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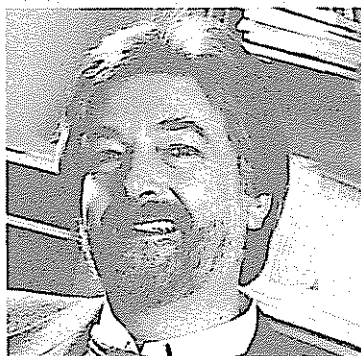
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Prospective thoughts by Alexander J.B. Zehnder

It is not an easy job to succeed Werner Stumm as the director of the EAWAG. Werner Stumm has created one of the world's leading institutions in environmental science and technology. He recognized very early that the environment can only be protected effectively if the cause and effects of pollution are analysed by scientific methods and that the conclusions are supported by hard scientific facts. Werner Stumm overcame some of the major and formidable barriers for environmental research:

He could inspire scientists and engineers from different disciplines of environmental research and stimulate them to combine their knowledge and skills for the analysis of environmental processes and ecological impact studies. He implemented environmental sciences into academic institutions which otherwise would have discovered the environment much later.

He recognized the importance of involving students at a very early stage in environmental science in order to convince them of the importance of environmental issues. He stressed the importance of international collaboration and promoted and supported it where he could. He actively contributed to scientific excellency in environmental research. Scientific excellency was needed in a field that historically covered a wide range of



Alexander J.B. Zehnder was born on 21st February 1946 in Goldach. Between 1974-1976 he worked for his PhD in the biology department of EAWAG on the ecology of methane bacteria under the supervision of Prof. Karl Wuhrmann. In 1977 he was appointed as a research fellow at the University of Wisconsin, Madison (USA), and in 1979 assistant professor in the department of Civil Engineering at Stanford University. In 1980 to 1982 he returned to the EAWAG and lectured at the ETHZ and university of Zurich. In 1982 he was elected as Professor of Microbiology at the University of Wageningen and headed a department of more than 60 collaborators.

more or less scientific research activities, the less rigorous endeavours of which tended to reflect poorly on the field as a whole.

In the seventies the EAWAG helped to develop the *image* and the *base* of excellent environmental research. In the eighties the EAWAG substantially contributed to the *implementation* and *incorporation* of environmental research and studies into the curricula of Swiss universities. Nowadays, every well-respected university has a program in one or the other environmental disciplines.

All this is the merit of Werner Stumm and his collaborators. So, it is perfectly justified to ask what more can the EAWAG do in the future as the environment has been discovered by almost everybody?

A special effort for our future

World-wide the EAWAG is still one of the few institutes with a "critical mass" of scientists and engineers closely collaborating in environmental disciplines. Such a "critical mass" and collaboration is absolutely necessary if the tasks of the future are to be seriously tackled. Where earlier work mainly concentrated on existing pollution and the prevention of it, concepts are now needed for *sustainable development* in view of a rapidly growing

human population that will double in the next century. Already now, more than 25% of the human population has no access to drinking water of adequate quality or is living in an environment where air and soil are polluted in such a way that health is negatively affected.

A special effort is needed to prevent a further degradation of the environment, ideally without the loss of the comforts we are used to. It seems impossible to combine further *industrialization*, increased *agricultural production*, the desire for better *individual life styles and mobility*, and more personal *safety and comfort* for a growing number of people while simultaneously *protecting our environment*. However, to hand down to our children an intact world and a quality of life similar to ours, such a seemingly impossible combination is precisely what is necessary.

The key is sustainable development. It is easier said than done since local, regional, and world-wide concepts are still missing. Sustainable development is a challenge for all of us, regardless of our occupation and position in society.

Principles

One of the major tasks of the EAWAG will be to contribute to sustainable development in the fields of its expertise. The third of the eight principles formulated by *The World Commission on Environment and Development*, also known as the *Brundtland Commission*, in their Tokyo declaration will act as guideline for the future work of the EAWAG:

Principle 3: "Conserve and enhance the resource base"

Sustainability requires the conservation of environmental resources such as clean air, water, forests, and soils; maintaining genetic diversity; and using energy, water and raw materials efficiently. Improvements in the efficiency of production must be accelerated to reduce per capita consumption of natural resources and encourage a shift to non-polluting products and technologies. All countries are called upon to prevent environmental pollution by rigorously enforcing environmental regulations, promoting low-waste technologies, and anticipating the impact of new products, technologies and wastes.

Agenda of Science for Environment and Development into the 21st Century

ASCEND -21 recommends:

- intensified research into natural and anthropogenic forces and their interrelationships, including the carrying capacity of the Earth and ways to slow population growth and to reduce overconsumption;
- strengthened support for international global environmental research and observation of the total Earth system;
- research and studies at the local and regional scale on: the hydrological cycle, impacts of climate change; coastal zones; loss of biodiversity; vulnerability of fragile ecosystems; impacts of changing land use, of waste and of human attitudes and behaviour;
- research on transition to a more efficient energy supply and use of materials and natural resources;
- special efforts in education and in building up of scientific institutions as well as involvement of a wide segment of the population in environment and development problem-solving;
- regular appraisals of the most urgent problems of environment and development and communication with policy-makers, the media and the public;
- establishment of a forum to link scientists and development agencies along with a strengthened partnership with organizations charged with addressing problems of environment and development;
- a wide review of environmental ethics.

Where appropriate, parts of the other seven principles should also guide the EAWAG's future activities. The International Conference on the *Agenda of Science for Environment and Development into the 21st Century (ASCEND 21)* formulated recommendations for the future directions of science which were used in preparation for the 1992 UNCED, and defined the highest scientific priorities, making eight recommendations for future research. All recommendations, though with different priorities, have been taken up by the EAWAG for its future activities.

Strategies

Recommendations and guidelines by international conferences and commissions are formulated in rather general terms. The EAWAG has to concretize some of the recommendations and guidelines that are important for its future work and for fulfilling its task within the system of Swiss universities and government and the international scientific community.

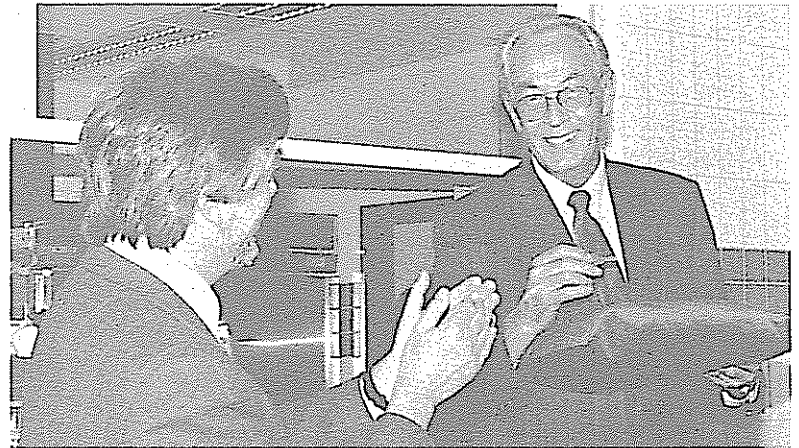
Besides the promotion of high caliber innovative research in the existing disciplines at the EAWAG and the intensification of collaboration between various disciplines to achieve substantive advances necessary for effective protection of our environment, the EAWAG will put special emphasis on integrating more strongly the engineering sciences and molecular aspects of the biological sciences into environmental research, education and consulting. The socio-economic aspects will be further developed and incorporated into the activities of the EAWAG as well.

Our institute will strengthen its *bridging function between fundamental sciences and engineering and their applications*. EAWAG offers support, cooperation and partnership to academia, industry, policy makers and government in general, and international organizations and activities.

Engineers play a decisive role in how our globe will look and how our society will function in the future, i.e. how sustainable our development will be. Thus, it is an absolute must that scientific and economic principles are incorporated into the training and education of modern engineers in order to make them aware of the ecological impact of their activities and how this impact can be optimized positively for the environment.



Professor Werner Stumm was presented with both practical and nostalgic gifts to mark his retirement from EAWAG: an album containing personal recollections, anecdotes and photographs, a computer (essential as the thinking man's workhorse), and a video recorded during his Friday EAWAG seminar on 31st January 1992, suitably entitled "Let the stones speak".



On 1st April 1992 Professor Roland Crottaz presented the keys to EAWAG to the new director Prof. Alexander J. B. Zehnder.

Contrary to the United States, such training has not heretofore received the necessary emphasis in Europe. It is time to correct this omission now. The EAWAG is an ideal place to *fuse both scientific and engineering approaches* and it can therefore help to develop engineers with a solid background in environmental science and technology. It is my personal concern to participate and to support the scientific education and training of our future engineers.

Recent advances in *molecular biology* have significantly contributed to making biological processes and interactions more predictable. These developments are just the beginning of what promises to become an exploding branch of the natural sciences. New molecular techniques provide biologists with the tools for a much more quantitative description, prediction, and -as a consequence- allows them to develop more general concepts. Environmental research can clearly profit from these developments. The EAWAG will not miss the opportunity to include this technology into its future activities.

First Steps

During three days in April, group leaders and the management of the EAWAG discussed the future activities of the institute. Besides many organizational aspects, future research directions were extensively discussed. Readers of the EAWAG-News will be given details in future issues about these activities. It also was decided to start a number of multidisciplinary projects in which the appropriate disciplines of the EAWAG will collaborate. Both scientists and engineers should be partners in these projects. Cooperation is also sought with groups from outside the EAWAG. The projects are

"Waste sites: environmental impact, remediation principles and technology, concepts for future handling of waste and pollutants" and

"Groundwater: influence of anthropogenic activities on groundwater quality". Other possible projects are

"Lake ecology: processes during oligotrophication" and

"Interaction man/environment - concepts for regional sustainable development".

