

Eawag

INews



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Late effects of eutrophication

The restoration of Swiss lakes is a success story. By around 1975, phosphorus concentrations in most lakes had increased dramatically. Across the country, there were reports of algal mats on lake surfaces, oxygen depletion in deep waters and fish kills. There followed a coordinated series of remedial measures: wastewater treatment plants were expanded, ring sewerage systems were constructed to prevent direct discharges into lakes, phosphates were banned in laundry detergents and there were efforts to improve the nutrient balance in agriculture. These measures soon proved effective: from around 1985, phosphorus concentrations declined significantly again, and in most lakes they have now reached levels not measured since the 1950s. Similar restoration efforts have also been successful in many other parts of Europe.

This example is encouraging – a problematic environmental condition such as eutrophication would appear to be reversible if remedial measures are taken over a period of decades. However, by no means all the late effects of overenrichment with nutrients have been eliminated. Like a patient who continues to limp long after his broken leg has healed, the late effects of eutrophication are still all too apparent in surface waters:

- ▶ In deep, permanently stratified waterbodies such as Lakes Zug and Lugano, phosphorus levels have only declined very slowly. However, Lake Lugano has now undergone complete mixing for the first time in about 40 years, which should further accelerate its recovery.
- ▶ The consequences of heavy fertilizer use are particularly marked in wetlands and river mouths. For example, because large amounts of phosphorus continue to run off agricultural areas in the Donau Basin, numerous small lakes in the Danube Delta remain highly eutrophic. This has given rise to substantial emissions of greenhouse gases (notably methane). In the future, agricultural measures will need to remain a priority.
- ▶ Comparison of a eutrophic and an oligotrophic lake reveals that there have been long-term changes in biomass production and the composition of phyto- and zooplankton.
- ▶ Resting stages retrieved from lake sediments can be used to trace the genetic effects of increased nutrient concentrations on water fleas. In Lake Constance and Greifensee, for example, a

Daphnia species that disappeared as a result of eutrophication has yet to be re-established, despite the marked improvement in the condition of the lakes.

In addition to the “in focus” articles, this issue of Eawag News includes reports on various other research projects:



- ▶ The overview article on wastewater treatment considers the question of when it may be advisable to use decentralized systems, presenting the views of researchers and other water professionals.
- ▶ Experiments conducted by Eawag show that ferrate can be used to remove micropollutants from treated wastewater. It offers the additional advantage of precipitating phosphate at the same time.
- ▶ Fish are preferred test organisms in ecotoxicology. With the aim of avoiding these animal experiments in the future, Eawag is developing a new test system involving fish cell lines.
- ▶ With the aid of substance flow analysis, the pathways of flame retardants can be traced throughout their life cycle. These persistent, endocrine-disrupting substances are used, for example, in plastic casings and textiles. Ubiquitous in our everyday lives, they also find their way into surface waters during use and disposal.

Environmental research generates knowledge and technologies which can help to prevent or mitigate environmental problems caused by nutrients and other water pollutants. But it also serves another function, as illustrated by a number of examples in this issue: Eawag researchers investigate how aquatic systems respond to remedial measures, thereby helping us to deal more effectively with future environmental problems.


Cover photo: Sorin Balan, a doctoral student at GeoEcoMar (the National Institute for Marine Geology and Geoecology in Bucharest), prepares for a dive. His task was to deploy and retrieve equipment used for sampling sediment pore water in a number of Danube Delta lakes. For more information on this project, see pp. 4–7. © Silviu Radan, GeoEcoMar, Bucharest

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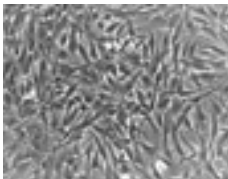
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Danube Delta: a leading source of greenhouse gases

Wetlands such as the Danube Delta act as huge natural water purification systems: anthropogenic nutrients are removed from the water column and incorporated into biomass. The decomposition of biomass in the Danube Delta gives rise to particularly large amounts of the greenhouse gases methane and carbon dioxide, which are released into the atmosphere.

Wetlands and lakes are major sources of greenhouse gases. For example, it is known that around 87 % of all lakes worldwide emit carbon dioxide (CO₂) to the atmosphere. However, their significance as a source of methane (CH₄) – a greenhouse gas ~20 times more potent than carbon dioxide – was long underestimated [1].

This was partly due to the fact that precise quantification of methane emissions from wetlands is complicated by their high degree of spatial and temporal variability. While carbon dioxide is produced by aerobic degradation of organic matter, methane is a product of anaerobic degradation. In addition, it is possible that

Different types of lakes in the Danube Delta

The Danube Delta comprises three main arms, as well as countless side or old branches, man-made channels, islands and lakes. The lakes are shallow (maximum depth 6 m), varying widely in terms of productivity, vegetation and hydrology. Lakes lying relatively close to the main arms are heavily influenced by the streamflows of the Danube. The other lakes are affected both by the Danube and by the Black Sea. Here, especially in the winter months, easterly winds may push brackish water into the lakes, where water levels tend to be low during this season. For our study, we chose three areas of the Danube Delta with a total of seven throughflow lakes:



- ▶ Lakes Uzlina and Isac (both close to the river) are mainly fed by water from the Sfântu Gheorghe arm, which only takes about 0.2 days to reach Lake Uzlina. They thus represent systems with very high nutrient inputs. Based on its vegetation (abundant aquatic macrophytes and filamentous algae) and high density of suspended matter, Uzlina is classified as a turbid lake. In contrast, Isac is a semi-turbid lake, mainly characterized by microscopic free-floating algae and turbid matter.
- ▶ Lakes Matita and Merhei represent typical wetlands with clear water, extensive reed belts and high abundance of aquatic vegetation. They receive river water via the meandering Lopatna channel. This channel is densely vegetated and transports large amounts of organic matter into Lake Matita.
- ▶ The more isolated Lakes Puiu, Rosu and Rosulet receive nutrient inputs from a channel but also receive relatively large amounts of organic matter and regenerated nutrients from the surrounding reed belts [2]. Lake Puiu is semi-turbid, with abundant phytoplankton and suspended matter. Rosu and Rosulet are turbid lakes, dominated by macrophytes and filamentous algae.

methane is also directly produced by plants and emitted to the atmosphere – although this process is a matter of considerable controversy among scientists.

