EAWAG
Federal Institute for Water Resources and Water Pollution Control
28/29
Swiss Federal Institutes of Technology
AUGUST 1990-EAWAG, CH- 8600 DÜBENDORF, SWITZERLAND

How Many Years Will The Swiss Mountains Exist Before They Are Washed To The Sea?

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Rocks and Rock'n'Roll

Sometimes an artist rather than a scientist finds the best words to bring a scientific problem to the point. Bob Dylan asked 20 years ago: "How many years can a mountain exist before it is washed to the sea?" At that time his song was hardly inspired by acid rain and the political controversy about ecological effects of accelerated weathering rates [1]. The final answer to Dylans grand question is still "blowing in the wind" although the yearly number of published papers on the subject of weathering kinetics is rapidly increasing. The overproduction of truth which is typical for today's science [2] has left us with hundreds of rate constants from the field, the laboratory and from theoretical studies.

In this article I invite the reader to follow a reductionistic downhill trail: We will start with an overview of alpine weathering rates in catchments of some 1000 km² area. Then we will discuss the usual attempts to mimic the dissolution of mountains in the laboratory. In typical batch experiments about 100 m² of mineral surface are exposed to aqueous solution. Finally we will descend to the molecular level. Computer simulations are now able to model the behavior of crystal surfaces over an area of some 100 nm².

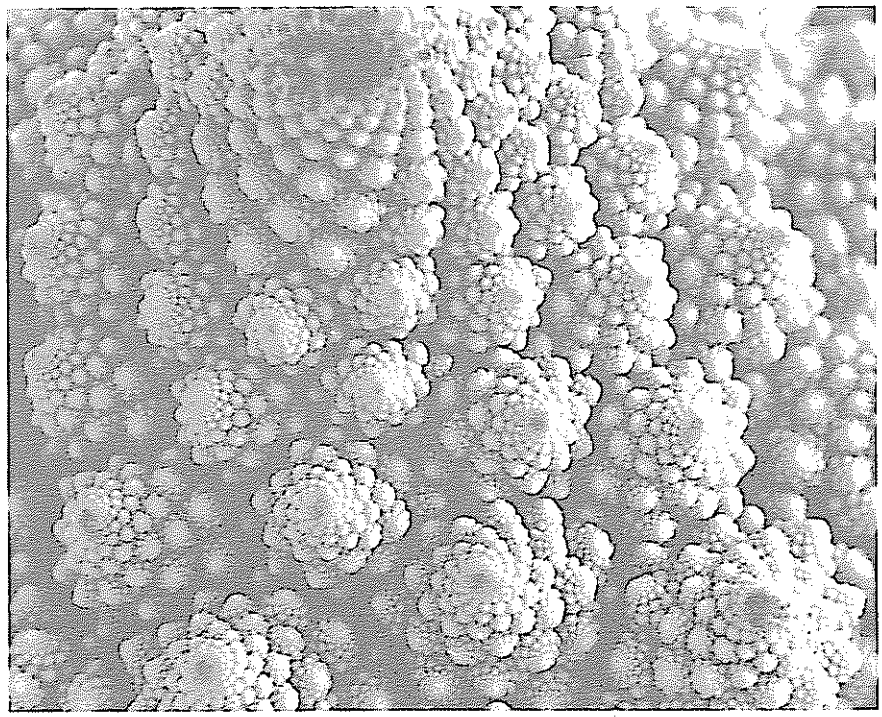


Fig 1
Self-similar cauliflower as a model for the fractal surface of mountains, rocks and mineral grains (sample by G. Furrer).

Alpine weathering rates

Geochemists distinguish operationally between physical and chemical weathering. Material which passes a 0.45 µm filter is called "dissolved" and is considered the result of dissolution of rock by water if other sources can be excluded. Suspended minerals, on the other hand, are attributed to the cracking of rock by mechanical forces such as the melting and freezing cycle of ice. The database for the suspended load of rivers is far less reliable than the collected results on the dissolved load because

most of the yearly particle flux occurs during few heavy rain events.

Mountains are built of a variety of solids, which react within different time scales with atmospheric water. At the natural pH of rain (pH=5.6) calcium carbonate dissolves about 10^6 times faster than aluminum oxide. Because crystalline bedrock dominates the geology of the central alps I choose the slow weathering rates of the silicates as the representative process. Representative weathering rates have been reported as results of the NADUF program [3-5], a long term project to monitor the composition of major Swiss rivers. Table 1 displays typical weathering rates in the range of 50-100 mmol silica $m^{-2} a^{-1}$. This corresponds to a yearly dissolution of 5-20 g silicates m^{-2}. We may use the density of silicates (~ 3 g cm^{-3}) to estimate the volume of rock lost by chemical weathering in alpine catchments. This yields about 2-7 cm^3 of rock $m^{-2} a^{-1}$. An idealized catchment would loose a few µm annually in altitude due to the chemical dissolution of rocks. Based on this estimate it would take more than 10^8 years to wash a 1000 m layer of alpine granite to the sea.

In comparison the estimated mechanical erosion in alpine catchments [4] may exceed 1000 g $m^{-2} a^{-1}$ which corresponds to a yearly "physical weathering depth" of about 0.4 mm. The transport of particles from alpine watersheds exceeds chemical weathering by more than two orders of magnitude. However, a large portion of this suspended load is retained in major Swiss lakes and is never washed to the sea.

Taking the mountains to the laboratory

At this point we could leave Mr. Dylan with this tentative answer from field studies. However, increased atmospheric deposition of strong acids from anthropogenic sources accelerates the chemical weathering rates in large areas of the earth's surface. As a result the concentrations of some toxic ions, such as Al^{3+} or Be^{2+}, are increasing in acid-sensitive areas. Laboratory studies under controlled conditions help us to predict the effects of this unintended ecotoxicological experiment. Furrer and Stumm [6] found the following rate law for the dissolution of aluminum oxide:

$$R_H = k\,[H^+]^{0.41} \qquad [\text{moles } m^{-2} a^{-1}] \quad (1)$$

Here the subscript 'H' marks a proton-promoted dissolution rate. An increase in the proton concentration by a factor of ten accelerates the dissolution rate only by a factor of 2.6. Therefore the neutralization of acid rain in catchments of crystalline rock is often kinetically controlled. The reason for the fractional rate order in the proton concentration has been attributed to the nonlinear adsorption isotherm of protons at many mineral surfaces [6, 7]. The adsorbed rather then the dissolved protons accelerate mineral dissolution.

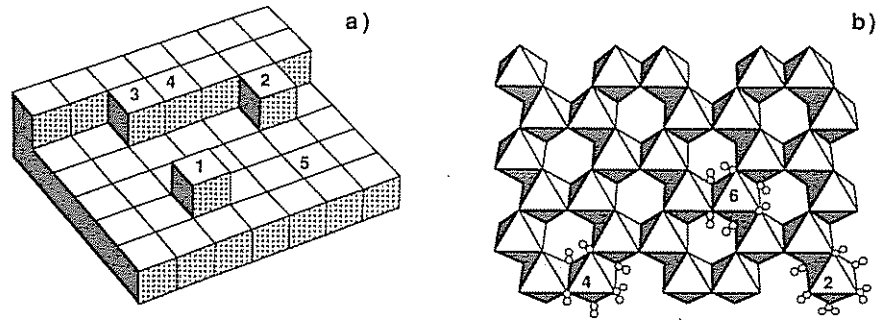


Fig 2
Surface structure determines reactivity:
a) Square-lattice model used in Monte Carlo simulations with five types of surface sites. Site 1 with a single bond to the surface dissolves very easily.
b) The coordination of octahedral aluminum centers in gibbsite or bayerite, $Al(OH)_3$.

In laboratory batch experiments often a pseudo-zeroth-order dissolution rate is observed. This implies that the surface area and the morphology of the mineral grains is in a steady state during the experiment. Pseudo-zeroth-order rate laws may be converted into first-order rates using the surface concentration of sites as determined by surface area measurements and crystallographic information. A typical distance between aluminum ions in a crystal lattice is 0.28 nm. From this we obtain a total surface concentration of sites St = 1.64 10^{-5} moles m^{-2}. At constant pH Eq.1 transforms to the following first-order rate law:

$$R_H = k_{obs} = k\,S_t \qquad [\text{moles } m^{-2} a^{-1}] \quad (2)$$

where k_{obs} is the observed pseudo-zeroth-order rate constant for given conditions and k [a^{-1}] is a first-order rate constant describing the mean reactivity of sites at the mineral-water interface. Table 2 lists typical data for the dissolution of aluminum and silicate minerals. They dissolve very slowly at pH ~ 5. It takes about one year to dissolve a layer of aluminum silicates. Comparing the laboratory data with the field observations in Table 1 we find a disagreement of 3-4 orders of magnitude. Many possible factors may contribute to this discrepancy. Dissolution rates slow down when dissolved concentrations approach the solubility equilibrium. Weathered rock surfaces may consist of more reactive material. Microorganisms may produce reactive organic ligands which accelerate the weathering process. The reactive surface area in a catchment may be many times larger than its "geographic" area. Therefore we should ask:

How large is the surface area of the Alps?

In 1967 B. Mandelbrot published an article in Science on the simple problem "how long is the coast of Britain?" Conventional wisdom would predict that the length L of the coastline will converge towards the true value if shorter and shorter yardsticks are used for the measurement. Empirical data show that a longer coastline is obtained if a shorter yardstick is used. The relation between the length L of the shoreline and the length λ of the yardstick is [8]

$$L \alpha F\,l^{1-D} \qquad (3)$$

where F counts how many times the

Table 1
Silicate weathering in the Alps

Catchment	Station	Rate m mol $m^{-2}a$	Ref.
Rhein	Hinterrhein	90	[4]
"	Basel	50	[4]
Rhone	Porte-du-Scex	66	[3]
Ticino	Riazzino	108	[3]
Inn	Martinsbruck	49	[3]
Aare	Brugg	43	[5]
Reuss	Melligen	40	[5]

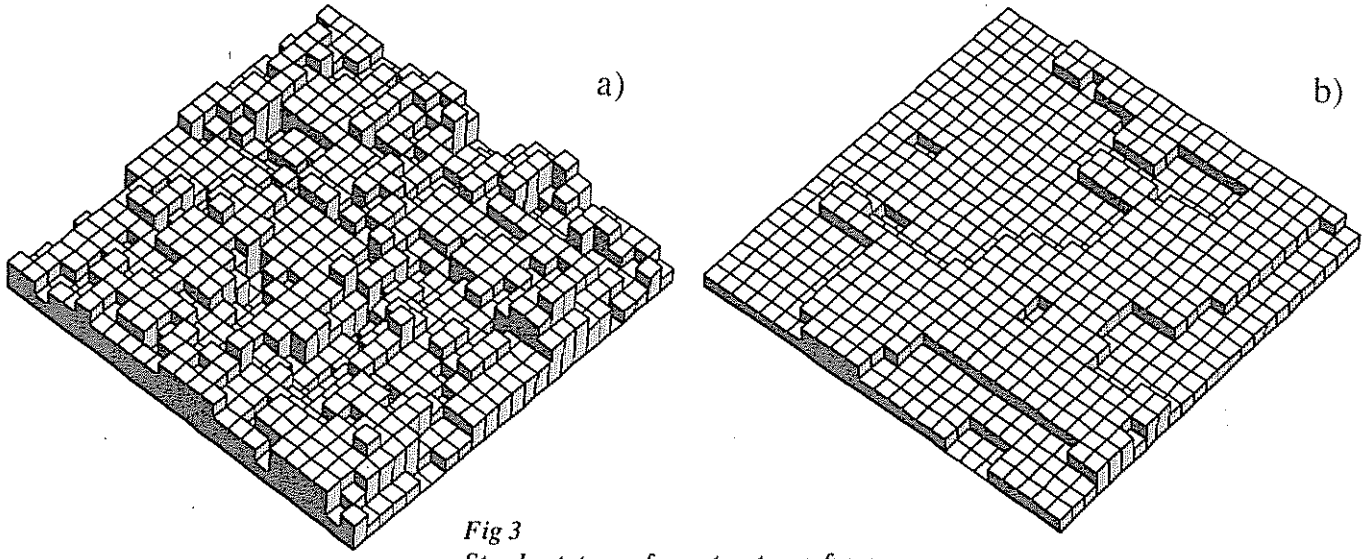


Fig 3
Steady-state surface structures from Monte Carlo simulations.
a) Rough surface at low activation enthalpy ($\Delta H^{\#}/RT = 1.0$).
b) Flat surface at $\Delta H^{\#}/RT = 3.0$.

yardstick has been applied and D stands for a geometric property of the coastline called the "fractal dimension" with 1<D<2. The fractal concept can be applied to any self-similar object. Fig. 1 shows a self-similar cauliflower: Each structural feature on the plant's surface represents a reduced image of the whole object. A fractal dimension of the cauliflower surface could in principle be determined with 2<D<3. Similar estimates of the fractal dimension of alpine landscapes, soil structure and of mineral surfaces would add significantly to our quantitative understanding of chemical weathering. In the future such geometric analyses will help us to perform a realistic scaling of laboratory data to the field situation.