The staff is of the unanimous opinion that the name of our institute should better reflect the present and future activities of the EAWAG and it is proposed to change the name to "Swiss Federal Institute for Environmental Science and Technology", but to keep the acronym EAWAG because of its world-wide familiarity. However, acceptance of this proposal is beyond our control.

Friends

I would like to see the EAWAG to function as the focal point for all those concerned about the environment, interested in the scientific analysis of processes in the environment, as well as the development of concepts and technologies to prevent adverse effects of anthropogenic activities on the environment. It is my desire that the EAWAG will remain a competent partner with its present friends and will do its best to make new friends in the future.

Before ending, I would like to thank everyone who made my start at EAWAG so easy and especially Werner Stumm for his warm welcome and the fine institute that he has handed over to me. ■

Microbes to the rescue?

Factors affecting the survival and maintenance of activity of introduced bacteria for environmental clean-up programmes.

C. Anthony Mason, Patrick Sticher and Geoffrey Hamer

1. Introduction

It is a fact of life that the environment has been harmed through both the misuse and improper disposal of chemical compounds for a significant period of time. We are now paying the price for this in terms of reduced access to and quality of natural resources and of the techno-economic and financial requirements to repair the damage so far done. One of the tools available for the treatment of contamination of the environment resides in the diverse flora of the microbial world, the omnipresent biology of which (except in extreme cases) offers some hope for a reversal of the current trends. Now that the requirement has been recognised, the effective and efficient clean-up of chemically contaminated sites in the environment, notably water (surface and ground), soils and sediments requires a concerted multidisciplinary effort. To achieve this, the environmental engineer has a range of physical, chemical and microbiological methods available as options to carry out the restoration of contaminated sites. The selection of the appropriate strategy will depend on a detailed understanding of the abiotic and biotic characteristics of the contaminated system and a thorough understanding of the mechanism of action of the particular processes involved.

This article will focus on the use of microorganisms for biotreatment of chemically contaminated environments and describe some of the philosophy behind ongoing research projects in the Technical Biology Department of EAWAG. The use of biological treatment strategies has advantages over methods such as incineration, solvent extraction, etc. in that it is cheaper and the possibility that either toxic compounds or derivatives are produced is considerably reduced. Nevertheless, despite (or perhaps more correctly as a result of) only a century of microbiological research, our understanding concerning the diversity, biochemistry, genetics and ecology of microorganisms is still very limited and very largely restricted to laboratory simulations. A prerequi-

site for the successful application of microorganisms is that fundamental knowledge concerning the interactions between microorganisms and each other as well as the influence of environmental factors on their activity and survival is available.

This article will explain why it is important that caution be exercised when making either claims or generalizations with respect to the potential of microorganisms to solve long existing problems. That microorganisms are important in nutrient and element cycling in the biosphere is indisputable and their biodegradative potential has been harnessed and to some extent optimized for example by the wastewater treatment industry. But even in this relatively well researched area, much remains unknown about the microbiology of the process cultures involved.

2. Bioremediation

Bioremediation is the process whereby the degradation of polluting compounds occurs as a result of biochemical activity of micro- and macroorganisms. Two options are available to utilize the biodegradative potential of microorganisms in polluted environments (see Fig. 1). These are:

a) **In-situ Biodegradation** whereby the activity of microorganisms already present in the particular environment is targeted. More effective biodegradation results from enhanced activity of such microbes, either by increasing their activity, e.g., by the addition of suitable additional nutrients which were otherwise limiting their activity, and/or by increasing their number so that their activity can be more effectively asserted in the particular system. After the Tanker Exxon Valdez accident in March 1989 off the coast of Alaska, this approach was one of the methods that was used for the clean-up operation. 150 Kilometres of the oil contaminated coast was sprayed with various nitrogen- and phosphorous- containing

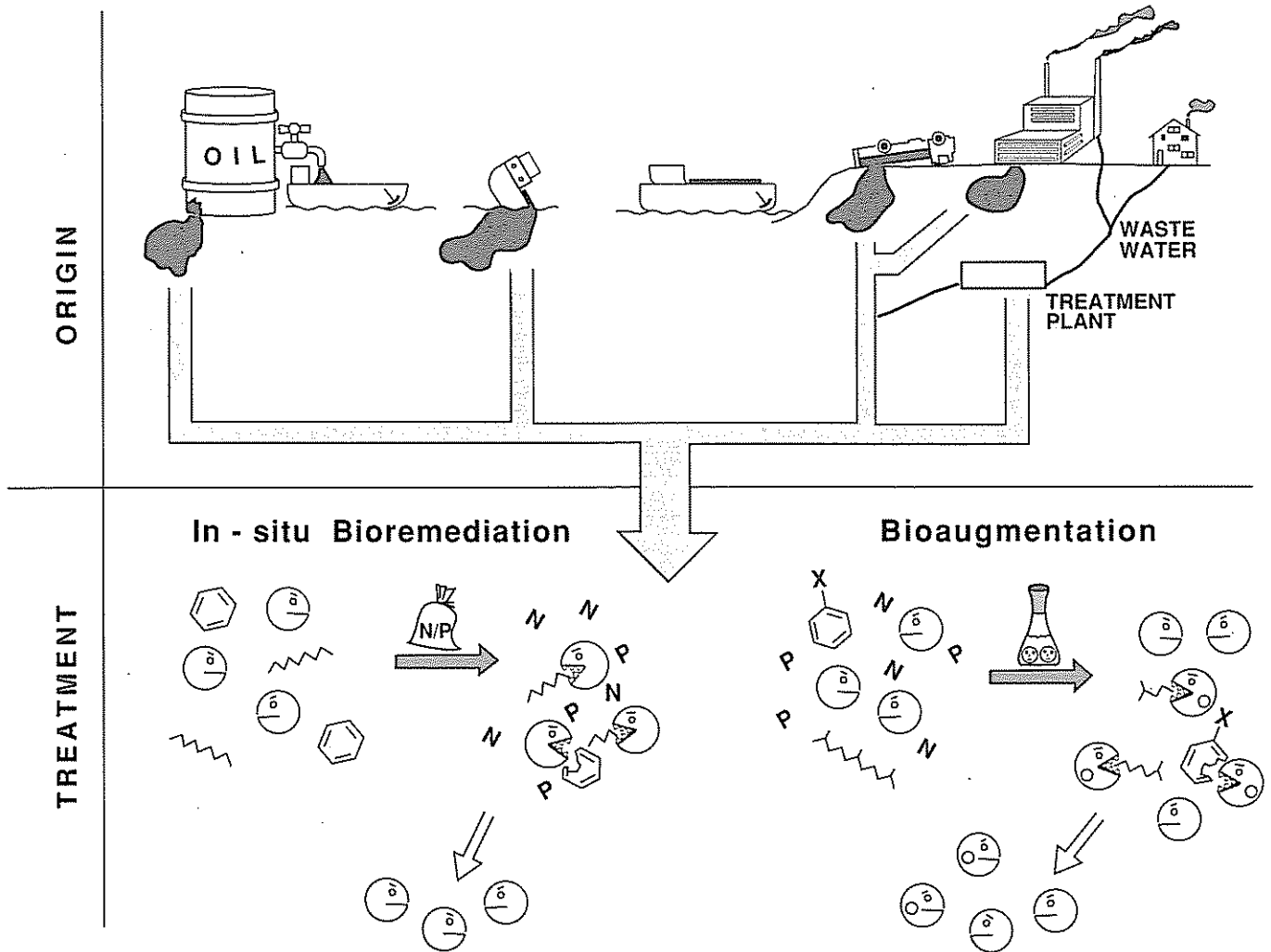
fertilizers. As a result, the biodegradation efficiency of the indigenous microorganisms was increased by a factor of ten. [1].

b) **Bioaugmentation** whereby specific microorganisms which possess a known specific biodegradative or other potential activity are introduced into the affected environment. The basis of this technique is to target the contaminating chemical pollutant with a microorganism known for its ability to degrade that particular compound. The strategy of introducing microorganisms into environments foreign to those where they are usually found or to where they may be present but in low numbers is surprisingly common in environmental biology and parallels can be seen for example in the use of biological pest control agents, in composting and in biofertilizers. The addition of the bacterium *Rhizobium* to soils to enhance nitrogen uptake as a result of a symbiotic relationship with the roots of plants has been common practice since 1890 [2].

3. Genetically Engineered Micro-organisms for Bioremediation ?

There has been much discussion (scientific, political and emotional) concerning the potential to apply genetically engineered microorganisms into the environment and in this connection, it is important to make a few important remarks.