Wetlands are often highly productive ecosystems. This is also true of the Danube Delta on the Romanian coast of the Black Sea; here, it is due in particular to the high nutrient content of the river water. As the Danube makes its way through ten European countries (many of which lack wastewater treatment facilities), the water becomes increasingly enriched with nutrients. We wanted to study the relationship between high nutrient concentrations, biomass production and degradation, and emissions of greenhouse gases. We also wanted to estimate how greenhouse gas emissions from the Danube Delta compare with those from other wetlands. In cooperation with researchers from the Romanian National Institute for Marine Geology and Geoecology (GeoEcoMar), we therefore carried out detailed studies of various lakes in the Danube Delta [3–5]. This involved the collection of both sediment and water samples.

Highly eutrophic delta. Covering an area of 5800 km², the Danube Delta is Europe’s largest – after the Volga Delta – and most natural wetland complex. Its biodiversity is comparable to that of the Amazon or Nile Delta. Since 1991, the Danube Delta has been included on the Ramsar List of Wetlands of International Importance and on the Natural World Heritage List. In 1992, it was also internationally recognized as a UNESCO Biosphere Reserve.

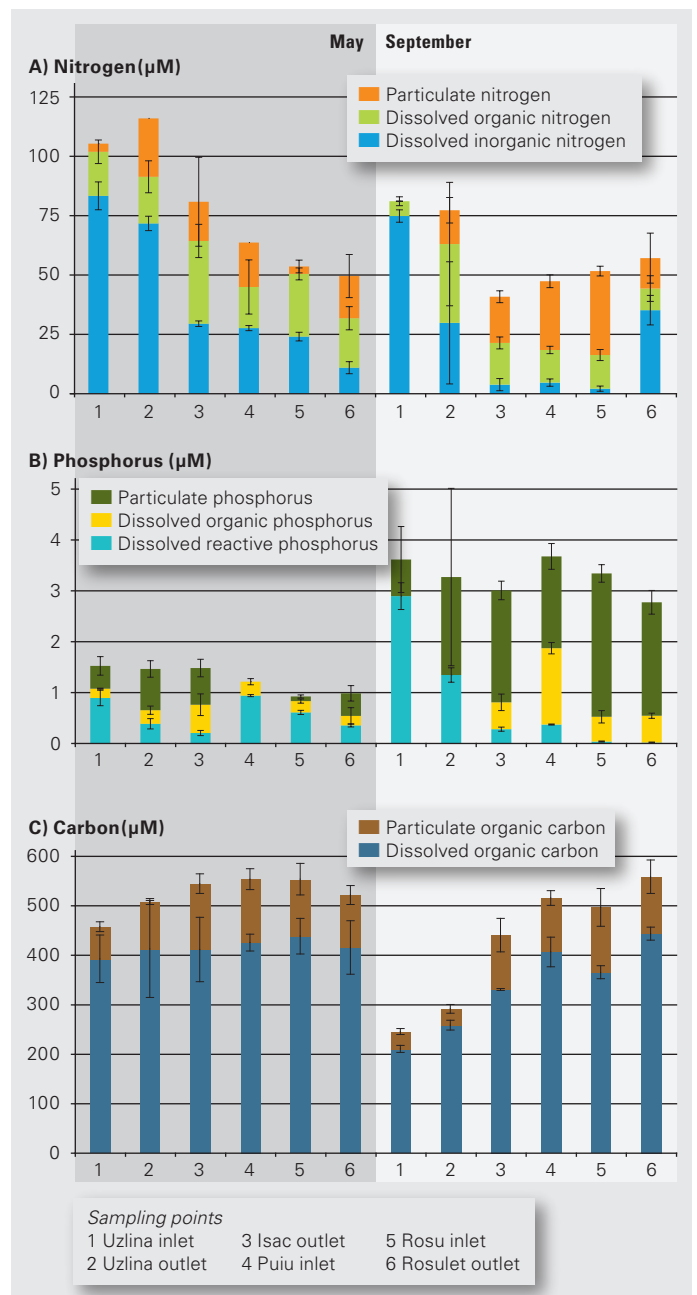
In spite of these conservation efforts, the Danube continues to export large quantities of nutrients (nitrogen and phosphorus) and biomass into the Delta lakes and the coastal waters of the Black Sea. Although the nutrient load declined over the past 20 years as a result of the economic downturn in Eastern Europe, inputs to the Danube from the catchment still amount to 750–1050 kilotonnes of nitrogen and 90–130 kilotonnes of phosphorus per year [6]. The resulting eutrophication has sharply increased the productivity of the entire wetland complex, and vast amounts of biomass (reeds, aquatic macrophytes and algae) are produced there.