Mineral dissolution on the computer

The ions in minerals impose a lower cutoff on the self-similar morphology of mountains, rocks and mineral surfaces. The distance l= 0.28 nm between two oxygen ions defines one of the shortest yardsticks for the characterization of mineral surfaces. At this length scale crystal lattices are perfectly described by classical geometry. A finite set of possible geometric arrangements at the lattice surface determines the reactivity. Fig 2a shows a cubic lattice with five different types of sites according to the number of "bonds" to the surface. The structure of a real mineral lattice is shown in Fig 2b. Only three distinct sites exist in the $Al(OH)_3$ plane. They are coordinated by 6, 4 and 2 lattice ligands. A general rate law has been developed based on the concept that

Table 2
Dissolution kinetics of Al minerals at pH 5

Mineral	rate R_H $\frac{\mu mol}{m^2 a}$	k a^{-1}	$t_{1/2}$ a	Ref.
Muscovite	8.2	0.50	1.38	[13]
Kaolinite	11	0.67	1.03	[13]
δ-Aluminum oxide	23	1.39	0.50	[6]
Bayerite	29	2.88	0.24	[14]

reactive sites at mineral surfaces match two requirements: (i) They are coordinated only by few surface ligands (sites 2 or 4 in Fig 2b) which favours detatchment from the surface and (ii) some of the surface ligands are protonated which weakens the surface bonds. The rate law can be stated as [7]

$$R_H = k\, x_a\, x_j\, S_t \qquad (4)$$

where x_a stands for the mole fraction of active sites and x_j represents the mole fraction of sites with j excess protons. The number j of protons was successfully determined from pH dependencies of dissolution rates (Eq. 1) and acidimetric titration of mineral surfaces [6]. The experimental determination of the mole fraction of active sites x_a, however, is not possible so far. Order-of-magnitude estimates were obtained by comparing reactivities of dissolved polynuclear complexes with the dissolution kinetics of minerals [9]. In addition Monte Carlo simulations [10] were used to find the answer to following problems: " Is x_a constant with time; in other words, will the simple lattice statistical model outlined in Fig. 2a reach a steady-state distribution of the active sites? What is the relation between structural parameters such as x_a and kinetic variables such as the activation energy?"

The geometric arrangement in Fig 2a was simulated with a 100 x 100 area of square sites. The well documented kinetic Ising model [11,12] was adapted on the basis of activated complex theory to define the dissolution rates. The overall rate is given as the sum of the five individual rates for sites i = 1..5:

$$R = S_t\, S\, k_i\, x_i \qquad (5)$$

with the rate constants: $k_i = \nu \exp(-i\, \Delta H^{\#}/RT)$

here ν represents a frequency factor and $\Delta H^{\#}$ stands for the activation enthalpy of the detachment of one surface bond. The simulations start with a perfect flat surface. Fig 3 depicts the resulting morphologies of the model after the dissolution of 200'000 sites. Unlike in real experiments the surface structure can be "monitored" continuously during a simulation and the key variable $\Delta H^{\#}$ can be varied over a wide range for different runs. Fig 4 outlines some of the results [10].

A steady-state morphology forms after a few layers have been dissolved (Fig 4a). In comparison the dissolution of one layer of aluminum silicates and oxides requires years. Changes in the solution chemistry in a soil environment are likely to occur at much shorter time scales. It is doubtful that the structure of the mineral-

water interface in a field situation remains in a perfect steady state. Acid-rain events may produce reactive surfaces which dissolve faster even if the pH of the rain water increases subsequentely.

The relation between surface structure and the kinetic parameter $\Delta H^{\#}/RT$ is shown in Fig. 4b. The higher the activation enthalpy the flatter the surface structure at steady state. Site 5 dominates in this case.

No rigorous lattice statistical derivation is available so far to predict the distribution x_i as a function of $\Delta H^{\#}/RT$. A simple empirical partition function, however, describes the Monte Carlo data (i = 1 to 5)

$$x_i = \frac{\exp(-a_i \Delta H^{\#}/RT)}{\Sigma \exp(-a_i \Delta H^{\#}/RT)} \quad (6)$$

with

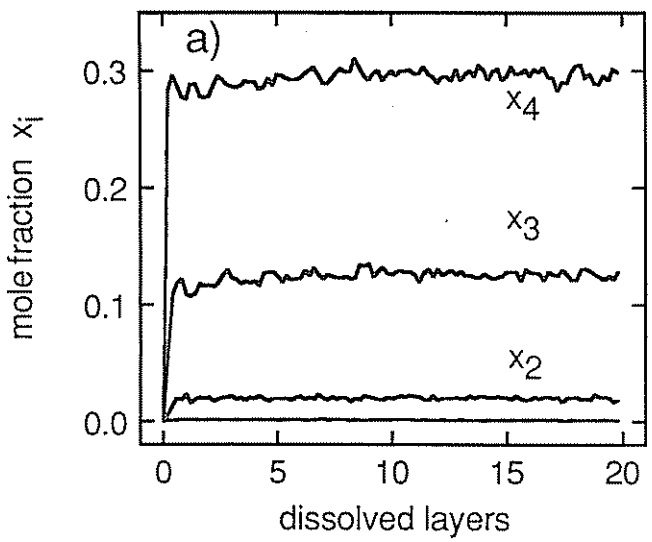
$a_1 = 5$ $\quad a_2 = {}^5/_2$

$a_3 = 1$ $\quad a_4 = {}^1/_2$

$a_5 = 0$

The equation implies that the activation enthalpy determines the steady-state structure of the surface. Fig 4c links the model parameter $\Delta H^{\#}/RT$ to experimental activation energies. This important link can be established if we consider the activation enthalpy, $\Delta H^{\#}$, constant and the temperature the main variable in the simulation runs. Fig 4c corresponds to an Arrhenius plot in this case and we may infer from the slope 4.0

$$E_a = 4\ \Delta H^{\#} \quad (7)$$



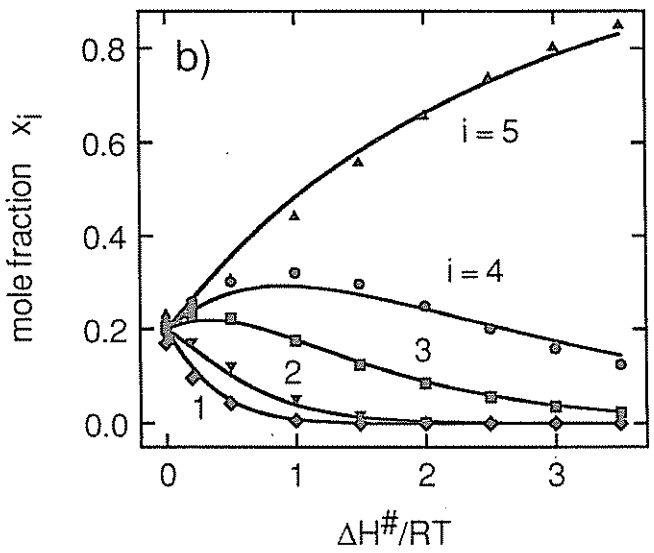
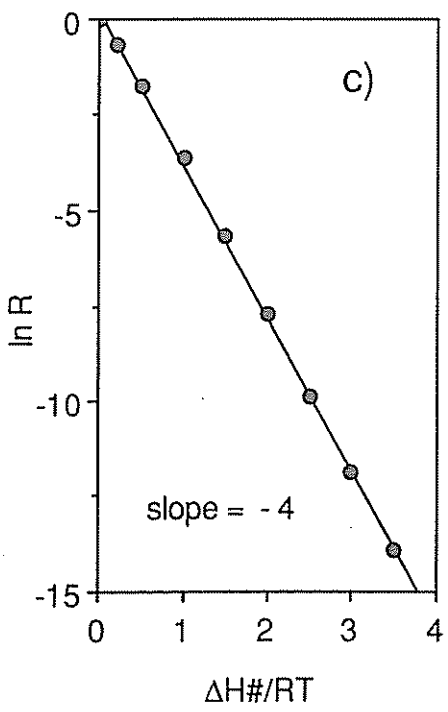
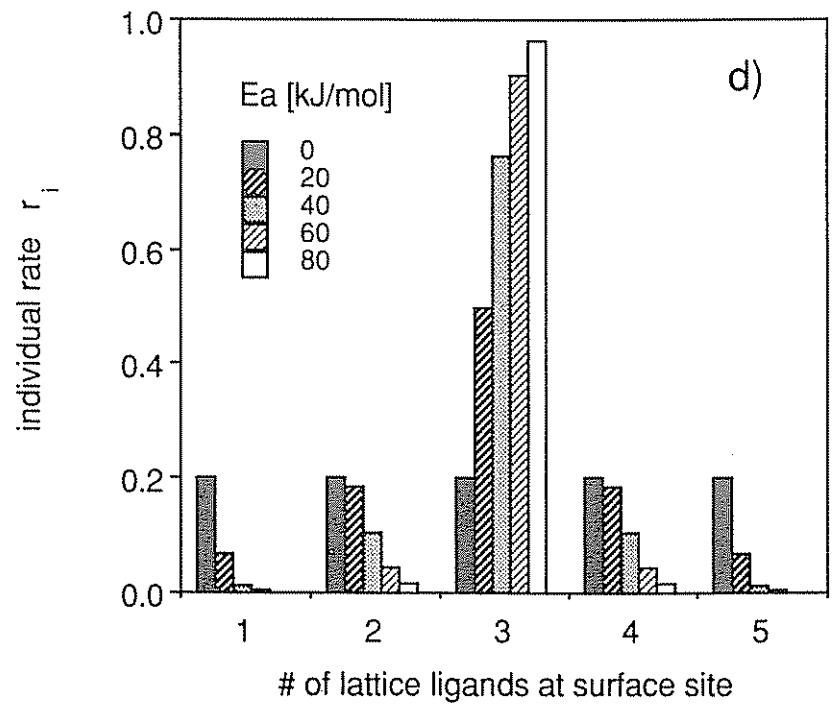


Fig 4
Results from computer simulations of dissolution kinetics.
a) A steady-state distribution of sites is observed after a few layers have been dissolved.
b) The activation enthalpy determines the distribution of sites in the steady state. Symbols represent Monte Carlo data, the lines are calculated from Eq. 6.





c) Arrhenius-plot relates the overall rate law to the activation enthalpy.
d) The individual rates of the five different sites were calculated from Eq. 8. All sites contribute with 1/5 to the overall rate in the diffusion-controlled limit of $E_a = 0$. At realistic activation energies site 3 controls the dissolution process.

Therefore a value of 3.0 for the activation enthalpy $\Delta H^{\#}/RT$ in Fig 3b corresponds to E_a = 12 RT ~ 30 kJ/mole which is a lower limit of the observed activation energies for mineral dissolution. We can now predict the relative importance of the five different sites for the dissolution process. Normlized to unit area the five individual rates are given by

$$r_i = k_i \quad x_i \qquad (8)$$

where the rate constant k_i is defined in Eq. 5 and the distribution of sites x_i is governed by the partition function in Eq. 6. The result is shown in Fig. 4d: At realistic activation energies (E_a > 40 kJ/mol) the "kink" sites with i = 3 surface bonds account for more than 80% of the dissolution flux.Thus the approximation that only one type of species is active can be justified. In the case of the ideal square lattice we would set the fraction of active sites in the general rate law of Eq. 4 to $x_a \sim x_3$.

Mountains, minerals and reductionism

We are at the end of our journey from the top of eroding Swiss mountains down to interactively dissolving crystal lattices. We escaped the fractal geometry of nature modelling dissolution at the length scale of oxygen ions. The results of the Monte Carlo simulations visualize the complex kinetic network which governs mineral dissolution. In this way they may improve the interpretation of laboratory experiments. However, simulations of some 1000 lattice ions will never produce the all-embracing theory of chemical weathering. Too many problems were left unanswered in reducing mountains to ionic lattices. Atomistic models in geochemistry represent just the narrowest ($\lambda \sim 0.3$ nm) of different complementary viewpoints. A single way of dealing with the hierarchy of length scales in nature is not enough [2]. The geochemical traditions of laboratory experiments ($\lambda \sim$ cm) and of field measurements ($\lambda \sim$ km) are equally essential to produce a convincing picture of a geochemical process. Convincing pictures are important if scientific insight should ever transform into political action. As Bob Dylan remarked in his song: We can turn our head many times and pretend that we just don't see...

Acknowledgement

I thank Gerhard Furrer, James J. Morgan, Werner Stumm, Erich Wieland and Jürg Zobrist for shared ideas, encouragement and productive discussions.

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The author, head of the group for anorganic chemistry, in the lake laboratory of the EAWAG at Kastanienbaum, was one of the participants of the conference "**Aquatic Chemical Kinetics; Reaction Rates of Processes in Natural Water**" (March 1989): *Janet Hering, Jürg Hoigné, Bernhard Wehrli (Front row, first from right), Barbara Sulzberger* and *Werner Stumm* (all from EAWAG), *Michael R. Hoffmann and James Morgan* (Caltech), *François Morel* (MIT), *Antonio C. Lasaga* (Yale), *Abraham Lerman* (Northwestern), *Patrick Brezonik* (Univ. of Minnesota), *Bozena Cosovic* (Univ. de Zagreb), *George W. Luther II* (Univ. of Delaware), *Jerald L. Schnoor* (Univ. of Iowa), *Jacques Schott* (Univ. Paul Sabatier, CNRS), *Charles R. O'Melia* (John Hopkins Univ.

Modelling of Pollutant Transport in Groundwater: Chemistry as a Key Factor

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Two kinds of pollutants can migrate in groundwater: conservative or reactive contaminants. The first ones are often used to study the hydrodynamic properties of water and porous media. Their transport is generally described by linear equations taking into account advection and dispersion mechanisms. On the other hand, transport of non-conservative solutes was and is still too often depicted by an empirical approach using distribution coefficient, determined from the so-called "isotherm curves". The main weakness of this concept is that this type of coefficient is only usable in particular conditions which fit very well the experiments [1]. A new step has to be overcome to go on and some questions arise: What are the chemical properties of the pollutants with regard to the solid phase and the aqueous phase? Then, the chemistry and the properties of the surface or the bulk solution have to be investigated in order to understand the possible exchange mechanisms or chemical reactions. From this point of view, chemistry becomes an important part of the modelling of the transport of such contaminants: each species is important and may affect the transport of the other species. The model appears as a set of non-linear chemical relationships associated with the mass transfer equations for each component. We apply such a model to describe the transport of metals in natural water and compare the results to field or laboratory data.

