., 1976). This study showed that Russell Fjord's deep circulation was driven by tidal addition of marine water over a 10 m sill at the north end of the fjord near Osier Island, adjacent the Hubbard Glacier. Tidal additions enter the fjord and are evident from nutrient measurements as distinct boluses. These boluses occupy different isopycnal surfaces through the year, reflecting seasonal changes in the density of shelf source waters. The deep waters of the fjord are renewed during oceanographic winter (February-March), when decreased runoff and cooling produce the densest near-surface shelf water. The boluses occupy progressively shallower depths in the fjord water column as increased runoff and warming in summer produce less dense source water. These seasonal changes in shelf source water density ensure that the entire water column is ventilated annually. The flushing rate, calculated by the tidal excursion and fjord volume, is about 1% per day. The notion of tidal flushing has been extended to explain flushing of other Alaskan fjords with deep, intermediate and shallow sills (MUENCH & HEGGIE, 1978).

The REEBURGH et al. (1976) study speculated on conditions that might result from glacial damming. A glacial dam would eliminate deep water renewal by tidal additions. Glacial damming would also result in rapid accumulation (28 m/a) of a surface freshwater layer, which would restrict atmospheric exchange. This isolation of the deep waters would permit biogeochemical oxygen consumption reactions to deplete dissolved oxygen and eventually lead to anoxia in the isolated fjord waters. It might also be possible for the freshwater surface layer to freeze. This study also indicated that the fjord level would rise until either the glacial dam failed or was breached, or until outflow occurred at the relict terminal moraine at the south end of Russell Fjord. REEBURGH et al. (1976) estimated the moraine outflow elevation to be 30 m; levelling during 1986 showed the moraine outflow level to be 39 m. Outflow at the southern moraine would enter the Situk river drainage, leading to large increases in river flow. The Situk River normally has a flow of 10 m^3/sec; estimates from the drainage basin area and precipitation indicated that the flow could increase to 270 m^3/sec, causing severe habitat disturbances and possible damage to public works.

The 1986 damming presented a unique opportunity to test the above suggestions and to provide direct runoff measurements. Detailed observations of the onset of anoxia on a scale like this are not available. Further, the dammed fjord could be viewed as a 'bucket' and estimates of runoff could be obtained from the rate of water level rise. This region of the Alaska coast is remote and ungauged, so runoff data are few. Studies have shown that the Alaska Coastal Current is driven by freshwater runoff and wind stress (ROYER, 1975, 1979, 1982, 1983; JOHNSON et al., 1988), so runoff measurements can be compared with seasonal variations in transport by this coastal jet. A continuous record of water level rise was obtained by deploying a data logging pressure sensor shortly after closure was reported. Hydrographic observations were obtained in September from an inflatable boat equipped with a winch for water sampling.

2. Tidewater Glacier Studies

Tidewater glaciers (glaciers terminating in the sea) are fairly common in Southcentral Alaska and have been the subject of study by the U.S. Geological Survey for some years. Glacier dammed lakes have been catalogued by POST & MAYO (1971).

Details of the circumstances leading to the 1986 advance of the Hubbard Glacier have been described by MAYO (1988a, b, 1989). The Hubbard Glacier is North America's largest tidewater glacier (3,400 km^2, 122 km long), and originates at Mt. Logan in the St. Elias Mountains. It has a positive material balance and is in a state of active advance. Further, a submarine terminal moraine ('toehold' moraine) is located at the snout. The presence of a submarine terminal moraine greatly reduces the calving rate at the face of tidewater glaciers (POST, 1975; MEIER & POST, 1987) and serves to both protect the snout and permit the net advance of the glacier. Such moraines are typically formed by pushing unconsolidated material ahead of the glacier and by transport of rock debris under the glacier. Retreat from the submarine terminal moraine is believed to result in rapid glacial retreat into water shallow enough to permit re-establishment of a submarine terminal moraine. The Columbia Glacier near Valdez has recently retreated from its submarine terminal moraine and provides an example of a glacier in rapid retreat (POST, 1975). An additional circumstance which aided the 1986 damming of Russell Fjord was the rapid advance of the Valerie Glacier, which joins the Hubbard Glacier on the west side of Yakutat Bay. This advance served to constrain the advance of the Hubbard Glacier to the east, where waters are shallow and the Hubbard Glacier's submarine moraine was maintained. The terminal moraine formed the actual dam as the Hubbard Glacier advanced onto Osier Island and against Gilbert Point.

3. Water Level Time Series

The glacial damming occurred on May 29, 1986. Two water level recorders were deployed on June 4, 1986, in a shallow bay near the south end of Russell Fjord (Fig. 1). The recorders were Aanderaa current meters equipped with a narrow range

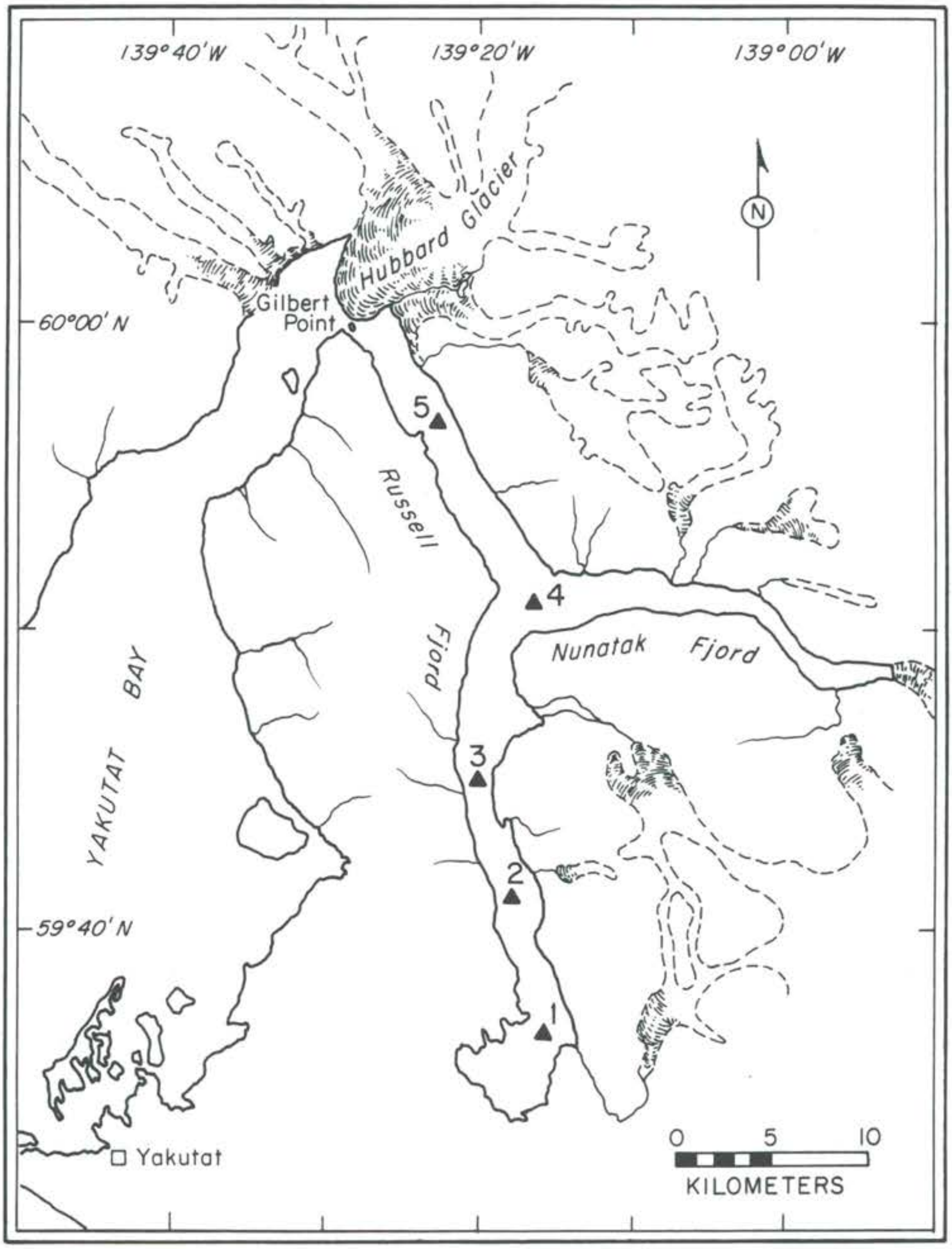

Fig. 1: Station locations. Five hydrographic stations were occupied during the 15-19 September 1986 study. The pressure recorders were deployed at station P at the south end of Russell Fjord. Osier Island is located between the Hubbard Glacier and Gilbert Point at the north end of the fjord.

pressure transducer. These pressure cases were fitted into PVC pipe collars to minimize corrosion and were anchored with a length of chain attached to a buoyant line and surface float for location and retrieval. The instruments have recording channels for direction, speed, pressure, temperature and salinity. The direction, speed and salinity channels were deactivated; pressure and temperature were recorded at 30-minute intervals. The float line was lengthened periodically as the fjord water level rose. Batteries and magnetic tapes were replaced in September, 1986, and the recorders were re-deployed. The recorders were recovered in January, 1987, when movement of surface ice threatened to carry the recorders to deeper water.

The depth resolution of the recorders is estimated to be 7 cm. The pressure recorders were deployed in 8 m of water; the cumulative water rise at the time of deployment was estimated to be 1.5 m. Our pressure record (converted to depth) and hand-level measurements made by U.S. Forest Service personnel are shown in Figure 2. Figure 3 shows a detailed plot of water level at outburst, showing that tides returned to Russell Fjord 26.5 hours after failure of the glacier dam. We recorded temperature as an independent means of monitoring instrument performance and present a portion of the temperature record bracketing the outburst in Figure 4. The recorder was deployed within a few meters of the halocline, which remained at the same distance above the bottom as the fjord level rose; the temperature channel fortuitously recorded internal waves. Power spectral analysis of oscillations in the

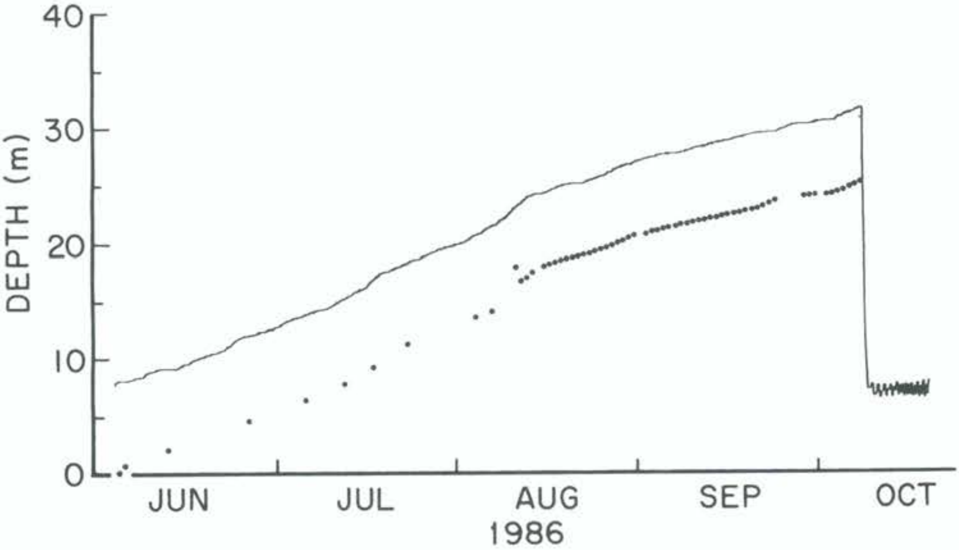

Fig. 2: Record from IMS pressure recorder deployed on bottom at Station P from 4 June 1986 to post-outburst. Instrument resolution is 7 cm. Discrete points are hand-level observations by U.S. Forest Service observers. The offset between the two records reflects deployment of the recorder in 8 m of water and permits comparison between the hand-level and instrument records. Note return of tides following outburst.

