EAWAG NEWS

20/21

Federal Institute for Water Resources and Water Pollution Control

Swiss Federal Institutes of Technology

JULY 1986 – EAWAG, 8600 DÜBENDORF, SWITZERLAND

Water, an Endangered Ecosystem; Some Reflections on the Fiftieth Anniversary of EAWAG

Werner Stumm

Byproducts of our civilization threaten one of its vital resources: clean water. The progressive interference by humans in hydrogeochemical cycles and new chemical pollutants require better ecological insights, improved control strategies and new research on ecotoxicology and on the coupling of water, land and atmosphere.

How are we to plan for the future?

How can we keep up with the steadily increasing pressures on our aquatic ecosystems and on the quality of our subsurface water reservoirs? Historically, impairment of water quality has occurred in three succeeding, but partly also overlapping phases (W.C. Clarke and C.S. Holling in *Global Change*, T.F. Malone and J.G. Roederer, eds., Cambridge Univ. Press, Cambridge, 1984).

First phase: acute, localized pollution by sewage and industrial wastes.

This kind of pollution created "unsanitary" conditions in the receiving waters, imparted odor and taste, lead to spreading of pathogenic organisms (water-borne diseases), created depletion of dissolved oxygen, favored saprobic "indicator" organisms, i.e. heterotrophic organisms responding to putrescible substances. Throughout the world, engineers have been very successful in ameliorating this kind of problem. Although we will continue to depend on more and more efficient sewage, waste and water purification and disinfection treatment, we need to apply our knowledge in a more integral way to entire water catchment areas and consider the interdependence of water supply and waste disposal. Despite of being far away from having solved all these problems, we realize that this kind of localized pollution is largely amenable to technological control.

Second phase: pollution by synthetic chemicals

Discards of modern industrial society (synthetic chemicals, mining products such as phosphates and heavy metals and byproducts of energy production) are distributed by various pathways into the environment and are in many instances perturbing aquatic ecosystems and occasionally may even be harmful to human health. It has been estimated that ca. 40 000 chemicals are in daily use and that this number increases by ca. 1000 substances every year. Many industrial chemicals reach receiving waters indirectly (via households, agricultural drainage, the atmosphere). Some of these substances are refractory (i.e. not biodegradable) and they progressively accumulate in aquatic ecosystems because self-purification and biological waste treatment are not very effective in eliminating such chemicals. Furthermore, many of these chemicals are introduced into the waters from non-point sources (via atmosphere, or from agricultural drainage) (Fig. 1).

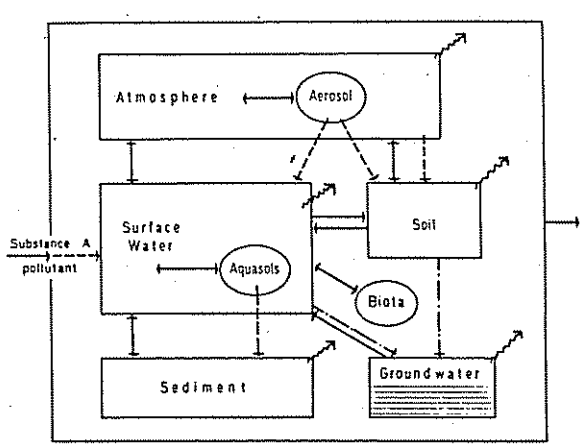


Fig. 1
A pollutant entering the environment becomes distributed – according to its substance specific properties, such as vapor pressure, adsorbability, lipophility, Henry's coefficient – in the various compartments of the environment. The atmosphere is a very important conveyor belt for many pollutants, of special ecological relevance is fat-solubility, the lipophility of a substance; lipophilic substances accumulate in organisms and the food-chain. Biodegradation and chemical or photochemical decomposition (indicated by the wavy lines) decrease the residence time and the residual concentration of individual pollutants.

Cultural evolution has been faster than natural evolution. In industrialized nations, industrial activities have grown faster than human population, agricultural production has been intensified by application of fertilizers and pesticides and energy production has increased exponentially. Many of the synthetic chemicals which have been added to the biosphere within the last decades bear little resemblance to the natural products of the biosphere. Because they are not readily biodegradable, many of these chemicals survive long enough in the environment. Some of these substances, even if they exhibit no acute toxicity, may nevertheless impair the self-regulation of aquatic ecosystems and damage their life support function, others tend to become concentrated in organisms, some may become harmful to human health.

The assessment of the potential ecological effects of pollutants is of central importance. This cannot be accomplished by merely evaluating the harmfulness or the basis of toxicity tests and by monitoring the environment for pollutants. Chemists and biologists are encouraged to participate in the solution of ecotoxicological problems. We need (1) the estimation – on the basis of physical-chemical generalizations – of the fate, the distribution, the potential for bioaccumulation in the food chain, and the approximate residence time of pollutants and thus the attainable residual concentrations in the environment; and (2) a better understanding of the impact of such substances on the functioning of ecosystems.

Third generation problem: interference in hydrogeochemical cycles.

Man in his social and cultural evolution continues to be successful in diverting energy to the advancement of his own civilization. Receiving waters reflect not solely the activities within their drainage area, but also the impact of emissions carried over large distances through the atmosphere. The rapid changes that have been observed in the last decades in chemical and biological properties of many coastal and fresh waters reflect the human influence on the environment. The burning of fossil fuels produces a variety of gaseous carbon, nitrogen, hydrogen and sulfur compounds and compounds of heavy metals. The oxides of nitrogen and sulfur can become converted into nitric acid and sulfuric acid which come down as acid rain. Of special concern here are substances that are dispersed over large distances and may adversely affect the ecology of natural waters. The dispersion of metals to the atmosphere as a consequence of industrial and agricultural activity appears to rival and sometimes to exceed natural mobilizations.

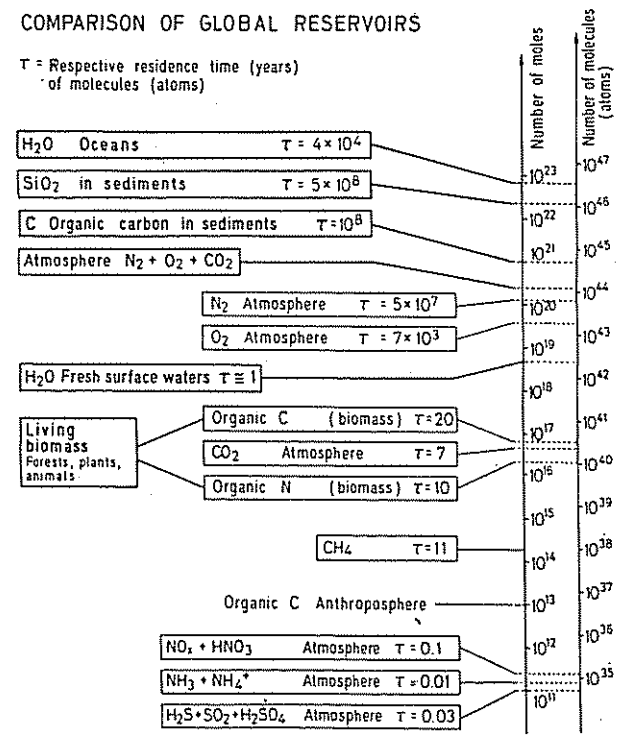
The water cycle is intimately connected to biogeochemical cycles. Humans have become more and more geochemical manipulators and agents of global change. Man has become a major force in the transport of solid earth materials and his chemical byproducts are changing the hydrosphere and atmosphere. The change on our planet involves a complex interaction between the inorganic physical processes and the biological processes. Although we depend on human intervention in the water cycle to provide adequate supplies for agriculture and people we are often not sufficiently aware of some of the negative effects that mammoth water diversion has on ecosystems. The consequences may often not be apparent for some time, and cause and effect may be displaced by huge distances. Identifying specific sources or causes may often be very difficult.

As has been pointed out by Clarke and Holling "We are moving beyond an age of acute localized, and relatively simple environmental problems reversible at economically measurable costs and politically realistic time and space scales. We are moving into a period of chronic, global, and extremely complex syndromes of ecological and economic interdependence". Despite intensive research, we understand only partially how chemical pollutants move among atmosphere, land and water and what changes they undergo in their transport. There is a degree of urgency to better understand the basic interactive processes that lead to a change of our environment. We need the collaboration of all scientific disciplines.

The sensitivity of aquatic ecosystems to perturbation

In Fig. 2 the sizes of the various reservoirs, measured in number of molecules or atoms, are compared. The mean residence times of these molecules in these reservoirs (years) are also indicated. The smaller the relative reservoir size and the smaller the residence time, the more sensitive is the reservoir towards perturbation. Obviously, atmosphere, living biomass (mostly forests), ground and surface fresh waters as reservoirs are most sensitive to perturbation. The anthropogenic exploitation of the larger sedimentary organic carbon reservoir (fossil fuels and by-products of their combustion, i.e. oxides, heavy metals, and the synthetic chemical, derived from organic carbon) can above all affect the small reservoirs. Over the past years we have started to recognize that biosphere processes play an important role in coupling the cycles of essential elements and in regulating the chemistry and

Fig. 2
Size of reservoirs. The comparison illustrates that the reservoirs atmosphere, surface fresh waters and living biomass (mostly forests) are significantly smaller than the sedimentary reservoirs of the oceans. Exploitation of sedimentary (fossile) organic carbon: its oxidation together with N and S and the concomitant release of heavy metals can perturb the atmosphere (CO_2 and acid rain) and influence terrestrial and aquatic ecosystems (data mostly from R.M. Garrels and E.A. Perry, in The Sea, E.D. Goldberg, ed. Wiley-Interscience, New York, 1974). The total groundwater reservoir may be two times that of the freshwater resevoir. But the quantity that is readily accessible is smaller than that of fresh surface water.



physics of our environment. The living biomass (Fig. 1) is a relatively small reservoir and thus subject to man's interference; each species forming the biosphere requires specific environmental conditions for sustenance and survival.
Impairment of ecological quality of a water is not synonymous with the addition of contaminants or pollutants to the environment, but can also result from many direct or indirect consequences of human action. Damming or diversing of rivers, deepening of channels to accomodate ships, modification of shorelines, reduction of runoff, amelioration of swamps and marshes, diking and filling of wetlands, all change the dynamics of biotic communities.

Some new priority research projects at EAWAG

In response to some of the reflections given, the collaborators of EAWAG have decided to amplify their priority research endeavors above all in two directions:

1. Ecotoxicology

Fig. 3 illustrates synoptically the realms and perspectives of aquatic ecotoxicology. Let us follow the various steps from the source to the potential ecological effects of a pollutant released into an aquatic ecosystem. The immission (immission gives the input load) is measured as a flow or load (capacity factor; mass per unit time or mass per unit time and volume or area). The resulting concentration is a consequence of dilution, transport, and transformation of this chemical. At any point, the water condition is characterized by the entity of interacting physical, chemical, and biological factors.
These variables, above all the concentrations, determine causally the doses (concentration × time) an organism or an ecosystem will receive and thus, in turn, the type of community or organisms present in the ecosystem (W. Stumm, R. Schwarzenbach and L. Sigg, From environmental analytical chemistry to ecotoxicology – A plea for more concepts and less monitoring and testing, Angewandte Chemie, Int. ed. Engl. *22*, 380–389, 1983). Thus, for an assessment of the exposure and an evaluation of the ecological and hygienic risk, we need to know the residual concentrations of pollutants. An estimate of the ambient concentration of a pollutant based on a prediction of its relevant fate and residence time (considering relevant pathways, exchange processes, biological and chemical conversions), or on the basis of analytical determinations in the receiving waters, is essential to any hazard assessment.

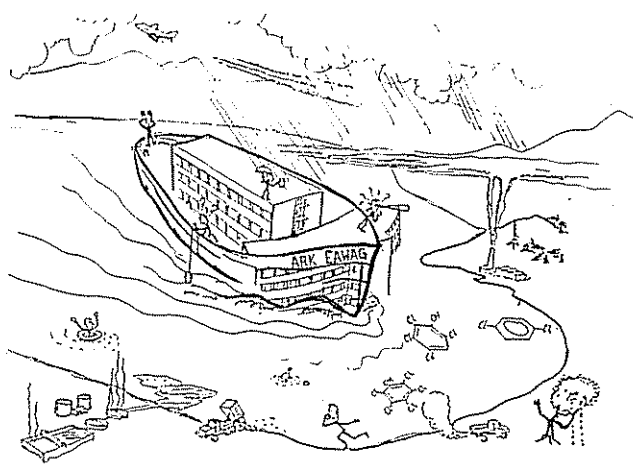


Fig. 3
EAWAG's function as a "Water Institute" is also to investigate atmospheric and terrestrial emissions which are released into the waters.