It is often very difficult to isolate a single microorganism able to completely mineralise a particular pollutant through to CO₂ and H₂O. It is more likely that the necessary enzymes to achieve the breakdown of a compound are found distributed in the metabolic potential of different microorganisms. One proposal that has been made is to pool all of the biodegradative enzymes of interest together into a single "superbug". Complete biodegradation can then be achieved by engineering the biochemical capability of a particular carrier microorganism [3]. Many of the genes which encode the necessary



enzymes for biodegradation some of the more persistent pollutants, are not found on the main chromosome of the bacteria in question, but are carried on extracellular "mini-chromosomes" known as plasmids [4]. These plasmids are in fact much more mobile than the main chromosome and their natural transfer is something that is a regular feature of genetic exchange and evolution in the environment. Various natural mechanisms also exist by which genes on the chromosome itself can be transferred in the natural environment [5]. The current technological status in molecular genetics has rendered these genes readily amenable to laboratory manipulation and transfer and construction of strains of bacteria with additional biodegradative phenotypes is realistically feasible. Since both natural and laboratory methods exist for manipulating the biodegradative capacity of microorganisms the questions of whether and how they can be used for biotreatment programmes require careful evaluation. Genetically engineered microorganisms

Fig. 1.
Two alternative strategies for bioremediation

a) During in situ bioremediation, the activity of the indigenous microorganisms is exploited. It is frequently necessary to enhance the biodegradation efficiency by the addition of suitable nutrients

b) Bioaugmentation - or the addition of laboratory grown, specialist microorganisms. This approach is necessary when the available population is unable to biodegrade the pollutant chemicals.

(GEMS) are already being tested in other countries outside of Switzerland to assess their potential for enhanced bioremediation.

4. Microorganisms, Consortia and Communities

Microorganisms are rarely, if ever, found in pure cultures. Microbial community structure in the natural environment is complex and unfortunately little understood (Figure 2). During the last few years the nature of community reactions has become a focal point of research. The reasons for this is that biodegradation and nutrient cycling reactions are mediated by interacting groups of highly specialized microorganisms operating together in concert to carry out the microbial transformations observed on the macroscopic level [6]. The biochemical flexibility of a microbial community in a particular environment is due to the nature of and interactions between the various microbial consortia present. That

biodegradation of contaminated environments should be a community level process rather than exclusively concerning the ability of an individual microorganism is both advantageous and disadvantageous. From the negative perspective it is unfortunate that, under most conditions, no single microorganism can be added whereby the pollutant is then completely mineralised by that particular microorganism. Indeed the common approach to examine the biodegradation ability of particular pure cultures of microorganisms has been to follow the removal of the original pollutant in bench-scale experiments in the laboratory. Often, microorganisms are selectively enriched using strategies designed to isolate that microorganism which can independently completely biodegrade a particular chemical compound. But such selection pressures do not necessarily pertain in nature. Here, the need for a single microorganism able to biodegrade a very wide spectrum of problem pollutants (the so-called "superbug") is an unrealistic prospect. The reason is as follows; in nature, the biochemical diversities of microbial communities are quite remarkable. When conditions in a particular environment change slightly, e.g., temperature changes, variations in nutrient supply etc, then the microbial community is able to accommodate this change with either slight or dramatic shifts in the balance between different individuals of the community. If a localized environment is severely contaminated with a particular substance that has been shown to be biodegradable in laboratory studies, this implies one of three possible causes: A) that the substrate is unavailable in the system due to either physical partitioning into an inaccessible site or because of chemical interactions binding the substrate to the surface, B) that a key stage in the biodegradation process is missing from the biochemical potential of the indigenous community or C) that the appropriate organisms have become restricted as a result of the lack of or limitation of a particular essential nutrient, e.g., N, P. This explains why natural in-situ bioremediation might not work without first amending the nutrient requirements of the indigenous population and how direct manipulation of the community can allow a change in the microbial balance thereby enabling biodegradation to occur through the concerted effort of new microbial consortia.

5. Survival and stability

Irrespective of the nature of its origin, the fact that a particular microorganism can be selected for or maybe engineered is only the first step in the overall bioremediation process. The second stage is to introduce that organism into the new environment in such a way that (a) it is able to establish itself without being excluded by competition, and (b) will remain active in the environment. There is already some information available concerning the survival and maintenance of introduced selected bacterial strains. In several instances it has been shown that, particularly in environments with low levels of hazardous pollutants, i.e., under those conditions where the selection pressure to maintain the introduced strain is low, then the introduced strain is unable to establish itself unless introduced at very high concentrations [7]. This is frequently an unrealistic strategy. The main reasons for the failure for successful establishment include predation by protozoa, infection by bacteriophage or non-availability of nutrients as a result of competition by other microorganisms with higher substrate/nutrient affinities. This scenario is particularly applicable to contaminated lakes and aquifers. The mechanisms involved in survival of bacteria in environments foreign to their indigenous environment are still poorly understood. Generalizations are difficult partly due to the enormous spectrum of microorganisms both from the points of view of taxonomic and biochemical diversity as well as a result of the different physical and chemical parameters which prevail in different environments and their influence on survival characteristics. How introduced strains interact with indigenous strains particularly with respect to genetic exchange and how the structure and function of the consortia are affected is also poorly understood (Figure 3). In addition there has been a tendency to rely on old established methods (e.g the plate count) for the detection of microorganisms in the environment despite the fact that the sensitivity of these methods has now long been shown to be totally inadequate [8].

6. Molecular Ecology and Detection Technology

The advent of molecular biology has also brought with it a new science, molecular ecology. This science is concerned

with the molecular mechanisms involved in the interaction of a microorganism and its environment. Research is now directed towards examining the interaction between a microorganism and its environment at the molecular level. This entails looking at what regulates the expression of particular genes, how microorganisms respond, at the genetic level when they encounter unfavourable physical conditions or when they are exposed to chemical pollutants. Characterization of the so-called "stress response" as a consequence of interactions with environmental contaminants is an active area of research in the Microbiology Department in EAWAG.

In addition, molecular ecology is concerned with the development and application of new molecular based techniques for the more precise enumeration of specific bacteria even in a background of a diverse range of numerous other species. It is indeed now possible to very carefully monitor the fate of a particular microorganism much more precisely than was previously possible. Detection technology is also a very important feature during the developmental and research phase of bioaugmentation programmes. One important feature of the newly developed methods for molecular ecology is that they are based not only at the level of the whole microorganism but also at the level of single genes and therefore allow one to follow the fate of particular genes in a system - techniques and data essential for scientific debate of the question of environmental release.

7. Single Substrates are Laboratory Myths: The Real Environment is Complex!

Most of this discussion has been limited to the somewhat special case of a single chemical pollutant. However when one critically examines the nature of polluted environments it can be seen that they can be broadly categorized into three groups. (a) those polluted by complex mixtures, i.e., crude oil, fuel oil, kerosine, coal tars etc, (b) those polluted by simple mixtures, i.e., simple solvents, explosives etc and the third category (c) those polluted by diverse wastes including off-specification chemicals and ill-defined/modified chemicals e.g., fire-damaged products. General solutions are possible for the first two categories but the complex and uncertain nature of the third category

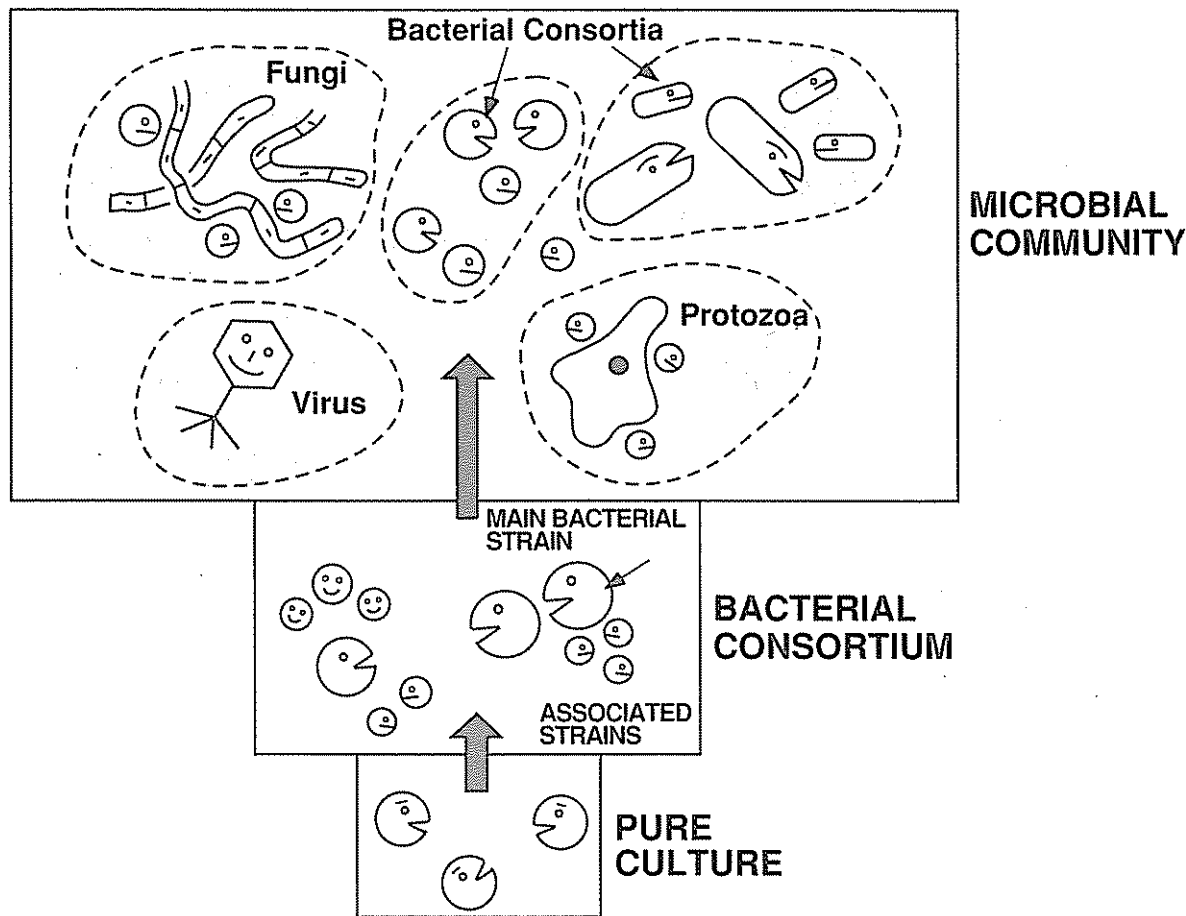


Fig. 2
Schematic representation of the composition of a microbial community

imposes the requirement to examine each on an individual basis. It is therefore not surprising that the pure culture mono-substrate approach cannot be applied in practise despite the voluminous data which has been produced from laboratory studies. Thus, the problem facing the environmental microbiologist is not only to develop strategies for successful application of a single microbial species but to define the mechanisms by which introduced populations consisting perhaps of one or several stable consortia capable of growth on or metabolic transformation of the mixed substrates will interact and compete in the natural environment.

