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Tracers: Elements of Evidence in Environmental Research

Determination of the Compound-Specific Isotope Signature of Chemical Pollutants





Biological Tracers in Ecotoxicology





Sediments - 10 Archives of Detergents

Interview with Ruth Gonseth "Emerging Water Contaminants"





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Detective Work

Tracers: Elements of Evidence in Environmental Research

2 Detective Work

Lead Article

3 Tracers - Making the Invisible Visible

Research Reports

- 6 Determination of the Compound-Specific Isotope Signature of Chemical Pollutants
- 8 Biological Tracers in Ecotoxicology
- 10 Sediments Archives of Detergents
- 12 RNA A Tracer to Detect Microorganisms
- 14 Silver as a New Tracer for Diatom Production
- 16 Temperature Microstructure as a Tracer of Turbulence and Mixing
- 18 Identification of Groundwater Habitats Using Radon as a Tracer
- 20 Conservative Elements on New Trails

Forum

22 "Emerging Water Contaminants" An Interview with Ruth Gonseth

In Brief 24 Publications 2870-2987, Books 27 In Brief

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Bernhard Wehrli, chemist and head of the department "Surface Waters"

Sherlock Holmes, Philip Maloney, Guido Brunetti, Stoner McTavish and other famous figures from the world of detective stories baffle the reader with their abilities to solve cases by assembling the whole scenario of a crime by observing minute details. Although environmental research is usually far less spectacular, it likewise involves the collection of clues and use of circumstantial evidence. Many processes occurring in water cannot be readily observed. Colorless nitrate, for example, is transformed by bacteria to invisible and odorless nitrogen gas. Despite the fact that our analytical methods can prove that nitrate disappears from the water, it remains difficult to determine how. where and by which microorganisms this transformation is accomplished.

Detectives often have the options of arresting, interrogating or observing a suspect in the hope of catching him/her in the act of committing another crime. Environmental research is faced with similar choices: one can bring nature into the laboratory and perform experiments under controlled conditions or attempt to uncover relevant processes with intensive and elaborate observations in the natural setting. Tracers are often extremely useful tools in the latter case; they expose otherwise invisible processes and put reseachers on the right track. Some of the "detective methods" employed in modern environmental research are documented in this issue of EAWAG news.

Over the past few years, EAWAG has invested heavily in the development of tracer methods. Our research interests cover a wide range of areas, including research on turbulence phenomena in aquatic physics, transport and degradation of environmental pollutants, and processes in molecular biology. This scientific detective work requires modern analytical tools. We have developed collaboration with research groups at the ETH-Zurich and with laboratories of the Canton of Zurich in order to share available infrastructure. The stable isotope mass spectrometer at EAWAG, for example, was acquired jointly with ETH-Zurich.

The introduction of such new techniques requires for mutual information and discussion. During the last winter semester, the Friday seminar of EAWAG was therefore dedicated to the topic of isotopic tracers. I am sure that these initiatives will improve our detective work for the environment.

Aller

Tracers – Making the Invisible Visible

Tracers are tools used in environmental research both to make processes more visible and to discover unknown processes. Tracers were used, for example in marine research, to answer the question about where the Gulf Stream ends. EAWAG is investigating similar questions about streams and lakes by using isotope tracers. Trace compounds in environmental repositories can be used to reconstruct changes in climatic conditions. A relatively recent development is the use of indicators of biological processes; biomarkers allow us to assess the effects of various pollutants on organisms.

Tracing the Gulf Stream

We enjoy a mild climate because the Gulf Stream directs warm water from the tropics towards Europe's shores. The Gulf Stream transports twenty times more water than all the world's streams combined; however, the water transported by the Gulf Stream must sink back down at some point or the North Atlantic would turn into a "water mountain". In the 1970s, a series of expeditions was undertaken to solve the mystery of the Gulf Stream. Temperature and salinity turned out to be reliable parameters to measure. Figure 1 shows two transects through the Atlantic Ocean [1]. On its way north, the Gulf Stream loses part of its volume through evaporation; western Europe receives this water in form of frequent well known precipitation. Evaporation increases the salinity of the Gulf Stream water. In addition, the water cools off on its way north and eventually mixes with the cold waters of the polar ocean, where the formation of the pack ice also increases salinity. North of Iceland, temperature and salinity reach a critical value. The density of the Gulf Stream water increases and the water masses drop to a depth of 3000 m, where it makes a turn south. After this point, the water is referred to as North Atlantic deep water. Near Gibraltar, warm and very salty water originating from the Mediterranean is layered above this deep current. At approximately the latitude of South Africa, two tongues of Antarctic water meet this current from the south. One part of the Antarctic water is colder but not as saline as the North Atlantic current and flows north along the ocean floor. This example demonstrates how we can make these very deep and slow currents visible with the help of just two parameters, temperature and salinity. Such parameters, revealing invisible processes, are called tracers. The temperature of a water body not only reveals the large-scale flow patterns; temperature measurements taken at a high spatial resolution can also give us quantitative clues about turbulent mixing processes on a small scale. The article by A. Wüest on p. 16 describes how such measurements of the temperature fine structure can be evaluated in a lake system.

Sources and Sinks

Since prehistoric times, humans have been curious about where the water in a spring comes from or where a stream that disappears in a seep hole ultimately goes. Tracer experiments in streams are almost 2000



Fig. 1: Cross-section through the Atlantic Ocean. Lines indicate (A) zones of constant temperature, expressed in °C, and (B) zones of constant salinity, expressed as ‰. Figure modified after [1].

years old. During Roman times, the waters of the Jordan River were marked with chaff in an effort to trace the subterranean connection to a karst spring [2]. Over the last 50 years, fluorescent dyes, added to the system from the outside, have been used for this purpose. It is more elegant, however, to use natural compounds that are already present in the environment. Such tracers can be either naturally occurring or of anthropogenic origin (coming from human activity). An example of a naturally occurring tracer is the ratio of the oxygen isotopes ¹⁸O/¹⁶O in rainwater [3]. The ratio of the two isotopes is a function of the elevation above sea level at which the precipitation fell (Fig. 2). Thanks to technical advances in sample processing, measurements of isotopic ratios in water are far less difficult today than they were even ten years ago. We are now able to obtain a very good estimate of the mean elevation at which the water in a surface stream or a groundwater aquifer fell.

Looking Back in Time

Information on the residence time of water in groundwater aquifers is important in drinking water production, risk analysis in the case of chemical spills, and in the analysis of ecosystems that depend on ground water, such as flood plains. Just as a detective asks a suspect about his or her whereabouts on a certain date and time, the "environmental detective" wants to know how long the water has been in a particular groundwater aquifer. A number of anthropogenic tracers are available for investigating this type of question. Freon or CFC's (chlorofluoro-carbons) did not exist in the past. Because of their special properties, CFC's were used more and more as propellants in spray cans and as cooling liquids in refrigerators. As a consequence, their atmospheric concentrations increased continually (see Fig. 3), until their devastating effect on the ozone layer was recognized [4]. Today, the production of freon is limited by the terms of the Montreal Protocol and substitute compounds are now being used. For the period of the last 50 years, there is a well-defined atmospheric CFC concentration at any point in time, corresponding to an equally well-defined equilibrium concentration of CFC's in water. Measuring freon concentrations in a spring, groundwater aquifer or a deep layer of a lake allows us to determine the time when the water was last in contact with the atmosphere. Noble gases are another class of tracers suitable for dating ground water, as is discussed in the article by R. Kipfer on page 20.

The best known tracers for the determination of ages and time constants in environmental processes are radioisotopes. Radioisotopes follow the laws of radioactive decay, and their half-lives are known precisely. In stream research, for example, it is important that the rate of water exchange between the stream and the pore spaces in the gravel bed at the stream bottom is known. Intensive exchange between stream water and near-shore ground water is essential for the health of a stream. The interstitial water in the streambed is an important habitat for benthic organisms, and it controls the exchange of nutrients between the stream and its surroundings. The article by E. Hoehn on page 18 discusses how groundwater habitats within a flood plain can be recognized using radon, a natural radioisotope. Fortunately, we now have extremely sensitive detection methods for radioisotopes. It is possible, for example, to detect radioactive ¹⁴C down to levels of 10⁻¹⁵ g (or one million atoms). The development of accelerator mass spectrometry has dramatically expanded the areas in which such tracer and age determination methods can be employed.

Rummaging in Environmental Archives

Other projects investigate the temporal dimension of environmental processes. Here the "environmental detective" faces a new kind of problem. In order to study the behavior of systems on large time scales, one has to have access to samples representing comparable periods of time. Typical research projects cover periods of a few years at most. Slow processes are typically studied by reconstructing the temporal development of the system under investigation. Obviously, one cannot expect that someone collected appropriate samples or even conducted the necessary measurements in wise foresight; one therefore has to rely on archives in which the relevant information has been stored or recorded in a temporal sequence.

A good example of such an archive is the sediment deposited in a lake. The sediments are a continuous, layer-by-layer record, storing a wide range of information on the chemical, physical and biological processes within the lake and its surroundings (Fig. 4). The challenge is to read and to interpret this information. The article by W. Giger on page 10 shows how detergents leave traces in the sediments and how sediment analyses can give us information about the original product composition and degradation processes in sewage treatment

plants. The sediments can also tell us about natural processes. Geochemical indicators are often used to gain information about the intensity of a natural process from environmental archives, as demonstrated in the article by G. Friedl on page 14. Other groups at EAWAG are currently participating in international research projects attempting to reconstruct environmental conditions in the distant past. They use ice cores from Greenland glaciers and sediment cores from Lake Baikal in Siberia. These interdisciplinary programs try to better understand current environmental conditions and future



Fig. 2: The oxygen isotope $\delta^{18}\text{O}$ in precipitation collected at three weather stations within the same geographical area, but at different elevations. $\delta^{18}\text{O}$: deviation of the $^{18}\text{O}/^{16}\text{O}$ -ratio from a standard in %.



Fig. 3: Increase of atmospheric CFC concentrations (CFC-11 and CFC-12) since 1950. Unit pptV = 10^{-9} volume parts.

developments by comparing them to conditions and changes over the last several thousand years. The beryllium radioisotope ¹⁰Be, for example, is formed in the atmosphere by cosmic radiation [5]. Its presence in Greenland ice may be used as a tracer for solar activity levels in the past. With these data, we can improve our understanding of the effect of solar radiation on climatic changes, which is important in determining the role that human activity plays in global climate change. A comparison between ¹⁰Be and ¹⁴C has revealed a reduction in the global ocean circulation at the end of the last ice age [6], which implies that even the Gulf Stream has a complex and ever changing history.

A Window into the Complexity of the Biosphere

The biosphere is a dynamic system of extraordinary complexity. With the sun as the driving force, innumerable biological processes occur on different temporal and spatial levels, but are usually coupled to one another. Three methodologies have become particularly useful in identifying individual processes: stable isotopes, gene probes

rm, EAWAG



Fig. 4: Sediment core from Lake Baldegg.

and biomarkers. In biological processes, such as photosynthesis or denitrification, the lighter isotopes of a particular element are processed slightly faster than the heavier ones. Generally, this leads to enrichment of lighter isotopes (12C or 14N) in the biological products, while the heavier isotopes ($^{13}\mbox{C}$ or $^{15}\mbox{N})$ become enriched in the substrate. A shift in isotopic ratio, as compared to the natural abundances, can therefore be used to assess the type and intensity of biological processes. Additionally, we can use substances enriched in a certain isotope (e.g., nitrate, ¹⁵NO₃) as a tracer. Stable isotope tracers have the advantage that they are not radioactive and can be used in environmental studies without doing any harm. Nitrate is used in biological systems in many different pathways. Heterotrophic microorganisms use nitrate to produce atmospheric nitrogen (N₂) or ammonia (NH₄⁺), while plants absorb nitrate as a nutrient and produce organically bound nitrogen. Using a mass spectrometer, we can, in some fortunate cases, follow the sources and the sinks of natural nitrate in the environment [7]. With isotopically-labeled nitrate, we can determine denitrification rates in surface waters [8]. The article by L. Zwank on page 6 illustrates the use of stable isotope tracers in studying the degradation of chemical pollutants in ground water. In this type of situation, the question often is whether an apparent drop in pollutant concentration along the flow path is simply a result of dilution or is due to microbial or chemical degradation. Biological degradation can typically be identified by a significant shift in isotopic ratios.

Modern microbial ecology, however, is interested in more than simply the question of which compound is transformed at what rate. One would like to know which microbes are active when and where. Today, gene probes allow us to determine the specific distribution of microorganisms in environmental samples. To achieve this, a short genetic sequence of ribosomal RNA is marked with a fluorescent tag. This type of biomolecular tracer marks specific groups of organisms, e.g., methanogens, in a water or sediment sample and can subsequently be analyzed microscopically. The advantage of this technique lies in the fact that we are examining active microorganisms, which often cannot be cultivated under laboratory conditions. The article by K. Zepp on page 12 discusses these techniques in more detail.

As information about the genetic make-up of organisms becomes available, we will have better tools to identify the players in complex interactions within the biosphere. Even more complex, however, is the information reflected in the wide array of proteins involved in the metabolism of organisms. This is where a relatively new tracer concept comes to the fore – that of biomarkers. Analyses of the metabolic products of an organism can tell us, for example, whether the organism had been exposed to toxic compounds. More about this new approach can be found in the article by R. Eggen on page 8.

This short overview has hopefully demonstrated how the various tracer techniques have evolved into extremely useful and very precise tools in environmental research. The success of this type of research, however, depends on whether the questions we are trying to answer are relevant, interesting and looking toward the future.



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Bernhard Wehrli, chemist and head of the department "Surface Waters". Professor of aquatic chemistry at ETH-Zurich. Research area: Nutrient and carbon cycles in surface waters.

- Berner E.K., Berner R.A. (1996): Global Environment. Water, Air, and Geochemical Cycles. Prentice-Hall, Upper Saddle River, New Jersey.
- [2] Käss W. (1992): Geohydrologische Markierungstechnik. Borntraeger, Berlin, 519 p.
- [3] Siegenthaler U., Oeschger H. (1980): Correlation of ¹⁸O in precipitation with temperature and altitude. Nature 285, 314–317.
- [4] IPCC (1996): Climate Change 1995. Cambridge University Press, 878 p.
- [5] Beer J., Mende W., Stellmacher R. (2000): The role of the sun in climate forcing. Quaternary Science Review 19, 403–415.
- [6] Muscheler R., Beer J., Wagner G., Finkel R.C. (2000): Changes in deep-water formation during the Younger Dryas event inferred from ¹⁰Be and ¹⁴C records. Nature 408, 567–570
- [7] Mengis M., Walther U., Bernasconi S.M., Wehrli B. (2001): Limitations of using ¹⁸O for the source identification of nitrate in agricultural soils. Environmental Science and Technology 35, 1840–1844.
- [8] Steingruber S.M., Friedrich J., Gächter R., Wehrli B. (2001): Measuring denitrification in sediments with the ¹⁵N isotope pairing technique. Applied and Environmental Microbiolog 67, 3773–3778.

