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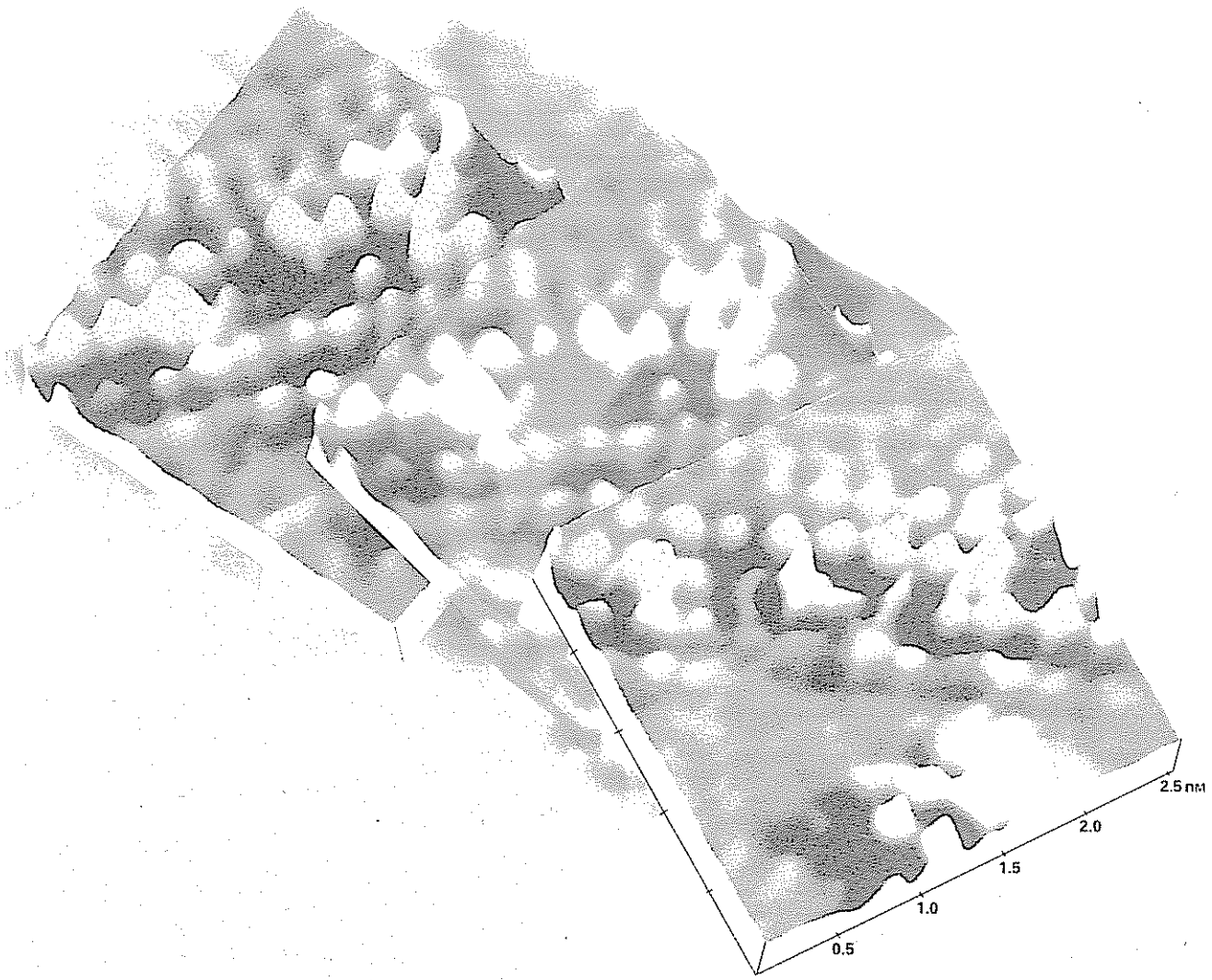

Looking Back to the Past?

One might expect someone who retires after 37 years at the EAWAG and with 22 years of service at the ETH in Zürich to reminisce about his career, reflect upon past successes and view any failures in an altogether favorable light. Actually, until recently, that was probably what I expected myself to do as well. Instead, I have a new story to relate which is briefly outlined in this issue of EAWAG news.

Since 1984, my colleagues and I in the Limnology Department at the EAWAG have collected "undisrupted" sediment samples from various Swiss lakes and prepared sectional views of the drilled cores in an effort to provide a photographic record of the current state of the lake floor. "Nothing new here", you might say. But in fact, the special technique we used allowed collection of samples with an unusually large core diameter (12 cm). The photographs were especially striking, providing us with a vivid impression of the fine structure of the material. Although this technique has been routinely used in the Greifensee for many years by field study students, it has never come into widespread use by the professional scientific community.

Photographs of samples taken between 1984 and 1986 from the Hallwilersee were particularly impressive with their sharply defined – even colorful – annual layers. We were encouraged by our initial efforts to continue to document this extraordinary sediment and to monitor its growth. Our first attempt in the Fall of 1992 failed; the top section of the core was disrupted – or perhaps had been disrupted by a flaw inherent in our collection method. We were no more successful the following year, despite repeated modification and testing of the drilling technique. We eventually came to realize that our "failure" was not, in fact, due to poor technique, but to changes in the structure of the lake sediment itself – apparently as a consequence of introducing compressed air and oxygen into the lake during restoration efforts.

Sediment formation in the lake today clearly differs from that of its pre-restoration days. The uppermost annual layers are now extremely watery and, therefore, more susceptible to external influences (e. g., burrowing organisms). As a result, we have completely revised our former impression of a clean, totally self-contained sediment. Though the original aesthetic and didactic motivation for undertaking these investigations has not produced the expected results, we nevertheless have made a surprising scientific discovery that raises a number of new questions about sediment formation and diagenesis.

Looking back to the past? I believe that looking to the future and to a whole host of new limnological problems is much more worthwhile. Even though as an emeritus professor I will be somewhat on the margins of such new and exciting research, my scientific curiosity and natural interests will continue to represent an expression of my close ties with the EAWAG.

H. Ambühl

Heinz Ambühl

EAWAG

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Title page picture

Two scanning tunneling microscope images of an iron oxide surface in water taken 8.4 seconds apart. "Bumps" are due to individual atoms.
A step with two kink sites crosses the images approximately horizontally. In the left image, two kink sites face each other (see article in this issue for details). In the top image, the kink site on the left has moved one site to the left. The metal-oxygen coordination complex that detached from the kink site is visible between the two kink sites. The middle image represents the transition from the left to the top image.

Heinz Ambühl

Lake sediment: ever fascinating but difficult

Freshly-deposited sediments, defined as materials that have been laid down in recent years, are difficult to deal with because they contain a high proportion of water. For this reason, sediment is almost liquid and has no resistance to mechanical influences. Taking an original, unchanged sample of this material requires an appropriately adapted technique.

Tried-and-true boring and preparation techniques have been in use for many years in working with sediments (e.g., [1, 2]). In our recent studies, new core samples were taken from several Swiss lakes in the Summer and Fall of 1993 in order to supplement sampling and photographic documentation dating from 1984–1987 and to document changes that have occurred in recent years.

During these sampling events, the opportunity was taken to refine the gravity plumb technique and to optimize the length of the core barrel, the total weight of the boring tool, and its operational height of fall. Preparation of the core, which is carried out immediately after boring, consists of making a longitudinal section with a thin glass disc sharpened to form a blade, a further development of the established method after Züllig [3]. One half is discarded; the other half, which remains behind the glass, shows (in the form of a "behind-the-glass image") the original stratification. This procedure is very difficult; it very frequently fails for a variety of reasons. The pattern must be photographed without delay using flash photography, overexposed by two stops in order to brighten the mostly very dark material. Because of the release of pressure, bubbles of carbon dioxide and methane are soon released which disrupt the pattern and make it essential to work fast. In Lake Lucerne, bubble formation is not a serious problem, while in the Baldeggersee it occurs immediately and turns the preparation process into a race against the clock with only minutes to work. Anyone working with sediments is bound to experience these same problems.

A few curious technical details: sampling is only possible from a sufficiently large boat; a row boat would not be stable enough. The boat shown in Fig. 1, formerly an army ferry, is just long

Fig. 2
Sampling crane with the coring tool. It consists of (from top to bottom) the trigger actuated by a messenger, the valve (movable end plate), the weight (ca. 15 kg) and the coring barrel (with the bonded preparation window). Photo: November 1993.

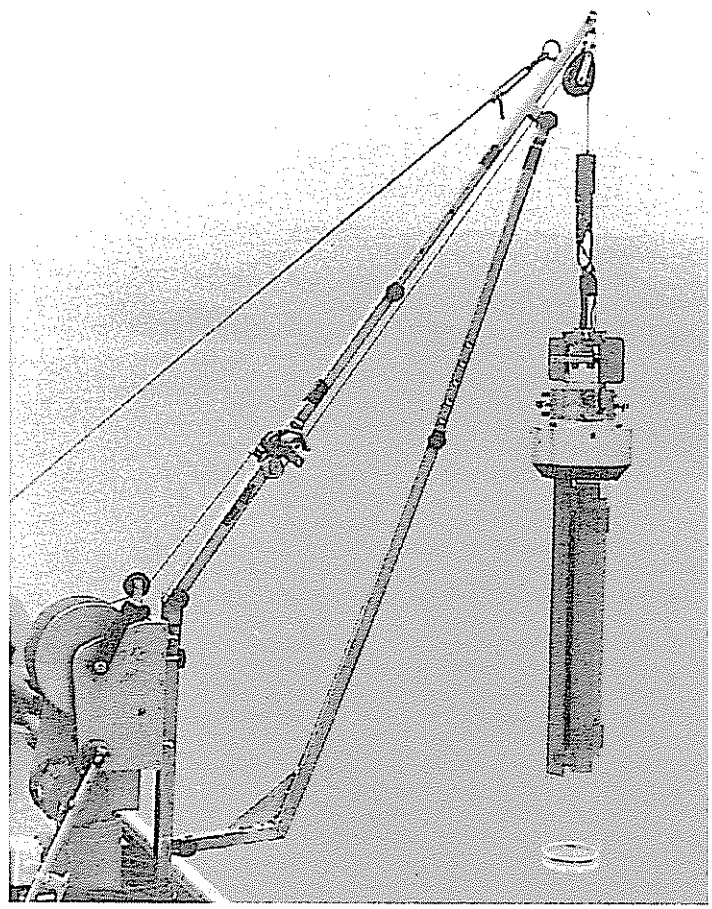
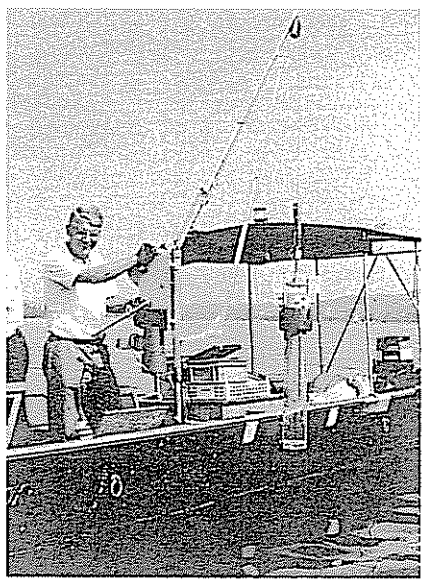


Fig. 1
A former ferry converted to a working boat, now named Redox *and moored on the Hallwilersee. The high sampling crane allows the coring tool to be retrieved in free-hanging fashion (and very carefully) from the lake. Photo: July 1986.*



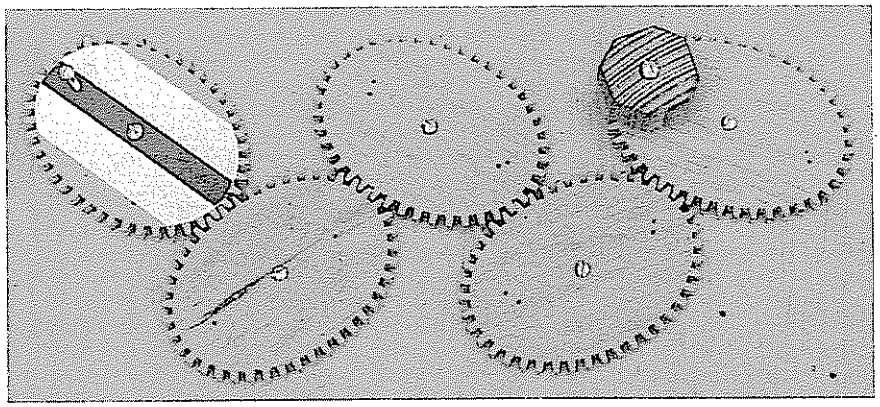


Fig. 3
Principle of the distribution of the crane cable on the cable drum (wooden model). This model was made, firstly, for the enjoyment of its inventors and, secondly, to convince doubters.

enough at 9 m. A larger boat would undoubtedly be better, but then it could no longer be towed on the road which would substantially restrict the choice of lakes we could sample.

One point concerning the boating equipment: when retrieving the coring tool, it must be free-hanging from the crane cable in order to keep the valve at the top of the barrel closed. This requires a correspondingly high sampling crane (see Fig. 2). The water depth from which the samples are taken is not limited, and the crane cable can, therefore, be 250 m long or more. This, in turn, requires that it be uniformly distributed over the cable drum. Mechanical distributing devices with cam control, for example, have been used for decades; unfortunately they require a lot of space. We set ourselves the task of designing an apparatus that could be accommodated in a small boot crane and developed a mechanism which converts a circular or sine motion into an admittedly imperfect but more practical zig-zag motion via oval gearwheels (with normal module gearing). The mechanism is configured in a single plane (see model in Fig. 3). It has proven to be very successful in some ten years' of operation, and all concerned – the designer (H. Ambühl), the model programmer (H. Bührer), the production engineer (H. Burkhalter) and the mechanic who carried out the work (H. Schälchli) – thoroughly enjoyed its development [4]. The following examples illustrate two new facts about sediments.

The fine structure of fresh sediment

The "fresh" sediment in those lakes which are more or less ideal for the sedimentation process (i. e., where the material is not affected by artificial influences such as turbulence caused by digging, burrowing, or whirling organisms) exhibits exceptionally fine, clear stratification. Our photographs from the Greifensee (Fig. 4) and from Lake Lucerne's Weggis-Vitznau Basin (Fig. 5) seem to show firm, solid stratification. In reality, the uppermost layers are extraordinarily fragile. A slight inclination of the core barrel during its movement from outboard to inboard can cause any excess water to slop to such an extent that the sedimentary material is

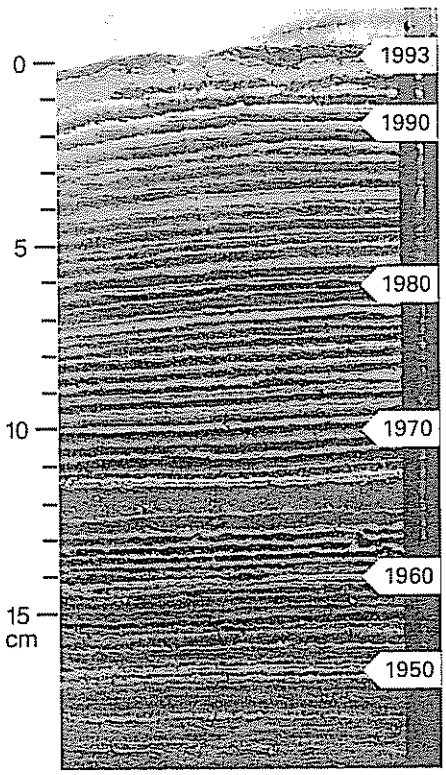
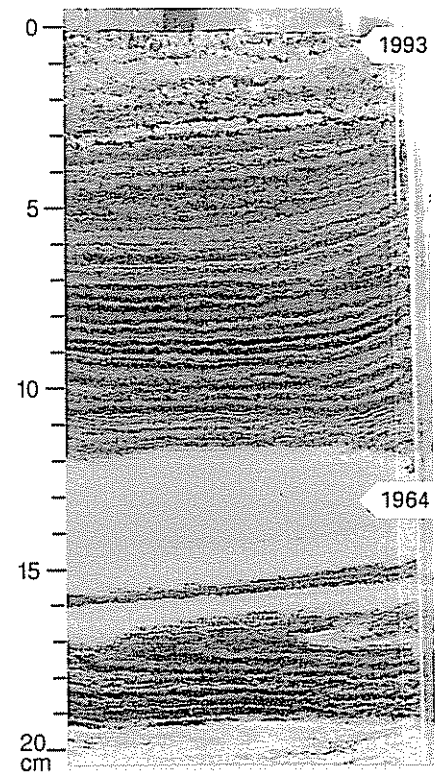


Fig. 4 (left)
No living organisms except bacteria can survive in the anaerobic sediment: therefore, undisturbed deposition.
Sediment core from the Greifensee, 20 October 1993, deepest location opposite the influx of the stream flowing through the village of Maur (1974 survey, Agency for Land Improvement and Reclamation of the Canton of Zürich), water depth 32 m. The core is sectioned longitudinally. Diameter of the full core cross-section 12 cm; 10 cm shown here.

Fig. 5 (right)
Lake Lucerne: An undisturbed sediment because it is anaerobic, even in the Weggis-Vitznau Basin, deepest location off "Obermatt", water depth 150 m. The lake is surrounded by high, steep mountains; it is, therefore, protected from the wind and is adversely affected by the weakness or frequent absence of winter turnover. The varve pattern corresponds to the type known from eutrophic lakes, although Lake Lucerne is considered oligotrophic at present. The thick, light stratum was deposited as a result of a landslide in August 1964.



mixed, and its structure is consequently disturbed. This then is also the reason for the recent uppermost part of sedimentary cores frequently being destroyed and being lost as turbid water if the borer and its use are not specially designed to retain this most sensitive layer.

Changes in sediment formation

Actually, the sampling technique we have employed since about 1974 [5] would have been adequate for obtaining new samples in 1993. In the period 1984–87, several cores were extracted from the Hallwilersee. They were notable for their regular, astonishingly clear stratification and colored spring strata. New cores were extracted in 1993 to document sediment growth since 1987. In absolutely every replication, the extracted extra strata turned out to be disturbed, for which sampling artifacts could not be excluded as the cause. The boring method was consequently modified in stages – at first with no success. Various samples of the Hallwilersee sediment were always disturbed in every area sampled. For verification purposes, a few cores were extracted using the now optimized technique from the Greifensee, which had an intact sediment and proved to be completely undisturbed (Fig. 4). Further sampling in the Hallwilersee yielded the above-described, most recent deposits which, on more accurate examination, showed partial disturbance (Fig. 6). The sediment was not changed externally as it had an intact surface (Fig. 7), and the excess water was clear. Disturbance by the coring or boring process could, therefore, be excluded as a cause; there must be other reasons. The beginning of the disturbance coincided with the start of restoration measures in the lake (i. e, aeration with compressed air and an oxygen supply from 1986 onwards). It remains to be settled whether deposition is being disturbed by mechanical or hydraulic effects, for example by sizeable, artificially-generated currents, or whether organisms are involved (e. g., larva of the *Chaoborus* midge). These organisms were present in the freshly-extracted samples dating from November 1993 at a concentration of around 10 individuals/dm^2 and were visible to the naked eye. The technical improvement work on the lake (the now aerobic environment) apparently enabled these organisms to reach the lake bottom and remain there. An equivalent pattern of varve disturbance to that in the Hallwilersee was also seen in the Sempachersee (also aerated and supplied with oxygen), and the Baldeggersee, the third of the lakes subject to such treatment. The significance of the change in sedimentation on the mass balance, in particular for redissolution of sedimentary phosphorus, is currently under study.

