

The Effects of NTA on the Growth of Phytoplankton with Particular Consideration given to Iron as a Microelement

Hans-Rudolf Bürgi

Phosphorus plays the key role in eutrophication of Swiss lakes. On the average 20 to 30% of the P-loading of our lakes originates from detergent builders.

Today NTA (nitrilotriacetate) is widely used both in Canada and Sweden. Culture experiments carried out by various authors indicated that an increase in photosynthetic production could result from addition of iron (III) in presence of NTA or EDTA. There was some concern that the iron remaining from phosphate removal treatment could trigger similar growth developments in lakes. We examined the effects of iron and NTA directly in a lake in a culture unit of 7000 liters (Fig. 1).

Experimental Procedures

In seven tests of three weeks duration (3 in mesotrophic Lake Lucerne and 4 in highly eutrophic Greifensee) the effects of addition of NTA (100–3000 µg/l), of Fe (III) (15–50 µg/l) and of NTA + Fe (III) on the growth response of phytoplankton were investigated, by measuring (1) productivity by C-14 of Steemann-Nielsen, (2) pigment analysis of (SCOR), and (3) by determination of biomass (cell counting of Utermoehl). Iron was determined spectrophotometrically with bathophenanthroline-di-sulfonate.

Chemical composition and characteristics of the two lakes (meand for epilimnion during summer) are given below.

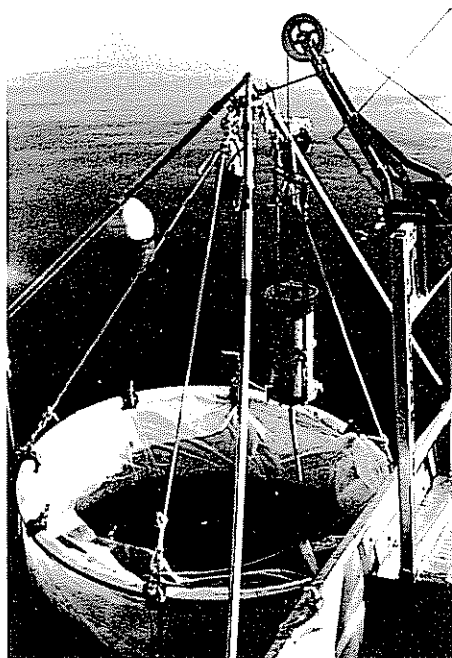


Figure 1
Culture units for in situ lake experiments.

Results and Discussion

The responses of the two lakes to the addition of Fe (III) and/or NTA was different (Figures 2 and 3). The addition of NTA, of Fe (III) or of both chemicals raises the productivity in Lake Lucerne but depresses the productivity in Greifensee.

In either case alterations in productivity and in biomass were transient. Iron does not appear to act as a growth limiting factor; for example, in Greifensee where the need for Fe must be larger than in Lake Lucerne because of six times larger biomass, the addition of Fe (III) decreases productivity. Fe (III) and/or NTA appear to affect the growth response of phytoplankton by altering the entire interdependent complex system of trace metals and inorganic and organic ligands. NTA is not capable of keeping Fe (III) entirely in solution. The dispersed Fe(OH)₃ or FeOOH acts as a cation exchanger, especially in solutions above pH=7. Hence addition of Fe (III), or NTA, or of both chemicals may cause the tying up (adsorption on complex formation, respectively) of some trace metals such as Cu (II) (Stumm 72) thereby either reducing the availability of an essential trace metal or reducing the concentration of a possibly inhibiting metal species. The different responses of the waters of the two lakes may perhaps be explained by such an argument. In an oligotrophic or mesotrophic lake, the addition of complexing agents may enhance temporarily photosynthesis because the concentration of some inhibiting metal ions may be reduced; in eutrophic lakes (e.g. Greifensee) on the other hand, where metal ions are to a larger extent complex bound than in less productive waters, addition of

	Lake Lucerne	Greifensee
PO ₄ -P	2 µg/l	50 µg/l
Total P	22 µg/l	600 µg/l
NO ₃ -N	130 µg/l	500 µg/l
NH ₄ -N	10 µg/l	300 µg/l
Total N	220 µg/l	1700 µg/l
Oxygen content	12 mg/l	10 mg/l
Alkalinity	1.7 equiv./l	3.7 equiv./l
Total Fe	25 µg/l	45 µg/l
Total Cu	10 µg/l	10 µg/l
Total Zn	8 µg/l	18 µg/l
Total org. C in filtered water	0.8 mg/l	5 mg/l
Visibility depth	4.6 m	1.2 m

complexing agents may tend to reduce the availability of some essential trace elements and thus mitigate the growth of phytoplankton. There was no significant change in the groupings of algal species within any of the brief 3-week test periods.

We may thus conclude that iron does not function as a limiting element in mesotrophic and eutrophic lakes. Similar to NTA, iron changes the complex chemistry of trace metals.

The use of P-free builders to replace polyphosphates in washing-products would effectively and rapidly reduce the pollution load in our lakes. Other investigations, reported by Little, indicate that NTA causes no acute or chronic toxicity effects. From a limnological point of view there are little objections to the use of NTA as a substitute.