Determination of the Compound-Specific Isotope Signature of Chemical Pollutants

New Perspectives in Contaminant Hydrology

Analytical methods have evolved to a point where it becomes possible to determine the isotopic composition of individual chemical compounds at low detection limits. These advances have opened new possibilities for the assessment of contaminated ground water. EAWAG intends to optimize established analytical methods for their application in contaminant hydrology.

Groundwater contamination by organic compounds is a common problem in industrialized countries. Chemicals that are used in large quantities, such as fuels or metal degreasing and dry cleaning agents, can reach the ground water directly from point sources (accidental spills, leaking underground storage tanks) or via diffuse pathways (atmospheric deposition, runoff from roads), and thereby compromise its use as a drinking water reservoir.

Problems in the Clean Up of Contaminated Ground water

In situ methods are becoming increasingly more important in the clean up of contaminated ground water. These include all methods where the contaminant is degraded directly in the subsurface, either by natural or by stimulated processes. The financial benefits of in situ over ex situ methods are tremendous. Ex situ remediation is typically very labor and resource intensive and reguires excavation and removal of contaminated material. In the case of readily degradable contaminants, in situ remediation may simply be a matter of following the concentration of the contaminant over time in order to determine whether or not and how fast degradation is occurring. It is often difficult, however, to conclusively show that degradation is taking place. Traditional approaches are based on mass balances for the contaminants in the ground water. In the case of slow degradation rates, this can lead to unreliable results, since balances have to be established for extended periods of time and because the spatial distribution of the contaminant plume often is poorly documented. Even in areas with well-



Following derailment of a train near Zurich-Affoltern in March of 1994, an estimated 70 tons of gasoline were spilled.

defined hydrogeological conditions and a dense network of monitoring wells, it is rarely possible to determine unequivocally degradation or transformation rates in ground water. Whenever contaminant loss is observed, it is usually not possible to discern whether the disappearance was due to dilution, evaporation, sorption, microbial degradation or abiotic reactions. To make matters worse, transformation processes may not necessarily form exclusively harmless products, but can lead to products that are more difficult to degrade or more toxic than the original compound (Fig. 1). Before we can use the so-called "monitored natural attenuation" approach in complex contamination situations, we need a better understanding of the system.

Assessment of Contaminant Behavior by Single Compound Isotope Measurements

The determination of stable isotope ratios for individual contaminants is an elegant method for gaining additional information about the efficiency of in situ degradation processes. Most elements occur in more than one stable isotopic form. The carbon atom, for example, can have a mass of 12 or 13 atomic units. Any organic molecule will contain both isotopes in a defined ratio (¹³C/¹²C). Today, we are able to measure stable isotope ratios of the elements H, C, N, O, S and Cl for individual compounds present in environmentally relevant concentrations. The various transport and transformation processes in the ground water change the isotopic signature of the elements in the contaminants in different ways. The stability of a chemical bond depends on the isotopic composition. Bonds be-



Fig. 1: Transport and transformation processes of organic contaminants in the ground.



Fig. 2: Effect of isotopic composition on bond energies and reaction rates.

The potential energy of a carbon-deuterium bond (C–D) is lower than that of a carbon-hydrogen bond (C–H). For this reason, the C–H bond is broken seven times faster than the C–D bond at room temperature. During the degradation of a compound, molecules containing lighter isotopes react faster. Reaction products become enriched in lighter isotopes, while the starting material becomes enriched in heavier isotopes (see example in Fig. 3).



Fig. 3: Degradation of toluene under anaerobic, sulfate-reducing conditions [3]. The disappearance of toluene corresponds to the formation of sulfide and vields a closed electron balance. Anaerobic degradation of toluene leads to isotope fractionation. The δ¹³C value of toluene increases, i.e., the remaining toluene becomes enriched in the heavier carbon isotope.

water quantitatively, single compound isotope ratio methodology is combined with methods for groundwater dating and groundwater modeling.



Luc Zwank is an environmental scientist and is participating in the project described above as a doctoral student. The work is performed in the group "Contaminant Hydrology" within the department "Water Resources and Drinking Water".

Co-authors: Torsten Schmidt, Rolf Kipfer, and Stefan Haderlein.

- [1] Bloom Y., Aravena R., Hunkeler D., Edwards E., Frape S.K. (2000): Carbon isotope fractionation during microbial dechlorination of trichloroethene, cis-1,2dichloroethene, and vinyl chloride: implications for assessment of natural attenuation. Environmental Science and Technology 34, 2768–2772.
- [2] Dayan H., Teophilo A., Abrajano J., Sturchio N.C., Winsor L. (1999): Carbon isotopic fractionation during reductive dehalogenation of chlorinated ethenes by metallic iron. Organic Geochemistry 30, 755–763.
- [3] Meckenstock R.U., Morasch B., Warthmann R., Schink B., Annweiler E., Michaelis W., Richnow H.H. (1999): ¹³C/¹²C isotope fractionation of aromatic hydrocarbons during microbial degradation. Environmental Microbiology 1, 409–414.
- [4] Beneteau K.M., Aravena R., Frape S.K. (1999): Isotopic characterization of chlorinated solvents – laboratory and field results. Organic Geochemistry 30, 739–753.

tween lighter isotopes (e.g., 12C-2H) are more readily broken than bonds between heavier isotopes (e.g., ¹³C-²H; see Fig. 2). Since chemical reactions occur at varying rates, depending on which isotopes are involved in the bonds being broken, the isotopic ratios in the reaction products are shifted relative to the ratios in the starting compounds. The isotopic signature of a particular compound as a function of location and time can, therefore, be used as a tracer for the type and rate of transformation processes occurring in the ground water (Fig. 3) [1-3]. Additionally, contaminants of different origin can have different isotopic signatures [4]. In such a case, isotopic ratios can be used to identify the source of the contamination or the polluters.

Isotope Ratios of Individual Compounds as a Research Project at EAWAG

Determination of isotopic signatures of groundwater contaminants is a new approach in contaminant hydrology, where the contaminants themselves are the tracers. In the department "Water Resources and Drinking Water", isotope analysis of individual compounds is currently being developed as a method specifically for the use in contaminant hydrology. The primary tool consists of a so-called GC-IRMS (gas chromatograph-isotope ratio mass spectrometer) that was recently purchased in cooperation with ETH-Zurich.

In a project that was initiated in 2000, EAWAG is studying the isotope effects of different degradation processes, both in the laboratory and in field experiments. Compounds being investigated include the solvents trichloroethylene, perchloroethylene, and the gasoline additive methyl tertiary butyl ether (MTBE). With the information gained from the project, we hope to identify degradation processes, quantify transformation rates, and identify the source(s) of contaminants in "real world" situations. In order to describe the behavior of persistent contaminants in the soil or in the ground

Biological Tracers in Ecotoxicology

Biomarkers are biochemical or physiological indicators of physical, biological or chemical stress on organisms. They are tracers for reactions that can take place on different biological levels – molecular, cellular, whole organism. This article discusses molecular biomarkers that are induced by chemical stress. Their detection enables us to assess very early the potentially negative effects of chemicals on organisms and ecosystems.

Despite improved legislation, large numbers of toxic chemicals are discharged into the environment even today. Often these contaminants, or contaminant mixtures, are present in very low concentrations, which makes the assessment of their toxic potential very difficult. This is where extremely sensitive biological methods, based on cellular systems, can be used to detect potential toxic effects on the cellular level.

Cellular Reaction to Stress

The first interactions between toxic compounds and biological systems take place at the cellular level, where proteins act as sensors (Fig. 1). Some sensors detect toxins directly, while others detect only the effects of the toxins e.g., damage to cell components (membranes, proteins or DNA)

and changes in the metabolic state, by reacting to changes in pH, osmotic pressure, or redox state. When the sensor detects stress, a cellular stress reaction is triggered. During this process, the sensor transfers the signal to a promoter element of certain stress genes, which are now turned on. As a result, the cell starts producing the corresponding messenger RNA (mRNA) which, in turn, serves as a template for the synthesis of stress proteins that are produced at the ribosomes (Fig. 1). It is the function of the stress proteins to remove the toxin or its degradation products, to repair or replace damaged cell components, and to re-establish the normal metabolic environment. If the stress proteins achieve this goal, the stress is overcome. If the stress proteins are unsuccessful, the stress can manifest itself



Fig. 1: Cellular reaction sequence from stress detection to the synthesis of stress proteins.

at a higher organizational level, i.e., in an organ, whole organism, population, community and/or ecosystem.

Molecular Stress Parameters as Biomarkers

A number of molecular parameters can be measured in order to assess the cellular stress reaction. These parameters serve as biomarkers in allowing us to estimate the toxicity of individual chemicals, mixtures of chemicals, or complex environmental samples.

One possibility is to measure the concentration or enzymatic activity of stress proteins after exposure to a toxin. The stress protein cytochrome P450 monooxygenase is a frequently used biomarker of a range of organic contaminants, such as PCBs, dioxin and dibenzofuranes. It is present in vertebrates as well as invertebrates and can be measured in cells or cell lines of both wild and laboratory animals [1]. Cytochrome P450 monooxygenase plays a central role in metabolic detoxification reactions. This is why the concentration and activity of this stress protein markedly increases after exposure to a contaminant.

Another method is to determine the concentration of mRNA [2]. Molecular methods for measuring changes in mRNA concentrations are highly specific, quantitative, sensitive, and quick (Fig. 2).

Parallel with the rapid progress made in molecular techniques, new biomarker methods have been developing at a rapid pace over the last few years [2]. Instead of measuring concentrations or activities of stress proteins, which are often very difficult to detect, or determining mRNA concentrations in a technically difficult procedure, we can now determine gene activity directly. To achieve this, promoters of known stress genes are linked with so-called reporter genes. Reporter genes code for easily detectable proteins, such as the enzyme luciferase, which produces light, or the "green fluorescing protein" (GFP), which fluoresces with a green color when it is exposed to light. The promoter-reporter gene



Fig. 2: Under oxidative stress (e.g., during the treatment with contaminants that induce the production of oxygen radicals), the concentration of glutathione peroxidase mRNA in the green alga Chlamydomonas reinhardtii increases significantly over time. It is assumed that glutathione peroxidase is a key enzyme in the defense against oxidative stress.



Fig. 3: Application of a recombinant biomarker system for the detection of contaminant-induced peroxide production. The promoter of a stress gene induced by peroxide was linked with the reporter gene luciferase and inserted into Escherichia coli, Increased peroxide concentrations inside the cell induce luciferase activity. Exposure of the cells to the contaminant catechol also causes induction of the luciferase activity because the presence of catechol triggers a chemical reaction inside the cell that produces peroxide [4].

Fig. 4: Gene analysis on a DNA chip. Each dot represents a gene. The darker the dot, the higher the activity of that particular gene.

constructs are inserted in bacteria or yeast cells. When these biomarker systems are exposed to a contaminated sample, both the promoter of the stress gene and the promoter of the reporter gene are activated, resulting in the production of the stress protein along with the reporter protein [3]. Figure 3 shows the activation of luciferase in recombinant bacterial cells after exposure to hydrogen peroxide and catechol [4]. This type of test system not only makes the detection of the reporter protein very easy, but it is also very sensitive. Extremely low concentrations of contaminants can be detected [5]. It is worth noting that often the actual bioavailable and stress-producing fraction of a contaminant is only a small fraction of its total concentration.

Future Biomarkers

The methods described above primarily target single stress genes or proteins. In the case of environmental samples, we often do not know the exact composition of the contaminants and it would be advantageous to monitor a number of stress genes and proteins simultaneously. Ideally, it would then be possible to identify contaminants based on the reactions that are observed. Furthermore, there is often only one toxic effect described for most contaminants, although we can expect that most contaminants will exhibit a complex toxicity pattern and that there are cellular effects, which are yet unknown [6]. New technologies, based on extensive gene and protein analyses, appear to be very promising. Large numbers of genes or partial genes are fixed on so-called DNA-chips and then subjected to tests (Fig. 4). With the sequencing of entire genomes, techniques in genome analysis are taking on a central role in toxicity research. At the same time, methods known as "proteomics" have been developed, where the protein composition of a cell as a whole can be characterized. Some of the more powerful methods can already separate more than 10,000 different proteins. These new methods will not only let

us identify new stress genes and proteins. but will allow us to examine the stress reaction of a cell or an organism as a whole, which is typically characterized by a complex interaction of a number of factors including stress factors.



Rik I.L. Eggen, molecular biologist and head of the department "Environmental Microbiology and Molecular Ecotoxicology". Research area: Molecular mechanisms of toxicity, development of bioanalytical methods.

- [1] Bucheli T.D., Fent K. (1995): Induction of cytochrome P450 as a biomarker for environmental contamination in aquatic ecosystems. Critical Reviews in Environmental Science & Technology 25, 201-268.
- [2] Power M., van der Meer J.R., Tchelet R., Egli T., Eggen R.I.L. (1998): Molecular methods can contribute to assessments of toxicological risks and bioremediation strategies. Journal of Microbiological Methods 32, 107-119.
- [3] Eggen R.I.L. (2001): Moderne biologische Analyse: Potenzial, Entwicklung und Anwendung. Gas Wasser Abwasser 3, 167-171.
- [4] Schweigert N., Belkin S., Leong-Morgenthaler P., Zehnder A.J.B., Eggen R.I.L. (1999): Combinations of chlorocatechols and heavy metals cause DNA degradation in vitro but must not result in increased mutation rates in vivo. Environmental & Molecular Mutagenesis 33, 202-210.
- [5] Jaspers M.C.M., Harms H.S., van der Meer J.R. (1999): Prokaryotic whole-cell living bioreporters expressing bioluminescence upon the presence of bioavailable concentrations of specific pollutants. In: Fass R., Flashner Y., Reuveny S. (eds), Novel approaches for bioremediation of organic pollution, Kluwer Academic/ Plenum Publishers, New York, p. 137-150
- [6] Schweigert N., Zehnder A.J.B., Eggen R.I.L. (2001): Chemical properties of catechols and their molecular modes of toxic action in cells, from microorganisms to mammals. Environmental Microbiology 3, 81-91.



