

Eawag News



In focus: Particles

Organic matter, light and contaminant degradation. Page 16

Modelling of benthic communities in rivers. Page 19

Promoting Sodis effectively. Page 22



Martina Bauchrowitz,
Editor of Eawag News.

Eawag News – a bridge between research and practice

Eawag News aims to serve as a link connecting scientists and practitioners, and to present the latest findings of our research in a reader-friendly way. The fact that we achieve this goal was shown by the results of last year's survey (see the inside back page). However, the constructive feedback we received also raised a number of suggestions which we are happy to take up. For example, we are moving away from the idea of devoting each issue to a single topic, and from now on Eawag News will offer something to interest every reader. Accordingly, this edition contains a mixture of current research projects from a wide variety of disciplines also including four articles focusing on the topic of particle analysis.

Particles are to be found not only in the air but also suspended in water. In view of the challenges involved in detecting such particles, Eawag established a laboratory dedicated to particle analysis. At the Particle Lab, researchers use state-of-the-art techniques of microscopy to get a detailed picture of these tiny specks of matter. This makes it possible to determine not only the size, concentration and external structure of individual particles but also their chemical composition. The Particle Lab deals with diverse projects, ranging from nanoparticles in drinking water and the analysis of iron particles produced in household arsenic removal systems, to the role of mineral particles in lake sediments – to mention just three of the studies presented in this edition of Eawag News.

In the "Current Research" section, the first two articles are concerned with aquatic ecosystems: the first explores the self-purification potential of surface waters – specifically, the degradation of micropollutants triggered by naturally occurring organic matter and sunlight. The second describes a new model developed at Eawag for simulating the dynamics of algae and invertebrates in watercourses.

Also included is an account of a large-scale social scientific study carried out by Eawag researchers in Bolivia and Zimbabwe. The aim was to find out why the Sodis (solar water disinfection) method developed by Eawag is not spreading as rapidly as might be hoped – despite the fact that access to safe drinking water still cannot be taken for granted in many developing countries.

Next, we turn our attention to water pollutants, traditionally a key concern for Eawag. In the light of findings from the US and Canada which showed that drinking water in some areas was contaminated with carcinogenic nitrosamines, Eawag pursued the question of whether Switzerland's water resources are also at risk. This involved the application of an analytical method pioneered at Eawag. Another article deals with nonylphenols – endocrine disruptors released by surfactants. New findings from Eawag demonstrate that the estrogenic potency of these substances can be further increased by a certain type of microbial degradation.

Finally, the "Forum" section features an interview with Eawag scientist Hong Yang. Here, she answers questions on water scarcity and how the concept of virtual water can be used to manage water resources more sustainably and reduce the environmental impacts of water use.

Once again, we would like to thank all those readers who took part in our survey. And if you have any more suggestions or comments – concerning the general approach of Eawag News or a specific research article – we look forward to continuing the dialogue with our readers!

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Martina Bauchrowitz

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Publisher, Distribution: Eawag, P.O. Box 611, 8600 Dübendorf, Switzerland, Phone +41 (0)44 823 55 11, Fax +41 (0)44 823 53 75, www.eawag.ch

Editor: Martina Bauchrowitz, Eawag

Copyright: Reproduction possible on request. Please contact the editor.

Translations: Jeff Acheson, Bottmingen

Copyright photographs: Eawag (if not otherwise specified)

Linguistic Revisions: Helen Brügger-Clarke, Zurich

Publication: 2–3 times per year in English, German and French. Chinese edition in cooperation with INFOTERRA China National Focal Point.

Figures: Peter Nadler, Fällanden

Design: TBS Identity, Zurich

Layout: Peter Nadler, Fällanden

Printed: On original recycled paper

Subscriptions and changes of address: New subscribers are welcome!
eawag.news@eawag.ch

ISSN 1440-5289

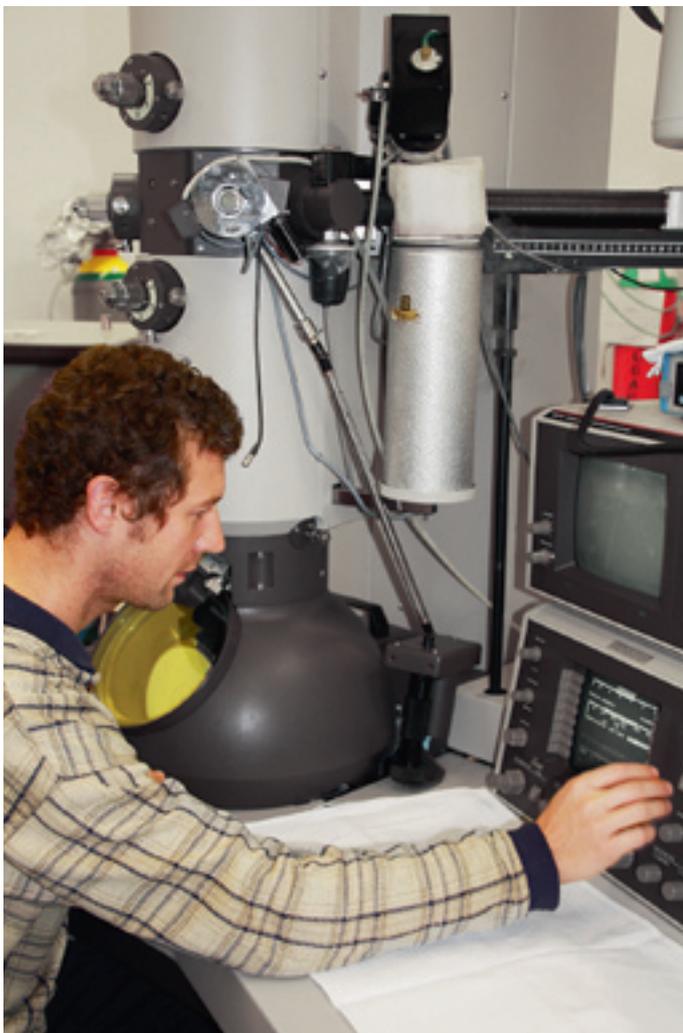
In focus: Particles

Studying the ultramicroscopic realm

The Eawag Particle Lab focuses on the analysis of colloids, which consist of particles measuring less than 1 μm . A wide variety of techniques are used to study, for example, colloidal particles in road runoff or the behaviour of synthetic nanoparticles in the environment.

After a long descent into the catacombs of the ETH Zurich, I stand in front of a door with a red light above it. I knock, and a few moments later the door opens. "Welcome to my subterranean

Ralf Kägi adjusts the TEM for his measurements.



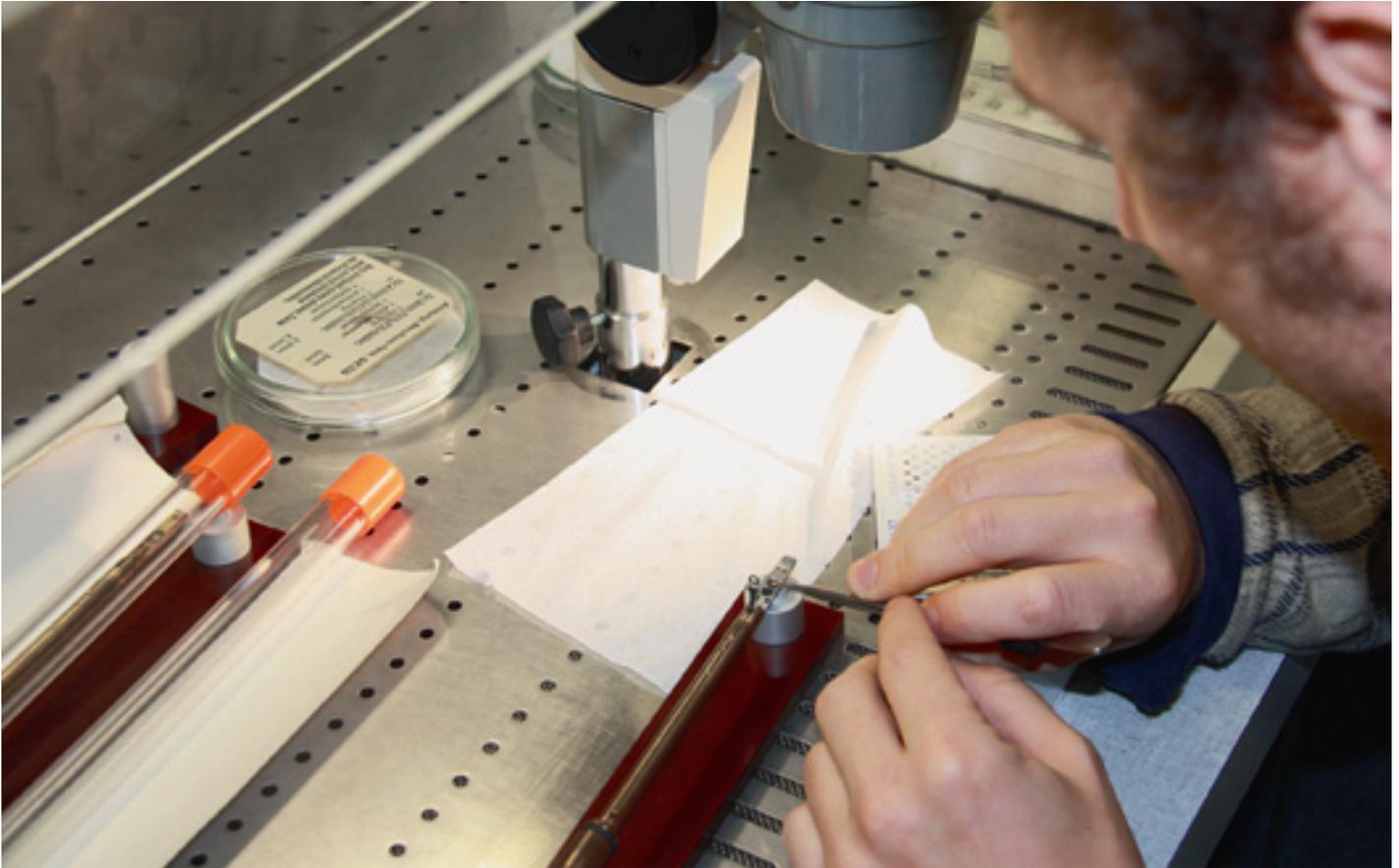
domain," says Ralf Kägi, Head of the Eawag Particle Lab. In the middle of the windowless room, illuminated by a single desk lamp, there is a transmission electron microscope (TEM). This high-resolution system belongs to the ETH Zurich, but Eawag is allowed to use it for its studies. Although it is twenty years old and was one of the first devices of its kind, Kägi emphasizes that it still produces excellent images. Nothing is automated on this microscope, so everything has to be adjusted by hand – a real challenge for its users.

Kägi has been in charge of the Eawag Particle Lab since February 2006. As he explains, he gravitated to microscopy from geology. His thesis had involved a lot of work with the electron microprobe, a special type of scanning electron microscope used to carry out quantitative chemical analyses e.g. on rock samples. Before finally working with the TEM, he had also gained experience with the Environmental Scanning Electron Microscope (ESEM). The ESEM makes it possible to image wet samples, which do not even need to be fixed or prepared in advance.

Supporting researchers in diverse projects. Together with biologist Brian Sinnet, Ralf Kägi provides advice and support for Eawag researchers in relation to microscopy for the analysis of particles. The range of questions to be investigated is very broad,

Microscopes used by the Particle Lab.

Type of microscope (location)	How does it work?	What can be analysed?
AFM = Atomic Force Microscope (Eawag)	A very fine tip scans the surface at a constant distance from the specimen.	Topography of the specimen
(E)SEM = (Environmental) Scanning Electron Microscope (Empa)	A focused electron beam is used to scan the specimen. At each point, numerous signals are generated by interactions between the electrons and the material.	Topography, chemical composition
TEM = Transmission Electron Microscope (ETH Zurich)	The specimen is illuminated by a parallel electron beam.	Size, crystallinity and chemical composition of individual particles

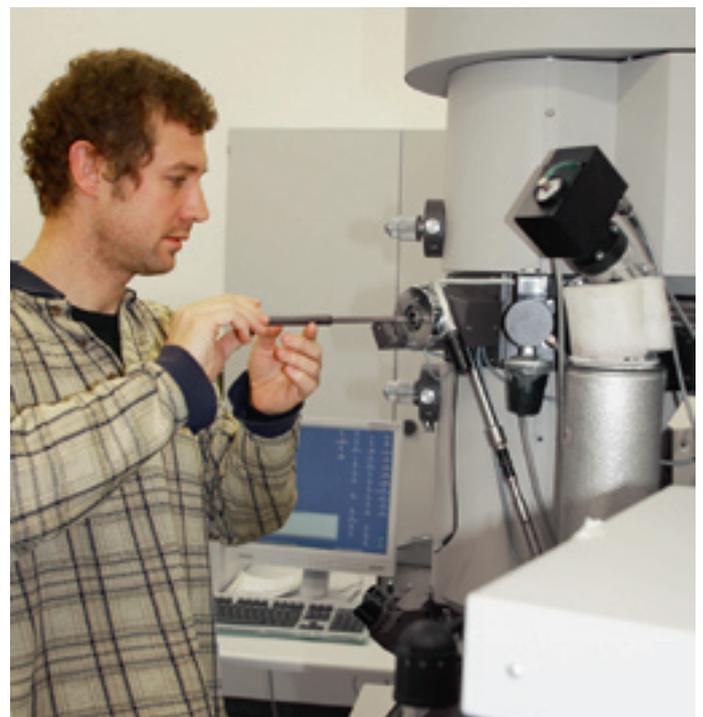


The specimen to be analysed is placed on the holder.

including for example the topical issue of nanoparticles (see the article on p. 7), sedimentology (see the article on p. 10), or analysis of the iron particles produced when arsenic is removed in the treatment of drinking water (see the article on p. 13). However, the Particle Lab focuses in particular on the wastewater field, which explains why it is attached to the Process Engineering department. The Particle Lab has a wide variety of instrumentation. As well as microscopes of different types (see Table), it is equipped, for example, with a state-of-the-art system – jointly acquired by Eawag and Empa – for the separation of particles by size (asymmetric field-flow fractionation) and a dynamic light scattering system for determining the size distribution of particles in solutions.

From external structure to chemical composition. In the meantime, Ralf Kägi has started up the TEM for his analysis. He places the specimen on the holder, which is then pushed into the TEM. As Kägi points out, there is a knack to inserting specimens: if air enters the system, the microscope shuts down and you have to start all over again. As usual, however, everything goes well. Now Kägi starts to make all the necessary adjustments: the specimen has to be brought into focus, the objective lens adjusted and astigmatism (an imaging error leading to distortion) corrected. Finally, the operator has to work his way towards the appropriate

A tense moment: the specimen is inserted into the TEM.





Assuring the continuity of expertise

US-born Brian Sinnet works as a technician in the Particle Lab. He came to microscopy from the field of sedimentology, where microscopes are used to analyse sediment samples. Having initially gained experience with scanning electron microscopy, he then became familiar with other methods. "It's an exciting area where you can always learn something new, as the technology is constantly developing," he explains.