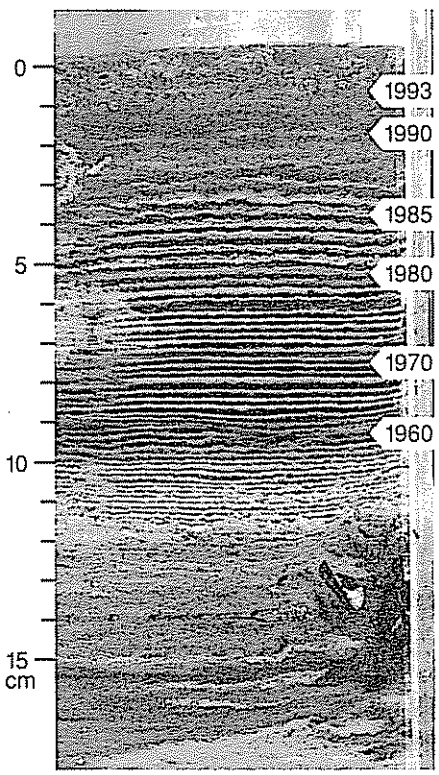


Fig. 6
One unresolved question: why have deposits in the Hallwilersee been disturbed for some years? Sample taken on 3 November 1993, 1 km south of the aeration point, water depth 45 m.
The annual strata since about 1987 can only be approximately identified; the pattern is disturbed. The patches at the top left and bottom right are sampling artifacts.

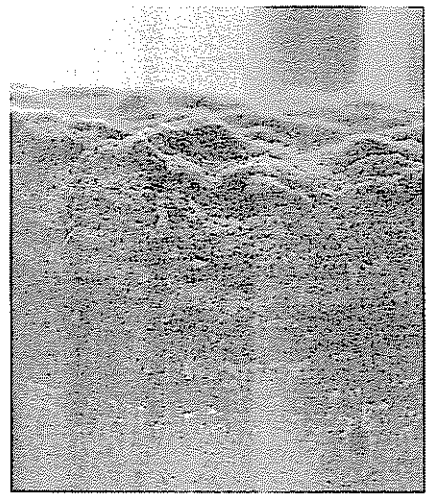


Fig. 7
This is what the lake floor looks like: Hallwilersee, 3 November 1993, sediment core in Fig. 3. View of the freshly-extracted sediment core. The excess water is clear, and the sedimentary material is intact. The Chaoborus *larva mentioned in the text were noticed because they released fine gas bubbles for a few seconds and then burrowed rapidly into the sediment.*

Acknowledgements

Sampling was only possible thanks to accurate teamwork with our colleagues *R. Illi, H. R. Bürgi* and *F. Stössel.* The photographs (from color negatives) were produced in *P. Schlup's* (†) photographic laboratory.

[1] Pollingher, U., H. Ambühl, H.R. Bürgi: A new method for processing clay rich unconsolidated sediments for paleoecological investigations. J. Paleolimnology 7: 95–101 (1992).

[2] Ambühl, H.: Technik der Präparation und Darstellung von Sedimentkernen mit grossem Querschnitt *[Technique for the preparation and presentation of sediment cores of large cross-section].* Schweiz. Z. Hydrol. 47, 2, 249–256 (1985).

[3] Züllig, H.: Untersuchungen über die Stratigraphie von Carotinoiden im geschichteten Sediment von 10 Schweizer Seen zur Erkundung früherer Phytoplankton-Entfaltungen *[Studies on the stratigraphy of carotenoids in stratified sediment from ten Swiss lakes to identify earlier phytoplankton growth].* Schweiz. Z. Hydrol. 44, 1, 1–98 (1982).

[4] Ambühl, H., H. Bührer: Transportables Kransystem für Probeentnahmearbeiten in beliebigen Booten *[Transportable crane system for sampling work in any boat].* Schweiz. Z. Hydrol. 47, 241–247 (1985).

[5] Ambühl, H., H. Bührer: Zur Technik der Entnahme ungestörter Grossproben von Seesediment: ein verbessertes Bohrlot *[Technique for extracting undisturbed large-scale samples of lake sediment: an improved bore plumb].* Schweiz. Z. Hydrol. 37, 175–186 (1975).

Carrick M. Eggleston

Mineral Surfaces and Surface Sites as Chemical Reactants: Direct Observation

In October 1994, EAWAG postdoctoral researcher Carrick Eggleston accepted a similar position at the Lawrence Livermore National Laboratory in California. In July 1995, he will join the faculty at the University of Wyoming in Laramie, Wyoming (USA) as an Assistant Professor in the Department of Geology and Geophysics. Stephan Hug (see p. 26) will continue the work with the RTM and ATM which was initiated at the EAWAG by Dr. Eggleston.

Our understanding of heterogeneous (solid-liquid) chemical reactions in natural systems is based primarily on characterization of dissolved species. Here, I concentrate on the other half of the problem: reactive sites on solid surfaces. Direct observation of "active" sites by scanning probe microscopy is beginning to advance our understanding of surface reactions, of what makes certain sites "active", and of how to predict the number of active sites available for reaction. Such knowledge enhances our ability to predict how heterogenous reaction systems will respond to changes in conditions.

Surface(s) of the Earth

The spherical surface of the Earth represents about 5×10^8 km^2 of area. This overall surface contains more than 10^{12} km^2 of mineral-water interfaces. Chemical reactions at these interfaces are a fundamental component of an overwhelming variety of natural chemical processes. Adsorption-desorption, dissolution-precipitation, and catalytic reactions involving surfaces control the chemical evolution both of natural waters and solids, whether in soil and ground waters, lakes and streams, or in oceans. Models of chemical interaction between surfaces and materials with which they come in contact are, therefore, important in many areas of environmental science, and an increasing amount of basic research is dedicated to improving these models or to defining their limits of applicability.

Surface sites in Chemical Reactions

Let us examine a simplified adsorption reaction to illustrate some of the problems encountered in understanding surface reactions. The adsorption of an organic ligand L^- to a mineral surface can be modeled using a stoichiometric ligand-exchange equation:

$$>SOH + L^-_{(aq)} + H^+_{(aq)} \rightarrow >SL + H_2O$$

$$K_L = [>SL]/[>SOH][L^-][H^+] \quad (1)$$

where >SOH represents a surface site, K_L is an equilibrium constant, and [ ] represents activity. Reaction (1) has stoichiometric significance only, although many spectroscopic studies have shown that the structure implied in (1) indeed occurs. However, most spectroscopic techniques employed for studying surface-complex structure probe the local coordination or magnetic environment, or vibrational properties, of the adsorbed species. The

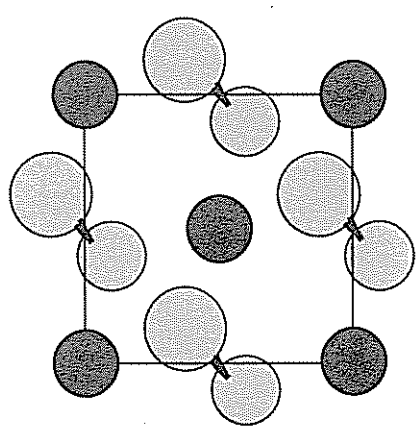


Fig. 1
Model of a surface unit-cell of the pyrite (100) surface. Filled circles represent Fe atoms, and shaded circles represent S atoms above (larger) and below (smaller) the plane of Fe atoms.

surface >SOH sites, by comparison, remain structurally undefined. This lack of definition limits our ability to model the complexity of natural systems, because not all surface sites are the same, even on a single mineral grain. Knowledge of what makes particular sites especially reactive, and how we might predict their abundance, could improve this situation.

For example, under most natural conditions mineral dissolution and precipitation is controlled by surface reactions. The dissolution rate R of a metal oxide can be written, in simplified form,

$$R = k_1[>SOH] + k_H[>SOH_2^+] + k_L[>SL] \qquad (2)$$

where k_1, k_H, and k_L are rate constants for pH -independent, proton-promoted, and ligand-promoted dissolution, respectively [1]. More terms can be added for more complicated systems. If the rate constants are known, the dissolution rate can be predicted from adsorption equilibria. For example, from reaction (1), [>SL] in the third term of equation (2) can be given as $K_L[>SOH][L^-][H^+]$. Each term in equation (2) will contain an expression for surface sites, >SOH. However, usually only a small number, $>SOH_{active}$, of the total surface sites, $>SOH_{tot}$, are "active" toward dissolution. The questions I wish to examine in this paper are: what are active sites, not only for dissolution but for other reactions as well, and how can we quantify them?

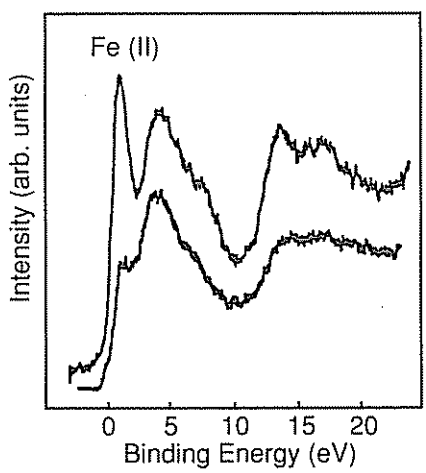


Fig. 2
This figure shows two X-ray photoelectron spectra from pyrite, taken and replotted from Ennaoui et al. [2] .The peaks in the spectra represent electrons from particular atomic orbitals of the solid. Quantum mechanical calculations aid in the interpretation of such spectra. The peak at 1 eV binding energy, for example, represents Fe 3d electrons in Fe (II). The broader peaks between 2 and 9 eV represent S 3p electrons, and the peaks between 12 and 20 eV represent S 3s electrons. The upper spectrum represents a fresh surface. The lower spectrum represents a surface after partial oxidation. Note the decrease in intensity of the Fe(II) peak in the lower spectrum.

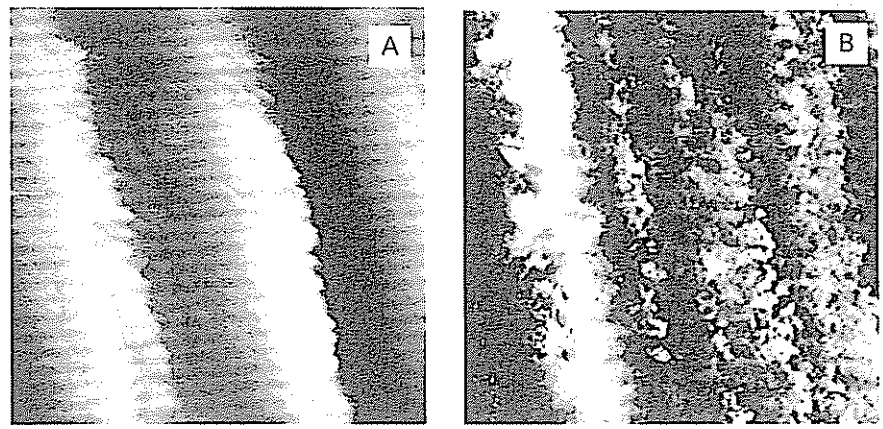


Fig. 3
(A) STM image of a fresh pyrite surface, taken in air with a Tungsten tip at a bias voltage of -316 mV and 1.0 nA. The image is 150 x 150 nanometers, with vertical relief of 1.5 nanometers (15 Å, equivalent to just over 3 atomic layers). Two steps, one atomic layer (left) and two atomic layers (right) run through the image near-vertically.
(B) STM image of a pyrite surface after one day in air. The conditions and image size are the same as in (A), except that bias is -40 mV. The surface appears corroded.

Reactivity and Predictability of Active States

What do we mean by ">SOH" and "$>SOH_{active}$"? I have chosen two examples: specific Fe(II) sites on oxidizing pyrite surfaces and kink sites on calcite surfaces.

A) Oxidation of pyrite (FeS_2) {001} surfaces

Pyrite is the most common sulfide mineral at the Earth's surface. Its redox chemistry is important in electron and elemental cycling in sediments, acid mine drainage, and photochemical reactions. Here, we discuss a very simple experiment in which a fresh pyrite surface is allowed to oxidize in air for one day.

Pyrite structure: where are the atoms and electrons?

Fig. 1 shows the pyrite {001} surface unit cell with an Fe(II) atom at each corner and one in the center. Because scanning tunneling microscope, STM, "sees" electronic structure, rather than atoms *per se*, we must understand the electronic structure of pyrite. Fig. 2 shows two photoelectron spectra [2]. The upper spectrum was taken from a fresh surface. Quantum mechanical calculations and specialized spectroscopic measurements show that the intense peak at 1 eV binding energy represents Fe 3d electrons in Fe(II) [3,4]. These

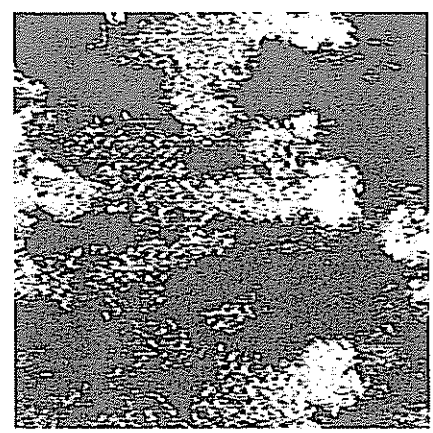


Fig. 4
STM image of a pyrite surface oxidized in air for one day (-40 mV, 1.0 nA). The image is 40x40 nanometers, and vertical relief is 8 Å. Although the image is slightly noisy, some areas are unoxidized, and the atomic periodicity of these areas (brighter) is visible. Other areas are oxidized and appear dark. A few individual oxidized sites appear within unoxidized areas. The borders between oxidized and unoxidized areas are crystallographically controlled.

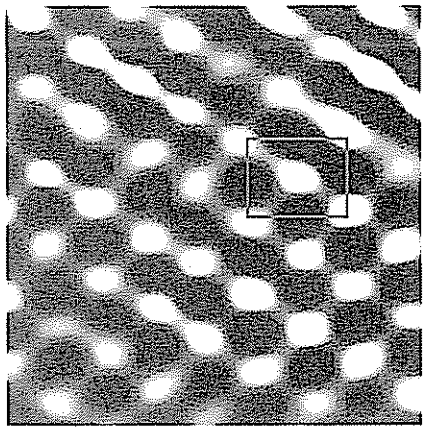


Fig. 5
STM image of a fresh, unoxidized pyrite surface. Compare the unit cell in this image to that drawn in Fig. 1. As expected from the electronic structure, we see only Fe (II) atoms at the surface. Image area is 2 x 2 nanometers.

electrons are the strongest reducing agents of the pyrite surface.

The lower spectrum in Fig. 2 was taken from a pyrite surface after partial oxidation [2]. The most important change is the greatly decreased intensity of the peak at ~1 eV. Oxidation has reduced the number of 3d electrons in Fe(II) at the surface. With an STM, we can "see" these 3d electrons and, therefore, "see" the Fe(II) atoms at the surface as well as their "disappearance" with oxidation progress.

Microtopography

Fig. 3a shows an STM image of an area of a freshly cleaved pyrite {001} surface, 0.15 mm on a side. The surface is relatively smooth (see figure caption for details). Fig. 3b shows an STM image of the same surface (in a slightly different place); the image area is the same size as in Fig. 3a, but the surface appears corroded. There are dark areas and light areas. Let us look more closely at the surface to examine the reasons for this.

Fig. 4 shows an image of the pyrite surface, 0.02 mm on a side. In the lighter areas, one can begin to see the atomic structure of pyrite. "Close-ups" of unoxidized areas (Fig. 5) show the structure expected of a fresh pyrite surface in which the bright "bumps" correspond to Fe(II) atoms (compare Fig. 5 to Fig. 1). Sulfur atoms are also present, but they are invisible to STM because they do not have electrons that the STM can "see" under the conditions used. In Fig. 4, some areas appear "dark"; these are the areas in which the electrons of Fe(II) have been lost by oxidation, the same electrons that are observed to "disappear" from the spectra in Fig. 2 after oxidation. Interestingly, the oxidized sites occur mostly in larger oxidized "patches", implying that oxidation occurs not by a randomly distributed process, but by a nucleation and growth process. In addition, the edges of the oxidized patches often occur parallel to particular crystallographic directions, often the [110], [100], and equivalent directions (compare Fig. 4 and Fig. 6).

Fe(III) and surface structure: different reactivities for different sites?

It is well known that Fe(III) plays an important role as an oxidant in pyrite oxidation. It is, therefore, reasonable to suggest that the number of nearest-neighbor Fe(III) sites around an unoxidized Fe(II) site is important in determining the overall oxidation probability for different surface Fe(II) sites. In Fig. 6, an Fe(II) site along a reaction border parallel to [110] (site 1) has only one oxidized nearest neighbor, whereas unoxidized sites at a "kink sites" (site 2) or along [100]-oriented reaction borders (site 3) have two Fe(III) nearest neighbors. This suggests that sites 2 and 3 in Fig. 6 should oxidize more rapidly than site1. If so, then the surface should become residually enriched in sites like site 1. This is the same as saying that we should see many reaction borders oriented parallel to [110] and equivalent directions. This is indeed seen in Fig. 4, but many sites like 2 and 3 in Fig. 6 also occur. This suggests that there is not a large difference in reactivity between the different sites modelled in Fig. 6, although sites like 1 are probably slightly less reactive than 2 and 3.

There are many more complicated interpretations that can be made. For example, we have only examined initial surface oxidation. Long-term oxidation probably consists of several parallel mechanisms. Direct oxidation of surface Fe(II), oxidation by adsorbed

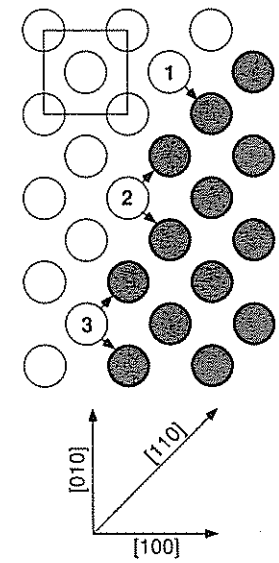


Fig. 6
Model of different Fe(II) sites along a border between an unoxidized area (unfilled circles represent (Fe(II)) and an oxidized area (filled circles represent Fe(III)). Site 1 has one Fe(III) nearest neighbor, whereas sites 2 and 3 have two oxidized nearest neighbors. Therefore, sites 2 and 3 are probably more likely to oxidize than site 1. A unit cell is included in the upper left (compare to Fig. 1), and the major crystallographic directions are given.

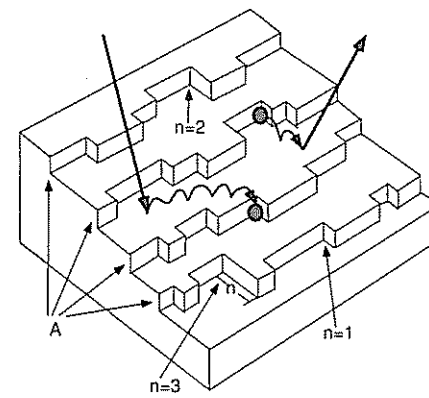


Fig. 7
Model of a crystal surface, showing four steps (A). Along each step are kink sites of various sizes defined by n. A kink site may have a size of 1, 2, 3 or more crystallographic units. Solutes from a solution may adsorb, surface-diffuse, and attach to kink sites during growth, or may detach from kink sites, surface diffuse, and desorb. Surface diffusion distances on minerals appear to be short [6,7]. Attachment or detachment from kinks causes the kink to move, and the motion of kinks causes the step to move. The overall rate of growth or dissolution of the area illustrated will depend on the number of kink sites, not simply on the total surface area.

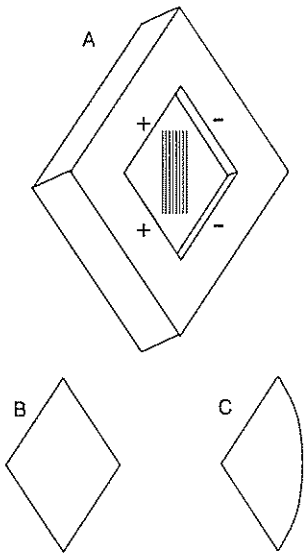


Fig. 8
A) Model of a calcite crystal (rhomb) with a pit in the center of a flat face. Steps marked "+" move faster than steps marked "–" during dissolution or growth [6]. The vertical lines are parallel to the atomic rows seen in Fig. 9.
B) The shape of a pit in highly undersaturated solution.
C) The shape of a pit on a surface that has approached equilibrium from undersaturation. The "–"-steps spontaneously curve, implying the spontaneous formation of kink sites.