8. Bioaugmentation Strategies

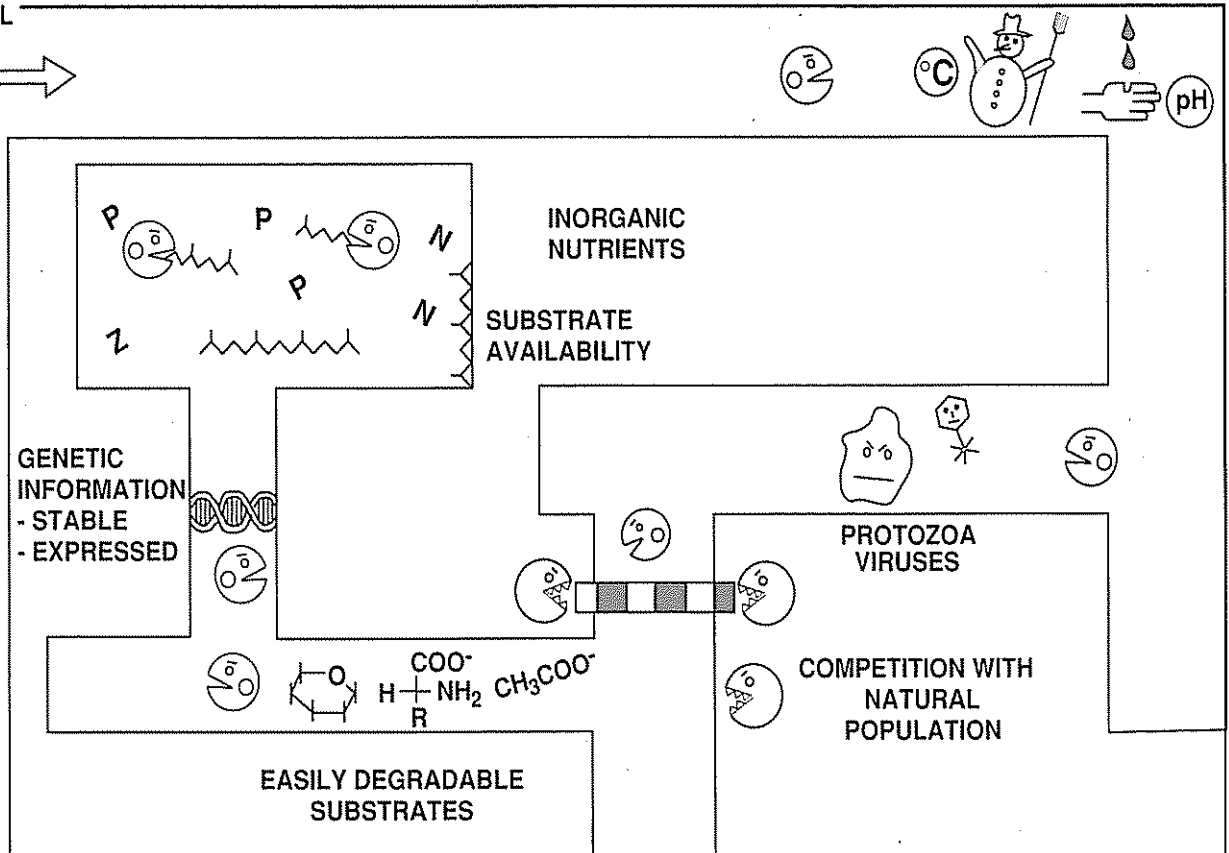
One unfortunately only too common pollutant which has both quantitative and qualitative effects on the natural environment is oil. Permanent damage to many biological processes can result from contamination with some of the hydrocarbons in oil resulting in mutagenesis even

when present at very low concentrations. The anthropogenic input of oil into the environment is relatively high as a consequence of its intensive use as a fossil fuel and as a raw chemical in the chemical industry. Complex transportation networks are also a major source for oil pollution. In the latter example. In 1981 an estimated 1 - 2.6 million tons of hydrocarbons were released into marine ecosystems. Of this, 0.3 - 0.4 million tons were due to tanker accidents. From institutional and private consumers in 1981 an estimated 0.6 - 3 million tons of hydrocarbons were released into marine waters in 1981, while 0.03 - 2.5 million tons were released into the marine ecosystem from natural sources [10].

Recently, bioaugmentation programmes have been employed for the purification of contaminated coastal areas and in wastewater treatment plants. In many instances the results were not very good or it was difficult to show that the resulting degradation was due to the activity of the

MICROORGANISM
WITH SPECIFIC
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introduced microorganisms. One research group in Buffalo (USA) tested the performance of 16 commercially bacterial strains recommended for bioaugmentation. In no instance was the biodegradation potential of the indigenous bacterial strains improved [11]. However, it is important that these results are not interpreted so as to imply that bioaugmentation is an inefficient process. What these results in fact show is that it is the uncontrolled addition of microorganisms to natural systems is unlikely to result in the achievement of the treatment objective. When sufficient knowledge and careful control of both the system and the system parameters are available, bioaugmentation can be a highly effective tool to combat environmental contamination problems. Moreover, given sufficient system data, it is a multi-faceted tool and with potential economic advantages for improved biodegradation by microorganisms especially in such systems as in industrial wastewater treatment. How efficiently a specialized microorganism will carry out its desired function in a natural system is very much dependent on the local environmental conditions and on the process control. For success of a bioaugmentation program it is necessary that the intro-

Fig. 3

The maze of physical, chemical and biological barriers which an introduced microorganism must overcome before it is in a position to degrade the chemical pollutants.

duced microorganisms can establish themselves on the one hand, and on the other hand the metabolic pathway(s) for the biodegradation of the problem compound(s) must be active under the prevailing environmental conditions. We are interested in the possibilities of influencing the behaviour and the interactions of a supplemented bacterial mixed culture by examining how it responds, with respect to culture survival and activity under different environmental conditions.

Particularly in the case of wastewater treatment, there have been a variety of approaches proposed as to the way in which microorganisms can be added to an existing culture to enhance the biodegradative capacity of a particular process [12]. In most municipal wastewater treatment plants such additions are largely restricted to the initial start up phase, while additions subsequent to this are frequently ineffective as a result of the overgrowth and out-competition by other members of the microbial and protozoan populations of this particular environment. This is somewhat of a problem because it is particularly in this system where the opportunity exists to retain

certain pollutants before they have the chance to enter into the environment. A good example in this respect concerns the hydrocarbon pristane. This branched chain (C-19) hydrocarbon is found both at the sites of oil spills and in the wastewater from oil refineries. Until recently this compound was regarded as being recalcitrant to biodegradation as it was consistently found at the sites of oil spillages without any change in concentration. Nevertheless, strains of microorganisms capable of the biodegradation of this compound have been isolated in our laboratory by C. Kroll. In all likelihood the reason that this compound is not biodegraded in the natural environment is not that the microorganisms capable of its biodegradation are not present but more likely is that these microorganisms are also capable of growing on other substrates, which are likely to be used preferentially to pristane (shorter chains, less branching etc.). However, as soon as the other substrates have been removed from this environment the pristane can no longer be degraded. One possible hypothesis to explain this is that other nutrients have become limiting (macro or trace elements as in the case of the marine environment) thereby inhibiting pristane metabolism. Thus in a wastewater treatment plant handling the wastewater from an oil refinery it is not surprising that the same processes occur, namely that the other nutrients are preferentially utilized causing pristane to persist and be released into the environment. One particular strategy for bioaug-

mentation uses the technique of immobilization. The immobilization of microorganisms results in dramatic changes in their physiology many of which appear to be beneficial as far as the biodegradative capacity is concerned. In addition, an immobilized system need not be subject to washout and competition events and is now an area of increased interest for treatment programmes.

8. Conclusions

This overview stresses the importance of understanding not only the physical and chemical and factors which can influence the successful outcome of a biotreatment programme but also the need to be able to comprehend the biology. In most instances individual situations have to be handled on a case by case basis and access to fundamental and applied research data is indispensable. That bioaugmentation strategies could in some instances have failed to be successful maybe due to inadequate consideration of the environmental factors rather than to a deficiency in this particular strategy. Many different approaches are possible and each has to be carefully evaluated to determine the most appropriate. Nevertheless, a lot remains to be learned about the problems involved in the survival of microorganisms in both natural and engineered environments and such information will serve as a valuable basis in the endeavour to achieve a cleaner environment.