1. Theory

1.1. The Chemical Model

It is very important to remember definitions of SPECIES and COMPONENTS [2]. Every chemical entity to be considered in chemical equilibrium problem is defined as SPECIES (C). Then, we can define a set of COMPONENTS (X) in such a way that every species can be written as the product of a reaction involving only the components, and no component can be written as the product of a reaction involving only the other components.

Example: CO_2 in water.

$H_2O \rightleftarrows H^+ + OH^-$	$K_1 = -14.00$
$CO_{2(gas)} \rightleftarrows H_2CO_3^*$	$K_2 = -1.47$
$H_2CO_3^* \rightleftarrows H^+ + HCO_3^-$	$K_3 = -6.37$
$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$	$K_4 = -10.33$

The chemical system may be defined with: 6 Species: H^+, OH^-, $CO_{2(gas)}$, $H_2CO_3^*$, HCO_3^-, CO_3^{2-} but 2 Components: H^+, $CO_{2(gas)}$, and 4 thermodynamical constants.

Then, the 4 previous equations can be rewritten by using the 2 components:

$H^+ \rightleftarrows H^+$	$\log K_5 = 0$
$H_2O - H^+ \rightleftarrows OH^-$	$\log K_6 = -14.00$
$CO_{2(gas)} \rightleftarrows CO_{2(gas)}$	$\log K_7 = 0$
$CO_{2(gas)} + H_2O \rightleftarrows H_2CO_3^*$	$\log K_8 = -1.47$
$CO_{2(gas)} - H^+ + H_2O \rightleftarrows HCO_3^-$	$\log K_9 = -7.84$
$CO_{2(gas)} - 2H^+ + H_2O \rightleftarrows CO_3^{2-}$	$\log K_{10} = -18.17$

Generalization.

In the case of m Species and k Components (l components are mobile) and for component j, we need a mass balance equation:

$$X_{tot_j} = \sum_{n=1}^{m} a_{nj} C_n$$

Chemical equilibria (for homo- or heterogeneous system) are described by relationships:

$$C_n = K_n \prod_{i=1}^{k} X_i^{a_{ni}}$$

In the case of precipitation or dissolution, we use the following relationship:

$$K_{sp} = \prod_{i=1}^{k} X_i^{a_{pi}}$$

where X_{totj} is total concentration of component j, a_{ni}, a_{nj}, a_{pi} stoichiometry coefficients, K_n thermodynamical constant, K_{sp} solubility product for species p.

1.2. The Transport Equation

For each mobile species, one mass balance equation is defined, but we only use the equation for each mobile component j [3-4]. This means that we will observe l breakthroughs at a location of sampling. The general equation becomes:

$$\frac{\partial X_{totj}}{\partial t} = D_l \frac{\partial^2 X_{aqj}}{\partial x^2} - u \frac{\partial X_{aqj}}{\partial x}$$

with $X_{totj} = X_{aqj} + X_{sj}$ (in mol/l), X_{aqj} total concentration of component j in the aqueous phase, X_{sj} total concentration of component j in / on the solid phase, D_l longitudinal hydrodynamic dispersion coefficient (L^2/T), u mean pore velocity (L/T), and

$$X_{sj} = \frac{\rho}{\theta} \bar{X}_{sj} = \frac{m_s}{V_p} \bar{X}_{sj}$$

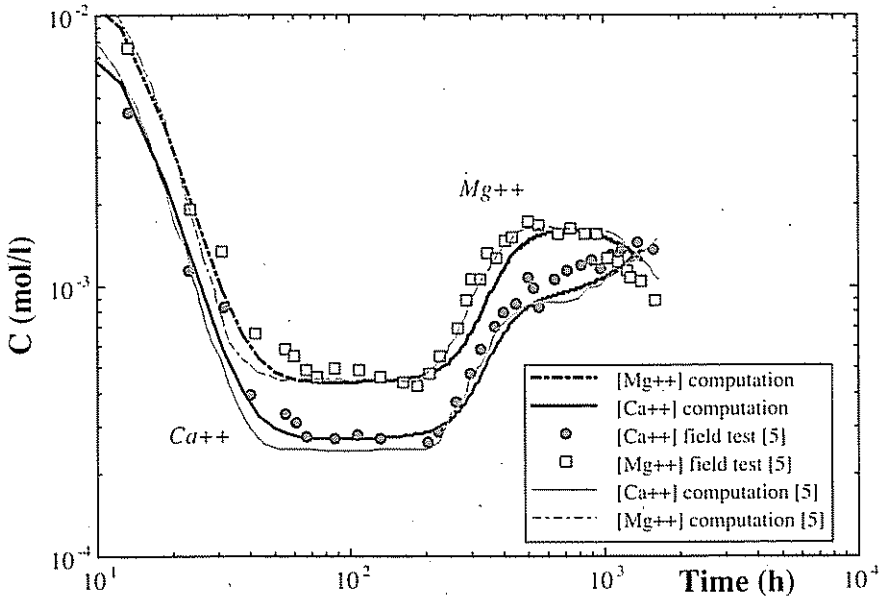


Fig. 1:
Comparison of field test [5] and simulated breakthroughs of Ca^{2+} and Mg^{2+}. Experiments (dots) and computation (thin lines) from [5], our computation (thick lines). Cl^- is used as a tracer to determine dispersivity (α=2.94 m) and mean pore velocity (u = 1.01 m/h). ρ = 1875 g/l; θ = 0.25.

where

ρ = bulk density of medium (g/l),
θ = medium porosity (-),
$\bar{X}_{sj}$ = concentration of component j on the solid phase (mol/g),
m_s = mass of porous medium (g),
V_p = pore volume (l).

For non-reactive component j, *i.e.* a tracer of water, $X_{totj} = X_{aqj}$

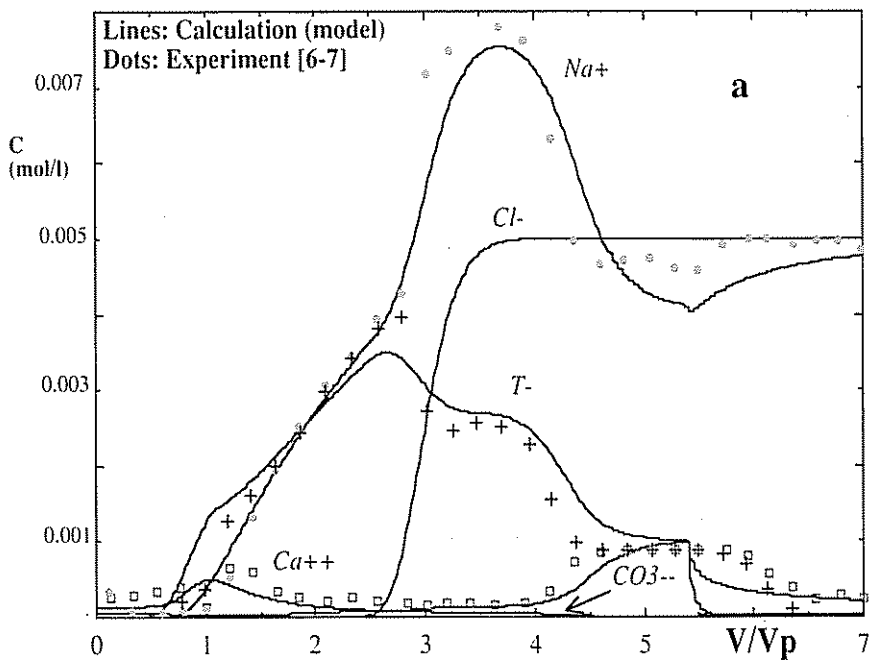
1.3. Numerical Solution Procedure

The set of chemical equations is solved by a Newton-Raphson method. A Finite Element method is used to integrate transport equations over space. The integration over time is achieved through a Finite Difference scheme with central weighting.

2. Validation: Field Experiment [5]

Case with ionic exchange between Na^+, Ca^{2+}, and Mg^{2+}

Water was injected into an aquifer. The concentrations of cations and chloride were followed in a well: length of flow path 16 m. In this simple case, there were no reaction in the aqueous



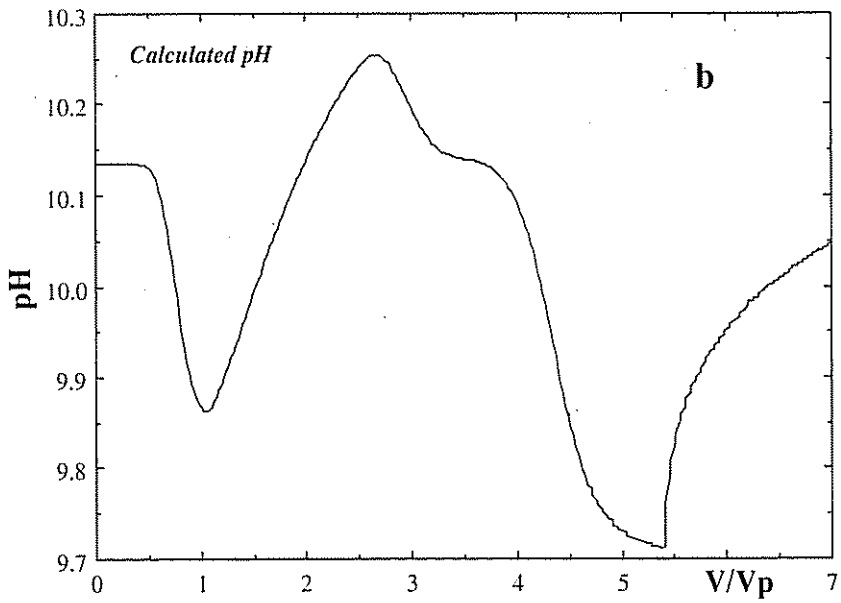


Fig. 2:
Comparison of column experiment [6-7] and simulation: response of the column to the injection of 2 pore volumes of surfactant at 5 mmol/l driven by NaCl at the same concentration.
(a) Ca^{2+}, Na^+, T^-, CO_3^{2-}, Cl^- vs V/V_p;
(b) pH vs V/V_p.
Cl^- is used as a tracer to determine dispersivity (a = 0.62 cm) and mean pore velocity (u = 1.52 10^{-3} cm/s). m_s = 146 g; V_p = 42.7 cm³.

there were no reaction in the aqueous phase, and no effect of pH. The two cationic exchange reactions are:

$$Mg^{2+} + 2Na^{+}_{s} \rightleftarrows Mg^{2+}_{s} + 2Na^{+} \qquad \log K_{11} = 0.355$$

$$Ca^{2+} + 2Na^{+}_{s} \rightleftarrows Ca^{2+}_{s} + 2Na^{+} \qquad \log K_{12} = 0.602$$

The chemical system:8 Species: Na^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, Na^{+}_{s}, Ca^{2+}_{s}, Mg^{2+}_{s}, , Surface; 5 Components: Na^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, Surface (Cationic Exchange Capacity). 4 are mobile: 4 breakthroughs. 2 selectivity coefficients.

Composition of water (mmol/l)

Comp.	Injected water	Total concentration in aquifer
Na^{+}	9,40	248
Ca^{2+}	2,12	165
Mg^{2+}	0,494	158
Cl^{-}	9,03	161
Surface		750

Field data and simulation results are in fig. 1. Our computer predictions agree very closely with the field results and the simulations done by [5]. Since this first step agrees with other data, we can take a more difficult example, and show the importance of the chemistry in such of modelling.

3. Role of the Chemistry

3.1. Column Experiment [6-7]

Case with ionic exchange between Na^{+}, and Ca^{2+}; precipitation / dissolution of CaT_2 (T^{-} is octylbenzenesulfonate); and equilibrium with calcite

A surfactant solution (NaT) following by NaCl solution was injected into a column (length of flow path 19.5 cm). The concentrations of Na^{+}, Ca^{2+}, T^{-}, Cl^{-}, and the pH were followed with time. In this particular case, the pH is not a constant. The set of different reactions is:

in the aqueous phase

$$H^{+} \rightleftarrows H^{+} \qquad \log K_{13} = 0$$

$$H_2O - H^{+} \rightleftarrows OH^{-} \qquad \log K_{14} = -14.18$$

$$CO_3^{2-} \rightleftarrows CO_3^{2-} \qquad \log K_{15} = 0$$

$$CO_3^{2-} + H^{+} \rightleftarrows HCO_3^{-} \qquad \log K_{16} = 10.38$$

$$CO_3^{2-} + 2H^{+} \rightleftarrows H_2CO_3^{*} \qquad \log K_{17} = 16.76$$

precipitation / dissolution

$$CO_3^{2-} + Ca^{2+} \rightleftarrows CaCO_3 \qquad \log K_{18} = -8.14$$

$$2T^{-} + Ca^{2+} \rightleftarrows CaT_2 \qquad \log K_{19} = -9.00$$

cationic exchange

$$Ca^{2+} + 2Na^{+}_{s} \rightleftarrows Ca^{2+}_{s} + 2Na^{+} \qquad \log K_{20} = 2.34$$

The chemical system:
14 Species: H^{+}, OH^{-}, $H_2CO_3^{*}$, HCO_3^{-}, CO_3^{2-}, Ca^{2+}, Na^{+}, T^{-}, Cl^{-}, $CaCO_3$, CaT_2, Na^{+}_{s}, Ca^{2+}_{s} Surface; 7 Components: H^{+}, CO_3^{2-}, Ca^{2+}, Na^{+}, T^{-}, Cl^{-}, Surface (Cationic Exchange Capacity). 6 are mobile: 6 breakthroughs. 1 selectivity coefficient.