The toxic effect
The ecological harmfulness of a substance depends on its interaction with organisms or with entire communities of organisms (Fig. 3). The intensity of this interaction depends on the specific structure and on the activity of the substance under consideration; but other factors such as temperature, turbulence, and the presence of other substances are also important. A thourough knowledge of the basic mechanisms by which toxic agents exert their injurious effects (pharmacokinetics, uptake, conversion, degradation, separation, and disturbance of regulatory mechanisms in the biological community) is fundamental for an understanding of biological responses.
An understanding of the interaction of chemical compounds in the natural system, that is the mode of their participation in various processes, hinges on the recognition of the compositional complexity of the environment. This requires an adequate analytic methodology, especially the ability to detect individual components (chemical species) selectively and to measure them accurately and with the greatest sensitivity.
Sociobiological effects
While we have some knowledge about the impact of xenobiotic substances on individual organisms, we know less about their impact on ecosystems. In considering biological communities (the biocenoses), various intra- and inter-species interactions of a sociobiological nature (e.g. chemotaxis and chemoreception) have to be taken into account.
The natural distribution of organisms depends primarily on their ability to compete under given conditions and not merely on their ability to survive the physical and chemical environment; a population will be eliminated when its competitive power is reduced to such an extent that it can be replaced by another species. The competitive abilities of an organism are an interplay of its reproductive rates which are related to food and physiological potential, and the mortality rates from all sources, including predation and imposed toxicity. There are many ways in which an organism can die, but there is only a verynarrow range of ways in which it can survive and leave offspring. Thus, in an ecosystem, a population may be eliminated by the presence of pollutants even at apparently trivial toxicity levels if its competitive ability is marginal, or if it is the most sensitive of the competitors. Often, contaminants at very low concentrations cause changes in the structure of the population by interfering through chemotaxis with interorganismic communication. For example, the survival of a fish population may be rendered impossible by a pollutant (even if it exhibits neither acute nor chronic toxicity to the particular species of fish) if it impairs the food source (zooplankton) or disturbs chemotactical stimuli or mimicks wrong signals (and thus, for example, interferes with food finding).

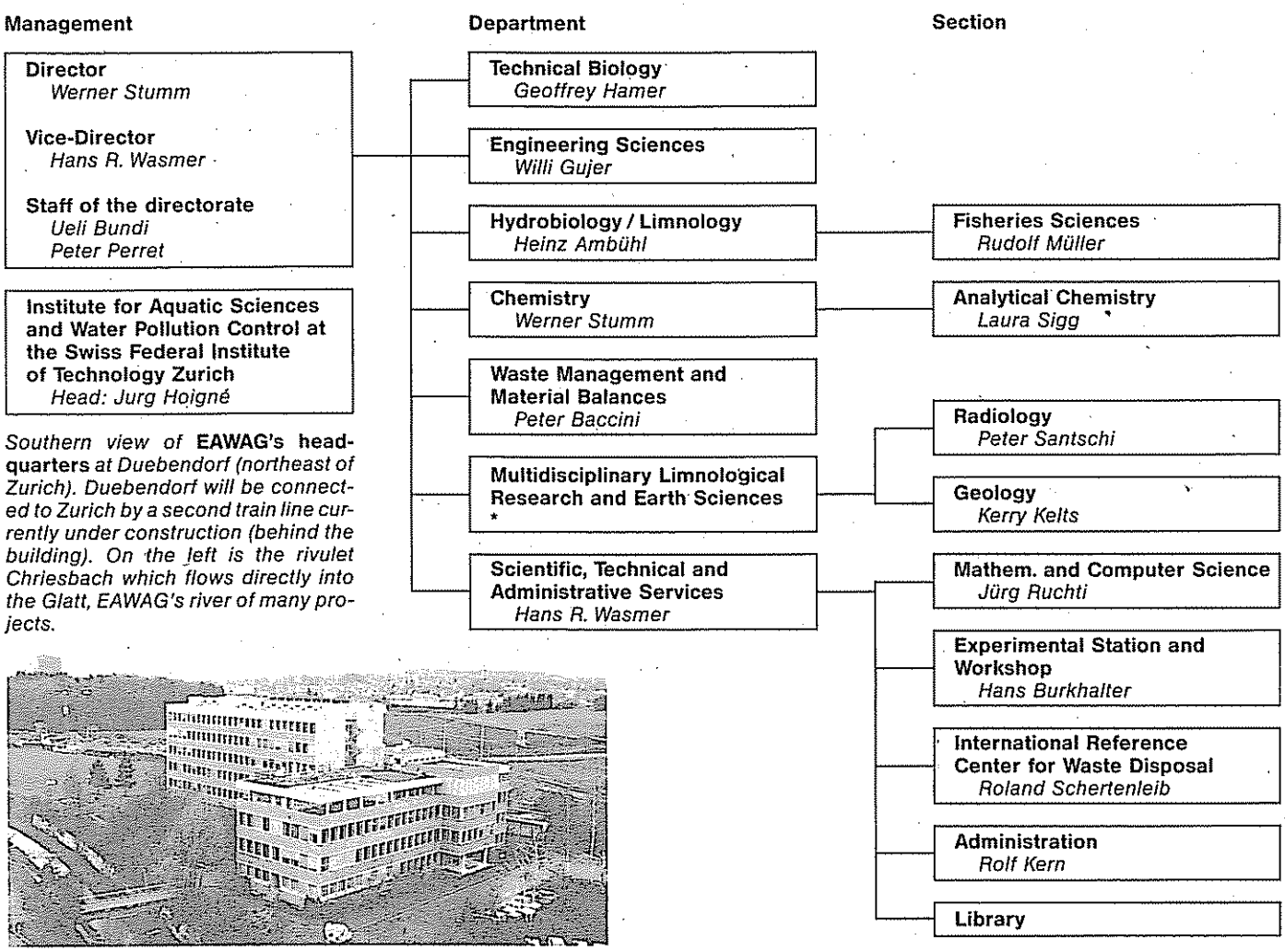
2. Coupling of land, water and atmosphere

Figs. 1 and 2 suggest that water as an ecosystem should no longer be considered independent of the material fluxes and cycles that couple land, water and atmosphere. As is also illustrated by the Chernobyl accident, the atmosphere is a powerful conveyor belt for many organic pollutants that ultimately find their way into aquatic ecosystems. At present, the open ocean and many lakes are more affected by pollution impacts of some metals through tropospheric transport than through riverine transport.
The chemists at EAWAG have been concentrating so far in analyzing and interpreting the inorganic and organic composition of atmospheric depositions (rain, fog, snow, aerosols and gases) emphasizing the processes occurring in

the gaswater transfers and in the acid-base neutralization reactions. We also plan to extend some of our aquatic chemical research on oxidation by ozone, hydrogen peroxide, hydroxyl radicals, on photo-induced reactions, etc., to processes occurring in the atmospheric water phase and its interface.
We have also started a research collaboration called "WaBoLu" (acronym for the German words Water, Soil and Air) with various institutes of the Swiss Federal Institute of Technology (ETHZ) (Laboratory for Atmospheric Physics, Laboratory for Solid State Physics, Laboratories of Soil Chemistry and Soil Physics).

While EAWAG remains a "water institute" (Fig. 3), we feel that we are well equipped to extend our know-how in water chemistry, our competence in inorganic and organic analysis and our understanding of oxidation mechanisms and kinetics to atmospheric chemistry.

Organizational chart of the Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG)

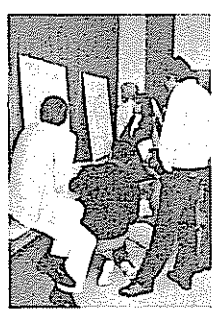


Southern view of **EAWAG's headquarters** *at Duebendorf (northeast of Zurich). Duebendorf will be connected to Zurich by a second train line currently under construction (behind the building). On the left is the rivulet Chriesbach which flows directly into the Glatt, EAWAG's river of many projects.*

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

From left to right, front row: *Dimitris Babalis, Eleni Giannopoulou, Eva Warnicki, Andreas Schwager, Alex Borer, Thomas Stauss;* second row: *Gregor Vogel, Dr. Thomas Strübin, Dariusz Gorczyca, Peter Krebs, Peter Baumann;* third row: *Stefan Drenkard, Felix Rutz, Paul Morgenthaler.*

* Head of associate department is a position which changes every second year among *René Gächter* (Biology), *Dieter Imboden* (Physics) and *René Schwarzenbach* (Chemistry) 1985–1987: *René Schwarzenbach.*



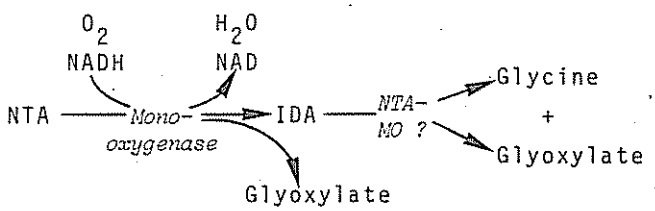
The workshop on **«Aquatic Surface Chemistry; Chemical Processes at the Particle Water Interface»** took place at the Wolfsberg Conference Center on Lake Constance, Switzerland, from January 22 to 25, 1986. Most of the program presented in EAWAG-News 18/19 and a few new articles will appear early 1987 in a book printed by Wiley-Interscience, New York.

Isolation of a Variety of Nitrilotriacetate-Degrading Aerobic Bacteria

Thomas Egli

Because phosphate is the growth-limiting nutrient for primary production of biomass in most aquatic ecosystems the extensive use of phosphates in washing powder and agricultural fertilizers has led to wide-spread eutrophication in lakes and rivers. To reduce the load of phosphate discharges to surface waters, legislation has been enacted in Switzerland and trisodium polyphosphates will be banned from washing powders with effect from July 1986. The main substitute for these phosphates will be nitrilotriacetic acid (NTA).

The biodegradation of NTA in the environment and in wastewater treatment plants has been studied extensively (for reviews see [1] and [2]). However, few reports have been published on the microbes involved in NTA-breakdown and the metabolism of this xenobiotic compound. To date only three bacteria have been isolated and studied in pure culture. They appeared to be physiologically identical and have been assigned to the genus of Pseudomonads [3, 4, 5]. In the two strains investigated the initial attack of NTA is catalysed by an enzyme requiring oxygen and NADH, NTA-monooxygenase (NTA-MO), which splits NTA to yield iminodiacetate (IDA) and glyoxylate:



It is postulated that the same enzyme is also responsible for the further breakdown of IDA to glycine and glyoxylate. The available information suggests that probably only a small group of specialized bacteria are able to degrade NTA and that the degradation is dependent on the presence of oxygen.

Isolation and characterization of new strains

By employing a different isolation strategy than was used previously, namely by setting up enrichment cultures with NTA as the sole nitrogen source and a mixture of glucose/acetate/methanol as carbon sources, several strains (TE 1-10) of non-pseudomonads were isolated in pure culture from both soil and wastewater. All the new isolates were able to grow with NTA as their sole source of carbon and nitrogen. The isolates have been characterized with respect to their cell morphology and physiology and were compared with the two reference strains *Pseudomonas* sp. 27109 and 29600 (from the American Type Culture Collection). Some of the physiological properties of isolates and reference strains are shown in Tab. 1. Based on those results the microbes were tentatively divided into five different groups:

1) Isolates TE 1 and 2 are short, Gram-negative rods which during exponential growth occur mostly as pairs (Fig. 1a). They are nonmotile and did not grow on any of the sugars tested. Both strains are physiologically and morphologically identical, except for the mucous appearance of TE 1 on Plate Count Agar plates. Amino acids and short chain alcohols and acids are preferentially utilized as carbon sources.

