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Microbial Competition in Biofilms

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1. Biofilms in waste water treatment

Biomass which grows in a thin layer on a solid surface is called biofilm. Such growth occurs in lakes and rivers as well as in some biological waste water treatment systems. For example, in a trickling filter, where waste water percolates over rock-media a biofilm will develop within a few days. Microorganisms grow on the solid surfaces, they utilize organic material for growth and thereby eliminate these pollutants from waste water.

In fixed film reactors the biomass adheres to a solid surface whereas in systems with suspended biomass, microorganisms are kept in free suspension by continuous turbulence. An example of the latter is the activated sludge process. Systems containing suspended biomass are complex, since the biomass must be kept from settling, microorganisms must be efficiently separated from the treated waste water and a portion of the biomass must be recycled to the reactor. This complexity of the activated sludge process has the advantage that the process may be controlled by different strategies and therefore optimisation of the treatment plant operation is possible. Such optimisations are frequently based on mathematical models which have been developed since about 1965. These models have today reached a significant level and will definitely be applied more frequently in the future.

Before such models can be routinely used for biofilm systems, many fundamental questions with regard to the structure and the performance of fixed biomass must be answered empirically, such as, what are the characteristics of a biofilm which develops in a waste water containing nutrients suitable for growth of a variety of organisms? How do fast- and slow-growing organisms compete for space in a biofilm? What happens if two species compete for a common nutrient? Why do major pieces of biofilm periodically slough from their support? All these questions could of course best be answered with the aid of specifically designed experiments.

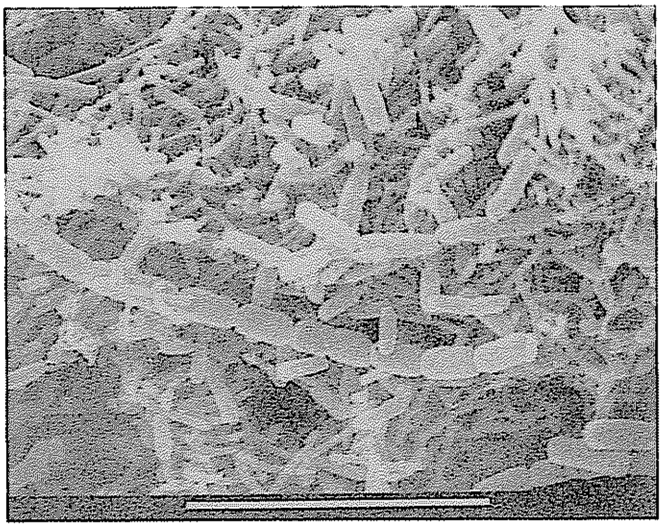


Fig. 1
Biofilm as shown by a scanning electron microscope [1] (Bar = 10 µm).

2. Experimental investigations are difficult

The amount of nutrients removed from the water or the thickness of a biofilm may be easily determined. Observation of processes within biofilms is almost impossible. Typical biofilms are only a fraction of a millimeter thick, and conditions may drastically change over this short distance. Microorganisms deeply inbedded in a film may lack important nutrients since these have already been consumed by organisms closer to the water. As such, it is insufficient to characterize the relative abundance of different species within the biomass and it is necessary to obtain information on their spatial distribution. With the aid of an electron microscope this may be possible (Fig. 1), however the sample is drastically perturbed in preparation and any information gained applies only to one instantaneous moment in time, and information on the distribution of the nutrients cannot be obtained.

Microelectrodes have been used with limited success to obtain profiles of nutrient concentrations within a biofilm. The traditional approach in biofilm research is based on macroscopic observation of biofilm behaviour. Such experimental procedures do not destroy the biofilm, neither do they provide direct evaluation of the situation within the biomass. Such evidence may be obtained indirectly with the aid of mathematical models. At EAWAG a range of experimental biofilm projects have been conducted on the laboratory- [1] as well as in pilot-scale [2,3]. Still, many questions remain unanswered.

In summary: Since microorganisms and nutrients interact, these must be observed simultaneously during experimental investigations of biofilms. It is important to obtain information on temporal and spatial changes. Direct observation of these variables is rarely possible.

In view of this situation, a major project which approaches biofilms with the aid of methods of system analysis was started at EAWAG. In close collaboration between process and informatics engineers our conception of the processes in the interior of a biofilm was developed and then translated into a mathematical form.

3. A mathematical model of microbial competition in biofilms

Fig. 2 visualizes our concept of biofilm growth. In mathematical form this concept may be expressed as:

$$\frac{dL}{dt} = u_L = \int_0^L \bar{\mu}\, dz \qquad \text{with } \bar{\mu} = \sum_{i=1}^{n} \mu_i f_i \qquad \mathbf{1}$$

These equations relate the velocity of biofilm expansion u_L to the mean specific growth rate $\bar{\mu}$, which depends on the specific growth rates μ_i and the volume fractions f_i of all n microbial species present in the film.

Whereas equation (1) establishes a relation between volume expansion and production of biomass, it does not describe the changes in microbial species in the biofilm in time and space. Therefore, additional equations have been developed:

$$\frac{\partial f_i}{\partial t} = (\mu_i - \bar{\mu})\, f_i - u \frac{\partial f_i}{\partial z} \qquad \mathbf{2}$$

This equation describes how the volume fraction f_i of the entire biomass of a microbial species i will change with time and space. The change of f_i with time depends on the relation of the growth rate μ_i of species i to the mean growth rate $\bar{\mu}$ of the entire biomass. It also depends on the velocity u at which the biomass expands at the specific location z and on the spatial change of f_i over the depth of the biofilm.

Equations **1** and **2** describe in general form the growth and and distribution of the microorganisms in a biofilm, such that the derivation of the equations does not depend on a specific reactor configuration or group of microbial species. Therefore the equations apply to any problem, their application requires only that the hydraulic and geometric parameters of the reactor as well as the laws that govern the growth and activities of the organisms are known. All of the known models of microbial distribution in biofilms describe special cases or approximate solutions to the equations presented here.

A further reason for the general validity of eqns. **1** and **2** stems from the fact that their derivation [4] relies only on a few very basic physical principles (mass balances). Therefore equations have been developed for microorganisms, which are equivalent to those which describe transport and consumption of nutrients in biofilms (based upon Fick's law). The latter have been known for many years [5] and are generally accepted. Together with eqns. **1** and **2** they estabtablish a comprehensive mathematical model of microbial competition in biofilms. The model may help to further our knowledge of processes deep within a biofilm, to identify the factors responsible for biofilm behaviour and to assess non-measurable variables by indirect experiments.

To describe a specific situation, numerical solution to the model is in practice only possible with the aid of computers. Fig. 3 which originates from a recently published report [4], illustrates the result of such calculations. This figure describes a freely growing biofilm with three different microbial species. Initially the thickness of the biofilm increases exponentially. After three days increase slows down due to nutrient deprivation deep within the film. With time, the increase in biofilm thickness approaches a constant value, controlled by the difference between the rates of growth and decay of the organisms.

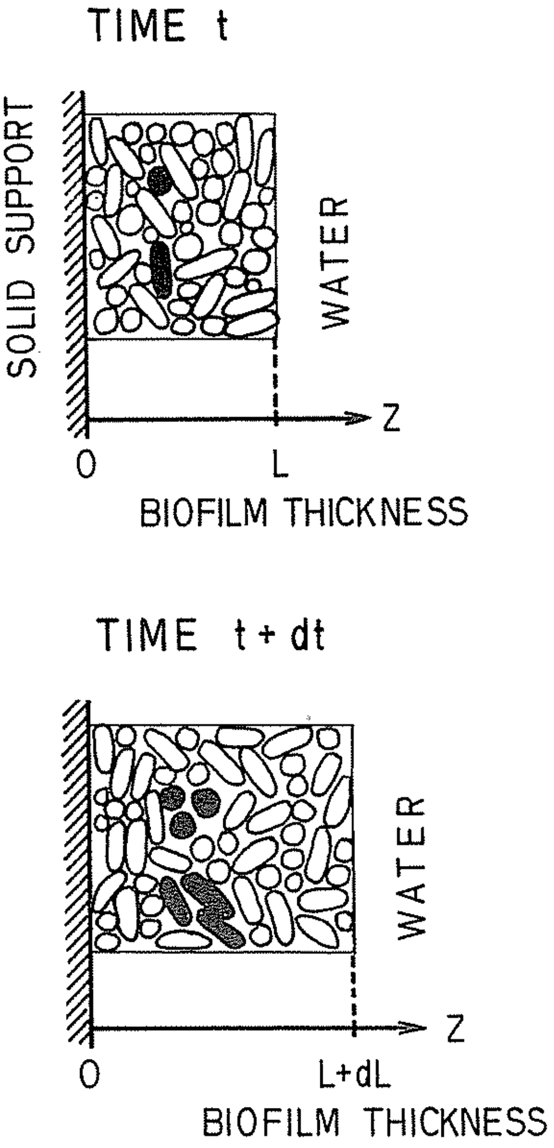


Fig. 2
Schematic representation of biofilm growth. During the time interval dt individual organisms grow and divide and thereby displace their neighbours: Biofilm thickness L increases by dL.

4. Mechanisms of biomass regeneration

If the water contains significant amounts of nutrients, as is typical for waste water, the biofilm would, according to Fig. 3, expand continuously. Therefore mechanisms must exist to limit biofilm growth. The shearing force exerted by the water flowing over a biofilm may continuously erode biomass from

the surface of the film or alternatively processes that occur in the depth of a biofilm may lead to the detachment of large pieces of biomass. In fact both mechanisms are known to occur and treated waste water contains significant amounts of microorganisms which originate from the biofilm.
With the aid of this model, these mechanisms may now be analysed in more detail. Fig. 4 indicates the result of such an analysis. On the left a case is presented where microorganisms continuously erode from the surface. After about 10 days an equilibrium is reached between erosion and production of biomass; biofilm thickness remains practically constant. The same applies to biofilm performance, i. e. the amount of nutrients which is removed from the water per unit surface area and per unit time. On the right, a case is presented where after 6.5 days a significant fraction of the biofilm is suddenly lost by sloughing. In this case no equilibrium is reached. If it is assumed that sloughing occurs periodically at different positions on a biofilm, a mean performance (nutrient removal rate) may be predicted (Fig. 4). The comparison of the different nutrient removal rates in the two cases indicates that biofilm performance depends strongly on the mechanisms governing the detachment of biomass from the biofilm. This is caused by the fact that the organisms differ significantly in their spatial distribution over the depth of the film and therefore they are affected in different ways by detachment processes. The model predicts that the mechanisms which control biomass regeneration and detachment are of utmost importance to the rate of nutrient removal – the ultimate goal of biofilm application in practice. The consequence of this prediction is that causes and mechanisms of biomass detachment should now be investigated with the aid of specifically designed experiments.

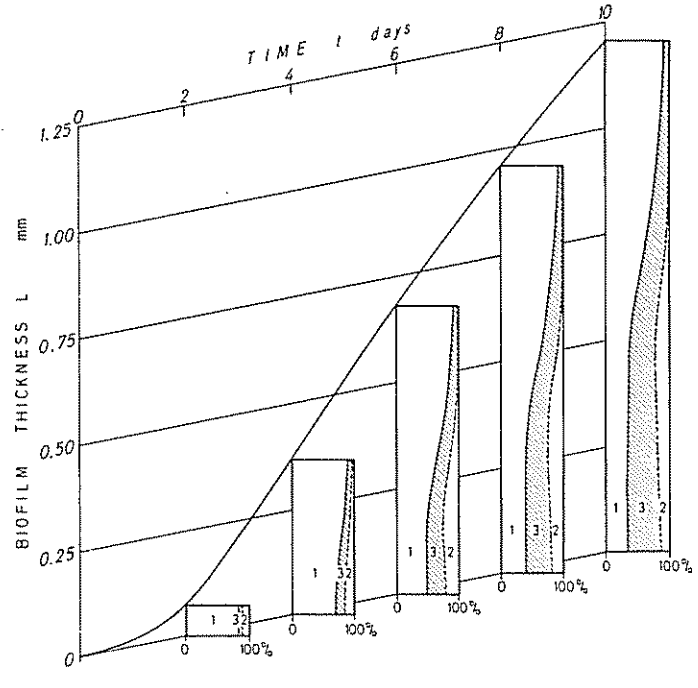
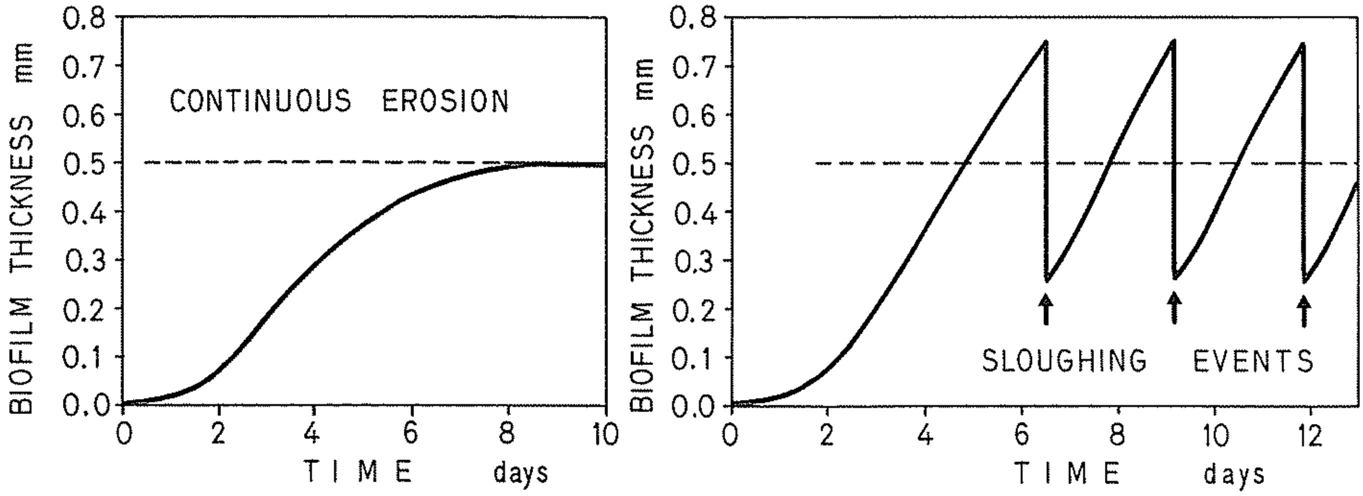


Fig. 3
Temporal development of biofilm thickness L and volume fraction f_i (0–100 %) of different microbial species. The example shows the relative abundance of heterotrophic (1), autotrophic (2) and inert particulate mass in a nitrifying biofilm between the biofilm's solid support (at the bottom of the figure) and the film-water interface [4].