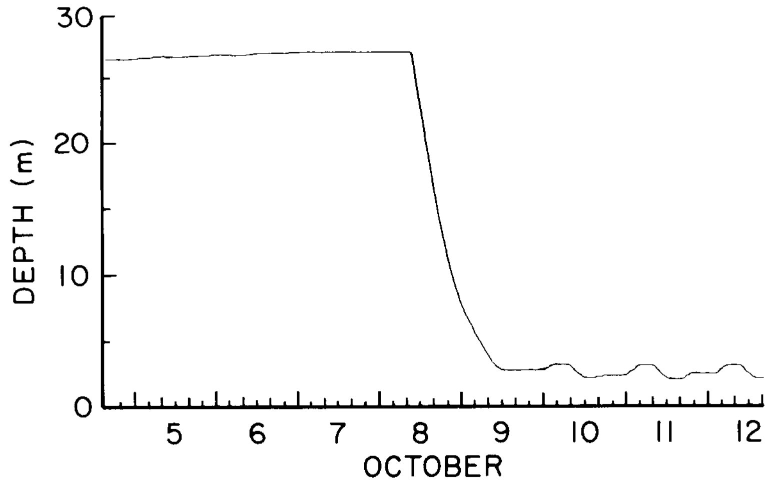

Fig. 3: Detailed plot of water level at outburst. Note that the fjord water level intersects the tide level about 26.5 hours after outburst.

pre- and post-outburst temperature record reveal two distinct periods. Temperature oscillations prior to the outburst have a 14-hour period and are in good agreement with the internal seiche period expected in a two-layer basin with the dimensions of Russell Fjord. Temperature oscillations similar to those shown in Figure 4 appear episodically through the temperature record; we suspect the pre-outburst oscillations are internal waves resulting from relaxation of set-up following along-fjord winds.

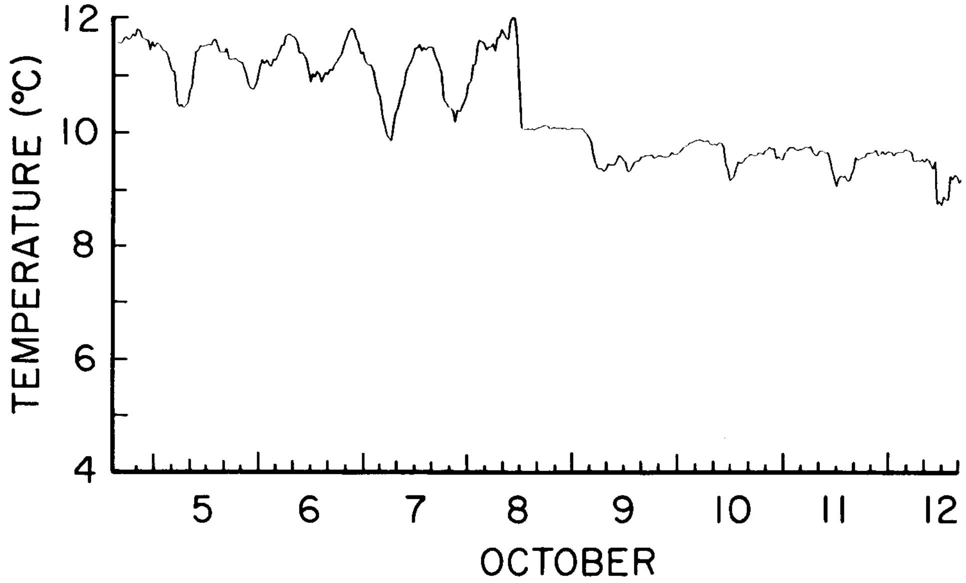

Fig. 4: Temperature record from pressure recorder at outburst. Temperature oscillations prior to outburst have a 14-hour period and are believed to result from an internal seiche at the freshwater/saltwater interface. Temperature oscillations following outbreak have a tidal period.

Temperature oscillations following the outburst have a period of about 23 hours, and are clearly tidal. The calculated surface seiche period is about 39 minutes, and is not evident in the record because of the 30-minute sampling interval.

Figure 5 shows air temperature, precipitation and fjord level rise rate records during the study period. The temperature and precipitation are from the Yakutat airport, about 20 km east of the south end of the fjord. The water level rise rate was

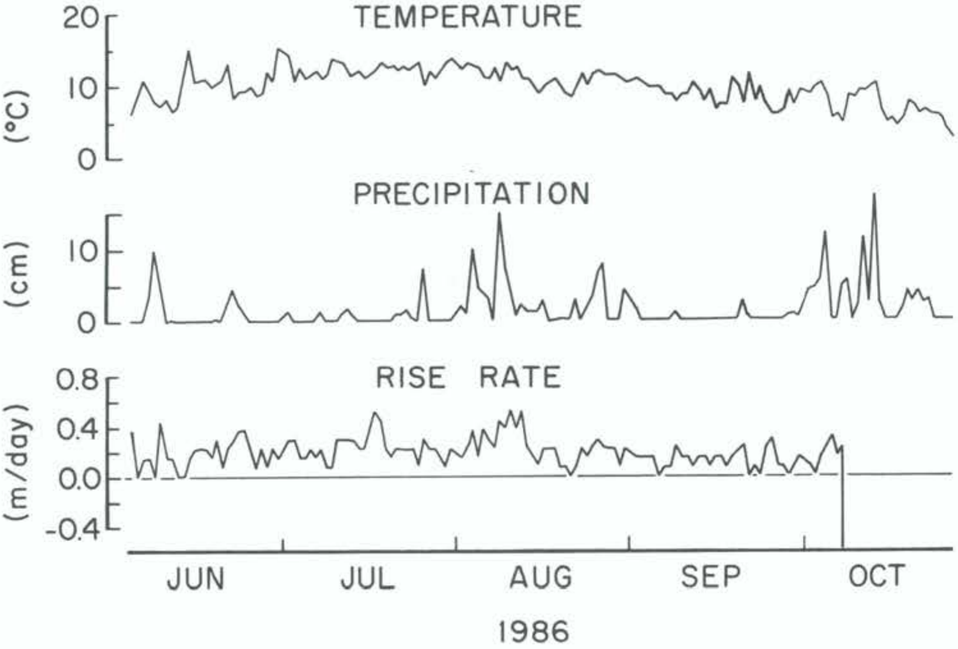

Fig. 5: Time-series of air temperature (°C, dashed line), precipitation (cm, dot-dashed line), and water level rise rate (m/d, solid line). Temperature and precipitation data are from the Yakutat airport (NOAA, 1986); water level rise rates were calculated from our pressure record. Time scales are identical, so effects of large precipitation events can be correlated with rapid level changes.

calculated from the data presented in Figure 2. The time scales in this plot are identical, so effects of major precipitation events can be correlated with rapid water level changes. The maximum water level rise rate was 60 cm/day.

4. Hydrographic Measurements

Five hydrographic stations were occupied from 15-19 September, 1986. Station locations are shown in Figure 1. Figures 6 through 9 show sections of temperature, salinity, oxygen and oxygen saturation. The sections show that strong stratification was maintained during the period that Russell Fjord was dammed. The sections also show that deep water characteristics are quite different from those observed 13 years before by REEBURGH et al. (1976). The bottom waters are 2°C warmer and 1 permil

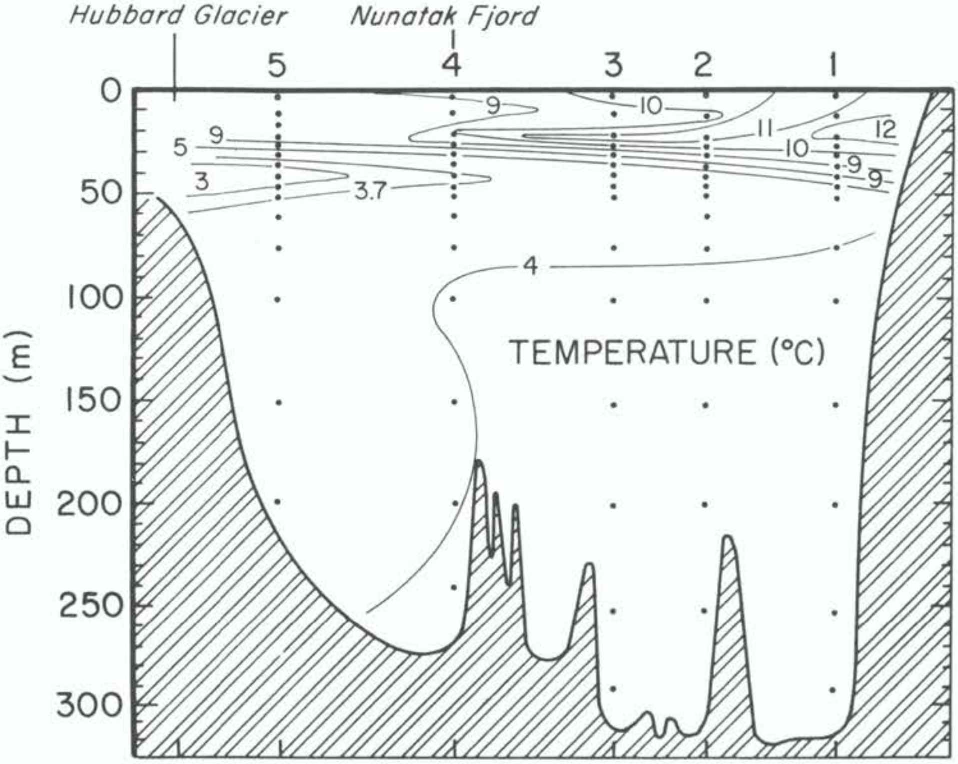

Fig. 6: Temperature section. 15-19 September, 1986. Note the tongue of cold water between 20 and 60 meters originating at the glacier. We attribute the shallow temperature maximum at the south end to down-fjord winds and the beginning of fall cooling. The bulge in the 4 degree isotherm is probably due to glacial cooling of waters below the halocline. The bottom waters are 2 degrees warmer than those observed in September 1973, reflecting an observed warming trend in the Gulf of Alaska source waters.

fresher than those observed in September, 1973. These observations are in agreement with the long-term warming trend observed in Gulf of Alaska source waters (XIONG & ROYER, 1984; ROYER, 1986).

The temperature (Fig. 6) and oxygen (Fig. 8) sections show several similar features in the upper 50 meters. We attribute the shallow temperature maximum at the south end of the fjord to down-fjord winds and the onset of fall cooling. The bulge in the 4°C isotherm is probably due to glacial cooling of waters below the halocline. A very strong pycnocline is evident in the salinity section (Fig. 7). The oxygen section (Fig. 8) shows a subsurface maximum at the south end of the fjord, reflecting a subsurface return flow due to along-fjord winds. The oxygen saturation section (Fig. 9) shows a bulge at the north end similar to the temperature distribution, suggesting glacial cooling. The levels of oxygen and oxygen saturation are not low enough to stress organisms. The oxygen decreases over the 3.5 month period between initial damming and our observations suggest that the fjord bottom

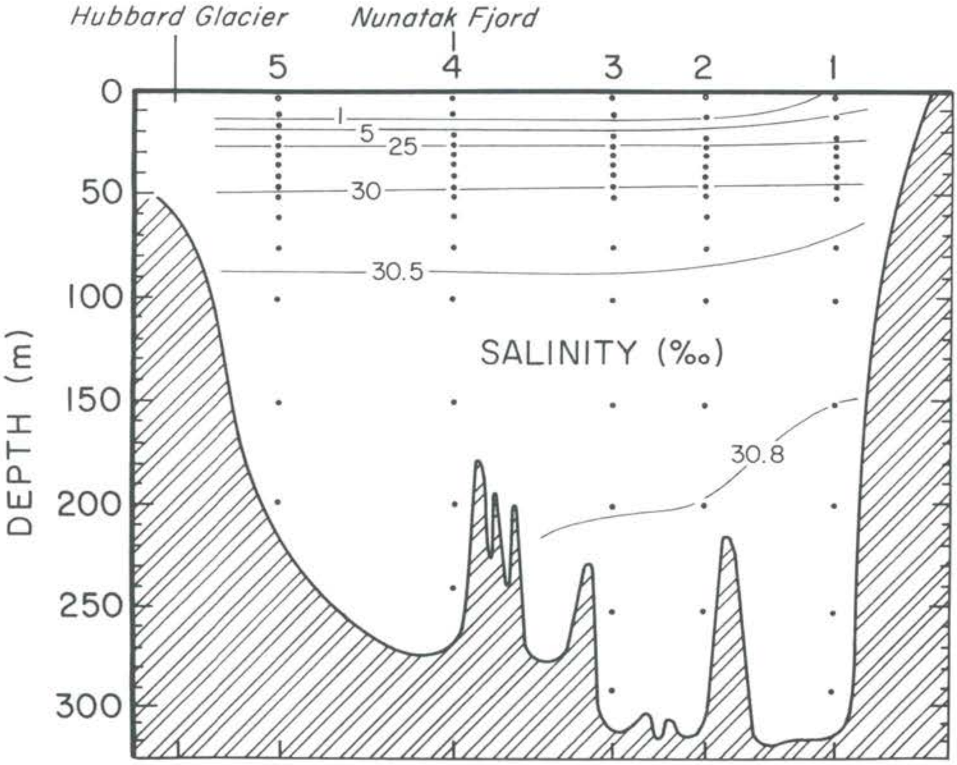

Fig. 7: Salinity section. 15-19 September 1986. The salinity depth distributions showed intense stratification and very little vertical mixing, as shown in this section. Several contours adjacent the intense halocline are omitted for clarity. Bottom waters were almost 1 permil fresher than those observed in 1973, again reflecting changes in the marine source waters. The freshwater lens functions as a lid.

waters would become anoxic about two years after isolation from coastal source water and atmospheric exchange.