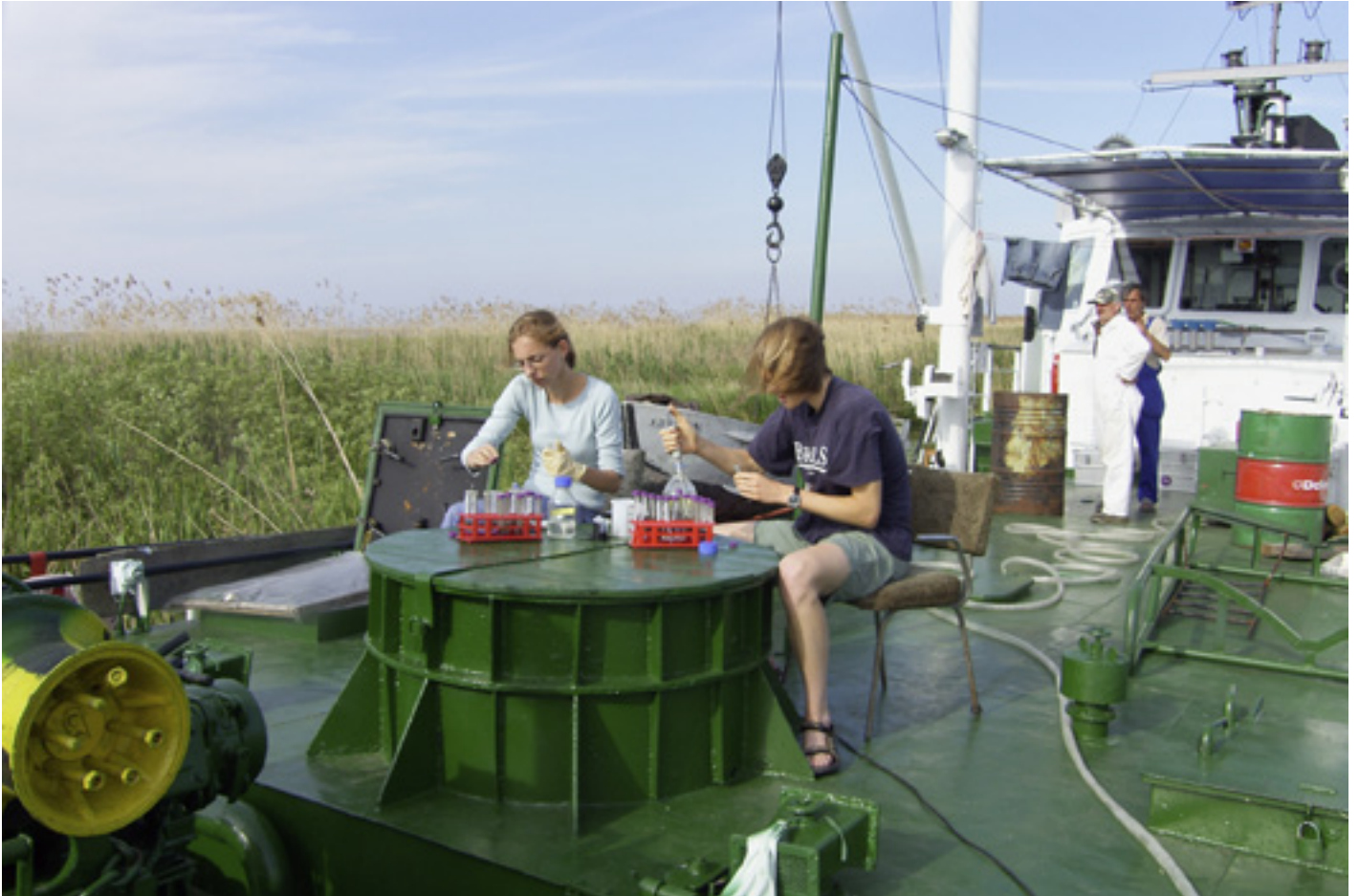
Danube Delta: a nutrient sink. As biomass is formed, nutrients are incorporated into the organic matter and thus removed from the water column. This means that the Danube Delta serves as a major sink for nutrients transported to the Black Sea. Nutrients are transformed most efficiently in the lakes lying close to the main branches of the Danube. Here, up to 77 % of dissolved nutrients are removed from the water column in the spring, when water levels are generally higher, and up to 97 % in the autumn, when water levels tend to be lower (compare the concentrations of dissolved inorganic nitrogen measured at the Uzlina inlet and the Isac outlet in May and in September, shown in Fig. 1A, and the concentrations of soluble reactive phosphorus shown in Fig. 1B). As a result, productivity is greatest in the autumn. After the organic matter produced has died off, it either sinks slowly to the lake bottom or – especially between April and June, when water levels are high – is carried away towards the Black Sea [3]. The more distant the lakes are from the main branches of the Danube, the less dissolved nutrients (Fig. 1A and B) and the more nutrients

bound in biomass – also from the extensive macrophyte and reed stocks (Fig. 1C) – are observed there.

Nutrient remobilization. When biomass is decomposed – either in the water column or in sediment – the bound nutrients are released and become available to the ecosystem again. This additional internal replenishment of the nutrient reservoir increases eutrophication and thus also biomass production – an effect which may persist for years, despite a decrease in nutrient inputs from

Fig. 1: Concentrations of various nutrient parameters at six different sampling sites (see map in Box on p. 4).





Diploma students Anna Doberer and Judith Reutimann prepare the water samples for nutrient measurements.

the Danube, thereby delaying the restoration of the Danube Delta to a more nutrient-poor and, as it were, pristine condition. This kind of “nutrient hysteresis” has also been observed for the Iron Gate 1 reservoir on the border between Romania and Serbia [7]. The term “hysteresis” describes a system whose state depends not only on the value of an input (in this case nutrients), but also on the past history of input variations.

If nitrogen nonetheless becomes scarce in the lakes distant from the Danube, the summer months see an increase in the growth of Cyanobacteria. These organisms can fix atmospheric nitrogen and thus supply the system with this nutrient in the form of ammonium.

Highly variable methane and carbon dioxide emissions. In addition to the analysis of nutrients, gas concentrations were measured at high spatial resolution in the surface water of the various lakes on a number of expeditions in the spring, summer and autumn. While the boat travelled slowly across the lake, following a grid pattern, water samples were continuously collected and the concentrations of dissolved methane and carbon dioxide were measured. This approach allowed us to analyse the gas distribution patterns in the lakes (Fig. 2): for instance, we often

found high greenhouse gas concentrations in the spring near lake inlets – e.g. in Lake Matita, which receives large amounts of dissolved gases via a richly vegetated channel. In the summer, by contrast, the highest methane concentrations were detected in lakeside reed belt areas, because the matter deposited in sediments there is readily degraded by methanogenic bacteria. It is interesting to note, however, that the seasonal distribution patterns for the dissolved greenhouse gases carbon dioxide and methane do not match the distribution patterns for total nitrogen and total phosphorus.

Relatively high emissions from the Danube Delta. The results of the gas measurements were also extrapolated so as to calculate greenhouse gas emissions for the total area of Danube Delta lakes. We estimate that emissions from lake surfaces to the atmosphere amount to 0.2×10^9 mol methane (3.2 kt) and 6.4×10^9 mol carbon dioxide (281.6 kt) per year. This makes the Danube Delta a leading source of emissions, compared with other wetlands and lakes – even though our estimates for methane do not include emissions from plants or via ebullition, which may account for up to 96 % of the total. In comparison with our conservative figures, the Black Sea estuary of the Danube (brackish

water zone) releases 75 % less methane than the Delta, and even the Pantanal region of Brazil – the world’s largest inland wetland – emits much less methane. One of the few wetlands where methane and carbon dioxide emissions are higher is the Amazon region.