Fig. 4
Variation of biofilm thickness with time. Left: Assuming loss of biomass due to a continuous erosion at the biofilm surface. Right: Assuming sequential sloughing events. Removal efficiencies on top are valid for steady state (left) or averaged over one period between two sloughing events. The biofilm contains heterotrophic as well as autotrophic organisms [4].

REMOVAL EFFICIENCY OF A BIOFILM in g $m^{-2} d^{-1}$:

	AT STEADY STATE	MEAN VALUE
ORGANIC COMPOUNDS COD	1.33	1.75
AMMONIUM	2.33	1.73
OXYGEN	11.01	8.75



5. May the model be applied in practice?

Our knowledge on the processes controlling the behaviour of fixed biomass is still limited. Further studies, similar to the one just presented, are necessary to improve our understanding of the processes occurring in the depth of the biofilm. With the aid of this model it is now possible to define experiments and analyse data in view of the complex behaviour of biofilm systems. The direct application of the model towards reactor systems and process optimisation and design is not yet feasible. First steps in this direction have been made [6]. However, they serve only to illustrate the purpose rather than to define a final approach. Despite the many unanswered questions, this model shows that mathematical simulation of biofilm behaviour is possible and points towards new areas of biofilm research.

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The Authors

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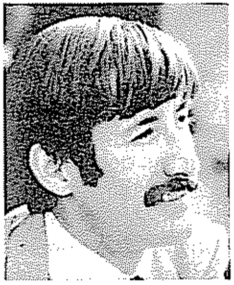

Dr. Oskar Wanner is a mechanical engineer specialising in system analysis and numerical mathematics. He worked several years at the Institute for Molecular Biology and Biophysics of the ETHZ, where he received his Ph.D. degree in Natural Sciences for the experimental and mathematical analysis of a hormone regulation system. Since joining the EAWAG in 1979 he has been doing interdisciplinary research in various fields. These include river quality modeling, the transport of chemicals in groundwater, and waste water treatment using fixed biomass.

The Artificial Rivers of EAWAG's Experiment Station Tüffenwies in Zurich

Elie Eichenberger

1. Introduction

In an early phase of the development of pollution control in Switzerland it was recognized that in order to effectively protect rivers the rational design of sewage treatment plants required additional knowledge on the following questions:

- what is the effect of untreated sewage on the biotic communities in rivers?
- to what extent do various treatment procedures modify the effect of sewage?
- which parameters do best characterize the biological effects of sewage?

For obvious reasons the answers to these questions were hard to get from the study of natural rivers. Therefore, in 1936 the first generation of "artificial rivers" was built at the sewage treatment plant of the town of Zurich [1]. The channels were later moved to the new research station Tüffenwies of EAWAG and extendend.

2. The artificial rivers

Artificial rivers are designed to offer advantages such as

- simplification of the structure of the running water ecosystem,
- manipulation and stabilisation of the chemical input and of some of the physical conditions,
- favorable conditions for measurements and good access to the working sites.

The primary aim of the construction of the experimental channels in Zurich was not the simulation of a particular natural river, but the establishment of an experimental system suited to the study of some deliberatly chosen and structurally or ecologically essential aspects of the smaller rivers typical of the Swiss Central Plateau.

The Tüffenwies rivers were conceived as outdoor throughflow systems. They are located on the outskirts of Zurich on

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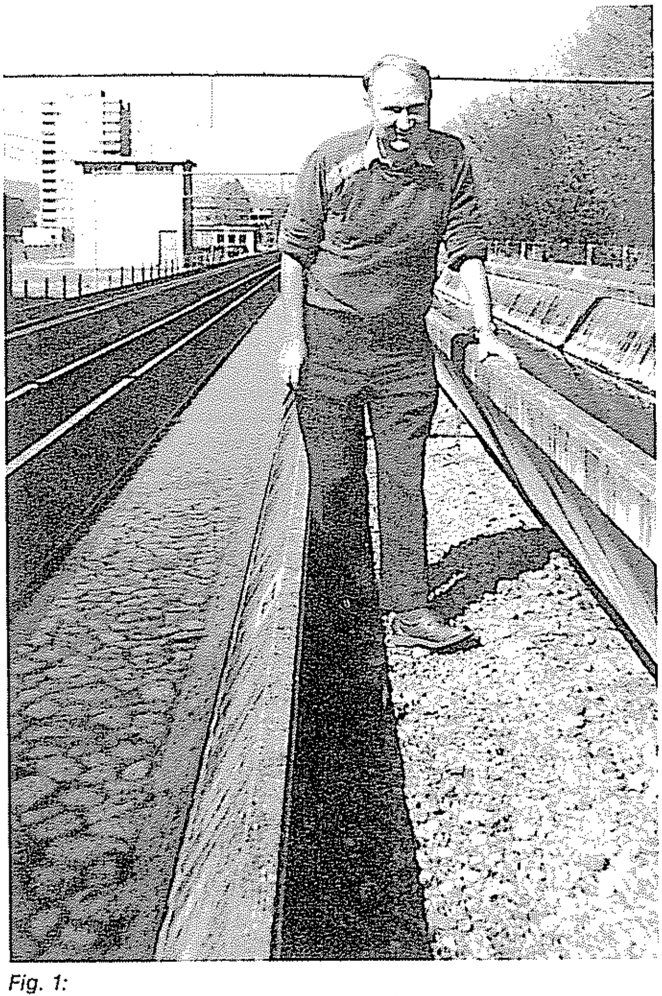

Fig. 1:
View of the artificial rivers in Tüffenwies

the outflow of the lake of Zurich (the river Limmat) and the main sewer of the town. As they also lie above the aquifer which supplies the town with drinking water, both artificial river systems – a small one for short term experiments, and a large one for the study of longer term successions (Table 1 and Fig. 1) – can draw their water from these three sources. Additional dosing of sewage and chemicals allows further manipulation of the water quality. The systems are usually run with groundwater thereby providing a carrier water without any physico-chemical daily variations at the point of inflow.

Table 1:
The river systems of EAWAG's experiment station, Tüffenwies

channel type	no	length m	profile cm	flow l/sec	arrangement¹⁾ m
small	9	75	rectangular 20 x 20	1–2	9 x 75 or 1 x 675
large	6	250	trapezoid 95/45 45 deep	<100	1 x 250 and 1 x 1250 2 x 250 and 2 x 750 250, 500, and 750

¹) this gives the possible combination of channels to rivers

However, seasonal fluctuations in water temperature and some chemical parameters are quite pronounced (Fig. 2). The shift of the water temperature amplitude with respect to the neighboring surface waters corresponds to about 2–3 months, with a minimum in April around 8° C and a maximum in October of around 17° C.

3. Some of the research topics past and present

In response to the practical needs for pollution control the effect of sewage on the microbial and microphytic benthos has been the central theme of the studies at the experiment station Tüffenwies. These studies have emphasized two aspects of the impact of the aquatic environment on the benthic communities, i.e. the chemical quality of the water, particularly its nutrient function, and the physical aspect, especially the role of the seasons and of the water flow.
Table 2 lists some of the topics studied and publications relating to them. In the following sections some aspects of these river studies will be presented in more detail.

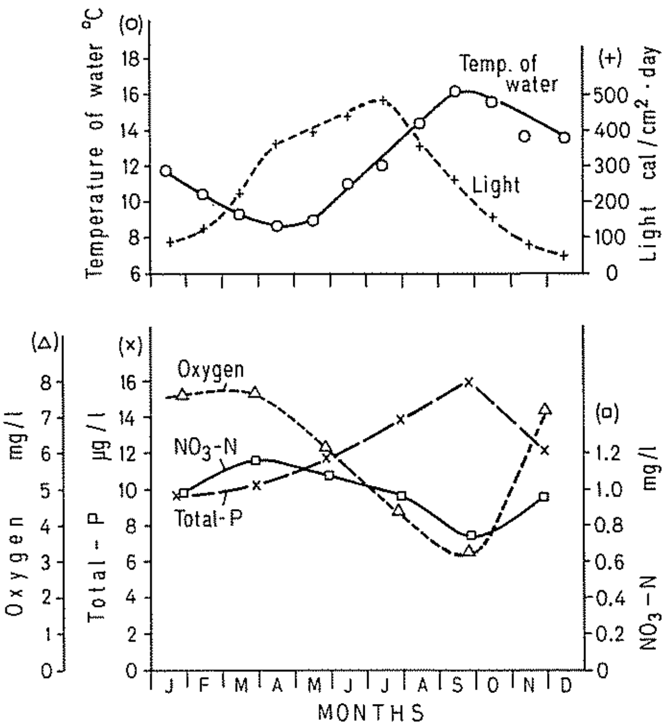

Fig. 2:
Yearly periodicity of some physical and chemical parameters of the groundwater in Tüffenwies fed into the channels (average of the years 1982–84)

3.1. Parameters used to characterize the activities of benthic communities

The description of benthic communities calls for an estimate of the number of organisms present and their biomass as well as for an appreciation of the contribution of characteristic groups of organisms, for example phototrophs and heterotrophs, to the overall physiology of the ecosystem. Number and mass have to be correlated to activities such as the incorporation of nutrients, photosynthesis, respiration, excretion and decomposition rates. Such information then provides a basis for an estimate of the exchange of nutrients between the organisms and their surrounding medium and the intensity of biologically induced changes on water chemistry.
The choice of parameters to describe a system is a function

Table 2:
Some topics studied on the artificial rivers

Effect of sewage on benthos	**Reference**
– effect of sewage on the phototrophic and heterotrophic growth of benthos	2,3,4,5
– selfpurification in microphytic communities with different ratios of heterotrophs and phototrophs	6,17
– effect of variable input of organic nutrient	8
– effect of light on the growth of *Sphaerotilus natans*	9,10
Eutrophication	
– can P or N supply simulate the eutrophying effect of sewage?	11
– effect of metals on the development of microphytic benthos	11
– photosynthetic efficiency of benthos	12
– effect of sewage on the growth of *Ranunculus fluitans*	Table 3
Effect of current and flow	
– interaction between flow velocity and sewage effect	13
– interaction between flow velocity and selfpurification	7
– role of hydraulic stress and flow on the interaction of trophic levels	14
Significance of grazing for the development of benthic communities	
– grazing of midge larvae *(Orthocladinae)* on algal benthos	15
– the effect of insecticides on the interaction between trophic levels	15
– grazing of crustaceans *(Gammarus)* on higher plants *(Ranunculus fluitans)*	16
– significance of grazing for the long term succession of microphytic benthos	17

of a number of considerations. Limitation in manpower has been essential for our choice of techniques especially for the description of sociological structures. In order to characterize the communities and their activities the following types of parameters were used: sociological structure, productivity and nutrient dynamics (for examples see Fig. 3, 4, 5 and 6).

3.2. The significance of hydraulic stress for the development of benthic communities in a low nutrient water

a) The stages of benthic succession

Initially benthic river communities fed with groundwater developed along comparable lines in both river systems, the small and the large, by going through similar colonization cycles. These cycles are characterized by a vegetation build-up followed by more or less severe biomass reduction caused by the activity of grazers. When the channels are new and have been cleaned and cleared of all vegetation, floating algal mats are quickly established; they are dominated either by green filaments *(Hormidium, Tribonema)* or brown filaments (diatoms such as *Diatoma hiemale, Melosira varians)* depending on the season. After a few weeks' existence the vegetation is grazed away by the larvae of midges *(Orthocladines)*. In a second colonization stage mosses and algae more resistant to grazing become established *(Vaucheria, Cladophora, Spirogyra)*. The small channels get so clogged up by the plant masses that frequently they have to be cleared before this second stage of the succession is reached. In the large channels very dense algal and moss communities are built up and maintained for 3-4 years. Gradually more powerful grazers such as snails *(Limnaea)* and crustaceans *(Gammarus)* get so numerous that they finally destroy both the bulky floating and the attached vegetation. The succession ends in a very stable epilithic crusty community devoid of mosses and filamentous algae (Fig. 3).