5. Possible Future Damming

At present (April, 1989) the Hubbard Glacier is grounded on Osier Island and is undergoing normal winter-spring advances and summer retreats (L.R. MAYO, pers. comm.). The width of the entrance varies between 300 and 500 meters. The Hubbard Glacier has an unusually large accumulation area and a small ablation area, and is expected to reclose Russell Fjord sometime in the future. The U.S. Geological Survey installed a lake level gauge in Russell Fjord prior to the 1986 outburst. This instrument telemeters data to GOES satellite at 15-minute intervals, and will provide early notice of future damming events.

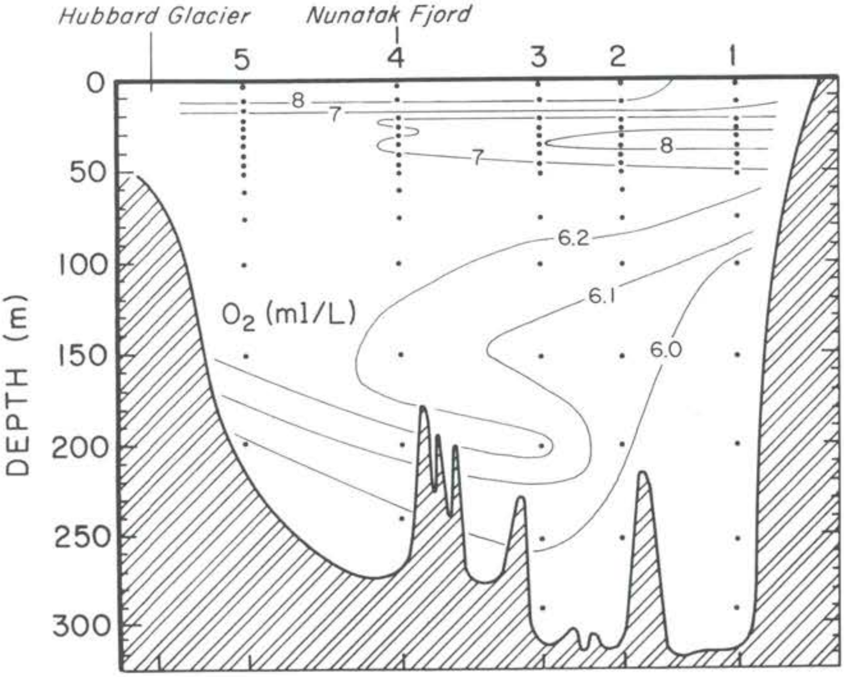

Fig. 8: Oxygen section. 15-19 September 1986. Measurements were made using the Chesapeake Bay Institute technique (CARPENTER, 1965). The oxygen section also shows many of the same features present in the temperature section. Deep water oxygen concentrations are comparable to those observed in September 1973, and are not low enough to stress organisms.

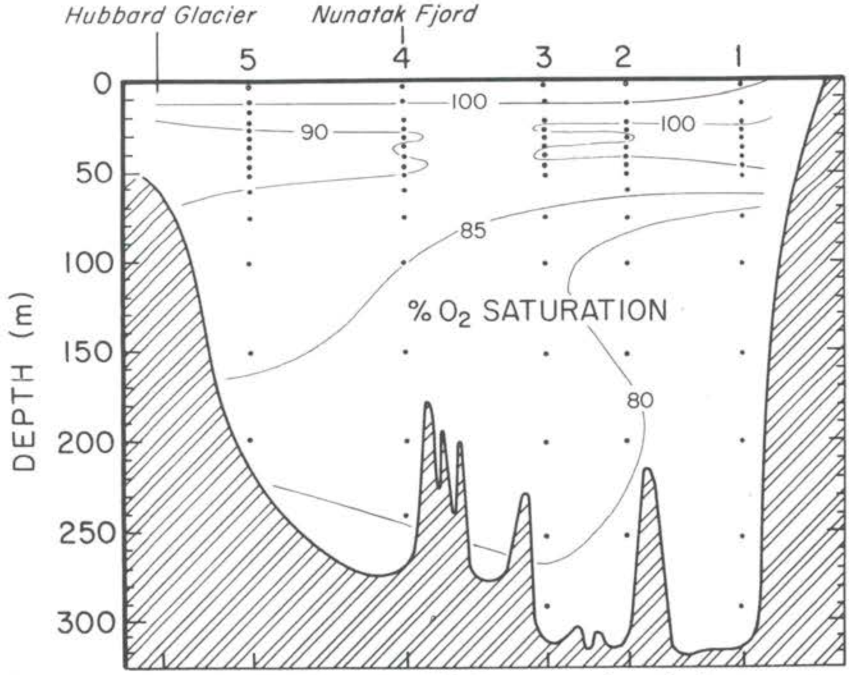

Fig. 9: Oxygen saturation section. 15-19 September 1986. Oxygen saturation at in situ temperatures and salinities was calculated using solubility values of WEISS (1970). Surface waters are in equilibrium with the atmosphere. The subsurface maximum at the south end is similar to the temperature section and reflects pile-up by along-fjord winds.

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Interactive System for Biogeochemical Modeling of Water Bodies

by
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With 6 Figures and 2 Tables

Contents

Abstract

Mathematical modeling in ecology in general and modeling of biogeochemcal cycles in particular calls for joint efforts of natural scientists - biologists, ecologists, chemists - and of specialists in mathematics and computer science. In order to bring together their interdisciplinary studies a user-friendly interactive modeling system may be of great help. Basic principles and advantages of one such system (SIMSAB) are discussed.

1. Introduction

Over the last 60 years methods of mathematical modeling have penetrated into theoretical ecology which not only gained new insights from mathematical findings but also provided quite interesting mathematical problems (SVIREZHEV, 1983).

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However, practical ecology was much more cautious with respect to mathematical methods, and only with the advent of computer models (traditionally known as simulation models) methods of mathematical modeling started to gain response among practical hydrobiologists and even decision-makers.

A number of models has been developed for the carbon and sulfur cycles, a survey of them can be found in LEONOV & AIZATULLIN (1977). Practically any more or less detailed ecosystem model can be regarded as a model of the carbon cycle, since the transfer of carbon through the trophic chain and its recycling due to decomposition are always reflected in such models (see for instance, JÖRGENSEN, 1976; SCAVIA, 1980; VOINOV & KOMILOV, 1986). The interaction of the two cycles within one ecosystem has not been adequately presented in models as yet, though there is already quite a lot of experimental and conceptual insights in this field. In general, there is a certain lag between experimental and modeling investigations, since only a few of natural scientists are ready to make use of mathematical methods in their studies.

This situation can be altered only if mathematical methods penetrate directly into the ecological media. By mathematical methods we mean not only statistical methods of information processing, which are already accepted by natural scientists and find more and more wide applications as more and more powerful and convenient software packages are developed (ABSTAT, STATGRAF etc.) We rather mean methods of simulation modeling, as a means of representation of experimental information for formulation and verification of hypotheses about operation principles for ecosystems and their separate units. Perception of methods of simulation modeling by poorly mathematized natural sciences - biology, chemistry, and ecology - is very much impeded by a lack of an interface, which could, just as in the case of statistics, provide workers not educated in mathematics and programming with a means to apply mathematical methods of analysis, allowing them to build and modify mathematical models all by themselves.

An attempt to create such an interface - the Simulation Modeling System for Aquatic Bodies (SIMSAB) - has been undertaken at the Computer Center of the USSR Academy of Sciences. Being most loosely linked to postulates of a certain school of mathematical modeling, the modeling interface is flexible enough to cover models of different kinds. Those principles which make up the invariant part of the system are identified in what follows and are open for criticism.

2. SIMSAB-Structure of Models

Spatial structuring of ecosystems. It is assumed that the whole water body can be split into a number of ecologically homogeneous segments (compartments). Within each of the segments ecosystem components are presented by spatially averaged variables (numbers, concentrations).

Temporal discreteness of processes. It is assumed that a sequence of events can be distinguished on the time axis, each event standing for some processes realized instantly, and no processes occur in between. Then the functioning of an ecosystem can be described as follows: at the time t boundary segments receive a nutrient load; next, for instance, at time (t + dt) concentrations of various components are altered, due to material transfer along trophic chains or in hydrobiochemical cycles (ecological block); then at time (t + 3dt) the wind induced currents are formed, determining the water exchange between segments (hydrodynamical block); next at time (t + 7dt), the whole water body is mixed up by water exchange and diffusive fluxes between segments, correspondingly changing the concentrations of ecological components, and so on.

Variables, parameters, and forcing functions. The model is specified by a number of variables, which represent those ecosystem components the dynamics of which we are interested in and time series for which we have data. Model parameters are the constants that appear in the formalizations of interactions between variables. It is best if the parameters are measured or at least estimated in experiments; however, usually most of them are selected during model calibration.

Forcing functions specify the time-variable effects which are independent of the ecosystem. These may be climatic factors, or the impacts of man, or in short all the functions that affect the ecosystem with no feedback from it. Obviously the set of forcing functions is defined by the boundaries of the modeled object in the representation of the researcher: varying these boundaries and hence the cause-effect relations one can turn forcing functions into variables and vice versa.

Dynamics of ecosystem variables. Within a segment dynamics of variables are described by a system of ordinary differential (difference) equations. Their right-hand sides may be specified in a file as a user-written FORTRAN program. If SIMSAB is applied, then the right-hand sides are calculated as sums of flows, specifying the material transfers from one ecosystem component into another. These flows are described in terms of a special SIMSAB flow language, using its library of functions, with any fragments of FORTRAN if necessary. The user who does not know any FORTRAN is restricted in his model formulations by the SIMSAB library of functions, which incidentally includes most of the widely used function.

The SIMSAB-monitor brings together all the subroutines, including those which compute the wind-induced currents, the material exchange between segments, and those which provide input of data and explanation of results. The general structure of SIMSAB is presented in Figure 1. In any case, SIMSAB results in a number of FORTRAN subroutines, calculating the right-hand sides of systems of differential equations, presenting various segments of the water body.