9

Sediments – Archives of Detergents

In the past, chemicals contained in detergents and cleaning agents were often very recalcitrant and were deposited in lake sediments. These chemicals can now be used as tracers to document the history of their release into the environment, which, in turn, allows us to assess the success of measures taken to reduce their use. Decreasing concentrations in the sediments can be attributed to changes in product formulations as well as to improved removal of these chemicals by wastewater treatment plants.

Lake sediments store information about environmental contaminants, which settled to the lake bottom while adsorbed to particulate matter. Such chemicals include heavy metals, lipophilic persistent organic pollutants, and so-called amphiphilic surfactants and their lipophilic degradation products.

Detergents – Product Development since the 1950s

During the 1950s, synthetic surfactants began to replace the soap in detergents and cleaning agents. The first surfactants synthesized from petrochemical raw materials and produced in large quantities were tetrapropyl benzenesulfonates (TPS, branched alkyl benzenesulfonates, Fig. 1). Unfortunately, these compounds are difficult to degrade under either aerobic and anaerobic conditions and their massive release into surface waters led to undesirable foam formation. For this reason, TPS were replaced by linear alkyl benzenesulfonates (LAS, Fig. 1) in the mid-1960s. LAS easily and rapidly undergo aerobic biodegrada-



Fig. 1: Chemical structures of detergents investigated in this study.

tion. In fact, they represent the most important group of surfactants worldwide. Another important class of surface-active compounds are the nonylphenol polyethoxylates (NPnEO), a group of non-ionic surfactants. They were used in large quantities in Switzerland during the 1970s and 1980s. Biodegradation of NPnEO in municipal wastewater treatment plants produces, among other metabolites, the lipophilic and highly recalcitrant degradation product nonylphenol (NP, Fig. 1). NP is far more toxic than its parent compound and has endocrine properties; i.e., it interferes with hormonal systems in humans and animals. Until the early 1990s, the primary compound used in fabric softeners was the cationic surfactant dialkyl (C16-C18) dimethyl ammonium chloride (DHTDMAC, Fig. 1). This compound is toxic to aquatic organisms and accumulates in sewage sludge. In Switzerland and in other European countries, DHTDMAC has been replaced by more easily degradable cationic surfactants, socalled ester quats.

Surfactants as Tracers in Sediments

Since active ingredients in detergents and cleaning agents represent high production chemicals and are discharged into the wastewater in considerable quantities, they deserve special attention. The primary goal of this study was to document to what extent the compounds TPS, LAS, NP and DHTDMAC were released into surface waters and to determine the success of reduction measures. Because these compounds are very persistent under anaerobic conditions, they are essentially fixed in the sediments and can now be used as tracers to reconstruct the history of their release into the environment. Dated layers of a sediment core from Wohlensee near Bern were examined for their concentrations of TPS, LAS, NP and DHTDMAC [1–4]. The concentrations of these compounds as a function of depth are shown in Figure 2. The time markers at 1963 and 1986 are based on Cs-137 measurements [5].

Changes in Product Composition

The continually increasing concentrations of TPS before 1963 document the use of this class of compounds in the period between 1950 and 1963. The maximum value of 3.4 mg TPS per kg dry weight was reached in the first half of the 1960s. In response to the environmental problem of excessive foam formation caused by TPS, many countries voluntarily stopped using these compounds and created legislations requiring that surface-active compounds used in detergents be degradable with 90% efficiency in a primary degradation step. Since TPS were not used in Switzerland after this time, the TPS concentrations in sediments fell below the detection limit after 1965 (Fig. 2).

The concentration profile for NP shows that NPnEO surfactants were introduced in Switzerland in the mid-1960s. Sediment concentrations of NP of 0.3-0.48 mg/kg dry weight reflect the substantial input of NPnEO surfactants between approximately 1965 and 1985 (Fig. 2). A risk assessment, performed according to EU methods, determined a PNEC value (Predicted No Effect Concentration) of 0.3 mg NP per kg wet sediment [6]; by 1986, this value was clearly exceeded. The introduction of the Swiss Ordinance on Chemicals Hazardous to the Environment ("Schweizerische Verordnung über Umweltgefährdende Stoffe") in 1986 banned the use of NPnEO in laundry detergents. At the same time, manufacturers voluntarily stopped using NPnEO in household

cleaners. As a result, NP concentrations in sediments decreased after the mid-1980s (Fig. 2). Since the early 1990s, NP concentrations have been around 0.05–0.08 mg/kg dry weight, which is clearly below the PNEC value.

Effect of Wastewater Treatment Plants

After the recalcitrant TPS were banned in the early 1960s, the more readily degradable LAS replaced them. The introduction of LAS is reflected in rising LAS concentrations in the sediments. The maximum values are around 2.4 mg LAS/kg dry weight and were observed towards the end of the 1960s (Fig. 2). In the early 1970s, the wastewater treatment plant of the city of Bern began operations. This treatment plant is by far the most important one in the watershed of the Aare River, which includes Wohlensee, the source of the sediments examined in this study. Anionic surfactants, like LAS, are effectively removed in the aerobic biological treatment step and through sorption on the sewage sludge. It is, therefore, not surprising that LAS concentrations in sediments from Wohlensee dropped after 1970, obviously in response to the introduction of aerobic wastewater treatment (Fig. 2).

The concentration profile for DHTDMAC indicates that this compound has been used in Switzerland since the late 1960s. The maximum DHTDMAC concentrations of approximately 70 mg/kg dry weight are observed in sediment layers that were deposited between 1970 and the early 1980s. A first significant reduction of DHTDMAC concentrations is observed in the years



Fortunately, pictures, like this one from the early 1960s, belong to the past.

after 1980 which coincides with the introduction of phosphate precipitation and subsequent flocculation/filtration in the pretreatment basin of the wastewater treatment plant in Bern. After 1990, there is a second reduction in DHTDMAC concentrations, which correlates with the replacement of DHTDMAC by ester quats.

This study illustrates that recently deposited lake sediments are archives for assessing the surfactant loadings that our surface waters have received over the past few decades. Measures reducing the use of certain compound classes are also clearly reflected in the sediment layers. It can be shown very clearly that legal bans, voluntary phasing-out, and better wastewater treatment plants have significantly reduced surfactant concentrations in the aquatic environment.



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Fig. 2: Vertical concentration profiles for TPS, LAS, NP and DHTDMAC in a dated sediment core from Wohlensee, Canton Berne, Switzerland.

Decreases in concentration are caused by different, consecutive reduction measures. A: replacement of TPS by LAS (1964); B: implementation of the wastewater treatment plant for the region of Bern (1970); C: introduction of phosphate precipitation and flocculation/filtration (after 1978); D: NPnEO is banned by Ordinance on Chemicals Hazardous to the Environment (1986). Measurements of Cs-137 provide time markers for 1963 and 1986.

- Reiser R., Toljander H.O., Giger W. (1997): Determination of alkyl benzenesulfonates in recent sediments by gas chromatography/mass spectrometry. Analytical Chemistry 69, 4923–4930.
- [2] Fernández P., Alder A.C., Suter M.J.-F., Giger W. (1996): Determination of the quaternary ammonium surfactant ditallowdimethylammonium in digested sludges and marine sediments by supercritical fluid extraction and liquid chromatography with postcolumn ion-pair formation. Analytical Chemistry 68, 921–929.
- [3] Reiser R., Toljander H., Albrecht A., Giger W. (1997): Alkyl benzenesulfonates in recent lake sediments as molecular markers for the environmental behavior of detergent-derived chemicals. In: Eganhouse R.P. (ed.), Molecular markers in environmental geochemistry. American Chemical Society Symposium Series, Washington DC, 13, 196–212.
- [4] Alder A.C., Giger W., Reiser R., Schaffner, C., Ahel M., Albrecht A. (2001): Detergentienchemikalien in Seesedimenten. Münchner Beiträge zur Abwasser-, Fischerei- und Flussbiologie 54, 289–301.
- [5] Albrecht A., Reiser R., Lück A., Stoll J.-M.A., Giger W. (1998): Radiocesium dating of sediments from lakes and reservoirs of different hydrological regimes. Environmental Science and Technology 32, 1882–1887.
- [6] European Commission. (2001): Draft European Union Risk Assessment Report: Nonylphenol and Phenol, 4-nonyl-, branched.

RNA – A Tracer to Detect Microorganisms

The group "Molecular Ecology" at EAWAG in Kastanienbaum uses 16S rRNA, a structural element of ribosomes, as a tracer in studies on the carbon cycle in anaerobic sediments. Two examples are presented here. Fluorescence *in situ* hybridization was used to identify active bacteria in 150 year old sediments from Baldeggersee. Two populations of methane-forming *Archaea* were characterized in Rotsee sediments; their depth distribution was correlated with the quality of available organic material.

RNA as a Molecular Tracer

According to recent estimates, less than 1% of the naturally occurring prokaryotes (bacteria within the domains *Bacteria* and *Archaea*) are identifiable by traditional culture methods. The recent development of molecular tracers, however, allows us to confirm the presence of microorganisms in the environment that have not yet been cultured in the laboratory.

Ribonucleic acid (RNA) can be classified as mRNA, tRNA, or rRNA, according to its specific structure and function. When there is need for a particular protein, mRNA (messenger RNA) transports the genetic information in the form of a copy to the ribosomes where protein synthesis takes place. The tRNA (transfer RNA) brings the necessary amino acids to the ribosome where they are linked together to proteins. Ribosomes themselves are made up of rRNA subunits (ribosomal RNA) of different size (i.e., 5S, 16S and 23S rRNA; S = Svedberg unit, representing the velocity at which suspended biomolecules sedimentate under standard centrifugation conditions).

16S rRNA (Fig. 1) is a particularly useful tracer in molecular ecology [1]. Comparative analyses of the molecular sequences of 16S rRNA isolated from a range of prokaryotes have shown that it possesses both highly conserved and highly variable regions [2]. Conserved regions, for example, show the same sequence for all prokaryotes, while highly variable regions can help to identify specific groups of prokaryotes. Based on these differences, it is possible to design RNA probes with different selectivity. RNA probes contain approximately 20 nucleotides that are complementary to the selected target region on the rRNA. An enormous number of gene probes for the selective identification of a wide range of groups of prokaryotes have been published to date [3]. Some examples are given in Fig. 1. Using fluorescence in situ hybridization [4], a given RNA probe is labeled with a fluorescent dye and mixed with an environmental sample in high concentrations. The probe diffuses into the prokaryotic cells and binds to (hybridizes with) its complementary target on the rRNA within the procaryotic cell without destroying its structure. Marked cells are visible under a fluorescence microscope and can be quantified by direct counting (Fig. 2).

Active Bacteria in 150 Year Old Sediments

We used fluorescence *in situ* hybridization to identify metabolically active prokaryotes



Fig. 1: Two-dimensional structure of 16S rRNA of *Escherichia coli* with conservative sections (A and B) and a variable section (C) which bind different genetic probes. Eub338 identifies organisms in the domain *Bacteria*; Arch915 detects organisms in the domain *Archaea*; the gene probes Rotc11 and Rotc12 identify two different populations of methanogenic *Archaea*.



Fig. 2: In situ hybridization of a sediment sample with the RNA probe Arch915 detecting Archaea [5] as indicated by arrows.



in a sediment core from Baldeggersee. Among others, we used the probe Eub338 [5], which detects all organisms of the domain *Bacteria* (Fig. 1). The density of bacteria was highest in the first few centimeters and then decreased with depth. Layers below 40 cm are older than 150 years and showed only minimal cell counts (Fig. 3). Using culturing techniques, however, we were able to confirm the presence of active microorganisms in these sediments, which are capable of completely degrading organic material in sediment layers that were as old as 6000 years.



Fig. 3: Cell counts in the top 50 cm of a sediment core from Lake Baldegg, Switzerland (number of cells per gram dry weight of sediment). Microorganisms were made visible by fluorescence *in situ* hybridization (FISH) and counted under a fluorescence microscope. The RNA probe used was Eub338.

Methanogens in Rotsee Sediments

In a second study, we investigated which specific methanogens are responsible for the anaerobic degradation of organic material in the sediments of Rotsee [6]. The first task was to find RNA probes that were selective for the methanogens present in this site. We extracted the total nucleic acid fraction from the top 10 cm of a sediment core. This fraction served as a template for a selective polymerase chain reaction (PCR) in which the 16S rRNA genes of the indigenous methanogens present in the studied sediment core were amplified [7]. Subsequent sequencing of the PCR fragments allowed us to synthesize two specific probes: Rotc11 identifies a group of methanogenic Archaea that form methane (CH₄) from CO₂ and H₂, while Rotc12 detects methanogens that transform acetate to CH₄ and CO₂ (Fig. 1).

These two probes Rotc11 and Rotc12 were used in fluorescence *in situ* hybridization assays to determine the depth profile of the



Fig. 4: Distribution of different groups of microorganisms in Rotsee sediment (per g dry wt). Identification with fluorescence *in situ* hybridization using various gene probes. two populations (Fig. 4). Results showed that the acetate-using *Archaea* were present at all depths, while the methanogens transforming CO_2 and H_2 to methane were restricted to the top two centimeters of the sediment. These bacteria appear to require freshly sedimented organic material.

Our Goals

The two projects described here demonstrate the versatility of methods using rRNA as a tracer. The group "Molecular Ecology" at EAWAG Kastanienbaum is using these methods, combined with chemical analyses, in an interdisciplinary effort to comprehensively characterize microbial communities in natural aquatic systems.



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anaerobic degradation of organic material.

- Olsen G.J., Lane D.J., Giovannoni S.J., Pace N.R., Stahl D.A. (1986): Microbial ecology and evolution: a ribosomal RNA approach. Annual Review of Microbiology 40, 337–365.
- [2] Woese C.R. (1987): Bacterial evolution. Microbiological Reviews 51, 221–271.
- [3] Larsen N., Olsen G.J., Maidak B.L., McCaughey M.J., Overbeek R., Macke T.J., Woese C.R. (1993): The ribosomal database project. Nucleic Acids Research 21, 191–198.
- [4] Amann R.I., Ludwig W., Schleifer H.-H. (1995): Phylogenetic identification and *in situ* detection of individual microbial cells without cultivation. Microbiological Review 59, 143–169.
- [5] Stahl D.A., Amann R.I. (1991): Development and application of nucleic acid probes. In: Stackebrandt E., Goodfellow M. (eds.), Nucleic acid techniques in bacterial systematics. John Wiley & Sons, Inc., New York, p. 205–248.
- [6] Zepp Falz K., Holliger C., Grosskopf R., Liesack W., Nozhevnikova A.N., Müller B., Wehrli B., Hahn D. (1999): Vertical distribution of methanogens in the anoxic sediment of Rotsee (Switzerland). Applied and Environmental Microbiology 65, 2402–2408.
- [7] Grosskopf R., Janssen P.H., Liesack W. (1998): Diversity and structure of the methanogenic community in anoxic rice paddy soil microcosms as exmined by cultivation and direct 16S rRNA gene sequence retrieval. Applied and Environmental Microbiology 64, 960–969.