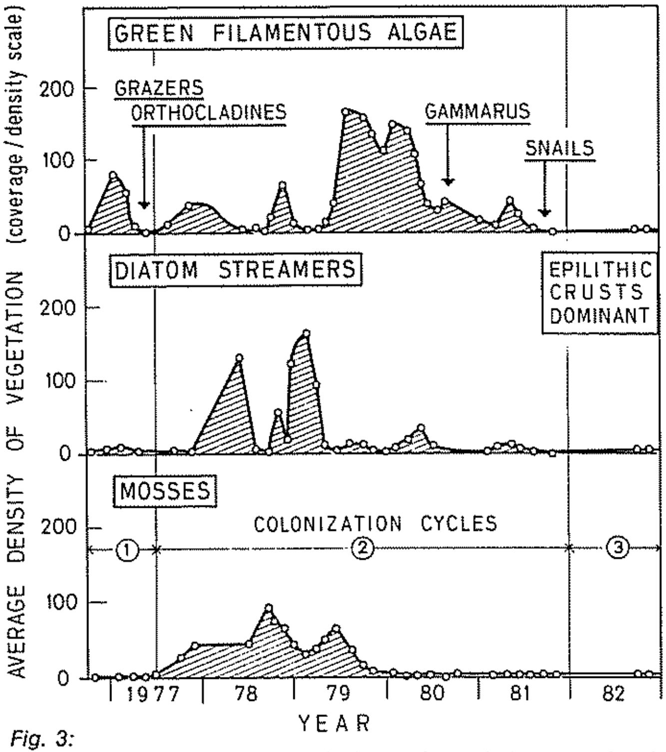

Fig. 3:
Time course of colonization of the large channels (average densities of the vegetation over the whole length of the channels). The average density is the product from coverage (0–100%) multiplied with the relative density of the growth form assessed (0–3), i.e. 0–300.

Although in this second, and long lasting colonization cycle the trend in the development in the different channels is similar, the structure of the communities shows considerable irregularities in the distribution of the organisms in time and along the length of the channels [17]. It appears that the lack of hydraulic stress, together with a reduced immigration rate causes a reduction of the competitive pressure on local colonization centers and thus tends to consolidate the stochastic distribution patterns generated in the initial settlements of animals and plants. The resulting mosaic-like distribution of organisms can be troublesome for those experiments where channels treated in different ways are compared with each other, as the reason for the different patterns may have to be attributed to chance alone.

b) The effect of variable discharge on colonization and succession

In nature variable discharge affects the interaction between plants and animals in various ways. An increase of flow may result in mechanical stress through abrasive actions of supended particles and the movement of the substrate. Depending on the depth of the bottom of the river and the presence of microhabitats resistant to displacement the chance for the survival of the macrofauna varies. The deposition of silt after a flood may bury organisms or reduce the exchange between organisms and their surrounding and will further affect the balance between the organisms of the different trophic levels i.e. producers, grazers and predators.

The consequences of mechanical stress on the development of the epilithic crust can be observed in the large channels when high flow is simulated by vigorously rolling the stones against each other. Filamentous algae may reappear after a short time. However, the success of such action is variable, suggesting that the process of recolonization depends on highly subtle biotic effects, including possible inhibitory exudates of the epilithon and grazing by microinvertebrates in the hydraulic boundary layer.

These observations in the large channels demonstrate the wide range in composition of biological communities that are possible under a clearly defined chemical condition, e.g. in low nutrient water, and they underline the central role of purely biological processes in the genesis of benthic communities.

3.3. The role of microphytic drift in the assessment of productivity of a river benthos.

The mechanical impact of current, grazers and burrowers continuously dislodges parts of the vegetation giving rise to microphytic drift or export. The quantitative measurement of microphytic drift presents a major technical problem. If we suppose that the export of a small channel with a surface of 15 m^2 corresponds to a production of 1 g dw/day m^2 (dw = dry weight), then the suspended biomass attains about 0.2 mg dw/l. As the drift has a pronounced diurnal activity, only collections over a 24 hour cycle can give a reliable estimate of the export. Therefore large volumes of water have to be filtered and as the biomass clogs the filters easily a considerable filter area is required. In our sampling station about 1000 l channel water are filtered daily, representing approximately 1% of the flow.

The microphytic drift is low when colonization starts. It increases fast and after a few weeks accounts for a large fraction of the total productivity (Fig. 4). Drift is considerably enhanced when senescence or reduced mass transport induces degradation of the benthos. Although always present, export becomes noticeable only when larger parts of the vegetation become detached.

The microphytic benthos has therefore only a limited residence time. When not consumed by grazers, it becomes pended drifting biomass, representing a riverplankton of benthic origin. The fraction of production remaining sessile as standing crop is a function of different factors, such as sociology, structure, age, nutrient supply and mechanical fac-

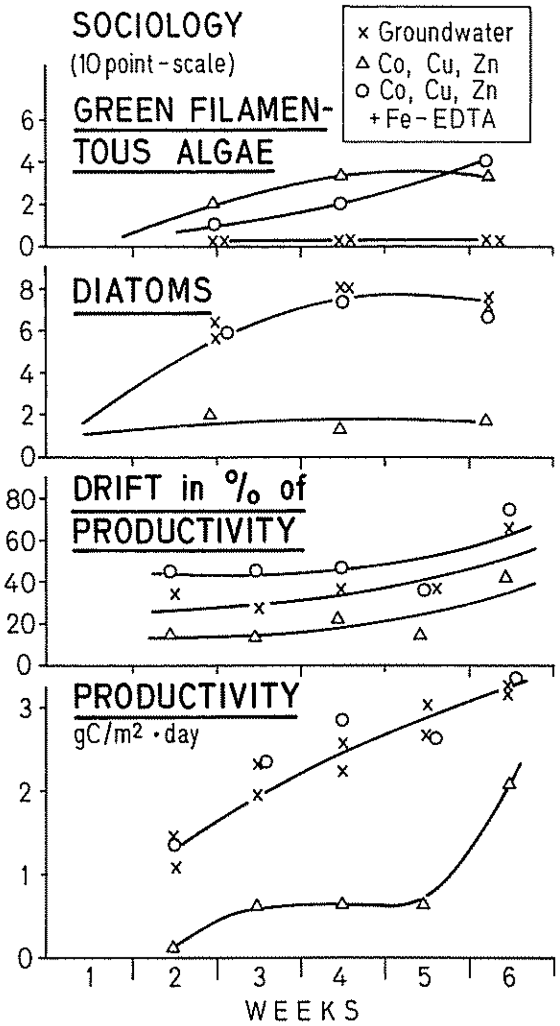

Fig. 4
Development of the benthic algae in the small channels after addition of essential heavy metals.
concentration of metals in µg/l (in groundwater): Co <2, Cu 2, Zn 3, Fe 10;
after metal addition: Co 50, Cu 20, Zn 200, Fe (as Fe-EDTA) 300

tors due to variable flow or animal activity. Changes in buoyancy caused by photosynthetic gas accumulation, for example, expose filamentous algae to stronger currents, contributing to a distinct daily periodicity of the drift of algal material (which may be easily detected by the color of the collection filters).

Determination of microphytic drift in channels run under the same hydraulic and chemical conditions is reproducible during the early stages of colonization (Fig. 4). This can be taken as confirmation that in initial phases of successions external and internal influences are very evenly distributed among the channels, in striking contrast with later development (as has been described for the large channels in section 3.2).

3.4. The role of chemical factors in eutrophication

Observations in our channels with turbulent flow have shown that addition of a few percent of domestic sewage to groundwater containing only 15 µg P/l significantly enhances the growth of algal communities. This increase in productivity and the simultanously occuring change in the sociological composition of the vegetation cannot be simulated by the addition of inorganic phosphorus alone, either at concentrations corresponding to the sewage input or higher (up to 300 µg P/l) [11]. However, mixtures of trace metals in very low concentrations or traces of iron at 300 µg/l alone or at 5.4 µmolar as Fe-EDTA may stimulate growth under certain conditions.

On the other hand the tolerance concentrations for the essential metals Co, Cu and Zn (50, 20, 200 µg/l or about 0.5 to 3 µmolar respectively) defined by the Swiss water protection law proved highly toxic to an algal benthos composed by streamer forming diatoms (e.g. *Diatoma hiemale)*. The addition of 5.4 µmolar Fe-EDTA, but not the corresponding concentration of EDTA alone, reverses this toxicity.

The data from these experiments are presented as an example of the response to chemical stress of different parameters characterizing a microphytic community. The mixture of essential trace metals Co, Cu and Zn or each metal alone at first completely suppresses the growth of diatoms typical for the season, so that initially no growth occurs. Instead, green filamentous algae become established and about a month after the start of the experiment they proliferate vigorously (Fig. 4).

The elimination of the nutrient N (from nitrate), P (from orthophosphate) and Si (from silicate) is clearly correlated with the productivity; the resulting ratios between the incorporation of carbon as determined from productivity and the uptake of the essential nutrients N, P and Si as determined by their elimination from the water are C/N 5.8, C/P 102,7 and C/Si 2.8, in molar units respectively (Fig. 5).

This experiment demonstrates some of the interactions between metals and some of the limits in predicting the biological reactions of the benthos with respect to metal pollution. *Ranunculus fluitans*, a higher vascular plant, the growth of which is causing much nuisance in European rivers, responds to domestic sewage by increased growth. But as with the algal communities studied so far in Tüffenwies its growth is not unequivocally stimulated by increased concentrations of inorganic phosphorus from the naturally occuring 17 µg/l to about 300 µg/l (Tab. 3).

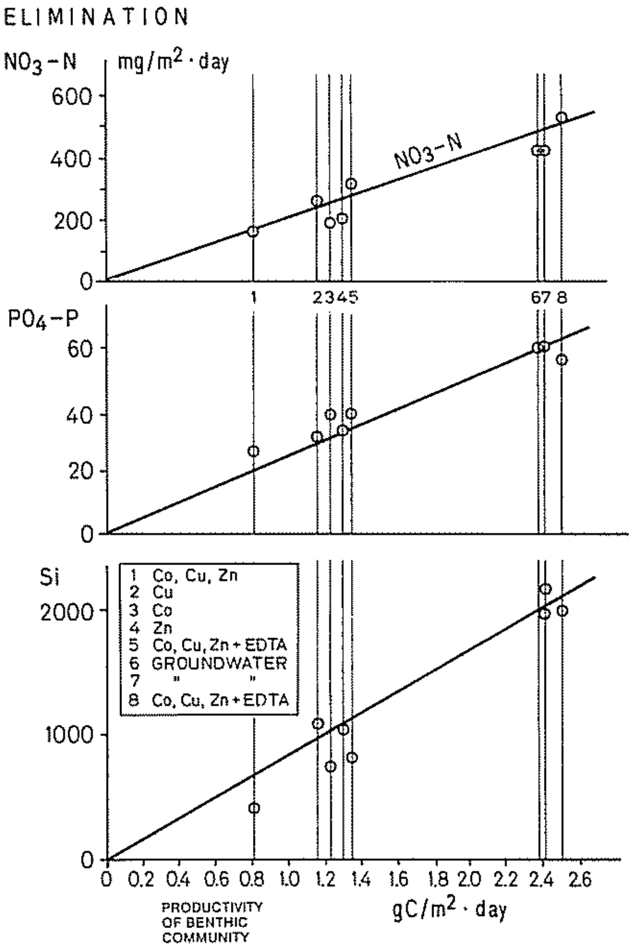

Fig. 5
Elimination of mineral nutrient ions (nitrate, orthophosphate and silicate) by the vegetation grown in various combinations of essential metals

Table 3:
The effect of sewage and phosphate on the growth of Ranunculus fluitans

	groundwater		PO_4-P	settled sewage		biologically treated sewage		
Channel	1	2	3	4	5	6	7	8
Substrate added								
- sewage								
a) settled				1%	1%			
b) biologically treated						5%	20%	50%
- PO_4-P (300 µg/l)			⊕		⊕			
Composition of river water								
DOC (mg/l)	0.4	0.3	0.4	1.4	1.2	1.0	1.7	4.4
PO_4-P (µg/l)	17	17	338	62	432	117	582	1643
Growth of plants								
average of 16 plants per channel								
initial fresh weight (g)	9.0	10.0	9.7	9.6	10.4	10.4	12.5	11.4
increase in fresh weight in 1 month (g)	6.5	5.0	8.0	22.2	27.9	32.8	48.0	38.0

On the basis of the observations in our channels we feel that the mechanism for eutrophication in rivers is far from being clearly understood. It cannot be explained as a direct reaction to one key nutrient alone.

3.5. Repression of benthic growth by grazing and its possible role in eutrophication

The contribution of the grazers in limiting the development of the benthos can be seen in the general succession of algal communities which is characterized by the transition from a vegetation composed of lush filamentous streamers to a rather inconspicuous epilithic community (described in section 3.2).
Therefore, it is not surprising that rivers subjected to grazing pressure respond to the application of insecticides by very fast resumption of algal growth [15].
It is possible to eliminate the grazers established in a large channel by leaving it dry for 2 weeks. After reflooding, a cover of floating algal streamers and mosses is quickly reestablished. This type of vegetation has been excluded from the channels several years earlier by the gradually increasing grazing pressure [14].
These findings in the channels suggest that the balance between grazers and plants is a major factor controlling the structure of benthic communities in natural rivers. Interference with the activity or the population dynamics of grazers can cause a proliferation of algal and macrophytic stands. Sewage is a stress factor which effects the interaction between trophic levels. It is tempting to speculate that the reduction of grazing pressure by the action of sewage may cause increased algal production and thus be at the root of local eutrophication symptoms.