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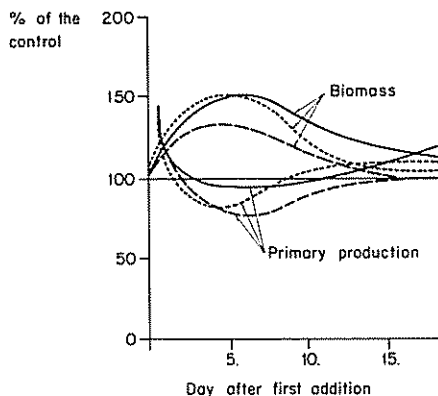


Figure 2
Lake Lucerne. Response of Phytoplankton to the addition of

- NTA + Fe (III)
- - - Fe (III)
- NTA

Experiments carried out in 7000 liter culture units during the summer. Mean for each separate addition for the three experiments.

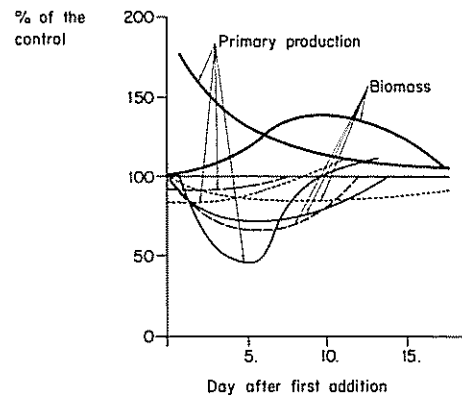


Figure 3
Greifensee. Response of Phytoplankton to the addition of the reagents

- March to April 1972
- - - June to July 1971
- August to September 1971
- October to November 1971 (overturn)

Mean of all reagents per experiment as the iron-curve runs parallel to the respective curves NTA and combined NTA + Fe (III), but shows variability with time.

Yuan-Hui Li and Peter Erni Calculate Erosion Rates in the Drainage Area of the Rhein River

Using factor analysis techniques and geochemical mass balance calculations, Li and Erni have shown on the basis of chemical data of the International Commission for the Protection of the Rhein against Pollution that the chemical composition of the Rhein water is mainly controlled by (1) the ion inputs from the dissolution of rocksalt, carbonate rocks and anhydrite, and $\text{NO}_3^- + \text{NH}_4^+$ from fertilizer and sewage, and (2) its subsequent modification by calcite buffering of

$[\text{Ca}^{2+}]$ and $[\text{HCO}_3^-]$, the seasonal biological uptake and release of NO_3^- and SiO_2 and the *in situ* formation of chlorite and hydroxyapatite in the rivers.

The total *chemical denudation* rates are quite similar in the various tributary drainage areas of the Rhein (range from 10-30 mg/cm^2 year) and average about 18 mg/cm^2 yr^{-1} . They are about 3-10 times the world average, on the other hand, the *mechanical denudation* rate in

the alpine Rhein area is exceedingly high ($\sim 115 \text{ mg}/\text{cm}^2$ yr^{-1}) as compared to that in the Rhein drainage areas below the Swiss lakes (3 mg/cm^2 yr^{-1}). Most of the detrital materials from the Alpine area were deposited in the Swiss lakes.

A detailed publication by Li and Erni on "The Factor Analysis and Geochemical Mass Balance of the Rhein and Upper Rhone Rivers" is forthcoming.

Petroleum-derived and Indigenous Hydrocarbons in Recent Sediments of Lake Zug, Switzerland (summary)

Walter Giger, Martin Reinhard, Christian Schaffner and Werner Stumm

Hydrocarbons of recent sediments of Lake Zug have been analyzed by infrared spectroscopy and gas chromatography. Samples of the sediment surface were taken at six locations near the shores in water depths varying from 2 to 9 meters. The amounts of the total extractable hydrocarbons were determined by IR-spectroscopy according to a modified API method. Gas chromatography was performed on glass capillary columns.

The gas chromatograms of samples collected near the densely populated northern shore show a continuous distribution curve of n-alkanes in the range of $n=10-24$, indicating a high content

(160-590 mg per 1000 g wet sediment) of petroleum and petroleum products. n-C₁₇ the main component in biogenic hydrocarbon mixtures is often found to be more abundant than the adjacent straight chain hydrocarbons. This fact is explained by a superposition of indigenous and polluting hydrocarbons.

The isoprenoids pristane (C₂₀) and phytane (C₂₁) which are major constituents of many crude oils are found in high abundance near the urbanized northern shore, whereas in the sediments adjacent to the less populated areas they are absent or present only in trace amounts. In the unpolluted areas the hydrocarbons

found (15-85 mg per 1000 g wet sediment) are produced by algae and other photosynthetic organisms. Near the mouth of River Lorze a remarkable increase in the concentration of odd numbered n-alkanes C₂₃, C₂₅ and C₂₇ is observed, which is also a typical feature of terrestrial plants. The n-C₁₇/pristane ratio of samples from the northern shore varies from 2.8 to 1. This may be attributed either to different sources or to different degrees of biodegradation of the fossil oils. The pristane/phytane ratio however remains close to unity. Studies are planned to evaluate the biological effects to this pollution (Figure 4).