Silver as a New Tracer for Diatom Production

Sediments from oceans and lakes contain a record of the history of the water body itself, of the nearby land masses, and of the climate. The art of paleoceanography and paleolimnology is to correctly interpret these archives. Metals generally serve as tracers, yielding information about primary productivity levels as well as redox conditions at the time of deposition. The use of silver as a specific indicator for the productivity of diatoms is a new addition to the arsenal of tracers.

In chemical paleoceanography, and increasingly in paleolimnology, sediment sequences are being examined for indicators that allow us to reconstruct the conditions prevailing at the time of deposition. The presence of layers rich in organic material might indicate increased levels of primary production or, alternatively, of reduced levels of decomposition due to a lack of oxygen in deeper waters at the time when



Fig. 1: The depth to which sulfate diffuses into the sediment defines the redox front. When the redox front lies close to the sediment-water interface, the diffusion (D) of metals into the sediment is high; when the redox front lies deeper within the sediment, the amount of diffusion is smaller.

those particular sediment layers were formed [1]. The challenge is to distinguish between these two different interpretations.

Metals as Indicators

In marine sediments, redox-sensitive trace metals such as rhenium (Re), molybdenum (Mo), uranium (U) and cadmium (Cd) have been used as tracers for years [2]. It is crucial that the biogeochemical cycling of these metals in water and in the sediments is well known.

Re, U and Mo behave largely conservatively in oceans, i.e., they do not participate in chemical or biological reactions. They diffuse from the deep water into the sediment, where they are reduced and accumulate. Re becomes reduced at suboxic conditions, i.e., under conditions where oxygen is depleted, but where bacterial sulfate reduction is not yet active. The reduction of U and Mo requires anoxic conditions, meaning that they will not be reduced until the redox potential is low enough to reduce sulfate to sulfide. The position of the sulfate reducing zone (redox front) determines the diffusion rate of the metals (Fig. 1). If the zone of sulfate reduction lies far within the sediment, the diffusion distance for the metals is large, and the gradient is flat. Under these conditions, only small amounts of Re, U and Mo diffuse into the sediment where they are fixed. Accumulation of these metals is, therefore, dependent on the depth to which sulfate infiltrates the sediment; in other words, on the redox condition at the watersediment interface. Re, U and Mo may, therefore, be used as tracers of historic redox conditions in deep water bodies.

In contrast, Cd is involved in the biological cycle since it is taken up by phytoplankton, similar to phosphorus. Cd reaches the sediments as part of settling organic particles. When the organic material is degraded in the sediments, Cd is released and diffuses back into the water column, thus being lost from the sediment. If free sulfide is present, the insoluble cadmium sulfide (CdS) precipitates and is retained in the sediment. The smallest traces of sulfide suffice in creating a Cd signal, which makes Cd a good tracer of primary production.

Silver Binds to Diatom Shells

Silver (Ag) behaves very similarly to Cd. It is taken up by phytoplankton, reaches the sediment and becomes immobilized as silver sulfide (Ag₂S) like CdS. In the case of both metals, a minimal concentration of free sulfide, and therefore sulfate reduction, is required for the precipitation of the insoluble sulfide. Under such reducing conditions, the Cd or the Ag signal of primary production is preserved. As in the case of Re, U and Mo, the concentration of the Ag and Cd in the sediment is dependent on the depth of the redox front.

In contrast to Cd though, Ag is not taken up into the interior of the algae but is primarily adsorbed to the exterior of the shell



Silicate shell of the diatom Cyclotella stelligera.

structure. It has been shown in laboratory experiments that silver binds more strongly to silica shells (diatoms) than to calcite shells (e.g., coccolithophores) [3]. This finding has led to the hypothesis that Ag may be used both as a tracer of primary production and as a specific indicator for the production of diatoms. The purpose of the study presented here was to test this hypothesis [4].



Fig. 2: Sedimentation rates of biogenic silica (dark blue, g m⁻² d⁻¹) and particulate silver (light blue, $\mu g m^{-2} d^{-1}$) in the open water of the Saanich Inlet (British Columbia, Canada).



Fig. 3: Cd and Ag profiles in a sediment core from the Pacific Ocean (Seamount Patton-Murray, Gulf of Alaska). The gray areas indicate the occurrence of diatom shells.

Silver in Sedimenting Particles

First, we needed to confirm that Ag binds to diatoms and sediments with dead algae. For this purpose, sediment traps were deployed in the open water in the Saanich Inlet (British Columbia, Canada) at a depth beyond light penetration. Sediment traps were emptied monthly and examined for their concentration of biogenic silica and Ag. During the summer months, the sedimentation rate of silica increases due to an increase of diatom production: silver concentrations augment concomitantly (Fig. 2). The maximum Ag concentration observed was up to 12 times higher than the average concentration in the sediments. Similar concentrations have only been reported in areas heavily impacted by anthropogenic activity, as for example in the sediments off Long Island near New York, where sewage effluent is discharged into the ocean at depth. The high concentrations of Ag in sediment trap material from waters with very low levels of anthropogenic input can only indicate intensive uptake by diatoms.

Concentration of Silver: A Measure for Diatom Productivity

In marine sediments, diatom shells are often completely dissolved, which makes the reconstruction of past levels of primary production from sediment data very difficult. Therefore, our next step was to determine whether Ag is suitable as a specific tracer for diatom productivity. For this purpose, we examined an 8 m long sediment core from the Gulf of Alaska. The core was previously documented as containing three layers of diatom shells (Fig. 3, gray regions). These layers were formed during episodes of increased primary production and are characterized by high silica concentrations (data not shown).

Ag and Cd were determined in individual layers of the sediment core. Figure 3 shows that the concentration profiles for both metals follow a similar pattern. There are several horizons with elevated levels of the two metals, indicating increased levels of primary production at the time of deposition. Closer examination of the Ag/Cd ratios reveals that the horizons can be divided into two distinct types: several horizons with a Ag/Cd ratio of approximately 0.2, and three horizons with a Ag/Cd ratio of about 0.4, reflecting enrichment in Ag relative to Cd. Since these three layers correspond to the layers showing increased silica concentrations, the higher Ag/Cd ratio can be attributed to a higher diatom production. The results demonstrate for the first time the usefulness of Ag as a tracer for diatom productivity.



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- Calvert S.E., Pedersen T.F. (1992): Organic carbon accumulation and preservation in marine sediments: How important is anoxia? In: Whelan J.K., Farrington J.W. (eds.), Organic matter: productivity, accumulation and preservation in recent sediments. Columbia University Press, New York, 533 pp.
- [2] Crusius J., Calvert S., Pedersen T.F., Sage D. (1996): Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. Earth & Planetary Science Letters 145, 65–78.
- [3] Fisher N.S., Wente M. (1993): The release of trace elements by dying marine phytoplankton. Deep-sea Research 40, 671–694.
- [4] Friedl G., Pedersen T.F., Crusius J., Donald D. (2002): Enrichment of silver in marine sediments as an indicator of high paleoproductivity. Paleoceanography, submitted.

Temperature Microstructure as a Tracer of Turbulence and Mixing

The smallest temperature variations in natural waters extend over fractions of millimeters. These so-called temperature microstructures can be used as a tracer of turbulent mixing processes and their small-scale dynamics. This methodology allows us to differentiate between different effects that cause mixing in natural waters such as wind and cooling.

In classic tracer applications, concentration variations of a substance are measured as a function of time and space, which allows us to determine transport and transformation rates for the water constituents of interest. "Standing" waters, such as lakes and oceans, are almost always density stratified and exhibit well-defined temperature gradients. In such situations, temperature variations ($\Delta T'$, Fig. 1) may be used as a natural tracer. Since temperature is a conservative parameter over time periods of seconds to minutes, temperature variations are a direct reflection of turbulent transport processes. This is the basis for the temperature microstructure method, which attempts to determine mixing rates from a large set of $\Delta T'$ measurements. In a stratified body of water, turbulent currents occur primarily in the horizontal direction, while vertical mixing is drastically reduced. However, the turbulent vertical mixing is still 100 to one million times faster than the ever present molecular diffusion (K_T or K_S; see Table 1). Since vertical mass transfer is calculated as the product of turbulent diffusivity, K_v (m² s⁻¹), times the concentration gradient, $\partial C/\partial z$ (mol m⁻⁴; z = depth), the determination of K_v is of great practical importance.

The Principle

What is the relationship between temperature microstructures and mixing rates? The basic principle is illustrated in figure 1 using a temperature profile from Lake Neuchâtel. If a temperature gradient $\partial T/\partial z$ is present, neighboring water parcels have slightly different temperatures. Turbulent mixing of



The Measurement

Complete resolution of temperature or velocity microstructures on a millimeter scale is critical for successful measurements of turbulence. Profiles are typically measured with free sinking or rising probes, often operated from ships, or in more recent developments, freely floating and controlled via satellites. The probe has to move at a speed that is faster than the turbulent velocity, w' (Table 1); however, the thermal equilibration time scale of the sensors of approximately one-hundredth of a second requires the lowest possible probe velocity. As a compromise, probes are typically moved at velocities of 5 to 10 cm s⁻¹, which yields a vertical resolution of the temperature profile of 0.5 to 1 mm. It is important that the fast responding temperature sensors are mounted at the tip of the probe in order to sense the undisturbed waters.



Fig. 1: Temperature profile in Lake Neuchâtel (left, T-measured) and the corresponding excursion profile of vertical displacements (L', on right). The excursions L' reach distances of up to 2 m relative to the stable equilibrium position (no turbulence; left, T-stable). The temperature variations $\Delta T'$ are created by turbulent mixing of neighboring water parcels of differing temperature.

Symbol	Property	Typical Range
$\Delta T'$	Temperature variations (local) in lakes	0.0001 to 0.1 °C
K _v	Vertical turbulent diffusivity (mixing rate $K_v = w' \cdot L'$)	10 ⁻⁷ to 10 ⁻⁴ m ² s ⁻¹
K _T	Molecular diffusivity (temperature)	1.4·10 ⁻⁷ m ² s ⁻¹
Ks	Molecular diffusivity of solutes	around 10 ⁻⁹ m ² s ⁻¹
Ľ	Vertical site of eddies	cm to several m
w'	Vertical velocity of eddies (w' = $(\epsilon/N)^{\frac{1}{2}}$)	0.01 to 10 cm s ⁻¹
ε	Dissipation of turbulent energy into heat	10 ⁻¹¹ to 10 ⁻⁶ W kg ⁻¹
N ²	Stability of the water column (N ² = -1/ $\rho \cdot \partial \rho / \partial z$)	10 ⁻⁹ to 10 ⁻² s ⁻²

Table 1: Range of turbulent properties in stratified natural waters.

The Application

Turbulent diffusion in stratified waters is important in many different ways. In oceans, for example, turbulence influences the fate of climate-controlling gases or of heat transfer between the equator and polar regions. In lakes, turbulence has an impact on the distribution of nutrients and pollutants, algal production, transport of oxygen and other redox parameters, and ultimately impacts the formation of sediments. The measurement of vertical diffusivity in natural waters is rather delicate, since mixing against the stratification occurs slowly and is spatially and temporally very heterogeneous. Figure 1 illustrates how turbulent and inactive zones alternate.

Traditionally, vertical mixing rates have been determined "indirectly" by following the distribution of a tracer over time or via heat budgets. In such an approach, we are only able to observe the integrated result of all turbulent mixing processes. However, it is not possible to identify inactive or particularly turbulent zones nor to determine the mixing intensity at any specific location or point in time. In contrast, direct measurement of temperature microstructures also

Cox number method: This method compares the gradient of temperature variations ΔT^{i} (or more precisely, $[\partial T'/\partial z]^{2}$) to the average gradient $[\partial T/\partial z]^{2}$. The ratio of these two numbers, the so-called Cox number, is a measure for determining how much larger the turbulent mixing rate compared to the molecular diffusion rate (see Table 1 for typical values) is.

Dissipation method: This method uses the information in the fine structure of the measured temperature fluctuations. The more intensive the turbulence, the smaller the eddies can be before they are smoothed out by the viscosity of water. From these smallest structures, we can draw conclusions about the dissipation of turbulent energy (Table 1). Dissipation is the classic measure for the intensity of turbulence in natural systems.

includes turbulent events and resolves them temporally and spatially. This allowed us, for example, to document the role that the sediment-water interface layer plays in turbulent mixing processes in the hypolimnion of medium and small lakes (Fig. 2) [2]. Measurements in Lake Baikal [3] and in nearshore areas of oceans indicate that, even in large water bodies, processes near the sediments largely control vertical mixing.

Another benefit of this method is that we can examine turbulence under different physical boundary conditions. We are now able to correctly represent and parameterize different physical mixing processes in models and can determine the paths and residence times of mechanical energy. This allows us, for example, to distinguish between wind impact and the effects of cooling – a task which was difficult to achieve using classic tracer methods.

This work has received long-term support from the Swiss National Science Foundation and EAWAG.



Fig. 2: Typical profile of turbulence intensity in a lake (here: Lake Alpnach). At the surface, turbulent energy is created by direct wind impact and by cooling. Turbulence decreases with depth and is additionally dampened by stratification. In the interior of the water body, conditions are extremely calm. Above the lake bottom, turbulence intensity increases, mostly due to friction with the bottom.



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- Gloor M., Kocsis O., Omlin M., Schurter M., Wüest A. (1995): Temperaturmikrostrukturen – Eine Methode zur Bestimmung der Mischungsintensität in geschichteten Gewässern. Gas Wasser Abwasser 75, 1087–1096.
- [2] Wüest A., Piepke G., van Senden D.C. (2000): Turbulent kinetic energy balance as a tool for estimating vertical diffusivity in wind-forced stratified waters. Limnology & Oceanography 45, 1388–1400.
- [3] Ravens T.M., Kocsis O., Wüest A., Granin N. (2000): Small-scale turbulence and vertical mixing in Lake Baikal, Limnology & Oceanography 45, 159–173.