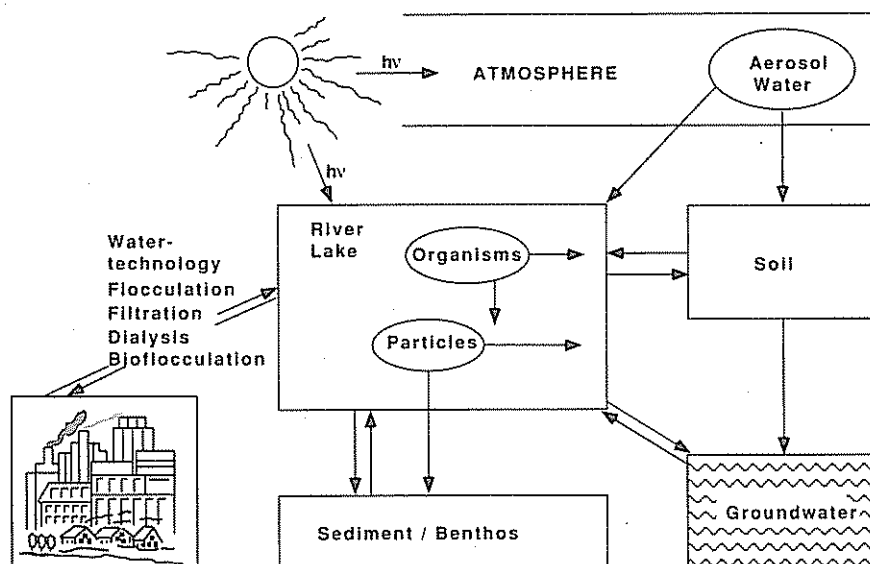
We would like to express our thanks to Mario Snozzi for his comments and contributions to this article.

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Interfacial Chemistry

A Key to the Understanding of Chemical Processes in Natural Waters and in Water Technology

Carrick M. Eggleston, Laura Sigg, Werner Stumm,
Barbara Sutzberger, Bernhard Wehrli, and Jürg Zobrist



1. Why Interfacial Chemistry?

It is often assumed that a water chemist occupies himself with chemical processes in solution. One overlooks the fact that most important processes, e.g. buffering of the water, many acid-base processes, dissolution and precipitation of minerals, reduction and oxidation processes occur to a large extent at the mineral-water, at the particle-water and the organism-water interface. Furthermore all processes of water technology - biological purification, coagulation, flotation, filtration, activated carbon adsorption - occur at interfaces (Table 1).

Fig. 1 depicts a scheme for the reciprocal interaction of the various reservoirs of our environment. The conveyor belt of aerosols in the atmosphere and the conveyor belt of aquasols (suspended particles and dispersed colloids in rivers and lakes) transport a significant fraction of pollutants and of reactive elements. The interaction between dissolved substances and particles and their surfaces and the processes at the sediment - water interface in soils and in aquifers (adsorption, desorption, dissolution, precipitation) determine the residual concentration of solutes.

Fig. 1

Chemical processes at interfaces regulate to a large extent the composition of dissolved aqueous constituents.

Suspended particles, colloids, and microorganisms (especially algae) are important adsorbents for metals, metalloids, phosphates, humic substances and organic pollutants. The affinity of the reactive elements and substances for the surfaces of these particles (which are transported in a continuous conveyor belt and settle) determine the residence time, the residual concentration and the ultimate fate of these substances.

The aerosols are important carriers of many atmospheric pollutants (especially less volatile substances) into surface waters.

Processes in soils and aquifers are also dominated by processes at the mineral - water interface. The interfaces in aquifers retard the transport of metals and of organic pollutants.

Colloids, the Neglected Dimension. Colloids - suspended particles with a size between 1 nm and 1 μm - are ubiquitous. They are present at concentrations often exceeding 10^6 colloids per cm^3 in oceans, lakes, rivers, and even in groundwaters. These colloids are characterized by very large specific surfaces ($>100 \text{ m}^2$ per cm^3) and may play a not yet well understood role in the transport of pollutants. In water technology colloids are brought to agglomeration (flocculation, coagulation) and settling or are removed by contact filtration.

From Nanocosmos to Global Ecosystems. The different reservoirs of our environment (atmosphere, surface- and groundwater, soils, sediment, biota) which participate in local and global cycles of elements and pollutants in our environment contain materials which are characterized by large area to volume ratios. These are the surfaces which are very efficient in the regulation of our environment; thus, we expect that the various surface chemical processes which are investigated at EAWAG, from different points of view, contribute also to an understanding of geochemical cycles. The particle surfaces and organisms couple

Table 1
Unit Processes in Water Technology

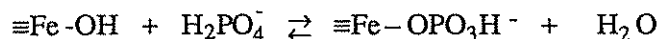
Examples of improvements of water technology by a better understanding of surface chemical processes	
Process	Concepts of Interfacial Chemistry
Coagulation	Surface-chemical reactions regulating surface charge
Filtration, Contact filtration	Mechanism of attachment of particles on filter grain
Flotation	Attachment of gas bubbles to particles
Ion Exchange	New synthetic ion exchange resins
Phosphate Elimination	Chemistry of phosphate precipitation, contact filtration
Activated Carbon Adsorption	Regeneration of activated carbon
Biological Treatment	Bioflocculation, adhesion of bacteria

some of the cycles and their interdependence; an analysis of these processes may assist our understanding of global ecosystems and how they are disturbed by our civilisation.

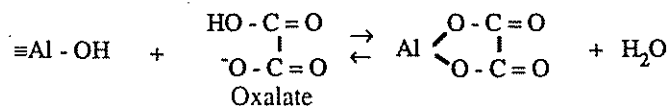
2. Structure and Reactivity

The structure of the surface, e.g., the type of functional groups and their arrangement at the surface, and how these groups interact with H⁺, OH⁻, metal ions and ligands (anions and weak acids), determine the reactivity surface, e.g. how fast a mineral is dissolved, how a surface behaves catalytically in a redox process or a photochemical process, or how colloids or suspended particles agglomerate or become deposited on surfaces.

The Surface Complex Formation Model. At the international Colloid Symposium 1976, Paul Schindler (Berne) and Werner Stumm (EAWAG, ETHZ) introduced the "Swiss Model" for the adsorption of metal ions on hydrous oxide surfaces. The model was later extended to ligand exchange (adsorption of anions and weak acids) (Stumm et al. 1980).



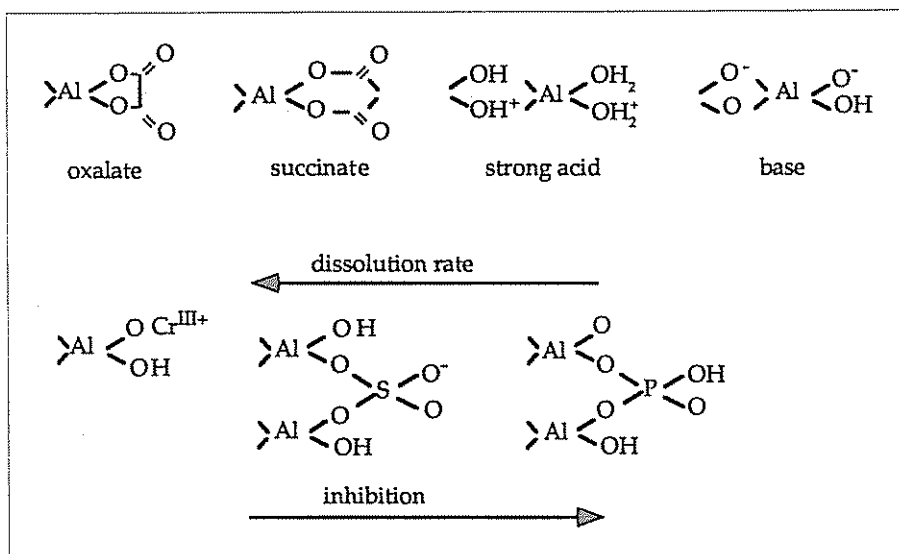
or



The model interprets adsorption in terms of the coordination chemistry at the solid-water interface, e.g., a chemical interaction of an oxygen donor atom with a metal ion or the interaction of the central ion of the surface lattice with a base (ligand). Chemical bonds (modification of the electron orbitals) are formed; the stability of surface complexes, similar as with complexes in solution, can be quan-

tified by mass law constants. The complex formation model, despite early criticism, now finds wide application (Dzombak and Morel, 1990, Stumm, 1992). The model permits the prediction of the distribution of reactive elements (heavy metals, metalloids, radionuclides phosphate and other anions) between particle surfaces and the solution as a function of pH and solution variables.

The Kinetics of Dissolution of a solid phase is controlled by chemical processes at the surface (and not, as has been previously believed, by transport processes). The dissolution rate of a mineral depends on the surface speciation, i.e., on the type of surface complexes. For example, the dissolution rate of Al₂O₃ decreases in the sequence shown:



The arrangement of the surface complexes and the distribution of electrons (orbitals) and the question whether mononuclear or binuclear complexes are formed determines whether a dissolution is enhanced or inhibited. The evaluation of these interdependences brings new insights into processes like mineral weathering and corrosion inhibition (passive oxide films).

The dissolution of silicates is influenced not solely by the hydrogen ions in solution but also by the possible presence of complex formers such as oxalate. This complicated dissolution reaction occurs only at preferential sites of the silicate surface (Fig. 3, see next page). Because of the resistance of silicates to dissolution, con-

centrations of dissolved ions, such as calcium, magnesium, potassium, sodium, and of silicic acid in the runoff are in the range of 0.01 to 0.2 mM.