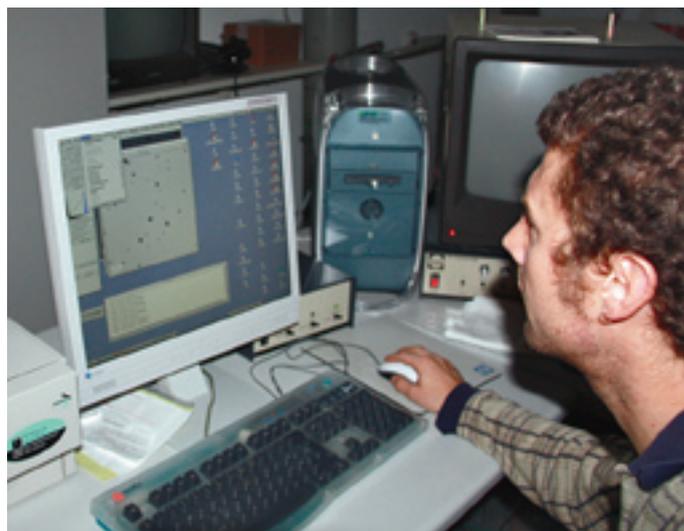
One of his special interests is atomic force microscopy, in which surfaces are mechanically scanned. At the moment, however, he is also closely involved with Eawag's new field-flow fractionation system, whereby complex samples can be separated into fractions. This is used, for example, to investigate the leaching of nanoparticles from facades, or to determine the content of trace elements in urban or road runoff. As the Particle Lab now has a wide range of systems at its disposal, the associated expertise needs to be continuously assured and further developed for Eawag – Brian Sinnet sees this as one of the core responsibilities of the Particle Lab.

imaging mode by varying the magnification, brightness and exposure time.

The problem with environmental microscopy, according to Käge, is that there is a temptation to concentrate on the most striking objects. But this is to focus on phenomena that are not representative. The aim, therefore, should be firstly to gain an overview of the specimen as a whole before subsequently selecting particles for detailed analysis. I am curious to know how long he spends on a single sample. It could be anything from half an hour to several days, he says, but in the latter case he would analyse, for example, just the morphology of a specimen on one day, before turning to the chemistry the next day.

With TEM, after all, it is possible to determine not only the external structure but also the elemental composition of particles. As the electrons pass through the individual particles, a wide variety of interactions occur, including the generation of X-rays, which can be captured using a special detector. For this purpose, however, the objective aperture has to be removed, the electron beam condensed and the detector mounted. Quantitative analyses of particles can then be carried out. It is even possible to analyse different areas of a single particle, thereby identifying heterogeneities within particles. Käge explains that these analytical capabilities of microscopes will become increasingly important in the future.

Having spent the morning at the TEM, I'm glad to return to daylight. Together with Christine Wenk (a master's student at



Brightness and exposure time are varied on the computer.

Eawag), Ralf Käge will also be spending the afternoon there, looking at ferric hydroxide particles (see the article on p. 13). He is not troubled by this – usually solitary – work in the dark. On the contrary, he feels it allows him to be completely focused – and oblivious to the passage of time. ○ ○ ○

Martina Bauchrowitz

Nanoparticles in drinking water



Ralf Kaegi, environmental scientist, is head of the Particle Lab at Eawag.
Co-author: Brian Sinnet

Synthetic nanoparticles are increasingly being used in everyday products, but little is known about environmental releases of these materials. Our knowledge of how many natural nanoparticles occur in drinking water is also inadequate. An initial assessment is presented here.

Drinking water is clear, and yet it contains millions of particles. Substances are described as particulate – as opposed to dissolved – if they are retained by a filter with a pore diameter of 0.45 μm . However, this operational definition overlooks the fact that water contains many smaller particles which can pass through such filters. These include particles measuring 1–100 nm, i. e. nanoparticles. It is not known how many of these naturally occurring nanoparticles are actually present in drinking water. Our aim, therefore, was to make an initial assessment of natural nanoparticles in drinking water, using various methods of microscopy.

On this basis, it should in future be possible to distinguish between natural and man-made nanoparticles. The latter are now widely used in consumer products, e. g. in sunscreens (titanium dioxide), textiles (silver) and cosmetics (fullerene), as well as in facades (photocatalytic titanium dioxide) and scratch-proof paints (silicon dioxide). However, little is known about releases or the fate of synthetic nanoparticles in the environment.

Samples prepared by sedimentation/centrifugation. Based on the method described by Perret [1], we developed a technique for the analysis of nanoparticles. After samples have been collected – we used drinking water from the Lengg waterworks in Zurich – the nanoparticles first need to be separated from the larger particles. The simplest and quickest way of achieving this is by filtration. In principle, small particles pass through the pores while larger ones are retained. During the filtration process, however, the filter pores become blocked, leading to the retention of ever-smaller particles. To avoid this problem, we opted for stepwise sedimentation/centrifugation. In this procedure, the

water sample is first allowed to stand for 2 hours in a 30-litre sedimentation tank. During this time, the large particles settle more rapidly than the small ones and can thus be separated out. Next, the uppermost 2 cm of water (= 1 litre) is carefully drawn off with a peristaltic pump (see photo). However, many of the particles in this water fraction are still larger than 100 nm. To allow these to be also separated from the nanoparticles, the sample is then centrifuged for 30 minutes at 330 g (g = acceleration due to gravity). The uppermost layer (2 cm) is once again removed with a peristaltic pump and undergoes a second centrifugation step (1 hour at 2700 g). The resulting supernatant contains mainly nanoparticles.

The nanoparticles now have to be mounted in such a way that they can be viewed under the microscope. This is done with the aid of ultracentrifugation (12 hours at 120 000 g). The fractionation steps, including the various particle diameter cut-offs, are summarized in the Table. As the cut-off diameter also depends on particle density, two different densities are given in each case.

Brian Sinnet preparing a sample at the Lengg lake water treatment plant (Zurich).



Fractionation steps used for sample preparation.

Fractionation method	Time	Force applied (g)	Cut-off (1.1 g/cm^3)	Cut-off (2 g/cm^3)
Sedimentation	2 h	1 $\times g$	9 μm	3 μm
Centrifugation 1	0.5 h	330 $\times g$	750 nm	250 nm
Centrifugation 2	1 h	2700 $\times g$	180 nm	60 nm
Ultracentrifugation	12 h	120 000 $\times g$	12 nm	4 nm

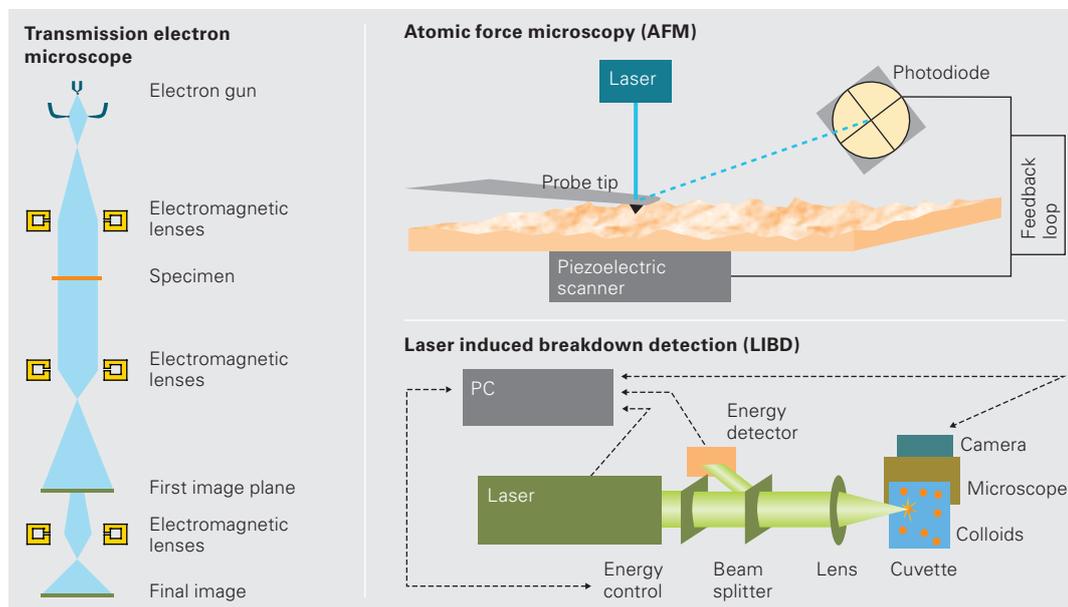


Fig. 1: Schematic view of the microscopy methods used (LIBD simplified from [3]).

The 1.1 g/cm^3 density is roughly equivalent to that of organic particles, and 2 g/cm^3 to that of clay minerals.

Particle surfaces scanned in the atomic force microscope.

To analyse the nanoparticles, we used various methods of microscopy. Each method provides specific information on certain properties of the particles, but also generates artefacts. However, by comparing the results derived from the various analytical procedures, it is possible to identify artefacts and produce a comprehensive characterization of the particles.

In atomic force microscopy (AFM), the surface of the particles is scanned with a very fine tip (Fig. 1). In the process, the probe tip is brought so close to the specimen that Van der Waals forces – relatively weak non-covalent interactions between atoms or molecules – become detectable. Using this technique, the topography of the sample can be mapped with a high degree of precision. However, the particles have to be placed on an extremely flat specimen holder. Freshly cleaved sheets of mica (a naturally occurring sheet silicate) are generally used for this purpose.

On the basis of the AFM findings and descriptions in the literature, two types of particles can be distinguished: spherical aggregates, probably humic acid aggregates, with a diameter (height) of up to 60 nm and fibrous particles, presumably polysaccharides, which are several hundred nanometres long and only a few nanometres high (Fig. 2). These results accord well with those obtained by Santschi, who studied marine particles [2].

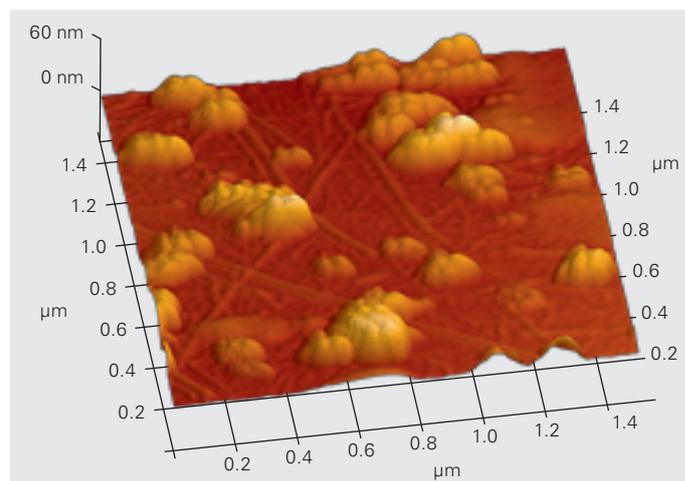
Particle size determined in the transmission electron microscope.

In transmission electron microscopy (TEM), a specimen is illuminated by a beam of electrons (Fig. 1). While the majority will pass unimpeded through the sample, electrons will be deflected when they hit matter, such as a particles deposited on

the sample carrier. The electrons transmitted through the sample are detected by a camera, forming the TEM image. Wherever a particle is located, the electrons are more strongly scattered, which translates into dark areas in the image. For TEM analysis, therefore, particles have to be mounted on a specimen holder that permits the passage of electrons. A copper grid coated with a thin film of carbon proved to be most suitable for our applications.

Figure 3 shows nanoparticles in drinking water imaged with a transmission electron microscope. The contrast was enhanced by strongly defocusing the electron beam, producing an image which is in principle of poor quality, but highly suitable for image analysis. In purely qualitative terms, the same types of particles are visible here as in the AFM analysis. With the aid of image

Fig. 2: Nanoparticles in drinking water, visualized by atomic force microscopy (AFM).



analysis tools, the particles can be detected and measured automatically. For our project, we studied 1800 particles on a total of 10 TEM images. On the basis of these data, the size distribution of nanoparticles in drinking water can be determined. With the TEM settings used, it is possible to measure particles down to a minimum diameter of 40 nm. The results indicate that the particle size distribution follows a power law. When the values are plotted on a log-log scale, the particle size distribution lies on a straight line with a slope of -3.3 . This accords well with textbook accounts of particle size distribution in natural waters [4].

Particle concentration and average size readily determined by laser-induced breakdown detection. The microscopy techniques applied to date provide detailed information on individual particles. In combination with digital image processing, large numbers of individual particles can be measured. However, this is extremely time-consuming, as the samples first have to be prepared and then manually analysed under the microscope. We therefore tested a new laser-based technique known as laser-induced breakdown detection (LIBD), which makes it possible to obtain information on the mean particle diameter and the total number of particles within a few minutes. Our measurements were carried out on a prototype LIBD system at the Research Center in Karlsruhe, Germany.

A schematic view of how the LIBD operates is given in Fig. 1. A 20-Hz pulsed laser beam (green, 532 nm) is focused into a measurement cuvette. Whenever a particle lies within the laser focus, it breaks down, and generates a plasma (an ionized gas containing free charge carriers such as ions or electrons). This emission of light in the visible spectrum is recorded by a specialised camera. The position of the particle on the image (x/y coordinates) together with the frequency (ratio of laser pulses delivered to plasma events detected) is used to determine the mean diameter and the concentration of particles in the sample. For our sample, it was shown that a litre of drinking water contains approx. 7×10^{11} particles. The mean particle diameter is around 15 nm.

Comparing the various techniques. Overall, the results we obtained with the three different microscopy methods show a good measure of agreement. With both AFM and TEM, two different particle types were identified – spherical aggregates (humic acid aggregates) and elongated, fibrous particles (polysaccharides). On the basis of several TEM images, the particle size distribution was calculated. For particles >40 nm, the size distribution follows a power law. In order to compare the results of the TEM (particles >40 nm) and LIBD (particles >10 nm) measurements, we had to extrapolate the size distribution determined experimentally by TEM down to 10 nm. The total concentration of particles >10 nm would then be around 1.1×10^{12} particles per litre, with a mean diameter of 13 nm, which is in close agreement with the results of the LIBD measurements (7×10^{11} particles per litre, 15 nm).

Needles in a haystack. We used various analytical methods to study the nanoparticles that occur naturally in drinking water.

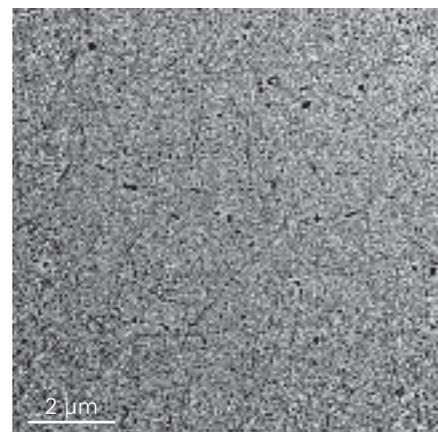


Fig. 3: Transmission electron micrograph of nanoparticles in drinking water.

A precise characterization of the natural nanoparticles already present is required in order to distinguish them from synthetic nanoparticles that could enter the water cycle in the future. As yet, however, little is known about the release and environmental behaviour of synthetic nanoparticles, or about the quantities to be expected in drinking water or untreated water. In addition, according to our findings, drinking water already contains vast quantities of natural nanoparticles; the detection of synthetic particles will therefore pose the next major challenge for researchers. ○ ○ ○

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Buried in lakes – how carbon is stored in sediments



Sebastian Sobek, biologist, was a postdoc in the Surface Waters Department.

Vast quantities of carbon are stored in lake sediments. By reducing concentrations of CO₂ in the atmosphere, the sequestration of carbon in sediments counteracts the greenhouse effect. An Eawag research team has now discovered how carbon is stabilized in lake sediments over long periods.

Across the earth, there are only a limited number of places where carbon dioxide (CO₂) is permanently removed from the natural cycle. These include the sediments of lakes, where – fixed as organic carbon – it is sequestered in dead biomass. This biomass is either produced in the lake itself – largely in the form of phytoplankton – or is washed into the lake from the drainage basin, and slowly sinks to the lake bed. As it passes through the water column or on the lake floor, part of the biomass is converted to carbon dioxide or methane by microbial degradation. The remainder is sequestered in the sediment (Fig. 1) – a process representing a long-term carbon sink [1–3].