Causal factors. A variety of factors are responsible for the high level of greenhouse gas emissions from the Danube Delta – above all, the substantial nutrient inputs and, associated with this, in-

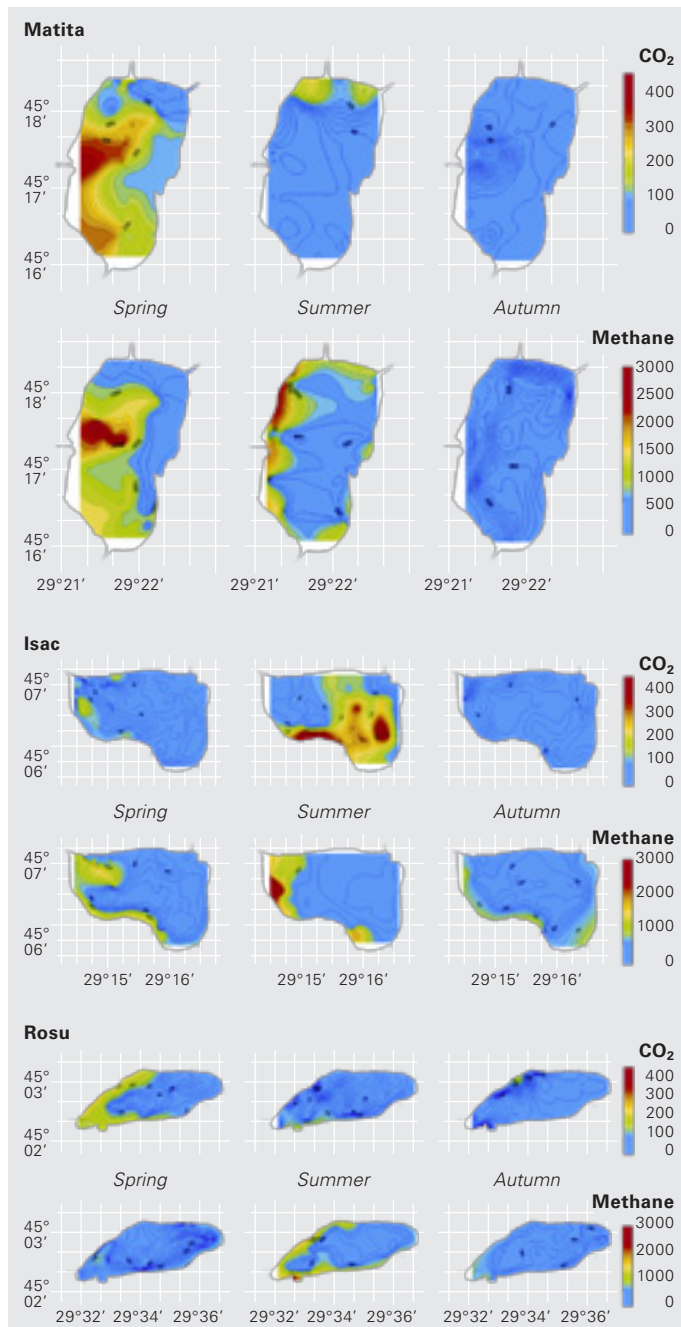
tense internal decomposition of accumulated biomass [8]. Other factors include:

- ▶ the specific hydrological conditions in the Delta,
- ▶ significant exchanges with standing water in reed belts,
- ▶ the shallowness of the lakes, which shortens the time required for transport of dissolved gases to the lake surface, especially near the shore,
- ▶ high wind speeds (due to the flat topography and proximity to the sea), which promote complete mixing of the water column and facilitate vertical gas transport.

Although nutrient inputs have been lower for some time now, the Delta must be expected to remain a major source of greenhouse gases for many years to come. Moreover, the accession of a number of Danube riparian states to the European Union and the associated economic upturn might even lead in the future to an increase in nutrient inputs and ultimately also greenhouse gas emissions. ○ ○ ○

We are grateful to everyone who collaborated on this project: Sorin Balan, Christian Dinkel, Anna Doberer, Silviu Radan, Judith Reutimann, Sebastian Sobek and Bernhard Wehrli.

Fig. 2: Distribution of greenhouse gas emissions from three of the Danube Delta lakes studied in the spring, summer and autumn.



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Daphnia populations affected by eutrophication



Nora Brede, biologist and postdoc in the Aquatic Ecology department.
Co-author: Piet Spaak

From 1950 onwards, habitats and species composition in Europe's lakes have been altered by excessive inputs of nutrients. The new environmental conditions favoured one particular water flea species, and genes were transferred across species via hybridization. Although eutrophication has now been successfully controlled, the original populations have not been re-established.

Despite their geographical proximity, Lake Constance and Greifensee could scarcely be more different as waterbodies. Lake Constance is among the largest lakes in the three bordering countries (Germany, Austria and Switzerland); Greifensee, near Zurich, can be classified as a small and shallow lake. Nonetheless, at around the same time, both of these lakes were affected by comparable overenrichment with nutrients (eutrophication). Indeed, the condition of Greifensee could even be described as hyper-eutrophication: in 1971, a total phosphorus concentration of 525 µg/l was observed. This resulted in a number of massive fish kills. Although the maximum phosphorus concentration measured in Lake Constance was only 87 µg/l (in 1971), it was transformed – in terms of productivity – from an oligotrophic (nutrient-poor) to a eutrophic lake.

Well-researched water fleas. Taking the example of water fleas, we aimed to reconstruct the changes in species composition and populations which had occurred over a relatively long period. We were mainly interested in determining the extent of the invasion

of *Daphnia galeata* (Fig. 1) caused by eutrophication, and of the subsequent interspecific hybridization with the existing species *Daphnia longispina* (formerly *Daphnia hyalina* [1]); what were the consequences of these processes for water flea populations [2]?

Daphnia are among the most important and hence well-researched zooplanktonic organisms. Therefore, it has long been known that, in the 1950s, *D. galeata* became established in both lakes alongside the indigenous species *D. longispina*. *D. galeata* generally hybridizes with other species of the subgenus *Hyalodaphnia* to which *D. longispina* belongs, and during the period of maximum eutrophication it was considerably more abundant in the two lakes studied than *D. longispina* [3].



Fig. 1: *Daphnia galeata* is found in many eutrophic surface waters – not only in Europe but also in Asia and North America.

Hybrids

When two species interbreed, the offspring are known as hybrids (crossbreeds). To differentiate this concept from that of hybridization in molecular biology and in animal or plant breeding, the term “interspecific hybridization” is frequently used in evolutionary biology.

Many species interbreed occasionally but remain differentiated if mechanisms exist to restrict gene flow. Some of the resultant hybrids are infertile; in this case, they are of no evolutionary relevance. Horse-donkey hybrids – mules and hinnies – are a typical example. Sometimes, however, hybrids are indeed fertile and form the basis for the development of new genotypes and species. But fertile hybrids will often gradually disappear again if they in turn mate with one of the original species (backcrossing). Via this pathway, genes are introduced from one species into another. This type of gene flow (introgression) has been demonstrated for *Daphnia* in both Lake Constance and Greifensee [2].