Similar considerations provide the theoretical basis for the understanding of reductive dissolution of higher-valent oxides such as Mn(III,IV)(hydr)oxide and Fe(III)(hydr)oxide and of photochemical processes occurring on the surface of naturally occurring semiconductor minerals; furthermore, better theories on the catalysis of reduction and oxidation processes, e.g. with reactions of organic substances, by the solid - water interface can be derived.

Precipitation, Crystal Growth, and Biomineralization. The functional groups at the surface also direct and control kinetically the processes involved in the formation of a new phase (nucleation, crystal growth). At the crystal interface, especially in biomineralization, a "molecular" recognition occurs; the surfaces of templates, nuclei and crystals can be thought of as being composed of "active sites" that interact stereospecifically with ions or molecules in solution, in a manner similar to the interaction of enzymes and substrates or antibodies or antigens. Crystals can be engineered with desired morphologies; molecular recognition by the surface determines which mineral phase is formed and whether the crystal grows as plates or needles.

3. The Nanocosmos: Atomic Surface Structure

Ultimately, chemical and biochemical processes depend on the atomic and electronic structures of the atoms and molecules that react with each other. It is clear that mineral surfaces and surface complexes play a crucial role in regulating the chemical interaction of natural waters with the rocks, soils, and sediments that they constantly encounter. Here, we look at the atomic structure of surfaces and surface complexes. It is said that "structure is the key to function"; direct study of surface structures will lead to a more thorough understanding of the function of mineral surfaces as environmental regulators.

Fig. 4 is an image of an iron oxide (hematite) surface taken using a scanning tunneling microscope (STM). The magnification is extreme - a line of five million of these blocks would be only one centimeter long. The array of bumps in

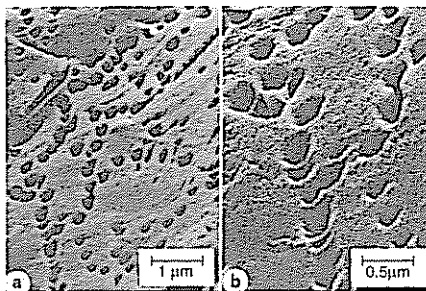


Fig. 3
Scanning electron micrograph of corroded feldspar grain. The enlargement shows the etch pits aligned along subgrain boundaries. Etch pits have narrow size distribution. (From Giovanoli, Schnoor, Sigg, Stumm and Zobrist, 1988)

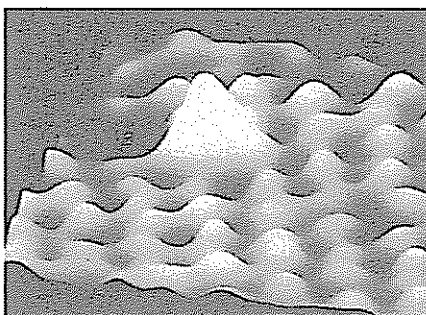


Fig. 4
Image of an iron oxide (hematite, $\alpha\text{-Fe}_2\text{O}_3$) surface taken with a scanning tunneling microscope (STM). The regular array of bumps corresponds to surface oxygen atoms. The large bump is a Cr(III) complex chemically bonded to three oxygen atoms (see text for discussion)

rows corresponds to surface oxygen atoms. The large bump is a chromium atom (or, more precisely, a surface complex containing a single chromium (III) atom and its coordinating H_2O ligands) which is chemically bonded to three of the surface oxygen atoms. The STM image shows the distribution of electrons around the oxygen atoms, and the disturbance of this distribution caused by the presence

of a chromium adsorbate. Because chemical bonding is by definition a shift in electron distribution around atoms, such images contain valuable information concerning the nature of bonding between adsorbed atoms or molecules and the mineral surface, and the structure of the adsorbed complex. Sequences of similar images show that chromium atoms move about on the surface, but only very slowly. This fact shows how strongly chromium is bonded to the surface, and can be used to calculate approximate surface diffusion coefficients. Surface and grain-boundary assisted diffusion is one of the less well known aspects of solute and contaminant transport in soils and groundwaters; such studies may lead to a better understanding of these processes.

Fig. 5 shows a somewhat larger area of a hematite surface, to which sulfate ions have been adsorbed. Layers of atoms at a solid surface are divided into terraces separated by steps, much like a staircase. Two such steps cross this image, from lower left to upper right. Steps have long been thought to be key structures in controlling the reactivity of mineral surfaces. This image shows that steps often adopt a unique structure never before observed (this is the reason that the rows of atoms along each step appear particularly bright), and that several foreign atoms or molecules are attached to the steps; they are seen as particularly tall white bumps. Note also that these atoms only occur in pairs. This and other evidence suggests that these are sulfate groups bonded to the steps. Such studies are aiding our understanding of the effects of sulfate and other anions on hematite reactivity, as well as our understanding of the role played by steps and other surface structures that have not previously been observable.

Fig. 6 shows the surface of a common mineral, calcium carbonate (calcite), imaged under water with a scanning force microscope (SFM), an instrument closely related to the STM. This demonstrates a uniquely powerful feature of STM and SFM: the ability to obtain images of molecules even with the sample immersed in water. The bumps in the image correspond to carbonate molecules or perhaps to water and/or carbonate molecules chemisorbed to the fresh cleavage surface. Double rows of carbonate molecules trend from lower left to upper right. Often, along these rows, a periodicity is observed which corresponds to a doubling

of the unit cell dimension expected from the bulk structure of the mineral; this shows that calcite surface structures do not correspond to that expected. Instead, upon creation of the surface, the surface atoms experience a new chemical and potential environment and may respond by rearranging themselves to form a new structure that only exists in two dimensions. Also, water and other molecules from the environment satisfy the broken bonds left behind by fracture. Some of these surface structures were previously unknown; they are important because they contain hints as to why surfaces often behave in unexpected ways. That is, surfaces can adopt unique structures with equally unique chemical properties.

4. Structural information from EXAFS spectroscopy

X-ray absorption spectra contain information of the chemical nature of neighboring atoms around an element. A mathematical analysis of this Extended X-ray Absorption Fine Structure yields bond lengths and the number of nearest neighbors of the absorbing element. Since the method is sensitive to short range order it provides crystallographic insight into the structure of adsorbed species and amorphous minerals. In collaboration with Dr. Alain Manceau at the University of Paris and the LURE-synchrotron facility in Orsay we use EXAFS spectroscopy to answer open questions of the manganese redox cycle in lakes.

It is well known that the oxidation of metal ions such as Mn(II) with molecular oxygen is catalyzed by mineral surfaces (Wehrli, 1990). A plausible mechanism for this reaction is based on the assumption that adsorbed Mn(II) ions form a direct coordinative bond to mineral surfaces. Using EXAFS spectroscopy we were able to verify this hypothesis. Spectra of Mn(II) on hydrous ferric oxide and goethite (α -FeOOH) show distinct =Fe-O-Mn(II) surface complexes. Products of the oxidation by O₂ could be identified as adsorbed Mn(IV). The coordination of Mn(IV) on iron hydroxides is influenced by the structure of the adsorbent: on hydrous ferric oxide we observe mainly Mn(IV) as edge sharing octahedra. Goethite samples show longer Fe-Mn(IV) distances. This points to a coordination geometry which is dominated by corner sharing Mn-octahedra. We are now performing kinetic experiments

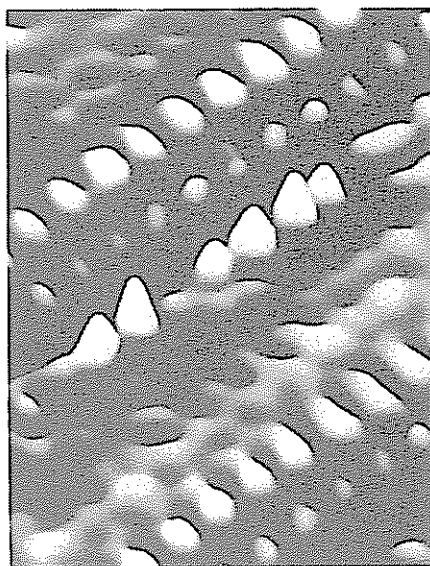


Fig. 5
A STM image at a somewhat larger area than in Fig. 4; you can see oxygen atoms arranged along steps on the surface. Several foreign species are adsorbed along the steps, in this case probably sulfate ions. See text for discussion.

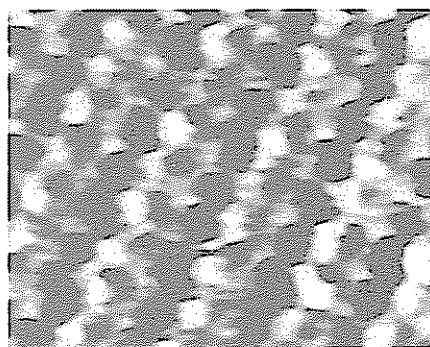


Fig. 6
Scanning force microscope (SFM) image of carbonate groups on a calcite surface. The image was taken under water, and shows a surface that differs from that expected (see text). This emphasizes the unique structure that surfaces can adopt, giving rise to unique chemical properties.

to test if such differences in the structure of adsorbed Mn(II) determines the reactivity in redox reactions.