Although lakes cover less than 2% of the Earth's surface, compared to 71% covered by oceans, lake sediments accumulate each year almost half as much organic carbon as do marine sediments. However, it is not yet known precisely how this effective carbon sink operates in lakes. An understanding of this process

is required if one wishes to predict how lake sediments will react to ongoing climate change: will this carbon sink tend to be strengthened or weakened in the future? Over the past 3 years, in an effort to answer this question, we have investigated the mechanisms of carbon sequestration in lake sediments, thereby making it possible for the first time to look into the future of lakes as a carbon sink.

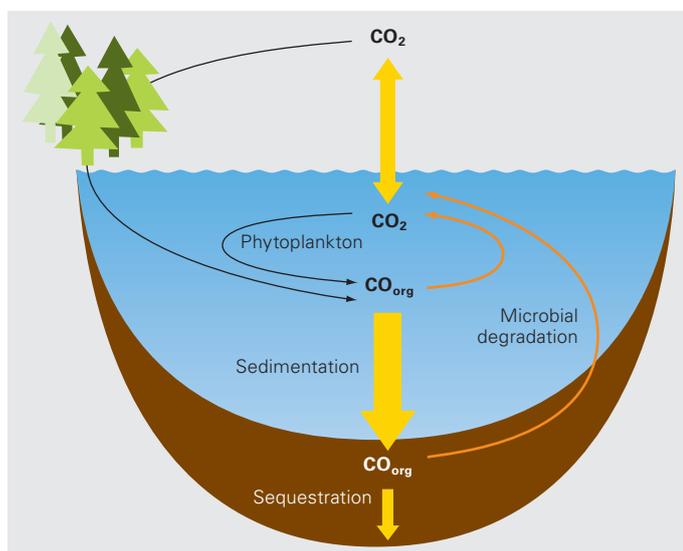
Comparing a wide variety of lake sediments. Because organic carbon sequestered in sediments over millions of years may be transformed into oil, gas and coal, sequestration processes are also of interest to the energy sector. Accordingly, numerous studies have already been carried out in marine sediments. Essentially, three main processes have been identified [4]:

- ▶ Organic carbon washed into the oceans from the land is generally less readily biodegradable and can be more efficiently sequestered in sediments than organic carbon produced in the sea by phytoplankton. This is presumably mainly due to the fact that terrestrial plants have a higher content of stable substances (e.g. lignin, cellulose and leaf waxes) which are relatively resistant to microbial degradation.
- ▶ In marine sediments, oxygen depletion seems to favour carbon sequestration, as organic matter is degraded at a much lower rate under anoxic conditions.
- ▶ As well as organic matter, inorganic matter is deposited in sediments – so-called mineral particles. These can bind organic compounds on their surface, thereby also inhibiting microbial degradation and promoting the sequestration of organic matter.

Each of these three factors could also be relevant in lakes, influencing the sequestration efficiency, i.e. the ratio between the amount of organic carbon deposited as sediment and the amount that is then actually sequestered (cf. Fig. 1). In our study, therefore, we collected data for 27 sediments from 11 lakes differing in precisely these respects (Table):

- ▶ *Origin of organic carbon* – for example, the organic carbon in the Swedish lakes studied derives almost exclusively from inputs of humus from the surrounding forests and mires, whereas the bulk of the sediment in the productive Lake Zug originates from phytoplankton.

Fig. 1: Sequestration of organic carbon (C_{org}) in marine or lake sediments means that carbon dioxide (CO₂) is removed from the atmosphere for geological timescales.



► *Oxygen availability* – while the deep waters of Lake Baikal are very rich in oxygen, the northern basin of Lake Lugano is permanently anoxic.

► *Properties of mineral particles* – Lake Constance appeared to be ideal for an investigation of the influence of mineral particles, as the particles found, for example, where the Rhine enters the lake were expected to differ from those found on the southern shore of Romanshorn.

Detailed analysis of mineral particles. In our study, attention was focused firstly on the analysis of mineral particles. Initially, we sought to find out whether the chemical composition and size of these particles affects the sequestration of organic carbon. For this purpose, we collaborated with the Eawag Particle Laboratory, developing a new method based on electron microscopy. After the organic constituents of the sediment had been removed, the remaining mineral particles were placed on a filter and analysed by environmental scanning electron microscopy (ESEM). Unlike conventional scanning electron microscopy, ESEM does not require high vacuum conditions. This offers the major advantage that environmental samples do not need to be fixed or specially prepared. Mite specimens, for example, have reportedly survived ESEM analysis.

The ESEM system incorporates image analysis software and an X-ray detector. The software detects and measures the size of more than 1000 mineral particles in each sample, and at the same time the X-ray detector determines the elemental composition of each individual mineral particle (Fig. 2). This method is extremely well suited for assessing the origin of sediments. As expected, the mineral particles in the Rhine inflow area of Lake Constance differ markedly from those on the southern shore of the lake (Fig. 3). While the sediment from the inflow area is mainly characterized by inputs of mineral particles from the Alps (mafic silicates, with high magnesium and iron concentrations, and dolomite), fluvial inputs of this kind are not evident on the southern shore. Here, the sediment is largely derived from internal production of mineral particles, e.g. silicate from diatoms, and calcite, which can

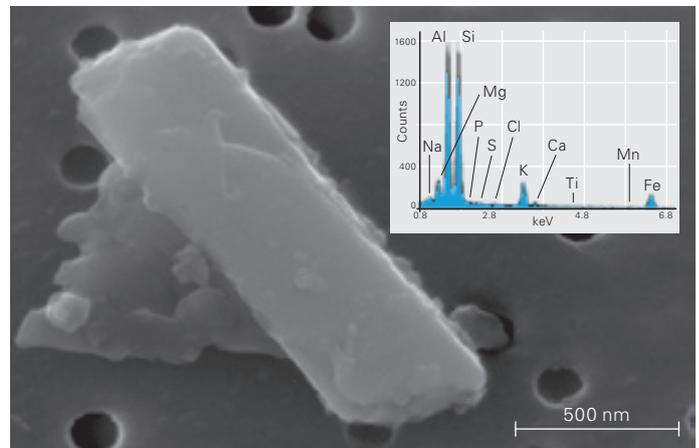


Fig. 2: Electron micrograph of a mineral particle. The X-ray spectrum shows the elemental composition.

be formed by internal processes. In spite of these differences, however, a subsequent statistical analysis of the results did not provide any evidence of an association between the chemical composition and size of mineral particles and the sequestration efficiency of organic carbon.

Mineral particles – not a significant factor. Secondly, we studied the surface of mineral particles. Our reasoning was that, the larger the surface area, the more organic carbon will become attached to mineral particles, with microbial degradation, presumably, being more strongly inhibited and sequestration efficiency increased as a result. We carried out this part of the project at the Soil Chemistry Laboratory of the Federal Institute of Technology (ETH) Zurich. After the organic matter had been removed, the sediment sample was heated in a vacuum to drive off the water vapour and finally cooled to -196°C . During the analysis, nitrogen gas was injected intermittently and at the same time the pressure over the sample was determined, with the amount of nitrogen

For our sediment study we selected a wide variety of lake types.

Lake	Country	Characteristic features
Constance	CH/D/A	Variable particle composition
Zug	Switzerland	Anoxic, organic carbon from phytoplankton
Wohlen	Switzerland	Reservoir, variable particle composition
Brienz	Switzerland	High particle inputs
Lugano	Switzerland	Anoxic
Gäddtjärn, Svarttjärn and Lilla Sångaren	Sweden	High humus content
Kinneret	Israel	Variable oxygen content
Baikal	Russia	Very oxygen-rich
Kivu	DR Congo/Rwanda	Anoxic

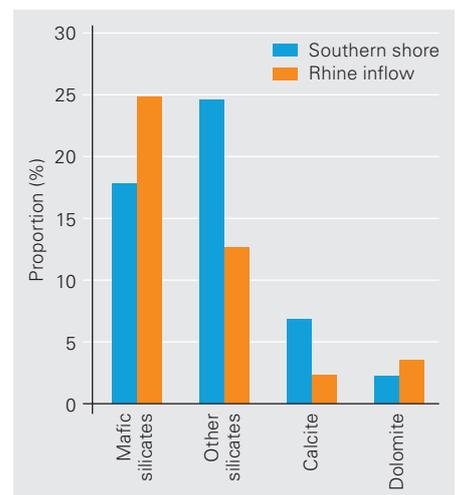


Fig. 3: Comparison of the composition of mineral particles in different parts of Lake Constance. Despite marked differences in chemical composition, we could not find any association with organic carbon sequestration efficiency.

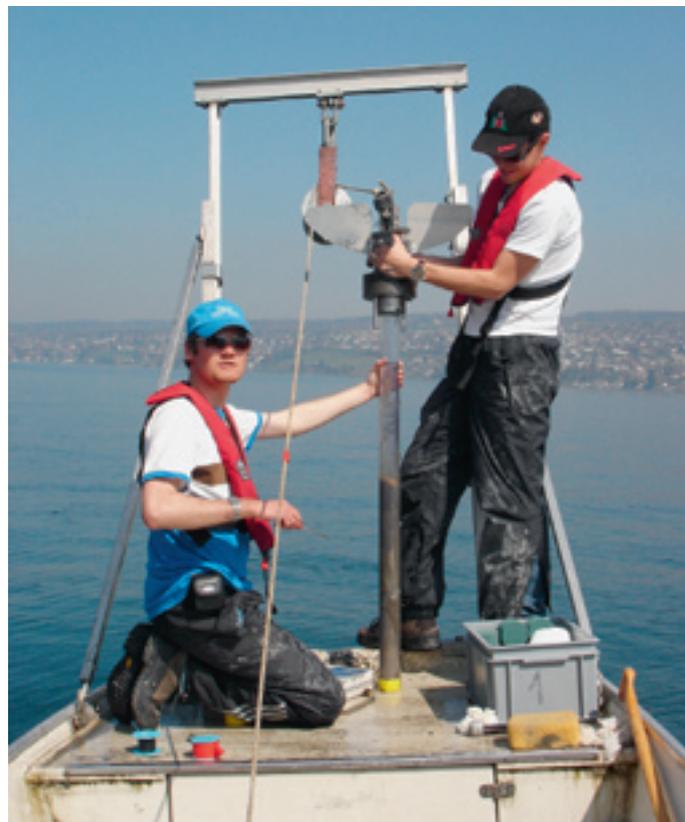
adsorbed to the mineral particles being proportional to the particle surface area.

To our surprise, it was shown that a large particle surface area is not associated with a high organic carbon sequestration efficiency (Fig. 4). In lake sediments – in contrast to marine sediments – this process appears to play only a subordinate role. This probably has to do with the fact that many lake sediments contain substantially more organic carbon than can be sorbed on mineral particles.

Importance of oxygen exposure and carbon source. This raises the question: if the composition of mineral particles and sorption on the particle surface do not play a significant role, then what processes do lead to the sequestration of organic carbon? How important are the duration of oxygen availability and the origin of organic carbon? In fact, both of these factors have a major effect on sequestration efficiency: up to 90 % of settling organic carbon was sequestered in sediments characterized by a very short oxygen exposure time (days) and a high content of poorly degradable terrestrial biomass. In contrast, the efficiency of carbon sequestration fell to 3 % in cases where sediments are in contact with oxygen over a long period (>2000 years) and, at the same time, a large proportion of the organic carbon is derived from phytoplankton production.

Overall, therefore, our results indicate that particularly large amounts of organic matter are sequestered in lake sediments when the bulk of the biomass is of terrestrial origin and the sediments are only exposed to oxygen for a short time.

Looking into the future. As a result of climate change, the properties of many lakes are also changing. For example, oxygen depletion in deep waters is expected to increase in the future, as stratification periods will probably become both longer and more stable. What this means for lake sediments as carbon sinks is that more carbon will presumably be sequestered owing to decreased oxygen exposure. That would be a favourable effect, which could possibly somewhat reduce the speed of climate change. At



A sediment core is collected by boat.

the same time, however, the production of methane – which is 20 times more potent than CO₂ as a greenhouse gas – will also be increased in anoxic sediments. In the future, therefore, lake sediments are likely to intensify rather than to mitigate the greenhouse effect. ○○○

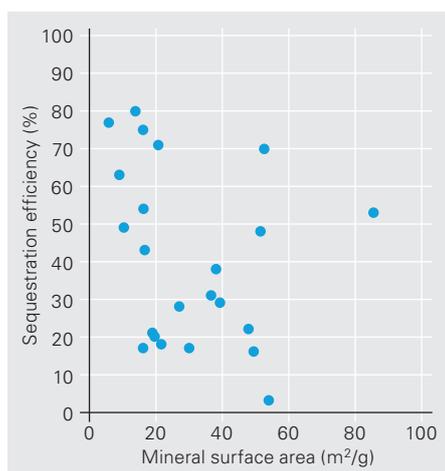


Fig. 4: A large mineral particle surface area is not associated with a high organic carbon sequestration efficiency. A sequestration efficiency of 60%, for example, means that 60% of the organic carbon deposited as sediment on the lake bed is sequestered, while the remaining 40% is biodegraded.

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Arsenic removal using iron colloids



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Co-author: Christine Wenk and Stephan Hug

Drinking water contaminated with arsenic can be treated using filters in which arsenic is adsorbed onto iron colloids. However, the performance of these systems may not be optimal, depending on the composition of the water. Eawag has now investigated the processes involved – and how the design of future filters could be optimized.

Worldwide, more than 100 million people – mainly in developing countries – are affected by excessive concentrations of arsenic in drinking water. Groundwater is tapped as an alternative to scant or polluted surface waters, but in many areas it contains natural (geogenic) arsenic dissolved from rocks and sediments. As water supplies in developing countries are often decentralized, there is a need to find solutions at the household or community level. In recent years, a variety of arsenic mitigation strategies have been developed in severely affected countries, such as Bangladesh; the success of these approaches depends on local circumstances [1]. For those regions where it is not possible to avoid arsenic-tainted water altogether, filter systems have been developed to permit removal of the toxic element (see Box). Particularly promising are sand filters that either take advantage of iron occurring naturally in water or contain additional iron in the form of filings or nails [2]. In these systems, iron colloids are formed which adsorb arsenic, thereby removing it from the water. However, the performance of the filters varies according to the water composition. For example, it has been shown that colloid formation decreases sharply within the first 30 days, leading to inadequate arsenic removal.

If these systems are to be optimized, a fundamental understanding of the chemical and physical processes in the filters is required. We therefore used electron microscopy methods, combined with chemical analysis of samples, to study the following questions:

- ▶ How are the iron colloids produced and what are their properties?
- ▶ Under what conditions are dissolved substances adsorbed onto existing surfaces (iron nails/filings, iron colloids), forming new layers?

Experimental set-up. As part of Christine Wenk's Master's thesis, the Kanchan filter was reconstructed and tested at laboratory scale. Since the removal efficiency depends on the water composition, we studied various synthetic waters. While all of these showed the elevated arsenic content characteristic of arsenic-tainted groundwaters, we varied the concentrations of calcium, silicon and phosphorus. The waters produced were allowed to

pass through a bed of iron nails corresponding to the Kanchan filter for several weeks (Fig. 1). Arsenic removal was determined by measuring the concentrations of arsenic in the effluent. In addition, to obtain information on corrosion rates for the iron nails used, the oxygen content of the filtered water was analysed. Electron microscopy techniques were used to examine the surface

Fig. 1: Bed of iron nails.