Species composition altered by eutrophication. In both lakes, *Daphnia* species composition changed dramatically from the onset of eutrophication (Fig. 2). In Lake Constance, *D. longispina* stopped reproducing sexually and continued to exist as a purely asexual organism, while in Greifensee – which was much more heavily polluted – it disappeared completely. In Greifensee, another species, *D. cucullata*, appeared briefly during the period of most severe eutrophication. Although it disappeared rapidly thereafter, genes from this species were introduced into existing *D. galeata* populations via hybridization (see Box on “Hybrids”).

Since the beginning of this century, thanks to major efforts to control water pollution, the original trophic status has been restored in both lakes. However, water flea populations have been changed irrevocably and now consist mainly of the species *D. galeata* and a broad range of hybrids.

Resting stages: a biological archive. As part of the study conducted from 2003 to 2008, sediment cores were collected from both lakes. The clearly visible light- and dark-coloured layers make it possible to determine the age of the deposits. Samples can be dated even more accurately with the aid of radiodated reference cores. Buried in the sediment layers are ephippia – the resting stages of water fleas. These saddle-shaped structures, only about 0.5 mm long, usually contain two eggs. These are produced in the course of a season and gradually sink to the bottom of the lake, where they are covered by newly deposited sediment.

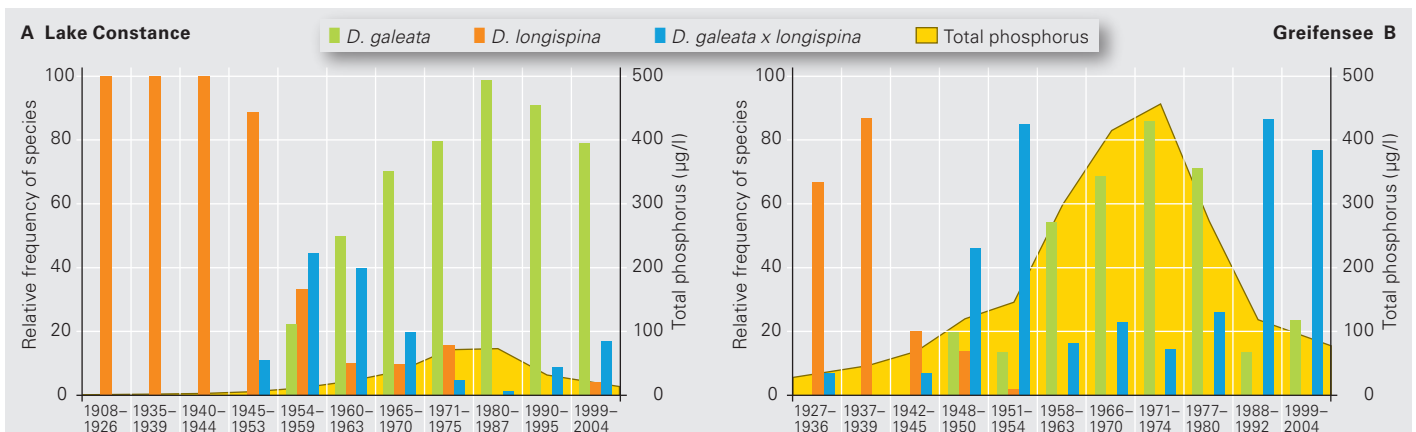
Most *Daphnia* species reproduce by cyclical parthenogenesis. This means that they reproduce asexually (clonally) during the spring and summer, and then start to produce both sexual females and males in the autumn. Ephippia, which arise only from sexual reproduction, generally start to develop in the spring. These “winter eggs” are thus able to survive the months when food sources are lacking and temperatures are too low. The resting stages of water fleas are extremely robust: it is known that they can withstand passage through the guts of waterbirds and fish, as well as drought or frost. We were able to hatch *Daphnia* even from eggs



Piet Spaak, head of the Aquatic Ecology department, collecting sediment cores on Greifensee.

that had been dormant for 45 years. Older eggs lose their capacity to develop, but even after 100 years the DNA they contain can still be readily used for molecular genetic analyses [4]. Resting stages thus represent an archive of the populations that were found in a lake decades earlier, allowing scientists to reconstruct historical processes (see Box on “Resurrection Ecology”).

Fig. 2: Changes in the relative frequency of various species (*D. longispina*, *D. galeata* and *D. galeata x longispina*) over time in Lake Constance (A) and Greifensee (B). Yellow shading: average phosphorus concentrations.



Resurrection ecology

The idea of hatching viable water fleas from resting eggs which have lain dormant for decades conjures up visions of “Jurassic Park”. In scientific research, this method – known as “resurrection ecology” – has also been used to breathe new life into the resting stages of other zooplankton. In the case of copepods (aquatic crustaceans), living creatures have been hatched from eggs more than 300 years old. Creatures dating from even earlier periods have not yet been restored to life. However, in contrast to palaeoecology, this technique can be used not only to analyse a creature’s DNA but also to compare genetic information directly with characteristics of the living organism – in particular, its adaptation to the environmental conditions of its former habitat.

Rapid adaptation due to hybridization. For a long time, it was believed that genetic variation – and therefore evolution as a whole – was based on mutations. However, mutations occur relatively rarely and in most cases their influence on selection is either neutral or even negative. In contrast, functional gene sequences which are recombined as a result of hybridization have already proved successful in nature [5]. One species can thus “acquire” particular advantages from another – a process which has long been exploited in animal and plant breeding.

Greater lead tolerance in the past. Under stable conditions, *D. galeata* and *D. longispina* occupy different habitats and are accordingly adapted to their respective niches: *D. longispina* colonizes large, oligotrophic lakes, and *D. galeata* smaller, eutrophic waters, which explains why the latter species is also more heat-tolerant. Water fleas hatched from the resting eggs of earlier years show adaptation to the conditions which originally prevailed. In Lake Constance, they indicate the different food quantities and qualities available during the eutrophication period: organisms whose parents lived in the lake at the time of maximum eutrophication thrived in the laboratory better than others when they received generous supplies of green algae with high phosphorus concentrations. *Daphnia* hatched from older sediment layers of Greifensee survived longer in high lead concentrations than those from more recent sediments. Evidently, they were better adapted to the conditions of that period, since lead concentrations declined sharply as the use of leaded petrol first decreased and was ultimately prohibited (in 2000).