Identification of Groundwater Habitats Using Radon as a Tracer

Floodplains harbor a complex network of aquatic habitats that are fed by surface water as well as ground water. With the help of the radon method, it is possible to identify habitats that are primarily influenced by ground water. In the "middle floodplain" of Valle di Blenio, we were able to distinguish three types of ground water by determining radon along with sulfate concentrations. Each type of ground water is characterized by a different proportion of freshly-infiltrated surface water.

Floodplains are sections of a stream system that are periodically flooded [1]. They are often found in gravel deposits along valley floors and have a characteristic plant and wildlife community, depending on the duration and frequency of flooding events. In floodplains, there is an intense exchange between surface water and ground water; surface water can infiltrate into ground water and vice versa.

Radon as a Tracer in Ground Water

Groundwater habitats in floodplains are characterized by varying mixing ratios of surface water and ground water and by variable residence times of the mixed water [1]. Using the naturally occurring tracer radon, we can estimate this mixing proportion. Ground water naturally contains the radioactive noble gas radon (isotope Rn-222, referred to as Rn; see box) in detectable concentrations. Surface water, in contrast,

Radon

The radioactive isotope Radon-222 (halflife 3.8 days) is produced by the natural decay of Radium-226, itself a decay product of Uranium-238. Chemically, radon is an inert noble gas. Radon has a strong ability to penetrate rock; if uranium and/or radium is present in permeable rock, radon can be released by diffusion and recoil (emanation). Thus radon can reach ground water or soil gas, from where it is released as gas into the atmosphere. Radioactivity is measured as number of decays per second, which is the definition of the unit Becquerel (Bg). The concentration of radioactivity in ground water is described as Bq/l.

contains virtually no Rn, since it is released as gas into the atmosphere. Surface water that has freshly infiltrated to the subsurface will take up Rn and reach a steady-state concentration after approximately 15 days (Fig. 2) [2].

Groundwater Influence in the Floodplains of Valle di Blenio

An EAWAG case study in the "middle floodplain" of Valle di Blenio (Acquarossa - Ponto Valentino, Canton Ticino; Fig. 1) aimed at determining the extent to which aquatic habitats in floodplains are influenced by ground water. Part of the middle floodplain is fed by hillslope water [3]. Hillslope water is ground water that flows from the valley sides towards the valley bottom and emerges in the floodplain as springs. Such springs, for example, can be found in the gravel deposits associated with the tributary stream Uregn. Additionally, there are springs and groundwater upwellings along the stream bed and banks of the Brenno that are fed by valley floor ground water. A relatively high proportion of freshly infiltrated surface water characterizes this ground water.

Nine sites in the middle floodplain were sampled on three days (July and October 1999, April 2000). At these sites, groundwater samples were pumped from depths of up to 10 m. For comparison, water from two springs of the sulfate-rich Trias formation and surface water from the tributary Uregn and the main channel of the Brenno was sampled (Fig. 1). Radon concentrations in the water samples were immediately measured in the field with a semiconductor detector.

Three Types of Ground Water

Measured Rn concentrations were between 5 and 45 Bq/l (unit Bq: see box). As expected, the surface water from the Brenno and the Uregn contained virtually no Rn. The water from the two triassic springs, on the other hand, showed high Rn concentrations (>33 Bq/l), reflecting the fact that this is older, unmixed ground water. The



Fig. 1: Map of the middle floodplain of the Valle di Blenio (Canton Ticino), with sampling locations.

samples from the 9 groundwater sites contained mixed water with Rn concentrations between 5 and 33 Bg/l. Because of the wide range of Rn concentrations found in the mixed water samples, no clear pattern could be determined. In some sampling locations, the Rn concentration changed between sampling dates. The additional determination of sulfate (SO₄²⁻) concentrations can give us a clearer picture of whether different types of ground water are present.

The water of the Brenno is known for relatively high SO²⁻ concentrations. The sulfate is generated by the dissolution of gypsum and anhydrite rocks of the Trias formation in the upper parts of the watershed [4, 5]. Sulfate concentrations were, in fact, between 1 and 2.5 mmol/l for most of the water samples. Groundwater samples and water samples from the Uregn, on the other hand, contained only little SO₄²⁻ (<1 mmol/l).



Fig. 2: Equation describing the increase in Rn concentration over time: after 15 days (approximately 4 half-lives, t1/2) 94% of the steady-state concentration (A $_{\infty}$) is reached. Solving this equation for measured Rn concentrations (A) allows us to calculate activity ratios A/A... and, therefore, residence times for the groundwater samples



The "middle floodplain" of Valle di Blenio, Canton Ticino.

Figure 3 demonstrates how Rn and SO₄²⁻ concentrations can be used to define three types of ground water. The first group is characterized by low SO₄²⁻ and intermediate Rn concentrations; this is thought to be relatively old ground water, probably being fed by hillslope ground water from the area of the tributary Uregn. The low SO₄²⁻ concentrations indicate minimal infiltration of surface water. The second group includes samples with intermediate SO_4^{2-} and low Rn concentrations. This combination indicates fairly young mixed water with a relatively high proportion of infiltrated Brenno water. The third group comprises the water samples from the triassic springs, characterized by both high SO_4^{2-} and Rn concentrations.

mixed water with low proportion

of surface water and high propor-

tion of ground water (11 samples

mixed water with high proportion

of surface water and low propor-

tion of ground water (18 samples

water from the triassic springs (6 samples from 2 locations).

from 4 locations).

from 8 locations).

These results illustrate how Rn concentrations, in this case in combination with SO₄²⁻ concentrations, allow us to determine mixing ratios and the age of ground water. Depending on the quality of the ground water, we can expect different subsurface habitats. In addition to the hydrological aspects described in this article, a comprehensive characterization of groundwater habitats must include detailed biological and geological investigations.



Eduard Hoehn, hydrologist and research scientist in the department "Water Resources and Drinking Water" and leader of the group "Wetlands" in the interdisciplinary project "Ecoelectricity". Research area: Exchange between ground

water and surface water, groundwater contamination, tracer methods.

Co-authors: Tom Gonser, Doris Hohmann and Ruth Stierli

- [1] Brunke M., Gonser T. (1997): The ecological significance of exchange processes between rivers and ground water, Freshwater Biology 37, 1-33.
- [2] Hoehn E., von Gunten H.R. (1989): Radon in ground water - a tool to assess infiltration from surface waters to aguifers. Water Resources and Research 25, 1795-1803
- [3] Holocher J., Kipfer R., Matta V., Aeschbach-Hertig W., Beyerle U., Hofer M. Combined hydrochemical and isotopic investigations to determine the hydrological system of an alpine floodplain, Valle di Blenio, Switzerland. Groundwater 39 (6), 841-852.
- [4] Mazor E., Vuataz F. (1990): Hydrology of a spring complex, studied by geochemical time-series data, Acquarossa, Switzerland. Applied Geochemistry 5, 563-569
- [5] Pastorelli S., Marini L., Hunziker J.C. (1999): Water chemistry and isotope composition of the Acquarossa thermal system, Ticino, Switzerland. Geothermics 28, 75-93.



Conservative Elements on New Trails

A new model describing the physical process of gas exchange between entrapped soil air and ground water is able to provide an explanation of excess air in ground water. The model postulates equilibrium conditions between the ground water and the entrapped air. Based on this model, we can more meaningfully interpret atmospheric gas concentrations and more accurately quantify radiogenic helium which, in turn, allows us to more accurately date young ground water.

Over the last three decades, tracer-based methods have been successfully applied in research on the renewal of deep water masses in oceans and large lakes [1, 2]. Conservative trace gases, such as the transient nobel gases, are of primary analytical interest. If one follows the concentration changes of these transient tracers over time, one observes certain simple regularities; for example, ³He (helium) accumulates in the water due to the decay of the radioactive hydrogen isotope tritium (3H). Hence the tritiogenic ³He concentration is a measure of the time that has passed since the water was last in contact with the atmosphere; in other words, of "the age" of that particular water body.

It has long been obvious that these powerful tracer methods could also be used to determine the residence time and exchange rates of ground water; however, since gas exchange between soil air and ground water is far more complex than gas exchange between open waters and the free atmosphere, the tracer methodology developed for oceans could not be simply transferred for use in groundwater studies. Specifically, the occurrence of excess air complicates the application of the ³H-³He dating method. Therefore, the EAWAG group "Environmental Isotopes" has focused its research over the past several years on gas exchange between the atmosphere, soil and ground water.

"Excess Air" in Ground Water

Since the solubility of the noble gases in water is strongly temperature dependent, the equilibrium concentration of these gases

is a direct measure of the temperatures prevailing during the gas exchange. In contrast to open waters, the concentrations of noble gases in ground water are clearly above expected equilibrium concentrations (Fig. 1). In order to obtain accurate temperature determinations, the measured noble gas concentrations have been corrected for the "excess air" component. The composition of this "excess air" is close to the composition of the atmosphere. Although it has been known for decades that this "excess air" occurs in ground water and that it limits the application of noble gases to date ground water and to reconstruct paleoclimate conditions, almost no attempts have been made to understand the origin and the formation of this "excess air" in ground water.

The noble gases, neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe), found in water are exclusively of atmospheric origin, while helium (He) has both atmospheric- and non-atmospheric sources. Therefore, we can use four of the noble gases to solve the equations for gas exchange between atmosphere and ground water (Fig. 1). The system of equations is determined by three free parameters: temperature, amount of "excess air", and its elemental fractionation (with respect to air). The pressure is usually fairly well known, since it is given by the elevation of the infiltration zone. The equations can be solved iteratively by appropriate statistical algorithms for temperature and the other free parameters [3].

Radiogenic 2.0 Excess air Equilibrium 1.5 Concentration Σ in ground water 1 0 0.5 0 He Ne Ar Kr Xe $C_{me}^{NG} = C_{mo}^{NG} (T, p, A, F)$ Inverse model for gas exchange → T, (p), A, F ⁴He_{rad}, ³He_{tri} Age determination He_{atm}, Ne, Ar, Kr, Xe Noble gas temperature

Fig. 1: Model explaining excess noble gas concentrations in ground water. Measured gas concentrations (Σ) are clearly higher

than concentrations expected on the basis of equilibrium with the atmosphere (gray). Equilibrium concentrations are determined by the total pressure (p). average soil temperature (T), and the specific solubility of a given gas. The lighter the gas, the more enriched it becomes in the gas phase ("excess air" A, light blue). The excess of the purely atmospheric noble gases (Ne, Ar, Kr, Xe) in ground water have a composition similar to air but the heavier noble gases are enriched (F. fractionation). Helium is the only noble gas that receives additional input from radioactive decay (4He: decay of U and Th; 3He: decay of 3H). The models describing gas solution in ground water are based on the following physical parameters: T, A, F and p. as well as the concentrations of the four atmospheric noble gases Ne, Ar, Kr, Xe (C^{NG}, me = measured, mo = modeled). Using statistical methods, the model calculates the radiogenic component of the measured He concentrations which, in turn, vields an accurate age determination for the ground water.

A number of models have been proposed to describe the concentrations of atmospheric noble gases in ground water. These models vary in their assumptions about the underlying physical processes that govern gas exchange; however, none have been able to adequately account for excess helium concentrations that are calculated from ³He and ⁴He measurements in relatively young groundwater bodies [3].

"Entrapped Air" in Soil

There is clearly a need for new approaches to describe gas exchange between ground water and soil air. The new models need to adequately represent real conditions in soils and better predict the observed concentrations of He isotopes.

In contrast to common terminology, there is a gradual transition between the vadose zone (pore spaces filled with air and water) and the saturated zone (pore space completely filled with water). Typically, there is a transitional zone, which would traditionally be called saturated, where 10–20% of the pore space is filled with trapped and im-

mobilized air. This so-called "entrapped air" has a crucial influence on the groundwater recharge because it forms an effective barrier against infiltration.

Despite the fact that "entrapped air" has been extensively studied in soil science, it was not until our recent studies that the functional relationship between "excess air" and "entrapped air" and its effect on gas exchange with ground water were described [4, 5]. Flow velocities in the quasi-saturated zone are extremely low (meters per day at most); additionally, the pressure in this zone is 5–10% higher than atmospheric pressure due to hydrostatic overburden. It can be assumed that the locally increased pressure will result in a new equilibrium between "entrapped air" and the dissolved noble gases in the ground water. Since the "entrapped air" is a finite reservoir of limited capacity, and since the pressure in the trapped gas phase must be equal to the external pressure, the partial pressures of the various gases within the gas phase will adjust accordingly. As a result, the entrapped air pockets become enriched in the lighter noble gases relative to unfractionated air. The water phase, on the other hand, will become enriched in the heavier and more soluble noble gases (Fig. 1).

This new gas exchange model, which postulates an equilibrium between ground water and "entrapped air", exactly predicts the elemental composition of the noble gas excess that is typical in ground water. What is particularly important is the fact that the nobel gas excesses are directly linked to observable physical parameters, such as the overpressure in the quasi-saturated



Conclusion: Accurate Age Determination for Ground Water

In summary, the new model has not only expanded our understanding of gas exchange in ground water but it also allows on a physical basis, the determination of the temperature by measuring noble gas concentrations. The new concept of gas exchange in ground water has also significantly improved the quality of ³H-³He dating methods for relatively young ground water. Our new model results in younger, more plausible groundwater ages; whereas previous fractionation models yielded unrealistically high residence times.



Rolf Kipfer is an environmental physicist and leader of the working group "Environmental Isotopes". His research focuses on environmental tracer methods in ground water and lakes, numerical methods for data analysis and modeling of aquatic systems.

Coauthors: Werner Aeschbach-Hertig, Urs Beyerle, Matthias Brennwald, Markus Hofer, Johannes Holocher, Frank Peeters

- Hohmann R., Kipfer R., Kocsis O., Peeters F., Schurter M., Sturm M., Imboden D. (1996): Den Geheimnissen des Baikalsees auf der Spur. In: EAWAG-Jahresbericht, Dübendorf, S. 3–8.
- [2] Imboden D. (1994): Der Vierwaldstättersee fast ein helvetischer Ozean: In EAWAG-Jahresbericht, Dübendorf, S. 7–12.
- [3] Aeschbach-Hertig W., Peeters F., Beyerle U., Kipfer R. (1999): Interpretation of dissolved atmospheric noble gases in natural waters. Water Resources Research 35, 2779–2792.
- [4] Aeschbach-Hertig W., Peeters F., Beyerle U., Kipfer R. (2000): Palaeotemperature reconstruction from noble gases in ground water taking into account equilibration with entrapped air. Nature 405, 1040–1044.
- [5] Holocher J., Peeters F., Aeschbach-Hertig W., Beyerle U., Braunwald M., Hofer M., Kipfer R. (2000): New insights into the processes controlling the formation of excess air in ground water. EOS, Trans. Am. Geophys. Union, San Fransisco, 81, F 441.
- [6] Aeschbach-Hertig W., Beyerle U., Holocher J., Peeters F., Kipfer R. (2001): Excess in ground water as a potential indicator of past environmental changes. In: International conference on the study of environmental change using isotope techniques, IAEA, Vienna, p. 34–36.
- [7] Peeters F., Beyerle U., Aeschbach-Hertig W., Holocher J., Kipfer R. (2000): Recharge temperature, excess air fractionation and groundwater dating: improving the analysis by including noble gas isotopes, EOS, Trans. Am. Geophys. Union, San Fransisco, 81, F 440–441.