3.6. Chemoperiodicity in rivers

A number of physiological processes going on in rivers follows a daily periodicity which depends either on natural variations of limiting physico-chemical factors such as light and temperature or on some variable input from the environment as a consequence of human activities.
In Fig. 6 the elimination of P_{total} along channel sections of 250 and 500 m length are displayed for two different days, one in December and the other in June. The channels received 1% of settled sewage. The concentration of P shows a pronounced daily periodicity with lowest values around 4 a.m., and maxima around noon between 80 and 180 µg P/l. The P-balance along the channels varies between elimination in June and a transition from elimination to release of P from the system into the water in December. This suggests that different processes go on simultaneoulsy which affect the P balance and that their activity depends on the concentration of the P input. However, in addition, the processes are influenced by some other day/night cycle effects, so that at the same input-concentration the balance will depend on the time of day. This example demonstrates the simultaneous expression of 2 different sources of chemoperiodism, i.e. of external or internal origin to the system.
Of practical relevance is the question whether the biological effect of a given load of organic substrate depends on the timing of its input. This was investigated in channels fed with the same daily average of 1 mg sucrose-C/l, dosed either continually or during 12, 6 or 3 hours of each 24 hour cycle in double or correspondingly higher concentrations [8].
Judged from the first 75 m below the outfall, i.e. the channels' length, the growth of heterotrophs was less when the application was intermittent (Tab. 4). Presumably the losses of biomass during the starvation phase of increasing duration are responsible for the progressively smaller utilization of the substrate. The results might be different if the total length of the affected river sections could be taken into consideration. When less nutrient is used upstream, more is left

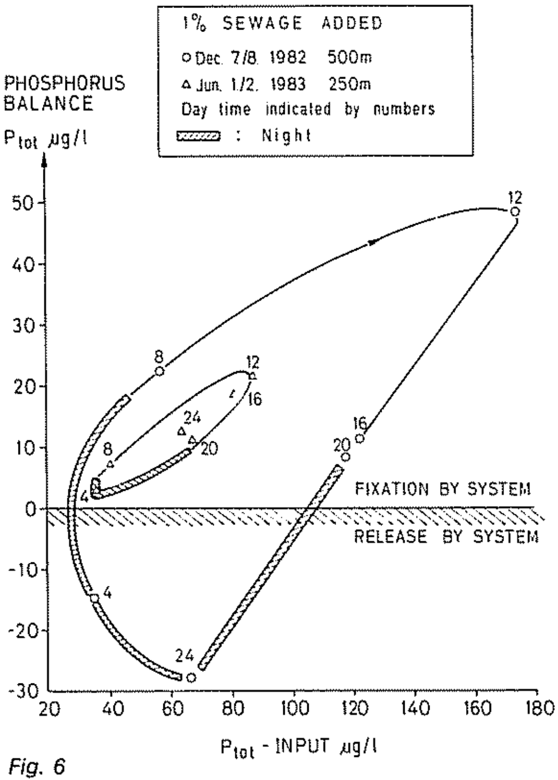

Fig. 6
Daily periodicity of the elimination of total phosphorus in the large channels

Table 4:
Effect of chemoperiodicity on the development of heterotrophic benthic biocenosis, when the same daily sucrose load of 86.4 g C/day/was applied.

channel	1	2	3	4
sucrose load (g C/day)	86.4	86.4	86.4	86.4
duration of dosing (hr/day)	24	12	6	3
concentration (mg C/l)	1	2	4	8
productivity[1]				
as standing crop increase	0.91	0.51	0.51	0.41
as drift	1.80	0.61	0.29	0.29
total	2.71	1.12	0.80	0.71
in %	100	41	30	26

[1] productivity expressed as average daily production over the length of the channel (75 m long) in g ash free biomass/m^2 day, data calculated from [8], p. 21.

to feed bacteria further downstream, in this particular case being outside the experimentally available space.

4. Other types of artificial rivers

The design of artificial rivers depends on what particular subsystem of the flowing water is intended to be studied. The target of our system was the benthos of smaller rivers as found in the Swiss Central Plateau. Other outdoor systems analyse the role of the suspended biomass in lowland rivers (System of Marienfeld in Berlin, 18), or the contribution both of the benthos and of the gravel river bottom (or subrheal) to the ecology of rivers (recirculating hard-water rivers in East Stoke, England, 19). As the supply of sufficient water of good quality represents a major limitation in the maintenance of artificial rivers they are frequently operated with recirculated water. In this respect the Zurich throughflow channels with a maximal flow of 100 l/sec are unique.

Some of the fundamental limitations in outdoor systems reside in the restricitions imposed on the manipulation of the composition of the biotic communities as well as some of physical factors such as light and especially temperature. This has called for the construction of laboratory streams [20] run at room temperature, or laboratory systems where the water temperature is controlled by heating and cooling (Rheodrom at EAWAG, [21]) or entirely located in climatized rooms (National Institute for Environmental Studies, Tsukuba, Japan).

The use of artificial outdoor river models is especially rewarding in close cooperation with a team of laboratory microbiologists. The study of the light inhibition of *Sphaerotilus natans* is in this respect an instructive example. In channels fed with a small addition of domestic sewage the first growth of *Sphaerotilus* prefered the wall side which was not exposed to the full afternoon-sun radiation and thus received a smaller light dose. Direct shading of the channels with wooden boards confirmed the inhibitory effect of sunlight. In vitro growth measurements of pure cultures in submerged vessels with breathing tubes demonstrated that the light effect directly affected the bacterium and was not the result of competition with other microphytes or grazers [10]. In the laboratory the effect of light of different wave-lengths on the growth of *Sphaerotilus* and on the medium was analysed [9] and it was shown that the inhibitory effect could be overcome by an adequate nutrient supply.

As a section of a natural river is an individual habitat and can not represent "the river", so are the different artificial rivers also unique and therefore embody some aspects found in natural rivers. The aspects considered essential in formulating research projects are themselves dependent on the progress of our knowledge and our expectations with respect to rivers. Future research on our Swiss rivers may pay more attention to the biotic interactions and the role of physical factors such as flow and temperature. This may call for more rigorous control of the environmental conditions and will probably result in the construction of more advanced river systems which will for practical and economic reasons be of smaller scale and supplement the possibilities offered by the existing systems.

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Structure and Properties of Coordination Compounds with Hydrous Surfaces: Spectroscopic Investigations

Herbert Motschi

Chemical reactions in natural waters tend to occur at the solid-solution interface. Particles of small colloidal size contribute the largest amount of active surface area. They may be either of biological or mineral origin. A typical perialpine Swiss lake contains on the order of 10^7 colloidal particles per ml of water. Nutrient rich lakes are loaded primarily with organic material, while processes such as mineralization and erosion increase the amount of inorganic material in suspension. Oxide minerals of Si, Al, Fe, Ti are abundant components of the earth's crust and are also found in and as atmospheric aerosols. If brough into contact with water, the oxide surfaces are transformed into hydrated oxides and/or hydroxides. Modification of the oxide minerals by the formation of surface functional groups provides an enormous potential for their adsorptive characteristics towards cations and anions, and for the processes of mineral weathering which constitute the main input of most elements into the hydrologic system. By settling processes, dissolved species are transported to the sediments dependent on the adsorptive characteristic. The distribution of a chemical species between the solution and solid phases can be treated mathematically as an equilibrium calculation of a multicomponent/multiphase system. Such a cycle is shown in a simplified lake box model for a metal ion (Fig. 1).

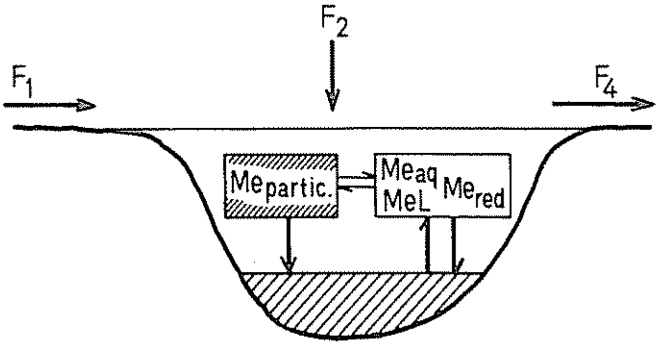

Fig. 1:
Distribution of metal cations in a lake.
F_1: Input from river inflow
F_2: Input from atmospheric precipitation
F_3: rate of sedimentation
F_4: river outflow
Metal ions are distributed between suspended particles and the dissolved state where they can undergo complex formation reactions (MeL) and redox reactions (Me_{red}). Reductive conditions in the hypolimnion can transport certain metal ions back into solution (e.g., $Fe(III)_{particulate} \rightarrow Fe(II)_{dissolved}$).

Functional groups on the surfaces of naturally occuring particles are normally of heterogeneous composition which limits their suitability as model surfaces. Hydrous oxides as well as organic polyelectrolytes have been thoroughly investigated for their adsorptive behavior towards metal cations [1–3]. Stumm and Schindler have outlined a thermodynamic model which takes into account the coordinative interactions of the surface hydroxyl functional group, i. e., the amphoteric nature against protons ($\equiv$MeOH can react as base and as acid, see reactions **1** und **2**) and the ambivalent characteristics towards protons and anions (reactions **3** and **4**). The acidity constants ($K^s_{a_1}$, $K^s_{a_2}$) can be derived from titration experiments as may be the stability constants of the surface complexes formed with metal cations and ligands ($K^*_{1_s}$ K^s_A). With this basic set of equilibria, adsorption isotherms can be formulated in a thermodynamically consistent fashion. Such equilibria are very sensitive to the nature of the surface as well as to the type of specifically sorbable metal cations and anions, suggestive of an inner-sphere binding (i. e., direct bonding) between surface and adsorbate.

Table 1:
Coordination reactions of the surface hydroxyle functional group ($\equiv$MeOH).

$$\equiv MeOH_2^+ \rightleftharpoons \equiv MeOH + H^+ \quad ; \quad K^s_{a_1} \qquad \mathbf{1}$$

$$\equiv MeOH \rightleftharpoons \equiv MeO^- + H^+ \quad ; \quad K^s_{a_2} \qquad \mathbf{2}$$

$$\equiv MeOH + M^{z+} \rightleftharpoons \equiv MeOM^{(z-1)+} + H^+ \quad ; \quad K^*_{1_s} \qquad \mathbf{3}$$

$$\equiv MeOH_2^+ + A^{z-} \rightleftharpoons \equiv MeA^{(z-1)-} + H_2O \quad ; \quad K^s_A \qquad \mathbf{4}$$

However, there is a number of consistent models which place the emphasis on the interaction of the electric field gradient at a charged surface with the dipolar moment of the adjacent water layer (Fig. 2).

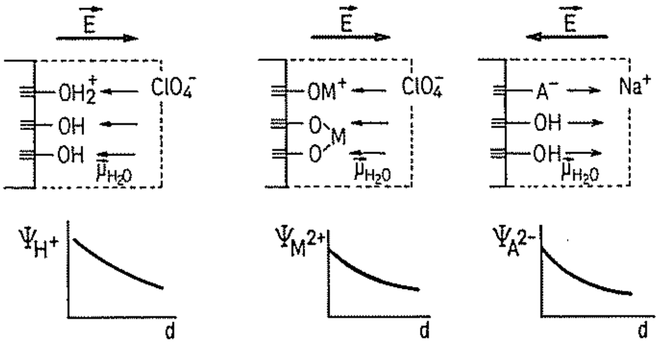

Fig. 2:
Electrical double layer.
Specific adsorption of potential determining ions (H^+, OH^-, metal cations (M^{2+}), and anions (A^{2-})) induces a field gradient at the solid solution interface. Depending on the sign of the surface charge (E) dipole moments (μ_{H_2O}) of the adjacent water molecules will be oriented.

As thermodynamic modelling does not necessarily relate to actually existing structural units, spectroscopic methods shall be presented in this article which provide direct information on the interactions between adsorbate and surface functional groups of hydrous oxides.

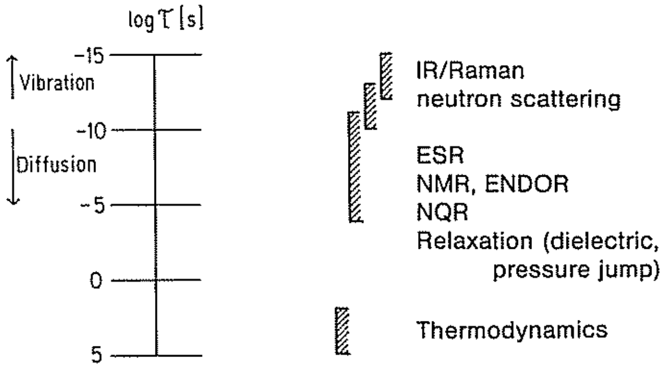

Fig. 3:
Comparison of time domains of molecular dynamics with characteristic frequencies of various spectroscopic methods.
If the mobility of a molecule is rapid compared to the time scale of a particular spectroscopy, an isotropic spectrum is observed; inversely, if the frequency of a spectroscopy is high compared to molecular motion, an anisotropic spectrum is resolved (cf. Fig. 4b). Molecular dynamics can be interpreted for spectroscopic methods which overlap with molecular dynamics. (E.g. Cu(II)-complexes normally are very labile: $k(NH_3) = 2.0 \cdot 10^8 M^{-1} s^{-1}$).