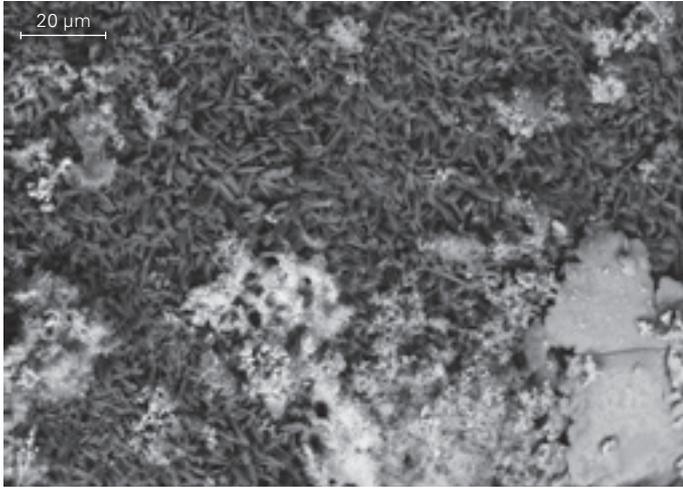


Fig. 2: Coating of calcite (dark areas) and iron colloids (light areas), which formed on iron nails after filtration with phosphate-free water.

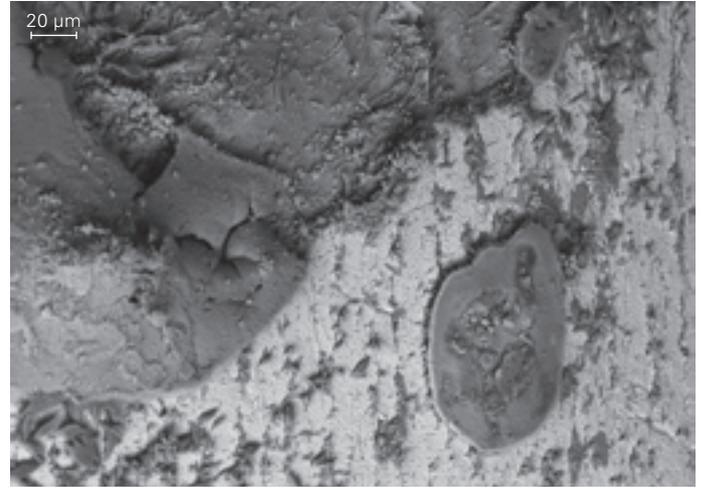


Fig. 3: If water containing phosphate is used for filtration, the surface of the iron nails remains largely clean (light areas).

of the corroded nails and of the iron(III) oxide/hydroxide colloids (particles between 1 nm and 1 µm) produced by the corrosion process.

Surface analysis of iron nails by environmental scanning electron microscopy. With the ESEM, in contrast to conventional scanning electron microscopy, non-conductive samples can also be imaged without special preparation. Depending on the signal type, information is acquired on the topography or the elemental composition of the specimen.

Initially, we worked with a phosphate-free water, which, however, contained calcium and silicon. It was shown that, after filtration, the surface of the nails is completely covered by a coating of dark crystals, with isolated lighter areas. Figure 2 is a backscattered electron image, providing both topographical and chemical information: bright areas represent heavy elements, and darker regions correspond to lighter elements. The chemical composition

of the two phases can be directly determined in the SEM by means of energy dispersive X-ray analysis. In this technique, the atoms in the sample are excited by the electron beam and emit X-rays with an energy characteristic of a specific element. We identified the darker areas as calcite crystals (CaCO_3) and the lighter areas as iron-rich colloids. The iron particles were formed in the course of corrosion and became attached to the surface of the calcite crystals. With water containing phosphate, in contrast, calcite formation is suppressed and the iron nails remain uncoated. In Fig. 3, the light areas clearly indicate that the surface of the iron nails is still largely free of coating layers.

Overall, our observations accord very well with the results concerning oxygen consumption and iron corrosion. In the absence of phosphate and with a high calcium content, a dense layer of calcite forms on the iron nails. This is undesirable, as the calcite reduces iron corrosion, i.e. the formation of iron(III) oxide/hydroxide colloids. Conversely, in the presence of phosphate,

Principle of filter systems used for arsenic removal

In Bangladesh, the main type of filter used comprises layers of sand and cast iron turnings (SONO filter) [3], while the type of device preferred in Nepal is the Kanchan filter, in which water first runs through a bed of iron nails (Fig. 1) and is then passed through a biosand filter [4]. In both cases, iron(III) oxides/hydroxides are produced – either from dissolved iron(II) already contained in the water, which oxidizes when groundwater is pumped to the surface, or as a result of corrosion from metallic iron(0) in the filings/nails. These iron colloids adsorb the dissolved arsenic and form larger particles, which can then precipitate or be deposited on sand grains or on the iron itself.

The performance reported for filters of both types varies from good to inadequate, according to the specific type of water and other factors. The form, composition and properties of the iron(III) oxides/hydroxides depend on the water composition. At the same time, phosphate, calcium and silicate present in the water are incorporated into the iron(III) oxides/hydroxides, which impedes the removal of arsenic. In addition, the oxidation of iron is coupled with the oxidation of arsenic(III) to the more readily removable arsenic(V) species – but this process is also significantly influenced by the water composition and the flow conditions in filters.

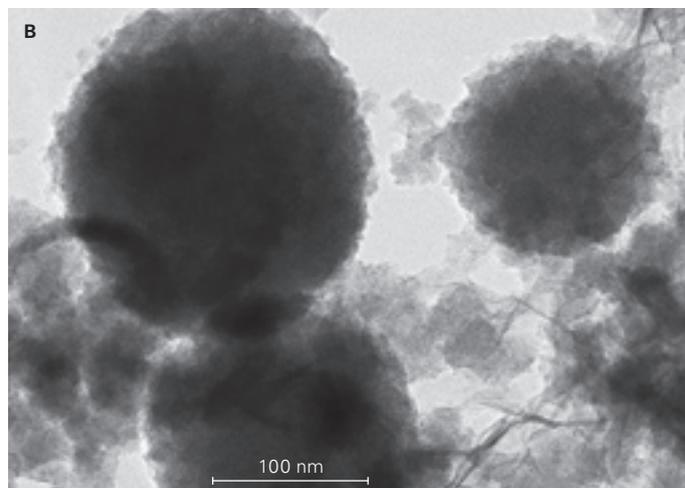
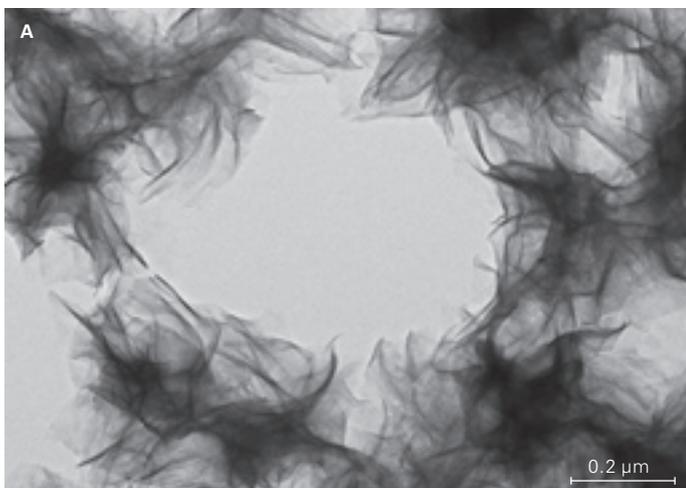


Fig.4: Lepidocrocite (A) and ferrihydrite (B), iron colloids that form in the filter system if the water contains sodium bicarbonate (A) or sodium bicarbonate and silicon (B). Both types of colloid adsorb arsenic.

calcite formation is prevented; as a result, the surface of the iron nails remains cleaner and the rate of corrosion higher. In fact, however, this finding was surprising because phosphate is also used as a corrosion inhibitor in water pipes.

Analysis of iron colloids by transmission electron microscopy. In the transmission electron microscope (TEM), samples are illuminated by electrons and therefore need to be thin. The newly formed iron(III) oxide/hydroxide colloids are generally only a few 100 nm thick and are highly suitable for analysis in the TEM. With this method – unlike the above-described ESEM, where larger samples can be directly inserted into the microscope – the colloids first have to be mounted on appropriate holders.

We first analysed iron colloids that had formed during the filtration of water which contained sodium bicarbonate but was silicon- and phosphate-free (Fig. 4A). We identified these colloids as lepidocrocite, an iron oxide/hydroxide mineral (γ -FeOOH) with an orthorhombic crystal structure (crystal system with three unequal axes at right angles to each other). If silica is now added to the water, the crystallization of lepidocrocite is prevented and ferrihydrite (structural formula not yet established), another iron oxide/hydroxide mineral, is formed (Fig. 4B). Dissolved arsenic can be adsorbed onto both types of colloid and is thus removed from the water.

If phosphate is added to the water, amorphous iron phosphate colloids are formed, but – as a result of the binding of phosphate to the iron colloids – the adsorption of arsenic is decreased and less arsenic is removed from the water overall. However, this negative effect of phosphate on arsenic removal is partly offset by the more rapid corrosion of iron turnings in contact with water containing phosphate.

How can arsenic filters be improved? The Kanchan filters that were reconstructed at laboratory scale and tested under various conditions rely on the corrosion of iron nails. The measurement

of oxygen concentrations showed that, although iron corrosion does not decline sharply within the first 30 days, arsenic removal is reduced from 90 % at the outset to approx. 60 %. The main reason seems to be that less iron(III) is released and the formation of iron(III) oxides/hydroxides is thus also decreased. However, after the initial deterioration in arsenic removal efficiency, it appears to stabilize at the 60 % level in subsequent months. One possible way of improving the filter system would be to use two nail beds separated by a space containing air. After passing through the first filter, the water would then be oxygenated again and the corrosion process would be restarted; as a result, the arsenic content would be reduced to an acceptable level. Another option would be periodic removal of the corrosion layers, e.g. by breaking up the nail bed and applying mechanical friction (vigorous shaking). ○ ○ ○

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Organic matter, light and contaminant degradation

Dissolved organic matter consists of organic compounds, mainly of natural origin. Although it is only present in trace amounts in surface waters, organic matter influences the fate of contaminants. Under the action of sunlight, it can either increase or decrease the rate at which contaminants are degraded.

Natural waters can take on a wide variety of hues – a characteristic that has always fascinated observers and inspired numerous artists. The colour of water is often affected by the presence of dissolved constituents that absorb daylight at specific wavelengths. One important group is the fulvic acids, which mainly absorb the violet and ultraviolet (UV) portions of the spectrum. These acids are part of what is known as dissolved natural organic matter (DOM). DOM comprises a vast number of largely unidentified organic chemical compounds, mainly deriving from the metabolism and decomposition of terrestrial and aquatic organisms.

When light is absorbed, the energy of the photons is transformed. As well as generating heat, this gives rise to compounds that are energy-rich, metastable and in some cases highly reactive. As a light-absorbing material, DOM thus decreases the direct effects of photons by removing them from the water and, at the same time, creates possibilities for chemical reactions, e.g. involving poorly degradable contaminants. For this reason, DOM is known as a photosensitizer (see Box). The effects of DOM on the fate of contaminants have been studied at Eawag for more than two decades. It has been shown, for example, that the widely used herbicide isoproturon would reside much longer in surface waters if the water did not contain DOM. Other contaminants – including substances of concern such as endocrine disruptors and antibiotics – may also be involved in degradation reactions of this

kind. According to our most recent findings, DOM can not only promote but also inhibit degradation. The precise mechanisms are explained in this article.

Contaminant degradation by excited triplet states of DOM.

The absorption of sunlight by DOM, nitrate and other substances contained in water can generate many different highly reactive species. However, even under direct sunlight, these are only produced in small quantities and are fairly unstable owing to their reactivity, which makes them difficult to identify and quantify by traditional chemical analysis. Over twenty years ago, methods were developed for determining two of the reactive species – the hydroxyl radical and singlet oxygen – in water, and for calculating the rate of the resultant contaminant degradation [1]. Though important, the hydroxyl radical and singlet oxygen only account for a small proportion of contaminant degradation in surface waters. The hydroxyl radical reacts highly effectively with almost all organic compounds, but the concentrations in which it occurs are generally so low that contaminants would only be degraded over a period of several months. In contrast, singlet oxygen is present in higher concentrations than the hydroxyl radical, but it only reacts effectively with a very limited number of contaminants.

It is interesting to note, however, that, when exposed to sunlight in surface waters, substituted phenols (found, for example,

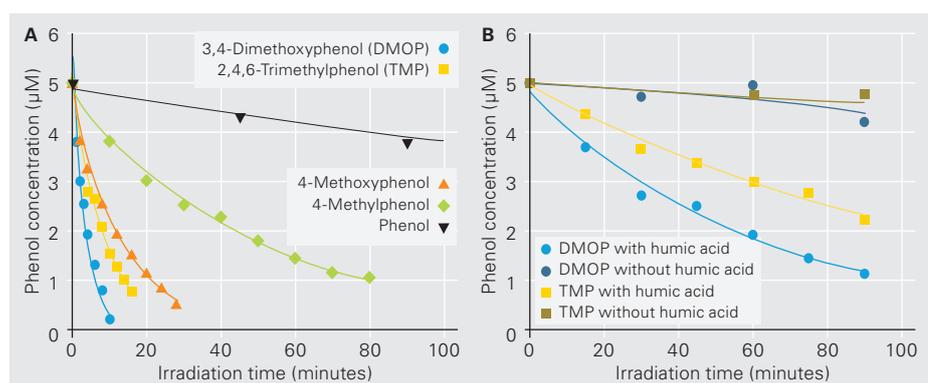


Fig. 1: Degradation kinetics of substituted phenols under laboratory irradiation with UV-A and visible light (A) and under natural sunlight (B). Humic acid was used as DOM (concentration 1.7 mg carbon per litre).



The yellowish colour of Lake Greifen indicates the presence of relatively high concentrations of organic matter.

in plastics, dyes, pharmaceuticals and pesticides) are degraded much more rapidly than could be explained by the mere action of the hydroxyl radical and singlet oxygen. Electron-rich, readily oxidizable phenols are more readily degradable than electron-poor, poorly oxidizable phenols (Fig. 1) [2]. We believe that the highly reactive species responsible for phenol degradation must be excited triplet states of DOM [2].

Role of model photosensitizers in oxidation of contaminants.

But how exactly is contaminant degradation induced by triplet states? We carried out further experiments using, rather than DOM, defined individual substances as model photosensitizers. For this purpose, aromatic ketones proved to be ideal compounds. A major advantage offered by these model photosensitizers over DOM is that their chemical structure and many physicochemical properties are known, which greatly facilitates the development of quantitative models to describe their reactivity. In addition, rapid spectroscopic methods are available that allow triplet states of individual compounds to be measured, which is not possible with DOM on account of its undefined chemical structure. Using one such method, laser flash photolysis, we showed that:

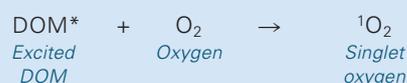
- ▶ the degradation of substituted phenols and phenylurea herbicides observed under environmental conditions is directly associated with the reaction between the excited triplet state of the photosensitizer – in this case, an aromatic ketone – and the contaminant [3, 4] and
- ▶ a quantitative relationship exists between the oxidizing capacity (known as the standard one-electron reduction potential) of triplet states and the rate of contaminant degradation. Thus, in the case of substituted phenols, it can be said that the more readily they are oxidizable and the higher the oxidative capacity of the triplet states is, the more rapidly they are degraded [3].