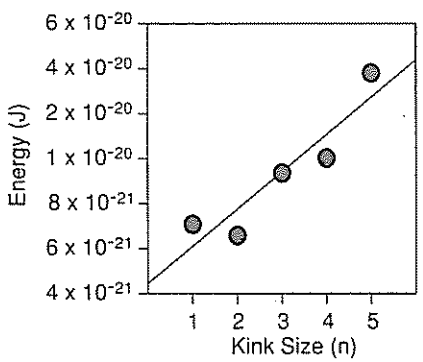


Fig. 10
A plot of kink energy versus kink size, n (n is defined in Fig. 7). The energies were calculated from statistical data on the numbers of kinks of various sizes n, denoted N(n), in comparison to the total number of possible kink sites (i.e., sites along steps), denoted N(0), using the Boltzmann equation, $N(n)/N(0) = \exp[E_n/kT]$. The resulting formation energies thus do not include the energy required to form a surface (ca. 24 kJ mol^{-1} of unit cells) or the energy required to form the steps along which the kinks occur (which is estimated to be similar to the kink formation energy because the formation of a kink requires the formation of a section of step).

Fe(III), and even electron conduction through thin layers of Fe(III) oxide may all occur simultaneously, and as oxidation proceeds different mechanims may become rate-controlling. Also, I have ignored sulfur. Fe(III) also acts as an important oxidant of sulfur, and better definition of the important reactive Fe sites may also help in understanding and modelling sulfur oxidation. Here, I wish only to show that the STM observations allow us to ask questions concerning the relative reactivity of different surface sites. For example, potentially important surface sites, such as those in Fig. 6, can be studied using quantum chemical calculations to quantify electron transfer probabilities. We can thus begin to form direct connections between the microscopic world, macroscopic oxidation rates and experiments, and eventually the behavior of pyrite in natural systems.

B) Kink site energetics and $CaCO_3$ dissolution

In this section, we will briefly discuss "active" sites in the dissolution and precipitation of calcite. The solid-solution equilibria and kinetics of calcite play a large role in global carbon cycling as well as in local water quality, the use of calcite to infer paleoenvironmental conditions, and the action of carbonates in absorbing trace metals from solution. What are "active sites" in calcite dissolution and precipitation, and how can we predict their behavior?

Perhaps the most widely-accepted model of crystal growth and dissolution is the Burton-Cabrera-Franck (BCF) model, in which adsorption and desorption equilibria create a steady-state population of adsorbed species that can move across the surface and interact with (attach to or detach from) kink sites (see Fig. 7). It has been shown [5] that kink sites are usually the "active" sites mentioned in the introduction. If we could predict the number of kink sites likely to occur in different conditions, we would have a much better understanding of ">SOH_{active}".

Direct, in-situ imaging of surface microtopography during dissolution

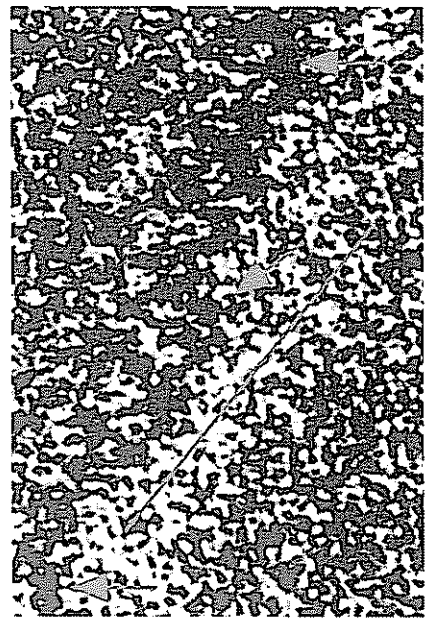


Fig. 9
Atomic force microscope (AFM) image of a calcite surface in equilibrium with water (closed to the atmosphere).
In AFM, unlike in STM, the image arises from forces rather than electronic conduction. Here, the forces are predominantly electrostatic [9], in the range of 10^{-10} Newtons. Under these conditions, ambient vibrations are enormous and contribute greatly to noise.
The image area is 10x15 nanometers, and atomic rows can be seen. A step runs through the image from lower left to upper right. The expected step direction is marked. Kink sites, which are sections of the step parallel to the atomic rows rather than diagonal to them, are visible (some are marked with arrows), and could be counted in many similar images.

and growth of calcite [6] has shown that steps indeed advance and retreat across the surface in accord with the BCF model. Interestingly, steps in different crystallographic orientations on calcite move at different rates. Fig. 8 shows which steps move quickly and which steps move slowly. This implies that some kink sites are either more reactive or more populous than others. Also, it has been observed that etch pits originally with the shape shown in Fig. 8b spontaneously evolve into the shape shown in Fig. 8c as equilibrium with solution is approached. This implies that kink sites form much more easily along the (-) steps than along the (+) steps. What is the formation energy of kink sites on the two steps?

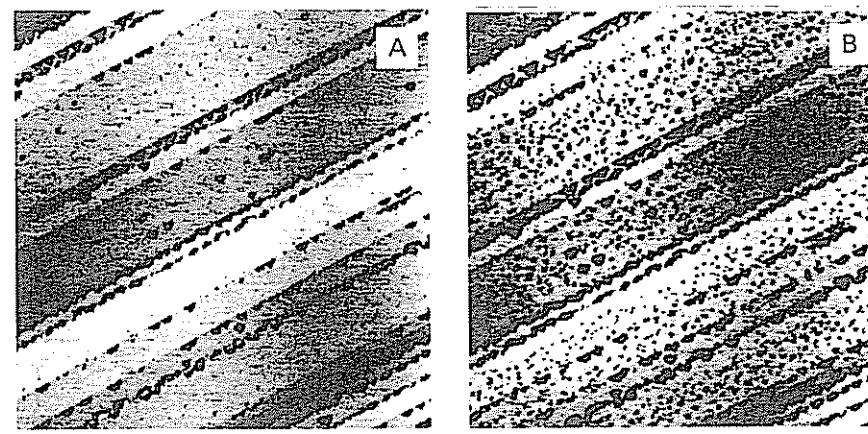


Fig. 11
Both images presented here are AFM images of microtopography, 8 x 8 mm. Vertical relief is 4 nanometers.
A) A calcite surface after 3.5 hours of exposure to air. Many pits have formed on the surface, mostly along steps.
B) after 6 hours of air exposure, pits have also formed on the flat terraces between steps.

Formation energy of kink sites

Direct, in-situ observation of steps by atomic force microscopy (AFM), with the surface in equilibrium with water, gave images similar to Fig. 9. The calcite structure can just barely be seen. The step is not parallel to the nominal step direction, but is curved and exhibits a number of kink sites.

To a first approximation, the kink site formation energy can be calculated from x_o in

$$E = kT \ln [(2x_o/a) - 2]$$

where a is the crystallographic constant in the step direction, E is the kink energy, x_o is the mean distance between kink sites, and k and T have their usual meanings [8].

From the images, x_o was measured and the energies of kink sites calculated. The formation energy of kink sites on (+) steps is constrained to be >8 kJ mol^{-1}, and along (-) steps is approximately 2 kJ mol^{-1}. Another statistical treatment of kink sites along (-) steps [9] (Fig. 10) gave formation energies of >3 kJ mol^{-1}, depending on kink size. Thus, two different models show that kink formation energies on calcite in water are very small, probably less than 10 kJ mol^{-1}. These numbers must be considered approximate, however, because they are based on a statistically small number of observations.

Surfaces change with time

With such small formation energies, we expect that steps and kink sites should form spontaneously on calcite surfaces in water at room temperature. This explains the spontaneous curving of steps illustrated in Fig. 8 (spontaneous curving during approach to equilibrium also shows that the kink population depends on undersaturation). In addition, Fig. 11 shows the spontaneous formation of small depressions on an originally flat surface exposed to air. To obtain Fig. 11, a calcite crystal was cleaved in air. The fresh surface was atomically flat except for a few steps from upper left to lower right. After 3.5 hours in air (Fig. 11a), pits or depressions had formed on the surface, mostly along the steps. After 6 hours in air (Fig. 11b), pits had also formed in the flat terraces between steps. This spontaneous thermal step and kink formation is consistent with low kink formation energies.

With knowledge of kink site formation energies, in turn, several models can be used to calculate kink site populations as a function of supersaturation, temperature, and other variables, thus allowing us to quantify what we mean by "$>SOH_{active}$" in equation (2). For example, if we can now begin to quantify the ratio

$$[>SOH_{active}]/[>SOH_{total}],$$

and to understand how this ratio varies with conditions, we may be able to extend dissolution models to non-steady-state conditions and thus make them more flexible for describing non-steady-state natural systems.

Outlook

I have discussed two examples of how microscopic observations can be used to constrain macroscopic models, particularly concerning what we mean by the symbolism ">SOH" for a surface site. Any physically realistic model must be consistent with microscopic observations, not only *structurally* (as spectroscopic studies have emphasized), but also *energetically*, in terms of population distributions and binding energies. New microscopic techniques are beginning to allow us to quantify these constraints, and thus to better define the surfaces and surface sites that act as key reactants in natural systems. The hope is that not only the speciation of dissolved species and adsorbed species, but also of the surface sites themselves, can eventually be predicted so that we can more accurately sort out the important mechanisms and pathways of heterogeneous reactions.

[1] Stumm W. *Chemistry of the Solid-Water Interface.* Wiley, 1992.
[2] Ennaoui A., Fiechter S., Jaegermann W., and Tributsch H., *J. Electrochem. Soc.* 133 (1), 97–106, 1986.
[3] Li E.K., Johnson K.H., Eastman D.E. and Freeouf J.L., *Phys. Rev. Lett.* 32, 470–472, 1974.
[4] Tossell J.A., Vaughan D.J. *Theoretical Geochemistry: Application of Quantum Mechanics in the Earth and Mineral Sciences.* Oxford, 1992.
[5] Wehrli, B., *J. Coll. Interf. Sci.* 132, 230–242, 1989.
[6] Gratz A.J., Hillner P.E. and Hansma P.K., Geochim. Cosmochim. Acta 57, 491–499, 1993.
[7] Eggleston C.M., and Stumm W. Geochim. Cosmochim. Acta 57, 4843–4850, 1993.
[8] Frenkel J. J. Physics, USSR, 9(5), 392–398, 1945.
[9] Eggleston C.M. EOS, 74(43), 626, 1993.

Hansruedi Siegrist

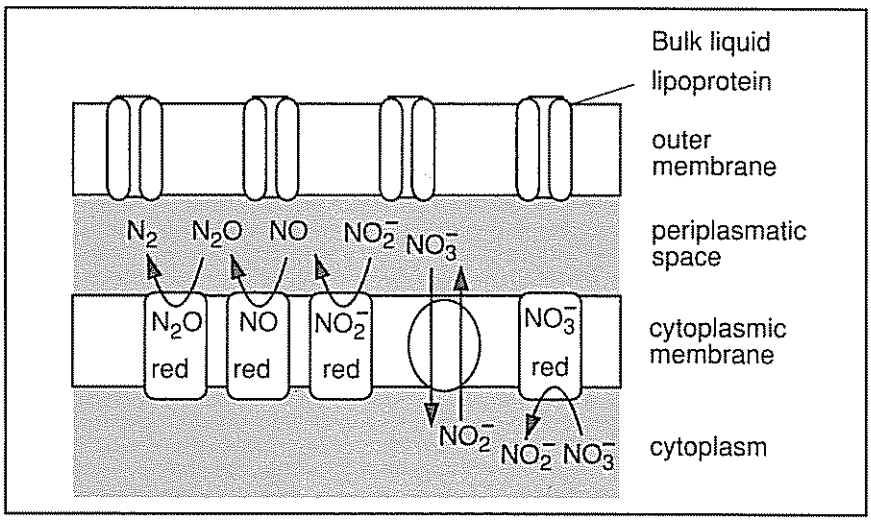
The Removal of Nutrients in Activated Sludge Systems

In its efforts to protect the North Sea, the EEC soon plans to stringently limit discharge of the nutrients phosphorus (P) and nitrogen. A number of sewage treatment plants have already been enlarged to include nitrification and chemical phosphate precipitation. Due to operation and energy management, denitrification might be added within the framework of future improvements of these plants. This will be possible in some cases without adding tank volume. In order to both save the amount of precipitating agent used and to decrease the volume of sewage sludge produced, the possibility of employing biological P removal in combination with chemical precipitation of residual P should be investigated parallel to the introduction of the denitrification process.

Introduction

As a consequence of the eutrophication of the North Sea's coastal waters, the larger sewage treatment plants in Switzerland will have to reduce their nitrogen load either to meet a certain standard level or by 70–80% according to the EEC directives 21 May 1991. In order to remove the nitrogen, supplementary denitrification could be added to those plants already carrying out nitrification in their activated sludge systems. Small and medium-sized sewage treatment plants will also operate a limited pre-denitrification process in order to improve the properties of the sludge and to reduce the amount of bulking and floating sludge.

Only a few domestic sewage treatment plants in Switzerland currently operate denitrification systems. Consequently, there is little operating experience upon which to design the extension of a sewage treatment plant to include an incoming denitrification system. Parallel to the introduction of denitrification, enhanced biological phosphorus removal should be investi-



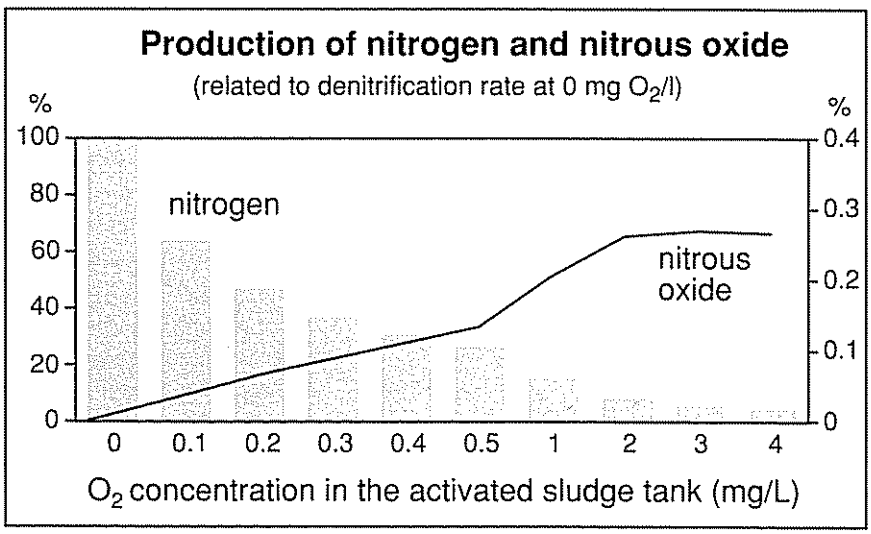


Fig. 1
Above: The enzymes of the respiratory chain of denitrification are localized in the cytoplasmic membrane of Gram-negative bacteria. The active site of nitrate reductase is on the inside of the membrane. The transport of nitrate through the cytoplasmic membrane occurs through a transport system involving the exchange of nitrite. The active sites of the nitrite, NO and N_2O reductases can be found on the outside of the cytoplasmic membrane in the periplasmatic space [3].

Below: Nitrous oxide-reductase (N_2O) is more strongly inhibited at low oxygen concentrations than the nitrite and nitrate reductases, which leads to increased emissions of nitrous oxide if the oxygen supply is insufficient (calculations made using an experimentally calibrated model [4]).

gated as a possibility for partially replacing the current methods of P removal by chemical precipitation.

If a sewage treatment plant is equipped with a filtration system, a fraction of the nitrate can be denitrified in the filter by adding an easily degradable organic compound (e. g., methanol). This means, however, that enhanced biological removal of phosphate in the activated sludge system would not be possible, as low nitrate values and a well-functioning denitrification system are prerequisites for enhanced biological phosphorus removal.

The removal of nitrogen by heterotrophic denitrification

Denitrification is carried out by heterotrophic bacteria that decompose organic compounds (CH_2O) and reduce nitrate (NO_3^-) to molecular nitrogen (N_2) in several steps (see Fig. 1 above):

$$4\,NO_3^- + 5\,CH_2O \Rightarrow CO_2 + 4\,HCO_3^- + 2\,N_2 + 3\,H_2O$$

In the process of denitrification, 50% of the acid buffer capacity (HCO_3^-) required for nitrification is recovered, which leads to more stable pH conditions at low bicarbonate levels. About 70% of the heterotrophic bacteria that can live in oxygen are able to reduce nitrate under anoxic conditions (i.e., nitrate present but molecular oxygen absent).

The efficiency of denitrification and enhanced biological phosphorus removal is dependent on the easily degradable, dissolved organic fraction in the inflowing sewage water. As a consequence of the pre-oxidation of the wastewater in the sewers and the high dilution of wastewater by external water, the fraction of easily degradable organic components in Swiss domestic wastewater is small, and practical results from foreign plants cannot be directly applied. Siegrist and Gujer [1] have described a static model for planning the construction of a denitrification system which takes into account the composition of the wastewater, the influent concentration of oxygen, the flow diagram of the entire system and temperature. This model will be tested in the sewage treatment plants of Neugut in Dübendorf and Zürich-Werdhölzli. At the same time, the dynamic behavior of the nitrification/denitrification processes will be followed by on-line surveillance. The degree of correlation to the behavior simulated by mathematical models will be continuously tested.

Preliminary trials in the sewage treatment plants of Zürich-Werdhölzli and Zürich-Glatt suggest that for typical Swiss domestic wastewater (BOD/N ca. 4), a 60-70% removal of nitrogen can be achieved with 30% anoxic (denitrifying) volume in spite of the considerable oxygen input into the denitrification zone (6–12 g O_2/m^3 inflow) [2]. The removal efficiency stands in relation to the influent nitrogen load and also accounts for the incorporation of nitrogen into microbial biomass. Supplementary measures (e.g., reducing oxygen input from inflow and return flow, adapting the aeration to the requirements of nitrification, reducing the volume of the preclarification tank and possibly adding an easily degradable substrate) would facilitate an even higher removal efficiency to be achieved.

Fears that denitrification could lead to increased nitrous oxide emissions are unfounded. Nitrous oxide emissions are highest where redox conditions are not clearly defined, as may be the case near the influent of strictly nitrifying activated sludge plants. Low oxygen levels inhibit nitrous oxide reductase significantly more strongly than nitrate and nitrite reductase, leading to an accumulation of nitrous oxide at low oxygen concentrations. In comparison, the emission of nitrous oxide in well-defined denitrification zones is less than 0.1% of the denitrified nitrogen load (see Fig. 1 *below* on page 11).

Process technology of denitrification

One can differentiate between two main types process technology for nitrogen removal in activated sludge systems [5]:

- Nitrification and pre-denitrification in *separate* tanks. This includes incoming denitrification and cascade denitrification.
- Nitrification and denitrification in a *single, unseparated* tank, in which a spatial or temporal separation of the two processes can be made. Simultaneous and intermittent denitrification, as well as alternating denitrification and the sequential batch reactor all belong to this classification.

In *pre-denitrification*, the front part of the activated sludge system does not receive aeration, and the activated sludge is kept in suspension by a stirrer. Nitrate enters the anoxic area of the tank through the return sludge. An additional internal recirculation from the end of the aerobic tank to the beginning of the anoxic tank can enhance the efficiency of denitrification; this also reduces the hydraulic load of the clarifier. Space permitting, pre-denitrification can be integrated rather easily into existing nitrifying systems.

During *cascade denitrification*, the anoxic and aerobic sections of the tanks alternate in the line of flow. Additional internal recirculation is not necessary as the nitrate always originates from the previous nitrifying zone. Optimally, the inflow should be distributed equally among the denitrification zones.