Spectroscopic methods to characterize hydrous surfaces

Due to the small exchange capacity of active surfaces (e.g., on the order of 0.1 to 1 µeq/m²) only a few spectroscopic methods are sufficiently sensitive. An additional limitation arises from the requirement to study the surface in an hydrated state, thereby eliminating a number of other techniques developed for the investigation of gas adsorption phenomena. Methods which fulfill these two criteria given above are shown in Fig. 3. The corresponding spectroscopic method is characterized by a typical time domain, i. e., structural parameters and molecular dynamics cannot be discussed separately.

Cu(II)-EPR-measurements to characterize surface coordination

Because of its unique electronic configuration (d^9), the Cu(II)-ion is especially well suitable for EPR(Electron Paramagnetic Resonance)-measurements. From the analysis of an EPR-Spectrum, information concerning the geometry around the Cu(II)-center can be obtained as well as some hints as to the nature and number of coordinating ligands. Important spectroscopic parameters are the so-called g-factors, which are influenced by the ligand field and the hyperfine interactions (A) which arise from the interaction of the unpaired electron with magnetic moments of adjacent nuclei [4]. Measurements on hydrous oxides have demonstrated that the EPR parameters $g_{\parallel}$ and $A_{\parallel}$ (i. e., axial components, cf. Fig. 7) are sensitive to the nature of the oxide [5]. A mapping of EPR-parameters of Cu(II) on various oxide surfaces is shown in Fig. 4.

A decreasing tendency of the $g_{\parallel}$-parameter is indicative of an increasing coordinative interaction, which is in qualitative agreement with stability constants derived from titration experiments (eq. **3**). A correlation has been obtained between the overall stability constants of Cu(II) complexes and $g_{\parallel}$-values for a series of model compounds:

$$Cu(II) + L_1 + L_2 + \ldots \rightleftharpoons Cu(L_1,L_2 \ldots L_n);\ \log K_{tot} = \sum_{i=1}^{n} \log K_i \qquad \textbf{5}$$

The result of this correlation is transposed for a number of $g_{\parallel}$-values for Cu(II) adsorbed on various surfaces and ion-exchange resins as shown in Fig. 5. Estimated stability constants of Cu(II) surface complexe with oxides, humic substances, and charcoal, which are known to contain carboxylic and phenolic functional groups, lie well within values obtained from titration experiments.

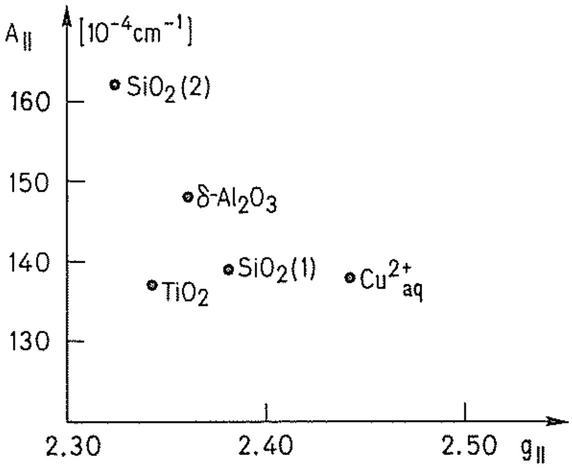

Fig. 4a:
Cu(II)-EPR parameters for oxide surfaces.
($g_{\parallel}$: g-factor in axial direction (see Fig. 7),
$A_{\parallel}$: Hyperfine splitting with isotopes ^{63}Cu, ^{65}Cu (axial component).
Cu^{2+}_{aq} = Cu(II)-aquo-ion in porous silica
$SiO_2(1)$ = Aerosil (300)
$SiO_2(2)$ = silica sol (hydrolysis of elemental Si)

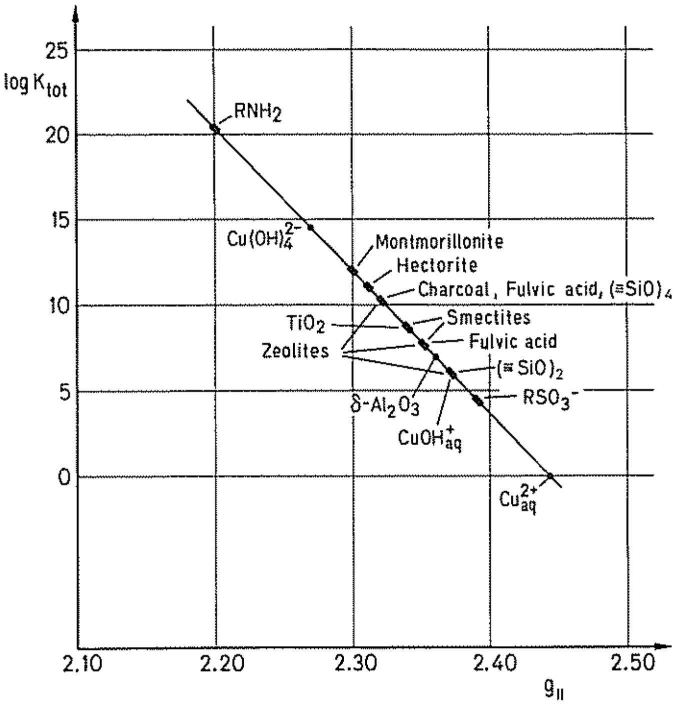

Fig. 5:
Stability constants of Cu(II) surface complexes for various adsorbents estimated from EPR ($g_{\parallel}$)
(RNH_2: amino ion exchange resin,
RSO_3^-: sulfonate ion exchange resin).

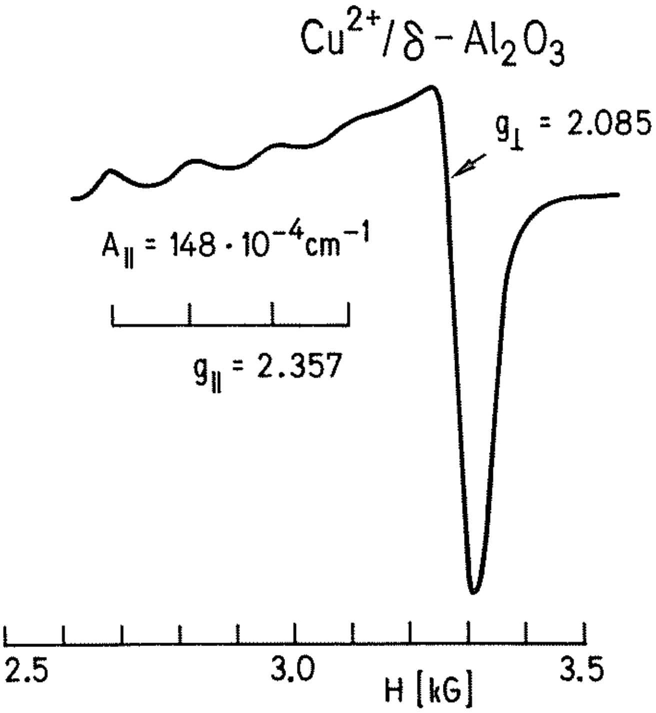

Fig. 4b:
EPR-Spectrum of Cu^{2+}_{aq}/δ-Al_2O_3 in an aqueous suspension. Anisotropic spectrum, i.e., spatial components ($g_{\parallel}$: axial, $g_{\perp}$: equatorial) are resolved on the EPR time scale (~$10^{11} s^{-1}$).

Ternary surface complexes on δ-Al_2O_3

Starting from the copper aquo-surface complex, two molecules of coordinated water may be substituted by ligands ($\overset{\frown}{L_1L_2}$ = bidentate ligand) of stronger coordination tendency. Ligands of increasing coordination strength again lead to a decrease in $g_{\parallel}$-parameters, which results in an enhanced stability of ternary surface complexes. Such a reaction is schematically written as

$$(\equiv AlO)_2\ Cu(OH_2)_2 + \overset{\frown}{L_1L_2} \rightleftharpoons (\equiv AlO)_2\ Cu\ \overset{\frown}{L_1L_2} + 2H_2O \qquad 6$$

Especially suitable ligands for Cu(II) contain amino functional groups (e.g. NTA as in Fig. 6, ammonia, glycine). The formation of ternary complexes has a significant effect on the distribution of heavy metals between the dissolved state and the solid phase.

ENDOR spectroscopy of surface complexes

In collaboration with the Physical Chemistry Department of the ETH-Zürich, ENDOR (= Electron Nuclear DOuble Resonance)-measurements have been performed in order to get more specific information at the molecular level. Application of ENDOR spectroscopy allows the resolution of weak interactions between the unpaired electron with nuclei within a distance of about 5Å. From these so-called hyperfine data, structural parameters can be derived, e.g., bond-distances of the paramagnetic center to the coupling nuclei of ligands. Cu(II)-complexes are typically of a tetragonal configuration what has also been confirmed for the surface complex $(\equiv AlO)_2\ Cu(OH_2^{eq})_2(OH_2)_2^{ax}$ (Fig. 7).
Bond distances can be accurately determined if the interaction between the magnetic moments of the electron and the nucleus is of a dipolar nature. However, through *chemical bonding* electron density can be *delocalized* to neighboring nuclei, in which case the observed coupling will be considerably larger than would be anticipated for a more dipolar interaction. The analysis of such spectra is rather complicated since adsorbed species are not oriented spacially and a three dimensional spectrum must be interpreted. In general, spectra simulations are considerably facilitated if parameters are available which have been obtained from single crystal measurements of model compounds [6].
However, this is not always the case. In the ENDOR spectrum of adsorbed oxovanadium (VO^{2+}/δ-Al_2O_3) signals caused by the coupling with the surface Lewis center (^{27}Al) are split much more strongly than is calculated from molecular modelling [7] (Cf. fig. 7: Cu is replaced by VO).

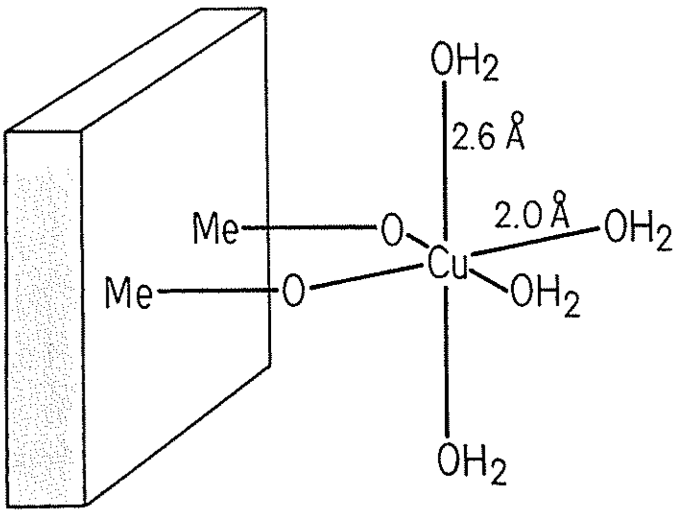

Fig. 7:
Bond distances of the surface complex $(\equiv AlO)_2\ Cu(H_2O)_4$ derived from the analysis of the ^1H-ENDOR spectrum.

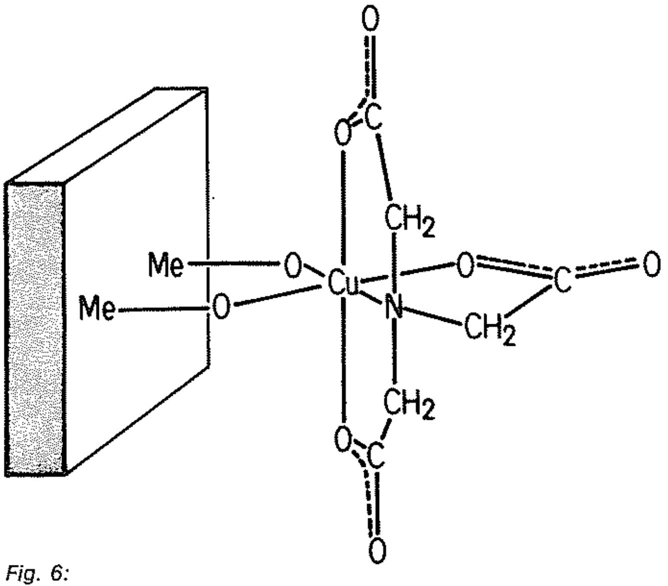

Fig. 6:
Schematic representation of the ternary surface complex $(\equiv AlO)_2Cu$ (NTA)

Delocalization of the unpaired electron form the vanadyle fragment to the surface functional group (≡AlO) is *direct evidence* of *inner-sphere coordination.*
Surfaces of naturally occurring particles are heterogeneous in composition, yet we can learn to understand many of their characteristics by studying model compounds. Spectroscopic investigations are complementary in resolving questions concerning the nature of surface interactions, such as as electrostatic forces, hydrogen-bridges, van der Waals energies, and Donnan potentials. Criteria for unambiguous assignments of the various contributions for adsorption processes are not readily available because they are generally superimposed. Processes of mineral dissolution and heterogenous nucleation are intimately coupled to surface adsorption and transport characteristics at solid/solution interfaces. It is the dynamics of such processes which contribute to the changing features of aquatic geochemistry.