2) Isolate TE 3 is a Gram-positive, nonmotile rod which is able to degrade cellulose. The cells often show birth scars on their cell wall. Because dividing cells frequently do not separate completely V-formation typical for coryneform

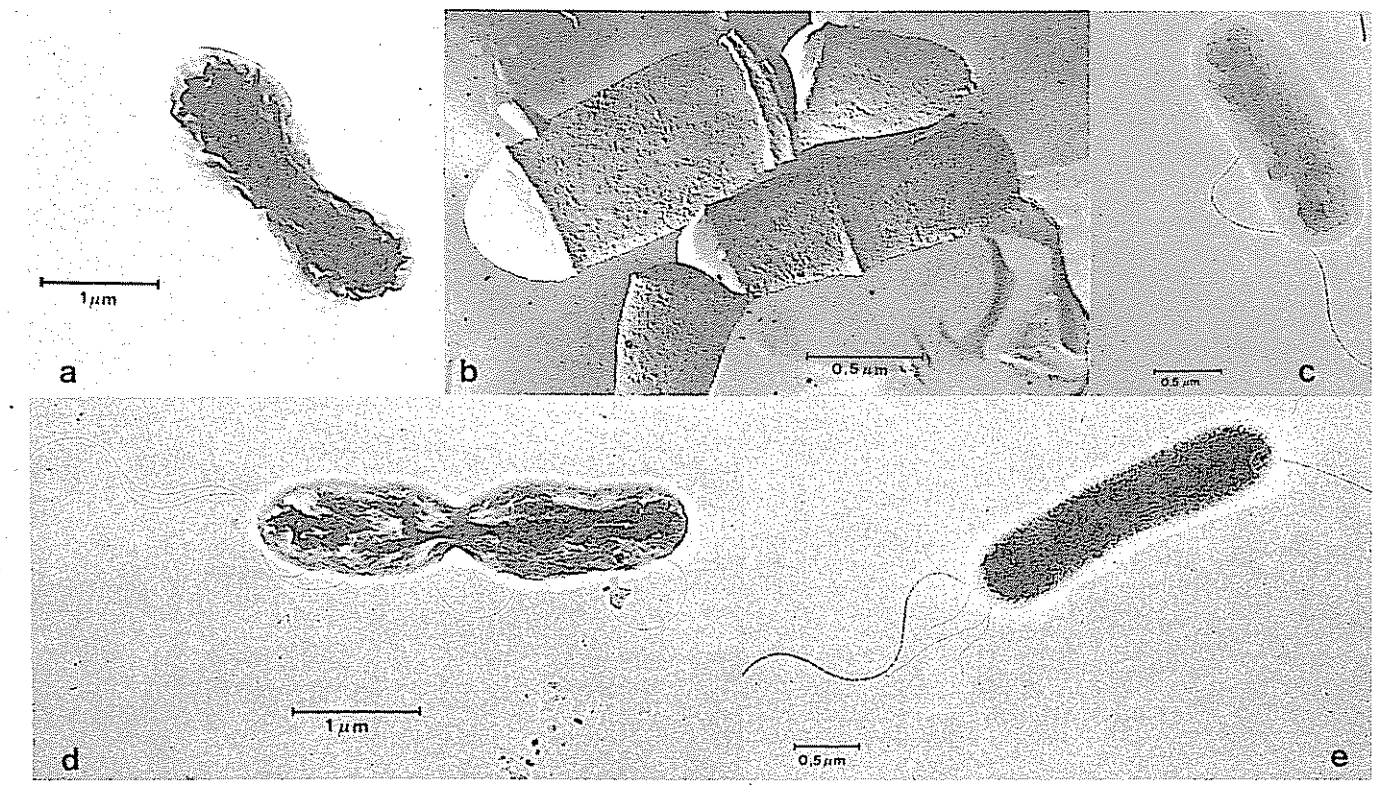


Fig. 1
Morphology of NTA-utilizing bacteria.
a) Isolate TE 1; b) Isolate TE 3; c) Isolate TE 9; d) Isolate TE 8; e) Isolate TE 10.
(Electron micrographs were taken by Dr. E. Wehrli from the «Labor für Elektronenmikroskopie», ETH Zürich.)

Tab. 1 Characterization of NTA-utilizing bacteria
where + is indicating growth (–: no growth) on the substrate or presence (–: absence) of enzyme activity

Strain	TE 1 TE 2	TE 3	TE 4	TE 10	TE 5 TE 7	TE 6	TE 8	PS 27109	PS 29600	TE 9
Gram reaction	–	+	–	–	–	–	–	–	–	–
Growth on C_1 compounds	–	–	–	–	+	+	+	+	+	+
Formation of Acetoïn (2-Butanone, 3-hydroxy [dl], $CH_3CHOHCOCH_3$)	–	–	+	+	+	+	+	–	+	+
Presence of Urease	+	+	–	–	–	–	–	–	+	+
Growth with Raffinose	–	–	–	–	+	–	–	–	+	–
Growth with Butyrate	–	–	+	–	+	+	+	+	–	+
Gelatine liquification	–	–	+	–	+	+	+	+	–	–

bacteria is observed (Fig. 1b). This isolate was identified as a *Cellulomonas* sp. on the basis of its morphology and substrate utlisation pattern.

3) The two Gram-negative isolates TE 4 and 10 are grouped together because of their inability to grow on methylated amines. Morphologically the strains differ with respect to their flagellar arrangement. Strain TE 4 is motile by several probably peritrichously arranged flagella and is morphologically identical to strain TE 8 (Fig. 1d), whereas strain TE 10 shows one single polar flagellum (Fig. 1e).

4) The four Gram-negative isolates TE 5–8 and the two reference strains *Pseudomonas* sp 27109 and 29600 are capable of growth on methylated amines, hence must be able to synthesize C_3-compounds for biosynthetic purposes via a C_1-assimilation pathway. Morphologically, these bacteria do not differ significantly from strain TE 8 shown in Fig. 1d. All strains are motile by several, probably peritrichous flagella.

5) Although also able to grow on methylated amines, isolate TE 9 differs morphologically considerably from the bacteria in the previous group. This isolate is bean-shaped and motile by one or two lateral flagella (Fig. 1c).

Except for the Gram-positive strain, the data collected so far do not allow classification of the strains isolated and the taxonomic position of the 9 new isolates, as well as the two reference strains, remains obscure. Properties like growth on C_1 compounds, production of acetoïn and non-motility clearly indicate that these strains do not belong to the genus of Pseudomonads.

Presence of NTA-MO in the new isolates

Investigations on cell-free extracts of NTA-grown cells showed that in all strains the initial attack on NTA is catalyzed by a monooxygenase (Tab. 2): the results indicate that NTA-MO is a flavin adenine dinucleotide (FAD)-containing enzyme. Except for *Pseudomonas* sp. 29600, NTA-MO activity was detected only if FAD was included in the assay as published previously [3,5]. This suggests that FAD is bound to NTA-MO only loosely and is easily lost during cell breakage. It further explains why attempts to purify NTA-MO from *Pseudomonas* sp. 29600 were not successful [6]. These authors reported the loss of catalytic activity of NTA-MO during the isolation procedure.

Conclusions and future work

The results show that the ability to utilize NTA is not, as previously thought, restricted to a small group of specialists, but is common to a variety of physiologically and morphologically quite different bacteria.
The uniform presence of NTA-MO and its requirements for NADH, Mn^{2+} and FAD indicates that in all these bacteria the metabolism of NTA does proceed via an identical metabolic pathway.
Future work will be directed to the elucidation of the complete metabolic pathway for NTA, including the transport of NTA into the cell and the purification of key enzymes. Once the relevant enzymes are established their regulation under growth conditions as they occur in nature and wastewater treatment plants, e.g. pulse addition of NTA or the influence of alternative carbon and/or nitrogen sources, will be investigated.
Additionally, the metabolism of NTA in the absence of oxygen will be studied using a recently enriched culture which is able to degrade NTA under denitrifying (anoxic) conditions [7].

Tab. 2
NTA-Monooxygenase activity in cell-free extracts of NTA-grown cells.

Strain	*a)*	*+FAD*
Pseudomonas sp 29600	+	++
Pseudomonas sp. 27109	–	+
Isolates TE 1–10	–	+

a) Enzyme assay according to [6] containing NADH, Mn^{2+}, O_2 and Tris. HCl-buffer.

[1] R.L. Anderson, W.E. Bishop, R.L. Campbell, A Review of the Environmental and Mammalian Toxicology of Nitrilotricetic, Acid, CRC Critical Reviews in Toxicology, *15,* 1 (1985).
[2] NTA. Studie über die aquatische Umweltverträglichkeit von Nitrilotriacetat (NTA). H. Bernhardt *et al.* (eds.). Verlag Hans Richarz, Sankt Augustin (1984).
[3] R.E. Cripps & A.S. Noble, Metabolism of Nitrilotriacetate by a Pseudomonad, Biochemical Journal *136,* 1059 (1973).
[4] D.D. Focht & H.A. Joseph, Bacterial Degradation of Nitrilotriacetic Acid (NTA). Canadian Journal of Microbiology, *17,* 1553 (1971).
[5] M.K. Firestone & J.M. Tiedje, Pathway of Degradation of Nitrilotriacetate by a *Pseudomonas* species, Mechanism of Reaction, Applied and Environmental Microbiology, *35,* 955 (1978).
[6] M.K. Firestone, S.T. Aust, J.M. Tiedje, A Nitrilotriacetic Acid Monooxygenase with Conditional NADH Oxidase Activity, Archives of Biochemistry & Biophysics *190,* 617 (1978).
[7] Th. Egli & H.U. Weilenmann, Biodegradation of Nitrilotriacetic Acid (NTA) in the Absence of Oxygen, Experientia *42,* (1986) (accepted for publication).

The Author

Dr. Thomas Egli studied microbiology and biochemistry at ETHZ. After obtaining his doctorate (Institute of Biotechnology, ETHZ) in 1980, he worked for 1½ years as a Senior Research Fellow in the Microbiological Departement of Sheffield University (U.K.). His special interest is Microbial Physiology. After joining EAWAG in 1982 he has been working on the utilization of substrate mixtures by microbes and the biodegradation of industrial chemicals.

Voltammetric methods for expedient determination of surface complex formation with metal ions

Maria de Lurdes Simões Gonçalves, Laura Sigg, Max Reutlinger and Werner Stumm*

Voltammetric techniques (differential pulse polarography, DPP, anodic stripping voltammetry, ASV, and differential pulse anodic stripping voltammetry, DPASV) are capable of distinguishing – without recourse to filtration or centrifugation – between dissolved and particulate metal concentrations (Pb, Zn, Cu, Cd). Colloids of FeOOH, MnO_2, SiO_2 and of bacteria have no effect on the electrode-kinetic measurement; i. e., metal ions adsorbed or bound to surfaces of colloids or particles are non-labile (low mass transfer to the electrode surface and slow dissociation) [1, 2].
The voltammetric technique is especially useful for the following reasons:

1) No centrifugation or membrane filtration is necessary (phase separations by either technique often give rise to artifacts partially because of incomplete phase separation, effects by charged colloids and by lysis of biological cells).
2) Very small concentrations of metal ions, i. e., concentrations lower than those which can be measured by ion selective electrodes, can be used in these experiments.
3) The electrode-kinetic response can aid in the identification of the species and in many circumstances in the detection of labile or non-labile solute complex formers.