In *simultaneous denitrification*, nitrification and denitrification take place simultaneously in different zones of the tank (carrousel plant). During intermittent denitrification, nitrification and denitrification are temporally separated but occur within the same reactor.

During *alternating denitrification*, denitrification and nitrification alternate between two linked tanks (bio-denitro-process). The inflow is lead into the non-aerated tank, whereas the outflow always moves out of the aerated one. In order to ensure that no anaerobic wastewater containing ammonium flows into the clarifier when switching over, an aeration phase has been inserted for both tanks.

In the *sequential batch reactor*, the wastewater is added in batches and is then denitrified, nitrified and subse-

quently decanted. This process can be applied when the catchment area is relatively small and possesses a separate sewer system (storm sewers).

Simplified model for describing the enhanced biological removal of phosphorus

The microbiological mechanisms of polyphosphate storage have only been partially elucidated. The activated sludge model assumed by process engineers [6, 7] (see Fig. 2) was recently corroborated by Ubukata and Takii [8] in pure cultures; however, only for a bacteria growing on amino acids. For this reason, there should be a closer collaboration between microbiology and the engineering sciences in order to more accurately describe the microbiological mechanisms occurring in mixed cultures and to develop a better working model.

The model which has been put forward by process engineers assumes that a phosphorus-accumulating organism (PAO) exists within activated sludge that requires two different redox conditions for P accumulation to occur (see Fig. 2):

- Under anaerobic conditions (without nitrate), the polyphosphate stored within the cell is released anaerobically and excreted as orthophosphate. The resulting, biochemically useful energy is utilized for maintaining the cell and for assimilating easily degradable substrates. As the bacteria cannot utilize the substrate under anaerobic conditions, it is stored in the cell in the form of long-chained compounds (e.g., polyhydroxy carboxylic acids).
- Under aerobic (and partly also under anoxic conditions), the anaerobically stored substrate is respired as a source of energy and utilized for cell growth. At the same time, some of the resulting energy is used for storing polyphosphate.

The proposed phosphorus-accumulating organism depends on respiration and anaerobically stored substrate for its cell growth. For this reason, the activated sludge should be able to run through several anaerobic/anoxic/aerobic cycles. The growth rate is lower than for other heterotrophic bacteria. The advantage of phosphorus-accumulating organisms is the capacity to store substrate in an environment which does not allow other bacteria to grow. Other bacteria can only utilize the easily degradable substrate efficiently when a corresponding electron acceptor is available (oxygen or nitrate), as the possibility of storage does not exist for them.

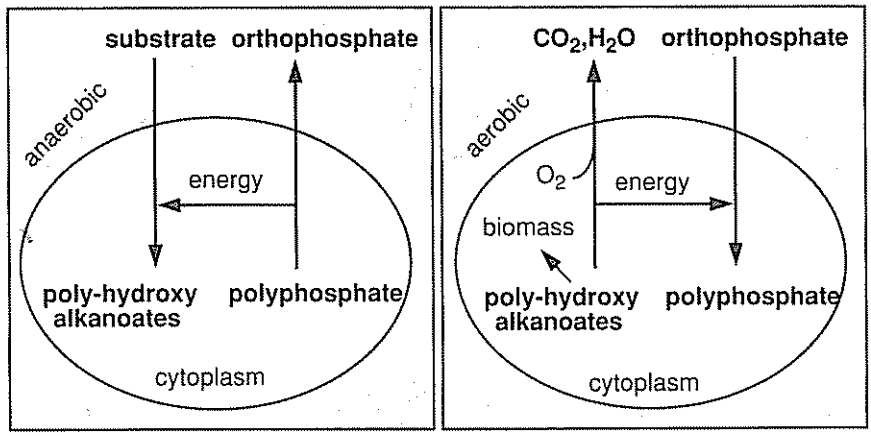


Fig. 2
Scheme of the anaerobic and aerobic processes in phosphorus accumulating bacteria.

For mixed cultures in an anaerobic environment, a definitive relationship between the disappearance of dissolved BOD (Biochemical Oxygen Demand) and an increase in the orthophosphate content of the water exists. The bacteria do not assimilate all substances equally well. Volatile fatty acids such as acetic acid, propionic acid or butyric acid are assimilated most efficiently. These substances, which are very easily degradable under either aerobic or anoxic conditions, are seldom found in high concentrations in the influent. There are exceptions; for example, for long residence times in the sewer or in the preclarification tank where through fermentation a substantial fraction of the BOD is made available in the form of volatile fatty acids for the redissolution of phosphate. The fraction of easily degradable substances could also be increased by adding volatile fatty acids from primary sludge acidification. Otherwise the substrate has to be «produced» *in situ* by fermenting the particulate substances during a sufficiently long anaerobic residence time.

In order to carry out the biological removal of phosphorus, the activated sludge has to be alternatingly exposed to aerobic and anaerobic conditions (see Fig. 3). At high concentrations of easily degradable substrate matter in the anaerobic tank, the nitrate from the returned sludge is denitrified and the phosphate is redissolved by the phosphorus-accumulating bacteria. To what extent the redissolution and assimilation of phosphate occur simultaneously under anoxic conditions cannot yet be quantified.

The role of nitrate is not clear at this time, and additional research is needed. Experiments show that an anoxic environment can inhibit the redissolution of phosphate. If the availability of substrate is low, the nitrate has to be denitrified before phosphate can be redissolved. For this reason, every biological phosphorus removing system also has to have a good denitrification system.

Inhibition of the biological removal of phosphorus by nitrous oxide (NO) at concentrations higher than 20 µM NO, as observed by Appeldorn [9], will probably not cause problems in continuously running systems since the concentration of NO in an incoming denitrification system is usually about 1000 times lower [10]. A decrease in overall denitrification capacity due to fixation of substrate in the anaerobic phase by polyphosphate-accumulating organisms has not yet been corroborated in practice suggesting that some of the

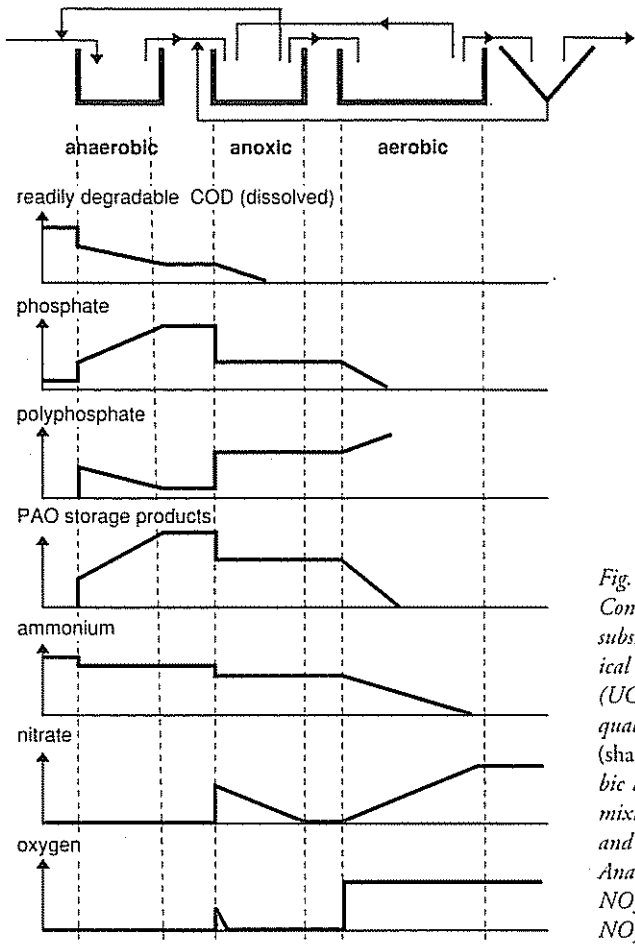


Fig. 3
Concentration profiles of various substances in an enhanced biological phosphorus removal plant (UCT-process). The graphs are qualitative and strong changes (sharp jumps) *before the anaerobic and the anoxic tanks suggest mixing effects with return sludge and internal recirculation. Anaerobic = without O_2, without NO_3. Anoxic = without O_2, with NO_3.*

PAO are carrying out denitrification based on a supply of stored substrate and so can already assimilate phosphorus under anoxic conditions.

The chemical process technology for biological removal of phosphorus

There are two main types of processes for the biological removal of phosphorus:

- In the *mainstream* process, the redissolution of phosphate occurs in the mainstream of the wastewater in an anaerobic tank series connected to the denitrification/nitrification process. Phosphorus is removed as polyphosphate with the surplus sludge.
- In the *side stream* flow process, part of the return flow of sludge is lead through a separate tank where anaerobic conditions enable the polyphosphate to be redissolved (pretreated sewage having been added). As the resulting dissolved phosphate is rather concentrated,. it can be precipitated with lime or iron (phostrip-process) after separating and returning the polyphosphate-poor activated sludge.

Maurer and Gujer [11] have developed a static model for calculating the efficiency of biological phosphorus removal, taking into account the composition of the wastewater, the input of oxygen, the layout of the system and temperature. This model will be verified in the sewage treatment plant of Neugut in Dübendorf and in a laboratory system. The Task Group on Mathematical Modelling of the IAWQ (International Association on Water Quality) has developed a dynamic model for describing the biological removal of phosphorus [12], which is also being tested on Swiss domestic sewage in the laboratory and in the Neugut sewage treatment plant.

A large number of flow diagrams for the mainstream process have been published and many patents issued. The UCT-process developed at the University of Cape Town is used for illustrating the course of the concentrations of various substances (see Fig. 3). The return sludge is first conducted into the anoxic zone. An additional return pipe into the inflow leads the nitrate-poor sludge into the anaerobic tank; the biologically stored phosphorus can be redissolved without the inhibiting presence of nitrate. The efficiency of denitrification can be increased by means of an internal recirculation between the aerobic and the anoxic zones.

As Swiss wastewater is rather dilute, the phosphate levels of the discharge cannot be kept at a stable level using biological P removal alone. Consequently, the standards of the (Swiss) Ordinance for Water Pollution Control cannot be met, and a residual phosphate precipitation with iron or aluminum salts is required. The precipitant may, however, only be added to the far end of the aerobic tank after the phosphate has been completely assimilated biologically. This process should be controlled by the on-line measurement of orthophosphate levels in the effluent of the activated sludge system. When using trivalent iron or aluminum salts, the precipitant could also be added to the outflow of the activated sludge system. The precipitation of residual phosphorus by means of a flocculation filtration would completely relieve the activated sludge system of precipitated sludge.

Since the amount of precipitated sludge is significantly reduced by the biological removal of phosphorus, the integration of a biological phosphorus removal system with a denitrification system is not expected to lead to a significant enlargement of tank space; however, the non-aerated tank space would be enlarged at the expense of the aerated space.

Removal of nutrients and sludge treatment

During the digestion of the sewage sludge, the nitrogen bound in proteins is released as ammonium with a stoichiometric amount of bicarbonate being formed simultaneously. If the digested sludge is dewatered, the ammonium load from sludge treatment amounts to about 15–20% of the inflow load (see Fig. 4).

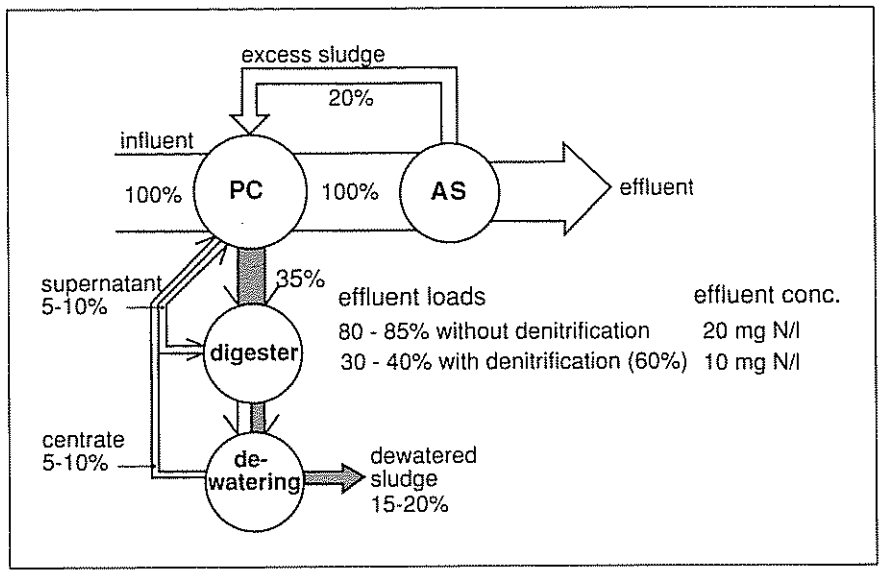


Fig. 4
Nitrogen loads in a sewage treatment plant containing sludge dehydration.
PC = primary clarifier. AS = activated sludge system.

The combined thickening of both primary and secondary sludges is not possible in a plant with biological phosphorus removal. The anaerobic conditions in the primary clarifier and in the pre-thickening tank causes a large amount of the biologically stored phosphate to redissolve thereby increasing the phosphate load for biological treatment. The excess sludge must be removed and immediately dewatered. If, however, the pre-dewatered excess sludge is digested together with the primary sludge, a fraction of the phosphate will be redissolved in the digester. The polyphosphate anion, stored in the microbial cells, is mainly stabilized by magnesium and potassium cations. These cations are also released during redissolution of phosphate. About 30% of the redissolved phosphate is precipitated in the digester in the form of magnesium ammonium phosphate ($MgNH_4PO_4$), and about 50% is precipitated as calcium hydrogen phosphate and adsorbed to sludge particle surfaces [13, 14]. If no aluminum or iron salts from phosphate precipitation are available, about 20% of the released phosphate salts remain dissolved in the digester supernatant. If about 50% of the P is stored as polyphosphate in the activated sludge system, this would lead to a phosphate reloading of the activated sludge system of about 10%.

After the release of biogas pressure, the precipitation of $MgNH_4PO_4$ and $CaHPO_4$ can lead to increased scaling in the digester supernatant piping and the simultaneous precipitation of calcium carbonate (decrease in the partial pressure of CO_2 increases pH) [15]. Whether the magnetic treatment of the supernatant could prevent increased scale formation of the piping is currently the subject of a doctoral dissertation at the EAWAG. The extent to which the precipitation of residual phosphorus with iron in the activated sludge system causes a decrease in the level of dissolved phosphorus in the supernatant and a binding of hydrogen sulfide in the digester is not yet known and requires further research.

In existing plants with biological phosphorus removal, differing rates of phosphate redissolution have been reported. In German sewage treatment plants, low concentrations of P are usually found (50–100 mg P_{tot}/L) in the supernatant with the phosphorus reloading amounting to less than 10% [16]. In a South African plant, however, as much as 130 mg PO_4-P/L were measured in the supernatant [17], leading together with particulate P to considerable reloading of the primary effluent.

If the precipitation of residual phosphorus is not needed in the activated sludge treatment, several possibilities exist for decreasing P in the digester supernatant:

- Direct dewatering of the excess sludge or pre-dewatering and mixing with digested primary sludge in the sludge storage tank. Due to the high solid retention time of the sludge in the activated sludge system (16–20 days), the excess sludge is usually largely mineralized, and additional digestion would not result in a further decrease in the amount of sludge. This procedure is, however, only possible when the sludge is subsequently dried or not used as fertilizer in agriculture as the disinfection step is omitted.
- Treating the digested sludge or the supernatant with iron or magnesium salts in order to precipitate the dissolved phosphorus.
- Removal of P stored in the form of polyphosphate from the activated sludge in the side stream flow (phostrip-process) and precipitation of the dissolved phosphate with lime, magnesium or iron. The phosphate-poor pretreated excess sludge can then be thickened and digested together with the primary sludge.

Summary

In order to decrease the nitrogen load, to improve the sedimentation properties of the sludge and to reduce the energy consumed by aeration, medium-sized and larger sewage treatment plants should run a limited *pre-denitrification* in the future. Preliminary experiments suggest that for typical Swiss domestic wastewater, a nitrogen removal of 60–70% can be achieved with 30% anoxic volume, in spite of considerable amounts of oxygen entering the denitrification zone. In the course of denitrification, a part of the alkalinity needed in nitrification is recovered, which leads to more stable pH conditions for soft water. Fears that denitrification might lead to increased emissions of nitrous oxide are unfounded.

As the amount of precipitating sludge can clearly be reduced by *enhanced biological removal of phosphorus*, one can assume that the integration of a biological phosphorus removal system into a well denitrifying system would not lead to a significant enlargement of tank space. The nonaerated reactor space

would be increased at the expense of the aerated space. The thickening or dewatering of the excess sludge has to take place separately, however, as the anaerobic conditions would cause a partial redissolution of the biologically bound phosphate.

To date, the microbiological mechanisms of polyphosphate storage are not well understood. Denitrification and the biological removal of phosphorus are very much dependent on availability of easily degradable dissolved organic compounds in the influent wastewater. As a consequence of the preoxidation of the wastewater in sewers and the dilution of wastewater by extraneous water, the fraction of easily degradable organics in Swiss domestic wastewater is usually small. Consequently, over the next 2–3 years, several projects at the EAWAG will focus on denitrification and the enhanced biological removal of phosphorus as well as interactions with sewage sludge treatment.

Current projects at the EAWAG in the field of nutrient removal

- Kinetics of nitrous oxide production in denitrifying sewage treatment plants (R. von Schulthess, W. Gujer)
- Acidification of primary sludge for the production of easily degradable substrate for the enhanced biological removal of phosphorus. Redissolution and precipitation of phosphate during the mesophilic digestion of excess sludge from enhanced phosphorus removal plants (D. Wild, W. Gujer, H. Siegrist)
- Population dynamics in the mixed biocenosis (I. Purtschert, W. Gujer)
- Dynamic modelling of enhanced biological phosphorus removal (M. Maurer, W. Gujer)
- Investigations on denitrification and enhanced biological phosphorus removal in the sewage treatment plants of Werdhölzli and Neugut (D.Baschnagel, C. Bernhard, I. Brunner, G. Koch, M. Kühni, H. Siegrist, W. Gujer)
- The microbiology of enhanced biological phosphate removal in domestic sewage treatment plants (R. Hesselmann, H.P. Kohler, A.J.B. Zehnder)
- Physiological regulation of the accumulation of polymers in bacteria (S. Frank, T. Egli).
- Mechanisms and practical areas of application of magnetic water treatment apparatus (R. Müller, B. Wehrli, H. Siegrist).

[1] Siegrist H. and Gujer W. (1994), Nitrogen removal in activated sludge systems including denitrification in secondary clarifiers, 17th Biennal International Conference, Budapest, Vol 1, pp. 247–256.

[2] Purtschert I. und Bühler R. (1993), Denitrifikationsversuche auf der Kläranlage Glatt, Diplomarbeit an der Abt. VIII der ETH Zürich.

[3] Stouthamer A.H., Dissimilatory reduction of oxidized nitrogen compounds. In: *Biology of Anaerobic Microorganisms*, Edited by A.J.B. Zehnder, pp. 245–303. John Wiley & Sons, New York, 1988.

[4] von Schulthess R., Wild D., Gujer W. (1994), Nitric and nitrous oxides from denitrifying activated sludge at low oxygen concentration, 17th Biennal International Conference, Budapest, Vol 1, pp. 93–102.

[5] Siegrist H. (1993) Gestaltung und Leistung von denitrifizierenden Anlagen, 35. VSA-Fortbildungskurs über Nährstoffelimination in der biologischen Abwasserreinigung, Engelberg.

[6] Wentzel M. C., Ekama G.A., Marais G.v.R. (1992), Processes and modelling of nitrification denitrification biological excess phosphorus removal systems – a review, Wat. Sci. Tech., 25, 59–82.