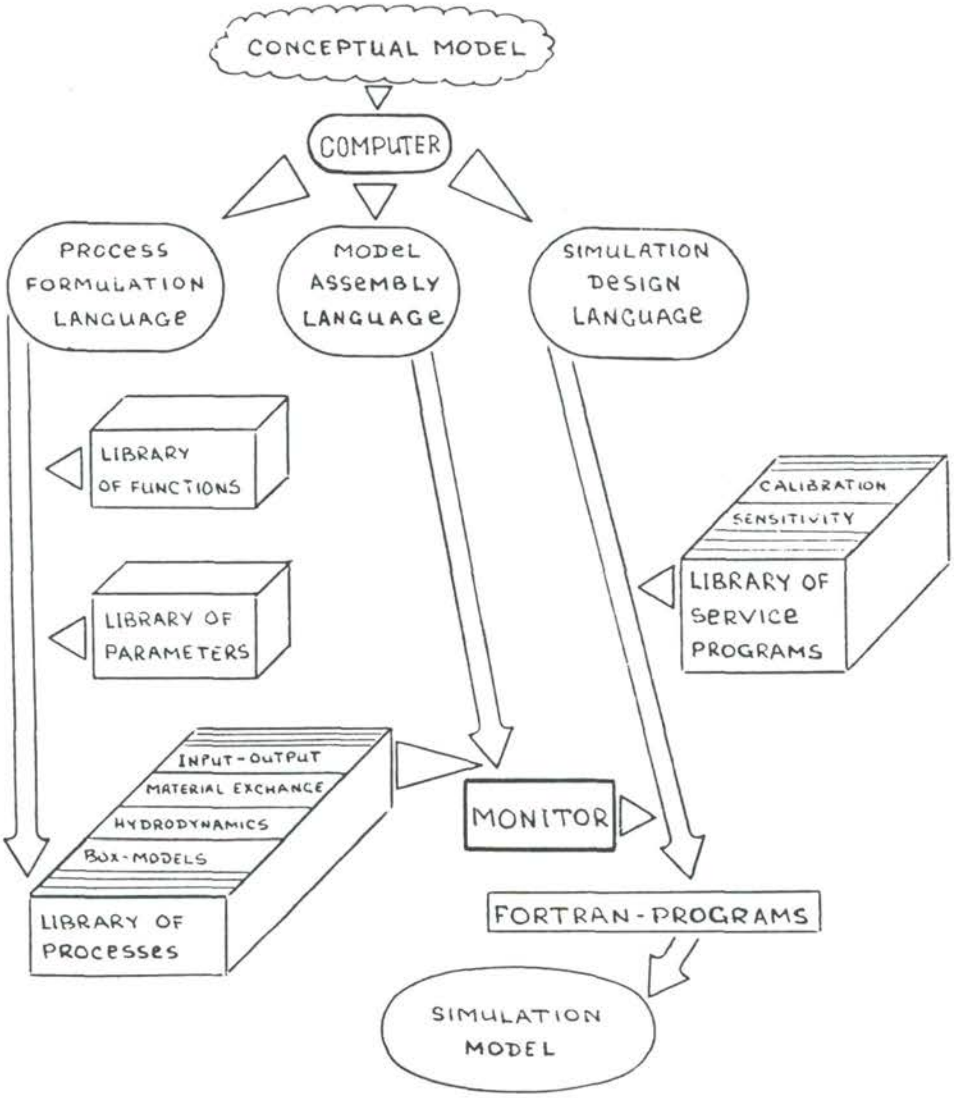

Fig. 1: General structure of SIMSAB.

3. A SIMSAB-Model with Comments

As an example let us look at a simple one-segment model of an aqueous ecosystem. Let it be one of those qualitative eutrophication models, which describe the general material cycle in a water body. Suppose that growth of phytoplankton (A) is limited by one of the nutrients: total mineral phosphorus (P) or nitrogen (N). Besides, phytoplankton is grazed by zooplankton (Z) and both of them die off turning into detritus (D). Figure 2 presents the diagram of material flows for such a

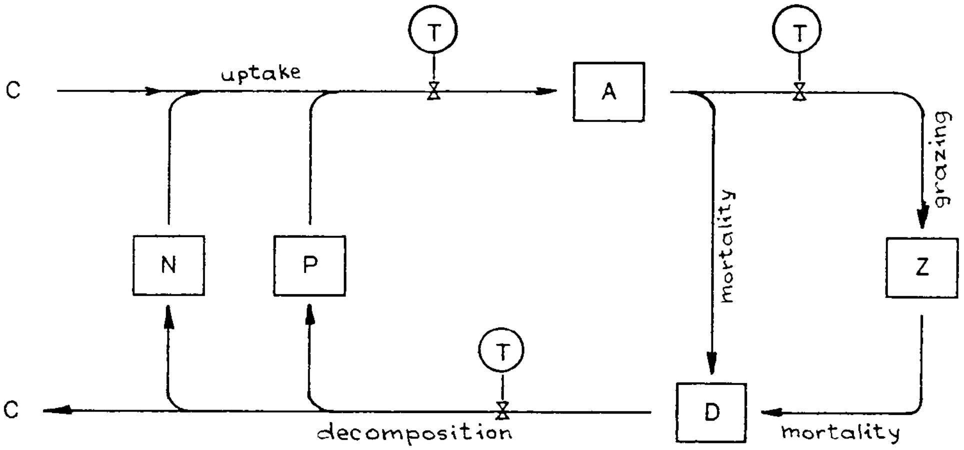

Fig. 2: Material flows in a simple eutrophication model.

model. The corresponding system of ordinary differential equations may be presented as follows:

$$dA/dt = f_1(T)*s*(C_n+C_p+C_c)*(1-B_a) - M_a*A$$

$$dZ/dt = f_2(T)*r(A,Z)*(1-B_z) - M_z*Z$$

$$dD/dt =$$

$$B_a*f_1(T)*s*(C_n+C_p+C_c) + M_a*A + B_z*f_2(T)*r(A,Z) + M_z*Z - f_3(T)*Des*D$$

$$dN/dt = f_3(T)*Des*D*C_n/(C_n+C_p+C_c) - f_1(T)*s*C_n$$

$$dP/dt = f_3(T)*Des*D*C_p/(C_n+C_p+C_c) - f_1(T)*s*C_p.$$

Here $f_1(t)$ and $f_2(T)$ are the temperature functions of the form as shown in Figure 3; $f_3(T)$ - is the Vant-Hoff temperature function (Fig. 4); $s = \min\{ r(N,A)/C_n; r(P,A)/C_p\}$ - describes the uptake of nutrients according to the principle of limiting factors; r(A,Z), r(N,A), r(P,A) - are s-shaped trophic functions (Fig. 5);

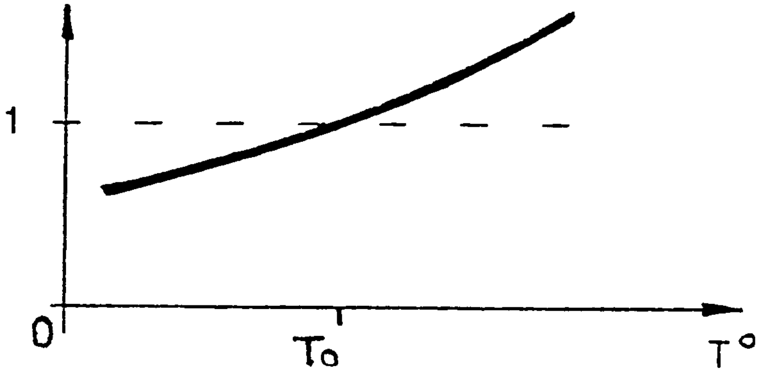

Fig. 3: Function of temperature limitation,

$$\text{e.g. } f_i(T) = \left\| \begin{array}{l} f_o**((T_{opt}-T)/T_{opt})**s_i \\ \\ 0.01**((T-T_{opt})/T_{max}-T_{opt}))**s_i; \quad s_1 > s_2. \end{array} \right.$$

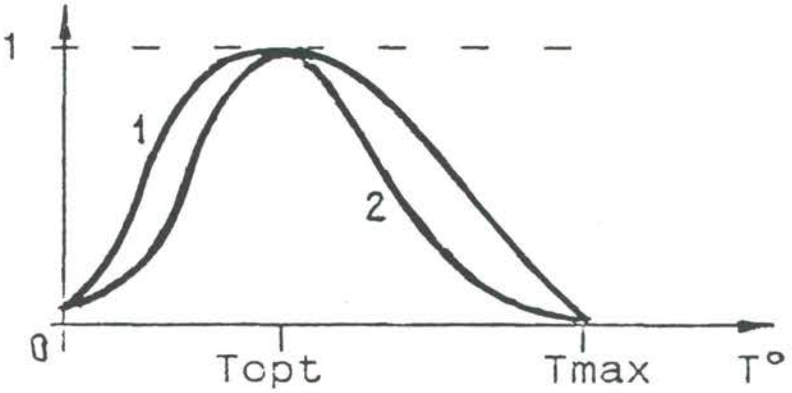

Fig. 4: Vant-Hoff's temperature function ($f_3(T) = 2^{**}((T-T_0)/10)$).

C_n, C_p, C_c - are the stoichiometric coefficients for nitrogen, phosphorus and carbon, respectively; B_a, B_z - are the metabolism coefficients for phyto- and zooplankton; M_a, M_z - are the corresponding mortality coefficients; Des - is the destruction rate coefficient.

Let us now formulate this system in terms of the SIMSAB flow language (AKHREMENKOV, 1988). We shall not go into the syntax details of this language, but just outline the main points:

- Q[X,Y] stands for the flow from component X to Y;
- QIN[X] and QOUT[X] stand for the inflow into X from outside of the system and for the outflow from X, respectively;
- Q[*,X] and Q[X,*] stand for the sums of flows entering X and leaving X, respectively;
- $ denotes a SIMSAB library function ($FT4, $LIM1, etc.);
- #VAR:NAME.EXT is a model parameter (here VAR, NAME and EXT are identifiers standing for the variable name, parameter name and its extension, respectively);
- if a SIMSAB function, returning several values, is used, then these values will be assigned to the flows in curly brackets {..} on the left-hand side.

As for the rest, the basic FORTRAN syntax rules are adopted ("C" starts the comments, entries start from the 6th position etc.).

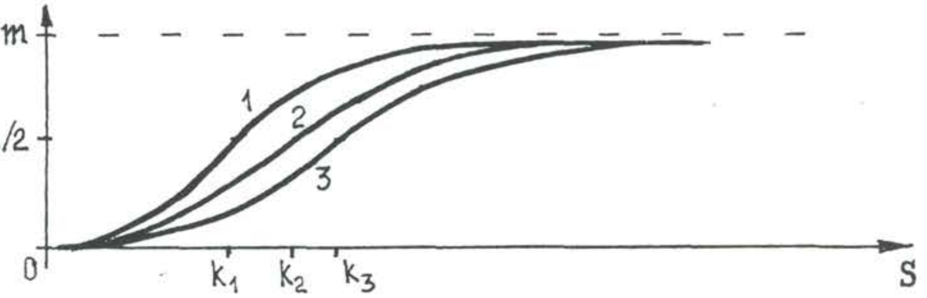

Fig. 5: S-shaped trophic function (e.g., $R(S) = m^*S^{**}a/(k^{**}a + S^{**}a)$).

The formulation of a box model is opened by its name, the names of the variables and forcing functions and the name of the file, which stores the information about model parameters. After that all the positive flows of the box model are specified in terms of the flow language (Table 1).

Table 1

Formulation of a box model.

```
MODEL A
VAR A,Z,D,N,P;
FORC T;
PARAM MOD-A.PRM;
C    Uptake of nutrients by phytoplankton with limiting by N
C    or P: $LIM1 returns two values, two flows are defined.
C    $R2 is a trophic function, $FT2 is a temperature function.
     {Q[N,A],Q[P,A]}=$FT2(T,A)*$LIM1(A,N,P,$R2(N,A),$R2(P,A))
C    Uptake of carbon described as an external flow
             QIN[A]=Q[N,A]/#A:C.*#A:C.C
C    Grazing of zoo- and phythoplankton limited by temperature
     Q[A,Z]=$FT2(T,Z) * $R2(A,Z)
C    Metabollic losses and mortality
             Q[A,D]=Q[*,A]*#A:MB + A*#A:MOR
             Q[Z,D]=Q[*,Z]*#Z:MB + Z*#Z:MOR
C    Decomposition of detritus into nutrients, $ST1 distributes the
C    flow of decomposed detritus $DES according to stoichiometry.
     {Q[D,N],Q[D,P],QOUT[D]}=$FT4(T,D)*$ST1(D,N,P,C,$DES(D))
END
```

Let us note that when using the SIMSAB library functions we do not define their parameters. All the necessary parameters are automatically selected from the SIMSAB library and copied to the model file of parameters. The missing parameters are inquired from the user during the first translation. If there are other segments in the model, a box model should be formulated for each of them.

Formulation of the model is concluded by the monitor which specifies the sequence of modeled events (Table 2). In the monitor we determine the initial values of variables, the variations of forcing functions, the method of numeric integration of equations, the form of explication of simulation results etc. Here we can also describe the lake hydrology and the spatial patterns of material exchange.

Besides, we should specify the data used by the monitor. In this case it is the weekly averaged temperature. The data may be presented either directly in the monitor or in separate files.

A model thus formulated is automatically translated into FORTRAN. Just for example in Figure 6 we present the trajectories calculated by this model.