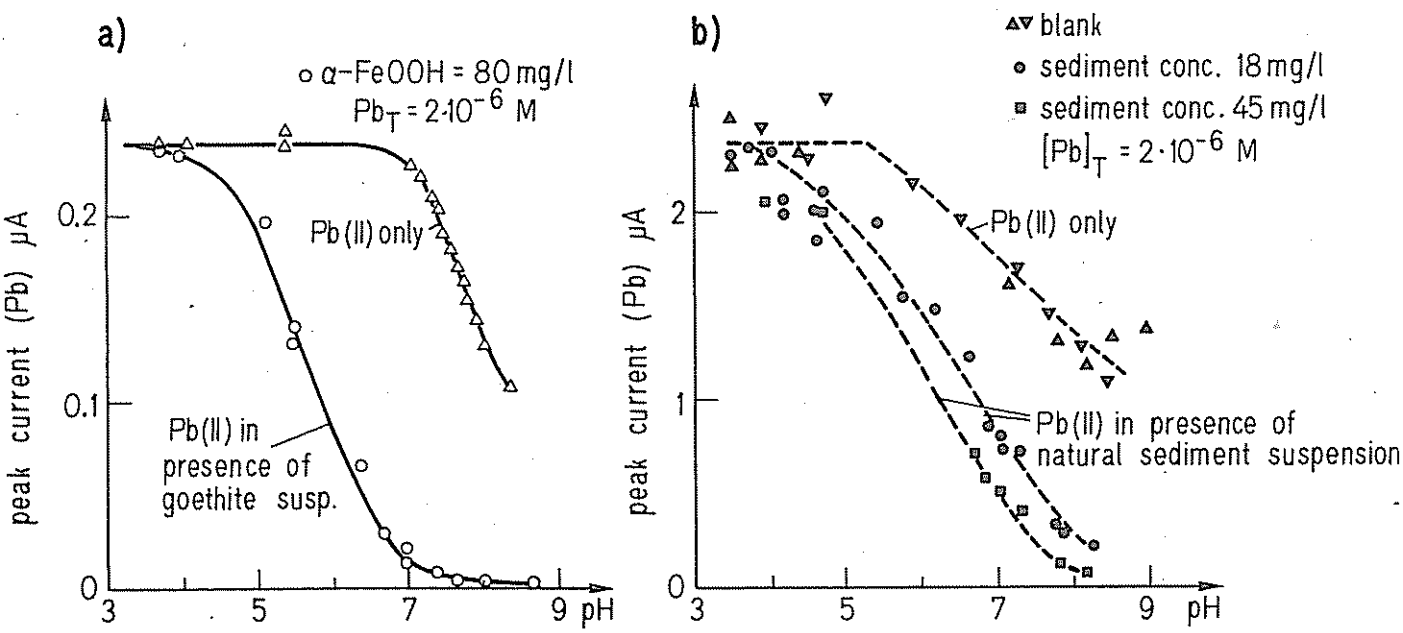


Fig. 1
Pb(II) – adsorption on a goethite suspension (a) and on a natural sediment suspension (b); the residual Pb(II) in solution is given by the voltammetric peak current.

* Centro de Quimica Estrutural, Instituto Superior Tècnico, 1096 Lisboa, Portugal

Voltammetric measurements in the presence of particles

Using voltammetric techniques, the adsorption of Pb(II) on a natural sediment suspension is compared with that on a goethite (α-FeOOH) suspension; a similar pH-dependence of the binding on these different suspensions is observed (Fig. 1).

Fig. 1a shows a representative curve of residual labile Pb(II) as measured by ASV peak current in presence and absence of the model colloid goethite. The binding of Pb(II) to the goethite surface, increasing with increasing pH, is reflected by a decrease in the peak current i_p; in the absence of goethite, adsorption of Pb(II) on the glass wall occurs (as determined by atomic absorption measurements) at higher pH values. This adsorption on the glass wall coincides with the tendency of Pb(II) to form hydroxo complexes (and their polymers) as is evidenced by a shift in the peak potential.

Fig. 1b shows the same kind of measurements of Pb(II) in the presence of partially organic lake sediments. The extent of surface complex formation, and its pH-dependence can be read off these curves.

Voltammetric methods allow in principle a distinction between metal ions in labile species (aquo ions, inorganic complexes etc.), non-labile species (e.g. strong organic complexes, which may be reduced at more negative potentials) and surface-bound metal ions.

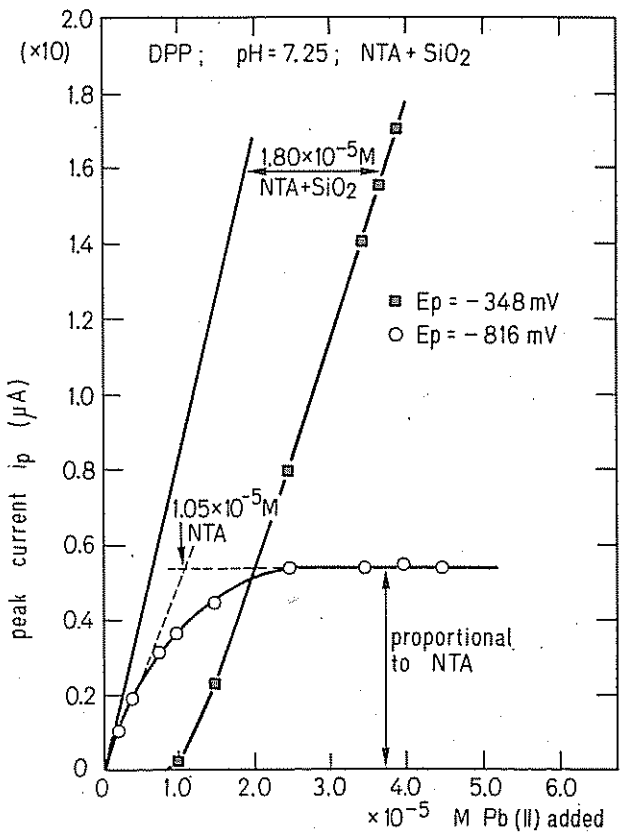


Fig. 2
Addition of Pb(II) to a suspension of SiO_2 in the presence of NTA. (Peak current measured at −348 mV proportional to $[Pb^{2+}]$; at − 816 mV proportional to $[PbNTA^-]$).

Fig. 2 illustrates a titration curve where Pb(II) is added to a suspension of SiO_2 in the presence of nitrilotriacetate (NTA). By measuring the DPP peak currents at different potentials as a function of [Pb(II)] added (at constant pH), it is possible to evaluate both the capacity of the SiO_2 surface, and of NTA respectively, to bind Pb(II).

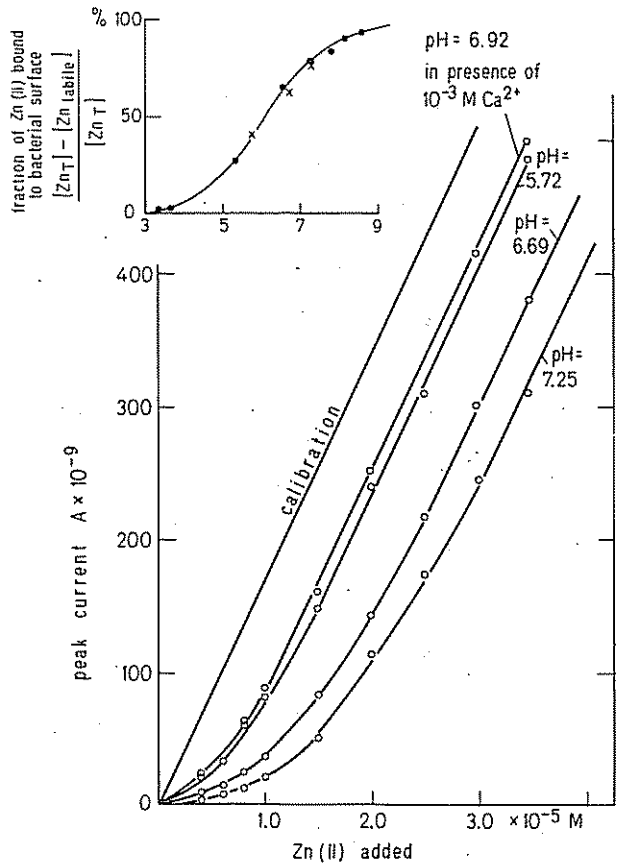


Fig. 3
Titration curves of bacterial cells Klebsiella pneumoniae (washed and treated with formaldehyde; 5.95 mg/l; dry weight) with Zn(II), where peak current (DPP) (proportional to residual labile Zn(II) in solution) is plotted versus [Zn(II)] added at various pH values. The inset illustrates the pH dependence of Zn(II)-binding to bacterial cell surfaces.

Binding of metal ions to bacterial surfaces

The interactions of metal ions with biological surfaces are important for their fate and transport in the aquatic environment. In order to estimate the role of biological surfaces as carriers of metal ions, simple chemical models may describe these interactions. Voltammetric methods were used in order to evaluate the binding of metal ions to bacterial cells [3]. The binding of metal ions to the cell surfaces may be treated as a pH and concentration dependent surface reaction. These experiments show a high affinity of the cell surfaces for the metal ions, especially for Cu(II).

Fig. 3 illustrates the binding of Zn(II) to the surfaces of bacterial cells *(Klebsiella pneumoniae).* With increasing pH, the capacity of the cell surfaces to bind Zn(II) is increased. In the presence of Ca^{2+} (10^{-3} M) less Zn(II) becomes tied up because of competition by the large excess of Ca^{2+}over Zn(II).

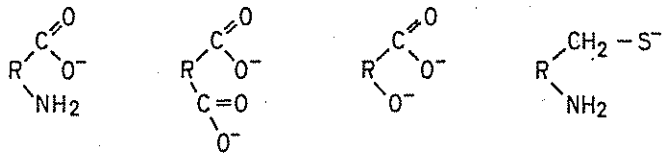
In the same bacterial suspension, Cu(II) forms complexes with the cell surfaces and with exudates released into solution by the microorganisms (Fig. 4).

With increasing pH, Cu(II) becomes better bound to the various functional groups of the cell surface. The extent of binding of Cu(II) by the cell surfaces is reflected by a decrease in peak current (in comparison to a Cu(II) solution in the absence of bacteria). The decrease in peak current, augmenting with increasing pH, is accompanied by a shift,

in the negative direction, of the peak potential. This indicates that soluble complexes are formed in addition to the surface complexes.
The extent of surface binding of metal ions on hydrous oxide surfaces or biological cell surfaces may be generalized by mass law equations, e. g., in case of bacterial surfaces, at pH values of natural waters:

$$\equiv SH^- + Cu^{2+} \rightleftarrows \equiv SCu^+ + H^+ \qquad \overline{K}_{SCu} \qquad (1)$$

where S designates a (deprotonated) bidentate surface chelating site, such as



Its acid-base properties are characterized by

$$\equiv SH_2 \rightleftarrows \equiv SH^- + H^+ \qquad \overline{K}_{a1} \qquad (2)$$

$$\equiv SH^- \rightleftarrows \equiv S^{2-} + H^+ \qquad \overline{K}_{a2} \qquad (3)$$

Different functional groups (e. g. carboxyl, amino, or sulfur groups) exist on bacterial surfaces, which would give different stability constants with metal ions. K_{SCu} of eqn. (1) represents thus an average stability constant of a mixture of surface chelating sites. The values of K_{SCu} measured under different conditions vary with the extent of Cu(II)-binding of the surface, since Cu(II) is tied up first with the surface chelate sites that have the highest affinity and then sequentially with other sites that have a progressively decreasing affinity for Cu(II) [4,5].

Conclusions

Voltammetric techniques allow a direct measurement of metal ions in solution in the presence of particle suspensions. They represent thus useful methods for the evaluation of the interactions of metal ions with different kinds of particles, including inorganic model colloids as well as biological particles and natural sediment particles.

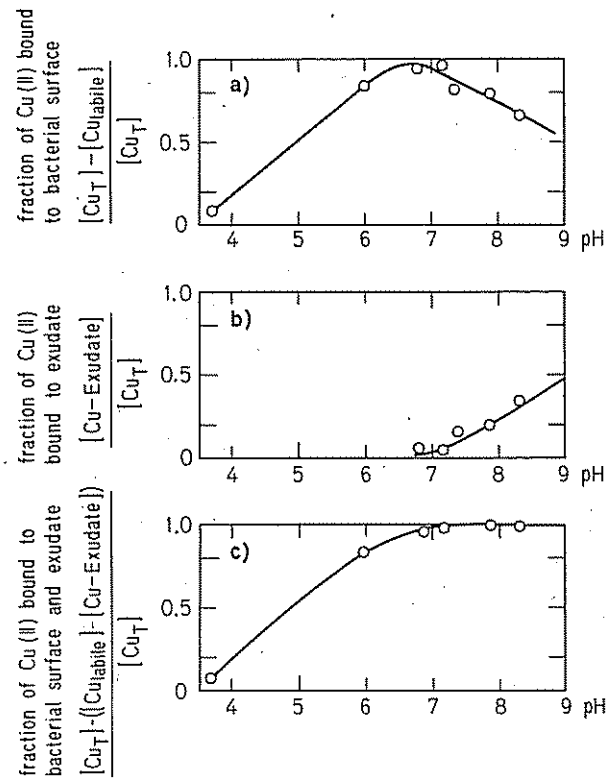
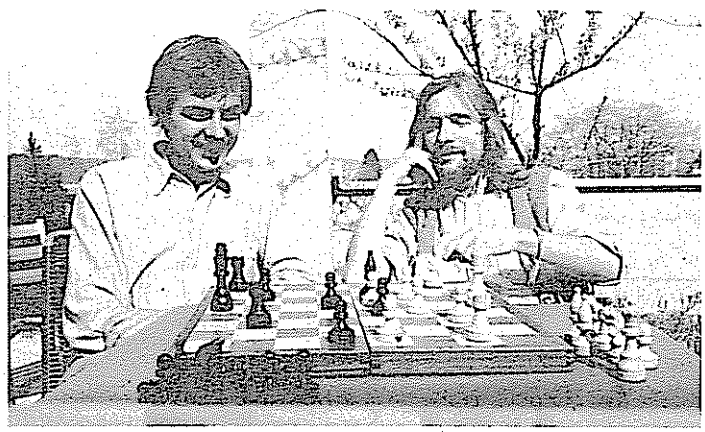


Fig. 4
Interpretation of differential pulse anodic stripping voltammetry (DPASV) measurements of Cu(II) in the presence of bacterial cells ($[Cu(II)_T] = 10^{-7}$ M, 5.95 mg cells/l; dry weight; cells washed and treated with formaldehyde). Cu(II) bound to the cell surface is determined from the decrease of Cu(II) in solution (proportional to the peak current) (Fig. 4a). The extent of Cu(II) binding to the dissolved exudate is obtained from the shift in peak potential (Fig. 4b). Fig. 4c gives the sum of Cu(II) bound to the cell surface and to the exudate.