[7] Tsuno H., Somiya I., Matsumoto M., A kinetic model for biological phosphorus removal incorporating intracellular organics and phosphorus pools. In: *Advances in Water Pollution Control: Biological Phosphate Removal from Wastewaters*, Edited by R. Ramadori, pp. 99–110. Pergamon Press, Oxford, 1987.

[8] Ubukata Y. and Takii S. (1994), Induction method of excess phosphate accumulation for phosphate removing bacteria isolated from anaerobic/aerobic activated sludge, 17th Biennal International Conference, Budapest, Vol 1, pp. 121–126.

[9] Appeldorn, K.J., Ecological aspects of the biological phosphate removal from wastewaters, Ph.D. Thesis, Wageningen, The Netherlands, 1993.

[10] von Schulthess R. (1994), Die Emmission von Lachgas (N_2O) in denitrifizierenden Belebungsanlagen, Diss. ETH Nr. 10790.

[11] Maurer M. and Gujer W. (1994), Prediction of the performance of enhanced biological phosphorus removal plants, 17th Biennal International Conference, Budapest, Vol 1, pp. 207–216.

[12] Henze M., Gujer W., Mino T., Matsuo T., Wentzel M.C., and Marais G.v.R. (1994), «Activated sludge Model No. 2», IAWQ Scientific and Technical Reports, No. 3, IAWQ, London, in press.

[13] Jardin N. and Pöpel H.J., Phosphate Fixation in Sludges from Enhanced Biological P-Removal During Stabilization. In: *Chemical Water and Wastewater Treatment III*. Edited by R. Klute and H. H. Hahn, pp. 353–372, Springer Verlag, Berlin, 1994.

[14] Wild D., Kisliakova A., and Siegrist H. (1994), Die Ausfaulung von Schlämmen aus der erhöhten biologischen P-Elimination: Ziele und gegenwärtiger Stand der Forschung an der EAWAG presented at the Workshop: "Auswirkungen der erhöhten Phosphorelimination auf die Schlammbehandlung", Darmstadt, 24.–25. 11.

[15] Borgerding J. (1972), Phosphate deposits in digestion systems, J. Wat. Poll. Control Fed., 5, 813–819.

[16] Baumann P. (1991) Untersuchung der biologischen Phosphatelimination bei gleichzeitiger Stickstoffelimination auf der Kläranlage Waiblingen, Korrespondenz Abwasser, 38, 192–198.

[17] Pitman A. R., Deacon S. L., Alexander W. V. (1991), The thickening and treatment of sewage sludges to minimize phosphorus release, Wat. Res., 25, 1285–1294.

Barbara Sulzberger

The Role of Iron in the Photochemical Transformation of Pollutants

Due to its ubiquity and reactivity in aquatic and terrestrial ecosystems, iron is a key player in the transformation of pollutants – in both aerobic and anaerobic environments. In aerobic systems – atmospheric waters, surface waters, and soil surfaces – light plays the same role as microorganisms in catalyzing some of the iron-dependent processes. The following examples illustrate the role of light-induced iron cycling, involving iron oxides, in the transformation of pollutants.

Iron-mediated photooxidation of EDTA in surface waters

Why do we have to consider iron oxides – not just dissolved iron species – in evaluating the role of light in the transformation of pollutants in surface waters? The reason is due to the extremely low solubility of ferric iron [Fe(III)] under surface water conditions which depends both on pH and the concentration of strong iron(III)-binding ligands. Examples of iron(III) (hydr)oxide phases that are commonly found in surface waters include γ-FeOOH (lepidocrocite), α-FeOOH (goethite), α-Fe_2O_3 (hematite), and amorphous iron(III) hydroxide (ferrihydrite).

Many hydrophilic compounds that form stable complexes with Fe(III) also form stable complexes on the surfaces of iron(III) oxides or hydroxide particles and colloids [1]. A good example is ethylenediaminetetraacetate (EDTA). In sewage treatment plants, EDTA is not removed by wastewater treatment [2]. A powerful chelating agent, the environmental hazard of EDTA lays in its potential to mobilize toxic metals that are associated with particles and colloids, thereby preventing them from being removed from the water column (e. g., by sedimentation lakes). Dissolved Fe(III)-EDTA complexes are readily photolyzed which results in oxidation of the EDTA and reduction of the Fe(III). This is an important pathway for EDTA degradation in surface waters where the EDTA input occurs in the form of dissolved Fe(III)-EDTA [2].

What about the fate of EDTA if its input to a natural water body does not occur in the form of dissolved Fe(III)-EDTA? Laboratory experiments have shown that EDTA is photooxidized in a lepidocrocite suspension to which EDTA has been added as uncomplexed EDTA [3]. In addition to CO_2, formaldehyde (CH_2O) is one of the oxidation products (see Fig. 1). Figure 1 shows that dissolved Fe(III)-EDTA is also formed and degraded upon irradiation of a lepidocrocite suspension containing uncomplexed EDTA. This means that the photooxidation of EDTA in such a heterogeneous system occurs through the interplay of surface and solution photoredox reactions. Photooxidation of EDTA is accompanied by photoreduction of Fe(III). At pH 7, however, dissolved Fe(II) is readily reoxidized by oxygen and other oxidants of Fe(II), and Fe(III) eventually re-precipitates.

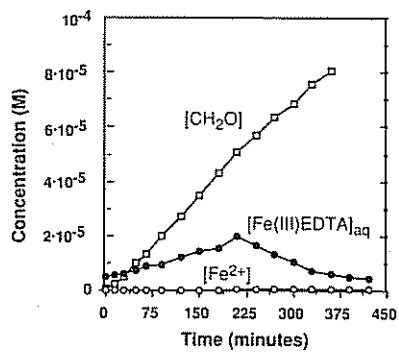


Fig. 1
Concentrations of CH_2O, Fe(II), and $Fe(III)EDTA_{aq}$ as a function of time upon irradiation of an aerated g-FeOOH suspension (0.05 g L^{-1}) at pH 7. EDTA was added as uncomplexed EDTA at an initial concentration of 10^{-4} M. The light source was polychromatic light from a 1000W high-pressure xenon lamp. The incident light intensity was about 0.5 kW/m².

Iron-mediated photooxidation of bisulfite (HSO_3^-) in atmospheric waters

Iron is emitted from the Earth's surface into the atmosphere in the form of particulate iron – so-called iron-containing aerosols. Aerosol particles are incorporated into cloud water through impaction or differential settling. In atmospheric waters, iron undergoes photoredox cycling to yield dissolved Fe(II) [4–8], one important reaction being photoreductive dissolution of particulate iron [4]. Apart from organic reductants (e. g., oxalate, formate, and acetate), bisulfite is also involved in reductive dissolution of particulate iron in atmospheric waters [4]. Bisulfite forms complexes on surfaces of atmospheric Fe(III) (hydr)oxides, followed by oxidation to the highly reactive SO_3^- radical with subsequent reactions with H_2O and O_2 to form sulfuric acid and superoxide (O_2^-), respectively. The electron transfer within the surface complex is enhanced by light. Photooxidation of

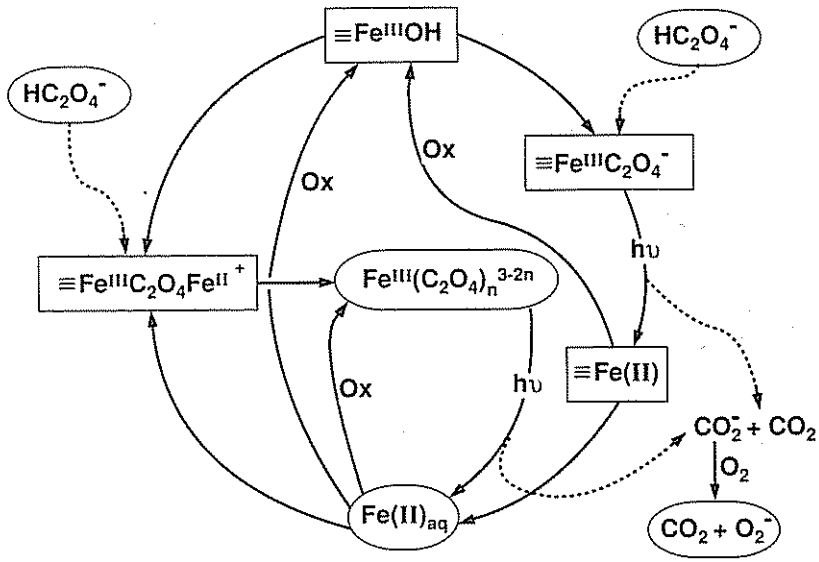


Fig. 2
Schematic representation of the redox cycling of iron in the presence of oxalate and light. The species surrounded by an oval are dissolved species, and those in a square frame are surface species. The symbol ≡ stands for the surface of an Fe(III) (hydr)oxide, and Ox for oxidants of dissolved and surface Fe(II), i.e., HO_2/O_2^-, H_2O_2, and O_2.

HSO_3^- is accompanied by photoreductive dissolution of the solid phase [4]:

$$HSO_3^- + \equiv Fe^{III}OH \leftrightarrows \equiv Fe^{III}OSO_2^- + H_2O$$

$$\equiv Fe^{III}OSO_2^- \xrightarrow{h\nu} SO_3^- + \equiv Fe(II)$$

$$SO_3^- + O_2 + H_2O \rightarrow H_2SO_5 + O_2^-$$

$$\equiv Fe(II) + 2\,H^+ \rightarrow Fe^{2+} + \equiv$$

(The symbol ≡ is a short hand notation of the surface of an iron(III) (hydr)oxide.)

Since the rate of Fe(II) oxidation increases with increasing pH and because atmospheric waters are often acidic, large fractions of total dissolved iron have been found in the reduced state [Fe(II)] [5]. Furthermore, in atmospheric waters with relatively low pH values and/or relatively high concentrations of Fe(III)-complexing agents such as oxalate, Fe(III) is prevented from precipitating. As a consequence, the redox cycling between dissolved iron species is likely to play a major role in the oxidation of HSO_3^- [6]. The iron-dependent photooxidation of S(IV) in atmospheric waters is also linked to the redox cycling of copper [6].

Aquatic iron cycling in the presence of oxalate

Aquatic iron cycling in the presence of oxalate and light has been studied thoroughly in both homogeneous and heterogeneous systems [7–9]. Although not a pollutant, oxalate is an important environmental compound for a number of reasons:

(i) relatively high oxalate concentrations are found in atmospheric waters as well as on soil surfaces in agricultural and forested ecosystems;

(ii) oxalate is a model compound for humic and fulvic substances which play a major role in light-induced iron cycling in surface waters; and

(iii) photoreactions of oxalate with iron lead to the formation of both reactive oxidants and reductants, as is discussed below.

The main reactions of the light-induced redox cycling of iron in the presence of oxalate are schematically shown in Fig. 2, a very much simplified scheme for complex natural systems! Oxalate is photooxidized by two pathways:

(i) via photolysis of Fe(III)-oxalate surface complexes (≡Fe$^{III}C_2O_4^-$), and

(ii) via photolysis of dissolved Fe(III)-oxalate complexes (Fe$^{III}(C_2O_4)_n^{3-2n}$).

Thereby, ferric iron is reduced. The oxalate photooxidation and subsequent decarboxylation result in the formation of the strongly reducing radical, CO_2^-. This radical reacts with oxygen to yield superoxide (O_2^-), an important precursor of hydrogen peroxide (H_2O_2). It has been shown that photolysis of Fe(III)-oxalate complexes and subsequent reaction of the photoproduct CO_2^- with oxygen is a major source of H_2O_2, another important oxidant of S(IV) in atmospheric waters [7]. Iron(II) is re-oxidized, either at the surface or in solution (≡Fe(II) or Fe(II)$_{aq}$ in Fig. 2), by oxidants such as HO_2/O_2^-, H_2O_2, or O_2 (summarized with "Ox" in Fig. 2).

Ferric iron resulting from the oxidation of Fe(II) either undergoes precipitation or is stabilized at low pH values by forming Fe(III)-oxalate complexes. These dissolved Fe(III)-complexes can also be formed by an additional pathway involving a ternary surface complex, ≡Fe$^{III}C_2O_4$Fe^{II+}. An important feature of the light-induced iron cycling shown in Fig. 2 is the following: photolysis of both the Fe(III)-oxalate surface and solution complex results in forma-

[1] W. Stumm (1992), *Chemistry of the Solid-Water Interface*, Wiley-Interscience, New York.
[2] F. G. Kari (1994), Umweltverhalten von Ethylendiamintetraacetat (EDTA) unter spezieller Berücksichtigung des photochemischen Abbaus, Dissertation ETH Zürich, Nr. 10698.
[3] G. Karametaxas, S. Hug, and B. Sulzberger, Photodegradation of EDTA in presence of colloidal iron, *Environ. Sci. Technol.*, submitted.
[4] M. R. Hoffmann (1990), Catalysis in Aquatic Environments, In: *Aquatic Chemical Kinetics*, W. Stumm, Ed., Wiley-Interscience, New York.
[5] N. Kotronaru, and L. Sigg (1993), SO_2 oxidation in atmospheric water: Role of Fe(II) and effect of ligands, *Environ. Sci. Technol.* 27, 2725–2735.
[6] D. L. Sedlak, and J. Hoigné (1994), Oxidation of S(IV) in atmospheric water by photooxidants and iron in the presence of copper, *Environ. Sci. Technol.*, in press.
[7] Y. Zuo, and J. Hoigné (1992), Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III)-oxalato complexes, *Environ. Sci. Technol.* 26, 1914–1022.
[8] D. L. Sedlak, and J. Hoigné (1993), The role of copper and oxalate in the redox cycling of iron in atmospheric waters, *Atmos. Environ.* 27A, 2173–2185.
[9] C. Siffert, and B. Sulzberger (1991), Light-induced dissolution of hematite in the presence of oxalate: A case study, *Langmuir* 7, 1627–1634.
[10] R. J. Kieber, and R. H. Helz (1992), Indirect photoreduction of aqueous chromium(VI), *Environ. Sci. Technol.* 26, 307–312.

tion of Fe(II), either at the surface or in solution, and the strongly reducing radical CO_2^- is also formed. These reductants may play an important role in the reduction of pollutants such as chromate [10]. The question is whether or not reaction of Fe(II) or CO_2^- occurs faster with such pollutants than with HO_2/O_2, H_2O_2, or O_2.

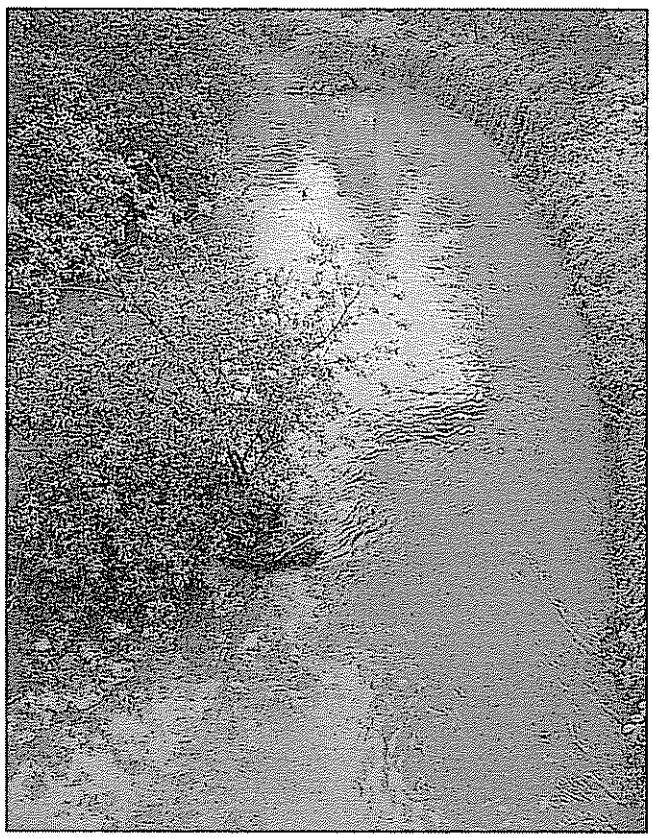
Conclusions

In evaluating the role of iron in the photochemical transformation of pollutants, both surface and solution processes have to be taken into account. This is because iron chemistry is heterogeneous. Furthermore, iron plays a diverse role: iron is likely to be involved in the *direct* photochemical transformation of many hydrophilic compounds such as EDTA and bisulfite, while it is also involved in the *indirect* photochemical transformation of pollutants since reactive oxidants (e. g., H_2O_2) and reactive reductants [e.g. Fe(II)] are formed through the light-induced redox cycling of iron. The role of photochemically formed Fe(II) as a reductant of pollutants needs to be further explored. The insights gained from the study of light-induced iron cycling, as it occurs in atmospheric waters, in surface waters, and on soil surfaces, are needed in light of using iron oxides for photochemical watewater treatment.

Reflections on High Water

Though the Chriesbach flows through an area of former marshlands, it still plots a well defined course over a consolidated river bed adjacent to the EAWAG in Dübendorf. The high population density in the regions precludes any attempt to restore the former marshlands, and the stream contains copious amounts of purified sewage and, therefore, possesses high nutrient levels. The plant life is incredibly rich and varied. In places, however, the result is an excess of aquatic macrophytes (=weed build-up).

During periods of very high flow, the floor of a natural stream is regularly churned up, thereby greatly increasing concentrations of suspended solids (readily identified by their color). As a result, high levels of particle-bound substances (e. g., total phosphorus or heavy metals) are transported during periods of high flow, with potentially negative implications for discharge into lakes. Nevertheless, the ecologically vital interstitial areas of a river bed (hyporheal) remain habitable for small animals. →



Photos: Andreas Fruitger

Left: Chriesbach on the rainy day of 19 May 94.

Right: the same location three weeks later.

Unfortunately, these mechanisms do not function in the Chriesbach. As revealed by the photo on the right (taken on 6 June 1994), even the force of the very high water occurring on 19 May 1994 (left) was insufficient to break up the river bed and eliminate infestation with flowing crowfoot. This was partly due to the high degree of obstruction. The minimal slope of the river bed has allowed it to become compacted, its soil pores have clogged up, and weed infestation is severe. Animal communities have become depleted. The problem is aggravated by the aquatic plants (particularly *Ranunculus fluitans*) which stabilize the stream bed and promote the sedimentation of fine particles. These aquatic plants are regularly cut to preserve the hydraulic performance of the watercourse. Studies by the Limnology Department [1,2] have revealed that the plant stock recovers within a few weeks and that rapidly growing plants are selectively encouraged by the regular cutting.

A free-flowing meadow stream serves as the ideal example of naturalization. Bordered on both sides by shrubs and trees, a meadow stream can meander freely, thus continually rearranging its bed with the passage of time. A corresponding redesign of the Chriesbach could keep weed infestation under control, since the main problem is not necessarily the high nutrient content, as is often assumed, but the excessive exposure to sunlight and the lack of bed-load transportation.

Diana Hornung

1993 EAWAG dissertations:

[1] Tania Schellenberg: «Ökologische Beurteilung und Renaturierungsmöglichkeiten des Chriesbaches» (Ecological assessment and renaturation options for the Chriesbach)

[2] Sandra Hocevar: "Ökologische Bedeutung der Makrophyten im Chriesbach" (Ecological significance of macrophytes in the Chriesbach)

Permanent Education

PEAK: EAWAG's Environmental Education Program

PEAK: Past and Future

On 13 September 1993, the first PEAK course was offered at the Limnological Research Center in Kastanienbaum. Thirteen participants attended the one-week applied course on "The Significance of Stream Morphology and Typology for Water Organisms". The positive response of early participants resulted in a great rush to sign up for other scheduled courses. All scheduled courses have taken place as planned, in addition to the 1993 InfoDay.

Courses A2/94 "Chemical Environmental Analysis: Concepts and Methods" and V2/94 "Metals in the Aquatic and Terrestrial Environment" were fully booked shortly after being announced. A2/94 was repeated in October 1994 and will again take place in late November 1995. Since PEAK's role is primarily to communicate new results and knowledge from current EAWAG research, course repetitions are the exception – not the rule.