Composition of water (mmol/l)

Com-position	1st Injection	2nd	Total conc. in column
Time	0 V_p	2,03 V_p	
pH	5,7	5,7	10,1
CO_3^{2-}	0,012	0,012	excess
Ca^{2+}	0	0	excess
Na^{+}	5	5	0
T^{-}	5	0	0
Cl^{-}	0	5	0
Surface			28.6

What does happen during this column experiment (fig. 2a)?

(i) In a first part, there is only ionic exchange between Na^{+} and Ca^{2+}, and we can see a small peak of Ca^{2+}. T^{-} behaves as a perfect tracer.

(ii) In a second zone, precipitation and cation exchange processes control the T^{-} transport and Ca^{2+} concentration.

(iii) The third part starts with the injection of Cl^{-}: The dissolution CaT_2 gives some Ca^{2+} ions into the aqueous phase which take replace Na^{+} (peak of Na^{+}).

(iv) At the end, there are only ionic exchange and calcite equilibrium. Experimental data and simulation results are in fig. 2. As shown in fig. 2b, the pH cannot be constant.

Computer predictions agree very closely with the experimental results [6-7]. We assume a local equilibrium with respect to the mean pore velocity in our computation. This is true for the two first parts when there are precipitation and ionic exchange; the difference between experimental data and simulation during the third and fourth parts could be due to dissolution which is not a so fast mechanism (fig. 2).

For this example: What does distribution coefficient K_d mean with respect to the precipitation or the dissolution of $CaCO_3$ and CaT_2? K_d means nothing since there is no relationship between the total concentration of Ca on the surface and the concentration of Ca in the aqueous phase.

3.2. Transport of metals: Computation from field data (Glatt river - Aquifer at Glattfelden)

The results described below are based on the work done for and by the students for the "Abschlußkurs NDS Sommersemester 1989". The questions were: What is the influence of Cd discharge into the river on the composition of the groundwater and of the water pumped at 500 m away from the river? What could be the effect of injection of strong complexing agent, *e.g.* EDTA (ethylenediaminetetracetate), on the metal concentrations? How does the retardation factor R, or K_d evolve during the simulation?

Case with complexation in the aqueous phase and surface complexation

Definition of the System:

* 1 metal: Ca + 3 transition metals: Cd, Cu, Zn.
* Dissolved ligands: EDTA, NTA, DOC, OH^-, CO_3^{2-}.
* 1 surface: ≡S-OH
* Buffered system with regard to H^+ (constant pH = 8.00)

Two Simulations were done:

1. Injection of Cd at a very high concentration, for a short time (5 days)
2. Injection of Cd (cf. 1.), then injection of EDTA (100 days)

The set of different reactions for the surface complexation is (logK from [8]):

$$Cd^{2+} + \equiv S\text{-}OH \rightleftarrows \equiv S\text{-}O_{Cd}^{+} + H^{+} \qquad logK_{21} = -3.70$$

$$Cu^{2+} + \equiv S\text{-}OH \rightleftarrows \equiv S\text{-}O_{Cu}^{+} + H^{+} \qquad logK_{22} = -1.50$$

$$Zn^{2+} + \equiv S\text{-}OH \rightleftarrows \equiv S\text{-}O_{Zn}^{+} + H^{+} \qquad logK_{23} = -3.60$$

$$Ca^{2+} + \equiv S\text{-}OH \rightleftarrows \equiv S\text{-}O_{Ca}^{+} + H^{+} \qquad logK_{24} = -6.50$$

The chemical system:
45 Species: 38 in the aqueous phase, 7 on the surface.
10 Components: H^+, $EDTA^{4-}$, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ca^{2+}, NTA^{3-}, CO_3^{2-}, DOC, ≡S-OH. 9 are mobile: 9 breakthroughs; 5 are conservative.

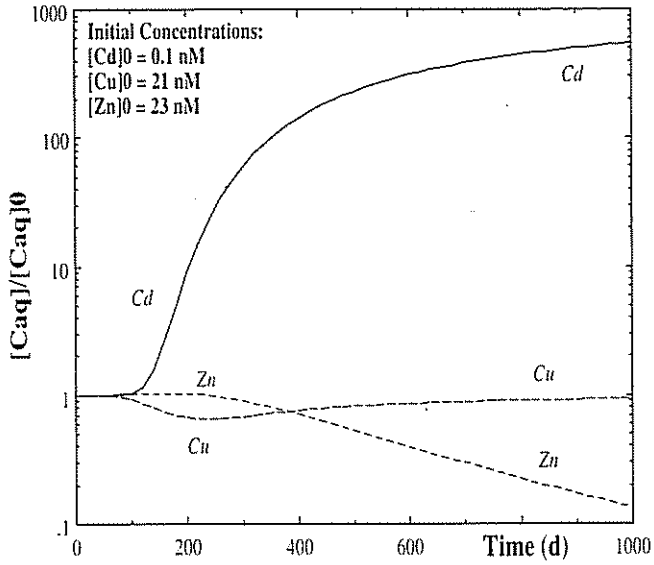


Fig. 3:
First simulation: Breakthrough curves of Cd, Cu, Zn at 500 m away from the injection source after an increase in Cd concentration. Dispersivity (α=50 m) and mean pore velocity (u = 10 m/d). Characteristic time of the field (for a tracer) = 50d.

First simulation: Composition of water

Comp. conc.	1st Step	2nd Step	Total in aquifer
Time (days)	0	5	
pH	8,0	8,0	8,0
$EDTA^{4-}$ (µM)	0,1	0,1	0,1
Cd^{2+} (µM)	1000	0,0001	0,0015
Cu^{2+} (µM)	0,021	0,021	0,088
Zn^{2+} (µM)	0,023	0,023	0,41
Ca^{2+} (mM)	1,08	1,08	2,06
NTA^{3-} (µM)	0,035	0,035	0,035
CO_3^{2-} (mM)	4,0	4,0	4,0
DOC (µM)	4,0	4,0	4,0
≡S-OH (mM)			46,0

Why do Cu_{aq}^{2+} and ZnS_{aq}^{2+} concentrations decrease with time (fig. 3)?

Let us reduce the system to 2 metals, Cd and Zn, and 2 ligands, EDTA and ≡S-OH. The mass balances for Zn, EDTA and ≡S-OH are:

$$Zn_{tot} = Zn_{aq} + Zn_s = [Zn^{2+}]\left(1 + \sum_r K_r' [EDTA^{4-}]^r + {}^*K_{23}^s [\equiv S\text{-}OH]\,[H^+]^{-1}\right)$$

$$EDTA_{tot} = "[EDTA]" + [CdEDTA^{2-}] + [ZnEDTA^{2-}]$$

$$\equiv S\text{-}OH_{tot} = "[\equiv S\text{-}OH]" + [\equiv S\text{-}OCd^{+}] + [\equiv S\text{-}OZn^{+}]$$

In our conditions, we have $Cd_{tot} >> EDTA_{tot}$ and $Cd_{tot} < \equiv S\text{-}OH_{tot}$ and according to stability constants for the complexes $CdEDTA^{2-}$ and $ZnEDTA^{2-}$, $EDTA_{tot}$ is almost equal to $CdEDTA^{2-}$ (fig. 4a). So, "EDTA" species and $ZnEDTA^{2-}$ become negligible (fig. 4b). Thus for given Zn_{tot}, ${}^*K_{23}^s [\equiv S\text{-}OH]\,[H^+]^{-1}$ is a constant, $[Zn^{2+}]$ has to increase and

$$[\equiv S\text{-}OZn^{+}] = {}^*K_{23}^s [Zn^{2+}]\,[\equiv S\text{-}OH]\,[H^+]^{-1}$$ too (fig. 4b). This first simulation exemplifies the competition between metals and the important role of a ligand in the migration of trace metals.

Second simulation: Composition of water

Comp.	1st Step	2nd Step	3rd Step	4th Step	aquifer
Time (days)	0	5	40	140	
pH	8,0	8,0	8,0	8,0	8,0
$EDTA^{4-}$ (µM)	0,1	0,1	100	0,1	0,1
Cd^{2+} (µM)	1000	0,0001	0,0001	0,0001	0,0015
Cu^{2+} (µM)	0,021	0,021	0,021	0,021	0,088
Zn^{2+} (µM)	0,023	0,023	0,023	0,023	0,41
Ca^{2+} (mM)	1,08	1,08	1,08	1,08	2,06
NTA^{3-} (µM)	0,035	0,035	0,035	0,035	0,035
CO_3^{2-} (mM)	4,0	4,0	4,0	4,0	4,0
DOC (µM)	4,0	4,0	4,0	4,0	4,0
≡S-OH (mM)					46,0

For the second computation, the question is: What is the effect of EDTA on the metal behaviour?

In our conditions, $\equiv S\text{-}OH_{tot}$ and $EDTA_{tot}$ are larger than Cd_{tot}, Cu_{tot} and Zn_{tot}. For Cd, Cd_{aq} is almost equal to $[CdEDTA^{2-}]$ (fig. 5a). In the mass balance,

$$Cd_{tot} = Cd_{aq} + Cd_s \approx [CdEDTA^{2-}] + Cd_s$$
$$\approx [Cd^{2+}]\,(K_{EDTA}\,[EDTA^{4-}] + {}^{*}K^{s}_{21}\,[\equiv S\text{-}OH]\,[H^{+}]^{-1})$$

For given Cd_{tot}, if the EDTA concentration increases, and ${}^{*}K^{s}_{21}\,[\equiv S\text{-}OH]\,[H^{+}]^{-1}$ is quasi constant, $[Cd^{2+}]$ decreases and

$[\equiv S\text{-}OCd^{+}] = {}^{*}K^{s}_{21}\,[Cd^{2+}]\,[\equiv S\text{-}OH]\,[H^{+}]^{-1}$ decreases too.

If ligand concentration is very high, the free metal concentration tends to a very low value and the concentration on the surface tends to 0. Strong ligand may "wash" porous medium contaminated by metals, with the exception of its possible secondary effects (fig. 5a).

For this example, since

$[\ S\text{-}OCd^{+}] \approx 0$, the retardation factor R tends to 1 ($K_d \approx 0$) (fig. 5b). eg.:

$$R = 1 + K_d = 1 + \frac{Cd_s}{Cd_{aq}}$$
$$= 1 + \frac{[\equiv S\text{-}OCd^{+}]}{Cd_{aq}}$$
$$\approx \frac{Cd_{tot}}{Cd_{aq}} \approx 1\,.$$

Conclusion

The goal here was to show the role of the chemistry in the transport of pollutants in groundwater. For that, it was necessary to couple chemistry and transport relationships to get a Multicomponent Transport Model. Three cases were shown:

(i) a simple case (field data) in order to validate the computer code (ion exchange);

(ii) a more complicated case where precipitation or dissolution and ion exchange occured. In this example, chemical approach can only help to solve the problem; and

(iii) a more theoretical situation issued

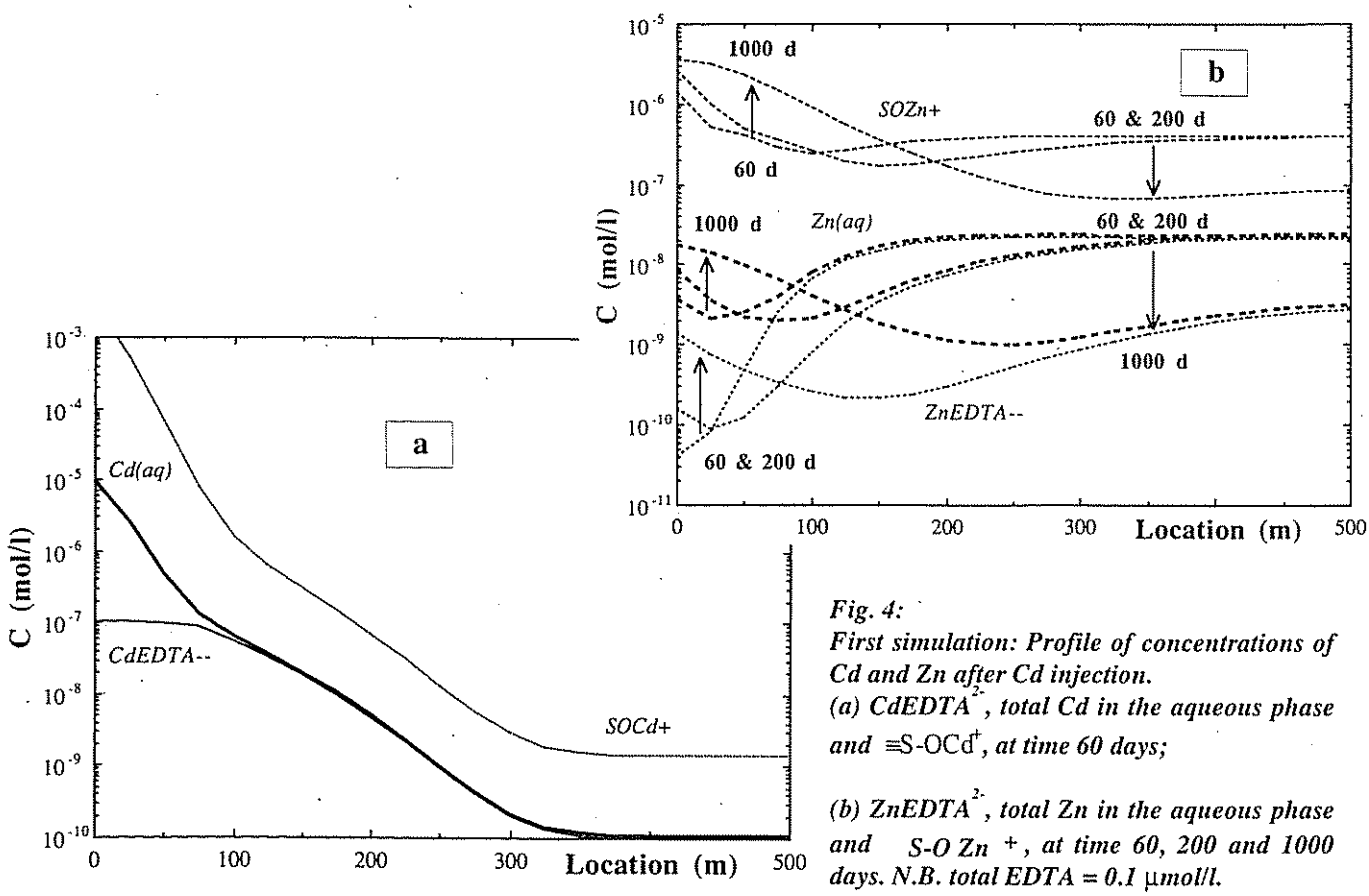


Fig. 4:
First simulation: Profile of concentrations of Cd and Zn after Cd injection.
(a) $CdEDTA^{2-}$, total Cd in the aqueous phase and $\equiv S\text{-}OCd^{+}$, at time 60 days;

(b) $ZnEDTA^{2-}$, total Zn in the aqueous phase and S-O Zn +, at time 60, 200 and 1000 days. N.B. total EDTA = 0.1 µmol/l.

from field case and studied by the students of Abschlußkurs NDS 1989.