[1] Plavsić, M., Kozar, S., Krznaric, D., Bilinsky, H. and Branica, M., Mar. Chem. *9*, 175, 1980
[2] Simões Gonçalves, M.L., Sigg, L. and Stumm, W., Env. Sci. Techn. *19*, 141, 1985
[3] Simões Gonçalves, M.L., Sigg, L., Reutlinger, M. and Stumm, W., Sci Tot. Env., 1986
[4] Buffle J., in «Aquatic Surface Chemistry», Stumm W., Ed., (1987), in press.
[5] Gamble, D.S., Underdown, A.W., and Langford, C.H., Anal. Chem., *52*, 1901, 1980

The Chessboard – A Model for Two-Dimensional Distributions of Interface Species

Bernhard Wehrli, Erich Wieland



1. Surface controlled geochemical reactions

Important geochemical processes like dissolution and nucleation are driven by surface controlled chemical reactions at the solid-aqueous interface. In most cases the change in the coordination sphere of dissolving or precipitating ions and not the transport processes involved determine the reaction rate. Recent kinetic studies on oxide dissolution [1], heterogeneous nucleation [2] and oxidation of adsorbed Mn(II) [3] were interpreted using rate laws solely dependent on surface concentration parameters. Furrer and Stumm [1] have suggested that the acid promoted dissolution of oxides is controlled by the formation of an active metal site with 2 or 3 nearest neighbor protons. As it happens very often in kinetics, the reac-

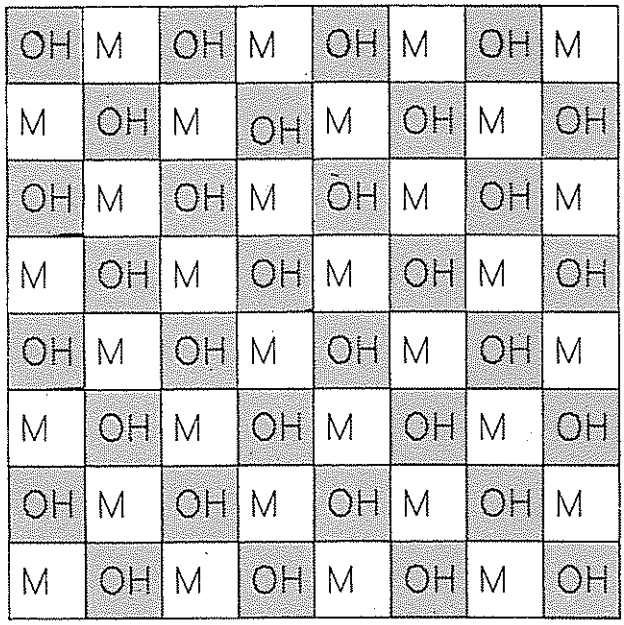


Fig. 1a
The chessboard model of an oxide surface establishes simple nearest neighbor relations between metal sites M and surface OH groups.

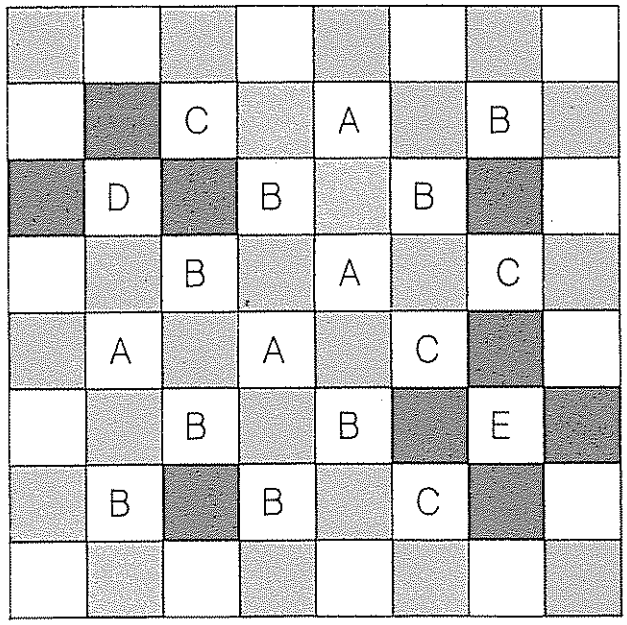


Fig. 1b
Types of metal centers. Within a binary mixture of protonated (black) and uncharged (hatched) OH-groups five types of metal centers (A,B,C,D,E) exist according to the number of nearest neighbor protons (0,1,2,3,4).

tive intermediates are not accessible to direct analytical determination. Here we propose a very simple geometrical model to estimate the surface concentration of such rate determining species.

2. The Chessboard Model

To make the two-dimensional distribution of surface protons a tractable problem of lattice statistics we arrange the surface hydroxyl groups and metal sites of an oxide in a chessboard geometry (Fig. 1). Let the metal centres be placed on the «white» chessboard fields and the hydroxyl groups on the «black» squares. If the hydroxyl species are allowed to be protonated or uncharged, then we may distinguish five different types of metal sites (A,B,C,D,E) according to the number n of nearest neighbor excess protons (n = 0,1,2,3,4). The fraction of protonated OH groups is defined by

$$\Theta_H = c_H^s / S \qquad 1$$

with c_H^s and S as the surface proton concentration and the total concentration of surface sites in moles · m^{-2}, respectively. If we assume that the protons are randomly distributed among the hydroxyl groups («random mixing condition», [4]) then the fractions Θ_i (i = A,B,C,D,E) of metal sites can be derived from probability theory: the probability of finding a specific OH group in the protonated or uncharged state is Θ_H or $(1-\Theta_H)$, respectively. Therefore the fraction Θ_i of metal sites surrounded by n protons and (4-n) uncharged OH group is

$$\Theta_i = \frac{4!}{n!\,(4-n)!} \cdot \Theta_H^n \cdot (1-\Theta_H)^{(4-n)} \qquad 2$$

This equation is in agreement with a simple Monte-Carlo [7] simulation of the chessboard model (Fig. 2). For low proton coverage ($\Theta_H \leqq 0.15$) and $n \geqq 2$ we may use the approximation

$$\Theta_i \approx \binom{4}{n} \cdot \Theta_H^n \qquad 3$$

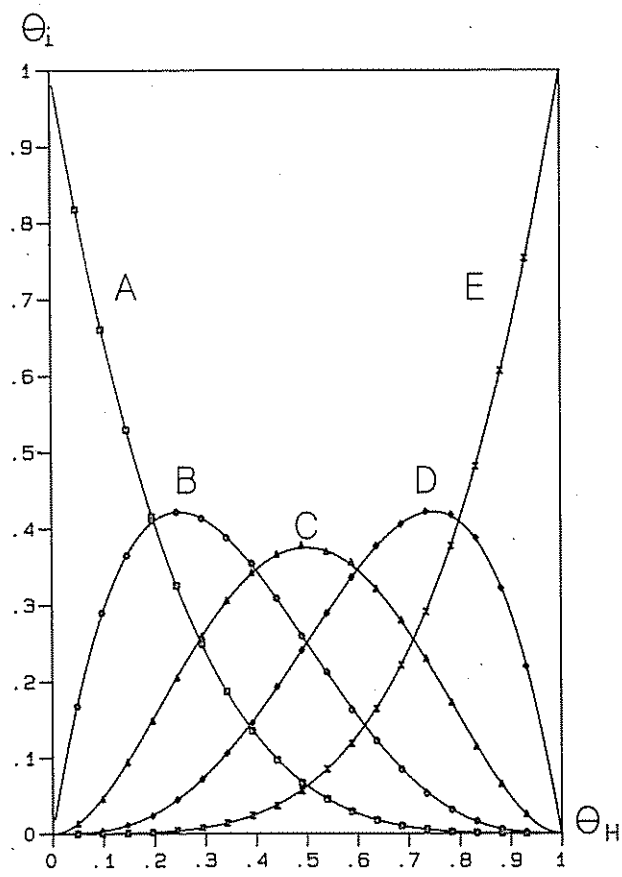


Fig. 2
Distribution of the five different metal sites as a function of surface protonation Θ_H. Lines: Calculated, using Eq. 2. Dots: Results of Monte-Carlo simulations.

Electrostatic interactions will modify the two-dimensional distribution toward lower configurational entropy. An assessment of this effect by a pairwise interaction model («quasi-chemical approximation» [4]) showed that the relative fractions of species C,D and E are shifted to lower values, but the qualitative behavior of the model remains unchanged.

3. Application to the dissolution of oxides

The dissolution of δ-Al_2O_3 [1] follows the rate law:

$$R_H = k_{exp} \left(c_H^s\right)^3 \quad 4$$

with R_H as the acid promoted dissolution rate. This rate law suggests that sites of type D (Fig. 1b) act as precursors of the rate-limiting step. With the basic assumption that an equilibrium between precursors and critically activated «dissolving» sites exists we may apply the transition state theory [5]:

$$R_H = f \cdot K^{\neq} \cdot c_D \quad 5$$

f: decay frequency of an activated site (=kT/h), [s^{-1}]
$f = 6 \cdot 10^{12}\ s^{-1}$ at T = 300° K
c_D: surface concentration of precursor D, [moles · m^{-2}]
$K^{\neq}$: constant for the equilibrium between precursor and critically activated site, [—]

The equation holds in this form for activity coefficients close to unity.
In principle the constant $K^{\neq}$ may be estimated from experimental data from the Gibbs free energy of activation, $\Delta G^{\neq}$:

$$\ln K^{\neq} = -\Delta G^{\neq}/RT \quad 6$$

Unfortunately the activation energy for the dissolution of δ-Al_2O_3 has not been measured, therefore we confine ourselves to a qualitative treatment. For an oxide with the mole fraction x_A of active sites (step-, kink-, edge-sites) the chessboard model predicts the following surface concentration of the precursor D:

$$c_D = x_A \cdot c_D^s = x_A \cdot 4 \cdot S \cdot \Theta_H^3 \quad 7$$

Here we have applied the low proton density approximation (Eq. 3). The surface protonation of δ-Al_2O_3 does not exceed a maximum value of $\Theta_H = 0.15$. Combining Eq. 1, 5 and 7 we arrive to:

$$R_H = 4 \cdot f \cdot K^{\neq} \cdot x_A \cdot S^{-2} \cdot \left(c_H^s\right)^3 \quad 8$$

Treating the product $K^{\neq} \cdot x_A$ as an adjustable parameter yields a perfect fit to experimental dissolution rates (Fig. 3).