We regard it as important to optimize the course contents and teaching methods. We, therefore, very much welcome criticism, requests and suggestions. We profit from the knowledge and experience of our participants and regard the events as a means of establishing new contacts. Not all the subjects covered by the EAWAG can be presented sufficiently frequently in PEAK events. Our staff consequently also participates in further education courses run by other institutions and lecture at a wide variety of functions.

1995 Program

Postgraduate Course in Urban Hydrology and Water Protection

From late 1994 onwards, the ETH Zürich is offering the postgraduate course "Urban Hydrology and Water Protection". Part of this postgraduate course will run in concentrated form; that is, in block modules, generally two-week courses on selected topics. Various PEAK events can be incorporated as block modules in the postgraduate course. To complete the course, postgraduate students must attend courses to a "value" of 20 credit units. Attendance for the entire course is compulsory for those wishing to receive a course certificate.

- The second date in the following table applies for all those who wish to gain a course certificate with credit units.
- For other participants, the second part of the courses is optional.
- PGC indicates those courses which can be incorporated into the postgraduate study course.
- The figure in brackets shows the available number of credit units (CUs).

For additional information, please contact Heidi Gruber or Herbert Güttinger:

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PEAK* Program for 1995 (CUs = credit units)

6–10 (–17) March 1995
PEAK Applied Course A3/95
PGC (5 CUs)

Systems Analysis and Reactor Technology

Waste water treatment systems: design, modelling and control of chemical reactors

Course Directors: Markus Boller, Willi Gujer, Hansruedi Siegrist

12–16 June 1995
PEAK Advanced Course V4/95

Water Supply and Sanitation in Developing Countries

Technical, social and medical principles of water supply systems: treatment and recycling of fecal material, wastewater and domestic waste

Course Directors: Roland Schertenleib, Martin Strauss, Martin Wegelin

3–7 (–14) July 1995
PEAK Advanced Course V5/95
PGC (5 CUs)

Chemistry and Treatment of Drinking Water

Principles, problems and applications of chemistry of drinking water theory and technology of drinking water treatment

Course Directors: Markus Boller, Urs Von Gunten, Jürg Hoigné

11–22 Sept 1995
PEAK Applied Course A4/95
PGC (5 CUs)

Stream Ecology and Hydraulic Engineering

Modern approaches to the assessment and evaluation of running waters: methods for the interdisciplinary treatment of hydraulic engineering projects and concepts for stream design

Course Directors: Michael Hütte, Armin Peter, Matthias Oplatka (VAW)

19–21 Sept. 1995
PEAK Advanced Course V6/95
PGC (2 CUs)

The Material Flow Analysis Method for Regional Resource Management

Coping with shortages in the regional use of resources (e. g. water, biomass, minerals). Early warning tools, resource planning and urban development.

Course Directors: Peter Baccini, Barbara Gamper

12 September 1995
Information Day 1995

Trace Elements in Water and the Environment

Coordinators: Theresa Büsser, Walter Giger

26–28 Sept 1995
PEAK Basic Course B3/95
PGC (2 CUs)

The Problems of Chemical Contamination of Ground Water

Sedimentological and hydrogeological system parameters. Concepts of ground water flow and mass transport in ground water, stimulus response principle, field reconnaissance methods (geophysics, drilling, tracers).

Course Directors: Peter Huggenberger, Eduard Höhn, Urs Von Gunten

2–6 (–13) Oct 1995
PEAK Advanced Course V7/95
PGC (5 CUs)

Environmental Biotechnology for Pollutant Degradation

Microbial transformations of organic compounds in the environment. Biochemistry and molecular biology of the degradation of selected pollutants. Influence of growth and environmental conditions on degradation properties. Aspects of *in situ* analysis of biodegradation.

Course Directors: Thomas Egli, Christof Holliger

29 Nov – 1 Dec 1995
PEAK Applied Course A2/95

Analytical Chemistry of Pollutants: Concepts and Methods

(2nd repetition of course A2/94 of 23–25 March 1994) State-of-the-art chemical analysis of water, soil and air. From sampling to data processing.

Course Directors: Walter Giger, Christoph Moor, Marc Suter

***PEAK** = German acronym for **P**raxisorientierte **EA**WAG-**K**urse

New Research Groups

Urban Hydrology Group

Personnel changes in the Departement of Engineering Sciencies ...

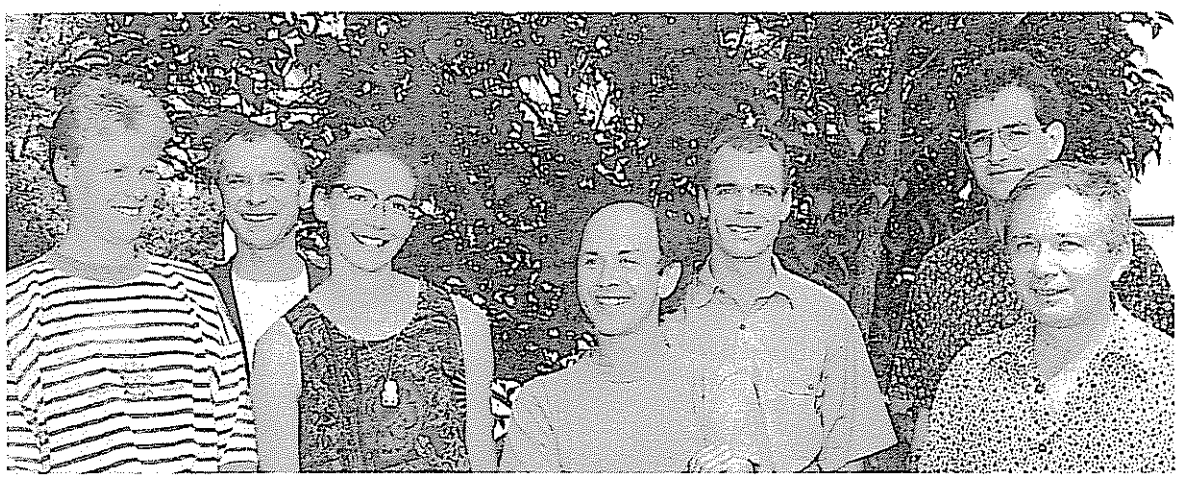
Two members of the Urban Hydrology Group were appointed professors in the summer of 1993: *Wolfgang Schilling* at the Trondheim Technical University in Norway and *Matthias Grottker* at Lübeck College. *Vladimir Krejci* has been working for several years in the Engineering Sciences Department, investigating and developing concepts for improving urban drainage. He is currently on a sabbatical year in his native Prague, where he plans to establish an urban hydrology group.

Two new individuals joined the our group in January 1993, filling the gaps left by the aforementioned departures and bringing in fresh perspectives. *Peter Krebs* studied civil engineering at the Federal Institute of Technology (ETH) in Zürich, completed the EAWAG postgraduate course in Sanitary Engineering and Water Pollution Control, and completed his doctoral dissertation on currents in secondary settling tanks at the Laboratory of Hydraulics, Hydrology and Glaciology (VAW). In recent years, he has been a research engineer at Karlsruhe Technical University, investigating the mathematical and experimental modelling of turbulence and density effects in hydraulics. In 1991, he was awarded the "Otto-Jaag Water Conservation Prize" and the following year received the "Pergamon Publications Medal" for his paper at the 1990 IAWPRC-Biennale in Kyoto, Japan. *Georg Smehil* emigrated to Switzerland in 1968 after studying surveying at the Technical University in Prague. He has since been involved with computer applications relating to geo-information systems (GIS) in surveying. He has directed an interdisciplinary project in which the basic survey parameters for the city of Zürich were numerically revised and transferred to a digital network information system. As a result, Zürich is now one of the best surveyed cities in the world. At the EAWAG, Smehil will be adapting the GIS, a system that can process much more than just survey data, to the needs of urban hydrology.

The rest of the group, composed of physicist *Dr. Rolf Fankhauser*, biologist *Sonja Gammeter* (doctoral student), drainage engineer *Peter Merz* (doctoral student) and electrical engineer *Bernd Harmuth*, is currently completing the project on "Integrated Urban Drainage – Fehraltorf: A Case Study", whose aim is to demonstrate appropriate technical and environmental solutions for urban drainage in Switzerland. The results of this study were presented at the VSA Conference on 2 September in Zürich. Their data will subsequently be evaluated in terms extending beyond the confines of the Fehraltorf project as part of a study on the effects of spatial variability of rainfall intensity on regional drainage. The integrated approach to urban drainage employed in the Fehraltorf study will remain a key element of the Urban Hydrology Group efforts and will be further developed in its subsequent research activities. In this context, the GIS can be used for preparing data structures that allow the topography of the catchment area to be correlated with data on ground sealing and permeability, siting, structure and inclines of sewage networks and with data on spatially-based precipitation. The GIS will also be used to incorporate, for example, information on groundwater protection zones or potential pollution sources in industrial areas within urban drainage plans. Suitable interfaces have been developed to allow urban hydrology programs to access the GIS database which until now, have had to be entered manually.

...and the development of future research activities based on updated principles

Methods for drawing up regional water surveys should be developed and refined and include informa-



From l. to r.: Bernd Harmuth, Georg Smehil, Sonja Gammeter, Rolf Fankhauser, Peter Krebs, Peter Merz and Vladimir Krejci

Surface Microbiology

tion, not only on the precipitation-drainage ratio, but also on seepage, groundwater formation and utilization, interactions with receiving waters at high water and control options for the drainage system. Finally, dynamic simulations of the water balance should be extended to include substance-specific data to allow their use as a tool for preparing suitable strategies for the long-term management of water resources.

The following marginal areas of urban drainage involving a number of specialist disciplines will be addressed via a comprehensive approach:

- the effects of type and frequency of sewer overflows on water quality and the ecology of the receiving water;
- the effect of meteoric water seepage on ground water in conjunction with the "Water as Resource" group; and
- the interaction between processes in the drainage system and in wastewater treatment plants in conjunction with the process engineering group.

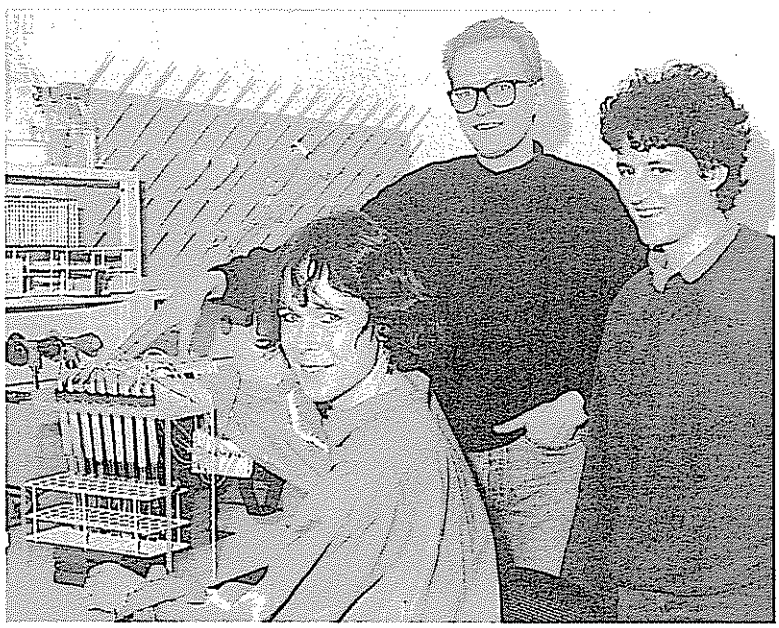
Although a knowledge of other respective specialist areas has until recently been considered a marginal requirement for performing one's own investigations, no attempt has been made to optimize the system as a whole. Control of the drainage network and utilization of the main sewer preceding the wastewater treatment plant as a reactor volume represent key sources of barely tapped potential for improvement. Although the Urban Hydrology Group is currently passing through a phase of staff change, its future is being planned in an inspiring environment.

Peter Krebs

In the popular imagination, bacteria busily swim about in liquids. In natural systems, however, this image only applies to a small proportion of microorganisms, since soils and sediments – not to mention whole bodies of water which are rich in particles – possess a variety of interfaces to which bacteria are attracted. The Surfaces Group was established last summer within the Department of Microbiology to investigate the interactions between bacteria and various types of solid, liquid and gaseous phase boundaries.

Bacterial adhesion to surfaces (biological or inanimate) initiates the formation of so-called biofilms, complex immobilized living communities made up of a variety of microorganisms embedded in a matrix of polymers. This lifestyle is evidently beneficial to bacteria since, in nature, the greatest contribution to microflora is made by biofilms. Conversely, biofilms may be detrimental to man. Most people are unaware, for example, that when brushing their teeth in the morning they are removing a biofilm that has grown overnight. Microbial growth on medical implants is just as harmful as is the bacterial contamination of the inner surfaces of drinking water pipes. Bacterial adhesion can, however, with the aid of biotechnology, be exploited to obtain environmental benefits. We are currently investigating the immobilization of specific pollutant-degrading bacteria at the site of contamination of soils or groundwater layers. As a rule, bacterial adhesion must be taken into account when applying the results obtained with bacterial liquid cultures to natural systems.

As part of her doctoral dissertation, *Barbara Jucker* is currently



The new Sufaces Group in the department of micorbiology (from left to right): Anke Schäfer, Hauke Harms and Barbara Jucker during a column test to investigate the transport of bacteria through porous media.

Hauke Harms studied biology at the University of Hamburg, specializing in microbiology, biochemistry and botany. In his doctoral dissertation, under the supervision of Profs. P. Fortnagel and W. Francke, he studied the bacterial degradation of dioxin-like compounds. He then spent a year investigating the "cold" degradation of explosive substances. As a Fellow of the EERO (European Environmental Research Organization), he spent the next two years investigating the activity of pollutant-degrading microorganisms in soil model systems at the Agricultural University in Wageningen, The Netherlands.

New Research Groups

investigating interactions at the molecular level between bacteria and surfaces. Her goal is to identify the specific forces involved in bacterial adhesion. She is analyzing the chemical composition of bacterial surfaces, using infrared spectroscopy and other sensitive measuring methods to identify the bonds that arise between bacterial surface polymers and solid surfaces during adhesion. The focus of *Anke Schäfer's* doctoral work is the effect of bacteria on pollutant transport in unsaturated (three-phase) soils. She is currently investigating the phenomenon of bacterial accumulation at the air/water interface.

The Surfaces Group is headed by *Hauke Harms,* who is studying surface influences on bacterial activity, e.g. the ability to degrade pollutants. To this end, he is using bacteria that use dioxin-like compounds as a growth substrate and investigating their breakdown performance in various ground model systems, e.g. using columns filled with glass, Teflon or sand.

Hauke Harms

Molecular Ecotoxicology

Organisms have an adaptation potential that allows them to grow under continuously changing conditions such as fluctuations in temperature, pH, salt concentrations, light intensities and substrate availabilities. For optimal metabolic activity, the conditions inside cells should, despite the changes in their environment, be kept constant (homeostasis). To maintain cellular homeostasis, organisms have complex regulatory circuits that somehow sense the changes in their environment or detect the presence of growth substrates and translate these signals to molecular cues inside the cell. Ultimately these signals will lead to an impulse-specific, fine-tuned response of the cellular metabolism such that the organisms can cope with the changed environment. In addition to environmental fluctuations, organisms are challenged by toxic compounds. Within certain limits, organisms can resist this challenge in often unknown ways and maintain cellular homeostasis. If adaptive responses fail for some reason or if the concentrations of toxic compounds are too high, damage may occur, leading to disturbed metabolic activities and ultimately to cell death. Irreversible toxic effects on single cells obviously affects the population and the entire ecosystem.

The purpose of the new research group in Molecular Ecotoxicology, which was established in January 1994 within the department of microbiology, is to understand the interactions between toxic compounds and organisms on the molecular level. The influence of toxic compounds on the adaptation potential of organisms – which is required for flexibility – will be examined. Likewise, the defense systems in organisms that are exposed to toxic compounds will be studied. Currently, green algae are used as model organisms in projects that are focused on the influence of increased concentrations of radicals in the cell or their environment. These radicals are present in the environment due to chemical reactions or may be generated by the algae themselves in response to various toxic compounds like heavy metals, nitroaromatics, herbicides or UV radiation.

Rik I. L. Eggen

Rik I. L. Eggen obtained his Ph.D in 1989 in the Department of Molecular Biology at the Agricultural University in Wageningen, The Netherlands. His research involved replication of plant viruses and was conducted under the supervision of Dr. A. van Kammen and Prof. Dr. R. W. Goldbach.

From 1989 to 1994, first as a postdoctoral fellow and then as a university lecturer, he was a member of the bacterial genetics research group of Prof. Dr. W. M. de Vos in the Department of Microbiology in Wageningen. His research during this period focused on enzymatic regulation in methanogens and on adaptation mechanisms of microorganisms that live at 100°C.

Molecular Surface Chemistry

Introduction

The goal of molecular surface chemistry is an understanding of surface structures and reactions at the molecular and atomic level. Only through such a detailed understanding is it possible to establish surface structure-reactivity relationships and to develop models which account for the complexity of surface reactions in the environment. Surface reactions occur in all compartments of the aquatic environment: in sediments, surface waters and in atmospheric water. A few examples are adsorption/desorption and transport of heavy metals and organic pollutants, release and retention of pollutants during the dissolution and formation of solid phases, chemical and photochemical transformations, formation of reactive oxygen species, adhesion of bacteria on surfaces, surface modifications by bacteria (e. g., by sulfate- and iron-reducing bacteria), and reactions on biological surfaces.

Previous investigations at the EAWAG

The interest in molecular surface chemistry has a long tradition at EAWAG. In recent years, it has become possible to probe surface structures directly by a variety of techniques. Our interest is mainly in methods that enable us to study surfaces in the presence of water and air; that is, under natural environmental conditions. In collaboration with Prof. A. Schweiger (ETH Zürich), magnetic resonance methods have been applied to study the surface structure of adsorbed heavy metals (Cu,Cr) [1]. In addition, we are collaborating with Prof. Alain Manceau (University of Paris) for the application of EXAFS (extended X-ray absorption fine structure spectroscopy) for the structural analysis of manganese (hydr)oxides [2]. About four years ago, the EAWAG acquired a Scanning Tunneling and Atomic Force Microscope (STM/AFM; see the article by C. Eggleston in this issue) and a Fourier Transform Infrared Spectrometer (FTIR) [3].

Current activities and developments

Our current research interests are in the application and further development of STM/AFM and FTIR. These methods are complementary in that FTIR is suited for the characterization of polyatomic surface adsorbates, while STM/AFM is useful for the investigation of atomic and topographic surface structures, as described below.

FTIR measures molecular vibrations with infrared light which provides information about the type and structure of surface adsorbates. During the past year, we have developed a method that employs ATR (ATR = attenuated total reflection) elements coated with mineral powders and that allows the measurement of surface spectra as a function of solution parameters. With this method, we can, for example, measure adsorption isotherms with IR and obtain quantitative and spectral information simultaneously. With multicomponent analysis, we have shown that oxalate forms different surface complexes on TiO2, depending on solution concentration and solution pH [4]. Also possible are direct FTIR measurements of solid phase transformations in aqueous environments. These studies will be extended to study adsorption and intercalation of organic compounds and of metals in clay minerals. IR-spectroscopy will also be applied to the characterization of certain minerals in sediments. In collaboration with the Department of Microbiology, we are investigating the adhesion of bacteria on solid surfaces using ATR-FTIR.

STM/AFM was introduced to the EAWAG by Carrick [5]. With STM/AFM, changes in the surface structure during chemical and photochemical reactions can be followed; for example restructuring of iron oxide surfaces during the photocatalytic oxidation of organic matter or the formation of Cr(III) phases with the reduction of Cr(VI) on surfaces. Reactions of this type are important in the transformation of minerals with the adsorption or release of heavy metals and of organic pollutants. Another goal is the imaging of surface modifications by microorganisms and the imaging of biological surfaces.