The system is not linear despite the low concentrations of metals present in the system. Once more, chemistry in the aqueous phase and on the surface is the key-point to explain the behaviour of the contaminants.

We are far away from the empirical approach since each parameter has to be known as a preliminary step. From fig. 6, we can ask the question: how is it possible to simulate the transport of trace metal such as Cu with one distribution coefficient?

Acknowledgements

We gratefully acknowledge D. Schweich and M. Sardin for stimulating discussions, and W. Stumm for his many encouragements.

Work supported in part by the research foundation of the chairman of the board of the Swiss Federal Institute of Technology. Ph. B. is partially supported by CNRS.

This work was presented at the VIIIth International Conference of "Computational Methods in Water Resources", Venice (June 1990).

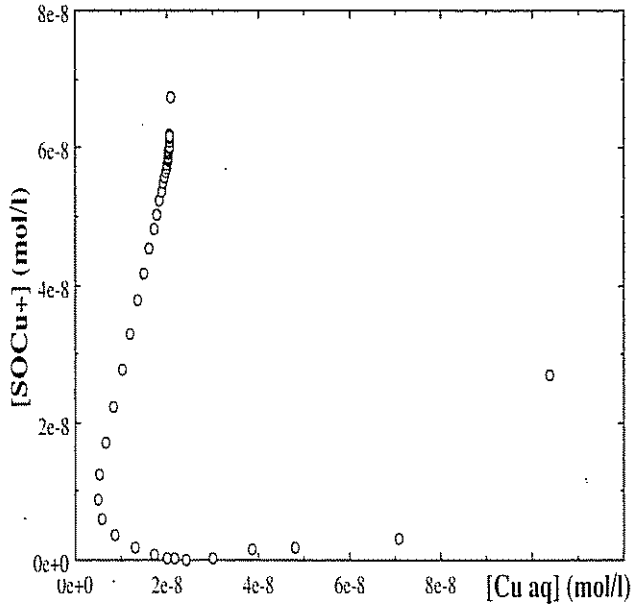


Fig. 6:
Variation of the concentration of Cu on the surface vs the total concentration of Cu in the aqueous phase. The data are from the second simulation. For some values of Cu_{aq}, there are two values of $\equiv S\text{-}OCu^{2+}$. This shows that the system is not linear.

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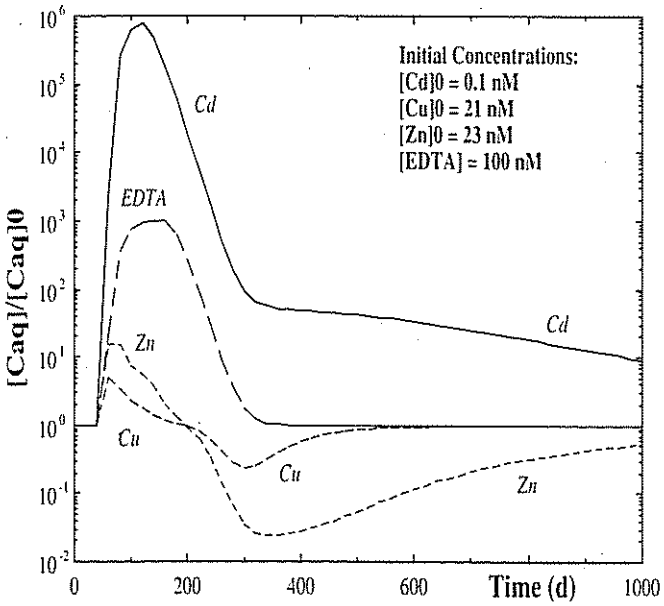


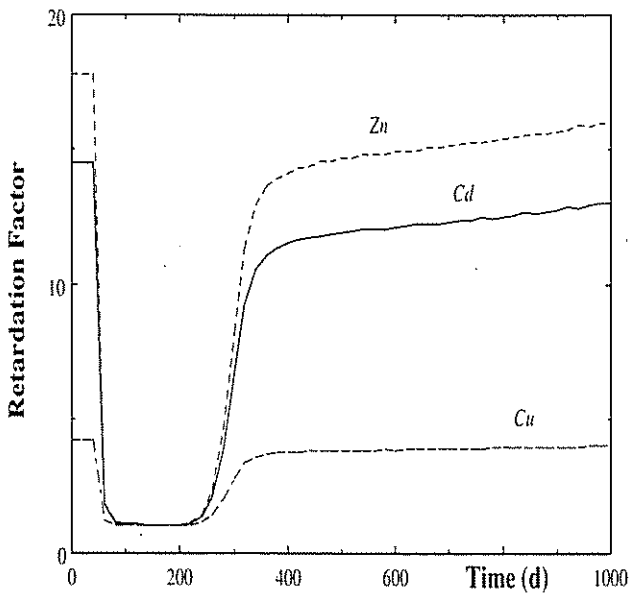


Fig. 5:
Second simulation:
(a) Breakthrough curves of Cd, Cu, Zn and EDTA; and (b) Variation of the retardation factor for Cd, Cu and Zn vs time at 500 m away from the injection source after an increase in Cd followed by an increase in EDTA.

TRACE METALS AND WHAT WE THINK THEY DO IN SURFACE WATERS

BEAT MÜLLER

One of the most characteristic attributes of heavy metals as pollutants compared with organics is their lack of degradability. Whenever metal ores are exploited and metals transformed to consumer goods, they end up as waste in the environment and are added to the natural fluxes. Somehow and somewhere many of these trace metals will cause major or minor problems because they do not go back to where they came from so easily. They gush through the exhaust of cars (which is called emission) into the lungs of the bicycle driver (which is called imission), they swell through chimneys and incinerators, they flow from some hidden waste pipe and from our own familiar sink into rivers and lakes, they leak quietly and secretly from some long forgotten dumping place into the groundwater, they spread over the fields and forests with rain and snow and dust. You can easily imagine that in air, water and earth we have a wild hullabaloo of metals and their complexes, mostly traces only, that behave according to their individual physical and chemical peculiarities. The current philosophy is to reduce pollution just below concentrations that cause visible toxic effects. This policy is often been defeated with the argument of the poor scientific knowledge of the behaviour of the metals in the environment and effects on organisms.

As a little contribution to this complex field I report here parts of the PhD work I did during the recent years with PD Dr. Laura Sigg as Ph.D. advisor.

1. METAL IONS IN SURFACE WATERS

One of the most important characteristics of trace metals in natural waters is their speciation, i.e. they take on various chemical modifications. The chemical form primarily determines behaviour and fate, toxicity and accumulation in the environment. For copper for example it is not the total amount of the metal that determines its damaging effect on organisms but the concentration of its free aqueous ion. Its journey in the water phase will be different if the particles on whose surfaces it has the tendency to adsorb originate from biogenic material like algae, phytoplankton or its debris, from precipitated $CaCO_3$ or from inorganic oxidic

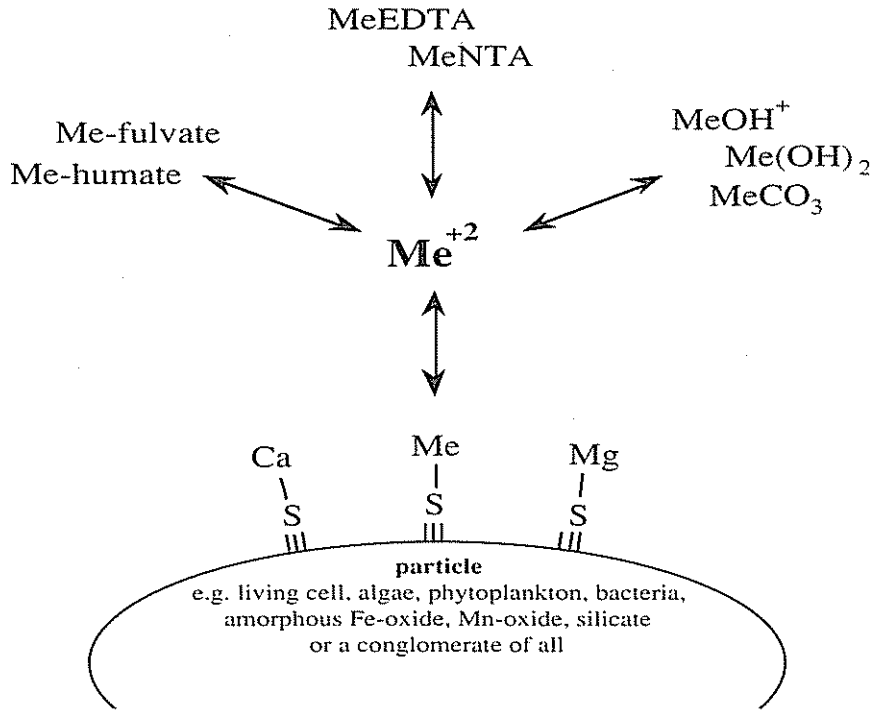


Fig. 1

Several complexation processes compete with each other to form complexes with trace metal ions, and trace metals and alkali earth metals (Ca, Mg) then compete for these ligands. The physical attributes and chemical behaviour of the trace metal ions depend mainly on the chemical form.

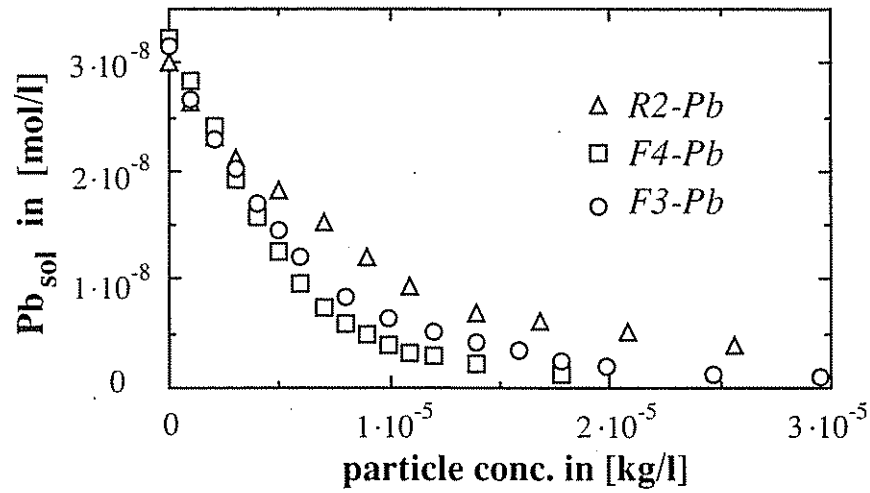
particles, (e.g. those of iron, manganese or silicates and other mineral phases). A metal ion also can undergo many complexing reactions with dissolved complex formers: it forms weak complexes with inorganic ligands and it has a strong tendency to form complexes with synthetic ligands such as EDTA, which originates mainly from metal-working industries but has also many other sources. It also forms complexes with complicated organic substances like fulvic and humic acids that are degraded products of phyto- and zooplankton, exudates of living cells, etc. Some competing reactions are schematically represented in figure 1. The interactions between metal ions and particles depend on pH and other dissolved ions that can either form complexes with metal ions or adsorb on the particulate surfaces. In addition to this, they also change with the concentrations of metal ions and particles.

Our intention was to investigate a method and mathematical procedure to determine the adsorption characteristics of some trace metals and then to apply them to interactions between dissolved and particulate complex formers, thereby simulating the distribution of metal ions between particle and solution phase measured in a river.

2. METHODOLOGY

To investigate the interaction of a metal ion with aquatic particulate matter we choose voltammetry as the analytical tool. Voltammetry not only has a very low detection limit for certain metals but also allows measurement of the concentration of the free non adsorbed metal in the presence of particles (without filtration or centrifugation). Separation procedures are difficult to handle since they are very sensitive to contamination or undesired adsorption. Voltammetric determination of trace metals is based on the reduction of metal ions on a negatively polarized mercury drop (accumulation step) and controlled re-oxidation from the mercury into the solution (oxidation step). The electrons gained through the oxidation can be measured as a current which is directly related to the amount of metal accumulated in the mercury drop. An important process in the course of the measurement is the transport of the metal ion or complex through the diffusion layer

Fig. 2
Curve resulting from the "titration" of $5 \cdot 10^{-8}$ M Pb(II) as determined by voltammetry with increments of various particle suspensionsat conc. of 2 g/l, pH 8.0 and 10^{-3} M HCO_3^-, buffered with 0.06% CO_2 in N_2. The concentration of dissolved lead decreases with increasing particle concentration due to adsorption on the particulate surfaces.



around the mercury drop. This transport obviously is much faster for a small dissolved complex than for a particle with a diameter of a tenth of a micron or more. A physical law can be applied to show that influences from particulate metals can be excluded from the measurement [1]. The system was tested extensively using lead and goethite as a well defined model surface [2, 3].