Trace Analysis of Organic Compounds in Water Using a Gas Chromatograph/Mass Spectrometer/Computer System

by Martin Reinhard

Recognizing the international scope of environmental pollution by persistent organic contaminants produced by industrial activity, the European Economic Community and associated states have established an administrative program to coordinate and to accelerate research work on the analysis of organic micropollutants in the environment. Such critical analytical steps as enrichment, separation, detection, identification and computer data processing are being studied and information is exchanged between collaborating institutions. The EAWAG is the Swiss member of this program.

The most promising tool for qualitative and quantitative analysis of micropollutants is the GC/MS combination with a computer data processing system. This combination overcomes many of the limitations of the gas chromatographic technique allowing an identification of individual compounds in terms of mass spectra.

By single or multiple peak monitoring, a detection of specific compounds or specific classes of compounds in the picogram range is possible even if two or more

constituents are present in one GC peak. Thus tedious physical and chemical pre-separations can be avoided. At the EAWAG, a Finnigan 1015 D GC/MS system with the interacting data system 6000 is used for micropollutant analysis.

One example of the application of this instrument, which has recently been tested in our laboratories, is the identification of chlorinated hydrocarbons, that may be partially removed by adsorption on activated carbon during water treatment of surface waters.

Samples of carbon have been collected from a water treatment plant and the organic compounds extracted after freeze drying with pentene.

Figure 5 shows the reconstructed gas chromatogram of this extract. The total ion current is plotted on the ordinate and the scan number (2 seconds per scan) on the abscissa. To determine the types of compounds present in a GC peak, one asks the computer to plot the spectra found in the corresponding peak. A more elegant and sensitive way to search for specific compounds is to plot separate limited

mass range chromatograms of fragments that are primarily sensitive for the types of compounds of interest. This is especially useful in the analysis of very complex mixtures of oil and polychlorinated aromatics.

Figure 6 shows a limited mass range plot for m/e 143-147 which is primarily characteristic of poly-chlorinated benzenes. The mass spectra of the positional isomers are difficult to distinguish so that positive identification must be confirmed by comparison of the retention time with reference compounds.

GC peaks of paraffin type hydrocarbons, of substituted benzenes and naphthalenes are accentuated LMR plots with m/e 43, 91 and 141 respectively.

Comparison of the various hydrocarbons present in the activated carbon extract with diesel fuel revealed close similarities. This could be easily shown by the specific gas chromatograms. However, the unused charcoal also provided hydrocarbons of similar composition so that no definite conclusions can be made about their origin. For tracing oil pollution, the technique of fingerprinting will be refined.

Professor Dennis Meadows spoke at the EAWAG Seminar

EAWAG, Direction and Heads of Sections

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Ph. D. in Chemistry, University of Zurich
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1956-1970
on faculty of Harvard University (Gordon McKay Professor of Applied Chemistry)

Since 1970
Professor and Director of EAWAG, Swiss Federal Institute of Technology, Zurich

Author of "Aquatic Chemistry" (with J.J. Morgan, Wiley Interscience 1970).

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Deputy Director
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1963
Diploma in Mechanical Engineering, Swiss Federal Institute of Technology, Zurich

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Since 1969
EAWAG. Head of the WHO International Reference Centre for Wastes Management

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Diploma in Biology, Swiss Federal Institute of Technology, Zurich

1937
Dr. sc. nat. (Swiss Federal Institute of Technology, Zurich)

1938-1939
Institute for General Botany, Swiss Federal Institute of Technology, Zurich

1939-1945
Federal Materials Testing Institute, St. Gall; organization and direction of the laboratory for biological testing methods

Since 1945
EAWAG, Head of the Biology Section

Professor for microbiology, mainly for water supply and wastewater purification at the Swiss Federal Institute of Technology;

Guest lectures; research, especially in microbial ecology, microbiology applied to water and wastewater treatment processes; ecology of running waters.

The co-author of the Club of Rome Report by an MIT-Group "The Limits to Growth" spoke at the EAWAG on the application of the methodology of the MIT study to water resources management.

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1947–1951
General construction engineering at a consulting office in Lenzburg

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Design of sewerage systems and water purification plants at an engineering office in Zurich

Since 1961
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Head of the Section (ad interim)

Studies and reports on problems of sewerage and water purification; courses at the Technical Training College, Zurich; author of the textbook "Abwasser"

Limnology
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Solid Wastes
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Radioactivity
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After immigration to Switzerland specialization in radiochemical methodology.

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Control of radioactivity in water and in the food chain.

Systems Sciences
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Dr. sc. techn. (Swiss Federal Institute of Technology, Zurich)

1961–1964
Postdoctoral Research Biochemist, University of California, Berkeley, USA

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(December 1972–August 1973)

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Munz, W.: Entlastungskonzeptionen im Mischsystem. "gwf"-wasser (1973).

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