Stephan Hug obtained his Ph.D. in physical chemistry from the University of California, Santa Cruz. Using nanosecond laser flash photolysis, he studied the kinetics of natural and artificial visual pigments and the excited states of polyenes and polyene cation radicals with a special emphasis was on the analysis of time resolved spectral data. From 1990–1992, he was a Swiss National Science Foundation postdoctoral fellow in the Chemistry Department at Stanford University where he investigated charge transfer transitions in porphyrins and transition metal complexes with Stark spectroscopy (electric field modulation of absorption and fluorescence). In the Spring of 1992, he joined the Chemistry Department at the EAWAG.

Current projects

- In situ measurements of photochemical surface reactions. Photochemical degradation of organic pollutants on titanium and iron oxides.
- Combination of quantitative surface complexation models,

including charge, with FTIR spectra.

- Transformation of solid phases during the photocatalytic oxidation of organic compounds on iron oxide surfaces by FTIR and STM/AFM (with C. Eggleston).
- Reductive dissolution of manganese oxides in the presence of oxalate, Fe(II) and light (with B. Sulzberger, H. U. Laubscher and E. Schtam).
- Adhesion of bacteria on solid surfaces detected by FTIR; possible conclusions about structural interactions (with B. Jucker, H. Harms and A. Zehnder).
- Molecular Orbital Calculations for the Interpretation of IR spectra (with Prof. G. Calzaferri, University of Bern).

Long-term projects

A molecular understanding of surface reactions pertinent to the environment and used in environmental technologies will require a combination of different methods, as well as their careful application and development. In collaboration with other EAWAG and external groups, we will continuously evaluate new chemical and physical methods and apply them to environmentally relevant questions. For the study of fast reactions on surfaces, we are considering the procurement of time-resolved spectroscopic instrumentation.

Our long-term goal is a detailed understanding of the interactions of natural and anthropogenic compounds with mineral and biological surfaces. We hope to achieve a better understanding of natural cycles and the fate of compounds in the atmosphere, in surface waters and in sediments. Risks, such as those posed by waste disposal sites, must be estimated dependably. A molecular understanding of surface reactions will also allow the development and optimization of technologies for the chemical and photochemical treatment of drinking water and wastewater and the remediation of contaminated soils and sediments. In order to evaluate contamination risks and remediation procedures, we need a detailed and comprehensive understanding of natural and anthropogenic cycles, in which surfaces obviously play a key role.

Stephan Hug

[1] Motschi, H., Aspects of the Molecular Structure in Surface Complexes: Spectroscopic Investigations in *Aquatic Surface Chemistry*, W. Stumm, ed., Wiley-Interscience, New York, 1987.

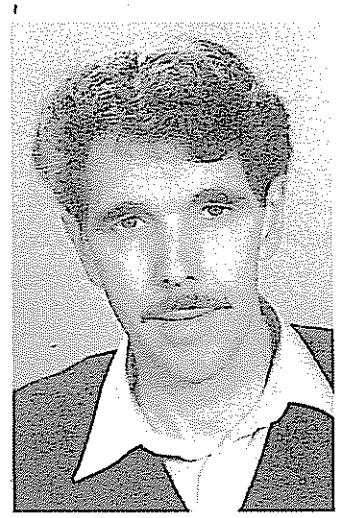
[2] Wehrli, B., G. Friedl and A. Manceau, Interface Reaction Products of Manganese Oxidation at the Sediment-Water, in Aquatic Chemistry in C.P. Huang et al., eds, *ACS Advances in Chemistry*, 1993.

[3] Biber, M. V. and W. Stumm, An in-situ ATR-FTIR study: the surface coordination of salicylic acid on aluminium and iron(III) oxides, Environ. Sci. Technol., 28, 763–768 (1994).

[4] Hug, S. J. and B. Sulzberger, In situ Fourier transform infrared spectroscopic evidence for the formation of several different surface complexes of oxalate on TiO_2 in the aqueous phase, Langmuir, 10, 3587–3597 (1994).

[5] Eggleston, C. M and S.J Hug, Raster-Tunnel und Raster-Kraft Mikroskopie in *Physikalisch-Chemische Untersuchungsmethoden in den Geowissenschaften*, Springer-Verlag, in press.

Farewell to Paul Schlup



Our 53-year-old photographer's busy life was cut short on the 12 July 1994 following a heart attack.

In 1966, Paul Schlup joined a much smaller EAWAG which then occupied several buildings. Though a trained photographer, he initially worked more as an illustrator. His photographic premises consisting solely of a cramped, tapering darkroom in the old villa on the Physikstrasse in Zürich. The simplicity of his equipment in no way impaired the quality of his work. When EAWAG relocated to Dübendorf in April 1970, the Photographic Service was provided with two darkrooms, a small studio and a modern reproduction system.

All who called upon the services of Paul Schlup were continually impressed both by the precision of his work and by his friendly nature and readiness to accept projects at short notice. You could always count on Paul whenever he promised to do anything. Even illness could not prevent him from completing his promised work. Only a much to premature death was able to curtail his sense of duty.

In Paul we have lost a sympathetic colleague who was always receptive to others' concerns, however trivial, willingly supporting all his colleagues in both word and deed. Even though his character was marked by a serious, religious approach to life and death, it did not prevent him from acting cheerfully and mischievously at times. Yet his little practical jokes which were such a feature of his early years at EAWAG were also marked by a human warmth.

In Paul we have lost a helpful colleague and friend and one who will always be remembered with fondness. We give thanks for his life.

Heinz Bachmann

New Techniques in Mass Spectrometry

In recent years, mass spectrometry (MS) has become an important tool in the hands of environmental scientists. It is widely used for the identification and quantification of organic as well as inorganic contaminants. The use of MS in conjunction with gas chromatography (GC) is a well established technique for the analysis of volatile organic compounds. Compared to classical GC detectors, for instance flame ionization, mass spectrometers provide additional information to molecular mass and structure. With the development of so-called soft ionization techniques such as electrospray ionization (ESI), a wide range of polar and non-volatile compounds has become amenable to MS analysis. Anionic and cationic surfactants, aromatic sulfonic acids, metal-organic complexes and proteins, to name a few, can now be introduced into a mass spectrometer without derivatization.

In 1992, the EAWAG acquired a mass spectrometer that provides tandem-MS, high resolution MS and LC-MS capabilities (the coupling of liquid chromatography with MS). Among others, tandem-MS allows analysis of molecules of interest directly out of a mixture. High resolution MS, on the other hand, allows us to determine the accurate mass (and thus the correct formula) of a molecule or fragment, generated during the ionization process. These techniques are used, for example, to differentiate between linear and branched alkylbenzenesulfonates (LAS and ABS) in sediments. ESI is being used for the analysis of ionic and polar compounds, either by directly injecting aqueous samples or after separation LC. Using this approach, we have been able to detect the intact Fe^{III}-EDTA (ethylenediaminetetraacetate) complex without prior derivatization. Further investigations will give us new insights into the mechanism of phototransformation of this compound. ESI also allows us to look at molecules of masses up to 100'000 daltons, which means that enzymes and their modifications can be investigated.

Current research:

- GC/MS/MS differentiation of linear and branched alkylbenzenesulfonates in sediment cores (Suter, Reiser, Giger)
- ESI-MS investigation into the phototransformation of Fe^{III}-EDTA (Suter, Karametaxas, Sulzberger, Giger)
- Investigation into the biodegradation of alkylpolyethoxylates using LC-MS. (Suter, Zanette, Marcomini, Giger)
- ESI investigation into the suicide inactivation of meta-ring cleaving dioxygenases. (Suter, Kohler)

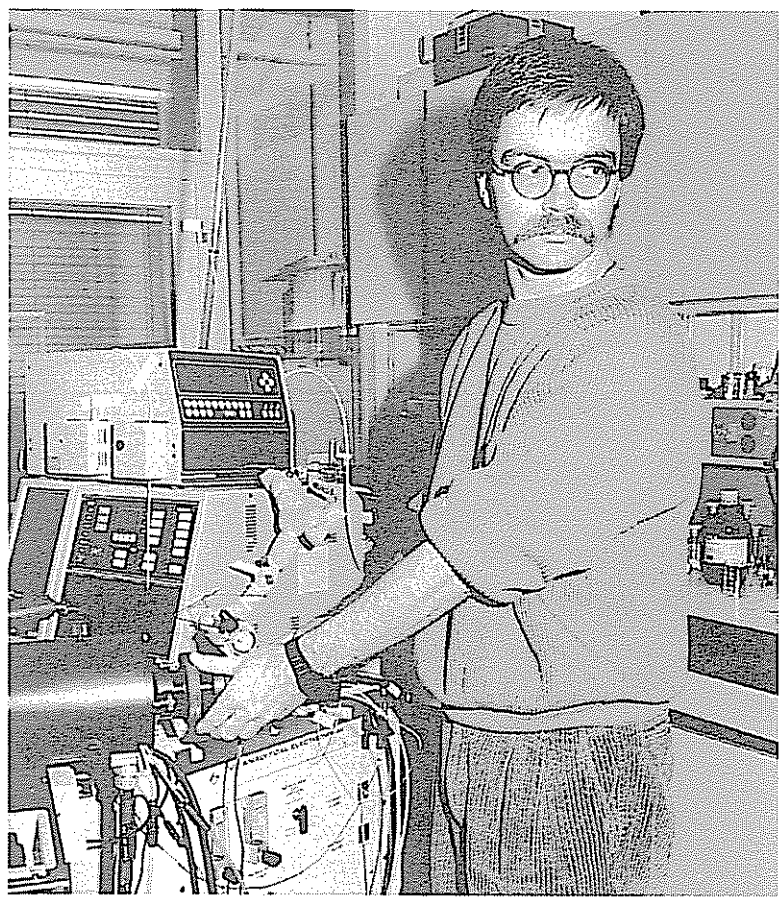
Marc J.-F. Suter

[1] M.J.-F. Suter et al., Int. J. Mass Spectrom. Ion Processes 86 (1988) 201–208.

[2] M.J.-F. Suter et al., Rapid Commmun. Mass Spectrom. 3 (1989) 62–66.

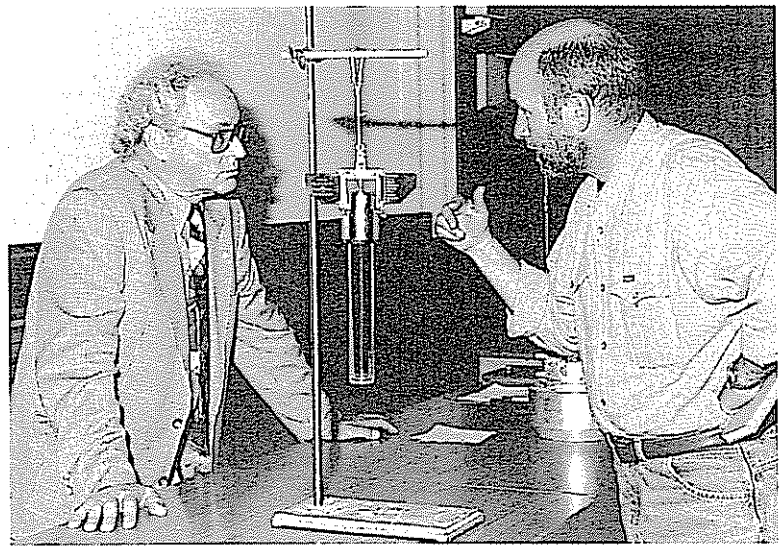
[3] M.J.-F. Suter, R.M. Caprioli, J. Am.Soc.Mass Spectrom., 3 (1992) 198–206.

[4] M.J.-F. Suter et al., Techniques in Protein Chemistry III, R.H. Angeletti, ed., Academic Press Inc., 1992, 447–55.



Marc Suter inserting the ESI probe while checking the control panel.
Scientific career: Studies in chemistry at the University of Bern. Diploma thesis on "MS Investigation of Rearrangement Mechanisms in the Gas Phase" [1] in 1982. Ph.D. under the supervision of Prof. Schlunegger (University of Bern) on the development of a hybrid BE-Quistor-Quadrupole-MS [2] in 1988. Postdoctoral studies with Prof. Caprioli (University of Texas, Houston) on "Biochemical and Medical Applications of MS using New Techniques like LC-MS, CZE-MS and MALDI" [3]. Joined Prof. W. Giger's group at the EAWAG in 1991.

Retirement of Professor Heinz Ambühl



On 25 May 1994, Professor Heinz Ambühl bade farewell to the EAWAG and presented a seminar on the status of sediment research. Prolonged applause is only one measure of the high regard with which his EAWAG and ETH colleagues hold him, serving as both head of the Limnology Department at the EAWAG and as ETH Professor. Deserving the highest tribute, his work has made a significant impact on limnological research in Switzerland and, in particular, on the subject of limnology as currently taught at the ETH.

Heinz Ambühl attended schools in Aarau. At the Aarau Cantonal School, he was fortunate enough to have had Professor Paul Steinmann, a teacher who knew how to enthuse his students about all things natural. Steinmann's work on whitefish and the fauna of mountain streams inspired Heinz Ambühl not only to study biology at the ETH but to go on to pursue his life's work in this field.

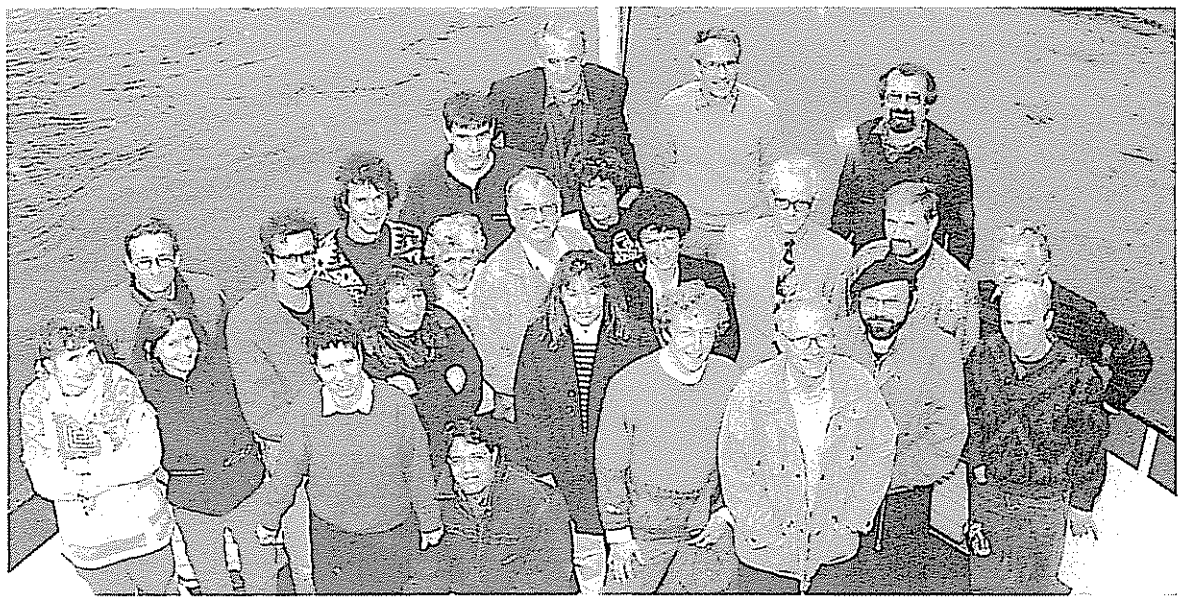
Working with Professor Otto Jaag at the ETH in Zürich, Ambühl began his dissertation research on "The Significance of Current as an Ecological Factor". In the scarce free time left to him while working as a hydrobiologist for the Canton of Aargau, he completed his doctoral work in 1959 for which he was awarded the rare distinction of the ETH Silver Medal.

Working as a cantonal hydrobiologist at a time when water conservation was still in its infancy, he recognized the importance of practical research. He accorded top priority to the collection of environmental samples and to precise analysis in the investigation of water quality and fish mortality. Analysis of lake water samples, often containing only trace quantities of nutrients, required a degree of precision that was unattainable in the early 1960s. Instead of simply complaining about the situation, he set to work to develop his own methods and equipment and to perfect them. His wide-ranging practical skills and broad general knowledge have stood him (and us) in good stead. The optimization of measuring and sampling techniques has remained one of his areas of expertise. During university holidays, he liked to develop his own ideas and turn them into workshop-ready plans – his particular way of "making holiday plans". Recently he has been concentrating on the collection of undisturbed lake sediment samples.

Even when appointed Head of the Department of Hydrobiology/Limnology at EAWAG/ETH in 1960, he retained a keen interest in practical matters. Many of the postgraduate theses and dissertations supervised by Professor Ambühl were based on practical problems of water pollution control. He was also pivotal in coordinating various infrastructure-related tasks, including the construction and expansion of EAWAG facilities in Dübendorf and Kastanienbaum. As his lecturing duties continued to expand under Professor Jaag at the ETH, he was appointed Associate Professor of Hydrobiology in October 1972. He was totally committed to his teaching at the ETH, always remaining up-to-date and discussing the latest findings from the limnological literature. The considerable impact he made on his students was annually reflected in the growing numbers of applicants wishing to register for Professor Ambühl's course in hydrobiology. The number of corresponding theses prepared each year increased from just one or two in the 1960s to his current rate of eight or 10. Likewise, the 35 doctoral dissertations supervised by Professor Ambühl during his career is particularly high.

His colleagues profited greatly from his varied gifts and extensive knowledge of limnological research. He devoted the few holidays he allowed himself, in addition to countless weekends, to study of the literature, which resulted in the production of a reference file of some 20'000 publications. This bibliography, together with his wealth of experience and role as editor of the *Schweizerische Zeitschrift für Hydrologie* (formerly *the Swiss Journal of Hydrology* and recently renamed *Aquatic Sciences*), has enhanced the presentation and scientific content of many a

Top photo: Professor Ambühl (left) in conversation with Dr. Mike Sturm.



The Limnology Department's farewell party for Professor Ambühl with (from left to right).

Front row: Christine Heller, Barbara Känel, Elisabeth Meyer (acting Head of Department 1994), Alexander Imhof, Heinrich Eisenmann, Bruno Ribi, Urs Uehlinger, Daniel Steiner.

2nd row: Andreas Frutiger, Markus Naegeli, Ursina Hartmann, Doris Hohmann, Christa Jolidon, Heinz Ambühl, Hans Ruedi Bürgi, Robert Berger.

3rd row: Günther Frauenlob, Sieglinde Gäbel, Heinrich Bührer, Ursula Tobler.

Back row: Rainer Zah, Fred Stössel, Heinz Bachmann, Peter Bossard (acting Head of Department 1995).

dissertation. Drafts of manuscripts were always returned to anxious students with numerous supplementary comments and helpful suggestions in the margins.

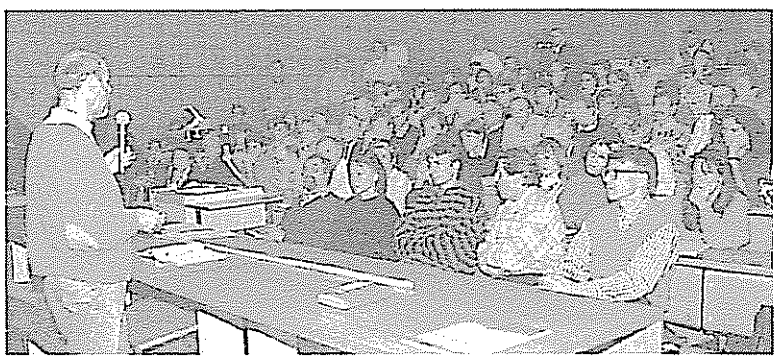
He tended to express fairly trenchant remarks about precipitate conclusions and carelessly researched work or emotionally-tinged reports in the media. This was in marked contrast with his otherwise very conciliatory nature. When speaking on specialist subjects in public, he knew how to express his concerns without diminishing the scientific quality of his message.