Fig. 2: "Excess air" in ground water of different geographical regions. Ground water from arid regions (Niger, Brazil) generally shows more "excess air" than ground water from temperate zones (Belgium, France, USA). Ground water from Niger, for example, which is older than 5000 years, shows exceptionally high amounts of "excess air". According to other paleoclimatic records, the climate in the region of the Sahel zone used to be significantly more humid than it is today ("green Sahara"). It can be assumed that under these more humid conditions, groundwater recharge was more intense, and groundwater levels were subject to large fluctuations. The resulting increased hydraulic overburden led to higher pressure in the quasi-saturated zone and hence more "excess air" can be dissolved in the ground water [6].

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"Emerging Water Contaminants"

An Interview with Ruth Gonseth

Dr. Ruth Gonseth was a representative of the Green Party in the Swiss National Parliament (Nationalrat) from 1991 to 2001. In this function, Dr. Gonseth was intensively concerned about contaminants in water and has submitted two legislative proposals "Research Need: Chemicals with Endocrine Effects" and "Reduction of Hormonally Active Substances". Dr. Gonseth has a dermatology practice and is an active member of the association "Doctors for Environmental Protection". EAWAG News interviewed Dr. Gonseth about the motives of her involvement in these issues, Switzerland's role in the international scene, and what she expects from research.

EAWAG news: You are very actively involved in issues of contaminants and pollution. What are your motives?

Ruth Gonseth: I have been interested in these kinds of problems for a long time. I have always taken special notice of reports on chemical spills, particularly when it involved chemicals that can have detrimental effects on animals and humans in even very low concentrations. At the same time, I always look at these incidents through the eyes of a physician. I am very disturbed by the increase in problems related to the male and female reproductive systems, particularly the rising number of cancers involving the breasts, testicles and prostate gland where a connection with endocrine environmental pollutants has been suggested. I only became really active after reading the report by the BUWAL (Federal Office of Environment, Forests and Landscape) on "Chemicals with Endocrine Properties in the Environment", which was coauthored by EAWAG. The document is a status report and is particularly interesting for how much it revealed that we do not know. I was



"We have to introduce the 'pay-as-you-pollute' principle, along with financial or other incentives and stricter liability laws."

shocked to learn that over the last five years, Switzerland has only spent about 500,000 CHF on research related to this very important topic. This is why I launched my first legislative proposal in 1999. I followed it up with a second interpellation in the spring of 2000 after the National Council (Bundesrat) failed to initiate any convincing measures. During the same period, the OECD had released a report on the loss of animal and plant species, which is more pronounced in Switzerland than in other countries. Among other factors, water contamination is quoted as one of the major possible causes. 45 out of 54 fish species in Switzerland are endangered. This is an absolutely terrifying number!

Are you satisfied with the outcome of your interpellation?

Yes, I am satisfied for the time being. After my second interpellation, the National Council established the national research program "Hormonally Active Chemicals in the Environment – Importance for Humans and Animals". The Federal government will be providing 15 Million CHF over the next five years. Switzerland has excellent scientists working in this field who will now be able to provide basic research in this problem area.

It appears that things have started to move on the research side. What measures do you think the government should introduce immediately in order to minimize the risk of hazardous substances in the short- to midterms?

Before we can make decisions of any kind, we need a comprehensive inventory of contaminant emissions. In such an inventory, we must compile the amounts and potential risks of environmental pollutants, similar to what we are already doing for atmospheric pollutants. I think it will be a wake-up call when we see the list of compounds that are actually released into the environment and into water in particular.

At the same time, many compounds that are currently in use must be re-examined for their hormonal activities, as is already

FORUM

being done for sun protection chemicals. In situations where toxic or other detrimental effects on organisms or the environment already have been documented unequivocally, as is the case for nonylphenols in detergents for example, I advocate a strict ban of use of these compounds.

But we cannot limit ourselves to fighting the symptoms after-the-fact. Producers and distributors of these compounds must shoulder more of the responsibility. We must introduce the "pay-as-you-pollute" principle, along with financial or other incentives and stricter liability laws. This would give industry some motivation to extensively test new chemicals and refrain from introducing such compounds if there is even the slightest sign of a problem.

Do you think the "pay-as-you-pollute" principle is enforceable?

It certainly is difficult; the lobby of the manufacturing industry is very powerful. At the same time, many of the users of these chemicals are also not interested in fundamental changes. Our intensive agricultural industry, for example, presents an enormous problem. Pesticides are still being used in huge quantities and end up in the environment. We have to move away from using these poisons. I am a strong advocate of biological agriculture. The increased demand for bioproducts by consumers is a huge opportunity for bringing about a fundamental change in our production methods, although I think that we need to increase the competitiveness of bioproducts by levying fees on pesticides.

The problem of environmental pollutants is a global one. What political goals should Switzerland pursue on the international level?

Switzerland has to become more engaged in international panels. It is an urgent goal to come to international agreements on pollutant levels. We are well off in Switzerland, being in the water reservoir of Europe, but countries farther downstream, along the Rhine for example, are still confronted with enormous problems. Despite the fact that pollutant concentrations have continually dropped over the last few years, we cannot cancel the alarm quite yet. This is why the work of the "International Commission for the Protection of the Rhine" is so important. It brings together all of the countries in the Rhine watershed at one table for a joint effort to find solutions.

A second important problem concerns southern countries. Many people do not have access to uncontaminated drinking water. We already know that the water supply will become even tighter in the future and that water will become a source of conflict. As a privileged country, we have the obligation to provide "know-how". An urgent issue, for example, is wastewater treatment, which is completely lacking even in large cities. Agriculture needs new water conservation technologies since approximately two thirds of the irrigation water is being wasted - it evaporates - although more appropriate irrigation systems could mitigate this problem. This is another area where Switzerland could provide useful research.

In your parliamentary proposal for an international water convention, you challenge politicians to become more active. What are the goals of such a convention?

I would like the National Council to become an advocate for an international water convention in the appropriate panels, e.g., in RIO 2002. The main points of the convention would be to effectively protect water as a common public good and to establish access to clean drinking water as a basic human right. It will require a huge effort to guarantee this basic human right, particularly because of the privatization tendencies in this area. This does not mean that I am against cooperation with private enterprises, but the government has to retain authority over the drinking water supply.

Finally, the question: what homework would the politician Ruth Gonseth like to give to the research community?

First, I am relieved that the Federal Government funds the national research program



"Water is a public and common good."

"Hormonally Active Chemicals in the Environment". The urgent task is now to fill the gaps in our scientific knowledge in order to understand the reasons for the disappearance of species, the increase of cancer and other phenomena. But I also think that the scientific community has to increasingly carry this topic into public discussions in order to raise the awareness that we have been treating "water" rather carelessly. Secondly I believe that scientists have to take on a more political role. Knowledge transfer is working well within the scientific community through scientific journals. The same transfer has to be possible between the scientific community and politicians.

I thank you very much for this conversation.

Interview by Martina Bauchrowitz

Publications and Books

Please use the order form in the center fold of EAWAG news to request reprints.

2870 **Von Gunten U., Salhi E.** (2000): Bromat im Trinkwasser – Ein Problem in der Schweiz? Gas, Wasser, Abwasser *80* (10), 705–710.

2871 Zah R., Niederöst M., Uehlinger U. (2000): Application of photogrammetry in freshwater ecology: analysing the morphology of a high Alpine flood-plain. Internat. Arch. Photogramm. & Remote Sensing 23 (B7), 1739–1746.

2872 Magnuson J.J., Robertson D.M., Benson B.J., Wynne R.H., Livingstone D.M., Arai T., Assel R.A., Barry R.G., Card V., Kuusisto E., Granin N.G., Prowse T.D., Stewart K.M., Vuglinski V.S. (2000): Historical trends in lake and river ice cover in the northern hemisphere. Science 289, 1743–1746.

2873 Boller M., von Gunten U., Pianta R., Solcà L. (2000): Modelling full scale advanced micropollutant oxidation. In: Chemical water and wastewater treatment VI, Proc. 9th Gothenburg Sympos. October 2–4, Istanbul, Turkey (Eds. H. Hahn et al.) Springer Verlag, Berlin, pp. 125–136.

2874 Bundi U., Peter A., Truffer B., Wagner W., Mauch U., Scheidegger A. (2000): The quality of aquatic ecosystems as an indicator for sustainable water management – country paper of Switzerland. In: Let the fish speak: the quality of aquatic ecosystems as an indicator for sustainable water management (Ed. J.A. van de Kraats). EurAqua technical review No. 4, pp. 205–215.

2875 **Bundi U.** (2000): Nachhaltige Wassernutzung in der Schweiz, in Europa und weltweit. Thema Umwelt (Hrsg. PUSCH – Praktischer Umweltschutz Schweiz) H. 1, 22–23.

2876 **Holm P.** (2000): Der Fischfangrückgang in den schweizerischen Fliessgewässern – Auslöser des Projektes "Fischnetz" und Konsequenzen für die Forschung. In: Festschrift 100 Jahre Sportfischer-Verein (Hrsg. Sportfischer-Verein, Bern), S. 109–113.

2877 Känel B., Bundi U., Peter A. (2000): Ansätze zur ökomorphologischen Analyse und Verbesserung von Fliessgewässer-Systemen. Protokoll der 34. Tagung des Cercl'eau der Vereinigung der kantonalen GewässerschutzlimnologInnen und -chemikerInnen, 23. März in Neuchâtel, 7 S.

2878 **Biedermann R., Bundi U., Traber H.** (1999): Wege zu einer nachhaltigen Landwirtschaft im Klettgau. Mitt. Naturforsch. Ges. Schaffhausen *44*, 21–30.

2879 Bonting C.F.C., Gerards R., Zehnder A.J.B., Kortstee G.J.J. (1999): Purification and properties of pyrophosphatase of *Acinetobacter johnsonii* 210A and its involvement in the degradation of polyphosphate. Biodegradation 10, 393–398.

2880 **Burkhardt-Holm P., Bloesch J.** (2000): Fish as bioindicators for pollutants in the Danube River: an approach. Proc. 33rd Internat. Assoc. Danube Res. Conf. Osijek, September 3–9, Croatia. Grafika, Osjek, pp. 375–382.

2881 Jaggy M., Schenker R., Riet R., Schenker F. (2000): Voruntersuchung einer Schiessanlage – Vorgehen am Beispiel des belasteten Standorts Grosswiyer, Goldau SZ. Schriftenreihe Umwelt-Materialien Nr. 124 (Altlasten/Gefährdungsabschätzung), BUWAL Bern, 49 S.

2882 **Krušpán P.R.** (2000): Natürliche und technische Petrogenese von Puzzolanen: Ein Beitrag zur Herstellung mineralischer Sekundärrohstoffe. Diss. ETHZ No. 13 732, Zürich.

2883 **Faist M.** (2000): Ressourceneffizienz in der Aktivität Ernähren: Akteurbezogene Stoffflussanalyse. Diss. ETHZ No. 13 884, Zürich.

2884 Kasemir B., Toth F., Masing V. (2000): Climate policy, venture capital and european integration. J. Common Market Studies 38 (5), 891–903.

2885 **Beer J.** (2000): Neutron monitor record in broader historical context. Space Sci. Rev. *93*, 107–119.

2886 **Beer J.** (2000): Long-term indirect indices of solar variability. Space Sci. Rev. *94*, 53–66.

2887 **Sigg L., Xue H., Kistler D., Schönenberger R.** (2000): Size fractionation (dissolved, colloidal and particulate) of trace metals in the Thur river, Switzerland. Aquatic Geochemistry *6*, 413– 434.

2888 Ahel M., Molnar E., Ibric S., Giger W. (2000): Estrogenic metabolites of alkylphenol polyethoxylates in secondary sewage effluents and rivers. Water Sci. Technol. 42 (7–8), 15–22.

2889 Strauss M., Larmie S.A., Heinss U., Montangero A. (2000): Treating faecal sludges in ponds. Water Sci. Technol. 42 (10–11), 283–290.

2890 Arscott D.B., Tockner K., Ward J.V. (2000): Aquatic habitat diversity along the corridor of an alpine floodplain river (fiume Tagliamento, Italy). Arch. Hydrobiol. *149* (4), 679–704.

2891 **Donath U., Robinson C.T.** (2001): Ecological characteristics of lake outlets in Alpine environments of the Swiss Alps. Arch. Hydrobiol. *150* (2), 207–225.

2892 **Gruber N., Wehrli B., Wüest A.** (2000): The role of biogeochemical cycling for the formation and preservation of varved sediments in Soppensee (Switzerland). J. Paleolimnology 24, 277-291.

2893 **Wüest A., Carmack E.** (2000): A priori estimates of mixing and circulation in the hard-to-reach water body of Lake Vostok. Ocean Model-ling *2*, 29–43.

2894 **Pinkernell U., Nowack B., Gallard H., von Gunten U.** (2000): Methods for the photometric determination of reactive bromine and chlorine species with abts. Water Res. *34* (18), 4343–4350.

2895 Looser P.W., Berg M., Fent K., Mühlemann J., Schwarzenbach R.P. (2000): Phenyland butyltin analysis in small biological samples by cold methanolic digestion and GC/MS. Anal. Chemistry 20 (20), 5136–5141.

2896 **Uehlinger U.** (2000): Resistance and resilience of ecosystem metabolism in a flood-prone river system. Freshwater Biol. *45*, 319–332.

2897 Landini P., Volkert M.R. (2000): Regulatory responses of the adaptive response to alkylation damage: a simple regulon with complex regulatory features. J. Bacteriol. *182* (23), 6543–6549.

2898 Volkland H.-P., Harms H., Müller B., Repphun G., Wanner O., Zehnder A.J.B. (2000): Bacterial phosphating of mild (unalloyed) steel. Appl. Environ. Microbiol. *66* (10), 4389–4395.

2899 Hoehn E., Johnson C.A., Huggenberger P., Amirbahman A., Peter A., Zweifel H.R. (2000): Investigative strategies and risk assessment of old unlined municipal solid waste landfills. Waste Managem. Res. *18*, 577–589.