It would make sense for quantitative relationships of this kind to be applied more generally, and this is being continuously re-

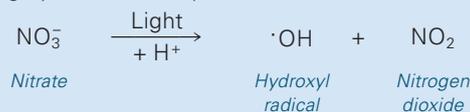
Photosensitizers

Substances which, through absorption of light, can induce a chemical reaction in another compound are generally known as photosensitizers. Substances of this kind, for instance nitrate and dissolved organic matter (DOM), are found in surface waters, where they can generate reactive species that play an essential role in the degradation of contaminants. Examples of these reactive species are given below:

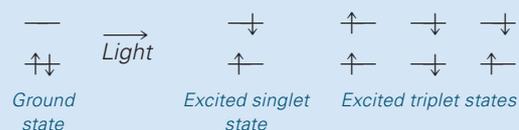
- ▶ Singlet oxygen, an excited state of the oxygen molecule, is mainly produced by the transfer of energy from excited DOM constituents; in contrast to normal oxygen, the electron spins are antiparallel.



- ▶ On account of its unpaired electron, the hydroxyl radical is a highly reactive compound.



- ▶ Excited triplet states of DOM owe their high reactivity to the presence of two unpaired electrons with three possible spin configurations. They act as strong oxidants if certain conditions are satisfied in their chemical structure. Unlike excited triplet states, excited singlet states of DOM are not able to oxidize contaminants effectively.



viewed on the basis of new experimental findings [5]. It is hoped that these theoretical tools will permit improved assessment of the environmental risks of chemicals, as required under the new REACH legislation [6] of the European Union. The fact that many other contaminants may also be affected by triplet-induced oxidation is shown by Fig. 2. In this experiment, we used both DOM (specifically, fulvic acid from the Suwannee River in the US, a widespread standard) and 4-carboxybenzophenone as photosensitizers. Here, an additional finding was that, in general, 4-carboxybenzophenone is a more powerful oxidant than fulvic acid.

Inhibitory effect of DOM on oxidation of contaminants. As mentioned above, DOM can also inhibit the degradation of contaminants. With regard to the oxidation of substituted anilines (used in dyes, synthetic fibres and pharmaceuticals), for example, a stronger than expected reduction in the reaction rate was noted in the presence of DOM. In addition, the degradation rates for anilines in the presence of DOM and light are much lower than for the methyl-substituted phenols (Fig. 2), even though anilines

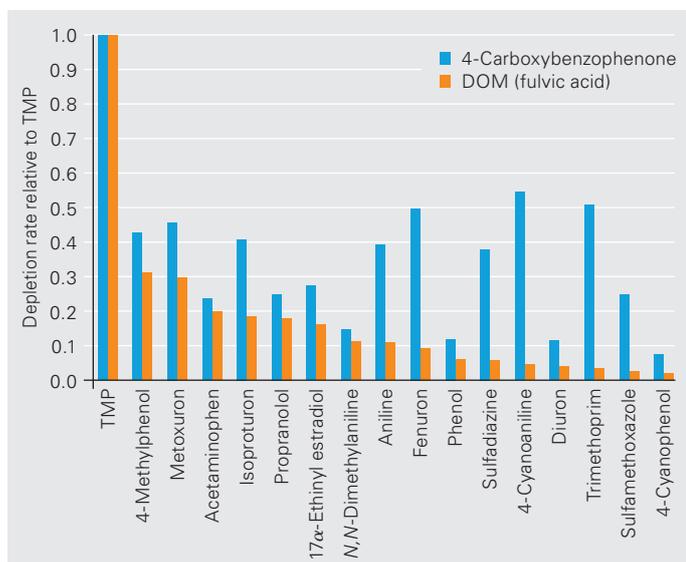


Fig. 2: Relative depletion rates for contaminants (each dissolved in water at a concentration of 5 μM) exposed to sunlight-like laboratory irradiation, using the model photosensitizer 4-carboxybenzophenone and Suwannee River fulvic acid (standard DOM) [based on Reference 7].

are more readily oxidizable and should react as least as rapidly as these phenols. To study this more closely, we exposed a series of contaminants to the model photosensitizer 4-carboxybenzophenone, both in the presence and in the absence of DOM [7]. Here, the experimental conditions were chosen so as to render negligible the effects of DOM as a photosensitizer.

As shown in Fig. 3, the oxidation rate for certain contaminants (e.g. most phenols and phenylurea herbicides) is virtually unaffected by the presence of DOM (values of the ratio of oxidation rates with and without DOM close to 1). In contrast, for a number of other contaminants, the oxidation rate is clearly decreased in the presence of DOM (values in Fig. 3 much lower than 1). In the case of the second group of contaminants, it is conjectured that their intermediate oxidation products react with readily oxidizable

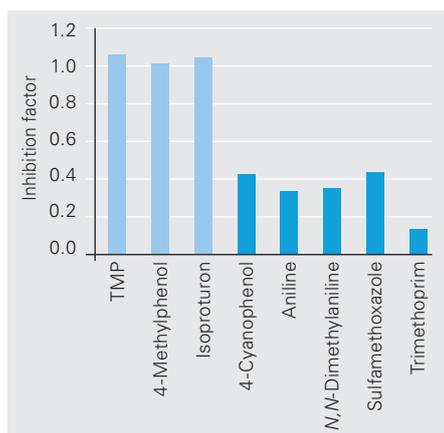


Fig. 3: Inhibition factor, defined as the ratio of oxidation rates with and without Suwannee River fulvic acid (standard DOM, concentration 2.5 mg carbon per litre), for selected contaminants [based on Reference 7].

components in DOM, leading to regeneration of the contaminant and hence to a decrease in the rate of degradation. Further studies are now under way to assess the validity of this hypothesis and to characterize more precisely this novel effect of DOM. Currently under investigation is whether the effect also occurs with other types of oxidation reaction – for example, those employed in water treatment processes.

Thanks to our experiments, we now have a much better understanding of the mechanisms that promote or inhibit degradation processes. Overall, however, research in this field is still in its infancy. ○ ○ ○

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Modelling of benthic communities in rivers



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Co-author: Peter Reichert

The Ecological River Model (ERIMO) developed by our group makes it possible to simulate key processes in running waters. Our modelling covers benthic algae and invertebrates and takes model uncertainties into account.

By simulating complex interactions, models can help to improve our understanding of rivers and the communities that live in them. Such models are also useful for predicting the future development of these ecosystems under constantly changing environmental conditions: for example, how will rivers be affected by climate change and other anthropogenic factors?

Although a number of river models are already available, these have crucial deficiencies: they frequently focus on water quality, excluding important parts of the system; they are not universally valid, having been developed and calibrated for specific rivers; or they fail to take uncertainties into account. Our goal is therefore to take a step towards a more comprehensive and generally applicable river model. In our newly developed Ecological River Model (ERIMO), the focus is on the benthic community, i.e. the animals, plants and microorganisms living on the river bed [1]. With ERIMO, it is possible to describe the most important processes occurring within this community and to simulate the effects produced by external factors. This model, which was initially applied to the Sihl river and a Spanish stream, is to be used in the future

on other small and medium-sized rivers, and will later be extended to include water quality.

Why are we interested in benthic communities? The answer to this question is that these communities are vital components in the material balance and food web of aquatic ecosystems. In shallow rivers, for example, transformation processes involving nutrients and organic matter are often dominated by algae, bacteria, fungi and other benthic microorganisms. These so-called biofilms play an important role in the self-purification of rivers and serve as a food source for a variety of macroinvertebrates (e.g. snails and insect larvae). By grazing biofilms and breaking down dead organic matter, the invertebrates in turn also influence the material transformation and self-purification capacity of rivers. In addition, they are themselves a food source, e.g. for fish.

What exactly does the model cover? Our model seeks to describe how the main groups of benthic organisms and the organic matter deposited on the river bed (detritus) vary over time. As it



Sampling in the River Sihl.

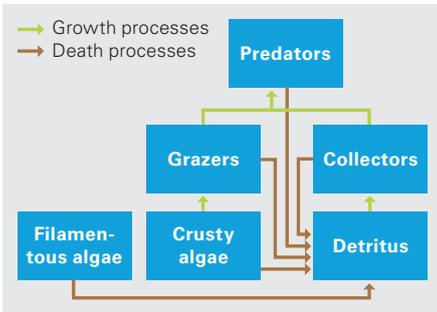


Fig. 1: Food web for the main benthic organisms in the Sihl.

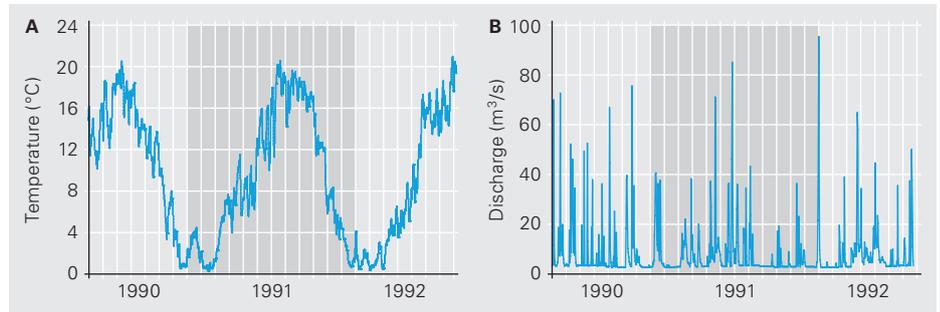


Fig. 2: Variation in external factors over time: water temperature (left) and discharge (right) in the Sihl.

would be far too complicated to include each individual species occurring in a river into the model, the invertebrates are combined into functional groups based on their food source – grazers (feeding on biofilm which grows on the river bed), collectors (feeding on particulate organic matter) and predators (feeding on other invertebrates). Also included in the model – as important components of biofilm – are sessile algae.

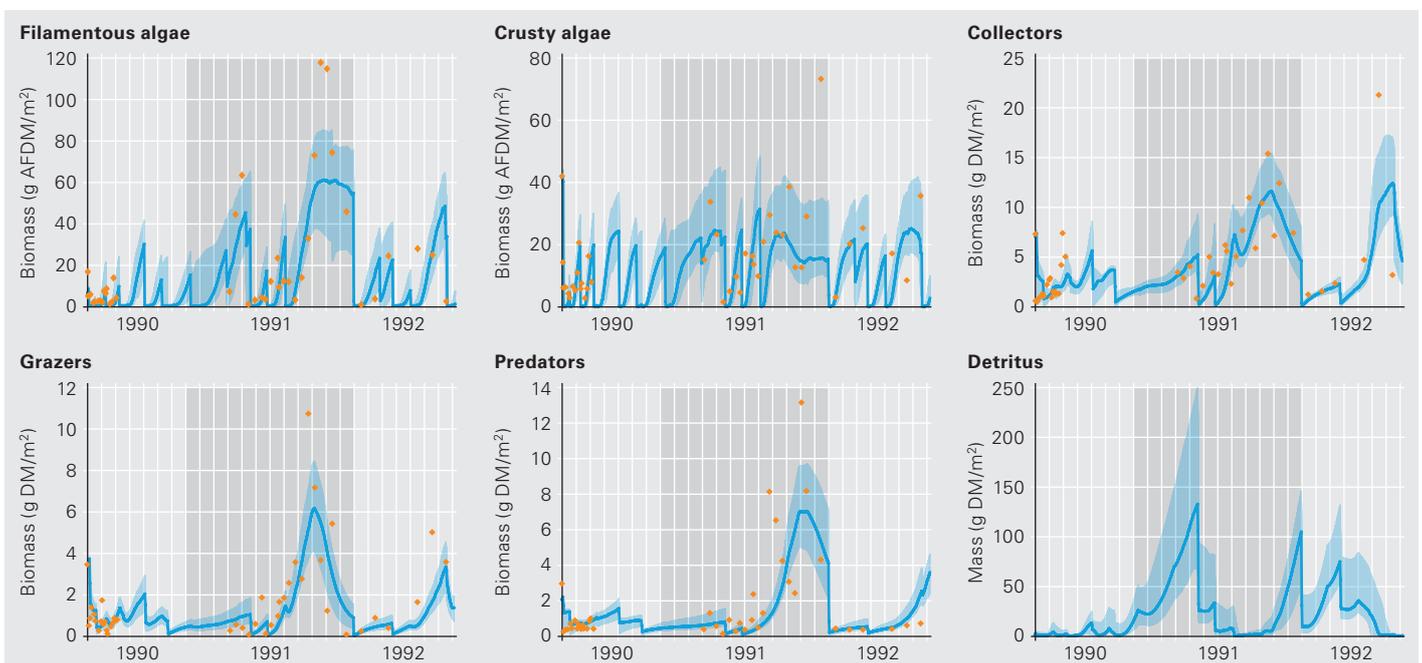
All the essential processes that are relevant to the modelled groups or detritus also have to be integrated. These include not only the colonization, growth and death of the benthic organisms, but also the loss of algae and invertebrates due to floods and the resuspension of sedimented detritus. Depending on the data available, the stoichiometric relationships between the various biological processes (e.g. when grazers feed on biofilm,

or invertebrate predators on collectors) are derived on the basis of the chemical composition or at least the biomass of the modelled groups of organisms and detritus.

Finally, the model also has to consider external factors, such as discharge, water temperature, sunlight and dissolved nutrients. The results are calculated using the AQUASIM program [2].

How can we calibrate the model and assess its predictive power? In order to be able to assess the predictive power of the model, it is important to consider the various sources of uncertainty and hence calculate the uncertainty of the results of modelling. Here, the following problem arises: reality is always much more complex than what we can describe with our models. While we simplify heavily to make the model as uncomplicated as possi-

Fig. 3: Seasonal dynamics of groups of benthic organisms and detritus in the Sihl. Orange dots = measurement data, blue curves = model results. The light-blue band (95% prediction interval) indicates the uncertainty in model results due to uncertainty in model parameters. The additional uncertainty due to the simplified model structure and the measurement process is not shown. AFDM = ash-free dry mass, DM = dry mass.



ble, we still have to deal with numerous unknown parameters that exert an influence (e.g. specific growth and death rates, and the critical discharge threshold for losses due to spates).

For each parameter, we need to specify a value – or at least a range of values – which is both itself realistic and yields realistic results for the model. For this purpose, one can try, for example, to determine the values experimentally in the laboratory, to find them in the literature, or to consult experts. However, as the composition of the groups of organisms varies from site to site and also seasonally, it is usually not possible to obtain accurate information. One can also use the population densities determined in the river to adjust the model parameters, so that the predictions agree closely with the measured data – a process known as calibration of the model. However, this is only possible in the case of parameters that have a decisive influence on the model results, but whose effects cannot be offset by other parameters (e.g. growth and death rates).

To generate the best possible predictions, it is therefore advisable both to draw on prior knowledge from experiments, literature review and experts, and to perform model calibration. By comparing measurement data and model results, one can then arrive at realistic values for parameters. An appropriate tool, here, is Bayesian inference – a mathematical method which, at the same time, can be used to calculate the uncertainty of the model results [3]. We applied this method using the UNCSIM program package [4].

Where have we applied ERIMO so far? Firstly, we developed a prototype of the ERIMO model for the River Sihl (Fig. 1) [1]. This river flows from Lake Sihl to Zurich, where it joins the Limmat. As part of hydropeaking experiments on the Sihl, the Canton Zurich Office for Waste, Water, Energy and Air (AWEL) and the AquaPlus consultancy measured the colonization densities of algae and invertebrates over a 2-year period (1991/1992). These data were used to calibrate our model. In addition, water temperature and discharge were measured over the same period (Fig. 2) – variables which, as known external factors, are required for the model calculations.