Since changes tend to occur very gradually in nature, scientific findings about whole ecosystems are seldom obtained during one or two year studies. Reliable conclusions can only be drawn from careful study over many years. Under Ambühl's leadership, the limnology of oligotrophic, mesotrophic, eutrophic and highly-eutrophic lakes has been compared. His unique, long-term limnological work has provided us with unimagined opportunities for hypothese testing and simulation. His data has already been used in the calibration of numerous computer models, some of which simulate the effects of internal lake-based measurements.

We offer Professor Ambühl our very best wishes and look forward to welcoming him to the EAWAG on many future occasions as a stimulating discussion partner and esteemed colleague.

Hans Rudolf Bürgi

Seminar Series on Sustainable Development



*"As inhabitants of this country, each and every one of us must reduce his or her current level of resource consumption to an average of one third of the present consumption in the next thirty years."**

In his lecture on the Infoday 1993, Prof. Zehnder has presented three theses in the context of sustainable development. This in turn has led to an internal seminar series. The aim of the series is to stimulate internal education and discussion about the changes at EAWAG and their implications for the future. The first talks are being given by speakers from within the EAWAG. The seminar series is very well attended.

* [Thesis 3, from EAWAG news 36E, p.3–5]

Publications

Can be ordered separately from the EAWAG library (use last page)

EAWAG-Publications

1823 **Bendinger, B., Rijnaarts, H.H.M., Altendorf, K., Zehnder, A.J.B.**: Physicochemical Cell Surface and Adhesive Properties of Coryneform Bacteria Related to the Presence and Chain Length of Micolic Acids. Appl. Environ. Microbiol. *59*, 3973–3977. (1993)

1824 **Bouwer, E. J., Zehnder, A. J. B.**: Bioremediation of Organic Compounds – Putting Microbial Metabolism to Work. TIBTECH *11*, 360–367 (1993)

1825 **Bundi, U., Leu, D.**: Stickstoffhaushalt in der Schweiz: Konsequenzen für Gewässerschutz und Umweltentwicklung. Bericht der Eidg. Gewässerschutzkommission. Schriftenreihe Umwelt, Nr. 209, Bern, 1993. 74 S.

1826 **Eggleston, C.M., Stumm, W.**: Scanning Tunneling Microscopy of Cr(III) Chemisorbed on α-Fe_2O_3 (001) Surfaces from Aqueous Solution: Direct Observation of Surface Mobility and Clustering. Geochim. Cosmochim. Acta *57*, 4843–4850 (1993).

1827 **Jannasch, W.H., Egli, T.**: Microbial Growth Kinetics : A Historical Perspective. Antonie van Leeuwenhoek *63*, 213–224 (1993).

1828 **Egli, T., Lendenmann, U., Snozzi, M.**: Kinetics of Microbial Growth With Mixtures of Carbon Sources. Antonie van Leeuwenhoek *63*, 289–298 (1993).

1829 **Bondietti, G., Sinniger, J., Stumm, W.**: The Reactivity of Fe(III)(hydr)oxides: Effects of Ligands in Inhibiting the Dissolution. Colloids & Surfaces A: Physicochem. & Engng. Aspects *79*, 157–167 (1993).

1830 **Kappeler, J., Gujer, W.**: Verification and Applications of a Mathematical Model for «Aerobic Bulking». Water Res. *28*, 311–322 (1994).

1831 **Eggleston, C.M.**: Direct Scanning Tunneling Microscope (STM) Observation of Cr(III) Complexes on Hematite (001) Surfaces. Aquatic Sci. *55*, 240–249 (1993).

1832 **Jaeger, C.C.**: The Cultural Evolution of Rational Choice. Int. Sociology *8*, 497–503 (1993).

1833 **Kappeler, J., Gujer, W.**: Development of a Mathematical Model for «Aerobic Bulking». Water Res. *28*, 303–310 (1994).

1834 **Barry, R.C., Schnoor, J.L., Sulzberger, B., Sigg, L., Stumm, W.**: Iron Oxidation Kinetics in an Acidic Alpine Lake. Water Res. *28*, 323–333 (1994).

1835 **Frutiger, A., Schib, J.-L.**: Limitations of FST Hemispheres in Lotic Benthos Research. Freshwater Biology *30*, 463–474 (1993).

1836 **Frutiger, A.**: Reply to Statzner. Freshwater Biology *30*, 485–486 (1993).

1837 **Münnich, M.**: On the Influence of Bottom Topography on the Vertical Structure of Internal Seiches. Diss. ETHZ Nr. 10434, Zürich 1993.

1838 **Hoigné, J., Zuo, Y., Nowell, L.**: Photochemical Reactions in Atmospheric Waters: Role of Dissolved Iron Species. In: «Aquatic and Surface Photochemistry», G.R. Helz, R.G. Zepp, D.G. Crosby (Eds.). Lewis Publ. Boca Raton, 1994. pp. 75–84.

1839 **Bürgi, H.R.**: Das Plankton – bizarre, schwebende Wasserlebewesen. In: «Sempachersee». Mitt. Naturforsch. Ges. Luzern *33*, 105–121 (1993).

1840 **Stumm, W.**: From Surface Acidity to Surface Reactivity; Inhibition of Oxide Dissolution. Aquatic Sci. *55* /4, 273–280 (1993).

1841 **Akeret, B.**: Ein neuer Fundort von *Aldrovanda vesiculosa* L. in der Nordschweiz und einige Bemerkungen zu *Stratiotes aloides*, L. Bot. Helv. *103*, 193–199 (1993).

1842 **Xue, H., Sigg, L.**: Free Cupric Ion Concentration and Cu(II) Speciation in a Eutrophic Lake. Limnol. Oceanogr. *38*, 1200–1213 (1993).

1843 **Xue, H., Sigg, L.**: Zinc Speciation in Lake Waters and its Determination by Ligand Exchange With EDTA and Differential Pulse Anodic Stripping Voltammetry. Anal. Chim. Acta *284*, 505–515 (1994).

1844 **Breedveld, M.W., Ludovicus C.D, Zevenhuizen, P.T.M., Zehnder, A.J.B.**: Response of Intracellular Carbohydrates to a NaCl Shock in *Rhizobium leguminosarum* biovar *trifolii* TA-1 and *Rhizobium meliloti* SU-47. J. Gen. Microbiol. *139*, 3157–3163 (1993).

1845 **Kotronarou, A., Sigg, L.**: SO_2 Oxidation in Atmospheric Water: Role of Fe(II) and Effect of Ligands. Environ. Sci. & Technol. *27* (13) 2725–2735 (1993).

1846 **Imboden, D.M.**: The Energy Needs of Today Are the Prejudices of Tomorrow. GAIA *2*, 330–337 (1993).

1847 **Häner, A., Mason, C.A., Hamer, G.**: Aerobic Thermophilic Waste Sludge Biotreatment: Carboxyclic Acid Production and Utilization During Biodegradation of Bacterial Cells Under Oxygen Limitation. Appl. Microbiol. Biotechnol. *40*, 904–909 (1994).

1848 **Häner, A., Mason, C.A., Hamer, G.**: Death and Lysis During Aerobic Thermophilic Sludge Treatment: Characterization of Recalcitrant Products. Water Res. *28*, 863–869 (1994).

1849 **Biesterveld, S., Oude Elferink, S.J.W.H., Zehnder, A.J.B., Stams, A.J.M.**: Xylose and Glucose Utilization by *Bacteroides xylanolyticus* X5-1 Cells Grown in Batch and Continuous Culture. Appl. Environ. Microbiol. *60*, 576–580 (1994).

1850 **Heijman, C.G., Holliger, C., Glaus, M.A., Schwarzenbach, R.P., Zeyer, J.**: Abiotic Reduction of 4-Chloronitrobenzene to 4-Chloroaniline in a Dissimilatory Iron-Reducing Enrichment Culture. Appl. Environ. Microbiol. *59*, 4350–4353 (1993).

1851 **Ochs, M., Cosovi˘c, B., Stumm, W.**: Coordinative and Hydrophobic Interaction of Humic Substances with Hydrophilic Al_2O_3 and Hydrophobic Mercury Surfaces. Geochim. Cosmochim. Acta *58*, 639–650 (1994).

1852 **Field, J.A., Field, T.M., Poiger, T. Giger, W.**: Determination of Secondary Alkane Sulfonates in Sewage Wastewaters by Solid-Phase Extraction and Injection-Port Derivatization Gas Chromatography/Mass Spectrometry. Environ. Sci. & Technol. *28*, 497–503 (1994).

1853 **Charlet, L., Dise, N., Stumm, W.**: Sulfate Adsorption on a Variable Charge Soil and on Reference Minerals. Agriculture, Ecosystems and Environment *47*, 87–102 (1993).

1854 **Uehlinger, U.**: Sauerstoff in der Glatt: Photosynthese, Respiration und Sauerstoffhaushalt in einem anthropogen stark beeinflussten Mittellandfluss (Glatt, Kt. Zürich). Gas, Wasser, Abwasser *74*, 123–128 (1994).

1855 **Hajdas, I., Ivy, S.D., Beer, J., Bonani, G., Imboden, D., Lotter, A.F., Sturm, M., Suter, M.**: AMS Radiocarbon Dating and Varve Chronology of Lake Soppensee: 6000 to 12000 ^{14}C Years BP. Climate Dynamics, *9*, 107–116 (1993).

1856 **Huggenberger, P., Meier, E., Pugin, A.**: Ground-probing Radar as a Tool for Heterogeneity Estimation in Gravel Deposits: Advances in Data-Processing and Facies Analysis. J. Appl. Geophys. *31*, 171–184 (1994).

1857 **Fent, K., Bucheli, T.D.**: Inhibition of Hepatic Microsomal Monooxygenase System by Organotins in Vitro in Freshwater Fish. Aquat. Toxicol. *28*, 107–126 (1994).

1858 **Peeters, F.**: Horizontale Mischung in Seen. Diss. Nr. 10476. Zürich 1994.

1859 **Urban, N.R.**: Retention of Sulfur in Lake Sediments. In: «Environmental Chemistry of Lakes and Reservoirs», L.A. Baker (Ed.). ACS Advances in Cemistry Series No. 237, Amer. Chem. Soc. 1994, pp. 323–369.

1860 **Kuhn, A., Johnson, A.C., Sigg, L.**: Cycles of Trace Elements in a Lake with a Seasonally Anoxic Hypolimnion. In: «Environmental Chemistry of Lakes and Reservoirs», L.A. Baker (Ed.). ACS Advances in Cemistry Series No. 237, Amer. Chem. Soc. 1994, pp. 473–497.

1861 **Poiger, T., Field, J.A., Field, T.M., Giger, W.**: Determination of Detergent-derived Fluorescent Whitening Agents in Sewage Sludges by Liquid Chromatography. Anal. Methods and Instrumentation *1*, No. 2, 104–113 (1993).

1862 **Ahel, M., Hrsak, D., Giger, W.**: Aero-bic Transformation of Short-Chain Alkylphenol Polyethoxylates by Mixed Bacterial Cultures. Arch. Environ. Toxicol. *26*, 540–5488 (1994).

1863 **Hoigné, J.**: Characterization of Water Quality Criteria for Ozonation Processes. Part I: Minimal Set of Analytical Data. Ozone Sci. & Engng. *16*, 113–120 (1994).

1864 **Hoigné, J., Bader, H.**: Characterization of Water Quality Criteria for Ozonation Processes. Part II: Lifetime of Added Ozone. Ozone Sci. & Engng. *16*, 121–134 (1994).

1865 **Leveau, J.H.J., de Vos, W.M., van der Meer, J.R.**: Analysis of the Binding Site of the LysR-Type Transcriptional Activator TcbR on the *tcbR* and *tcbC* Divergent Promoter Sequences. J. of Bacteriology *176*, 1850–1856 (1994).

1866 **Zuo, Y., Hoigné, J.**: Photochemical Decomposition of Oxalic, Glyoxalic and Pyruvic Acid Catalysed by Iron in Atmospheric Waters. Atmospheric Environ. *28*, 1231–1239 (1994).

1867 **Ahel, M., Giger, W., Koch, M.**: Behaviour of Alkylphenol Polyethoxylate Surfactants in the Aquatic Environment – I. Occurrence and Transformation in Sewage Treatment. Water Res. *28*, 1131–1142 (1994).

1868 **Ahel, M., Giger, W., Schaffner, C.**: Behaviour of Alkylphenol Polyethoxylate Surfactants in the Aquatic Environment – II. Occurrence and Transformation in Rivers. Water Res. *28*, 1143–1152 (1994).

1869 **Vojtyla, P., Beer, J., Stavina, P.**: Experimental and Simulated Cosmic Muon Induced Background of a Ge Spectrometer Equipped with a Top Side Anticoincidence Proportional Chamber. Nuclear Instruments & Methods in Physics Res. *B 86*, 380–386 (1994).

1870 **Boller, M., Schwager, A., Eugster, J., Mottier, V.**: Dynamic Behavior of Intermittent Buried Filters. Water Sci. Tech. *28*, No. 10, 99–107 (1993).

1871 **Zeh, M., Dönni, W.**: Restoration of Spawning Grounds of Trout and Grayling in the River High-Rhine. Aquatic Sci. *56*/1, 59–69 (1994).

1872 **Jaeger, C.C., Rust, A.J.**: Ethics as a Rule Systems: The Case of Genetically Engineered Organisms. Inquiry *3*, 65–84 (1993).

1873 **Lendenmann, U.**: Growth Kinetics of *Escherichia coli* with Mixtures of Sugars. Diss. ETHZ No. 10658, Zürich 1994.

1874 **Biesterveld, S., Zehnder, A.J.B., Stams, A.J.M.**: Regulation of Product Formation in *Bacteroides xylanolyticus* X5-1 by Interspecies Electron Transfer. Appl. & Environ. Microbiol. *60*, 1347–1352 (1994).

1875 **Fent, K.**: Einfluss von Umweltschadstoffen auf Fische. Wasser, Energie, Luft *86*, 26–30 (1994).

1876 **Bundi, U.**:Neue Ansätze für den Gewässerschutz. Von rein technischen zu integrierenden Schutzmassnahmen. Technische Rundschau 25.3.1994.

1877 **Bundi, U.**: Umfassende Umweltpolitik – Stickstoff-Problematik als Wegweiserin. VGL Information Nr. 1 (1994).

1878 **Bosma, T.N.P., Cottaar, F.H.M., Posthumus, M.A., Teunis, C.J., van Veldhuizen, A., Schraa, G., Zehnder, A.J.B.**: Comparison of Reductive Dechlorination of Hexachloro-1,3-butadiene in Rhine Sediment and Model Systems with Hydroxocobalamin. Environ. Sci. & Technol. *28*, 1124–1128 (1994).

1879 **Egli, T., Zehnder, A.J.B.**: Phosphate and Nitrate Renoval. Curr. Opinion in Biotechnol. *5*, 275–284 (1994).

1880 **Haderlein, S.B., Schwarzenbach, R.P.**: Sensing Reactive Mineral Surfaces in Natural Sediments by Nitroaromatic Model Compounds. In: «Transport and Reactive Processes in Aquifers», T. Dracos, F. Stauffer (Eds.). Balkema, Rotterdam 1994, pp. 67–72.

1881 **Ahel, M., Scully, F.E., Hoigné, J., Giger, W.**: Photochemical Degradation ob Nonylphenol and Nonylphenol Polyethoxylates in Natural Waters. Chemosphere *28*, 1361–1368 (1994).

1882 **Rothen, S.M.**: Carbon Dioxide Reduction in an Optimization Model – A Case Study for Switzerland. Swiss J. Economics & Statistics *130*/2, 145–170 (1994).

1883 **Höhener, P., Gächter, R.**: Nitrogen Cycling Across the Sediment–Water Interface in an Eutrophic, Artifically Oxygenated Lake. Aquatic Sci. *56*/2, 115–132 (1994).

1884 **Bloesch, J.**: A Review of Methods Used to Measure Sediment Resuspension. Hydrobiologia *284*, 13–18 (1994).

1885 **Gloor, M., Wüest, A., Münnich, M.**: Benthic Boundary Mixing and Resuspension Induced by Internal Seiches. Hydrobiologia *284*, 59–68 (1994).

1886 **Boller, M.**: Trends in Water Filtration Technology. J. Water SRT – Aqua *43*, 65–75 (1994).

1887 **Biber, M.V., dos Santos Afonso, M., Stumm, W.**: The Coordination Chemistry of Weathering: IV. Inhibition of the Dissolution of Oxide Minerals. Geochim Cosmochim Acta *58*, 1999–2010 (1994).

1888 **Wüest, A.**: Interaktionen in Seen: Die Biologie als Quelle dominanter physikalischer Kräfte. Limnologica *24*,/2, 93–104 (1994).

1889 **Behra, R.**: Interaction of Cadmium, Lead and Zinc With Calmodulin From Rainbow Trout, Sea Mussels And a Green Alga. The Sci. of the Total Environment, Suppl. 1993, pp. 647–653.

1890 **Güttinger, H.**: Combined Interpretation of Biological and Chemical Field Data to Evaluate Ecotoxicity of Chemical Substances. The Sci. of the Total Environment, Suppl. 1993, pp. 1539–1545.

1891 **Bundi, U.**: Stickstoffmanagement – Vehikel für integrierten Gewässerschutz. Gas, Wasser, Abwasser *74*, 482–487 (1994).

1892 **Biber, M.V., Stumm, W.**: An *In-Situ* ATR-FTIR Study: The Surface Coordination of Salicylic Acid on Aluminum and Iron(III) Oxides. Environ. Sci. & Technol., *28*, 763–768 (1994).

1893 **Huggenberger, P., Rauber, M., Stauffer, F.**: Integration of Geophysical and Sedimentological Information in the Stochastic Description of Inhomogeneities in Fluvial Gravel Deposits. In: «Transport and Reactive Processes in Aquifers». T. Dracos, F. Stauffer (Eds.). A.A. Balkema Rotterdam & Brookfield 1994, pp. 177–181.

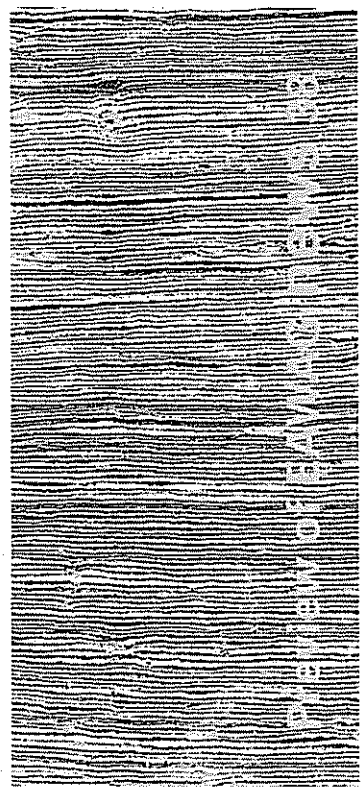
1894 **Xue, H., Schnoor, J.L.**: Acid Deposition and Lake Chemistry in Southwest China. Water, Air & Soil Pollution *75*, 61–78 (1994).

1895 **Stumm W.**: Acquisition of Solutes ans Regulation of the Composition of Natural Waters. In:«Chemistry of Aquatic Systems: Local and Global Perspectives», G. Bidoglio, W. Stumm (Eds). ECSC, EEC, EAEC, Brussels & Luxembourg 1994, pp. 1–31.

1896 **Sigg, L., Xue, H.**: Metal Speciation: Concepts, Analysis and Effects. In:«Chemistry of Aquatic Systems: Local and Global Perspectives», G. Bidoglio, W. Stumm (Eds). ECSC, EEC, EAEC, Brussels & Luxembourg 1994, pp. 153–181.

1897 **Kari, F.G.**: Umweltverhalten von Ethylendiamintetraacetat (EDTA) unter spezieller Berücksichtigung des photochemischen Abbaus. Diss. ETHZ Nr. 10698, Zürich 1994.

1898 **Aeschbach-Hertig, W.**: Helium und Tritium als Tracer für physikalische Prozesse in Seen. Diss. ETHZ Nr. 10714, Zürich 1994.



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