2900 Kasemir B., Dahinden U., Swartlin A.G., Schüle R., Tabara D., Jaeger C.C. (2000): Citizens' perspectives on climate change and energy use. Global Environ. Change *10*, 169–184.

2901 Zobrist J., Dowdle P.F., Davis J.A., Oremland R.S. (2000): Mobilization of arsenite by dissimilarory reduction of adsorbed arsenate. Environ. Sci. Technol. *34* (22), 4747–4753.

2902 Looser P.W., Fent K., Berg M., Goudsmit G.-H., Schwarzenbach R.P. (2000): Uptake and elimination of triorganotin compounds by larval midge *Chironomus riparius* in the absence and presence of aldrich humic acid. Environ. Sci. Technol. *34* (24), 5165–5171.

2903 Ingallinella A.M., Sanguinetti G., Fernandez R.G., Strauss M., Montangero A. (2000): Cotreatment of sewage and septage in stabilization ponds. International Conference on Waste Stabilisation Ponds, Cali, Colombia, October.

2904 Montangero A., Strauss M. (2000): Faecal sludge management – strategic aspects and treat-

ment options. International Workshop on Biosolids Management and Utilization at Nanjing and to the Forum on Biosolids Management and Utilization at Hongkong, 14 pp.

2905 **Montangero A., Strauss M.** (2000): When septic tanks are full – challenges in faecal sludge management and treatment. AIDIS Conference, Mendoza, Argentina, 14 pp.

2906 **Strauss M., Heinss U., Montangero A.** (2000): On-site sanitation: when the pits are full – planning for resource protection in faecal sludge management. In: Water, sanitation and health – resolving conflicts between drinking-water demands and pressures from society's wastes (Eds. I. Chorus et al.) Schriftenreihe des Vereins Wasser-, Boden- und Lufthygiene *105*, IWA Publishing House and WHO Water Series pp. 353–360.

2907 Montangero A., Strauss M., Dembélé A. (2000): Gestion des boues de vidange: Parent pauvre de l'assainissement et défi à relever. 12e conférence des centres du réseau international de formation à la gestion de l'eau et des déchets (RIF/ITN) d'Afrique, Ouagadougou, Burkina Faso, 12 pp.

2908 **Goss K.-U., Schwarzenbach R.P.** (2001): Linear free energy relationships used to evaluate equilibrium partitioning of organic compounds. Environ. Sci. Technol. *35* (1), 1–9.

2909 Wick L.Y., Colangelo T., Harms H. (2001) Kinetic of mass transfer-limited bacterial growth and solid PAHs. Environ. Sci. Technol. *35* (2), 354– 361.

2910 Wagner G., Masarik J., Beer J., Baumgartner S., Imboden D., Kubik P.W., Synal H.-A., Suter M. (2000): Reconstruction of the geomagnetic field between 20 and 60 kyr BP from cosmogenic radionuclides in the GRIP ice core. Nuclear Instruments and Methods in Physics Res. *B* 172, 597–606.

2911 Schweigert N., Hunziker R.W., Escher B.I., Eggen R.I.L. (2001): Acute toxicity of (chloro-) catechols and (chloro-)catechol-copper combinations in *Escherichia coli* corresponds to their membrane toxicity *in vitro*. Environ. Toxicol. Chem. 20 (2), 239–247.

2912 Eichler A., Schwikowski M., Gäggeler H.W., Furrer V., Synal H.-A., Beer J., Saurer M., Funk M. (2000): Glaciochemical dating of an ice core from upper Grenzgletscher (4200 m a.s.l.). J. Glaciology *46* (154), 507–516.

2913 **Beer J.** (2000) Solar activity: long-term records. In: Encyclopedia of astronomy and astrophysics (Eds. O. Sol et al.) Nature Publishing Group, Vol. 3, pp. 2475–2479.

2914 Wüest A. (2000): Archaisches Leben im verborgenen Extrem? Anspruchsvolle Erkundung eines einzigartigen Ökosystems. Neue Zürcher Zeitung, Nr. 261, 8. November.

2915 Wedekind C., Müller R., Steffen A., Eggler R. (2001): A low-cost method of rearing multiple batches of fish. Aquaculture *192*, 31–37.

2916 Yang H., Zehnder A.J.B. (2001): China's regional water scarcity and implications for grain supply and trade. Environ. Planning *A 33*, 79–92.

2917 Malard F., Tockner K., Ward J.V. (2000): Physico-chemical heterogeneity in a glacial riverscape. Landscape Ecology *15*, 679–695. 2918 Pianta R., Boller M., Urfer D., Chappaz A., Gmünder A. (2000): Costs of conventional vs. membrane treatment for karstic spring water. Desalination *131*, 245–255.

2919 **Bucheli-Witschel M., Egli T.** (2001): Environmental fate and microbial degradation of aminopolycarboxylic acids. FEMS Microbiol. Rev. *25*, 69–106.

2920 Goudsmit G.-H., Lemcke G., Livingstone D.M., Lotter A.F., Müller B., Sturm M. (2000): Hagelseewli: a fascinating high mountain lake – suitable for palaeoclimate studies? Verh. Internat. Verein. Limnol. *27*, 1013–1022.

2921 Emmenegger L., Schönenberger R., Sigg L., Sulzberger B. (2001): Light-induced redox cycling of iron in circumneutral lakes. Limnol. Oceanogr. 46 (1), 49–61.

2922 **Muscheler R., Beer J., Wagner G., Finkel R.C.** (2000): Changes in deep-water formation during the younger dryas event inferred from ¹⁰Be and ¹⁴C records. Nature *408*, 567–570.

2923 Bernet D., Schmidt H., Wahli T., Burkhardt-Holm P. (2001): Effluent from a sewage treatment works causes changes in serum chemistry of brown trout (*Salmo trutta* L.). Ecotoxicol. Environ. Safety *48 B*, 140–147.

2924 **Durner R., Zinn M., Withold B., Egli T.** (2001): Accumulation of poly(R)-2-hydroxyalkanoates in *Pseudomonas oleovorans* during growth in batch and chemostat culture with different carbon sources. Biotechnol. Bioeng. *72* (3), 278–288.

2925 Xue H.B., Jansen S., Prasch A., Sigg L. (2001): Nickel speciation and complexation kinetics in freshwater by ligand exchange and DPCSV. Environ. Sci. Technol. *35* (3), 539–546.

2926 **Zehnder A.J.B.** (2001): 21st century, a challenge for microbes, engineers, and environmental scientists. The Internat. Symposium of the COE, University of Tokyo, February 5–7.

2927 **Kipfer R., Peeters F.** (2000): Some speculations on the possibility of changes in deep-water renewal in Lake Baikal and their consequences. In: Lake Baikal, (Ed. K. Minoura) Elsevier, Amsterdam, pp. 273–280.

2928 Muscheler R. (2001): Letzte Kaltphase mit reduzierter Ozeanströmung. Neue Zürcher Zeitung, Nr. 1, 3. Januar.

2929 **Burkhardt-Holm P., Studer C.** (2000): Hormonaktive Stoffe im Abwasser – Sind Fische und andere wasserlebende Tiere betroffen? Gas, Wasser, Abwasser *80*, 504–509.

2930 **Gächter R.** (2000): Zehn Jahre Seenbelüftung. Ein Erfahrungsbericht. Gewässerökologie Norddeutschlands *4*, 158–165.

2931 **Pimenov N.V., Rusanov I.I., Yusupov S.K., Fridrich J., Lein A.Y., Wehrli B., Ivanov M.V.** (2000): Microbial processes at the aerobic-anaerobic interface in the deep-water zone of the Black Sea. Microbiology *69* (4), 436–448.

2932 Ivanov M.V., Lein A.Y., Miller Y.M., Yusupov S.K., Pimenov N.V., Wehrli B., Rusanov I.I., Zehnder A.J.B. (2000): The effect of microorganisms and seasonal factors on the isotopic composition of particulate organic carbon from the Black Sea. Microbiology 69 (4), 449–459. 2933 Balmer H., Hoehn E., Boller M. (2001): Zuströmbereiche für Grundwassererfassungen – Konzeptionelle Überlegungen zu Zweck und Abgrenzung. Gas, Wasser, Abwasser *81*, 21–28.

2934 Brancelj A., Sisko M., Lami A., Appleby P., Livingstone D.M., Rejec-Brancelj I., Ogrin D. (2000): Changes in the trophic level of an Alpine lake, Jezero v. Ledvici (NW Slovenia), induced by earthquakes and climate change. J. Limnol. 59 (Suppl. 1), 29–42.

2935 Lotter A.F., Hofmann W., Kamenik C., Lami A., Ohlendorf C., Sturm M., van der Knapp W.O., van Leeuwen J.F.N. (2000): Sedimentological and biostratigraphical analyses of short sediment cores from Hagelseewli (2339 m a.s.l.) in the Swiss Alps. J. Limnol. 59 (Suppl. 1), 53–64.

2936 Ohlendorf C., Bigler C., Goudsmit G.-H., Lemcke G., Livingstone D.M., Lotter A.F., Müller B., Sturm M. (2000): Causes and effects of long periods of ice cover on a remote high Alpine lake. J. Limnol. *59* (Suppl. 1), 65–80.

2937 Ventura M., Camerero L., Buchaca T., Bartumeus F., Livingstone D.M., Catalan J. (2000): The main features of seasonal variability in the external forcing and dynamics of a deep mountain lake (Redó, Pyrenees). J. Limnol. 59 (Suppl. 1), 97–108.

2938 **Burgherr P.** (2000): Spatio-temporal community patterns of lotic zoobenthos across habitat gradients in an Alpine glacial stream ecosystem. Diss. ETHZ Nr. 13 829, Zürich.

2939 Weirich D. (2000): Influence of organic ligands on the adsorption of copper, cadmium, and nickel on goethite. Diss. ETHZ Nr. 13 917, Zürich.

2940 Zah R. (2000): Patterns, pathways, and trophic transfer of organic matter in a glacial stream ecosystem in the Alps. Diss. ETHZ Nr. 13 998, Zürich.

2941 **Burgherr P.** (2000): Struktur der Wirbellosenfauna an der Flusssohle eines voralpinen Fliessgewässers (Necker SG). Ber. St. Gall. Naturwiss. Ges. 89, 137–154.

2942 **Enz C.A., Schäffer E., Müller R.** (2000): Growth and survival of Lake Hallwil whitefisch (*Coregonus* sp.) larvae reared on dry and live food. Arch. Hydrobiol. *148* (4), 499–516.

2943 **Livingstone D.M., Hajdas I.** (2001): Climatically relevant periodicities in the thicknesses of biogenic carbonate varves in Soppensee, Switzerland (9740–6870 Calendar yr BP). J. Paleolimnol. *25*, 17–24.

2944 Mattle N., Kinzelbach W., Beyerle U., Huggenberger P., Hoosli H.H. (2001): Exploring an aquifer system by integrating hydraulic, hydrogeologic and environmental tracer data in a threedimensional hydrodynamic transport model. J. Hydrol. *242*, 183–196.

2945 Johnson C.A., Schaap M.G., Abbaspour K.C. (2001): Model comparison of flow through a municipal solid waste incinerator ash landfill. J. Hydrol. *243*, 55–72.

2946 **Tockner K., Malard F., Ward J.V.** (2000): An extension of the flood pulse concept. Hydrol. Process. *14*, 2861–2883.

2947 Gurnell A.M., Petts G.E., Hannah D.M., Smith B.P.G., Edwards P.J., Kollmann J., Ward J.V., Tockner K. (2001): Riparian vegetation and island formation along the gravel-bed Fiume Tagliamento, Italy. Earth Surf. Process. Landforms 26, 31–62.

2948 Genoni G.P., Behra R., Montague C.L., Güttinger H., Ternay-Aegerter R. (2001): Complex dynamics of adaptation in a nonaxenic *Microcystis* culture – 1. Effects of dinitrophenol on population growth. Ecotoxicol. Environ. Safety 48, 235–240.

2949 Montague C.L., Behra R., Bosma T.N.P., Genoni G.P., Güttinger H. (2001): Complex dynamics of adaptation in a nonaxenic *Microcystis* culture – 2. Computer simulation of dinitrophenol effects. Ecotoxicol. Environ. Safety *48*, 241–254.

2950 Wagner G., Livingstone D.M., Masarik J., Muscheler R., Beer J. (2001): Some results relevant to the discussion of a possible link between cosmic rays and the earth's climate. J. Geophys. Res. *106* (D4), 3381–3387.

2951 **Beer J.** (2000): Polar ice as an archive for solar cycles and the terrestrial climate. Proc. 1st Solar and Space Weather Euroconference, Santa Cruz de Tenerife, Tenerife, Spain.

2952 Beardall J., Berman T., Heraud P., Kadiri M.O., Light B.R., Patterson G., Roberts S., Sulzberger B., Sahan E., Uehlinger U., Wood B. (2001): A comparison of methods for detection of phosphate limitation in microalgae. Aquatic Sci. 63, 107–121.

2953 Kominkova D., Kuehn K.A., Büsing N., Steiner D., Gessner M.O. (2000): Microbial biomass, growth, and respiration associated with submerged litter of *Phragmites australis* decomposing in a littoral reed stand of a large lake. Aquatic Microb. Ecol. *22*, 271–282.

2954 **Eggen R.I.L.** (2001): Moderne biologische Analyse. Gas, Wasser, Abwasser *81* (3), 167–171.

2955 **Soldo D.** (2000): Tolerance analyses in algal communities and populations exposed to pollutants. Diss. ETHZ No. 13 768, Zürich.

2956 Gerecke A.C. (2001): Phenylurea herbicides in the aquatic environment – sources and elimination processes. Diss. ETHZ No. 14111, Zürich.

2957 Lendenmann U., Senn H., Snozzi M., Egli T. (2000): Dynamics of mixed substrate growth of *Escherichia coli* in batch culture: the transition between simultaneous and sequential utilisation of carbon substrates. Acta Universitatis Carolinae Environmentalica *14*, 21–30.

2958 Klein B., Tockner K. (2000): Biodiversity in springbrooks of a glacial flood plain (Val Roseg, Switzerland). Verh. Internat. Verein. Limnol. *27*, 704–710.

2959 Robinson C.T., Gessner M.O. (2000): Leaf breakdown in an Alpine spring brook. Verh. Internat. Verein. Limnol. *27*, 744–747.

2960 **Frutiger A., Niederhauser D.** (2000): Effects of water abstraction on new-winged midges (Diptera: Blephariceridae). Verh. Internat. Verein. Limnol. *27*, 942–946.