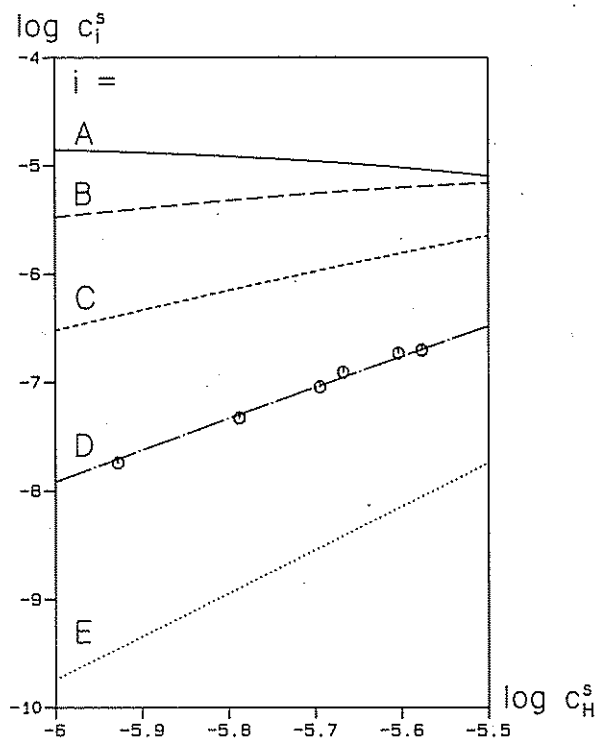


Fig. 3
Chessboard model applied to the dissolution of δ-Al_2O_3. Lines calculated with Eq. 2. The concentration of the total surface sites is $S = 1.77 \cdot 10^{-5}$ moles · m^{-2}. Dots: Concentrations of sites D derived from experimental dissolution rates [1] using Eq. 8. The adjustable parameter $K^{\neq} \cdot x_A$ takes a value of $9 \cdot 10^{-15}$.

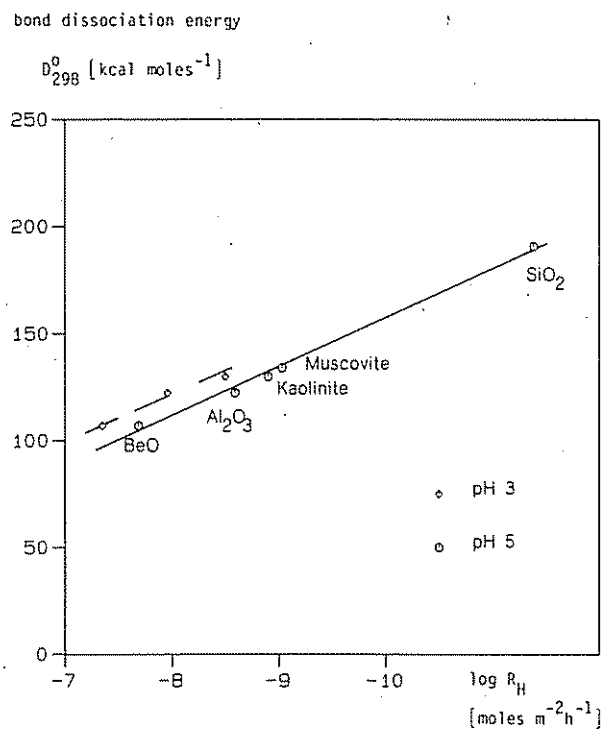


Fig. 4
Proton promoted dissolution rates R_H for various oxides and silicates vs. the bond strength, D^0_{298}, of diatomic molecules.

4. Discussion

In order to apply the «chessboard model» to the wide variety of mineral surfaces we need to be aware of the model's basic assumptions and the possible extensions.
a) Our model describes a truly two-dimensional ensemble of uniform sites. Real-world oxide surfaces however are not strictly two-dimensional. There is a general agreement, that the dissolution proceeds chiefly at step-, kink-, and edge-sites. Recent research presents evidence that the number of these active sites may be related to the fractal dimension of a surface [6]. If the mole fraction x_A of active sites to total sites is determinable we may easily include this parameter in a lattice statistical description, since x_A represents the general probability of a site to be found in an active conformation. A similar approach is possible in the case of layer silicates like kaolinite. Here the dissolution process occurs at distinguished faces of a crystal and consequently the model parameters S, Θ_H etc. have to be evaluated relative to these reactive faces.

b) The power n in Eq. 2 or 3, respectively, is equivalent to the number of nearest protons in the conformation of a precursor. In the case of δ-Al_2O_3 the dissolution rate is proportional to $(c_H^s)^3$ (Eq. 4) and in the case of BeO it is proportional to $(c_H^s)^2$ [1]; this corresponds to a mechanism in which sites of type D (3 neighboring protons) or sites of type C (2 neighboring protons) act as precursors

of the activated complex. With the objective to extend our understanding of dissolution processes to other oxides and silicates it is of further interest to know whether or not the number of protons promoting the rate limiting step is influenced by factors such as the valency of the metal centre, the structure of the crystal lattice or the bond energy.

c) Another limit to a merely statistical treatment of dissolution processes is set by the fact that in dissimilar minerals different chemical bonds are broken in the rate limiting step. Among oxides with similar surface charge properties and a corresponding dissolution mechanism one should observe a correlation between bond energy and reaction rate (Fig. 4).

Outlook

The simple geometry of the «chessboard model» allows a straightforward application of the well developed methods of lattice statistics. It offers a possibility to treat different surface controlled processes such as dissolution or reactions between adsorbed species within the same concept.

We hope that the improved understanding of the «molecular steps» in geochemical dissolution processes will help in the research of such important fields as the acidification of soils and the increase in weathering rates through acid deposition.

[1] Furrer, G., Stumm, W., «The role of surface coordination in the dissolution of δ-Al_2O_3 in dilute acids», Chimia *37*, 383 (1983)

[2] Swoboda-Colberg, N.G., «The role of specific adsorption in heterogeous nucleation», Ext. Abstr. Nat. Meet. Amer. Chem. Soc. *25* (2), 337 (1985)

[3] Davies, S.H.R., «Mn(II) oxidation in the presence of metal oxides», PhD. Thesis Cal. Tech. (1985)

[4] Hill, T.L., «Introduction to Statistical Thermodynamics», Addison Wesley (1960), (387, 252)

[5] Lasaga, A.C., in «Kinetics of Geochemical Processes» (eds. A.C. Lasaga and R.S. Kirkpatrick), Mineral. Soc. Amer. Rev. in Mineralogy *8*, 135 (1981).

[6] Avnir, D., Farin, D., Pfeifer, P., «Surface geometric irregularity of particulate materials: The fractal approach», J. Coll. Interf. Sci. *103*, 112 (1985)

[7] Schmitz, N., Lehmann, F., «Monte-Carlo-Methoden», Meisenheim (1976)

News about EAWAG Collaborators

Professor Karl Wuhrmann †

Dr Karl Wuhrmann, emeritus Professor for Microbiology at the Swiss Federal Institute of Technology (ETH) in Zurich and former Head of the Biology Department of the Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG) in Duebendorf, died on 16 September 1985 at the age of 73. Only his intimate friends knew of his severe heart condition to which he so suddenly and unexpectedly succumbed.

Professor Wuhrmann was an acknowledged specialist and scientist in the field of applied microbiology and aquatic ecology. He is the author of several fundamental studies on the application of the activated sludge process in the treatment of wastewaters. His biochemically derived method for the investigation of microbiological processes contrasted markedly with other mostly descriptive publications. He studied the effect of eutrophication on the biocenosis of flowing waters and vigorously supported the development of improved analytic methods for water quality determination. His artificial channels at Tüfenwies experimental station of EAWAG which simulated self-purifying processes in flowing waters were well-known and remained for a long time a rather unique experimental installation.

Professor Wuhrmann attached great importance to phosphate precipitation as supplementary wastewater treatment process. However, he also knew very well that it was not the final answer to the wastewater problem. He was concerned about the increase in abiotic chemical compounds in wastewater and their still unknown effects on ecology.

His studies on the toxic effects of ammonia and cyanide on freshwater fish were not only of great scientific interest but contributed to the revision of the Federal Law on Fisheries in 1973.

Karl Wuhrmann was a very critical specialist. Anybody who consulted him on research matters had to be well informed. This is precisely why his independent opinion was sought after by many fellow-colleagues. His quest for answers was sustained by the idea of finding the best possible solution for humanity. He was thereby not afraid to offend his interlocuters.

His death is a great loss not only to water scientists but to all branches of environmental protection.

Peter Perret

Alfons Zehnder †

Dr Alfons Zehnder died unexpectedly in November 1985 at the age of 65. Many years ago, he interrupted his teaching activities at the Teachers' Traning College in Wettingen regularly once a week to dedicate himself to the cultivation of the EAWAG's algal collection. He specialised in the isolation and cultivation of blue-green algae (Cyanophyta). As president of the International Association for Cyanophyte Research, he dealt with professional colleagues from all over the world, and was also in charge of organizing the symposium which had been initiated by Professor Jaag in 1960. The last one was held 2 years ago at the Lake Research Laboratory in Kastanienbaum on Lake Lucerne and at the EAWAG in Duebendorf.

Alfons Zehnder was a reserved person of a hidden versatility. In the course of his research, he spent several years working in Canada, Cameroon, Nepal, and India where he gained insight into the essence of human existence in an endangered environment. His talent as a natural scientist in the microscopic field to make and describe new discoveries on one hand, and his quest for ecological correlations on the other, stimulated several of his students to view nature and the environment with an open mind.

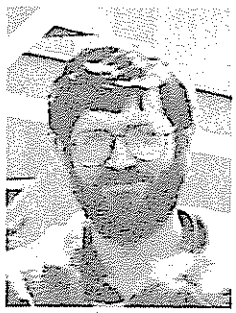
To his colleagues at the EAWAG, particularly at the hydrobiological/limnological department he was like a father. Unfortunately, although relieved from his teaching activities, fate did not grant him the pleasure of continuing his studies of the blue-green algae during retirement. We

thank Alfons Zehnder for his dedicated work and his valuable cooperation.

Peter Perret

Awards

In 1985, the American Chemical Society initiated a program of **Graduate Student Awards** in order to recognize outstanding graduate students in the field of environmental Chemistry.
Marijan Ahel of the Center for Marine Research in Zagreb, Yugoslavia, is one of the 22 graduate students who won an award in 1985. He has been a guest graduate student at EAWAG several times and a participant of the collaboration program between EAWAG and the «Rudjer Bošković« Institute, Yugoslavia. The topic of his doctoral dissertation is the fate of alkylphenol polyethoxylate surfactants in wastewater treatment and in natural waters.



The **Otto Jaag Prize 1985** for the most outstanding thesis in the field of water resources and water pollution control has been awarded to *Hansruedi Siegrist* for his thesis entitled «Mass Transfer Processes in a Nitrifying Biofilm». His thesis deals with the characterization of the properties of fixed biofilms and the interrelationship of transport mechanisms and microbiological processes. His findings will facilitate the understanding of biofilms in natural water systems and in waste-water treatment plants.

The **Albert Einstein World Award of Science** has been awarded by the World Cultural Council to the scientist *Professor WernerStumm* for his merits in environmental interdisciplinary research.
The prize was handed over in Stockholm in November 1985, where Prof. Stumm took the occasion to talk about «Man and the Hydrogeochemical Cycles; an Ecological Perspective».

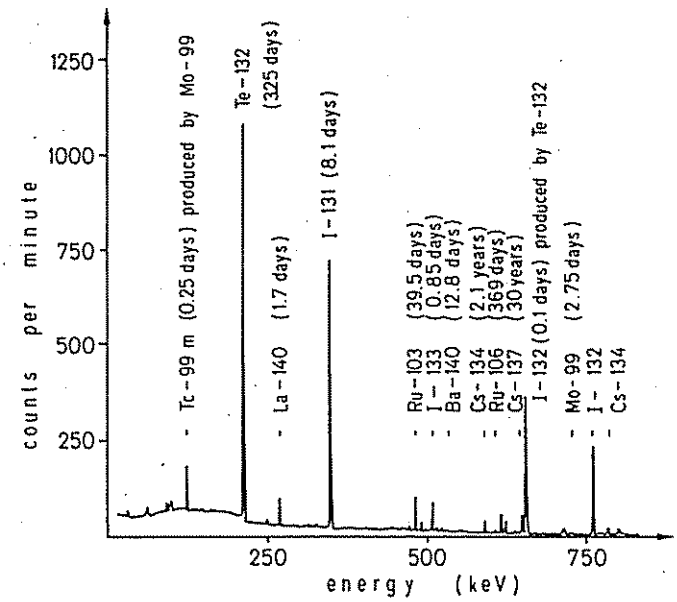
The **John and Alice Tyler Prize** of $ 150 000 has been awarded in equal parts to the Swiss aquatic chemist *Prof. Dr Werner Stumm* and to the Swiss-born scientist *Prof. Dr Richard Vollenweider.*
The award was presented in Los Angeles on 17 May 1986. The prize honors scientists or institutions for their outstanding scientific accomplishments in the field of enviromental protection and preservation of our biosphere.
The award is a recognition of Prof. Stumm's chemical and ecological contributions in the field of aquatic systems and for his future-oriented commitment to the conservation of a balanced environment.