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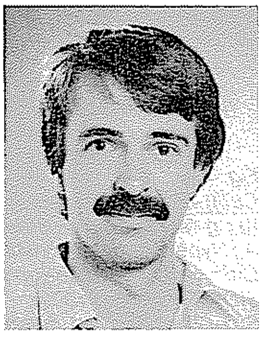


Atmospheric Pollutants: their Potential Impact on Aquatic and Terrestrial Ecosystems

Laura Sigg, C. Annette Johnson, Fritz Zürcher, Jürg Zobrist and Werner Stumm

The oxidation of C, S and N – resulting mostly from fossil fuel burning – rivals oxidation processes induced by photosynthesis. The occurrence of acid precipitation in regions of the northern hemisphere is a consequence of these redox processes; they reflect a disturbance of cycles that couple land, water and atmosphere [1–3]. The atmosphere is an efficient conveyor belt for the transport of pollutants, such as heavy metals and organic chemicals, which can impair aquatic and terrestrial ecosystems. This may be illustrated by two examples. Many heavy metals, especially the potentially more hazardous B-metals may be transported – predominantly adsorbed on aerosols – through the atmosphere over large distances. Fig. 1 shows that atmospheric deposition may make up a significant fraction of the mass balance of heavy metals entering a lake. Fig. 2 gives gas chromatograms of rain samples. The response of flame ionization detection (FID) and electron capture detection (ECD) reflect the presence of relatively non-volatile polycyclic aromatic hydrocarbons (including benz(a)pyrene) and chlorinated hydrocarbons, above all PCB's.

Fig. 3
Effects of atmospheric pollutants on terrestrial and aquatic ecosystems.
There are various pathways and interactions:

(1) *Direct absorption of gaseous pollutants; possible synergistic effects by the presence of ozone and of sunlight.*
(2) *Precipitation carries dissolved substances and suspended aerosols to the surface of trees and vegetation.*
(3) *Slow sedimenting or wind-drifting fog interacts with the trees; needles and leaves intercept fog droplets and thus high concentrations of pollutants become deposited on the tree tops. Larger drops can be formed and subsequently their concentrations can be further increased due to evaporation; the substances deposited may become modified photochemically by sunlight and ozone.*
(4) *Acid depositions can acidify the soils and cause elution of base cations (among others the biologically important ions K^+, Ca^{2+}). Al^{3+} released at lower pH values may damage the roots of trees and mycorrhiza living in symbiotic association with the roots.*
(5) *Atmospheric depositions carry significant loads of pollutants (heavy metals and organic pollutants) into aquatic ecosystems, especially lakes. The substances deposited can impair water quality and affect the biocoenosis.*

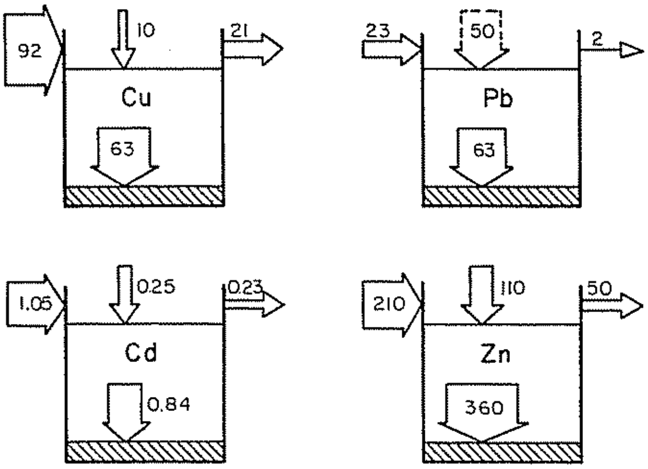


Fig. 1
Mass balance for some heavy metals in Lake Constance. All fluxes are given in mg m^{-2} yr^{-1}. The relative size of the arrows indicates the relative contributions of, respectively, atmospheric deposition and river inflow (left) for the inputs, and of sedimentation and outflow (right) for the outputs. Due to the imprecisions in the experimental determination of the various fluxes, the mass balances do not exactly match. [4]

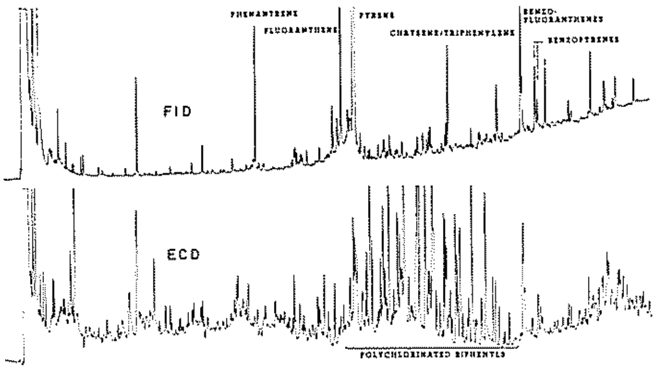
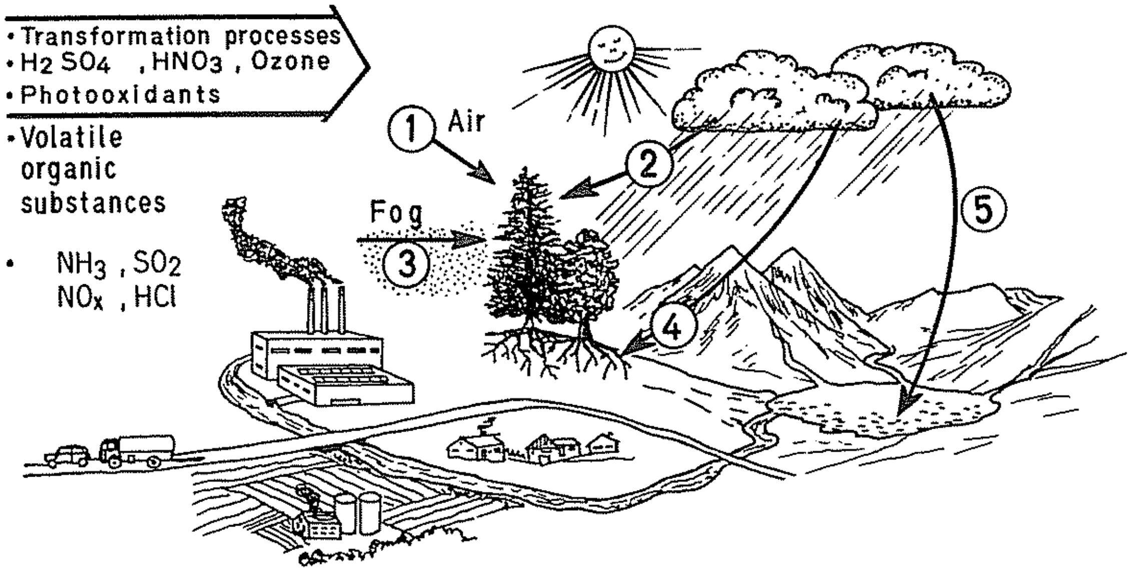


Fig. 2
Aromatic hydrocarbons in a rain sample. Gas chromatograms with flame ionization detection (FID) for polyaromatic hydrocarbons, including benz(a)pyrene; and electron capture detection (ECD) mostly for chlorinated hydrocarbons, including PCB's. [5].

Fig. 3 illustrates schematically how pollutants emitted into the atmosphere interact, subsequent to various transformations, with terrestrial and aquatic ecosystems. Swiss fores-



try research has recognized that a special risk for forest damage occurs at the upper level of fog layers during fall and winter and of smog layers during summer. In addition to gaseous pollutants and rain droplets, fog has to be considered as a carrier of potential pollutants with possible phytotoxic effects.

Here we report on the chemical inorganic composition of rain and fog samples collected during 1984*. Rain and fog samples were collected in the proximity of Dübendorf as individual events, i.e., rain samples were taken for a period of hours or days in which weather conditions remained constant. Large differences in composition may be observed from one rain event to the next one (the differences are averaged out if samples are taken weekly or monthly), on the other hand, since we did not sample every event our results do not represent a statistical distribution of rain events and cannot be used in order to derive a mean composition.

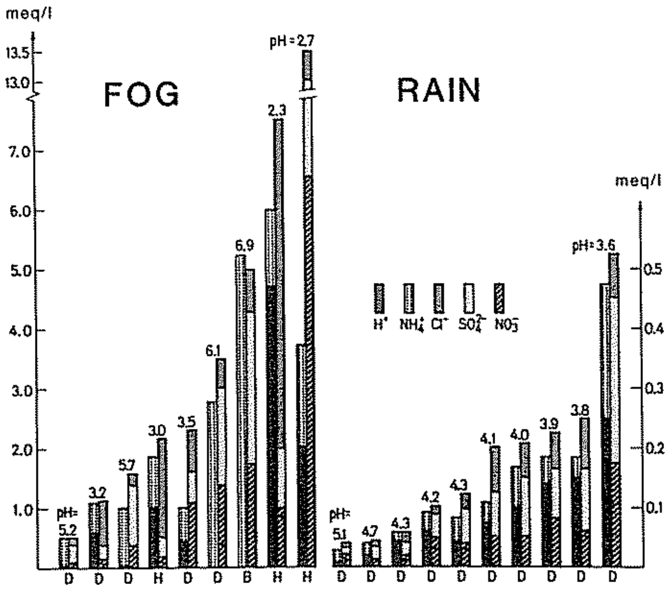
The Inorganic Composition of Rain.

Fig. 4 illustrates the composition of rain samples. The ratio of the cations (H^+, NH_4^+, Ca^{2+}, Na^+ and K^+) and anions (SO_4^{2-}, NO_3^-, Cl^-) reflects the acid-base titration that occurs within the rain droplets. Total concentrations (sum of cations or anions) vary typically between 20 µeq l^{-1} and ca. 500 µeq l^{-1}. Dilution effects, i.e. washout by atmospheric precipitation, can – at least in part – explain the differences observed; for example, highest concentrations are observed after a long dry period, while lowest concentrations are typically recorded at the end of a prolonged rain event.

pH is measured in terms of H^+ ion concentrations (p^cH) in samples adjusted to a constant ionic medium (0.05 M) by adding KCl [6]. Determination of acidity and pH calibration is carried out by coulometric Gran plot titration. A typical Gran plot of a rain water sample is given in Fig. 5. Most rain samples show pH values between 4 and 4.7. Extreme values down to pH values of 3.5 have been observed. The relative extent of neutralization of strong acids by ammonia is characterized by the relative concentration of NH_4^+. One noteworthy difference in our samples, in comparison to those typically observed in USA, is that most of the Cl^- concentration results from HCl which has been emitted to the atmosphere through refuse incineration plants (combustion of Cl-containing plastic such as polyvinylchloride).

Fig. 4

Examples of the composition of rain and fog in Dübendorf and surroundings of Zürich (1984); please note that the ordinate scales are different. The range of composition varies widely. The composition of fogs reflect, to a larger extent than rain, the influence of local emissions close to the ground, e.g., NH_3 from agriculture or HCl form refuse incinerators. The samples contain, in addition to the components given in the figure, alkali and earth alkali ions, heavy metals and organic material. Some fog samples contained appreciable concentrations of sulfite (up to 25% of that of SO_4^{2-}). Dissipating elevated fog layers are often characterized by high concentrations. D = samples form Dübendorf and environment, H = Elevated fog layer, B = Ground fog.



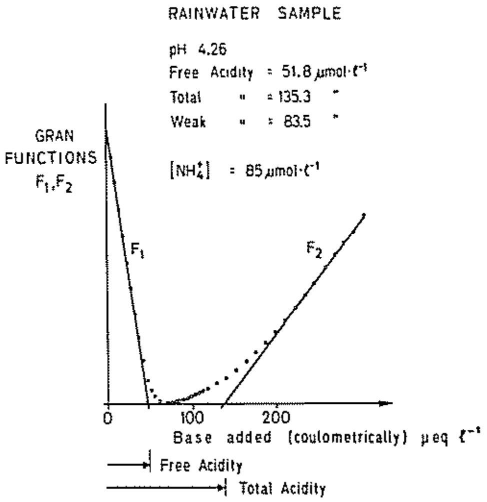


Fig. 5

Gran plot of a typical rain water sample. Base is generated coulometrically (1µeq l^{-1} represents base consumed by 1µmol l^{-1} H^+); linear extrapolations of the Gran functions $F_1 = V_o 10^{-p^cH}$ and $F_2 = V_o 10^{p^cH}$ to zero give free (strong) acidity and total acidity, respectively. Weak acidity = 83.5 µmol l^{-1} (mostly as NH_4^+). [6]

Fog as a Carrier of Concentrated Pollutants

When fog is formed from water saturated air, water droplets condense on haze or aerosol particles. In addition to components of the aerosols, the fog droplets can absorb gases such as NO_x, SO_2, NH_3 and HCl; they form a favorable milieu for various oxidation processes in which H_2SO_4 and HNO_3 are formed. Fog droplets (10–50 µm diameter) are much smaller than rain droplets; the liquid water content of fog is often in the range of 1×10^{-4}l per m³ air, so that fog typically contains concentrations that are about 10 to 50 times more concentrated than those of rain. Rain clouds are transported over large distances and thus are able to absorb gases and aerosols from a large region; because fog is formed in the lower air masses, fog droplets are efficient collectors of pollutants close to the earth surface. The composition of fog reflects thus the local situation. Ambient fog was collected with a rotating arm collector which sweeps as an external impactor through the air at high velocity (50 m sec⁻¹). This collector was developped and tested at the California Institute of Technology [7]. In Switzerland we often encounter, in addition to radiation fog (commonly known as ground fog), during fall and winter an elevated fog layer, resulting from inversion conditions.