Table 2

Formulation of the monitor.

```
MONITOR MOD A;
INITIAL
C  Input of the initital values of variables:
   $READ(0,5, 0.1, 2, 0.01, 0.005) VAR
C  Period of simulation is 60 days :
DYNAMIC TEND=60;
ST=0,7;
C  Input of temperature starting from time 0 and every 7 days
   $READ(TEMP) T
ST=0,0.5;
C  Every 12 hours (0.5 days): output of variables A & Z as graphs:
   $GRAPH A(0,2), Z(0,2)
C  Compute the system of equations by Adams method:
   $ADAMS A,VAR,FORC,5
END

DATA
TEMP: 0, 8.5, 13, 18, 14, 17, 13, 11, 20;
```

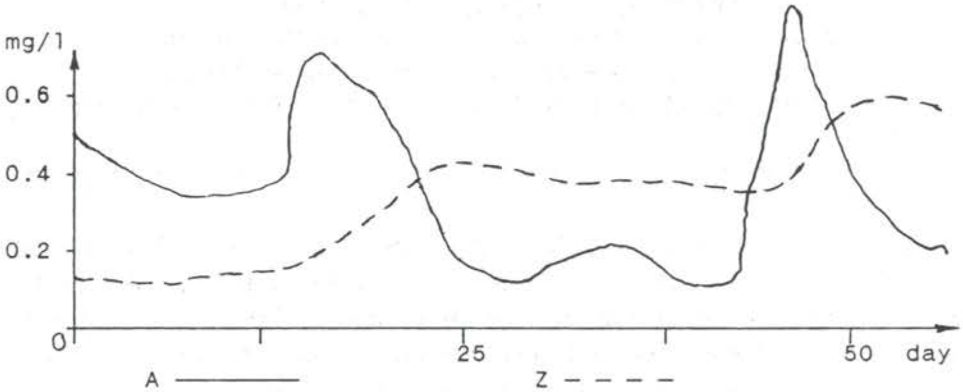

Fig. 6: Simulated phyto- and zooplankton dynamics.

Various alterations of the conceptual diagram (aggregation and desaggregation of variables, new links and interactions) can be readily included into the SIMSAB model and it is much easier to make these modifications in SIMSAB terms than to rearrange a program written in one of the traditional programming languages (Basic, FORTRAN etc.).

4. Model Analysis

The process of modeling is only started by the formation of the formalized representation of the object as a set of equations transformed into a FORTRAN program. In this form, models can in fact claim only to be "representations of the accumulated ... empirical information about the ecosystem and can solve only tasks of quantitative interpretation of the observations and verification of their mutual consistency" (AIZATULLIN & SHAMARDINA, 1980, p. 155). Actually, a large system, the water body, is substituted by another large system, the model, the dynamics of which are still to be studied.

Recently, more and more attention has been drawn to problems of model analysis - to estimations of their sensitivity, adequacy, accuracy of forecasts, to various methods of their calibration. Only a well analyzed model can serve as a tool of ecosystem research and provide new knowledge about aquatic bodies.

The SIMSAB-88 procedure of model analysis includes a number of modules which can:

- estimate model sensitivity with respect to parameters and forcing functions;

- estimate model stability and robustness (that is, define the extreme deviations of parameters and forcing functions which do not result in inadequate model trajectories - those tending to the negative domain or to infinity);

- calibrate models according to experimental data (adjust the most essential parameters to get the best fit of model trajectories to the experimental time series).

Besides, since SIMSAB allows one to modify the model itself easily, the structural sensitivity of models can be estimated, that is, the model sensitivity to variations of its structure: addition or exclusion of variables and/or links, modification of formalizations of interactions.

In all the service programs we follow the general lines of SIMSAB, according to which all products of the modeling system are portable FORTRAN programs. Thus, complicated models of high dimensionality can be analyzed on big computers, while the assembly of programs and analysis of simple models is performed on personal computers.

5. Conclusions

As computers become more and more widespread, methods of mathematical analysis become available for an increasing number of users and it becomes most urgent to develop a convenient user-friendly tooling, which requires no special mathematical background. It is only natural that most popular is the software which encloses its conceptual nucleas into a special environment, that facilitates learning and applications of the software.

SIMSAB-88 for instance, is accomplished by auxiliary programs which give an overview of some basic principles of simulation modeling in general and describe basic SIMSAB postulates in particular, allowing even a layman to master this system.
- SIMSAB-HELPER provides the user with all necessary information when working with the package.

It is this user orientation that allows us to hope, that SIMSAB and similar modeling packages will bring together ecological and mathematical studies in an interactive mode to obtain new insights into principles of ecosystem operation and more adequate representations of ecosystem dynamics.

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Model Averaging of Mass and Energy Cycles in Aquatic Ecosystems

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Contents

Abstract

In this paper we outline and illustrate methods for the averaging and closure of mathematical models of aquatic ecosystems. There is a wide spectrum for applications for such procedures in different areas of limnology, including the transition from distribution models to concentration models, recalculating laboratory experimental data to apply to natural conditions, calculating coefficients of averaged models and so on.

1. Introduction

Aquatic ecosystems are known to be a complex multitude of biotic and abiotic processes connected by various branched chains of trophic, biochemical and other interactions. In mathematical models this fact is reflected in that the equations are connected by chains of reverse bonds in the system. From the point of view of mass and energy circulation in ecosystems, the reverse bonds correspond to cycles of nutrients and energy of different ranges. For example, a chain such as phytoplankton,

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zooplankton, fish fauna, detritus, bacteria plankton, and nutrients, corresponds to a cycle which embraces all trophic levels. There are other cycles within it, for example the chain resourcer-consumer of precedent trophic level, primary predator, secondary predator, metabolites of this chain and precedent trophic level. There are many examples of different cycles in ecosystems. We also point out the availability of spatial cycles in the ecosystems, for example, primary producers, i.e., phytoplankton in the euphotic zone, consumers in the entire water column and at the bottom and the transfer ladder in the euphotic zone. All these cycles are characterized by certain time scales characteristic of transfer of certain substances. Since cycles of wide ranges exist in the ecosystem at the same time, it is necessary to coordinate the cycles of hydrothermodynamic processes of different spatial and temporal scales. It should be mentioned that for water bodies such as Lake Baikal, where the biotic influence on hydrothermodynamics can be disregarded, abiotic factors can be treated as independent variables.

2. Results and Discussion

The procedure of temporal and spatial averaging with the subsequent closure of model equations is one of the techniques of scale coordination. In this case, cycles with scales which are smaller than the averaged scale will be involved in the averaged model only parametrically. This means that the bond structure in model will change and new conformities to natural laws will appear. Thus, this procedure may be considered a new level of phenomenon description. Since the ecological models satisfy the laws of conservation of mass and the equations of each model are balanced equations, so averaging changes the balance of the system of cycles. The averaging problem with its subsequent closure may be solved successfully by a recursive closure method (REM). Since the REM and its modifications have already been considered in detail (GALKIN, 1980; GALKIN & KORNEYCHUC, 1981; ALEXANDRENKO & GALKIN, 1986), the discussion will be not repeated here. We only shall illustrate the averaging procedure and its applications. The REM allows phenomena such as inertia (or memory) of ecosystem elements to be taken into account, i.e., dependence of the system over a finite time interval upon previous states and their controlling factors and to find coefficients of the averaged model using fluctuation characteristics of the independent variables.

As an illustration, we consider the averaging of a model containing the chain of certain aquatic ecosystem elements of local nutrient circulation (cycle). To reduce complicated calculations we take as the ingredients of the chain state vector the following concentrations: $\mathbf{S}_1$ - phytoplankton, $\mathbf{S}_2$ - detritus (dead cells of $\mathbf{S}_1$), $\mathbf{S}_3$ - limiting nutrient. In this case, the equations of the distribution model are:

$$\frac{\partial S_\alpha}{\partial t}+\frac{\partial u_i S_\alpha}{\partial x_i}=K_\alpha \frac{\partial^2 S_\alpha}{\partial x_i^2}+S_\alpha\left(\sum_\beta R_{\alpha\beta}-\sum_\gamma P_{\alpha\gamma}\right)+Q_{\alpha m}+Q_\alpha-V_\alpha \frac{\partial S_\alpha}{\partial x_3} \tag{1}$$

where Greek indices signify various chain ingredients, $\mathbf{U}_i$ = environment velocity components, $\mathbf{K}_\alpha$ = diffusion coefficients, $\mathbf{R}_{\alpha\beta}$, $\mathbf{P}_{\alpha\tau}$, $\mathbf{Q}_{\alpha\mu}$ = coefficients of reproduction, mortality, and of sources, respectively. They are functions of α and μ x $\mathbf{Q}_\alpha$ = external sources, $\mathbf{V}_\alpha$ gravitational settling velocity; and where Latin indices i, j, k, n denote various spatial components. Repeated Latin indices imply summation over these indices.

In real conditions and in turbulent environments, $\mathbf{S}_\alpha$, $\mathbf{U}_i$, $\mathbf{R}_{\alpha\beta}$, $\mathbf{P}_{\alpha\tau}$ and $\mathbf{Q}_{\alpha\mu}$ contain a random component. So in this case we can write them as $\phi = \phi + \phi'$, where the barred term is the averaged quantity and the primed term denotes fluctuations about this average. Substituting this expression into equation (1) and applying the averaging procedure to it, we obtain:

$$\begin{aligned}\frac{\partial \bar{S}_\alpha}{\partial t} + \frac{\partial \bar{u}_i \bar{S}_\alpha}{\partial x_i} = {} & K_\alpha \frac{\partial^2 \bar{S}_\alpha}{\partial x_i^2} + \bar{S}_\alpha \left(\sum_\beta \bar{R}_{\alpha\beta} - \sum_\gamma \bar{P}_{\alpha\gamma}\right) + \bar{Q}_{\alpha\mu} + \bar{Q}_\alpha - V_\alpha \frac{\partial \bar{S}_\alpha}{\partial x_3} \\ & - \frac{\partial}{\partial x_i}\left(\overline{u_i' S_\alpha'}\right) + \overline{S_\alpha' \sum_\beta R_{\alpha\beta}'} - \overline{S_\alpha' \sum_\gamma P_{\alpha\gamma}'}\end{aligned} \tag{2}$$

The difference between equations (1) and (2) yields the equation system for the fluctuations of $\mathbf{S}'_\alpha$. By integrating it over time at every point in space, we obtain the equations that define $\mathbf{S}'_\alpha$ (with some loss of information):

$$\begin{aligned}S_\alpha' = {} & \int_{t-\tau}^{t} \left(-\frac{\partial u_i' \bar{S}_\alpha}{\partial x_i} + Q_\alpha\right) d\theta + \int_{t-\tau}^{t} \left[\sum_\beta Q_{\alpha\beta}' + \bar{S}_\alpha' \sum_\beta \left(R_{\alpha\beta}' - P_{\alpha\beta}'\right)\right] d\theta \\ & + \int_{t-\tau}^{t} \left[-\frac{\partial \bar{u}_i S_\alpha'}{\partial x_i} - \frac{\partial (\bar{u}_i S_\alpha')'}{\partial x_i} + S_\alpha' \sum_\beta \left(\bar{R}_{\alpha\beta} - \bar{P}_{\alpha\beta}\right) + \left(S_\alpha' \sum_\beta \left(R_{\alpha\beta}' - P_{\alpha\beta}'\right)\right)'\right] d\theta\end{aligned} \tag{3}$$

where primed brackets are fluctuations about these averages. It follows from (3) that if we disregard all addenda containg $\mathbf{R}'_{\alpha\beta}$, $\mathbf{S}'_\alpha$ and $\mathbf{P}'_{\alpha\beta}$, then $\mathbf{S}'_\alpha$ can be expressed in terms of derivatives of $\mathbf{S}_\alpha$ and the external parameters $\mathbf{U}'_i$ and $\mathbf{Q}'_\alpha$. The system of equations becomes independent. We denote this situation the zero approximation $\mathbf{S}'^{(0)}_\alpha$. To arrive at the first approximation $\mathbf{S}'^{(1)}_\alpha$, we disregard only the addenda with $\mathbf{S}'_\alpha$ and we substitute the first approximations of primed values into the second integral. This unites the equalities in the dependent system. To get the second approximation $\mathbf{S}'^{(2)}_\alpha$, we substitute approximations $\mathbf{S}'^{(1)}_\alpha$, $\mathbf{R}'^{(2)}_{\alpha\beta}$, $\mathbf{P}^{(2)}_{,\alpha\beta}$ and $\mathbf{Q}^{(2)}_{,\alpha\beta}$ in equality (3) instead of the primed values. Thus, the nth-approximation is expressed by the (n-1)th-approximation of $\mathbf{S}'_\alpha$ and the nth-approximation of the remaining primed values. With this method, we can express any approximation of $\mathbf{S}'_\alpha$ by means of $\mathbf{S}_\alpha$, its derivatives and the moments of the external parameters $\mathbf{U}'_i$ and $\mathbf{Q}'_\alpha$. Substituting different approximations $\mathbf{S}'_\alpha$ in the unknown moments of equation (2) $\mathbf{U}'_i\mathbf{S}'_\alpha$, $\mathbf{S}'_\alpha\Sigma_\beta\mathbf{R}'_{\alpha\beta}$, $\mathbf{S}'_\alpha\Sigma_\tau\mathbf{P}'_{\alpha\tau}$, we can derive the expression for it by means of $\mathbf{S}_\alpha$, its derivatives and moments of external parameters $\mathbf{U}'_i$ and $\mathbf{Q}'_\alpha$ of one or the other approximation, i.e., the problem of closure of the equations is solved.