Our results indicate that the model is capable of providing a sufficiently accurate reproduction of the data measured (see Fig. 3 for a comparison of the results of modelling and the measurement data). The development of algae and invertebrates over time shows an alternating pattern of losses due to flood events and subsequent regeneration. The simulation of the dynamics of predators – especially the rapid recovery after the major spate in June 1991 – is somewhat poorer than for the other functional groups. This could be due to the fact that the organisms in the predator group are more mobile and better able to seek refuge during flood events.

Secondly, we used the model for the simulation of a small Spanish stream (Fuirosos). Here, however, as the climatic and hydrological conditions are very different from those on the Sihl, the model had to be modified in several respects. For example, the fact that the stream dries up during the summer had to be taken into consideration. In addition, two other groups of inverte-

brates (filter-feeders and shredders) had to be included. The input data were gathered by Vicenç Acuña in the course of his dissertation. Here, again, it has been shown that the model is capable of reproducing the measurement data, and that uncertainty can be reduced for a number of parameters by Bayesian inference [5].

What is planned for the future? In the future, we intend to use the model for further rivers, and to find out which processes are important in each case and how the ranges specified for the parameters differ from one river to another. On the basis of this experience, the model should become increasingly widely applicable in the longer term and ultimately also facilitate predictions, e.g. simulating the impacts of changing external factors (increased temperature, altered discharge, elevated nutrient concentrations) in future scenarios.

Another aim is to extend the model to include the biofilm and processes occurring in the water column. It would then also be possible, in conjunction with the River Water Quality Model No. 1, to simulate factors that influence water quality, such as oxygen and nitrate concentrations [6]. In this case, closed mass balances could be calculated and the material balance of the main elements could be used to constrain the model. However, this would require a data set containing, for the same site, all the groups of organisms (invertebrates, algae, bacteria, etc.) and materials (dissolved substances, suspended and sedimented organic matter, etc.), as well as external factors. These values would have to be recorded at a temporal resolution corresponding to the variability of the groups of organisms over time. As this is highly time-consuming, no such data set has been available to us so far. However, we hope that in the future a joint project can be undertaken with the relevant field experts, so that this important advance can be achieved. ○ ○ ○

We are grateful to our colleagues Vicenç Acuña, Martin Kühni, Steffen Schweizer, Klement Tockner and Urs Uehlinger as well as to the Canton Zurich Office for Waste, Water, Energy and Air (AWEL) and the AquaPlus consultancy.

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Promoting Sodis effectively

The basic idea of solar water disinfection (Sodis) is simple: water is purified by being exposed to direct sunlight for 6 hours in a PET bottle. But despite the straightforwardness of the method and the benefits to health, Sodis has not been adopted as widely or rapidly as people might think.

Sodis, the solar water disinfection method developed at Eawag, has been promoted by various NGOs in Latin America, Asia and Africa for over 10 years. This method is ideal for the preparation of small amounts of drinking water for household use [1]: transparent plastic bottles filled with contaminated water are placed in the sun for a period of 6 hours to 2 days, depending on the cloud cover. Sunlight destroys the pathogenic microorganisms in the water by two mechanisms – ultraviolet radiation (UV-A, wavelength 320–400 nm) and increased water temperature.

Especially in countries where safe drinking water cannot be taken for granted, people should apply this method consistently and spread the message by word of mouth. However, this is not the case. Experience has shown that it is not sufficient merely to inform people about the problem (water contains pathogens that cause diarrhoea, which is associated with increased [child] mortality) and the method, and then to assume that they will incorporate Sodis into their daily routine. After all, the process leading to behavioural change is a complex one [2, 3]: it comprises problem awareness, the acquisition of knowledge, the development of a

Poster-type reminder (left): “Have you already placed your bottles in the sun today?” Table-top reminder (right): “Your bottles have to be placed in the sun”.



Andrea Tamas and Silvie Krämer, environmental psychologists and PhD students in the Systems Analysis, Integrated Assessment and Modelling department. Andrea Tamas received her doctorate at the beginning of 2009.

positive attitude and, ultimately, (tentative) adoption of the new behaviour. Crucial to the success of behavioural change is the final phase, habit formation – when the behaviour passes from the cognitively demanding trial phase into a routine (everyday) practice, requiring minimal cognitive resources (i.e. conscious reflection on the procedure involved).

In three field studies in Bolivia and Zimbabwe (see Table), we sought to identify the most effective strategies for the diffusion of Sodis (see Box on p. 23) and appropriate interventions for supporting the process of habit formation (see Box on p. 24) [4]. The effectiveness of the measures implemented was subsequently analysed with the aid of personal interviews.

Interpersonal strategies: more effective and less costly than mass communication. How did the various diffusion strategies fare in the three different projects? With information events, only 10% of the participants were persuaded to use Sodis permanently [2]. After such an event, self-diffusion also tends to be fairly limited. In contrast, the deployment of professional instructors has an excellent success rate: with this approach, 73% of the interviewees in Project 1 [5] and over 90% in Project 3 [2] became regular Sodis users within 2 months. The promotion of Sodis via voluntary disseminators was also effective: after a period of 2 months, 67% of interviewees reported that they had adopted the method. In addition, Sodis was more widely discussed among people thanks to the efforts of voluntary disseminators who came from the study areas themselves. As they “worked” on a voluntary basis, they are less efficient – but also less costly – than professional instructors [5]. A combined strategy, involving both professional instructors and voluntary disseminators, would probably be a promising approach, which should be tested in a future project.

Health fairs are often organized by NGOs as a way of simultaneously addressing as many people as possible. However, the number of people who had actually heard about Sodis at one such fair was very limited – only 20% of the interviewees – and the number of people adopting Sodis as a result was correspondingly low [5]. One novel strategy was that of incentive-based self-diffu-



The Sodis stand at a health fair.

sion, in which – alongside the activities of professional instructors – vouchers for PET bottles were distributed. Applied alone, however, the strategy only persuaded 26 % of the interviewees to use the Sodis method in future to prepare their drinking water. Accordingly, this approach is more suitable as a maintenance strategy following a successful diffusion measure [2].

More sustained effects with reminders than with public self-commitment. The two habit formation measures studied, i.e. reminders and public self-commitment, increased the likelihood of Sodis being used in households by a factor of 2 to 3 [3]. In Zimbabwe, these two measures also made it possible to keep the number of Sodis users constant, to reinforce the habit and to reduce forgetting [2]. In Bolivia, this result was achieved with reminders inside the home even after an intervention-free phase of 7 months. In the great majority of cases, however, the posters or stickers announcing the households' intention to use Sodis (public self-commitment) were destroyed by the elements after only a few weeks, as they were displayed outside the buildings. On the basis of calculations with a habit formation model, we showed

Diffusion strategies

Information events, organized by professional instructors, are designed to raise awareness of the problem and communicate knowledge on the application of Sodis. At these events, bottles of Sodis water should be distributed for sampling.

Professional instructors are responsible for visiting as many households as possible over a given period of time to promote the use of Sodis. If necessary, they can distribute additional materials such as flyers or bottles. Instructors are trained for this work and receive a salary.

Voluntary disseminators are people who are locals of the area where Sodis is being promoted. They are generally women interested in the method who, after intensive training, try to persuade their neighbours and acquaintances to adopt Sodis.

Health fairs are used to promote healthy behaviour (nutrition, hygiene, drinking water) among as many people as possible. They are attractive for participants, as they offer music, food and entertainment. One disadvantage is that Sodis is only presented as one topic among many others. In addition, such events require substantial organizational efforts and financial resources.

Incentive-based self-diffusion strategies

encourage people from the target area to pass on information about Sodis. Incentives take the form of vouchers that can be exchanged for PET bottles at a bottle centre. With each bottle handed out, the recipient obtains another voucher to pass on.

that both reminders and public self-commitment indirectly had a positive influence on the extent of Sodis use, i.e. Sodis-treated water as a percentage of total daily consumption.

An analysis of all the factors involved in the overall behavioural change process also yielded the interesting finding that, what-

Overview of projects evaluating different strategies for the diffusion of Sodis.

Project	Period	Location	No. of households / people	Diffusion strategies applied	Habit formation measures applied	Duration of campaign	No. of Sodis-using households after campaign *
1	2005	Suburban area in Bolivia	1000 / 5000	Professional instructors Voluntary disseminators Health fair	Reminders Public self-commitment	2 months	400
2	2007	Rural area in Bolivia	3500 / 18 000	Professional instructors	Reminders	6 months	2200
3	2007 to 2009	Slum in Harare, Zimbabwe	43 000 / 216 000	Professional instructors Information event Incentive strategy	Reminders Public self-commitment	12 months	20 000 (plus 8500 **)

* Extrapolations based on surveys.

** Households in surrounding areas informed about Sodis by self-diffusion.



A professional instructor at work.

ever type of water was drunk (boiled, untreated or Sodis-treated), similar factors influence the amount of water consumed. The behavioural intention was found to be more marked the more an individual is attached to a specific type of water (e.g. on account of the taste) and the more he or she likes the method. Although the availability of plastic bottles is also relevant, it is not as fundamental as originally assumed.

Recommendations for future projects. On the basis of the findings from these three projects, we recommend that the diffusion of Sodis should always be accompanied by a monitoring programme involving a standardized questionnaire. The information obtained in this way is helpful for the development of subsequent promotion strategies or the adjustment of ongoing interventions. While the “hard” arguments for Sodis – easy to use, healthy, cost-saving, etc. – should always be presented, the question of taste should not be underestimated. Accordingly, it is important that when Sodis is introduced, potential users should be given an opportunity to sample the water.

Particularly promising, in our view, are interpersonal and incentive-based self-diffusion strategies, as well as reminders to support habit formation. If resources permit, public self-commitment can also be used. In addition, alternative methods may be used to

Public self-commitments: “Here we drink Sodis water and protect our health” (left). “We pledge to drink water treated by the sun” (right).



Habit formation strategies

Reminders, e.g. in the form of table-top cards, posters or stickers, should if possible be displayed where water is prepared on a daily basis. In all projects, reminders proved to be very popular as decorations for the generally rudimentary dwellings.

Public self-commitments indicate to other people in the neighbourhood the households where Sodis is being used. They may take the form of water-resistant posters or stickers prominently displayed on the outside of the building.

increase the visibility of Sodis, e.g. wall paintings and radio advertisements. We would, however, advise against the use of health fairs in view of the high costs and limited effectiveness.

The long-term goal should be to move away from primarily external promotion strategies towards self-sustaining models. Here, we see significant potential in voluntary disseminators, who could gradually take over the responsibilities of professional instructors. For this, they should periodically receive supervision and recognition. Overall, a Sodis implementation project should not run for less than a year, or preferably 2 years, as behavioural change and sustained habit formation is a slow process, with a risk of reversion to former practices. ○○○

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Nitrosamines – a water safety risk?



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Co-authors: Philipp Longrée and Juliane Hollender

Nitrosamines are probable human carcinogens. As well as being ingested with food, these substances are produced by chemical reactions in the stomach. In the light of findings concerning contamination of drinking water in the US and Canada, we investigated whether nitrosamines could also pose a risk to water resources in Switzerland.

In the mid-1990s, high concentrations of *N*-nitrosodimethylamine (NDMA) were found in chlorinated and chloraminated drinking water in parts of the US and Canada. Subsequent studies revealed that NDMA in drinking water is mainly formed by the reaction of organic nitrogen precursors with chloramine [1] (Fig. 1). These nitrogen precursors derive primarily from wastewater and are not completely degraded at wastewater treatment plants (WWTPs). Common to these compounds is the presence of a dimethylamine group, as occurs in many pharmaceuticals, pesticides (e.g. diuron) and industrial chemicals (e.g. dimethylamine). Chloramine, in contrast, is either added to water directly in the chloramination process or is formed during chlorination from hypochlorite and available ammonium. Increased concentrations of nitrosamines are therefore to be expected in cases where drinking water is – knowingly or unknowingly – abstracted from waterbodies receiving wastewater inputs and disinfected with chlorine or chloramine.

NDMA and other *N*-nitrosamines can enter wastewater from a variety of sources. These compounds are formed from amines in a range of technical processes, e.g. in roasting, in the production of rubber, paints and detergents, in tanneries and when semisynthetic cooling lubricants are used. In Switzerland, these sources are more relevant since drinking water in this country is rarely chlorinated and never chloraminated. Swiss water resources are not generally exposed to significant wastewater inputs, but local releases of contaminated wastewater cannot be ruled out. We therefore wished to find out whether and to what extent wastewater in Switzerland is contaminated with nitrosamines, and whether these substances are effectively eliminated in the course of treatment. For this purpose, we used a high-performance analytical method newly developed by our group, which is also

suitable for determining not previously detectable – non-volatile and thermally unstable – nitrosamines [2].

Nitrosamines in Swiss wastewater. To gain an overview of nitrosamine contamination of wastewater in Switzerland, studies were carried out at 20 WWTPs. Here, 24-hour composite samples were collected on a single occasion at various stages of the treatment process – after primary and secondary treatment and (where applicable) after sand filtration. In addition, in order to document variability over time, 24- to 72-hour composite samples were collected at the WWTP Wüeri in Regensdorf on 16 occasions between 2006 and 2008. In each case, we analysed samples for eight different nitrosamines down to a concentration of 1 ng/l.

Nitrosamines were detected at all 20 WWTPs. The highest concentrations were measured in primary effluent, lying between 1 and 89 ng/l for NDMA (Fig. 2) and between 4 and 31 ng/l for *N*-nitrosomorpholine. NDMA concentrations at the WWTP in Regensdorf varied over time from not detectable to maximum levels close to 1 µg/l (Fig. 3). In contrast, concentrations of nitrosomorpholine (between 3 and 30 ng/l) showed considerably lower variation. Another four of the target nitrosamines occurred less frequently in the wastewater samples, with concentrations up to 25 ng/l. Two of the nitrosamines were not detected at all.

Biological wastewater treatment substantially reduced nitrosamine contamination at most of the WWTPs, with post-treatment concentrations generally lying below 20 ng/l. On average, the elimination rates were 70 % for NDMA, 40 % for *N*-nitrosomorpholine and 70–90 % for the other nitrosamine compounds, although the rates varied (in some cases widely).

Our results indicate that substantial peak concentrations of certain nitrosamines may be attained in wastewater, which are

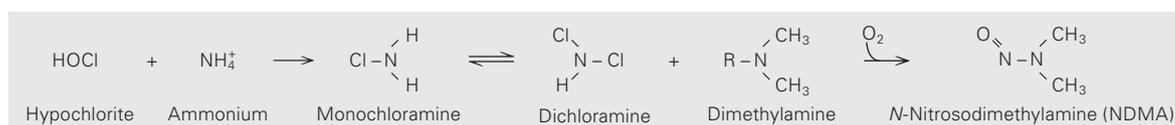


Fig. 1: Formation of *N*-nitrosodimethylamine from dimethylamine and chloramine.