The prizes awarded to Prof. Stumm are not only a tribute to the fundamental ecological work carried out at the Federal Institute of Technology and at the EAWAG, but also an encouragement particularly to multidisciplinary and ecologically-oriented water pollution control research in Switzerland.

Dr Laura Sigg has been **promoted to Privatdocent*** for Chemical Limnology at the Federal Institute of Technology (ETHZ, Dept. Natural Sciences). The title of her habilitation thesis is: «Chemical Interactions and Transport Mechanisms of Metals in Lakes». Laura Sigg joined the Chemistry Department of EAWAG in 1980 and became head of the Analytical Section in 1981.

The course on **«Hydraulics and Pollution of Ground Water»** was again held at the ETH Hönggerberg from March 3rd to 7th, 1986. The lecturers were Prof. T. Dracos, Prof. W. Stumm, Dr. R. Schwarzenbach (ETH) and Prof. J. Cherry (Canada).

As with many other laboratories in Europe, EAWAG's Isotope Geochemistry and Radiology section has been heaviliy involved in measuring radionuclides from the **radioactive fallout** of Chernobyl's burning reactor.
Samples taken and analysed included air, rain, surface waters, ground waters, grass, vegetables, milk, soil, etc. Transfer factors from the chains air → rain → grass → milk and air → rain → vegetables were determined. Of concern were both the relatively high concentrations of various short-lived radionuclides (see graph below) and the longer-lived radionuclides of Cesium (Cs) and Strontium (Sr). The inventory of ^{137}Cs in Duebendorf due to the Chernobyl fallout was as high as 70% of the levels measured during atomic testing in the 1950's and 1960's.
Concentrations were such that the Swiss government recommended that children under 2 years of age and pregnant women refrain from drinking milk and eating salads and vegetables grown in open fields during the first few weeks after the incident.
Apart from the tragedy for the people involved in the accident this incident again demonstrates that technology can create global scale experiments with impacts far from the source. It further points to the need for an ecological view of the close linkage between air, water, soil and biota reservoirs in any accident scenario.



Gamma spectrum of a rainwater sample in Duebendorf on the fifth day after the accident (1. 5. 86) showing a great number of radionuclides (in brackets: their half-lives).

Since summer 1985, the EAWAG was honored by the visit of the following **guest scientists:**

Ahel Marijan, Dipl. Chem., Rudjer Bošković Inst., Zagreb, Y, (Aug.–Oct. 85).

Bryers James, Dr Ing. Chem., Duke University, Durham N.C., USA (Aug. 85)

Capri Silvio, Dipl. Chem.-Ing., Ist di Ricerca Sulle Acque, Roma, I, (Jan.–June 86)

Cošović Bozena, Dr. Chem. Ing., Chief Lab. Physicochem. Separations, Rudjer Bošković Inst., Center for Marine Res., Zagreb, Y, (Oct–Dec. 85)

Christensen Erik, Assoc. Prof. of Civil Eng., Univ. of Wisconsin, Milwaukee, USA, (June–Aug. 86)

Czuczwa Jean, Dr Analyt. Chem., Indiana University, Bloomington, USA (Jan. 85 – May 86)

Devol Allan, Prof., University of Washington, Seattle, USA (Nov. 85)

Gonçalves Maria de Lourdes, Prof., Centro de Quimica Estrutural, Instituto Superior Tecnico, Lisboa, Portugal (July–Aug. 85)

Johnson Carola Annette, PhD, Chemist, Imperial College, Geology Dep., London (Febr. 84 – March 86)

McKenzie Judith, PhD, Geologist, University of Floridy, Gainesville, USA (May–Aug. 85)

Marcomini Antonio, Dr Chem., Dipt. di Scienze Ambientali, Università di Venezia, Venezia, Italy (since June 85)

Masten Susan, Dipl. Ing., Harvard University, Cambridge, Mass., USA (Jan. 85–Apr. 86)

Morgan James, Prof for Environm. Eng. Sci., Cal. Inst. Technol., Pasadena, LA, USA (July–Aug. 85)

O'Melia Charles, Prof. Dept. of Geogr. and Env. Eng., John Hopkins Univ., Baltimore, Maryland, USA (July–Aug. 85)

Pytkowicz Richard, Prof., Oregon State Univ., OR, USA, (Jan.–March 86)

Schnoor Jerald, Prof., Dept. of Civil & Environmental Eng., Univ. of Iowa, Iowa City, USA (May–June 86)

Sharefkin Mark, Dr, Lawrence Berkeley Lab., USA (June–Aug. 85)

Shuval Hillel, Prof., Dir., Environmental Health Lab., Hebrew University, Jerusalem, Israel (July 85)

Stephanou Euripides, Prof. for Env. Chem., University of Kreta, Heraklion, Greece (July–Aug. 85)

Yu Jun Qing, Geologist, Qing Hai Salt Lake Research Institute, Academia Sinica, Xinhing, China (Sept. 85 – 86)

Xue Hanbin, Inst. of Environm. Chemistry, Academia Sinica, Beijing, China (since March 86)

Fourth International Conference on Urban Storm Drainage (4ICUD)

The Fourth International Conference on Urban Storm Drainage will be held at Lausanne, in the Ecole Polytechnique Fédérale (Switzerland), concurrently with the XXIIth Congress of the International Association for Hydraulic Research, from August 31th to September 4th, 1987. Together with some seminars on timely themes, the following sessions have been proposed for presentation of contributions: topics in

1) Urban Drainage Hydraulics and Hydrology
2) Urban Storm Water Quality
3) Planning and Management.

In order to obtain more information (second announcement) please write to: Dr W. Gujer, «4IUCD», EAWAG, CH-8600 Duebendorf, Switzerland, or mark the respective box on page 16.

EAWAG-Publications:

Reprints may be obtained by writing to: EAWAG, Library, CH-8600 Duebendorf

1054
Leuenberger, C., Giger, W., Coney, R., Graydon, J. W., Molnar-Kubica, Eva: Persistent Chemicals in Pulp Mill Effluents – Occurrence and Behaviour in an Activated Sludge Treatment Plant. Water Res. *19,* 885–894 (1985).

1055
Schwarzenbach, R. P., Giger, W., Schaffner, C., Wanner, O.: Groundwater Contamination by Volatile Halogenated Alkanes: Abiotic Formation of Volatile Sulfur Compounds under Anaerobic Conditions. Env. Sci. Technol. *19,* 322–327 (1985).

1056
Gächter, R., Mares, A.: Does Settling Seston Release Soluble Reactive Phosphorus in the Hypolimnion of Lakes? Limnol. Oceanogr. *30* (2), 364–371 (1985).

1057
Hamer, G.: Lysis and «Cryptic» Growth in Wastewater and Sludge Treatment Processes. Acta Biotechnol. *5,* 117–127 (1985).

1058
Neftel, A., Beer, J., Oeschger, H., Zürcher, F., Finkel, R. C.: Sulphate and Nitrate Concentrations in Snow from South Greenland 1895–1978. Nature *314,* No. 6012, 611–613, 18. April 1985.

1059
Schwarzenbach, R. P., Giger, W.: Behavior and Fate of Halogenated Hydrocarbons in Ground Water. In: «Ground Water Quality» (C. H. Ward, W. Giger, P. L. McCarthy, Eds.). J. Wiley & Sons, Inc., New York 1985, pp. 446–471.

1060
Zinder, Bettina: Phosphatrücklösung aus Sedimenten als Folge der Reduktion von Eisenoxiden. Diss. ETHZ Nr. 7738, Zürich 1985.

1061
Stumm, W.: Deposition of Atmospheric and Metal Pollutants and Their Impact on the Freshwater Environment: Case Studies in Switzerland. In: «Environmental Inorganic Chemistry», K.J. Irgolic & A.E. Martell (Eds.). VCH Publ. Inc., Deerfield Beach, Florida, USA 1985, pp. 401–417.

1062
Ahel, M., Giger, W.: Identifikacija specifičnih organskih zagadivala u rijeci Savi kromatografskim metodama visokog razlučivanja i spektrometrijom masa opremljenom računalom. Kem. Ind. *34,* (5), 295–309 (1985).

1063
Hoigné, J., Bader, H., Haag, W.R., Staehelin, J.: Rate Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water – III: Inorganic Compounds and Radicals. Water Res. *19,* (8), 993–1004 (1985).

1064
Stöckli, A.: The Role of Bacteria and Algae in Phosphorus Regeneration Using Linked Continuous Cultures. Verh. Int. Verein. Limnol. *22,* 2773–2779 (1985).

1065
Stumm, W.: Interpretation and Measurement of Redox Intensity in Natural Waters. A. Comment to T. Frevert's Paper «Can the Redox Conditions in Natural Waters be Predicted by a Single Parameter?» Schweiz. Z. Hydrol. *46/2,* 291–296 (1984).

1066
Bürgi, H.R., Egli, Beatrix: Crustaceen-Plankton des Vierwaldstättersees. Grössenfraktionierung und Abundanzdynamik in den Jahren 1976 bis 1979. Schweiz. Z. Hydrol. *46/2,* 247–268 (1984).

1067
Motschi, H.: Cu(II) EPR: a Complementary Method for the Thermodynamic Description of Surface Complexation. Adsorption Sci. & Technol. *2,* 39–45 (1985).

1068
Hamer, G.: The Impact of Government Legislation on Industrial Effluent Treatment. Conservation & Recycling *8,* No. 1/2, 25–43 (1985).

1069
Bryers, J.D., Berger, J., Hamer, G.: Interpretation of Thermophilic Anaerobic Digestion Experiments Using a Dynamic Structured Model. Conservation & Recycling *8,* No. 1/2, 251–266 (1985).

1070
Hamer, G., Bryers, J.D.: Aerobic Thermophilic Sludge Treatment. Some Biotechnological Concepts. Conservation & Recycling *8*, No. 1/2, 267–284 (1985).

1071
Bryers, J.D.: Structured Modeling of the Anaerobic Digestion of Biomass Particulates. Biotechnol. & Bioengng. *27*, 638–649 (1985).

1072
Ahel, Marijan, Giger, W.: Determination of Alkylphenols and Alkylphenol Mono- and Diethoxylates in Environmental Samples by High-Performance Liquid Chromatography. Anal. Chem. *57*, 1577–1583 (1985). (Vgl. auch Publ. Nr. 1097)

1073
Davis, Joan S., Fahrni, H.-P., Liechti, P., Spreafico, M., Stadler, K., Zobrist, J.: Das nationale Programm für die analytische Daueruntersuchung der schweizerischen Fliessgewässer – eine Standortbestimmung. Gas-Wasser-Abwasser *65*, 123–135 (1985).

1074
Boller, M., Böni, H.: Versickerung von Dachwasser. Gas-Wasser-Abwasser *65*, 393–402 (1985).

1075
Baccini, P., Brunner, P.H.: Behandlung und Endlagerung von Reststoffen aus Kehrichtverbrennungsanlagen. Gas-Wasser-Abwasser *65*, 403–409 (1985).

1076
Imboden, D.M., Schwarzenbach, R.P.: Spatial and Temporal Distribution of Chemical Substances in Lakes: Modeling Concepts. In: «Chemical Processes in Lakes», ed. by W. Stumm. J. Wiley & Sons, New York 1985, pp. 1–30.

1077
Baccini, P.: Phosphate Interactions at the Sediment-Water Interface. In: «Chemical Processes in Lakes», ed. by W. Stumm. J. Wiley & Sons, New York 1985, pp. 189–205.

1078
Sigg, Laura: Metal Transfer Mechanisms in Lakes; the Role of Settling Particles. In «Chemical Processes in Lakes», ed. by W. Stumm, J. Wiley & Sons, New York 1985, pp. 283–310.

1079
Schnoor, J.L., Stumm, W.: Acidification of Aquatic and Terrestrial Systems. In: «Chemical Processes in Lakes», ed. by W. Stumm, J. Wiley & Sons, New York 1985, pp. 311–338.

1080
Gächter, R., Imboden, D.M.: Lake Restoration. In: «Chemical Processes in Lakes», ed. By W. Stumm. John Wiley & Sons New York 1985, pp. 365–388.