Thus, to solve this problem it is necessary to have information on the dependence of $\mathbf{R}_{\alpha\beta}$, $\mathbf{P}_{\alpha\tau}$ and $\mathbf{Q}_{\alpha\mu}$ on $\mathbf{S}_{\alpha}$, which can be obtained from experiments or from phenomenon theory. To illustrate this method let us take the simple dependence of these parameters on $\mathbf{S}_{\alpha}$, which follows from theory. For phytoplankton we consider both Libich's law and that reactions often can be described by a diffusion approximation where $\mathbf{R}_{\alpha\beta}$ depends linearly on the limiting nutrient, i.e., $\mathbf{R}_{13} = b\mathbf{S}_3$. Naturally, this term describes also nutrient consumption, therefore $\mathbf{Q}_{31} = b\mathbf{S}_1$. Phytoplankton mortality is defined by the rate of grazing by zooplankton. Since zooplankton is not included in the considered cycle, we can suppose that the mortality coefficient is a time function known from experiments or a constant, i.e., $\mathbf{P}_{1\beta} = d$. Likewise, the decomposition rate of detritus is a constant, i.e., $\mathbf{P}_{2\beta} = m$. Since detritus decomposition and phytoplankton mortality replenish nutrients and detritus, we can set $\mathbf{Q}_{32} = m\mathbf{S}_2$ and $\mathbf{Q}_{21} = d\mathbf{S}_1$. By analogy, the distribution sources $\mathbf{Q}_{\alpha}$ of nutrients and detritus depend on trophic level parameters not included into the cycle. Thus, we approximate them by an experimental function $\mathbf{Q}_2 = f_2(t)$ and $\mathbf{Q}_3 = f_3(t)$. Nutrients are consumed by phytoplankton, thus $\mathbf{P}_{31} = b\mathbf{S}_1$. In laminar environments described by system (1), the diffusion coefficients for phytoplankton $\mathbf{K}_1$ and $\mathbf{K}_2$ are equal to zero, since their dimensions are larger than Brownian motion. In non-turbulent environments they therefore remain stationary. This fact has served as a basis for the "concentration method" of phytoplankton experiments (KISILEV, 1980) and created great difficulties when working with microcosms (ALEKSEEV, 1980; DE BLOCK, 1975; PILSO et al., 1977).

Let us consider the realization of zero and first order approximations of the closure of equation systems. To simplify, let us suppose that the environment is incompressible, i.e., div $\vec{\mathbf{U}} = 0$. Substituting zero approximation $\mathbf{S}'_{\alpha}$ in turbulent flow $\overline{\mathbf{U}'_i\mathbf{S}'_{\alpha}}$ and in the moments of reverse bonds in system (1) $\overline{\mathbf{S}'_{\alpha}\Sigma_{\beta}\mathbf{R}'_{\alpha\beta}}$, $\overline{\mathbf{S}'_{\alpha}\Sigma_{\beta}\mathbf{P}'_{\alpha\beta}}$ we obtain:

$$\overline{U'_i S'_\alpha} = -D_{ij}\frac{\partial \bar{S}_\alpha}{\partial x_j} + Q_{i\alpha}, \quad \overline{S'_1 R'_{13}} = \overline{S'_3 P'} = -M_{ij}\frac{\partial \bar{S}_1}{\partial x_j}\frac{\partial \bar{S}_3}{\partial x_i} - G_{i3}\frac{\partial \bar{S}_1}{\partial x_i} \tag{4}$$

where $D_{ij} = \int_{t-\tau}^{t} \overline{U'_i(t)\,U'_j(t+\theta)}\,d\theta$, $\quad Q_{i\alpha} = \int_{t-\tau}^{t} \overline{U'_i(t)\,f'_\alpha(t+\theta)}\,d\theta$

and $\mathbf{M}_{ij}$ = averaged values of integrals over time for $\mathbf{U}'_i$ and $\mathbf{U}'_j$, $\mathbf{G}_{i3}$ = averaged values of analogous integrals for $\mathbf{U}'_i$ and $\mathbf{f}'_3$, the other moments are equal to zero as well as $\mathbf{Q}_{i1}$. It is not difficult to see that the zero approximation adds the flows in equation (2). In equation (2) terms with second derivatives describe diffusion, those with first derivatives advection, and those with zero derivatives kinetics, but independent of $\bar{\mathbf{S}}_{\alpha}$ distributed sources. From this it follows, that equalities (4) introduce additional turbulent flows with the diffusion coefficient $\mathbf{D}_{ij}$, advective flows for phytoplankton and nutrients, and distributed sources for detritus and nutrients into all equations. It changes the cycle balance terms considerably, i.e., new properties appear in system (1). One is a result of averaging, which we can consider as a result of transition on the new level of description with the new time scales. From equality (4) it follows that the first approximation introduces only the additional flows and sources leaving the system (2) quasi linear similarly to system (1). We like to discuss one more property, that is phytoplankton in the equality (4). Let us suppose that D_{ij} = constant, $\Sigma_{\beta}\overline{R}_{1\beta}$ = constant and that nutrients are distributed evenly. In this case the equation for phytoplankton is turned into an equation for $\mathbf{C}(\mathbf{X}_{i,t})$ without gravitational settling and reproduction by substitution:

$$\overline{S}_1 = C(x_i, t)\exp\left[\frac{V}{2D_{33}}x_3 + \left(A - \frac{V^2}{4D_{33}}\right)t\right], \quad A = \sum_{\beta} R_{1\beta} - \sum_{\gamma} P_{1\gamma}$$

The solution approaches zero for t → ∞. The factor $\exp(\mathbf{A}\text{-}\mathbf{V}^2/4\mathbf{D}_{33})t$ can compensate for this. It follows that $\mathbf{A}\text{-}\mathbf{V}^2/4\mathbf{D}_{33} > 0$. Quantity $4\mathbf{D}_{33}/\mathbf{V}^2$ defines the time during which the turbulence retains phytoplankton cells in the euphotic zone. If during this time a cell can realize more than one division then a phytoplankton bloom will develop. Otherwise it will perish. The parameter $\mathbf{V}^2/4\mathbf{D}_{33}$ in a turbulent environment can be called "floatation". Let us note that the availability of floatation will complicate the expression. Let us consider the first approximation. For it as well as for the zero approximation the equalities (4) are correct, but there $\mathbf{S'}_{\alpha}^{(0)}$ is substituted by $\mathbf{S'}_{\alpha}^{(1)}$, which is according to equation (3)

$$S_1'^{(1)} = S_1'^{(0)} + b\overline{S}_1\int_{t-\tau}^{t} S_3'^{(0)}\,d\theta, \quad S_2'^{(1)} = S_2'^{(0)} + d\int_{t-\tau}^{t} S_1'^{(0)}\,d\theta, \tag{5}$$

$$S_3'^{(1)} = S_3'^{(0)} + \int_{t-\tau}^{t} b\overline{S}_3 S_1'^{(0)}\,d\theta$$

Comparing equalities (4) and (5) it is concluded that the first approximation is obtained by addition to moments $\overline{U'_i\mathbf{S}'_{\alpha}}$, $\overline{\mathbf{S}'_{\alpha}\Sigma_{\beta}R'_{\alpha\beta}}$, $\overline{\mathbf{S}'_{\alpha}\Sigma_{\beta}P'_{\alpha\tau}}$ of the zero approximation to become addenda

$$b\overline{S}_1\frac{\partial\overline{S}_3}{\partial x_i}W_{ij}, \quad d\frac{\partial\overline{S}_1}{\partial x_i}W_{ij}, \quad -b\overline{S}_3\frac{\partial\overline{S}_1}{\partial x_i}W_{ij} \qquad \text{for } \overline{U_i' S_\alpha'} \tag{6}$$

$$b^2\overline{S}_1\left(\frac{\partial\overline{S}_3}{\partial x_i}\frac{\partial\overline{S}_3}{\partial x_j}W_{ij} + \frac{\partial\overline{S}_3}{\partial x_i}F_i + \phi_{33}\right) \qquad \text{for } \overline{S_1' R_{13}'}$$

$$-b^2\overline{S}_3\frac{\partial\overline{S}_1}{\partial x_i}\frac{\partial\overline{S}_1}{\partial x_j}W_{ij} \qquad \text{for } \overline{S_3' P_{31}'}$$

accordingly, where $W_{ij} = \overline{I_i J_j}$, $F_{i\alpha} = \overline{I_i J_\alpha} + \overline{I_\alpha J_i}$, $\Phi_{\alpha\alpha} = \overline{I_\alpha J_\alpha}$

$I_i = \int_{t-\tau}^{t} \varphi_i \, d\theta$, $J_i = \int_{t-\tau}^{t} \int_{t_1-\tau}^{t_1} \varphi_i \, d\theta \, dt_1$, $\varphi_i = U_i'$, $\varphi_\alpha = f_\alpha'(t)$

From equation (6) it follows that the first approximation added to the convective terms and kinetic parameters of the first and third equations make the equations non-linear but make it sources, when added to the second approximation. Besides the change of flows and kinetic parameters the following approximations will increase the order of these equations by two units.

Thus, averaging changes the model bond structure markedly and parametrizes cycle description with scales which are smaller than the average scale. It also transfers the system to a new level of description, revealing the new conformity to natural laws of behavior, which is not an original characteristic of this system. Let us add that the coefficients W_{ij}, $F_{i\alpha}$, $\phi_{\alpha\alpha}$ are the integrals of auto- and cross-correlation functions. The values of which statistically take into account the influence of the previous state of the system.

The conclusion is that spatially averaged equations describing dynamically interacting elements of an ecosystem are similar to temporal averaged equations and closure is based mainly on the closure modified recursive method (MREM; ALEXANDRENKO & GALKIN, 1986). In spatial averaging as well as in temporal averaging, every different level has its own conformity, which is most fully and synonymously described by averaged variables with scales that correspond to the given level. While transferring to macrovariables, all processes with smaller spatial scales are parametrized with the MREM scheme. In consequence of this, the model structure, the meaning of coefficients, the bond character on the right sides and others change. As a result of the averaging procedure (and closure), such problems as the decreasing of equation dimension (i.e., the reduction of the number of independent spatial variables), transfer from distribution to specialized models, recalculations to apply to natural conditions, calculating coefficients of averaged models and others are solved.

3. Conclusion

Finally, it can be concluded that the procedure of averaging with subsequent closure makes it possible to reveal some new properties peculiar to the collective behavior of the interacting elements of the ecosystem and not inherent to individual elements. On these grounds one might anticipate the application of methods advanced in this work in the search for development characteristics of ecosystems and for the study of cycling of mass and energy in natural systems.

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Local Unconformities in Satellite Images of Water Surfaces

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With 4 Figures

Contents

Abstract

This paper analyzes the origin of unconformities in remote sensing pictures of estuaries and adjacent areas in coastal marine and limnic settings.

1. Introduction

In nutrient rich coastal seas zones of higher primary production develop. These zones include frontal interfaces, upwelling areas, eddies, i.e., phenomena that have a significant vertical flow component.