The transfer of such detailed mechanistic studies to a field situation is often hampered by inadequate characterization of mineral phases. Manganese and iron minerals in sediments are usually X-ray amorphous if conventional powder diffraction techniques are applied. Fig. 7

illustrates the EXAFS spectroscopy, which yields structural information even of "amorphous" material from sediment traps. The spectra were recorded at the K-edge of manganese. The Fourier transforms of the "fine structure" can roughly be interpreted as radial distribution functions (RDF) around the absorbing atom. However, several corrections have to be made in order to extract bond lengths from the position of the peaks and coordination numbers from the peak intensity. The first peak in the RDF is due to six coordinated oxygen atoms. From the Mn-O bond length (1.9 Å) we conclude that the material consists of a Mn(IV) oxide. The second peak is produced by neighboring Mn atoms which are connected by edge sharing octahedra. The tunnel structure of the Mn(IV) oxide todorokite shows also a small amount of corner sharing octahedra. They are responsible for a third peak in the RDF which is completely absent in the layered structure of birnessite. We conclude that our amorphous Mn(IV) oxide from the sediment trap consists chiefly of edge sharing octahedra. We are now extending our studies to transformation reactions of iron and manganese minerals in sediments (Wehrli et al. 1992). With the help of EXAFS spectroscopy we are for the first time able to directly assess the structure of these amorphous solid reactants in sediments.

5. Photochemical Reactions at the Mineral-Water Interface

As described in the previous sections, many organic and inorganic compounds undergo specific chemical interactions at the mineral-water interface. Therefore, surface catalyzed reactions play an important role for the transformation of organic and inorganic compounds in natural water systems. In the photic zone of surface waters and in atmospheric water these transformation reactions can be catalyzed by light. The photochemical oxidation of compounds that are specifically adsorbed at mineral surfaces such as iron(III) (hydr)oxides is often accompanied by the photochemical reductive dissolution of the solid phase, i.e., the photochemical formation of dissolved iron(II) species from particulate iron(III) (Fig. 8). In atmospheric water the photochemical reductive dissolution of iron(III) (hydr)oxides is coupled to the photochem-

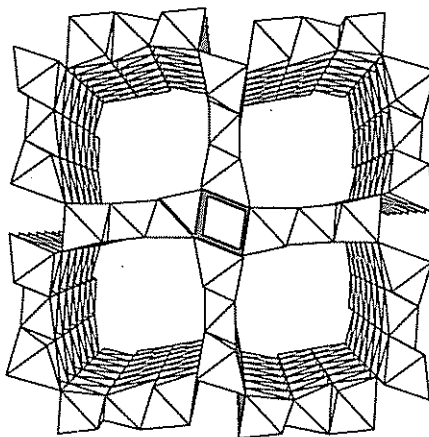
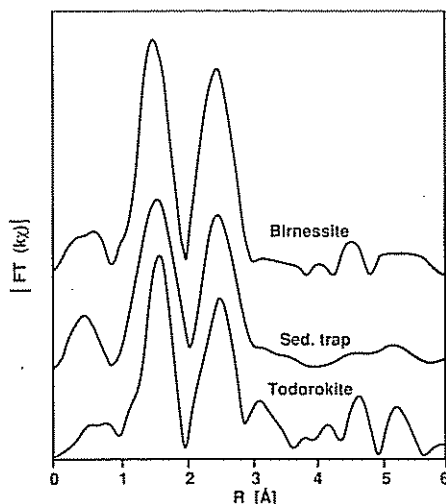


Fig. 7
Fourier transformation of EXAFS spectra. Above: Birnessite—a Mn(IV) oxide with layer structure. Middle: Sample from a sediment trap in Lake Sempach in 81 m depth. Below: Todorokite — a Mn(IV) oxide with tunnel structure. Right: Structure of Todorokite.

ical oxidation of S(IV) leading to formation of sulfuric acid. In the photic zone of surface waters the photoredox cycle of iron is primarily interdependent with the carbon cycle. Dissolved organic carbon present in surface waters may be either biogenic (i.e. humic or fulvic substances) or anthropogenic (i.e. organic pollutants). Upon photochemical oxidation these compounds are either mineralized to CO_2 and water or transformed into CO_2 and other oxidation products. The photochemical degradation pathway may be the rate limiting process for the removal of a large fraction of oceanic dissolved organic carbon. The involvement of iron in this photochemical degradation appears likely, although no data are available yet. Presumably, the iron(II,III) photoredox cycle also plays an important role for the photochemical oxidation of organic pollutants such as EDTA. In laboratory experiments EDTA is photochemically oxidized in the presence of a solid iron(III) phase, formaldehyde being one of the oxidation products (Karametaxas and Sulzberger, in preparation). These studies of the role of particulate iron for the photochemical oxidation of EDTA are part of a common project within the chemistry and the analytical departments of EAWAG which should answer the following questions:

- (1) Which are the main processes that control the fate of EDTA in surface waters?
- (2) Can laboratory experiments with well defined systems combined with mathematical models help to interpret the field data of EDTA in natural waters, such as the river Glatt and in Greifensee?

The photochemical oxidation of organic compounds is a major source of hydro-

gen peroxide. H_2O_2 is an important oxidant in atmospheric water and in surface waters. Fig. 9 shows preliminary results of the formation and consumption of H_2O_2 in an irradiated lepidocrocite ($\gamma\text{-FeOOH}$) suspension in the presence of fulvic acid. In the photochemical oxidation of fulvic acid, i.e. of the carboxylic groups of fulvic acid, radicals are formed which react with dissolved molecular oxygen to form O_2 and eventually - depending on pH - H_2O_2 . The photochemical oxidation of fulvic acid is accompanied with the reductive dissolution of $\gamma\text{-FeOOH}$, yielding dissolved iron(II), (Fig. 9). The rate of the photochemical formation of dissolved Fe(II) depends on the light intensity and its energy and on the concentration of fulvic acid that is specifically adsorbed at the surface of lepidocrocite. Since the extent of adsorption of an organic acid at the surface of particulate iron(III) is strongly pH-dependent, the rate of the photochemical reductive dissolution of iron(III) (hydr)oxides also exhibits a strong pH-dependence. Iron is a phytoplankton nutrient. However, it is only available to the biota in dissolved form. Hence, in environmental systems the bioavailability of iron depends on the kinetics of the formation of dissolved iron species, where the photochemical reductive dissolution of particulate iron is one

major pathway.

6. Role of particle surfaces for the regulation of trace elements in lakes and rivers

Trace metals in natural waters are strongly influenced by interactions with particle surfaces. The fate and the effects of trace metals depend upon the extent of their binding to the particulate phase. Primarily the dissolved fraction is involved in the interactions with organisms (toxic effects and availability of essential elements).

The concentrations of trace elements in lakes are determined by their binding and retention in sediments. Studies of trace metals in the water column and settling particles of lakes show that the trace metal fluxes to the sediments are significant; efficient elimination from the water column results from the high enrichment of these elements in particles and from the high sedimentation rates (in eutrophic lakes $1 - 3 \text{ g m}^{-2} \text{ d}^{-1}$). Consequently, very low concentrations of trace metals are observed in lake water columns, e.g. copper in the range $5 - 10 \times 10^{-10} \text{ M}$, zinc $5 - 40 \times 10^{-10} \text{ M}$ in Lake Zurich and Lake Greifen, lead $0.1 - 1 \times 10^{-10} \text{ M}$ in Lake Zurich. Low concentration ranges are thus observed in these lakes, although the inputs are quite high.

In rivers, the distribution of metal ions between suspended particles and water influences the transport of trace metals in the water phase, their binding in sediments and their possible infiltration into groundwater (Fig. 10).

Processes at the surfaces of natural particles determine the distribution of trace elements between solution and solid phase: adsorption to the surfaces is often the most significant process for the binding of trace elements. Suspended particles in lakes and rivers consist for one part of mineral particles (oxides, clay minerals, carbonates), and for another part of organic material (algae, bacteria and their decomposition products). On all these different particle surfaces, complexation with the surface functional groups (OH groups on oxides, $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, $-\text{SH}$ groups on organic material) is a likely mechanism of the binding of metal ions. Adsorption processes have been extensively studied in laboratory experiments with pure solid phases; binding of

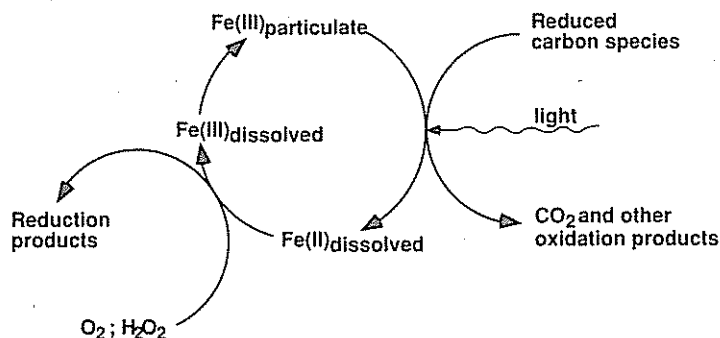


Fig. 8
Interdependence of the iron(II,III)
redox cycle with the carbon cycle.

metal ions to surface groups is favored in the pH range of natural waters (7-8.5). The distribution of metal ions between particulate and dissolved phase may be understood as a competition between binding to surfaces on one hand, and to ligands in solution on the other hand (Fig. 10).