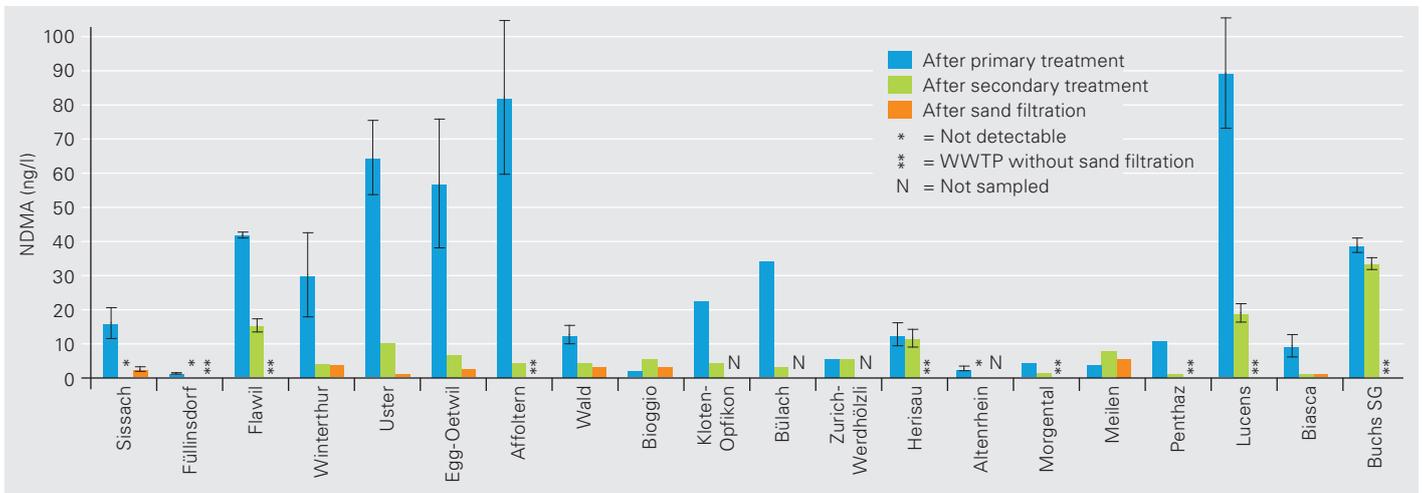


Fig. 2: *N*-Nitrosodimethylamine concentrations in wastewater at various stages of treatment in 20 Swiss plants.

presumably attributable to individual releases from as yet unidentified industrial sources. However, thanks to the generally high treatment efficiency at WWTPs, nitrosamine contamination of treated wastewater is relatively low in Switzerland.

Nitrosamines in water recycling. In contrast to Switzerland, drinking water resources are overexploited in many parts of the

world, and as a result wastewater is increasingly being recycled as drinking or process water. As part of the EU-funded RECLAIM WATER project [3], we studied the occurrence of nitrosamines at the Wulpen/Torreele plant on the Belgian North Sea coast. At this facility, municipal wastewater is treated in a conventional two-stage WWTP and additionally undergoes ultrafiltration and reverse osmosis so as to largely eliminate pathogenic microorganisms, macro- and micropollutants. The purified wastewater is infiltrated through ponds into an overexploited aquifer in the dune area to prevent seawater intrusion. After a residence time of about 40 days, the groundwater is abstracted for drinking water production (Fig. 4).

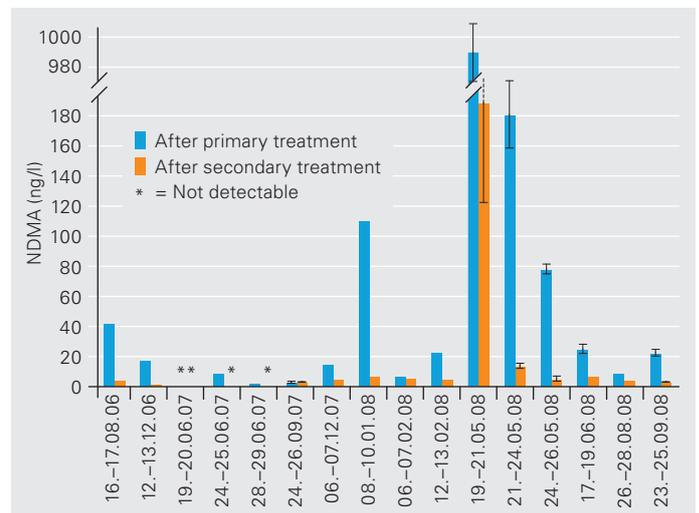
Before and after the two-stage treatment process, only low concentrations of NDMA and *N*-nitrosomorpholine were found in wastewater (less than 10 ng/l).

Nitrosamines derived from food and produced in the body

Since the 1970s, nitrosamines have been known to occur in foodstuffs in concentrations of up to several micrograms per kilogram – in smoked and nitrite-cured meat and fish, and in malt products such as beer. Nitrosamines have also been and continue to be found in a variety of other consumer goods, such as rubber products (e.g. dummies) and cosmetics, as well as in tobacco smoke. Even though, as a result of modified production processes, foodstuffs now contain significantly lower levels of nitrosamines, recent estimates assume that the dietary intake for adults is about 80–300 ng per day [4].

In addition, endogenous nitrosamine formation contributes to total exposure: in the stomach, nitrate is reduced to nitrite, which under acidic conditions reacts with food-borne amines to form nitrosamines. Estimates in the literature vary widely, ranging from 100 ng to as much as 20 µg per day. Endogenous nitrosamine formation is thus probably responsible for the largest portion of the total load, but is strongly dependent on dietary habits [4].

Fig. 3: Variation in concentrations of *N*-nitrosodimethylamine at the Regensdorf wastewater treatment plant.



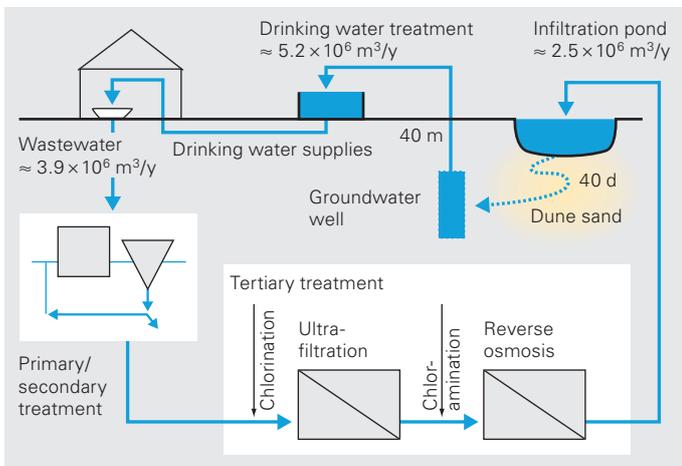


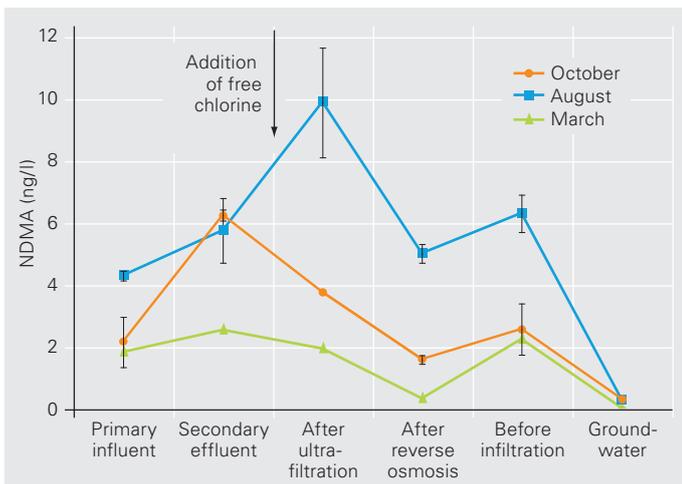
Fig. 4: Flow diagram of wastewater treatment, artificial groundwater recharge and drinking water production at the Wulpen/Torreele plant in Belgium.

When higher doses of chlorine or chloramine are used – as is the case in the summer – to prevent fouling of the ultrafiltration and reverse osmosis membranes, NDMA is formed (Fig. 5). In contrast to most inorganic ions and organic micropollutants, only about 50% of this substance is removed by reverse osmosis, as the small, uncharged and highly polar NDMA molecules can pass through such membranes. NDMA is however degraded in groundwater, and it was therefore not detected either in groundwater or in the treated drinking water. The low concentrations of *N*-nitrosomorpholine are reduced to below the detection limit by reverse osmosis.

Our studies furthermore demonstrate that nitrosamine precursors are retained by reverse osmosis with an efficiency of more than 98%. Accordingly, the formation of nitrosamines is very unlikely even if drinking water is chlorinated.

Fig. 5: Concentrations of *N*-nitrosodimethylamine measured on three sampling occasions at the Wulpen/Torreele plant.

Free chlorine added: March and October 1.5 mg/l, August 2.75 mg/l.



Nitrosamine limits

Nitrosamines are carcinogens or, more precisely, procarcinogens, which have to be activated in the body before they can exert any harmful effects. For substances of this kind, it is not possible to define specific limits on the basis of classical dose-response relationships. Limits are therefore based on the tolerable excess risk of developing cancer, which is extrapolated from animal experiments. For *N*-nitrosodimethylamine (NDMA), the US Department of Health and Human Services in 2005 determined the 1-in-a-million cancer risk level with lifetime consumption of drinking water to be 0.7 ng/l; for other nitrosamines the values lie in the range 0.2–16 ng/l.

In Switzerland, nitrosamine levels in drinking water have not been regulated to date, while in the Netherlands, Germany and some US states, (provisional) guideline or action levels of 10 ng/l have been proposed or specified for NDMA.

Nitrosamines to be avoided as far as possible! Our results indicate that, unlike in the US and Canada, drinking water supplies in Switzerland are unlikely to be contaminated with nitrosamines. Far greater quantities are ingested with our food or produced by our own body (see Box on p. 26). Compared with the overall daily intake, which for an adult may lie in the microgram range, the guideline values of approx. 10 ng/l proposed for drinking water (see Box on p. 27) appear to be very low. Nonetheless, any additional intake of carcinogenic substances in drinking water is to be avoided – especially for infants and children, whose ingestion of nitrosamines with food is certainly much lower. ○ ○ ○

We are grateful to Johan Cauwenberghs (Aquafin) and Emmanuel van Houtte (IWVA) for the collection of samples at Wulpen/Torreele. The studies were supported by the Federal Office for the Environment and the European Commission.

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Nonylphenols: degradation and estrogenicity



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Nonylphenols, which are endocrine disruptors, always occur as a mixture of different isomers. New findings indicate that the isomers are differentially degraded by bacteria, and the estrogenic risk posed by the mixture may even be increased in the process.

Nonylphenols are highly toxic environmental contaminants with endocrine-disrupting effects. Since the 1980s, Eawag has been studying the behaviour of these substances at wastewater treatment plants and in the aquatic environment. So-called technical nonylphenol, produced on an industrial scale from phenol and propylene trimer, is mainly used in the synthesis of nonylphenol polyethoxylates, an important group of non-ionic surfactants. Nonylphenol provides a striking example of how toxic compounds can arise in the environment from relatively harmless anthropogenic starting materials. When the relatively unproblematic nonylphenol polyethoxylates in wastewater enter a treatment plant, the nonylphenol used in surfactant production is released as a result of progressive microbial degradation of the polyethoxylate chain. In the EU and Switzerland, the use of nonylphenol and its ethoxylates has been heavily restricted by legislation for some years. In the US and most other countries, however, no legal restrictions are in place as yet.

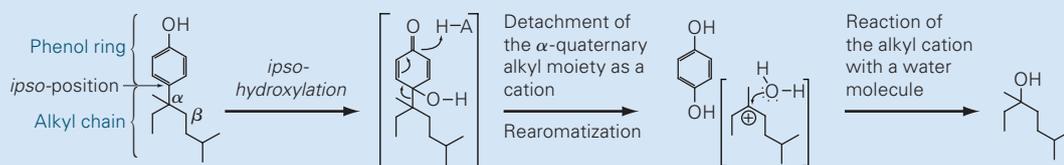
As a result of the manufacturing process, technical nonylphenol is a complex mixture containing more than 100 isomers, which

differ in the branching pattern and position of the alkyl chain (Fig. 1). About 85 % of the isomers in the technical mixture are 4-nonylphenols, i.e. the alkyl chain is located at position 4 – opposite the OH group in the phenol ring. Although the contamination of a wide variety of environmental compartments with nonylphenol has been addressed in numerous scientific publications, little is known about how the isomer composition changes during the degradation process. We therefore carried out experiments using the nonylphenol-degrading bacterium *Sphingobium xenophagum* Bayram (see Box “Microbial degradation of nonylphenols”) [1–4]. As the estrogenic effects (see Box “Estrogenic activity of nonylphenols” on p. 30) of the individual nonylphenol isomers appear to depend on the branching pattern of the alkyl chain, we also – in cooperation with the research group led by Professor Sumpter in the UK – studied a series of pure nonylphenol isomers in an estrogenicity test [1].

Microbial degradation of nonylphenol mixtures. In degradation experiments, we offered *S. xenophagum* Bayram technical

Microbial degradation of nonylphenols

In recent years, several bacterial strains – belonging to the Sphingomonad group – that can degrade nonylphenol and use it as a source of carbon and energy have been isolated from activated sludge of wastewater treatment plants. Surprisingly, the strains isolated on different continents all use the same novel degradation mechanism: the entire alkyl side chain is detached from the ring and appears as the corresponding alcohol derivative in the nutrient medium. To explain the degradation of nonylphenol by *Sphingobium xenophagum* Bayram, a strain isolated at Eawag from activated sludge of the Kloten-Opfikon WWTP [2], we have suggested an *ipso*-substitution mechanism [3, 4]. The strains isolated in Belgium, Japan and the US seem to use the same mechanism (see references in [1]).



Degradation of α -quaternary nonylphenols via *ipso*-substitution by *Sphingobium xenophagum* Bayram. The intermediates shown in square brackets are unstable.

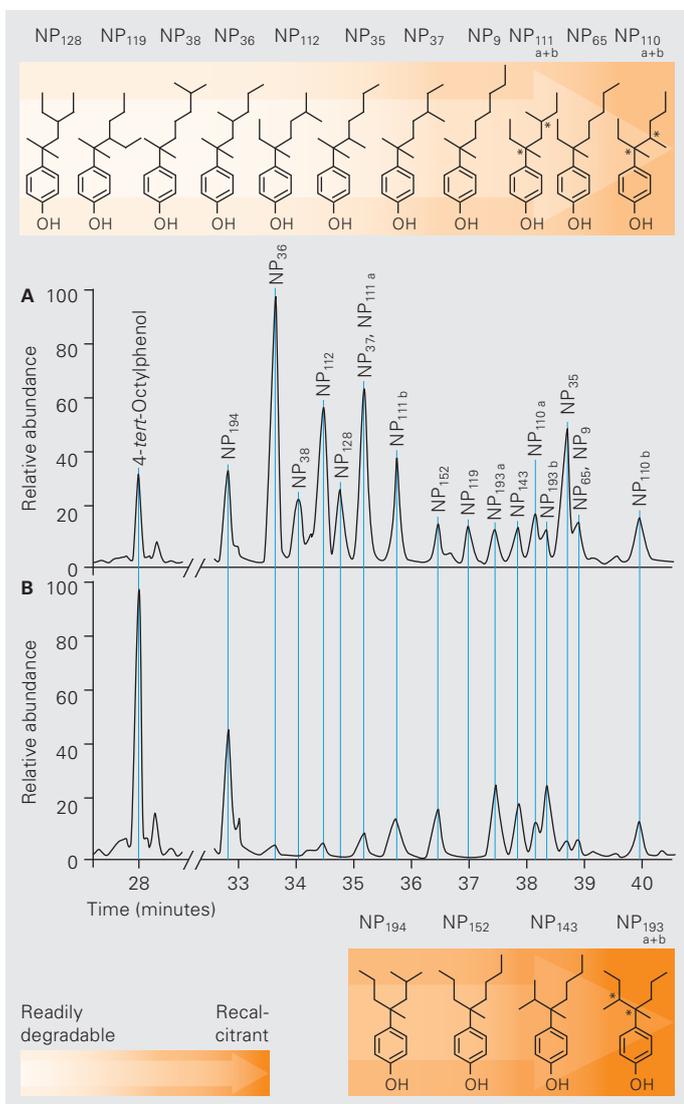


Fig. 1: "Aging" of technical nonylphenol as a result of degradation by *Sphingobium xenophagum* Bayram. The gas chromatography-mass spectrometry total ion current (TIC) traces show the nonylphenol mixture at the start of the experiment (A) and after 9 days' incubation (B). Abundance values are calculated relative to the internal standard (4-tert-octylphenol).

nonylphenol as the sole source of carbon and energy. Within 9 days, the bacteria transformed approx. 86% of the 4-nonylphenol. However, depending on the structure of the alkyl chain, degradation was more or less complete. In general, isomers with bulky groups at the α -position of the alkyl chain were more recalcitrant, and they were enriched in the resultant mixture (compare Fig. 1A and B). This is probably due to the fact that the branched alkyl chains of these nonylphenol isomers sterically hinder hydroxylation at the neighbouring *ipso*-position (see Box "Microbial degradation of nonylphenols"). It was shown by experiments involving defined mixtures of individual isomers that a lengthy alkyl chain also impedes *ipso*-hydroxylation.