We chose lead and zinc as two trace metal ions to adsorb on natural particulate matter from the river Glatt, in Switzerland. This small, highly polluted river was subjected to an extensive study and we obtained analytical data for particle composition and water phase. The particulate material was sampled by continuous centrifugation and freeze drying at two sites of the river. The first site was Fällanden ("F") right after the outflow from Lake Greifen, and the second at Rümlang ("R") after the inflow from some sewage treatment plants.

In this approach we look at the interaction of metals with particles as the formation of dissolved complexes. We performed titration experiments where we added increments of the particle suspension to a small amount of Pb or Zn at pH 8. We then determined the concentrations of the free non adsorbed metal by differential pulse anodic stripping voltammetry (DPASV). Some sample curves of this "inverse" titration are given in figure 2. As we expected from Murphys law, however, the analysis was not a simple matter of mixing metal ions and particles in the polarographic vessel. The surfaces of beaker and electrodes in contact with the sample caused significant adsorption. We were able to overcome this problem by certain arrangements described in [2], [3] and [4].

So, we define a conditional surface binding constant, K^s by formulation of the surface adsorption very generally as the ratio of concentrations from the

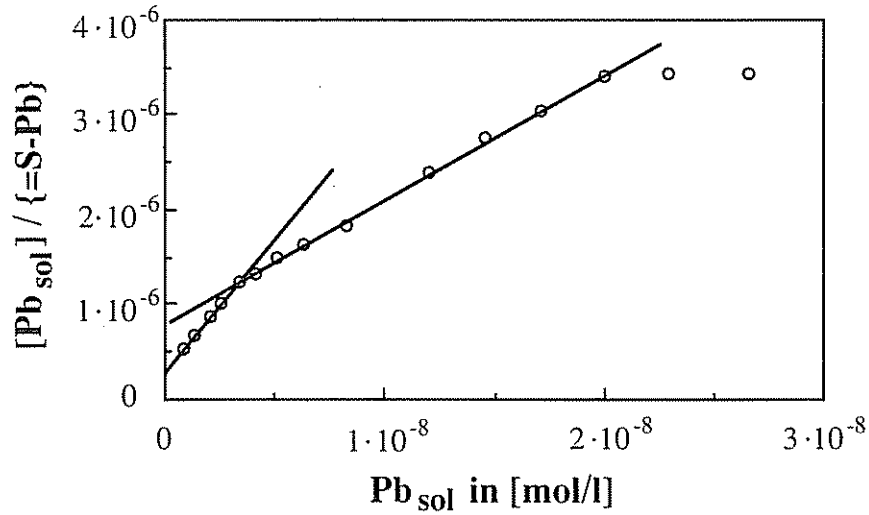


Fig. 3
Example of a linearized titration curve for Pb(II) of the type and conditions of fig. 2. The titration points fit a straight line except the first few points where the surface is overloaded with lead (low Me/surface ratio), and some lead samples that show sites with higher affinity (see text).

equilibrium $\equiv S + Me^{2+} \leftrightarrow \equiv S\text{-}Me$

K^s is valid for a certain pH, ionic strength, surfaces, and for the ligands and metal ions used in the experiment. If we introduce the maximum adsorption capacity Γ_{max} [mol/kg] as a measure for the number of surface binding sites for the concerned metal, we are able to arrange an equation of a straight line for the titration curve. We obtain the maximum binding capacity of the particles, Γ_{max}, and the complexation constant for the formation of surface complexes, K^s, through the slope and intercept of the resulting straight line, as is shown in figure 3 [2,4].

3. Some concluding points:

1. The binding constants of Pb and Zn with twelve different particle samples from river Glatt are very similar. The data from twelve titration experiments are shown in figure 4a. Since the compositions of the particles are quite different, the similarity of the binding constants is striking. The surface binding of lead is stronger than that of zinc by more than one order of magnitude. We obtained the following mean conditional binding constants (pH=8, 10^{-3}M HCO_3^-) for Pb(II) 9.44 ±0.18 and for Zn(II) 8.17±0.20. Obviously no special type of surface groups dominate the adsorption, or in any case there are no

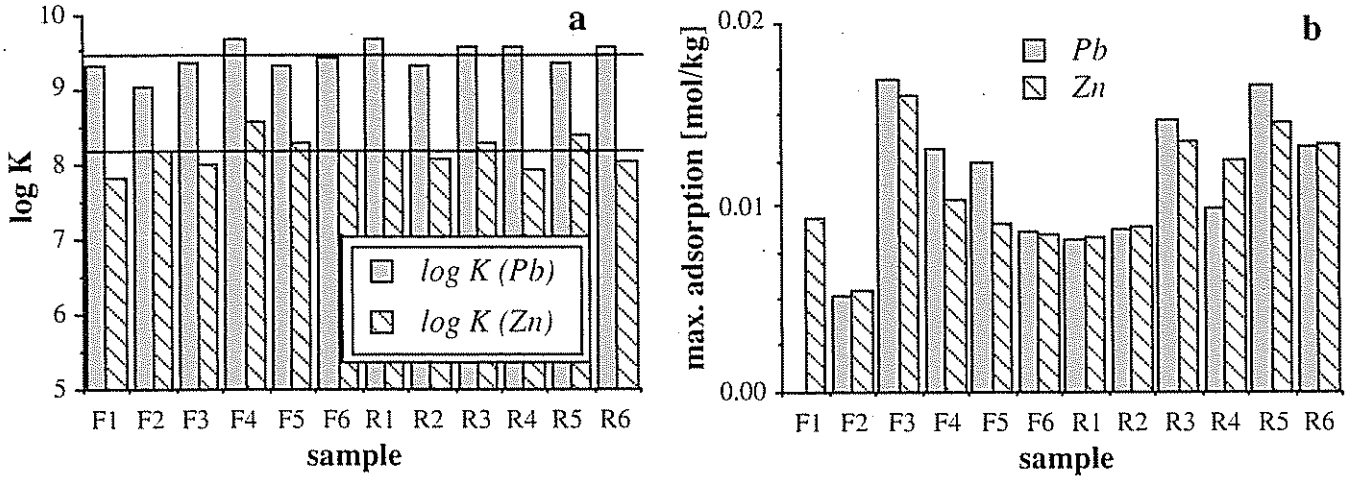


Fig. 4

Conditional surface binding constants (a) and maximum adsorption capacities (b) for Pb(II) and Zn(II) obtained from titration experiments with particle samples from river Glatt. Mean binding constants were calculated log K^{s}_{Pb} = 9.44 ±0.18 and log K^{s}_{Zn} = 8.17 ±0.20. Maximum binding capacities were calculated considering the amount of metal (Pb or Zn) already present on the particles from their natural environment.

particular differences in their metal binding abilities.

2. Adsorption capacities were found to vary by up to a factor of three (see figure 4b.). This variation is connected with size and composition of the particulate matter. The Rümlang samples ("R") which are mainly influenced by the sewage treatment plants and not much by seasonal variations showed a clear correlation of the binding capacity with the Fe(III) content. It was not possible to quantify the contributions of the constituting parameters in detail, but there is clear evidence that particles with high contents on either organic carbon, manganese and/or iron also adsorb high amounts of lead and zinc.

3. There is a competition of Pb(II) and Zn(II) for surface sites. If we calculate maximum adsorption for either Pb(II) or Zn(II) we must take into consideration the metals already adsorbed onto the particles in the river environment. We then obtain a striking agreement between the binding capacities for Pb(II) and Zn(II). The assumption of common adsorption sites is confirmed by the good data fit obtained from equilibrium calculation. These calculations were done using the MICROQL speciation program originally introduced by J. Westall [5].

4. Beneath the ordinary range of surface sites with similar binding constants we found evidence for a fraction of surface sites with much higher affinity towards Pb(II). The complexing sites whose binding constants are almost one order of magnitude higher than the ones with lower affinity, were found through careful analysis of the titration curves (see fig. 3). They reach up to 50% of the total sites in some samples. These high affinity sites are preferentially complexed with Pb(II) and are therefore already occupied in the situation of polluted natural waters. Our findings were also expected and discussed by Ruzic [6].

5. About half of the determined adsorption sites (for Pb(II)) are occupied with Ca^{+2} under the conditions of natural waters with 10^{-3}M Ca^{+2}, 10^{-3}M HCO_3^- and pH=8.0. Ca^{+2} therefore displaces Pb(II) from the surface sites. The same tendency, but much less pronounced, is observed with Zn(II).

6. NTA diminishes the adsorption of Pb(II) by moving the equilibrium to the solution side, a result of the formation of dissolved complexes. We can thereby observe how the binding constant for the Pb(II) adsorption increases with decreasing surface coverage. NTA acts as a metal buffer. The model assumption is fully able to describe the adsorption and complexation processes: the Pb-surface titration curve of an experiment in presence of NTA and Ca^{+2} was in perfect agreement with the MICROQL speciation calculation, as shown in figure 5.

7. Based on the analytical information (pH, concentrations of floating particulate matter, Ca^{+2}, alkalinity, Pb total and Pb filtered, Zn total and Zn

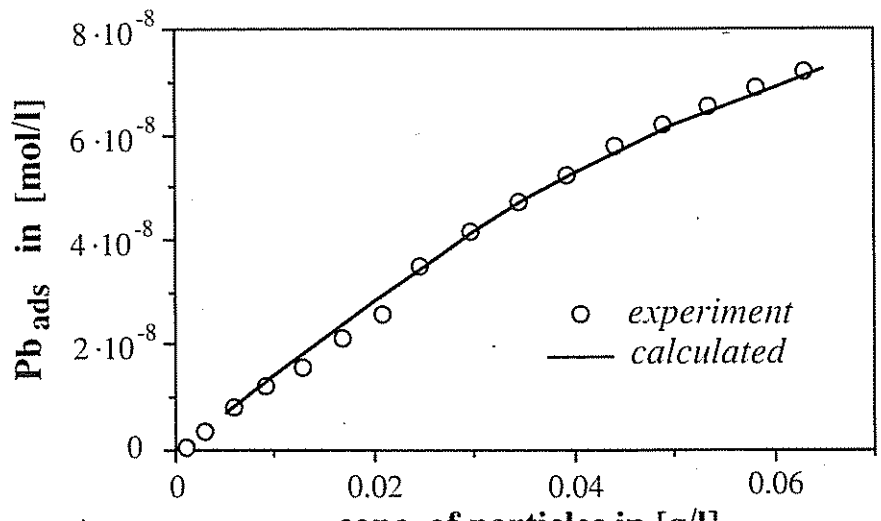


Fig. 5

Titration experiment with $5 \cdot 10^{-8}$M Pb, 10^{-3}M Ca, 10^{-6}M NTA, 10^{-3}M HCO_3^-, pH=8.0 with a particle sample from River Glatt. Dots are experimental data. The line is calculated with the speciation program using the experimental values for K^s and Γ_{max}.

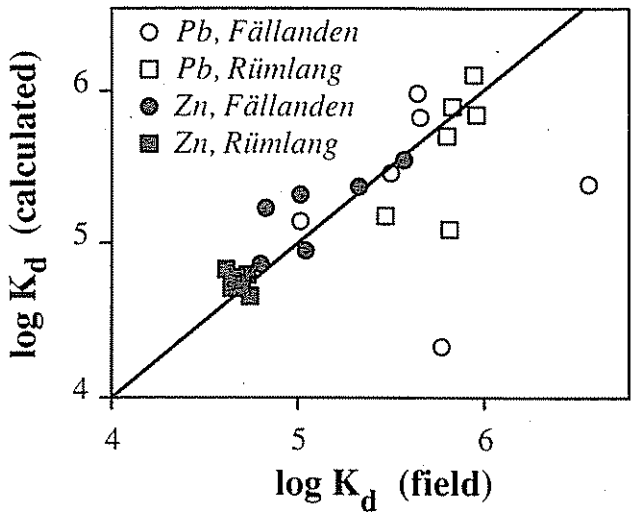


Fig. 6
Comparison of distribution coefficients for the metals Pb(II) and Zn(II) (defined as K_d = conc. in particles/conc. in water) measured in the river Glatt and calculated with data from adsorption experiments.

filtered, etc.) we were able to simulate the distribution of the metals between solution and particulate phase with species calculation on the basis of the adsorption parameters determined in our lab experiments with the corresponding particulate matter. As represented in figure 6. *we obtain satisfying agreement of the distribution coefficients (K_d = concentration of particulate metal / concentration of metal in solution) calculated and measured for almost all samples.*

8. Using the speciation program MICROQL and experimental adsorption parameters we followed the behaviour of Pb(II) and Zn(II) for stormwater conditions where large amounts of heavy metals are carried into the waterphase through the resuspension of particulate material. Since we then obtain an excess of surface sites we do not obtain large concentrations of dissolved metal but decreased free concentrations instead. This is indeed what was observed on the occasion of a high water level due to strong rainfall that was sampled in 1981 [7].

On the other hand however, if the river is contaminated with a certain amount of a trace metal, the metal binding capacity of the particles is increasingly exhausted and an increasing part of the trace metal is in the non-adsorbed state. This means that the concentration of the free aqueous metal ion (and therefore its toxicity) increase overproportional with increasing total metal concentration!