2961 Reichert P., Borchardt D., Henze M., Rauch W., Shanahan P., Somlyódy L., Vanrolleghem P. (2001): River water quality model no. 1 (RWQM1): II. Biochemical process equations. Water Sci. Technol. *43* (5), 11–30. 2962 Jacquinot P., Müller B., Wehrli B., Hauser P.C. (2001): Determination of methane and other small hydrocarbons with a platinum-nafion electrode by stripping voltammetry. Analytica Chimica Acta *432*, 1–10.

2963 **Oellers S., Singer H. P., Fässler P., Müller S.R.** (2001): Simultaneous quantification of neutral and acidic pharmaceuticals and pesticides at the low-ng/l level in surface and waste water. J. Chromatogr. *A 911*, 225–234.

2964 Weyhenmeyer G.A., Bloesch J. (2001): The pattern of particle flux variability in Swedish and Swiss lakes. Sci. Total Environ. *266*, 69–78.

2965 Schweigert N., Zehnder A.J.B., Eggen R.I.L. (2001): Chemical properties of catechols and their molecular modes of toxic action in cells, from microorganisms to mammals. Environ. Microbiol. *3* (2), 81–91.

2966 Egli K., Fanger U., Alvarez P.J.J., Siegrist H.-R., van der Meer J.R., Zehnder A.J.B. (2001): Enrichment and characterization of an anammox bacterium from a rotating biological contactor treating ammonium-rich leachate. Arch. Microbiol. 175, 198–207.

2967 Andren A.W., Mackay D., DePinto J.V., Fox K., Thibodeaux L.J., McLachlan M., Haderlein S. (2000): Inter-media partitioning and transport. In: Evaluation of persistence and long-range transport of organic chemicals in the environment (Eds. G. Klecka et al.) Soc. Environ. Toxicol. Chem. (SETAC), pp. 131–168.

2968 **Royer T.V., Robinson C.T., Minshall G.W.** (2001): Development of macroinvertebrate-based index for bioassessment of Idaho Rivers. Environ. Managem. *27* (4), 627–636.

2969 Larsen T.A., Boller M.A. (2001): Perspectives of nutrient recovery in DESAR concepts. In: Decentralised sanitation and reuse: concepts, systems and implementation (Eds. P. Lens et al.). IWA Publishing, London, pp. 387–410.

2970 **Bosma T.N.P., Harms H., Zehnder A.J.B.** (2001): Biodegradation of xenobiotics in environment and technosphere. In: The handbook of environmental chemistry, Vol. 2, Part K , Biodegradation and persistence, (Ed. B. Beek) Springer-Verlag, Berlin.

2971 **Canonica S., Freiburghaus M.** (2001): Electron-rich phenols for probing the photochemical reactivity of freshwaters. Environ. Sci. Technol. *35* (4), 690–695.

2972 Larsen T., Alder A., Eggen R., Maurer M., Muncke J., Peters I. (2001): Testlauf im Kraftwerk1. Magazin UniZürich 1/01 – Bull. ETHZ Nr. 281, 47–49.

2973 Alder A.C., Giger W., Reiser R., Schaffner C., Ahel M., Albrecht A. (2001): Detergentienchemikalien in Seesedimenten. In: Moderne Wasch- und Reinigungsmittel – Umweltwirkungen und Entwicklungstendenzen. Münchner Beiträge zur Abwasser-, Fischerei- und Flussbiologie, Bayerisches Landesamt für Wasserwirtschaft, München, Band 54, 289–301.

2974 Larsen T.A., Udert K.M. (1999): Urinseparierung – ein Konzept zur Schliessung der Nährstoffkreisläufe. Wasser & Boden 51 (11), 6–9.

2975 **Tillman D.** (2000): Entscheidungsabläufe in der Wasserversorgung. 4. Lippuner Seminar in

Vaduz FL: Fachtagung Wasser 2000 "Wasserverteilung". Verlag Lippuner, Bad Ragaz, S. 21–24.

2976 **Boller M.** (2000): Nutzen der Netzwerkanalyse für die Qualitätssicherung in der Wasserversorgung. 4. Lippuner Seminar in Vaduz FL: Fachtagung Wasser 2000 "Wasserverteilung". Verlag Lippuner, Bad Ragaz, S. 25–31.

2977 Schmidt T.C., Duong H.-A., Berg M., Haderlein S.B. (2001): Analysis of fuel oxygenates in the environment. Analyst *126*, 405–413.

2978 Larsen T.A. (1999): Nährstoffkreisläufe in der Siedlungswasserwirtschaft. Schweiz. Ingenieur & Architekt 19, 394–392.

2979 Zehnder A.J.B. (2001): Sind wir zur Nachhaltigkeit bereit? Gaia *10* (1), 25–26.

2980 Jung D.K.J., Klaus T., Fent K. (2001): Cytochrome P450 induction by nitrated polycyclic aromatic hydrocarbons, azaarenes, and binary mixtures in fish hepatoma cell line PLHC-1. Environ. Toxicol. Chem. 20 (1), 149–159.

2981 **Boller M.** (2001): Belastung des Regenwassers mit Schadstoffen und neue technische Reinigungsverfahren mit Adsorbern. VSA-Hauptmitgliederversammlung 30. März, Entsorgung des Regenwassers, 1–15.

2982 **Steingruber S.M.** (2001): Nutrient transformations in a wetland pond. Diss. ETHZ No. 13 939, Zürich

2983 **Rinke K., Robinson C.T., Uehlinger U.** (2001): A note on abiotic factors that constrain periphyton growth in Alpine glacier streams. Internat. Rev. Hydrobiol. *86* (3), 361–366.

2984 **Stemmler K., Glod G., von Gunten U.** (2001): Oxidation of metal-diethylenetriaminepentaacetate(DTPA)-complexes during drinking water ozonation. Water Res. *35* (8), 1877–1886.

2985 von Gunten U., Driedger A., Gallard H., Salhi E. (2001): By-products formation during drinking water disinfection: a tool to assess disinfection efficiency? Water Res. *35* (8), 2095–2099.

2986 Schmidt-Posthaus H., Bernet D., Wahli T., Burkhardt-Holm P. (2001): Morphological organ alterations and infectious diseases in brown trout *Salmo trutta* and rainbow trout *Oncorhynchus mykiss* exposed to polluted river water. Diseases Aquat. Org. 44, 161–170.

2987 Mengis M., Walther U., Bernasconi S.M., Wehrli B. (2001): Limitations of using δ^{18} O for the source identification of nitrate in agricultural soils. Environ. Sci. Technol. 35 (9), 1840–1844.

Books

Jaggy M., Schenker R., Tietz R., Schenker F. (2000): Voruntersuchung einer Schiessanlage – Vorgehen am Beispiel des belasteten Standorts Grosswiyer, Goldau SZ. Schriftenreihe Umwelt-Materialien Nr. 124 (Altlasten/ Gefährdungsabschätzung), BUWAL Bern, 49 Seiten. [2881]

Larsen T.A., Gujer W. (2000): Waste design and source control lead to flexibility in wastewater management. Preprint 1st IWA World Water Congress, Paris, Book 5, pp. 93–300.

Sigg L., Behra P., Stumm W. (2000): Chimie des milieux aquatiques, Dunod, Paris, 3ème éd., 567 p.

IN BRIEF

EAWAG at the Hannover Trade Fair 2001

EAWAG participated in a booth shared by the ETH Domain and by the initiative "Technology Made in Switzerland" at the Hannover Trade Show, which took place April 23–28, 2001. The goal of EAWAG's presence was to introduce EAWAG to a broad international public and contribute to information and technology transfer.

EAWAG had the opportunity to demonstrate its activities in research, teaching and consulting in a very interesting and stimulating environment. The project by Michele Steiner on "Copper in the Environment – New Filters Prevent Its Release" formed the central theme. Copper has excellent properties as a building material and is used as a roofing

New Face for Aquatic Sciences

The journal *Aquatic Sciences* has a long standing tradition. In 1920, the journal was launched under the name of the *Journal of Hydrology* by the Hydrobiological Commission of the Swiss Society for the Study of the Natural Sciences. Since its beginning, EAWAG has contributed the majority of the journal's editors.



ic Sciences will appear with a new focus, format and editorial board. The changes were prompted by a desire to give the journal stronger inter-

In 2002, Aquat-

national recognition. According to its new subtitle, "Research Across Boundaries", emphasis will be shifted to the publication of interdisciplinary research dealing with aquatic systems and the influence of human activity on those systems. Research on the sustainable management of natural waters will be of particular interest.

Aquatic Sciences – Research Across Boundaries will not only publish original research papers, but also review articles. In addition, some issues will be dedicated to topical themes. You are invited to submit your manuscripts or suggestions for special issues for publication in Aquatic Sciences. For more information:

http://www.eawag.ch/publications/ aquatic_sciences/ material, as the outer layer on facades, and in water pipes. Via rain water and sewage treatment sludge, copper is transported into the soil and surface waters where it exhibits toxic effects on a broad range of organisms. In order to prevent the spread of copper in the environment, EAWAG is recommending a novel iron-hydroxide-limestone sand filter as a means of immobilizing it.

Thanks to EAWAG's presence at the Hannover Trade Show, the public learned about the problems related to copper and about the new filtration system. The trade show also fostered interesting new contacts; applications of the new filtration system in related areas were also discussed.



CEAC-Workshop: Detection of Chemical Pollutants

Last year's summer workshop by the Center for Excellence in Analytical Chemistry (CEAC) of the ETH Zurich took place on July 12–13 at the EAWAG/EMPA Akadamie. The general topic was "Analytical methods of separation and detection in the new millenium". Specialists from the fields of analytical chemistry in the environment, in food and in drugs presented overviews of recent developments and current applications of various chemical and biological methods. Directly coupled methods, methods that combine separation and detection in one step such as GC/MS, were of particular

PKD – C'est quoi?

"Proliferative kidney disease", a kidney disease in fish, may be partially responsible for decreasing fisheries yields and generally deteriorating fitness of fish in Swiss streams. Possible connections between the disease and observations of fish health are being investigated as part of the project "Fish Net".

In July of last year, the project "Fish Net" invited an international group of experts to a workshop at EAWAG's facility in Kastanienbaum. During two days of talks and discussions, the current knowledge base was compiled and gaps in our understanding were identified. We now know that the intermediate host of the parasite causing PKD, a moss animal (bryozoan), prefers warm, slow-moving streams. This piece of information, together with information about interest. Most methods discussed focus on the detection of chemical pollutants which are currently of extreme importance. The discussions included persistent organic pollutants, hormonally active substances, the doping drug erythropoietin (EPO), a well known peptide hormone, as well as genetically manipulated organisms and prions causing BSE.

The workshop was organized jointly by Walter Giger and Hans-Peter Kohler of EAWAG and by Peter Schmid of EMPA. More information about the workshop may be found at www.ceac.ethz.ch

conditions found in Switzerland, was crucial in the development of a set of recommendations for mitigation which will shortly be passed on to the authorities in charge of fisheries in an effort to halt the spread of PKD.



IN BRIEF

"Festival of Science"

The "Festival of Science", sponsored jointly by the University of Zurich and ETH-Zurich, took place in the large hall of Zurich's main train station on May 4–12, 2001. The festival was part of a larger event, organized by the foundation "Science et Cité" and held at 10 different locations throughout Switzerland, with the goal of promoting dialogue between scientists and the public.

EAWAG presented two projects: "Solar Disinfection of Water" (SODIS) and the "NoMix Toilet". Both the unusual toilet, which allows the separate collection of urine, and the astonishingly simple SODIS technology for the disinfection of drinking water, attracted a great number of visitors. The public ap-



peared to be very interested in the opportunity to have direct conversations with the researchers and to learn about EAWAG's activities in general. There was also considerable interest in the pilot project "Round Table", in which EAWAG scientists and citizens meet in regular discussions.

With approximately 100,000 visitors spending an average of 30 minutes each at the festival, and intensive national media coverage, the first "Festival of Science" in Zurich was a great success.

For more information:

www.eawag.ch/events/science_et_cite/

Switzerland and EAWAG set international Standard for Certification of Ecoelectricity

On June 27, 2001, approximately 40 experts from Europe, USA, Canada and Japan met in Zurich to discuss the future of environmentally responsible hydroelectric power generation. The main topic of the "Second International Conference on Hydropower as Green Electricity" was the development of a credible and internationally equitable procedure for the certification of "ecoelectricity". The delegates reached consensus that simple certification procedures, as they are currently used in various European countries, will not be adequate in the long term. Since these procedures simply set limits for how



much power can be produced or how long a plant may be in operation, they largely ignore local and regional impacts on stream ecosystems.

The ecolabel "naturemade star", developed in Switzerland, proved to be a useful starting point for a designation that is both scientifically credible and applicable to the real world. The basis for the certification process under "naturemade star" is the "green hydro" process that was developed at EAWAG. The process has been proven to be practicable in the case of several Swiss hydroelectric power plants, as demonstrated by a representative of EWZ, the Electricity Power Plant of the City of Zurich. According to the representative of the "World Commission on Dams", the Swiss approach is suitable to become an "international guideline for the certification of power

greenhydro ••

Standard for environmentally compatible hydropower, EAWAG Switzerland

plants producing ecoelectricity". All delegates agreed that the parties present at the assembly should continue to work together closely and that the development of an internationally accepted and equitable concept for the certification of "green" energy should be their top priority.

For more information, see Bratrich C., Truffer B. (2001): Ökostrom-Zertifizierung für Wasserkraftanlagen – Konzepte, Verfahren, Kriterien. EAWAG Ökostrom Publikationen *6*, 1–113.

www.hydropower.ch, www.naturemade.org

Second Meeting of Barges in Gersau

On July 7 and 8, the second barge meeting took place near Gersau on Lake Lucerne.



André Steffen and Daniel Steiner from the limnological research station in Kastanienbaum represented EAWAG with a variety of presentations on the topic of "Life Under Water". The two technicians guided the guests through the exhibit and answered many questions with great enthusiasm. A short movie and several posters represented EAWAG and described its activities. In a PowerPoint presentation, the audience was taken into the world of phyto- and zooplankton. The highlight, however, was the microscopy room where young and old alike could use stereomicrocopes to examine water samples that had been freshly taken from the lake just minutes before. In fact, it was difficult to get a place at one of the microscopes. In all, over 3000 guests were drawn to the second barge meeting.

New Editor



Martina Bauchrowitz is editor of the EAWAG news since March 2001.

Please feel free to submit questions or suggestions any time via e-mail to

martina.bauchrowitz@eawag.ch