Areas with significant gradients in their hydrological and hydrobiological characteristics are not only of primary interest to fisheries, but also to remote sensing, at least as long as these gradients are also influencing hydrooptical

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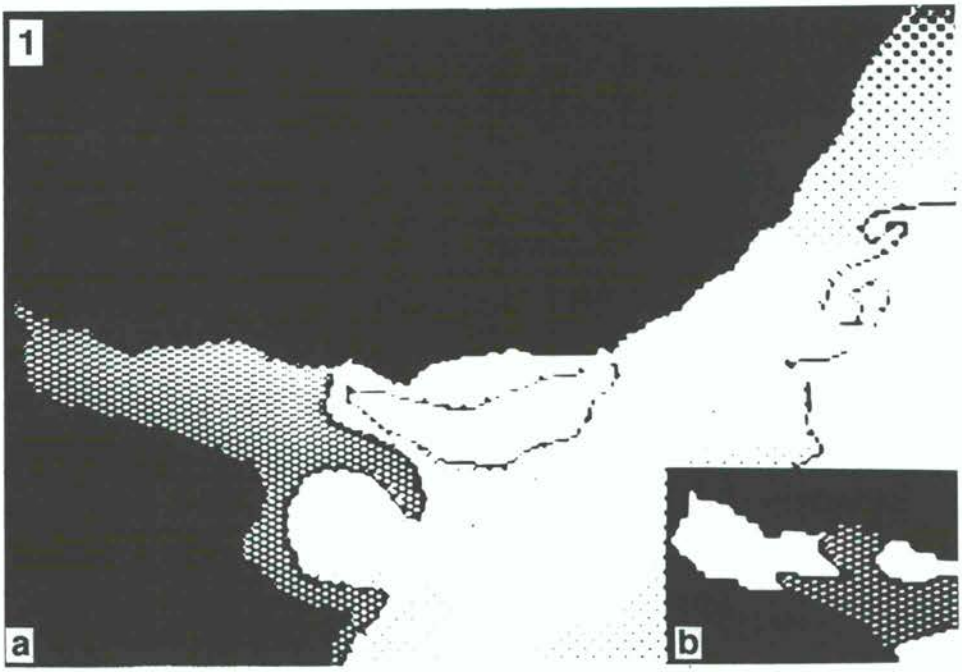
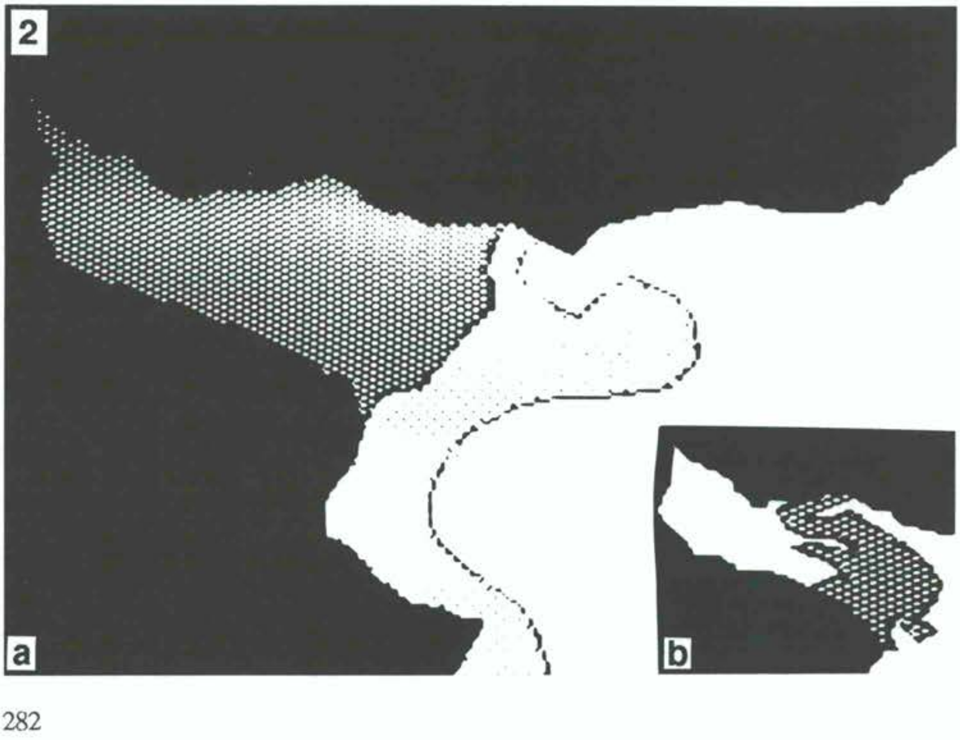
characteristics. The main scientific attraction to such areas is the fact that the processes generating the gradients are understood in general.

Defining character and quantity of a substance which alters detectable optical signals is the task of hydrooptics and atmospheric optics. The few attempts to solve





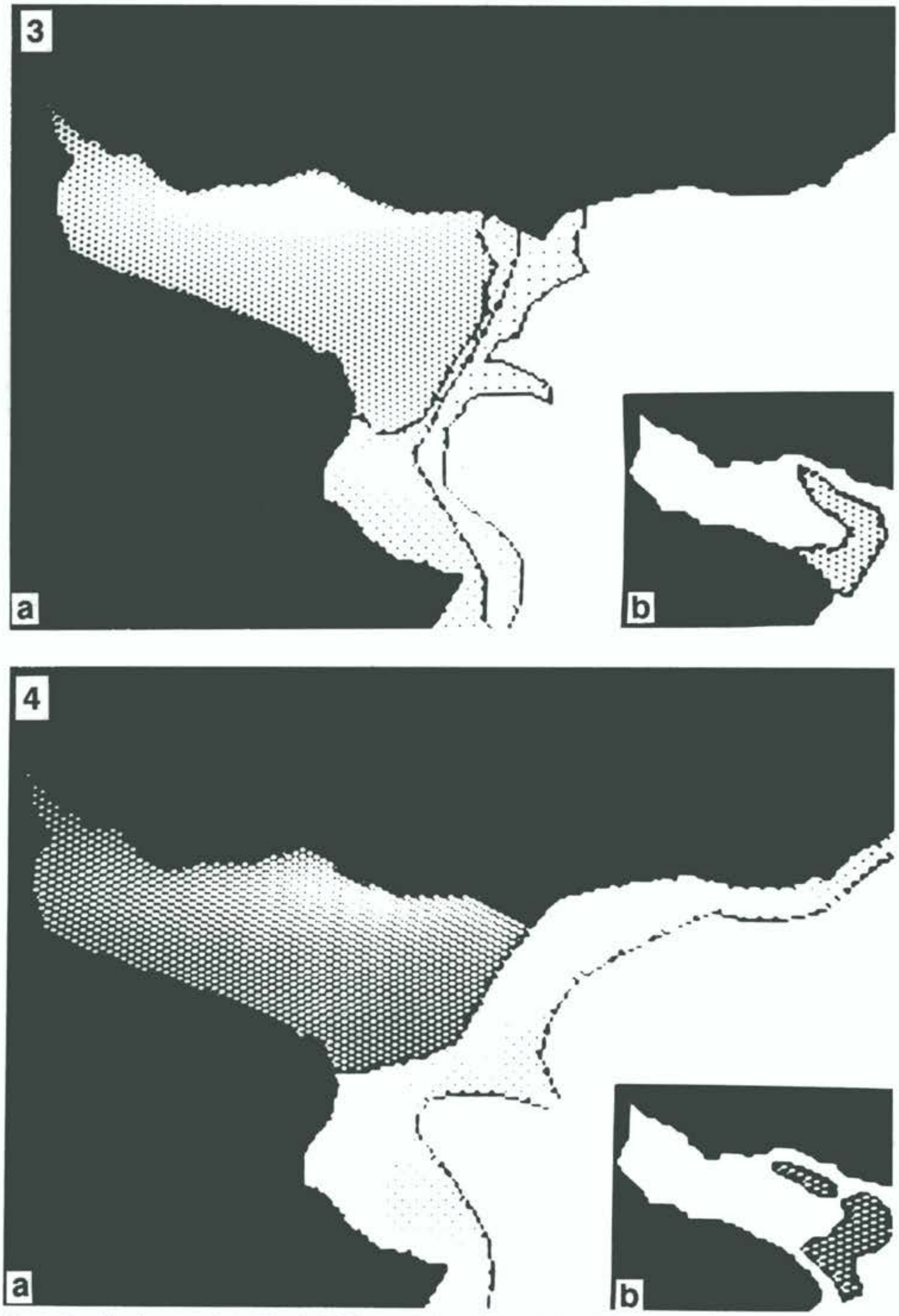


Fig. 1: Satellite images of the Rio de la Plata and the adjacent Atlantic Ocean obtained by multi-channel scanning device (MSD-S) using optical sounding, large pictures (a) show the microwave range 0.5-0.6 µm; insets (b) show the microwave range 0.8-0.9 µm. 1. February 24th, 1986; 2. March 3rd, 1986; 3. March 16th, 1986; 4. March 19th, 1986;.

the problems with the help of ground truth experiments required high financial and organizational expenditures. Nevertheless, the results are rather limited in use. Hence, when analyzing the measurements within spectral ranges inherent to scanners, we have no a priori knowledge, what substance or factor causes the observed unconformities.

In this paper, which deals with spectral images of zones with large plankton abundances we restrict ourselves to the areas (i) in which the origin of high plankton concentrations is connected with various oceanic phenomenon, and where (ii) horizontal unconformities in plankton concentrations outline the structure of these phenomena.

Phytoplankton blooms are as a rule accompanied by high zooplankton abundances (or by other suspensions of biological origin). For the spectral resolution of satellite scanners (0.1-0.2 μm) it cannot be made sure which component contributes to the contrasts in the scanned image: abiogenic suspended matter, biogenic suspended particles, or dissolved substances.

So, the aim of the paper is narrowed to describe characteristics of satellite images and of mechanisms occurring in zones with high biological productivity.

2. Unconformities in Estuaries and Adjacent Areas

The optical contrast between turbid riverine and clear oceanic water masses is used to define some hydrophysical phenomena. In images obtained with multichannel devices such as MSD-S, MSD-M, MSD-Sc, the interfaces between the two water masses are distinct.

The La Plata Estuary, formed jointly by the Paraná and the Uruguay at the east coast of South America is a suitable object for a remote sensing study of such interfaces. Furthermore, it is mostly free of clouds facilitating repeated and long-term observations by remote sensing.

In the analysis of the hydrophysical state of this estuary we will use multiband spectral information obtained by the MSD-S device. We shall start with the simple idea about light penetration depth into turbid water. According to results by GORDON (1979) we shall assume that the optical contrasts on the images of the La Plata obtained in the 0.8-1.1 μm range (Fig. 1.1-1.5) are connected with the unconformities in the concentration field of the suspended matter in the shallow surface layer. Optical contrasts obtained in the scanning range from 0.6-0.7 to 0.5-0.6 μm give an idea of the distribution of suspended matter in a layer approximately 1.5 m and 1.7 m thick, respectively.

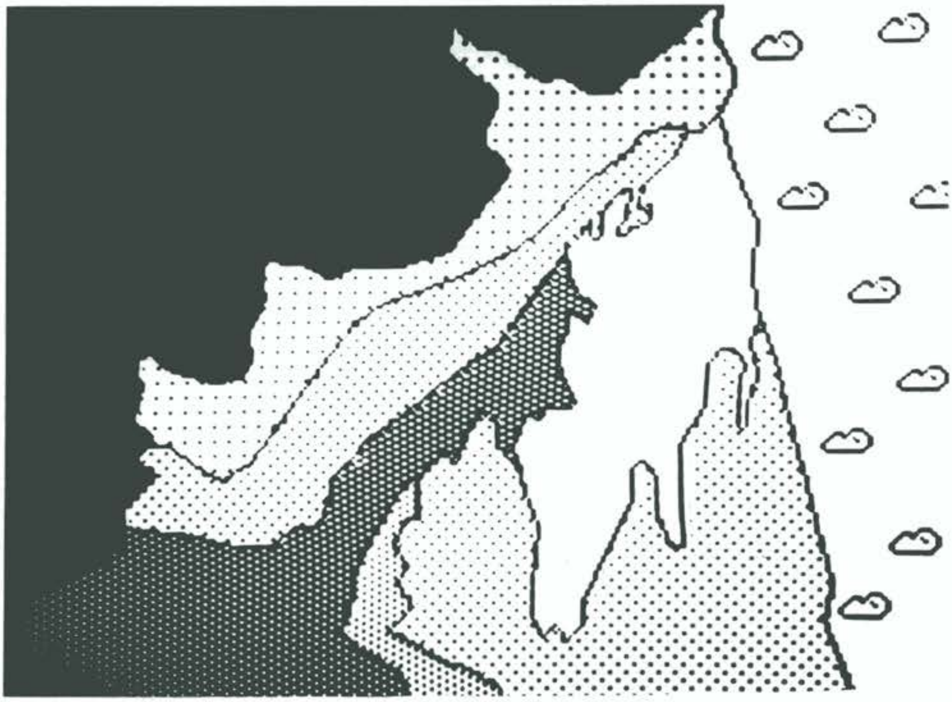


Fig. 1.5. Satellite image of the south Atlantic ocean off the La Plata, obtained in the infrared range by NOAA-4, May 22nd, 1976 (LEGEKIS, 1978). The dark areas correspond to warm surface waters, light areas correspond to cold waters.