The microevolutionary processes demonstrated by our research reflect the strong selection pressure exerted on the water flea populations by anthropogenic habitat changes [6]. However, our findings also underline the flexibility of the zooplanktonic organism *Daphnia*, which is a result of its capacity to survive unfavourable periods as a resting egg and also to acquire

characteristics from other species via hybridization. The water flea can thus adapt even to profound changes in its habitat. For this reason, it will remain an important model organism for the ecological and evolutionary sciences.

Preservation more important than restoration. Our results have clear implications for practical conservation and species protection: for example, from the point of view of population genetics, the restoration of earlier ecological conditions in a habitat is of limited value. It is apparent that the consequences of species invasions, interspecific hybridization and selection cannot be reversed. Priority should therefore be given to the protection of intact or near-natural habitats. At the same time, the question of what still counts as pristine – in view of the extensive environmental changes caused by humans – has been little researched to date. This makes it all the more important for researchers to establish what type of habitat protection promises the greatest long-term success. ○ ○ ○

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CO₂ fixation in Lake Brienz and Lake Lugano

Carbon dioxide (CO₂) is removed from the natural global cycle and sequestered in lake sediments in the form of organic carbon. But how is CO₂ fixation affected by nutrient concentrations and oxygen availability in lake water? To answer this question, Eawag explored the depths of two lakes, carrying out analyses at the molecular level.

Lakes generally act as carbon sinks: as plant biomass accumulates, CO₂ is removed from the atmosphere. Biomass is either produced in the lake itself – e.g. as phytoplankton, algae and reeds – or enters surface waters from the surrounding area. The resulting organic matter provides the basis for the lake food web. Standing in contrast to accumulation processes are degradation processes, in which part of the biomass is converted back to CO₂ by microorganisms as it passes through the water column. However, the part which is not broken down can be permanently sequestered in sediment.

By fixing CO₂ in this manner, lakes can counteract the greenhouse effect [1–3]. Accordingly, assessments of lakes' effectiveness as carbon sinks are important inputs for modelling the future impacts of climate change. We therefore wished to find out what internal parameters influence the process of CO₂ fixation in lakes. Specifically, we were interested in nutrient concentrations and the associated primary productivity (amount of biomass produced), as well as oxygen availability in lake water. In our research project, we compared two lakes of different trophic levels.

Organic matter production and degradation revealed by lipid biomarkers. The efficiency of sequestration of organic matter in sediment is described by the ratio of organic carbon available in the lake to carbon actually sequestered in sediment. It is thus partly influenced by the amount of biomass present: the higher the content of nutrients – especially phosphate and nitrate [4] – the greater the production of biomass in the lake. However, sequestration efficiency is also determined by the intensity of microbial degradation processes in the water column: if sufficient oxygen is available even in deeper layers, the organic matter may be almost completely mineralized to CO₂ in the water column, with only a small amount entering the sediment. We therefore selected two quite different lakes for our study: the oligotrophic Lake Brienz in the Bernese Oberland – characterized by relatively low levels of nutrients (phosphate <5 µg/l) and biomass and a high oxygen content – and the eutrophic Lake Lugano in Canton Ticino, with substantially higher concentrations of nutrients



Achim Bechtel, mineralogist, worked as a postdoc on an EU research fellowship in the Surface Waters department. Co-author: Carsten Schubert

(phosphate 50–60 µg/l) and biomass, and anoxic deep-water conditions (Fig. 1A).

The aim was to analyse the lipid composition of particulate organic matter collected from different water depths (10, 40, 70, 100, 150 and 200 or 250 m). Lipid biomarkers provide an indication of the sources of organic matter and thus the contributions of different organisms to the biomass [5–7]. More important for us, however, was the fact that we could use biomarkers to track degradation processes in the water column. The samples of suspended matter collected in the spring (June) and autumn

Eawag researcher Carsten Schubert prepares the mass spectrometer for measurement of samples, adding liquid nitrogen.