1081
Santschi, P.H.: The MERL Mesocosm Approach for Studying Sediment-Water Interactions and Ecotoxicology. Env. Technol. Let. *6*, 335–350 (1985).

1082
Karl, D.M., Bossard, P.: Measurement and Significance of ATP and Adenine Nucleotide Pool Turnover in Microbial Cells and Environmental Samples. J. Microbiol. Meth. *3*, 125–139 (1985).

1083
Gräzer-Lampart, Suzanne Dorothea: Chemostatstudie über die Regulation der ammoniumassimilierenden Enzyme in Hyphomicrobium ZV 620. Diss. ETHZ Nr. 7790, Zürich 1985.

1084
Sollfrank, U., Gujer, W.: Kontinuierliche Messung der Respiration im Belebungsverfahren. Das Gas-und Wasserfach *126*, 397–406 (1985).

1085
Zürcher, F.: Ausblasbare Organohalogen-Verbindungen – POX, eine bewährte Messmethode zur Beurteilung der Wasserqualität. Vortrag «Haus der Technik», Essen, 21. Febr. 1985, 20 S.

1086
Frutiger, A.: The Production Quotient PQ: A New Approach for Quality Determination of Slightly to Moderately Polluted Running Waters. Arch. Hydrobiol. *104*, 513–526 (1985).

1087
Frutiger, A.: A Versatile Flow Channel for Laboratory Experiments with Running Water Macroinvertebrates. Schweiz. Z. Hydrol. *46*/2, 301–305 (1984).

1088
Frutiger, A.: Gefährdete Mikrofauna der Fliessgewässer – Limnologische Aspekte des Gewässerschutzes. Neue Zürcher Ztg. Beil. «Forschung & Technik», Nr. 169, 24. Juli 1985, S. 41.

1089
Hamer, G.: Chemical Engineering and Biotechnology. In: «Biotechnology – Principles and Applications», I.J. Higgins, D.J. Best, J. Jones (Eds.). Blackwell Scientific Publ. Ltd. London 1985, pp. 346–414.

1090
Furrer, G.: Die oberflächenkontrollierte Auflösung von Metalloxiden: Ein koordinationschemischer Ansatz zur Verwitterungskinetik. Diss. ETHZ Nr. 7737, Zürich 1985.

1091
McEvoy, J., Giger, W.: Accumulation of Linear Alkylbenzenesulphate Surfactants in Sewage Sludges. Naturwiss. *72*, 429–431 (1985).

1092
Giger, W., Conrad, T.: Phosphatersatzstoffe in Waschmitteln und ihre aquatische Umweltverträglichkeit. In: «Wasser Berlin '85». Wissenschaftsverlag Spiess, Berlin 1985, S. 362–377.

1093
Uehlinger, U.: An in situ Pulse Light Fluorometer for Chlorophyll Determination as a Monitor for Vertical and Horizontal Phytoplankton Distribution in Lakes. J. Plankton Res. *7*, 605–615 (1985).

1094
Zinder, Bettina, Stumm, W.: Die Auflösung von Eisen(III)-oxiden; ihre Bedeutung im See und im Boden. Chimia *39*, 280–288 (1985).

1095
Siegrist, H., Gujer W.: Mass Transfer Mechanisms in a Heterotrophic Biofilm. Water Res. *19*, 1369–1378 (1985).

1096
Haag, W.H., Hoigné, J.: Degradation of Compounds in Water by Singlet Oxygen. In: «Water Chlorination – Chemistry, Environmental Impact and Health Effects», Vol. 5 (R.L. Jolley et al.). Lewis Publ. Inc., Chelsea, Mich. 1985, Chapter 79, pp. 1011–1020.

1097
Ahel, Marijan, Giger, W.: Determination of Nonionic Surfactants of the Alkylphenol Polyethoxylate Type by High-Performance Liquid Chromatography. Anal. Chem. *57*, 2584–2590 (1985).

1098
Hamer, G.: The Adequacy and Effectiveness of Government Regulations for Aqueous Industrial Effluents. In: «Biotechnology and Bioprocess Engineering», T.K. Ghose, Ed. Indian Inst. of Technology 1985, pp. 573–586.

1099
Erten, H.N., Von Gunten, H.R., Rössler, E., Sturm, M.: Dating of Sediments from Lake Zurich (Switzerland) with ^{210}Pb and ^{137}Cs. Schweiz. Z. Hydrol. *47*, H. 1, 5–11 (1985).

1100
Gächter, R., Bloesch, J.: Seasonal and Vertical Variation in the C:P Ratio of Suspended and Settling Seston of Lakes. Hydrobiologia *128*, 193–200 (1985).

1101
Karl, D.M., Bossard, P.: Measurement of Microbial Nucleic Acid Synthesis and Specific Growth Rate by $^{32}PO_4$ and [^{3}H]Adenine: Field Comparison. Appl. & Environ. Microbiol. *50*, 706–709 (1985).

1102
Lemmin, U., Schurter, M., Imboden, D.M., Joller, T.: An Instrument for Measuring Small Bottom Currents in Lakes. Limnol. Oceanogr. *30*, 1116–1122 (1985).

1103
Boller, M.: Full-Scale Experience with Tertiary Contact Filters. In: «Chemical Water and Wastewater Treatment», Schrr. Verein Wasser, Boden- und Lufthygiene *62*. G. Fischer Verlag Stuttgart u. New York, S. 152–166.

1104
Hoigné, J.: Organic Micropollutants and Treatment Processes: Kinetics and Final Effects of Ozone and Chlorine Dioxide. The Sci. of the Total Environ. *47*, 169–185 (1985).

1105
Hamer, G., Bryers, J.D., Berger, J.: Thermophilic Anaerobic Digestion for Sewage Sludge Stabilization. Acta Biotechnol. *5*, 3, 225–234 (1985).

1106
Stumm, W., Morgan, J.J.: Comment on the Conceptual Significance of p . A Comment to J.D. Hostettler's Paper «Electrode Electrons, Aqueous Electrons, and Redox Potentials in Natural Waters». Amer. J. Sci. *285*, 9, 856–859 (1985).

1107
Kuhn, E.P., Colberg, Patricia L., Schnoor, J.L., Wanner, O., Zehnder, A.J.B., Schwarzenbach, R.P.: Microbial Transformations of Substituted Benzenes During Infiltration of River Water to Groundwater: Laboratory Column Studies. Environ. Sci. & Technol. *19*, 961–968 (1985).

1108
Joller, R.: Untersuchung vertikaler Mischungsprozesse mit chemisch physikalischen Tracern im Hypolimnion des eutrophen Baldeggersees. Diss. ETHZ Nr. 7830, Zürich 1985.

1109
Santschi, P.: Radionuklidmigration in den Problemkreisen Radioaktiver Abfall – Chemodynamik – Sedimentologie. EIR-Bull. Nr. 54, 65–72, Januar 1985.

1110
Haag, W.R., Hoigné, J.: Photo-Sensitized Oxidation in Natural Water via ·OH Radicals. Chemosphere *14*, 1659–1671 (1985).

1111
Santschi, P.H., Nixon, S., Pilson, M., Hunt, C.: Accumulation of Sediments, Trace Metals (Pb, Cu) and Total Hydrocarbons in Narragansett Bay, Rhode Island. Estuarine, Coastal and Shelf Sci. *19*, 427–449 (1984).

1112
Nyffeler, U.P., Li, Y.-H., Santschi, P.H.: A Kinetic Approach to Describe Trace-Element Distribution Between Particles and Solution in Natural Aquaric Systems. Geochim. et Cosmochim. Acta *48*, 1513–1522 (1984).

1113
Guojiang, W., Santschi, P., Farrenkothen, K., Sturm, M., Stumm, W.: Distribution and Dating of ^{137}Cs for Recent Sediments in Lake Greifen (Switzerland). Acta Scientiae Circumstantiae (Beijing, China) *5*, 3, 360–365 (1985). [Engl. Summary]

1114
Tschui, M., Brunner, P.H.: Die Bildung von 4-Nonylphenol aus 4-Nonylphenolmono- und -diethoxylat bei der Schlammfaulung. Vom Wasser *65*, 9–19 (1985).

1115
Mechsner, K., Hamer, G., De Paolis, Annemarie: Denitrification with Methanotrophic/Methylotrophic Bacterial Associations in the Presence of Oxygen. In: Proc. Nitrates dans les eaux, 22.–24. Oct. 1985, Paris.

1116
Hamer, G., Egli, T., Mechsner, K.: Biological Treatment of Industrial Wastewater: a Microbiological Basis for Process Performance. J. Appl. Bacteriol. Sympos. Suppl. 127S–140S (1985).

1117
Hamer, G.: Microbiology of Treatment Processes. In: «Comprehensive Biotechnology», Vol. 4, eds. M. Moo-Young, C.W. Robinson, J.A. Howell. Chapter 45, Pergamon Press, Oxford, New York 1985, pp. 819–832.

1118
Siffert, Ch.: Forêts: Overdose d'acide. Nouvelle Cité, Paris, no. 275 (Janv. 1986), p. 14–16.

1119
Irvine, R.L., Bryers, J.D.: Stoichiometry and Kinetics of Waste Treatment. In: «Comprehensive Biotechnology», Vol. 4, eds. M. Moo-Young, C.W. Robinson, J.A. Howell. Chapter 44, Pergamon Press Oxford, New York 1985. pp. 757–772.

1120
Bossard, P., Karl, D.M.: The Direct Measurement of ATP and Adenine Nucleotide Pool Turnover in Microorganisms: a New Method for Environmental Assessment of Metabolism, Energy Flux and Phosphorus Dynamics. J. Plankton Res. *8*, 1, 1–13 (1986).

1121
Motschi, H., McEvoy, J.: Influence of Metal/Adsorbate Interactions on the Adsorption of Linear Alkylbenzenesulphonates to Hydrous Surfaces. Naturwissenschaften *72*, 654–655 (1985).

1122
Hoigné, J.: Verhalten anorganischer Ionen und Desinfektionsmittel bei der Ozonung von Wasser (Übersicht). Gas-Wasser-Abwasser *65*, 773–778 (1965).

1123
Staehelin, J., Hoigné, J.: Decomposition of Ozone in Water in the Presence of Organic Solutes Acting as Promotors and Inhibitors of Radical Chain Reactions. Environ. Sci. Technol. *19*, 1206–1213 (1985).

1124
Mechsner, K., Hamer, G.: Denitrification by Methanotrophic / Methylotrophic Bacterial Association in Aquatic Environments. In: «Denitrification in the Nitrogen Cycle», ed. by H.L. Golterman. Plenum Publ. Corp. New York and London 1985, pp. 257–271.

1125
Stöckli, A.P.: Die Rolle der Bakterien bei der Regeneration von Nährstoffen aus Algenexkreten und Autolyseprodukten, Experimente mit gekoppelten, kontinuierlichen Kulturen. Diss. ETHZ Nr. 7850, Zürich 1985.

1126
Moore, W.S., Santschi, P.H.: Ra-228 in the Deep Indian Ocean, Deep-Sea Res. *33*, 1, 107–120 (1986).

Impressum

Editor: Diana Hornung
Copyright: Reproduction of article/s is permitted if the source is mentionned and both author/s and editor/s are informed of the intention to print part or whole excerpts.
Printed on 100% recycled paper, i. e. made with very little water consumption, no bleaching and no coloration.

Please inform us of any **change in your address.**

Subscription for EAWAG-News
New subscribers are welcome: the English version appears annually in summer, the French/German editions are available twice a year. Please complete this subscription form and return it to EAWAG, Library, CH-8600 Dübendorf, Switzerland

With the entry into force of the Federal Law relating to the protection of the environment of October 1983 (set by the Federal Council to January 1985) Switzerland is trying to reduce pollution – among others – by the principle of causality (Art. 2: Anyone who causes measures to be taken under the provisions of this law shall bear the costs). The text of this law is now available in English at: Publikationsdienst, BUS, 3003 Berne, Switzerland.

Index of articles
All articles having appeared in the German/French editions of the EAWAG-News *1–20* (1973–1985) have been compiled on a sheet, which is available, if you write to the Library of the EAWAG.

Please send me
- ☐ regularly the EAWAG-News in English ☐ in German/French ☐
- ☐ second announcement for 4th Int. Conf. Urban Storm Drainage (autumn 1987)
- ☐ the Index 1973–85

☐ Change of address:

Name/Title: _____

Position/Company/Institute: _____

Full Mailing Address: _____