The influence of local emissions (e.g. NH_3 in the proximity of agricultural activity or HCl in the vicinity of refuse incinerations) is reflected in the fog composition. The upper level of the elevated fog layers has a tendency for higher concentrations and lower pH. Fog waters investigated contain typically total ionic concentrations between 0.5 and 15 meq l^{-1} (Fig. 4). The variation in the ratios of individual cations and anions differ from sample to sample much more than in rainwater. Thus, remarkably different pH values are observed. In addition to neutral fogs (pH 5–7) – some of which had very high anion concentrations – we found remarkably acid fogs (extreme value: pH = 2.3). The following ranges of anion concentrations were found in the fogs investigated: SO_4^{2-}: 0.2–

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* A report on the results regarding organic constituents in rain and fog will be given by W. Giger et al. in one of the next issues.

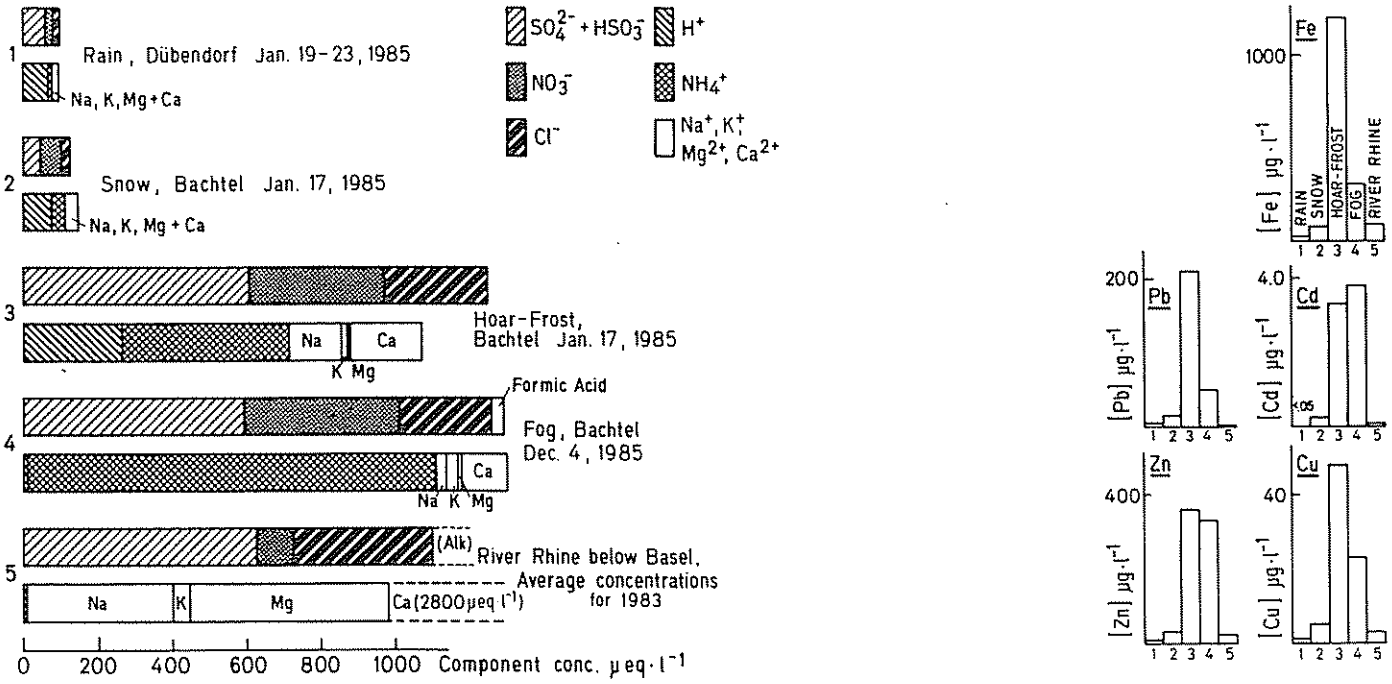

Fig. 6
Comparison of the composition of individual samples of rain, snow, hoarfrost and fog (although not necessarily representative of mean compositions, the samples were collected around the same time in the same prealpine area, 15 km south of Dübendorf) with those of the Rhine River below Basle. The atmospheric depositions are characterized typically by high concentrations of NH_4^+ and H^+; surface waters, on the other hand, contain as a result of weathering relatively large concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+ and HCO_3^-.

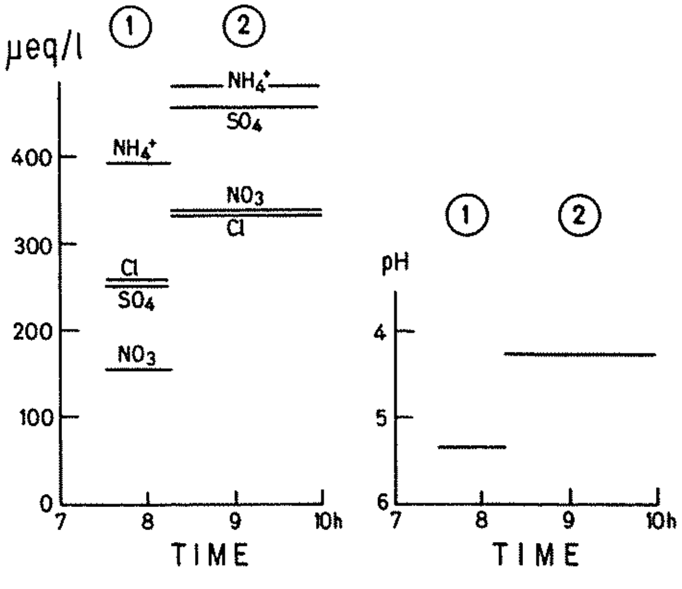

Fig. 7
Temporal variation of the concentrations of NO_3^-, SO_4^{2-}, Cl^-, NH_4^+ and pH during a fog event. During the dissipation of the fog, the liquid water content decreased from fraction 1 to fraction 2 by a factor of about 2.

5.8 meq l^{-1}, NO_3^-: 0.2–7 meq l^{-1}; Cl^-: 0.1–6.6 meq l^{-1}. In some cases the sulfur was not fully oxidized in the samples, i.e., up to 25% was present as sulfite. The concentrations of NH_4^+ and H^+ as well can be as high as a few meq l^{-1}. They also contain significant concentrations of organic pollutants and heavy metals. The latter have been found in the following concentrations: Fe: 0.2–4 mg l^{-1}, Zn: 100–300 µg l^{-1}, Cu: 10–100 µg l^{-1}, Cd: 1–6 µg l^{-1}, Pb: 40–600 µg l^{-1}.

In Fig. 6 the main chemical composition of rain, snow, hoarfrost and fog are compared with that of river water (Rhine River in Basle). The differences in the concentrations of the atmospheric deposition samples found can – in a first approximation – be accounted for by assuming that different atmospheric liquid water contents were prevalent when the rain, snow, hoar-frost or fog respectively was formed. The concentrations of gases and aerosols in the air contributing to the composition of these samples may also have been different at the various times. Hoar-frost has a composition similar to that of fog, being much more concentrated than snow collected at the same place. Of particular interest are the respective heavy metal concentrations in these samples. It is noteworthy (Fig. 6, right side) that atmospheric depositions contain heavy metal concentrations that are significantly larger that those found in surface waters of polluted rivers or lakes (by a factor of at least 10 for rivers, respectively 100 for lakes).

We are interested in understanding how the composition of fog waters is affected when fog is formed, when it becomes more dense, or when it becomes dissipated. Fig. 7 gives an example of a concentration change observed during a morning in Dübendorf.

Objectives in the near future

We plan to emphasize the *specific* and sensitive analytical measurement of important pollution species in air, water (rain, snow, fog) and in particles, respectively. A better knowledge on the forms of occurrence (which species in what phase) appears to be a prerequisite *i)* for a better appreciation of the atmospheric reaction sequences, and the chemical processes occurring during the formation of rain and fog and the distribution of pollutants between gas, water and aerosol phases; *ii)* for a more quantitative interpretation of the so-called "dry" and "wet" deposition of pollutants to various receptors (soil, water, forest); and *iii)* an improved understanding of potential ecological impacts of atmospheric depositions on aquatic and terrestrial ecosystems.

Acknowledgement: Careful sampling and exacting analysis carried out by (from left to right) *Claude Jaques, Claudia Mäder* and *Ursula Michel* is acknowledged.

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The Authors

C. Annette Johnson has a Ph.D. from Imperial College (UK); she is a research fellow at EAWAG.

Dr. Laura Sigg is the head of EAWAG's Chemical-Analytical Laboratory and a lecturer of Aquatic Chemistry at ETHZ.

Dr. Jürg Zobrist is a member of EAWAG's Chemistry Department and responsible for collecting atmospheric depositions and fog.

Fritz Zürcher is a chemist in EAWAG's Chemical Analytical Laboratory and a specialist in ion chromatography.

Werner Stumm is a Professor at ETH and Director of EAWAG.

News about EAWAG Collaborators

On July 11th, Professor *Kurt Grob* will celebrate his 65th birthday. Professor Grob has made pioneering contributions to the field of high-resolution gas chromatography. In particular, he has developed glass capillary columns with long life expectancies and broad applications. He introduced procedures for evaluating the column quality ("Grob test") and developed new injection methods (splitless and on-column injection). His contributions to the improvement of gas chromatographic techniques were based on systematic investigations of the surface properties of glass and of the chemical characteristics of the various stationary phases. Grob's methodological developments have established the basis for the success of high-resolution gas chromatography in many areas such as environmental, geological, forensic and clinical chemistry. In water analysis the "Grob closed-loop stripping analysis" allows for the quantitative determination of as little as 10^{-9} g/l of a chemical constituent in water. The methods developed by Grob are in daily use by numerous university, industry and government laboratories. Grob has aided in promoting the application of his procedures by regularly publishing his results and by teaching "hands-on" courses at EAWAG and at other institutions all over the world. He has been awarded two honorary doctoral degrees: one from the University of Berne and one form the Swiss Federal Institute of Technology, Zurich. Professor Grob was assisted during his entire scientific career by Mrs. Gertrud Grob.
With his extraordinary high scientific productivity, his unusually great didactic talent and with his rigorously and consequentially performed research, Grob has rendered a great service to his colleagues, to EAWAG and to the ETHZ. His presence will greatly be missed, when he retires from EAWAG late this summer.

Dr. Jürg Hoigné has been promoted to the rank of a Professor at the Swiss Federal Institute of Technology. Jürg Hoigné has carried out pioneering research on the kinetics of oxidation processes. Especially his work on the interaction of ozone and the hydroxylradical ($OH^{\cdot}$) with inorganic and organic solutes is well known. Jürg Hoigné has established the fundamentals necessary for the intelligent application of ozone in water supply technology. His collaborators and he are now also engaged in aquatic photochemistry. Much of their results is applicable as well to the oxidation reactions occurring in the atmosphere which are important for understanding the processes leading to acid rain and fog. Jürg Hoigné will continue to teach at ETHZ his classes on aquatic chemistry and on unit processes in water treatment.

Dr. Johannes Stähelin whose dissertation was carried out under Jürg Hoigné's supervision received in April 1985 the Jacques Hallopeau Prize (awarded only every second year by the International Society on Ozone) for his thesis research.

The following presents some food-for-thought on evolving directions within the Geology Section of the Department of Multidisciplinary Limnological Research (MLF).
Geology is traditionally considered a historical, deductive science. As such it has made major contributions to the understanding of the Swiss environment. The early pioneers of

alpine geology gave Switzerland a reputation for excellence that still forms a measuring stick for quality in field observations.

What distinguishes a geologist from other scientists? Perhaps, a unique feature is the grasp of physical and chemical processes seen on a vast time scale. Few others can visualize the Alps "moving" on the centimeter per year scale that we know is the rate at which continents go crashing around.

How does this affect the EAWAG? Firstly, a bit of history. During and after the last World War, the need for mapping, understanding and protecting the groundwater drinking resources became apparent. The EAWAG played a key role in the education of the public to those ends, and many communal, cantonal of federal agencies turned naturally to the EAWAG for advice for everything from locating springs to groundwater-protection zones. In the meantime, the general protection of groundwater has grown on sound footing in Switzerland and a large net of consulting geology offices is available to give advice on routine projects. The EAWAG Geology can now turn to research projects which both compliment government and industrial capabilities, and which look beyond the immediate needs.

Today, Geology takes on new form, largely as a result of the outgrowths of marine research which fostered new methodology and a multi-disciplinary approach to interactions on a global scale. The unifying theory of plate tectonics, e. g., has added a new dimension of geodynamic predictability. Geologists are also being asked to make predictions for our environment which extend hundreds to hundreds of thousands of years into the future. Only recently have we realized that man has become an agent of change which equals the potential of natural geologic processes. We do not yet know how, e. g., deforestation would affect our hydrologic budget, or how the anthropogenic increase of trace gases in the atmosphere will affect our climatic, hydrologic, and carbon budget.

How do we make predictions on the feedbacks of change? One approach is to look at the past. Sediments are the memory banks of geology which store information on many ancient environmental experiments. Water is the main datatransfer agent.