The main reason causing large differences in optical properties is connected to turbulence which maintains particles in suspension. Particles with a density different from water settle with a velocity V_p according to Stoke's Law:

$$V_p = 2\,g\,r^2(d_p-d_w)\,/\,9\,v\,\phi_p \qquad (1)$$

where g = acceleration of gravity; r = radius of the particle; d_p = particle density; d_w = water density; v = fluid velocity; and ϕ_p = a coefficient accounting for particle shape.

Hydrodynamic instability and bottom friction cause the outflowing river water to be turbulent with a vertical velocity fluctuation denoted as σ_w. The turbulence creates a resistance for the settling particle. If the fluctuation is large and if particles are caught in ascending water parcels so that there is no time to settle (i.e., if $\sigma_w > V_p$), then particles can be kept buoyant and stay in suspension. Otherwise (i.e., if $\sigma_w < V_p$) particles sink (BARENBLATT & MONIN, 1979).

An estuary front is formed where clear ocean and turbid water converge (FYODOROV, 1983; Fig. 3.35). The patches on the La Plata Estuary images obtained by the MSD-S (range of 0.8-0.9 μm; Fig. 1.1-1.4, b) may show such accumulations of buoyant suspension bound to the turbulence at the mixing front.

The mixing of the river water in deeper areas is accompanied by an exchange of energy and mass from the fresh water forming a wedge on top of the salt water. With the decrease of the flow velocity in the fresh water plume, turbulence decreases, concentration of suspended matter drops and optical properties of the fresh water change.

MSD-S images of the range 0.8-0.9 μm of the La Plata (Fig. 1.1b-1.4b, inset) taken in February and March 1986 show that significant changes can develop within a few days. Between frames Figure 1.1 and 1.3 the frontal patch has decreased in size and its outer boundary shifted towards the sea by 30 km.

In contrast to this, the images obtained in the 0.5-0.6 μm range (Fig. 1.1-1.4, a) do not show much alteration within the time of observation. The principal changes are observed towards the ocean. Optical contrasts of these pictures are connected with sharp changes of the concentration of suspended matter.

Turbulence in the estuary depends on mixing intensity which decreases towards the ocean causing sediment to settle. In Figure 1.4 (b) the turbid water interface observed follows the 10 m isobath, i.e. the mixed layer touches the bottom allowing sediments to be resuspended.

If d_p is similar to d_w, then water density changes (e.g. due to seasons) may lead to the change of the sign of the density difference in (1). Such changes in the sign of the density difference could come about by seasonal fluctuations in the composition of the particles, in salinity changes or in temperature changes (the Atlantic water varies from 10 to 15°C; MUROMTSEV, 1963). Temperature changes are easily detectable off the coast of Argentina where the Falkland and the Brazil currents meet (Fig. 1.5; LEGEKIS, 1978).

Turbulence and hence resuspension capacity of the outflowing river plume is connected in shallow waters to bottom topography or to the velocity of the flow over the salt wedge if the plume happens to flow out into deep coastal seas (e.g., the Amazon for an oceanic example and the Selenga in Lake Baikal for an limnic example). In the case of the Amazon largest optical contrasts are found in the outer plume where sufficient salinity changes occur (Fig. 2). Toward the ocean front, suspended matter concentration fall off almost in a jump (MONIN & KOPELEVITCH, 1983).

The gradients in the optical characteristics of the Selenga plume in Lake Baikal (Fig. 3) are possibly caused by two main factors:

(i) the density differences between the lake and river waters (the Selenga water is warmer as a rule);

(ii) the differences in the turbulent mixing intensities between lake and river water.

Both factors are seasonal. The Selenga plume spreads much further during periods of vertical stratification. In Figure 3 the plume extension as detected by scanning in the wave length range 0.5-0.7 μm is marked with a dashed line.

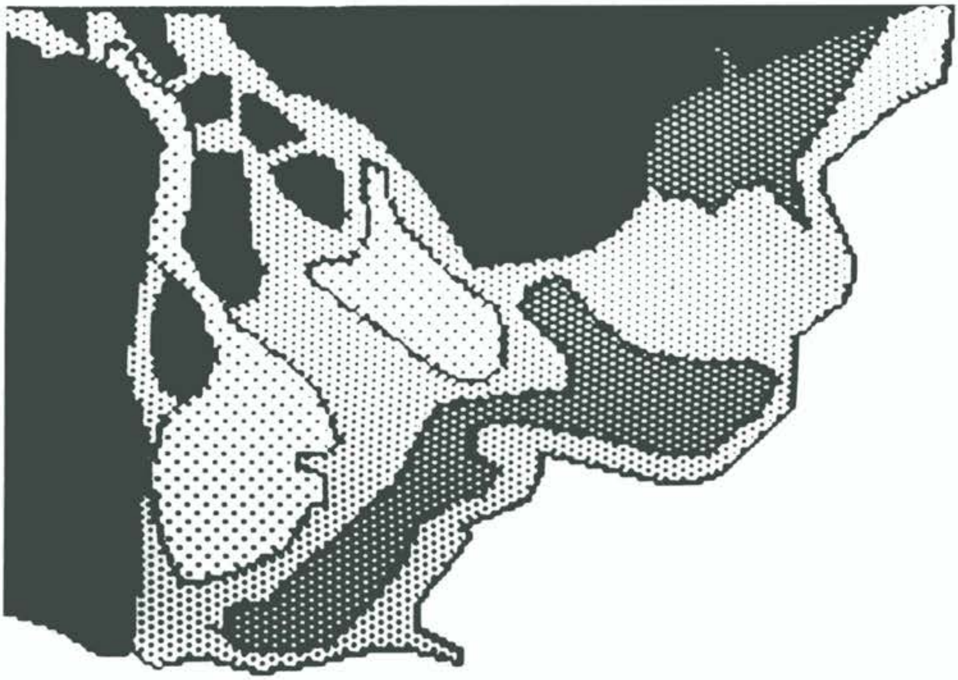


Fig. 2: Satellite image of the Amazon delta and the adjacent coastal sea obtained by MSD-S soundings in the range of 0.5-0.7 μm, June 27th, 1986.

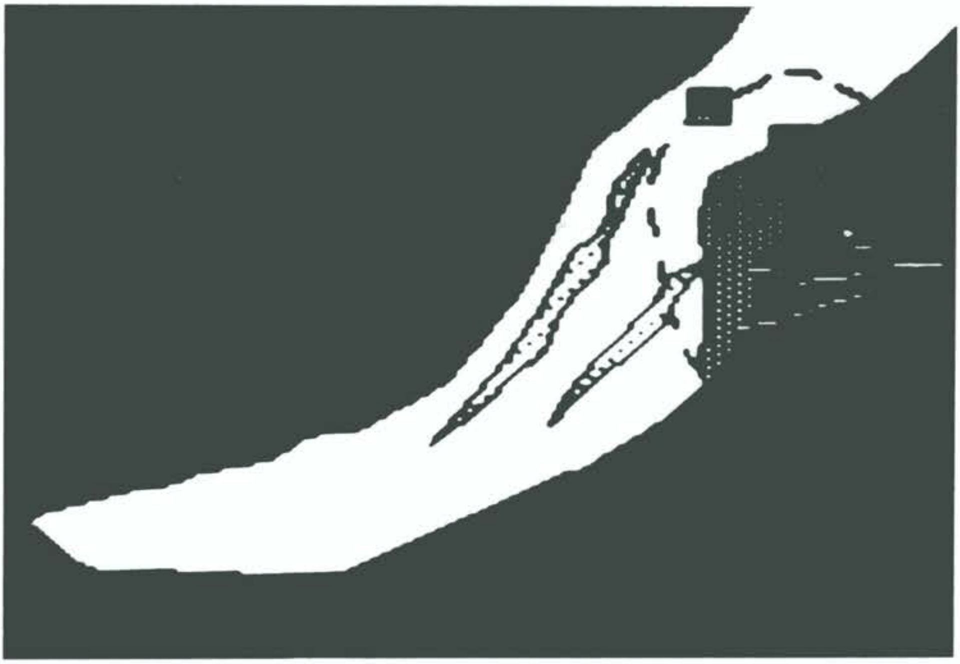


Fig. 3: Satellite image of the Selenga plume/Lake Baikal obtained by the normal resolution multi-channel scanning device (msd-m) using optical sounding, June 27th, 1983.

3. Optical Unconformities in Lake Sevan

Lake Sevan, Armenia, provides an excellent example to study optical unconformities by remote sensing in an limnic environment because the limnology of the lake is well known. Compared to Lake Baikal, Lake Sevan has a higher phytoplankton concentration, reaching 18 g/m^3 during blooms, and it shows stronger seasonal alterations its current pattern. In summer the warm surface layer of the Bolshoi Sevan develops cyclonic movements with upwelling in the center and downwelling along the shores (AKOPYAN & DYOMIN, 1982). In the Malyi Sevan, which is less deep, surface flow is controlled by local winds entering through gaps in the surrounding mountains to a greater extent than in Bolshoi Sevan.

In order to discus the current pattern in connection with the unconformities in remote sensing images of Lake Sevan (Fig. 4) we have to consider the vertical temperature profile, the vertical suspended matter distribution and phyto- and zooplankton profiles (RUMYANTSEV et al., 1986). Furthermore, during plankton blooms, blue green algae occur in large quantities in the mixed surface layer (KISELYOV, 1980; TIMOFEYEV, 1960).

Strong upwelling in the lake during summer causes the thermocline to crop out at the surface. These areas then appear presumably as clear patches in the satellite images while the turbid areas correspond to the downwelling areas where the thick mixed layer contains more light absorbing plankton and other suspended particles.

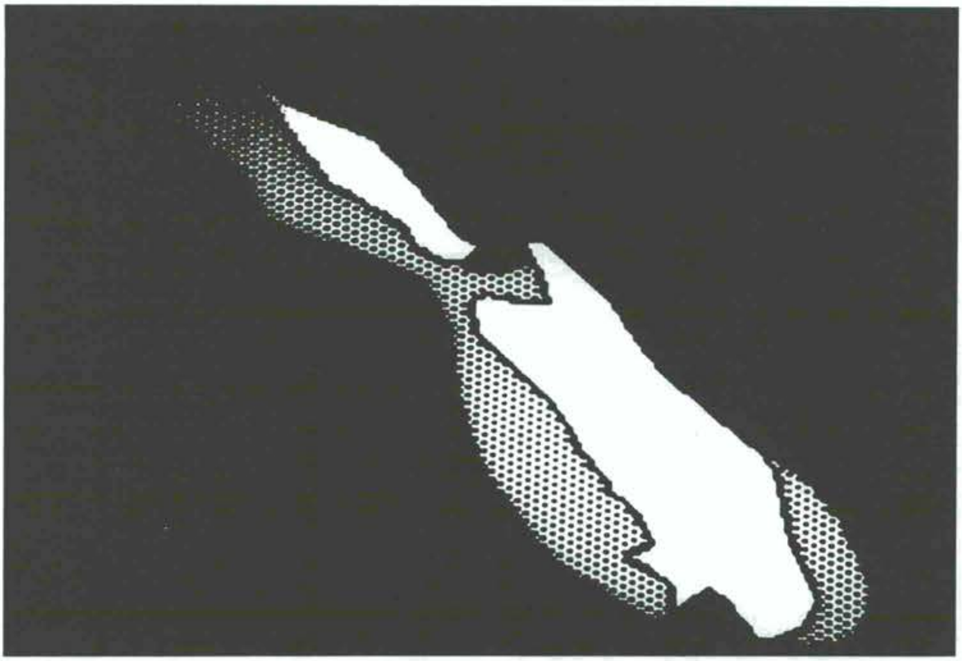


Fig. 4: Satellite image of Lake Sevan obtained by MSD-ms soundings in the range 0.5-0.6 µm, October 8th, 1985. Northern part of lake is called Malyi Sevan, southern part Bolshoi Sevan.

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