A quantitative description would require quantification of adsorption to the natural particle surfaces. This quantification is difficult, since natural particles consist of a complex mixture of different solid surfaces, and heterogeneous surface groups with different adsorption properties exist. Natural suspended particles from the Glatt river were character-

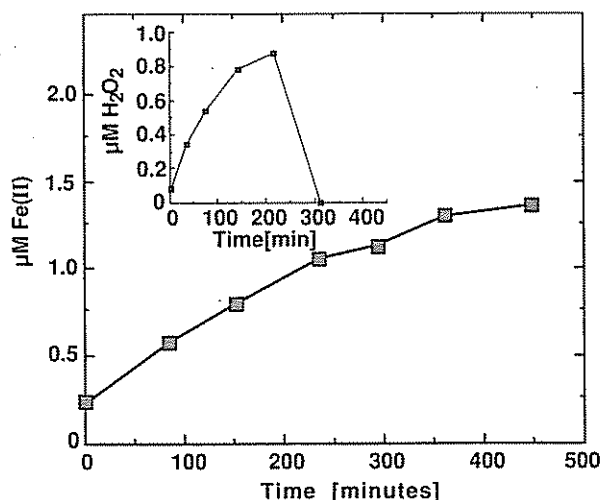


Fig. 9
Photochemical formation of hydrogen peroxide and photochemical iron(II) formation in an irradiated iron(III) (hydr)oxide suspension (ca. 30 mM Fe in form of γ -FeOOH, pH = 5.0) in the presence of Suwannee River fulvic acid (10 mg L^{-1}). The disappearance of H_2O_2 may be explained in terms of reaction of precursor radicals with dissolved Fe(II), where the rate of this reaction depends on the Fe(II) concentration (Bartschat and Sulzberger, in preparation).

ized in laboratory experiments with respect to their adsorption of metal ions; the adsorption properties of particles collected at different times and sites were similar (Müller and Sigg 1990). Lead was more strongly adsorbed than zinc on these particles.

These studies allowed evaluation of the effects of different variables on the distribution of metal ions between solution and particulate phases. In rivers the concentrations of suspended solids may vary in a wide range with the water flow. A significant increase of suspended solids at high water flow usually means also an increase of the total concentration of

metal ions, of which a large fraction is bound to particles. The concentrations in solution, however, may relatively decrease in such cases, since the number of available surface sites increases with particle concentrations (Müller and Sigg 1990). The effects of complexing ligands such as EDTA (ethylenediaminetetraacetate) and NTA (nitrilotriacetate) must be evaluated in the framework of the complex interactions between metal ions, dissolved components, suspended solids and sediments.

7. The role of interfaces in unconsolidated deposits in regulating the water composition and transport of contaminants in groundwater

Knowledge of the processes occurring at the rock-water interface are the basis for understanding the factors regulating the changes in the water composition during infiltration of rain- and river waters, as well as the factors controlling the transport of pollutants underground. When water is percolating through a porous medium its contact surface with the solid phase increases by a few orders of magnitude. Consequently, the following processes become very important :

- Dissolution (weathering) of rock-forming minerals by the acids found in the infiltrate, as already discussed in the section on structure and reactivity.
- Sorption of certain groups of chemical compounds, e.g. heavy metals, lipophilic organic pollutants, at the surface of the solid matrix.
- Redox processes mediated by microorganisms and microbial degradation of organic substances. In these cases, the solid matrix gives a physical support to the microorganisms and hence facilitates the formation of a biofilm.

The concentrations of most constituents are changing when pollutants are transported in an aquifer or when river water infiltrates into groundwater. These changes may also be due to sorption processes (adsorption and desorption). If there is a reversible sorption equilibrium, the transport of the substance will merely be retarded, or a concentration pulse will be flattened out. However, if the sorption is irreversible or the sorption capacity of the

aquifer is large, then we will observe a decrease in concentration of the substance considered (Fig. 11). In field systems, sorption processes are usually coupled with transformation processes.

The formation of a bio-film on the solid matrix enhances the rate of microbially mediated reactions by orders of magnitude compared to the bulk water. If considerable amounts of degradable organic substances are present in the infiltrate, the available oxidants (electron acceptors) in the aquifer, such as oxygen, nitrate, sulfate and the solid manganese and iron (hydr)oxides, are stepwise reduced by microbially mediated reactions (von Gunten und Zobrist, 1992). As a consequence, the chemical environment of the aquifer has changed and further reactions can be in-

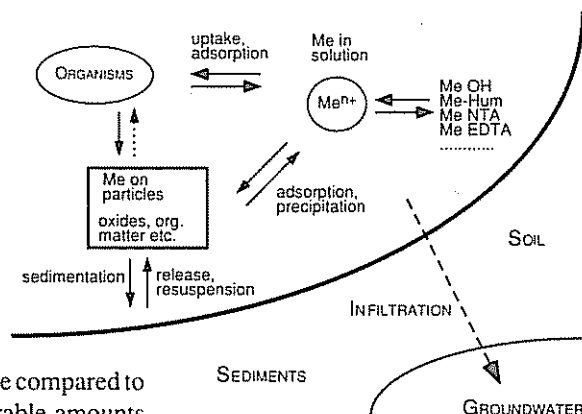


Fig. 10 Schematic representation of the interactions of metal ions with particle surfaces and ligands in solution; transport of metal ions in the water phase and to the sediments, infiltration into groundwater and interactions with organisms depend on these interactions.

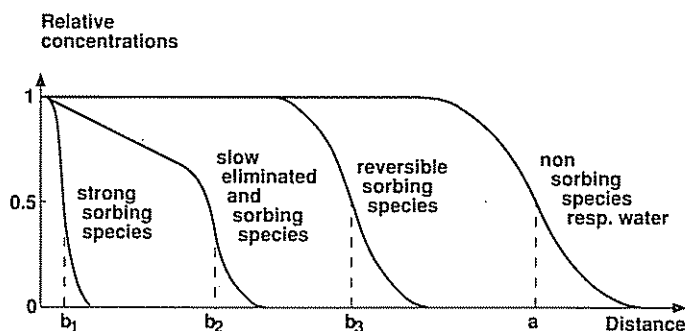


Fig. 11 Schematic representation of substances transported in a homogeneous porous media. After a given running time t , in the column, a substance has been transported over a distance characteristic for the sorption behaviour of the species considered. The concentration profiles also show the effect of the dispersion. The ratio of a to b , represents the retardation factor.

duced, for example the reductive dissolution of iron (hydr)oxides by sulfide or the reduction of aromatic nitro compounds to the corresponding anilines. In an anoxic environment the pathway of the microbial degradation of pollutants also changes.

8. Final Remarks

We have made here a few excursions into the chemistry of the mineral-water and particle-water interface; the phenomena discussed cover a wide range of space and time scales. Our considerations went from split-second processes between atoms and molecules in the nanorange to global geochemical cycles and to water technological processes. The common feature of all these processes is that they are influenced or regulated by processes at the interface.

Among the various experimental procedures which are useful in interfacial chemistry, we should mention the scanning probe microscopes (scanning tun-

elling microscopy, and scanning force microscopy) that have been added recently to the laboratory facilities at EAWAG. Probe microscopy is one of the few experimental techniques, which which a surface can be investigated in the presence of water and, thus, offers broad and innovative possibilities to study processes within the atomic scale at the surface. Nevertheless none of the techniques mentioned here is unequivocally able to as-

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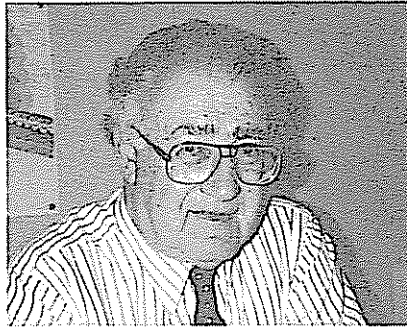
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sess the surface processes. We need a complementarity of different experimental methods and procedures to obtain better answers to many yet unresolved questions on the interactions on interfaces.

But progress in understanding the dependence of the macroscopic world on the microscopic world and in technology will depend on the collaboration with interfacial chemistry.

Stable isotopes in the surface water/atmosphere system

The lecture series by Prof. Joel Gat from the Department of Environmental Science and Energy Research at the Weizman Institute of Science, Rehovot, Israel on "Stable isotopes in the surface water/atmosphere system" addresses the variations in the abundance of the stable isotopic species of water in the water cycle. In the isotopic water molecules, the heavy isotopes of oxygen and hydrogen (namely ^{18}O and ^2H , the latter also named deuterium, D), substitutes for the more common light isotopes thus yielding the isotopic species of H_2^{18}O and ^1HDO . The natural relative abundance of the heavy oxygen water and deuterated water molecules is respectively 2.038×10^{-3} and 2.992×10^{-4} , but differences of a few permil (‰) in the abundance are found throughout the natural water cycle. These differences are caused primarily by an isotopic fractionation during the process of evaporation from open water surfaces, on one hand, and during the formation of precipitation (rain, hail or snow) by condensation of air moisture, on the other hand. Thus various water bodies in the



ocean and in the terrestrial water cycle acquire characteristic differences in isotopic composition, which enables one to study such processes as the mixing of waters or to determine the water balance of lakes or groundwater systems and also global aspects of the origin of water resources and their change in time.

In his scientific work Joel Gat has utilized this stable isotope methodology in studies on the water cycle of the semi-arid and arid regions, with special emphasis on saline waters, the Dead Sea as a prime example. Furthermore, he has studied the global water balance in major evaporitic regions, including the tropical rain forests of the Amazon, the Great Lakes region in North America and marine systems such as the Mediterranean Sea.

During his stay in EAWAG his main research interest is the lake-atmospheric interaction as it affects the water balance, but also the gas exchange process, as a function of the scale of the systems and in particular, the effect of turbulence and wave breaking along the shores.

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