Current trends in geological sciences emphasize the interpretation of "Geological Events", in particular those rare, but sudden changes which affected global biogeochemical cycles. Controversies have flared, which opened hundred-year-old wounds of catastrophists versus those who prefer to imagine the smooth continuity of earth and its life forms. One example concerns a sudden event at the Cretaceous/Tertiary boundary. When the demise of the dinosaurs was linked to the feedbacks caused by the impact of a comet, many dismissed the discussions as purely academic. Yet, recent scenarios for a nuclear winter borrowed heavily from this Impact-Hypothesis and its explanation of the large scale mass mortality 65 million years ago. Clearly, this example is outside the realm of EAWAG Geology. It illustrates, however, how we seek to integrate the implications of current research progress on the high-resolution sedimentary record of global geological changes into an EAWAG program to recognize future problems that might affect our environment.

The Geology Section of MLF is small, and its foremost role is that of a critical partner for advice and direct stimulus within the Multi-Disciplinary Lake Research Group, and as a catalyst in hydro- and limno-geology for the EAWAG as a whole. Clearly a broad program can hardly be realized without the expected close ties to institutes of the ETH Department of Earth Sciences. A teaching and research program is envisaged which aims at some contributions to the following themes:

- *Comparative Lacustrine Sedimentology:* Lake sediments act as integrators of the ecological history of their basins. One way to understand a possible effect of pCO_2 on climates is to compare the rate of change patterns in different lakes for critical periods of known climatic change such as 20 000 to 10 000 years ago and 8000–5000 years ago. This is done by stratigraphic analysis of drill core samples. Our problem is to develop better criteria for interpreting the signals in these ancient deposits. Often carbonate minerals hold key information on primary and diagenetic reactions which can be extracted with isotopic and other geochemical methods. Combined with sedimentogy, stable isotopic studies are now routine tools for paleoenvironment and paleohydrological analyses and we plan to integrate these into the EAWAG through a close cooperation with the Stable Isotope facility at the Geological Institute, ETHZ. Correlation and dating of sequences are part of a cooperative project with a group of the ETH-Inst. for Middle Energy Physics.

The EAWAG is now the headquarters of an international UNESCO-IGCP (International Geological Correlation Program) project on comparative lacustrine sedimentology in geologic history.

- *Energy and Lakes:* The hydrocarbon potential of lake basins is a newly recognized frontier. China, for example, derives much of its petroleum from ancient lake deposits. Present lakes are the key to past lakes. Applied research at the EAWAG is thus planned which will help us understand biogeochemical cycles of carbon sedimentation and preservation in various lacustrine systems, and their controls on methane or oil generation.
- *Quaternary Processes:* Newer Quaternary studies show perialpine valleys and lakes to be deeply incised and filled with a multitude of fine and coarse sediments from different glacial stages. The obvious and important question of groundwater communication between lakes and deep stockwerk systems is quite difficult to answer. It requires an integrated approach combining seismic geometry and facies analyses with geochemical, isotopic and other tracer methods.
- *Groundwater Contaminants:* Long term, where and how will we deposit the toxic sewage sludge of the future? In USA, there is a trend towards deep-well injection but do we know enough about deep hydraulic circulation patterns in Switzerland? How do we follow fluid motion in fine-grained, possibly fractured rocks? To gain experience in these questions before the problem arrives, we plan, in cooperation with internal EAWAG departments, the VAW-ETH and EIR, to work with various hydrogeological physical modelling techniques and their field application. Where possible, these will include experiments with stable isotope hydrogeology. Both alpine and lowland areas are under consideration.
- *Technical Aid:* EAWAG is a world leader in the research on aquatic systems. One of our most valuable resources therefore is knowledge. Because geological problems commonly cross national borders, we can also gain much from a lively interchange with lesser developed regions while at the same time transfering technologies which may also help protect our own environment through the links of global feedback.

Kerry Kelts

Dr. Kerry Kelts has recently begun as the new head of the Geology Section of the EAWAG. His work on problems of aquatic geology has received wide recognition, particularly for studies on lacustrine environments, marine sedimentology and isotope geochemistry. He received his Ph.D. in Nat.Sci. from the Geological Institute ETHZ where he developed programs in marine- and limno-geology as a lecturer and senior research associate with Prof. K.J. Hsü.

Workshop on Aquatic Surface Chemistry

Chemical Processes at the Particle/Water Interface

Tentative Program

1. The Solid-Solution Interface

- The Continuum of Adsorption Mechanisms from the Hydrophobic Effect through Donnan Equilibria and Ion-Exchange to Surface Complexation. *John C. Westall,* Oregon State University, Corvallis, Oregon, USA.
- The Electric Double Layer at the Solid/Solution Interface. *Roger Parsons,* School of Chemistry, The University, Bristol, Great Britain.
- A Unified Model for the Interpretation of Proton and Metal Ion Binding to Natural Polyelectrolytes Present as Gels or Colloidal Dispersions. *Jacob A. Marinsky,* Chemistry Dept., State University of New York, Buffalo, N.Y., USA.
- The Surface Chemistry of Oxides, Hydroxides and Oxide Minerals. *Paul Schindler,* Dept. of Chemistry, University of Berne, Switzerland.

2. The Formation and Dissolution of Solid Phases

- The Dissolution of Oxides and Alumium Silicates. (Authorship under Negotiation)
- The role of Defects in Controlling the Dissolution and Precipitation Rate of Silicates. *Antonio C. Lasaga,* Kline Geology Laboratory, Yale University, New Haven, Conn., USA.
- Reductive Dissolution of Oxides. *James J. Morgan,* California Institute of Technology, Pasadena, California; and *Alan Stone,* the Johns Hopkins University, Baltimore, Maryland, USA.
- Surface Chemical Processes in Soil. *Gerhard H. Bolt,* Agricultural University, Wageningen, The Netherlands.
- Iron Hydroxide Formation in Synthetic, Aquatic and Biological Media. *Walter Schneider,* Swiss Federal Institute of Technology, Zurich, Switzerland.

3. Regulating the Composition of Natural Waters

- The Nature of Aquatic Particles. *François Morel,* Massachusetts Institute of Technology, Cambridge, Mass., USA.
- Particle/Particle Interactions. *Charles R. O'Melia,* Johns Hopkins University, Baltimore, Maryland, USA.
- The Role of Particles in Regulating the Composition of Natural Waters. *Michael Whitfield,* Marine Biological Association, Plymouth, Great Britain.
- Catalytic and Photochemical Processes at the Particle/Water Interface. *Richard G. Zepp and N. Lee Wolfe,* Environmental Protection Agency, Athens, Georgia, USA.
- Heavy Metals Interaction with Particles. The Chemical Dynamics of Metals in Aquatic Systems. *Laura Sigg,* Swiss Federal Institute of Technology, Zurich, Switzerland.
- The Solid/Solution Interface and Geosphere Exchange Processes. *William S. Fyfe,* University of Western Ontario, London, Ontario, Canada.

This workshop takes place at the *Wolfsberg Conference Center* on Lake Constance, Switzerland, from January 22 to 25, 1986. It is organized

1) to treat some quantitative features of interfacial chemistry in the context of aquatic systems (oceans, fresh water, soils);
2) to strengthen our understanding on specific chemical interactions at the particle/water interface;
3) to stimulate innovative research in aquatic surface chemistry; and
4) to bring together surface chemists, geochemists, oceanographers, limnologists and environmental engineers who need to collaborate for a better understanding of the chemical processes occurring at aquatic interfaces.

In order to optimize a stimulating discourse, we plan to restrict participation to about seventy participants. We select on the basis of scientific expertise in the subject of the conference and give a certain preference to participants form Europe. (No additional talks can be added to the program.) Registration fee (including meals and all accomodations in single rooms) is Swiss Francs 700.– (ca. US $ 270.–).
If you would like to be considered for participation, please drop a note to Prof. *Werner Stumm, EAWAG, 8600 Dübendorf.*

In 1984/1985, the EAWAG was honored by the visit of the following **guest scientists:**
Ahel Marijan, Dipl. Chem., Institut Rudjer Bošković, Zagreb, Yugoslavia, (Aug.–Oct. 84).
Brooks Norman, Prof., Keck Laboratory of Hydraulics and Dir. Environ. Quality Lab., Cal. Inst. Technol., Visiting Professor ETHZ, (Sept. 84–July 85).
Carroll-Webb Susan, Dipl. Geol., Dept. of Geol. Sci., Northwestern Univ., Evanston, Illinois, USA, (June–Sept. 84).
Ćosović Božena, PhD, Chem. Ing., Chief Lab. Physicochem. Separations, Rudjer Bošković Inst., Center for Marine Res., Zagreb, (Oct.–Dec. 84).
Gonçalves Maria de Lurdes, Prof., Centro de Quimica Estrutural, Inst. Superior Technico, Lisboa, Portugal, (July–Aug. 84 and 85).
Lewandowski Zbigniew, Dr. Ing. Polish Academy of Sci., Inst. Environ. Eng., Zabrze, Poland, (Oct.–Dec. 84).
Masten Susan, Dipl. Ing., Harvard University, USA, (Jan.–Dec. 85).
McKenzie Judith, PhD, Geologist, University of Florida, Gainesville, USA (May–Aug. 85).
Morgan James, Prof. for Environ. Eng. Sci., Cal. Inst. Technol., USA, (Aug.–Sept. 84).
O'Melia Charles, Prof. of Environ. Eng., Dept. Geogr. and Environ. Eng., The John Hopkins Univ., Baltimore, Maryland, USA, (July–Sept. 84 and 85).
Ruzić Ivica, PhD, Research Associate., Rudjer Bošković Inst., Zagreb, Yugoslavia, (Oct.–Dec. 84)
Schnoor Jerald, Prof. and Head of the Dept of Civil and Environ. Eng., Univ. of Iowa, Iowa City, USA, (May–June 84 and 85).
Scully Francis, Prof., Old Dominion Univ. Dept. of Chem. Sci., Norfolk, Virginia, USA, (June–Dec. 84).
Stiller Mariana, PhD, Chemist, Weizmann Inst., Rehovot, Israel, (March–June 85).
Tang Hong-Xiao, Associale Prof., Division Deputy-chief, Inst. Environ. Chem., Chinese Acad. Sci., Beijing, PR China, (June 84–July 85).
Wang Zi-Jian, Chemist, Inst. Environ. Chem., Acad. Sinica, Beijing, PR China, (July 84–June 85).
Webb Bruce, PhD, Chemist, Exeter Univ., UK, (March–April 85).
Zepp Richard, PhD, Chemist, Environ. Proc. Branach, Environ. Res. Lab., Athens, Georgia USA, (May–Aug. 85).
Zhen Zhen, Chemist, Inst. Photogr. Chem., PR China, (Jan.–June 85).

Participants of the fifth postgraduate course in Sanitary Engineering and Water Pollution Control (offered by the Institute for Water Pollution Control, IGW, and the Institute for Hydraulics and Water Ressources Management, IHW, of the ETHZ).

From left to right, front row: *Thomas Burg, Heinz Mutzner, Dieter Raab, Siglinde Schiele, Georg Cassimatis;* second row: *Asterios Podas, Steven Banwart, Heinz Böni, Margareth Meyer, Jean-Claude Pulver, Lorenz Tschudi, Dorrit Marti* and (not in the picture) *Ewa Warnicke.*

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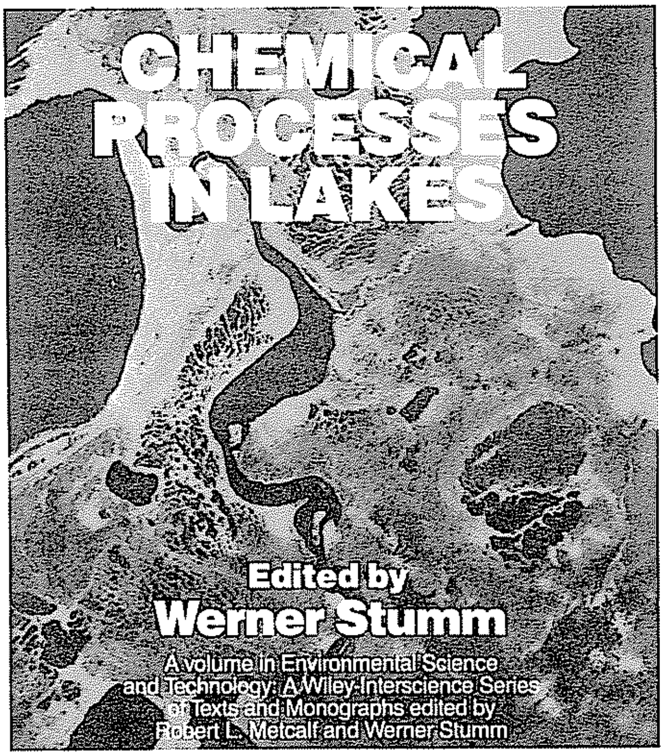

EAWAG edited books
"Chemical Processes in Lakes", Stumm, W., Ed. 435 pages, Wiley Interscience New York, 1985, ISBN 0-471-88261-5, $ 59.95 (See EAWAG 16/17 for table of contents).
In another book to be printed this summer, *Walter Giger* (EAWAG) is a co-editor: "Groundwater Quality", Ward, C. H., Giger, W., and McCarthy, P. L., Eds., Wiley-Interscience New York, 1985

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