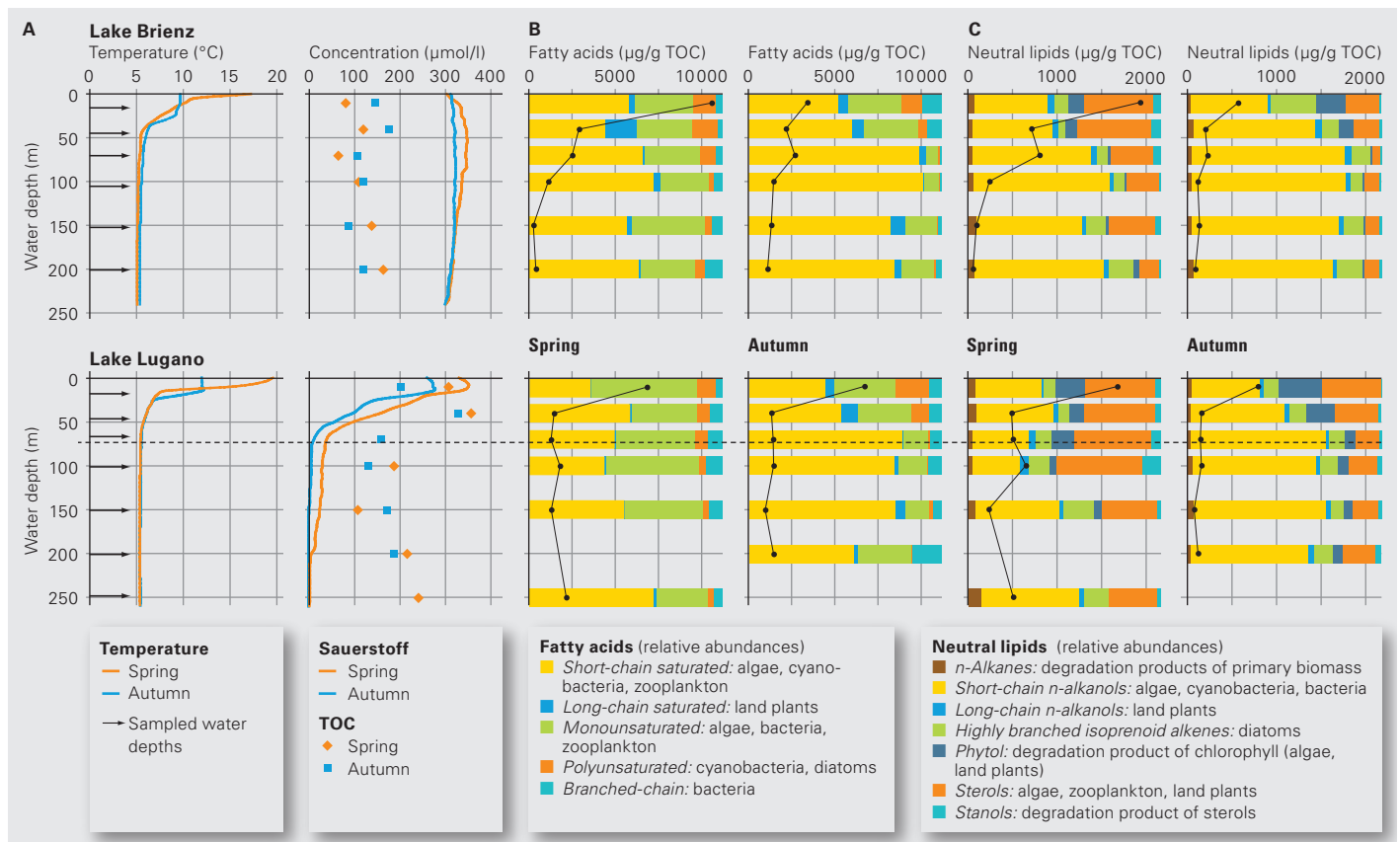


Fig. 1: Parameters studied at various depths in Lake Brienz and Lake Lugano (spring and autumn sampling campaigns).

A) Bioproductivity (expressed as total organic carbon concentration [TOC]) and oxygen content.
 B) Total fatty acid concentrations (curves) and relative abundances of fatty acid groups (bars).
 C) Total neutral lipid concentrations (curves) and relative abundances of neutral lipid groups (bars).
 The dashed line indicates the oxic-anoxic interface in the water column of Lake Lugano

(October/November) of 2007 were therefore separated into fatty acid and neutral lipid fractions, and the molecular composition was then analysed.

Detailed analysis of fatty acids. As a first step, we analysed in detail the fatty acid compositions and concentrations for both lakes. The following conclusions can be drawn from our data:

- ▶ Both lakes show roughly comparable fatty acid concentrations, if these are normalized to total organic carbon (TOC; cf. curves in Fig. 1B). However, the absolute fatty acid concentrations in micrograms per litre of water filtered are approx. 4 times higher in Lake Lugano. This clearly reflects the differences in primary productivity resulting from the different nutrient concentrations in the two lakes.
- ▶ In deeper water layers, fatty acid concentrations decline (curves in Fig. 1B). At the same time, there is an increase in the proportion of unsaturated as against saturated fatty acids (bars in Fig. 1B). The biomass available in the lake is thus reduced as water depth increases. However, fatty acid concentrations tend to rise again in the deep waters of Lake Lugano – here, degradation appears to proceed more slowly.

- ▶ In both lakes, the fatty acid fractions mainly consist of short-chain, saturated and monounsaturated substances, indicating the predominant contribution of phytoplankton to the biomass. For example, monounsaturated fatty acids with 16 carbon atoms are markers for diatoms. We detected a high relative abundance of these compounds in the euphotic zone of Lake Brienz in the spring and autumn. The euphotic zone is the well-illuminated upper layer of water, where photosynthesis can occur. Only a small proportion of the organic matter is attributable to land plants – identifiable by the long-chain fatty acids which are components of waxes (bars in Fig. 1B).
- ▶ Branched-chain fatty acids are biomarkers for bacterially derived biomass. Elevated relative abundances of these fatty acids were found in Lake Lugano at the interface between oxic and anoxic water at a depth of around 70 m (spring) and in deep water layers (autumn). The relatively high abundances of branched-chain fatty acids in the anoxic deep waters of Lake Lugano indicate the presence of bacteria which are active in the absence of oxygen.
- ▶ Polyunsaturated fatty acids indicate the occurrence of cyanobacteria (i. e. blue-green algae = bacteria capable of photosynthesis) and diatoms. In particular, polyunsaturated fatty acids with

18 carbon atoms are of cyanobacterial origin. These were found, for example, in the euphotic zone of Lake Lugano in the spring. By contrast, polyunsaturated fatty acids occurring in Lake Brienz and in the euphotic zone of Lake Lugano in the autumn derive mainly from diatoms.

► High contents of short-chain saturated fatty acids with 18 carbon atoms in both lakes suggest an increased contribution of zooplankton to the biomass in deeper parts of the water column at the time of sampling in the autumn (bars in Fig. 1B).

Valuable information provided by neutral lipids. Additional insights are also to be gained from the neutral lipid fractions, which include alcohols, alkanes and alkenes. Our findings were as follows:

► As with fatty acids, concentrations of neutral lipids decrease as water depth increases (curves in Fig. 1C), reflecting the degradation of biomass in the water column.

► The predominance of short-chain over long-chain *n*-alkanols (saturated hydrocarbons with one or more hydroxyl groups) confirms the finding – already obtained with reference to fatty acids – that the biomass present in the lake is mainly derived from phytoplankton, with only a small contribution from land plants (bars in Fig. 1C).

► In all the samples, we also detected alkanols of microbial origin (branched-chain *n*-alkanols with 15 or 17 carbon atoms).

► Phytol – a component of chlorophyll – serves as a marker for photosynthetically active organisms. It is therefore not surprising that it mainly occurs in the upper layers of both lakes.

► Sterols are constituents of plant cell membranes, with individual sterols being attributable to specific groups of organisms. Thus, sitosterol is considered to be a marker for land plants, while a particular sterol with 28 carbon atoms is typical of diatoms. Both of these sterols were detected in the samples collected in the spring from Lake Brienz and Lake Lugano. By contrast, the autumn samples contain much lower concentrations of plant sterols. Here, the predominant sterol is cholesterol, which suggests an increase in the relative contribution of zooplankton to the biomass, especially in deeper parts of the water column.

► In deeper water layers, the stanols/sterols ratio increases. This may be regarded as evidence of degradation of organic matter in the water column.

► Also noteworthy is the high relative abundance of highly branched isoprenoid alkenes – another characteristic marker for inputs from diatoms.