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[7] Gujer W., V. Krejci, R. Schwarzenbach and J. Zobrist (1982), Von der Kanalisation ins Grundwasser - Charakterisierung eines Regenereignisses im Glattal, Gas-Wasser-Abwasser, 999. 298-311

Beat Müller ist collaborator in the section "Chemical Analytics" and, starting this fall, a lecturer at ETH for water chemistry courses in the graduate program (postgraduate course in sanitary engineering and water pollution control)

Visit of Prof. Nikolay N. Vorontsov, Head of the Comitee for Environmental Protection of the UDSSR, on 21. November 1989 in the Lake Laboratory at Kastanienbaum

Prof. Dr. Nikolay N. Vorontsov, biologist (evolution of mammals), and since mid 1989 head of the environmental department of the UDSSR, was accompanied by the director of the Baikal Museum, Prof. Dr. Grigory Galazy, on his visit to the Lake Laboratories in Kastanienbaum.

He has a personal relationship to Switzerland: Vorontsov and Prof. Robert Matthey, zoologist at the University of Lausanne († 1982), exchanged letters for many years. Vorontsov regards Matthey as his teacher, although they only met once on a congress. On the first day of his stay in Switzerland Minister Vorontsov visited the tomb of Prof. Matthey in Pully.

Minister Vorontsov and his Swiss colleague, Bundesrat Cotti, signed an agreement, where common research was one of the goals. Vorontsov thinks of projects for the russian lakes above 2000 meters above sea level.

At Kastanienbaum collaborators of the EAWAG and the knowledgeable scientist discussed such topics as eutrophication problems, ecotoxicology and the relation between eutrophication and fish density.

TRAINING OF APPRENTICES IN SWITZERLAND: THE EAWAG AS A MODEL

MAX REUTLINGER

1. HISTORICAL ASPECTS

The training of specialized workmen in Switzerland has a long tradition. As early as the 14th century workmen in guilds trained apprentices. With industrialization in the 19th century, training was handicapped by the decreasing influence of guilds and traditional professions in factories. On the other hand, Swiss industry was confronted with the fact that products of foreign countries (e.g. England, USA and Prussia) were of better quality than those of Switzerland. The reason was the superior professional training of the foreign workmen. When this fact was recognized in Switzerland, more attention was focused on improved training. As early as 1870, Sulzer founded a training workshop for locksmiths in Winterthur. In 1879, the Swiss trademen's union was founded; this organization was especially involved in the further development of the professional training. In 1884, vocational school attendance was the subject of state legislation. For a long time, lessons were held only on Sundays. Only in 1930 did a governmental law state that a minimum of 5 lessons must be given during working time. The law of professional training of 1980 mandates not only obligatory school attendance, but also introductory courses and requirements for the workshop and teachers. For every profession, regulations define the course content and the training goals.

PROFESSIONAL TRAINING TODAY

After 9 years of schooling, young people must follow a professional training for 2 to 4 years. This training prepares young people for their profession. Usually the training consists of three parts:

a) Training "off the job" in workshops, for example laboratories, and teaching of fundamental knowledge. The training uses simulated problems presented didactically (proceeding from easy problems to more difficult ones). The lessons are given by special teachers and instructors. Small enterprises co-operate and teach their apprentices together in courses which are partially supported by the government.

b) *Training "on the job" in the workshop or laboratory* (Practical application of expertise and methods). The specifics of training are determined by the nature and quantity of the work in progress. Instruction is given by skilled workmen, dealing with daily tasks.

c) The *continuation school* teaches professional and general education. School attendance (1 - 1.5 days per week) is compulsary. Talented pupils can attend the vocational high school which grants access to a technical college.

The apprenticeship ends with an examination, which includes practical and theoretical parts, and indicates if the apprentice will be able to practice his profession. The apprentice who passes the examinations successfully receives a certificate of ability and may call himself a trained workman.

In 1984, 240'000 apprentices were registered in about 400 professions. Most of them were trained in small or mid-sized enterprises.

Costs ...

Estimations of the costs of training an apprentice covers a wide range from 6000.- to 30'000.- Swiss francs per year. The rather small salary of the apprentices minimizes the training expenses and thus stimulates the willingness of private industry to train workmen. The school-fees are supported by the government; all other expenses are covered by the training institute.

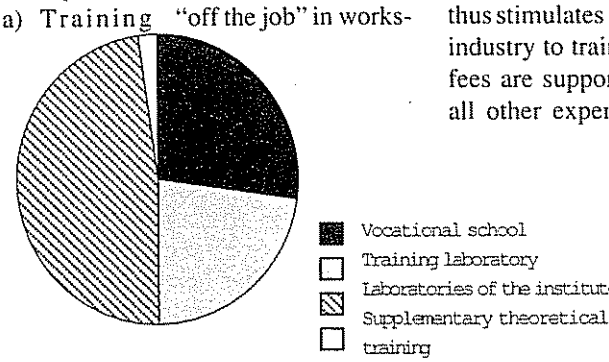


Fig. 1
Distribution of the 3-year training period among school, training laboratory and work place

... and benefits

During the training, the apprentice is partly involved in productive work which decreases training costs. The institution of apprenticeship yields the number of qualified workmen of a profession required by private and public economy. It guaranties a constant and high level of knowledge and therefore excellent quality and efficiency of work.

And last but not least, a well supported professional education is an important economic factor affecting social stability and results (among other things) in a lower unemployment rate for young people than in foreign countries.

2. THE PROFESSIONAL TRAINING OF LABORATORY TECHNICIANS AT EAWAG

At EAWAG we train apprentices in order to supply laboratories of water works and water treatment facilities with young specialists trained in water chemistry. The training methods must be continuously adapted to evolving professional requirements. In earlier days, professional knowledge was transferred directly from an experienced laboratory technican to the apprentice. Now, a part of basic knowledge is acquired in collective courses of instruction in a training laboratory, while the practical application of the methods is learned in analytical and research laboratories. In this way, professional competence is efficiently and intensively developed.

2.1 The education in the training laboratory

The courses are divided up in three parts:

1st year	introduction and analytical chemistry
2nd year	organic synthesis
3rd year	repetition and preparation for the examinations

Introduction

The new apprentices learn fundamental methods with the main focus on analytic chemistry which will be the special field of work of the future laboratory technicians. The training begins

with basic methods such as the use of analytical balances, filtration, distillations, determination of physical constants and gravimetric analysis, but is also extended to more complex proceedings such as chromatography, volumetric analysis and spectroanalytical methods which are often used in the analytical laboratory. Safe handling of toxic, inflammable and even explosive substances is very important and also the methods of ecological disposal of chemical wastes.

Organic synthesis

The official regulations governing the training of laboratory technicians specify that synthetic techniques and procedures (as well as analytical methods) must be learned. These are the object of the second year course which also includes instruction on separation and purification. Every apprentice must perform about 12 experiments including literature research, assembly of appropriate apparatus, synthesis of a product, and purification by distillation or recrystallization. Physical and chromatographic methods are applied in order to determine the quality and purity of the product.

Repetition and preparation of the examinations

At the end of the training the apprentice must pass an examination which will certify him as a chemical laboratory technican. In the 3rd year, the apprentice prepares for this examination. The entire subject matter is repeated. A simulated examination indicates to the apprentice whether his knowledge will allow him to meet the requirements of the examination.

2.2 Laboratories of the institute

Between two courses in the training laboratories, the apprentices are employed in the laboratories of the different research departments of EAWAG: Chemistry, Limnology, Technical Biology and Radiation Chemistry. They are involved in all daily activities. This is a good opportunity to apply their basic knowledge of the analytical methods.

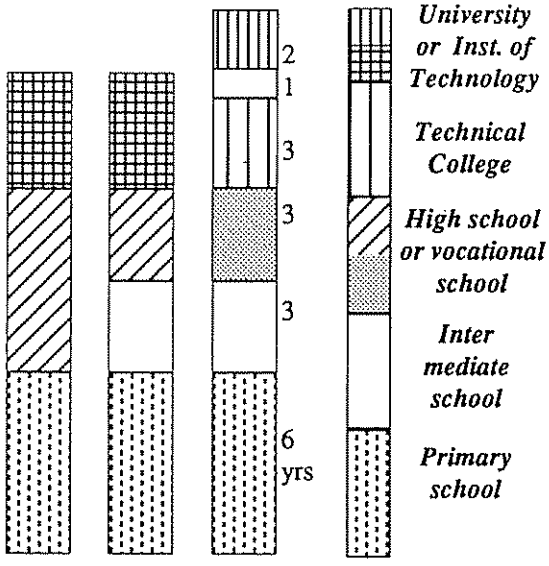


Fig. 2
School system of the Canton of Zurich
After 6 years in the Primary School children can take an examination to enter High School (6 1/2 years) or to enter the Intermediate School (3 years). At age 15 or 16, Intermediate School pupils again have the choice between a vocational school as an apprentice and High School. After the apprenticeship, they can continue their education in a technical college if they pass the entrance examination.
The "Matura" is the equivalent of High School and a bachelor's degree.
With this certificate all studies at a University can be started. After completion of studies at the technical college and an additional course , it is possible to enter the Swiss Federal Institute of Technology and skip the first 4 semesters.

As a rule, the apprentice spends 3 - 6 months in the same laboratory. In this way, the apprentice is introduced to the varying activities of the different departments, resulting in overall professional development. During this important part of professional education, the apprentices are also confronted with the less attractive aspects of their profession, e.g. routine work.

2.3 Supplementary theoretical training at the institute

In addition to a thorough training in sophisticated instrumental analytical methods, some of the basic subjects treated in school are repeated in a more comprehensive form . The apprentices of EMPA (The Swiss Federal Laboratories for Materials Testing and Research) participate in the theoretical and practical courses in the training laboratory.

3. School Training

The attendance at school is obligatory. Here the apprentices are trained for 1 1/2 days per week in professional knowledge and general subjects (inorganic chemistry, organic chemistry, knowledge of material science and ecology, technical mathematics, english, german, political knowledge (civics), economic and business policy, sports).

4. Perspectives of the profession

After graduation most of our young laboratory technicians are employed in the field of analytical chemistry. Some of them work in private laboratories for water quality control or in official laboratories of the government.

5. Possibilities of subsequent development

Continuous improvement of professional knowledge is essential for qualified workmen who are confronted daily with new laboratory equipment, modern instruments and methods.

Professional associations and the government offer a wide variety of advanced training courses.

Many laboratory technicians apply to a technical college or a university, after a special training du

ring the apprenticeship or after a successful entrance examination. The degree of a chemical engineer obtained after the final examination of the technical college grants access to university chemistry departments.

6. Co-operation in cantonal committees

Introductory courses and final examinations are (like many other things in Switzerland) organized in a militia system, i.e.- members of a laboratory staff are delegated for this kind of special function for a short time. Laboratory technicians of EAWAG also act as experts during the final examinations and participate in the examination-board or the commissions for introductory courses.

7. Future

The technical aspects of this profession are rapidly and continuously changing as a consequence of automation and the use of computers. This also requires a steady adaptation of the methods of professional training, which are influenced by any new technology. The professions need a certain number of specialists. It is important to give every laboratory technician the chance to improve his professional knowledge in order to enable him to weather the fluctuations of the labor market and to control his future and his career.

Courses are organized by

- the vocational schools
- the professional unions
- commercial institutes
- government institutes
- colleges for continuing education

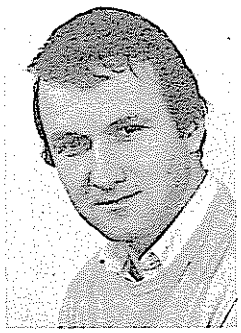
Continuous development of knowledge is an economic necessity for competition on the national and international level.

In the last 18 years, about 70 laboratory technicians (consisting of about equal numbers of women and men) have been trained in this special field of water chemistry. Many of them still work in this function in private or public laboratories. So the expertise of EAWAG is brought to these institutions.

E. Wettstein, R. Bossy, F. Dommann, D. Villiger: "Die Berufsbildung in der Schweiz"
DBK (Deutschschweizerische Berufsbildungsämter-Konferenz)1985.

News about EAWAG and its Collaborators

Professorship in Environmental Chemistry at ETHz



I remember my frist impression upon meeting him for the first time in 1977. René Schwarzenbach, witty, stimulating, engaging, recently returned from the mecca of Science across the Atlantic, and now breaking into the framework of a National Research Program on "exotic" chemicals in Swiss groundwater. It was not long before he delved into the offices and laboratories of the diverse departments at EAWAG, always ready to ask - and answer - questions. I was impressed with his intrepidity in applying physical and mathematical methods and making use of computers.

Now, the federal government has elected René Schwarzenbach as professor in Environmental Chemistry at the ETH Zürich beginning November 1, 1989. It surely was no accident that he was entrusted with the position, because this position plays a central role in the framework of the new Environmental Science program at ETH. After his return to Switzerland in 1977, the bold, precedent-setter Schwarzenbach soon turned out to be a source of ideas and a bridge-builder between the various disciplines. His first effort linked Groundwater Chemistry to Groundwater-Hydrology and Geology. Through work with substances in lakes and rivers, he later brought about contact with lake physicists and mathematical modelers. He had just made the transition from a national foundation scientist to a permanent government employee, when in 1983 he was nominated to the leading panel for the Multi-disciplinary Limnological Research (MLF) group. With that he strengthened additional bridges, those to Microbiology and Ecology.

In spite of the large span of interests he had obtained, he concentrated his efforts further in the area of Environmental Science (in the general area of Chemistry) in writing habilitation thesis, for which he received the venia legendi (the permit to teach university courses required in Germanic-speaking countries) at the ETH Zürich in 1984. I had the pleasure of being his partner for the first course on anthropogenic substances in the environment.