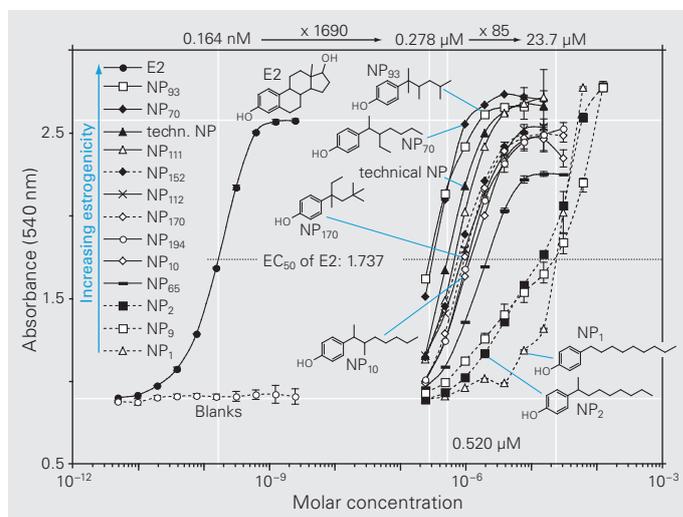


Fig. 2: Estrogenic activity (mean values and standard deviations from two assays) of individual nonylphenol isomers and of the female sex hormone 17 β -estradiol (E2) as a function of concentration, determined using the yeast estrogen screen (YES) assay. For formulae not shown here see Fig. 1.

Enrichment of nonylphenol isomers with bulky groups at the α -position had already been found in river water samples from around Tokyo Bay and in composting plants (see references in [1]). The *ipso*-hydroxylation mechanism that we have proposed may possibly be the decisive factor in the development of these nonylphenol fingerprints. In addition, we suspect that the isomer composition depends on the degree of "aging" of the nonylphenol mixture and on the predominant aging process (e.g. microbial degradation or photochemical decomposition). In cases where the aging process scarcely differentiates between the various isomers or where no transformation whatsoever occurs – for example, because nonylphenols escape degradation by adsorption to solids – the composition of the nonylphenol mixture will be very similar to that of the original technical mixture. This could explain why, in certain sediments, no change was observed in the nonylphenol pattern.

Estrogenicity of nonylphenol isomers. The estrogenicity of nonylphenol isomers has been shown by three studies to depend on the structure of the alkyl residue, but the principles underlying this relationship have yet to be fully elucidated. However, on the basis of the available results, the estrogenic potency of nonylphenol mixtures can be expected to vary according to differences in isomer composition. This conclusion is relevant for the risk assessment of environmental contaminants, since the isomer distribution pattern of nonylphenol in some biological systems differs markedly from that of the technical mixture.

Figure 2 shows the estrogenic activity of 12 different nonylphenol isomers as a function of concentration in the yeast estrogen screen (YES) assay. In general, the isomers studied attained the same maximum activity as the female sex hormone 17 β -estradiol, although this required 1700- to 140 000-fold higher concentra-

Estrogenic activity of nonylphenols

On account of their structural relationship to the female sex hormone 17β -estradiol, nonylphenols can have endocrine-disrupting, estrogenic effects on many vertebrates. In the 1990s, nonylphenols were believed to be implicated in the feminization of fish in heavily contaminated rivers in the UK: male juveniles living downstream of WWTP effluent outlets had abnormally small testes and produced vitellogenin, an egg yolk protein normally only found in females.

tions. The EC_{20} of technical nonylphenol – i.e. the concentration producing 20 % of the maximum response for 17β -estradiol in the YES assay – is in the same order of magnitude (approx. 61 $\mu\text{g/l}$) as the dissolved nonylphenol concentrations that were actually measured in the mid-1990s in heavily polluted river stretches in the UK (24–53 $\mu\text{g/l}$). According to a pioneering study, a high degree of branching at the α -carbon atom of the alkyl chain could be an important structural characteristic of highly estrogenic nonylphenol isomers. In our experiments, however, the NP_{93} and NP_{70} isomers were especially potent. These two isomers have an alkyl substituent at the β -position and a main chain with 5 and 6 carbon atoms respectively. Isomers with a side chain of similar length (4–6 carbon atoms) but no β -substituent (e.g. NP_{65}) and those with a β -substituent but a longer side chain (NP_{10}) are less potent, even if they have a quaternary α -carbon atom (i.e. one bonded to four other carbon atoms). We therefore conclude – as did a Japanese research group – that not α -substitution, but β -substitution, together with an optimal length of the main chain, is the key factor for high estrogenic activity in nonylphenol isomers [1]. If both of these activity-promoting structural characteristics are lacking, the isomers tend to have low estrogenic activity. Given their structure, the as yet untested but recalcitrant isomers NP_{193a} and NP_{193b} could therefore be highly estrogenic.

For the estrogenic effect to develop, the active substance must interact with a matching cavity in the protein receptor (lock-and-key principle). The structure of 17β -estradiol, in particular, is well adapted to the receptor binding site. Even so, in the hormone-receptor complex, large cavities adjacent to two positions of the ligand remain unoccupied. This is also the case when nonylphenols bind to the receptor. These cavities can accommodate further groups of a ligand (e.g. appropriately shaped β -substituents of certain nonylphenols), thereby increasing the stability of the ligand-receptor complex and hence also the estrogenic effect.

Influence of microbial degradation on estrogenic activity. Of the 18 main isomers occurring in technical nonylphenol, only 11 have so far been synthesized and tested for estrogenicity. Remarkably, all these isomers were less estrogenic than the technical mixture. If this cannot be explained by a synergistic effect (i.e. if

the whole is indeed equal to the sum of the parts), these findings imply either that certain as yet untested main components are at least moderately more potent than the technical mixture or that certain minor components are highly estrogenic. For example, it would need to be investigated whether such highly estrogenic isomers as NP_{167} , which appears to be 153 times more potent than technical nonylphenol, are minor components of the technical mixture. Obviously, only small amounts of such a compound would need to be present in technical nonylphenol to account for its estrogenicity.

In one way or another, isomer-specific degradation certainly influences the endocrine-disrupting activity of nonylphenol mixtures. If recalcitrant isomers such as NP_{193a} and NP_{193b} prove to be highly estrogenic, there is a significant risk that microbial degradation by *ipso*-substitution will increase the estrogenicity of nonylphenol mixtures [1]. Effective monitoring – as required by the EU for nonylphenols – is therefore only possible if individual isomers are measured. ○ ○ ○

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No food without water

Water shortages pose a serious threat to humanity and will have wide-ranging consequences in various sectors, including agriculture. An interview with Eawag scientist Hong Yang.

Global water demand is constantly increasing. What are the reasons? It's certainly due to a combination of factors, such as population growth, rapid economic development and climate change. However, there's another crucial aspect that is often underestimated, i.e. changes in diet structure. Take China as an example. Of course, its population is growing and the economy is expanding rapidly. But these are not the main causes of the growing water scarcity in China. The main reason is the change in patterns of food consumption – people are eating more and more meat as they become more and more prosperous.

How does this influence water requirements? In China, it takes 4,000–12,600 litres of water to produce a kilogram of meat, whereas a kilogram of cereals needs only 800–1,300 litres. So, the recent rise in meat consumption has led to an increase in China's annual per capita water requirement for food production from 255 m³ in 1961 to 860 m³ in 2003.

Is this comparable to the situation in fully industrialized countries? No, China's water requirement for food production is still well below that of many developed countries. The United States, for example, uses 1,820 m³ per capita per year. But the steady increase in the amount of meat in Chinese diets is also worrying from another point of view.

Namely? I am thinking of the health aspect. Meat consumption is already 50% higher than the optimal amount recommended by the Chinese Nutrition Society. A dietary shift may thus also have detrimental effects on the population's health, as is known from developed countries. Raising public awareness about healthy eating would therefore kill two birds with one stone: it would help to keep people in



Hong Yang received her PhD from Adelaide University (Australia) in 1994. She worked as a postdoctoral fellow at Adelaide University and as an assistant professor at Hong Kong University before joining Eawag in 1999. She is currently a senior scientist and leader of the group «Water scarcity, environment and food» in the department «System Analysis, Integrated Assessment and Modelling» at Eawag.

good physical shape and to mitigate water scarcity.

India is another rapidly growing country. For India, it's a different story. There, population growth itself is the number one cause of water scarcity because economic development is not as fast as in China and for religious reasons the Indian diet is more vegetarian than the Chinese diet.

Your research focuses on the relationship between water usage and food production and the implications for water resources and the environment.

That's right. In order to improve the efficiency of water use and reduce its impact on the environment, we are especially interested in exploiting the virtual water strategy.

What is "virtual water"? In a country with limited water resources, you have to restrict the use of water for irrigation. Consequently crop production will decline and there will not be enough food for the

people. So what do you do? Either you transfer real water into the region or you import food which is produced elsewhere. This is virtual water! The water is "spent" somewhere else, and by importing food you balance the water budget.

Which countries would profit in particular from the virtual water strategy? All those with pronounced interregional variation. Look at Iran. This country not only has a wide range of climatic conditions but also the socioeconomic situation varies between regions. So they produce different crops, and the productivity of water differs a lot. In a project financed by the National Science Foundation of Switzerland we are investigating the advantages of the virtual water strategy for Iran.

How does this work in detail? First we assess water availability and the amount of water actually used in the various regions. Then we compare these data and identify those areas where water problems are serious, where practices are not sustainable and where the system could collapse. Finally, we communicate our results to local high- and low-level officials. However, things change slowly and concrete implementation of the virtual water strategy is a task for policymakers. What we can do is feed our findings into the policymaking process. ○ ○ ○

The interview was conducted by Martina Bauchrowitz.

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Where does Eawag News go from here?

Since it was first launched in 1973, Eawag News has been addressed to a steadily growing circle of subscribers – both nationally and internationally. But who exactly reads Eawag News? And does Eawag News meet its readers' requirements? Answers are provided by the survey conducted in April 2008.

"This is an excellent way of presenting complex subjects. These magazines are not to be missed!" These were just some of the encouraging comments elicited by the Eawag News survey. Altogether, our questionnaire was completed by more than 650 readers from 40 different countries. Thank you for your participation!

Target audience and reading patterns.

Eawag News is read by people of all ages, with 46- to 55-year-olds making up the largest group. The respondents come primarily from the water sector (research, administration and private sector) and are educated to a high level: 75% of those who took part in the survey have a degree and 40% also have a doctorate.

Around 90% of the respondents reported reading Eawag News regularly or reading selected articles closely. Just under two thirds find the information in Eawag News useful for their work and hope it will help them to keep in touch with research.

Eawag News: from research, for practice

The first issue of Eawag News appeared in January 1973. The magazine was established by the then Director, Werner Stumm. It is thus the oldest institutional magazine in Switzerland's research landscape – and also the only one produced in four different languages. Current circulation figures for Eawag News: German edition 3500, English 1600, French 900 and Chinese 2000.



Level and organization. The great majority of respondents consider Eawag News to be pitched at an appropriate level. They find the research reports comprehensible and the degree of detail and complexity of the articles just right. It was also interesting to note that more than two thirds of all respondents do not want Eawag News to be written in a less scientific style.

Overall, the survey participants welcome the fact that individual issues of Eawag News focus on specific topics. Nonetheless, half of the respondents would also like to read more up-to-date articles and a mixture of contributions from different areas of research. The layout of the magazine and the frequency of publication – an average of two issues per year – are generally appreciated.

Constructive criticism. As well as the numerous compliments that we received for Eawag News, some critical views were, of course, also expressed: these ranged from "Why go to the expense of producing a paper version?" to "It would be good to make additional information available online" and even "A bit more political bite in statements on environ-

mental topics wouldn't go amiss". We welcomed this criticism, as it is important for us that Eawag News should continue to provide a strong link between research and practice.

New directions for Eawag News. How can Eawag News now be developed? From now on, each issue of Eawag News will offer something for every reader. We aim to achieve this by including a mixture of articles from different fields. In addition, we will be featuring overview articles, which will also increasingly provide a forum for external water professionals. But Eawag News will also continue to focus on specific questions, illustrating how Eawag approaches a research topic from various angles.

Even though individual respondents were opposed to the print editions of Eawag News, we have decided to continue producing the publication in this form. We believe that the vast majority of readers prefer a print edition. Eawag News will of course also continue to be available for download from our website:

www.eawag.ch/eawagnews ○○○

Martina Bachrowitz

In Brief

Reaping the rewards of sustainable construction

A five-storey office and research building that accommodates 220 people, but requires little more energy for heating and cooling from external sources than a couple of single-family homes? Eawag's internationally renowned Forum Chriesbach proves that this is possible.

At a meeting held in January 2009, architects, planners and clients concluded

that the building had performed well over the first two years – in terms of both energy use and costs. At CHF 30 million, the construction costs for Eawag's new headquarters were well below the credit limit approved by the Federal Parliament. The additional investments – compared with a similar, conventionally constructed building – amounted to just under 5%.

However, this is offset by the lower operating costs: the annual (capital and operating) costs are already CHF 10,000 lower than for a conventional building. If energy prices rise as expected, the benefits will become even more marked over the years. Forum Chriesbach is already regarded as a model for a new generation of buildings. ○ ○ ○



Vietnamese medals awarded to Eawag scientists

In March 2009, four Eawag scientists received official medals from the Vietnamese government for their achievements in the areas of drinking water quality and sanitation. The medals were awarded in recognition of "outstanding contributions to education and training in Vietnam".

With financial support from the Swiss government, the scientists successfully strengthened capacity at two research centres in Northern Vietnam and improved the quality of local water supplies and wastewater management. For more information, visit www.eawag.ch



Antoine Morel, Michael Berg, Walter Giger and Roland Schertenleib (from left to right) received their medals from the Vietnamese ambassador in Switzerland.

Jurassic Park from a Swiss lake?

Ecological changes caused by humans affect natural biodiversity. For example, the eutrophication of Lake Constance and Greifensee in the 1970s and 1980s led to genetic changes in the population of water fleas. At the beginning of the 20th century, only one species of water flea (*Daphnia hyalina*) occurred abundantly in the two



lakes studied. As eutrophication developed, this was displaced by another species (*Daphnia galeata*).

In the transitional periods before and after peak nutrient inputs, hybrids also developed. However, although the lakes are now once again much cleaner (thanks to major efforts in the urban wastewater management sector), the original species has not yet re-established. This was demonstrated by researchers from Eawag and from two German universities (Frankfurt and Konstanz), who analysed genetic material from *Daphnia* eggs up to 100 years old. Biological archives such as the resting eggs of *Daphnia* in lake sediments are thus a valuable tool for investigating how organisms respond to changes in the ecosystem. www.eawag.ch/medien/bulletin/20090310/index_EN