Being a physicist for whom the field of Organic Chemistry has always been a discipline full of unspeakable names, I was fascinated with René Schwarzenbach's gift for giving Environmental Chemistry a quantitative structure by relating physical-chemical methods and by introducing space-coordinates into the test tube.

In the fall of 1987 - the first students in Environmental Science had just begun their program - the planning commission started to look into the details of the study program in the second part of the curriculum. René Schwarzenbach served as chemist on the commission. His input into the commission's work was not confined only to his own discipline, however. Again and again he proposed a holistic approach as the focal point of the new program. Thus, it was largely due to his intervention that the commission expanded their original concept of the program to include a chemical-microbiological component.

The interests of René Schwarzenbach have value for both teaching and research. His persistent search for understandable and fundamental concepts and his central theme, namely, the fate of anthropogenic substances in the environment, make his teaching an adventure for chemists and non-specialists alike. Teaching, for its part, is fueled by research, which for René Schwarzenbach, is not confined only to the laboratory, but also is conducted in the field. Naturally, he does not avoid practical questions.

In spite of his new position, René Schwarzenbach will not leave EAWAG or MLF. Rather, he will strengthen the interaction between EAWAG and ETH in the area of Environmental Science. In the name of my colleagues, I would like to congratulate the new professor and welcome him in his new position. I hope to hear his engaging voice in our hallowed halls for years to come.

Dieter Imboden

New Group Atmospheric Chemistry

Professor J. Alistair Kerr from the University of Birmingham, England and *Dr. David W. Stocker* from the University of Denver, U.S.A. have recently joined the staff of EAWAG where they are setting up an Atmospheric Chemistry Group. Initially they will concentrate on developing a continuing programme of laboratory studies of the rates and mechanisms of important atmospheric homogeneous gas-phase reactions. The studies will be carried out in smog chamber reactors under simulated tropospheric conditions. At present a major interest in tropospheric chemistry lies in determining the pathways of photochemical oxidative degradation of organic molecules (hydrocarbons and oxygenates) in NO_x containing atmospheres, which lead to the generation of photochemical oxidant (ozone plus peroxyacyl nitrates). Later a programme of field studies will be started concentrating on the measurement of the fluxes of trace gas species over various surfaces. It is hoped that at a future date studies of atmospheric modelling will also be added to the group to complete the three major aspects of atmospheric chemistry

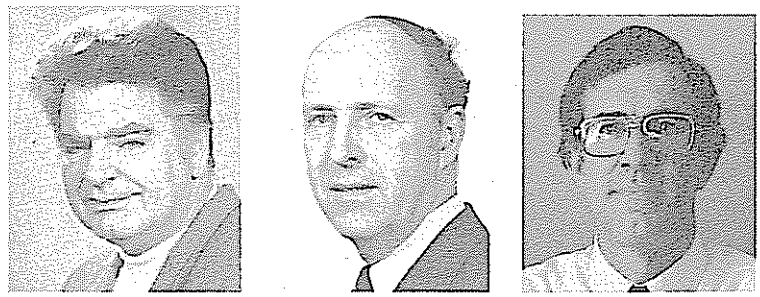
(i) field measurements of trace atmospheric species
(ii) laboratory studies of the reactions taking place in the atmosphere
(iii) computer modelling to apply laboratory data to atmospheric situations with a view to testing possible control strategies for maintaining air quality standards.

Professor Kerr will be responsible for developing the curriculum for atmospheric chemistry at ETHZ for students enrolled in the Department of Environmental Sciences. Professor Kerr is well known in the atmospheric chemistry community for his chairmanship of the IUPAC Subcommittee on Kinetic and Photochemical Data Evaluation widely applied in Stratospheric modelling.

Dr. Stocker has spent the past 2 years collaborating with the U.S. Forest Service making measurements of the flux of NO_x over a Prairie Ecosystem.

Awards

The Office of Research and Development of the United States Environmental Protection Agency (EPA) has cited the paper "Nitrate-Induced Photo-oxidation of Trace Organic Chemicals in Water" by *Heinz Bader (left)* and *Professor Jürg Hoigné* from the EAWAG and the EPA

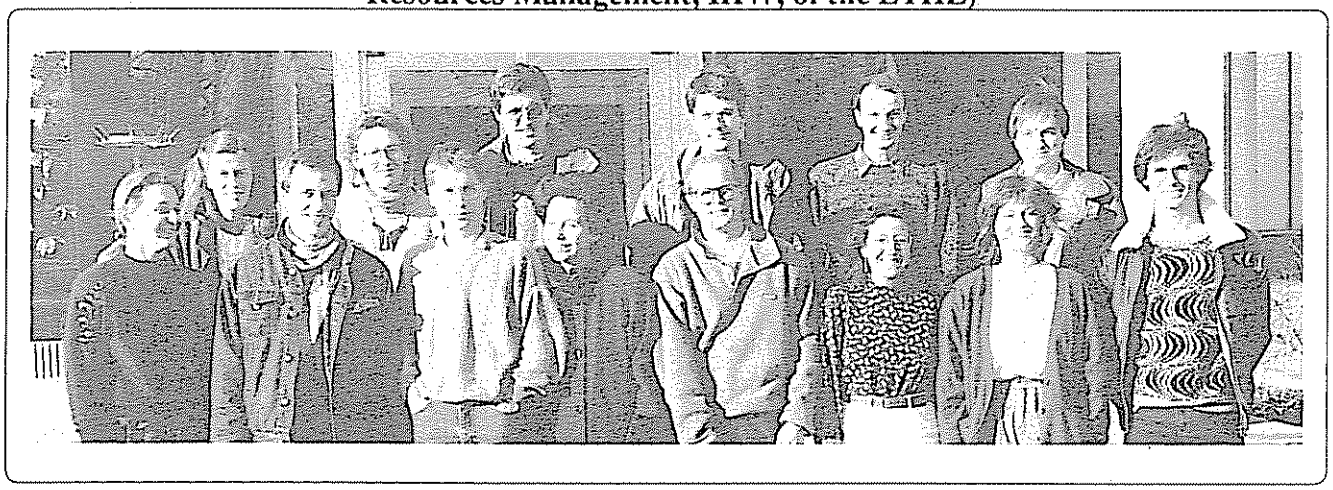


employee Dr. *Richard Zepp (right)*, who spending his sabbatical at the EAWAG laid the ground for the special research publication which appeared in the jounal of *Environmental Sci. & Techn. 21 (1987)* for recognition and accorded to them an award in the annual **Scientific and Technological Achievement Awards (STAA) Program 1989.**

Prof. *Werner Stumm* was awarded a **honorary doctoral degree by the Northwestern University in Evanston** (Illinois, USA, June 1989) and a **honorary Ph.D. from Technion, the Israel Institute of Technology.**

Already a Decade:
Participants of the Tenth Postgraduate Course in Sanitary Engineering and Water Pollution Control

(offered by the Institute of Aquatic Sciences, IGW, and the Institute for Hydraulics and Water Resources Management, IHW, of the ETHZ)



From left to right (front row): Andrea Robien, Tobias Schaller, Ulrich Fischer, Gertrud Fluhr-Meyer, Roland Boller, Carmen Romero- Muther, Yael Mason, Markus Egli. Second row: Barbara Gamper, Marlis Bernauer, Martin Rauber, Markus Greiner, Ralf Ronald Weber, Thomas Schöndorf.

On January 26th 1990 Dr. *Peter Reichert* (at left), Dr. *Jürg Ruchti* (middle) and Dr. *Oskar Wanner* (right) were awarded with the **Seymour Cray** Prize of Switzerland 1989 in the ETHZ.

Beat Müller, doctorand of Dr. Laura Sigg, received the **Silver Medal of the ETH 1990** for his thesis "On the adsorption of metal ions on the surface of aquatic particles".

IAWPRC Pergamon Publication Medal 1990 for the paper "Generalised Model of the Effect of Different Control Measures in Reducing Health Risks from Waste Reuse" by *U.J. Blumenthal, M. Strauss* (IRCWD/EAWAG), *D. D. Mara*, and *S. Cairncross*, which was presented on July 30, 1990 at the Kyoto Intern. Conference Hall.
The Otto Jaag Prize 1989 for the most outstanding thesis in the field of water resources and water pollution control has been awarded to *Nader Al-Awadhi* doctorand of Prof. Geoffrey Hamer, for his thesis entitled "The characterisation and physiology of some thermotolerant and thermophilc solvent- utilizing bacteria".

The distinguished journal "**Environmental Science and Technology**", one of the 24 journals of the American Chemical Society, has appointed new editors additionally to the prevailing ones.

One of their important tasks will be to select thehonorary reviewers ant to get in direct contact with the authors for neccessary correction. For the first time an **editor** is not an U.S. citizen: *Walter Giger* of the EAWAG!

Aquatic Chemical Kinetics

Reaction Rates of Processes in Natural Water

Edited by Werner Stumm

Emphasizing intellectual stimulation over extensive documentation. Aquatic Chemical Kinetics has been designed with a threefold intention:

- to provide an understanding of the general principles of aquatic chemistry:
- to discuss the application of kinetics to the exploration of naturally-occurring processes: and
- to inspire and develop new engineering practices.

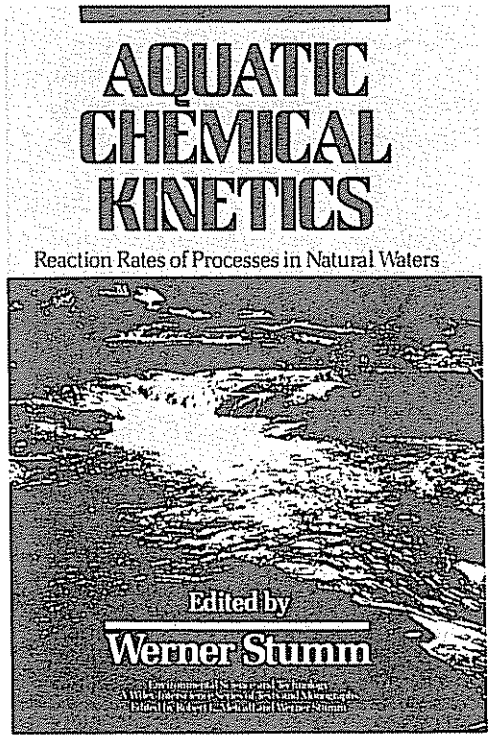
With these objectives in mind, kinetics is introduced with a set of basic principles stressing the elementary reaction as a basic unit of chemical processes. Coverage then progresses from simple concepts to applications in natural water, soil, and geochemical systems.

Discussion of environmetal factors and rates of chemical transformations, chemical catalysis, and linear free-energy relationships follows.

A treatment of the features of chemical kinetic in aqueous solutions and in the context of aquatic systems (oceans, fresh water, atmospheric water and soil), is also included along with disussion of reaction mechanisms and specific reaction rates in natural waters and in water technology.

Special attention is paid to the kinetics of surface reations, ranging from *ab initio*-quantum mechanical calculations and frontier molecular orbiaatl theories to extracellular enzymatic reactions, the adsorption of organic solutes, and redox processes.

Finally discussion is offered on weathering rates as they pertain to the kinetics of colloid chemical processes, as well a the role of surficial transport processes in geochemical an biogeochemical processes.



For professionals involved in physical and inorganic chemistry, surface and colloid chemistry, aquatic chemistry, geochemistry, oceanography, and chemical and environmental engineering, **Aquatic Chemical Kinetics** offers a solid foundation for understanding the general principles and features of chemical principles in aqueous solutions and in the context of aquatic systems.

The book can be ordered from Wiley Interscience 605 Third Ave., New York, N.Y., 10003 (Tel. 212-850 6000).

Guests to the EAWAG in 1989/90

Ahel Marijan, Rudjer Boskovic Inst., Zagreb, Yugoslalvia

Jordi Bruno, Royal Institute of Technology, Stockholm, Sweden

Ingmar Grenthe, Royal Inst. of Technology, Stockholm.

Maria L.S. Gonçalves, Instituto Superior tecnico, Lisboa, Portugal

Zhang Jian, Eng./Computer scientist , Beijing, China

James J. Morgan, Caltech, Pasadena, CA

Manuela Motta, Universidad de Evora, Portugal

James O'Leckie,Civil Engineering Dept., Stanford University, California

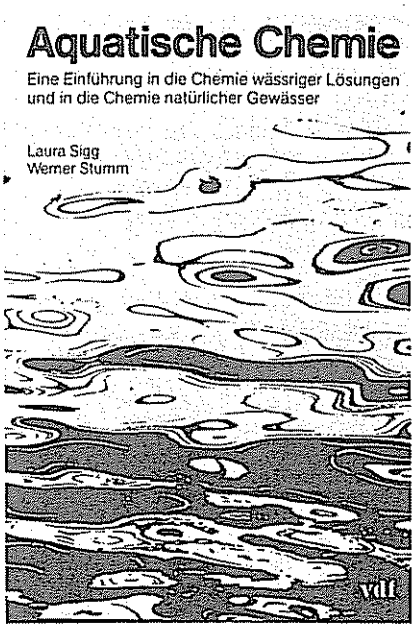
Charles O'Melia, Johns Hopkins University, Baltimore, Maryland USA

Jerald Schnoor, University of Iowa, College of Engineering, Dept. of Civil and Environmenttal Engineering, USA

David van Senden, University of Western Australia, Australia

Aglaia Xyla, University of Patras, Greece

Hanbin Xue, Institute of Environmental Chemistry, Academia Sinica, Beijing, China



Book (German)

Aquatische Chemie

Eine Einführung in die Chemie wässriger Lösungen und in die Chemie natürlicher Gewässer,

Laura Sigg and *Werner Stumm*, vdf (Verlag der Fachvereine, Voltastr. 24, 8044 Zürich), 1989, SFr. 48.-

EAWAG-Publications

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

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