Organic matter dynamics and CO₂ fixation. In summary, what can be concluded from our findings? As expected, less organic matter is produced in the oligotrophic Lake Brienz than in the eutrophic Lake Lugano. At the same time, organic matter is more efficiently degraded in Lake Brienz than in Lake Lugano, so that overall more organic carbon is sequestered in the sediment of Lake Lugano. At first glance, therefore, Lake Lugano is the larger carbon sink. However, the other side of the coin shows Lake Lugano as an ecosystem which has undergone major changes since the 1970s. Until the late 1980s, nutrient levels rose continu-

ously as a result of human impacts. Since then, while increased efforts to protect the environment have achieved some initial success, there is still evidence today not only of unnaturally high biomass production but also of changes in the composition of phytoplankton and zooplankton. Our analysis of lipid composition, for example, demonstrates the predominance of cyanobacteria (which can adversely affect water quality) and green algae in Lake Lugano, while diatoms predominate in the oligotrophic Lake Brienz. As a result of the elevated nutrient concentrations, oxygen levels in Lake Lugano are only comparable to Lake Brienz in the uppermost water layers (Fig. 1A). From a depth of around 70 m, there is virtually no oxygen in Lake Lugano, which accounts for the less marked degradation of organic matter. At the same time, however, organic matter is transformed by microorganisms even under these anoxic conditions – producing not CO₂, but methane, which is about ~20 times more potent as a greenhouse gas. The significance of Lake Lugano as a larger carbon sink is thus substantially reduced. Overall, our study shows that nutrient and oxygen levels in water are crucial factors determining carbon turnover and hence also CO₂ fixation in lakes. ○ ○ ○

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Why Lake Lugano's waters remained unmixed for decades

In 2009, Eawag published a study on the mixing behaviour of Lake Lugano. In this interview, Rolf Kipfer, Head of the Water Resources and Drinking Water department and Titular Professor at the ETH Zurich, explains how eutrophication and climate change may affect water circulation in lakes.

Why did you decide to study Lake Lugano?

Well, Lake Lugano had not been completely mixed for around 40 years, and the deep waters had been anoxic for all that time.

How did you know that?

Temperature, oxygen levels and electrical conductivity at various water depths have always been measured sporadically by Canton Ticino, and in fact since 1991 these parameters have been recorded regularly – every two weeks. Also, Eawag had previously carried out sampling campaigns on Lake Lugano. We used this data to monitor water quality and oxygen concentrations in Lake Lugano and suddenly, for a short period in the winter of 2005, traces of oxygen were found in the bottom layer.

Does this mean that mixing had occurred?

Yes, but what happened in 2005 was a brief – though important – initial mixing event. It was only in the following winter that Lake Lugano was completely mixed over a period of two months.

Is it normal for an “overturn” to occur so rarely in Lake Lugano?

It's certainly not a lake which – like many other (shallow) lakes in these latitudes – is mixed twice a year, in the spring and autumn. That's because it's a narrow, deep lake with a low throughflow. But the fact that it took so long this time was partly due to eutrophication.

So a rise in nutrient inputs can also affect physical processes such as mixing?

That's right.

Could you explain how that happened?

Well, in the second half of the last century, Lake Lugano experienced huge changes in geochemical conditions as a result of elevated nutrient inputs. First, there was an increase in primary production which led to oxygen depletion in the deep waters. And under these anoxic conditions, ions were remobilized from sediments. So, from the bottom up, the lake became laden with dissolved ions, and the density and conductivity of the deep

waters increased. As salinity increased with depth, the lake was chemically stratified and complete mixing was no longer possible. That's a typical eutrophication problem.

And it couldn't be reversed even when water pollution was better controlled with the aid of wastewater treatment plants from the early 1970s onwards?

It could, to a certain extent, but only in the upper layers. Because the lake is so deep and the salinity gradient – the stratification – was so stable, no large-scale mixing was possible. That only happened during the two relatively cold winters of 2005 and 2006. And the aim of our study was to reconstruct precisely how those mixing events occurred.

“Eutrophication is one reason why it took so long for complete mixing to occur.”



To do so, you carried out a detailed analysis of the cantonal data going back from 2006 to 1991. What did that tell you?

Let's take the temperature data first. It showed us that, over the years, the deep water was gradually warmed up by heat from the underlying rock. And the water was also increasingly heated from above by a process known as turbulent transport.

That involves warmer water moving up or down?

No, at least not over any great distance. What happens is that, as a result of small-scale turbulence, heat is passed on vertically from one water parcel to another. The fundamental conditions required for large-scale vertical water transport, i.e. for complete mixing, only occur in winters where the surface and deep-water temperatures are identical – or if the surface water is actually colder than the deep water. In Lake Lugano, that was only the case again in the winter of 1999.

But why did it take another six years for complete mixing to occur?

It was because of the extremely stable chemical stratification. From the conductivity data, we could see that during the period between 1999 and 2005 surface water with low conductivity was slowly but surely mixed to greater depths and the density gradient was reduced. As a result, the chemical stratification was also erased from 2005 to 2006, and only then was the winter cooling strong enough to trigger the mixing process.

Is the deep water of Lake Lugano now enriched with oxygen?

Probably not, as the deep water was practically anoxic again by the end of 2006. Because of the prolonged anoxic period, there are just too many reducing substances remaining which rapidly consume any oxygen – even if supplies are constantly replenished by mixing processes.

You tried to quantify the renewal of deep water.

That's right. We calculated that in the winter of 2006 about half of the deep-water volume was exchanged.

And you did that by looking at conservative tracer data.

Yes, after we'd seen that, in the winter of 2005, Lake Lugano had been completely mixed again for the first time for many years, we collected samples from the lake in the spring of 2005 and 2006 and performed tracer analyses. We were also able to draw on a previous Eawag tracer campaign from 2001.

What exactly are conservative tracers?

These are substances which undergo physical mixing processes, but without being degraded or consumed like oxygen. So the tracers indicate how oxygen would behave if it was biochemically conservative. They allow you to calculate how much gas exchange has occurred and how much water has been renewed.

And these tracers occur naturally in lakes?

They are present in lakes, but not naturally. In some cases, they have been released into the environment as a result of human



"You can't judge the condition of a lake by the mixing behaviour alone."

activities and stem from technical applications, like the trace gas SF₆ (sulphur hexafluoride). This was designed to be chemically inert, as it was used in electrical systems to prevent flashovers. Or CFCs (chlorofluorocarbons), which were used in refrigeration systems.

So you're making a virtue of necessity.

Yes, I'm afraid so. Mostly, these gases are very well studied. We know how the atmospheric concentrations have changed over the years, and that can be traced in the water – because the water is coupled with the atmosphere via gas exchange. So it's possible to draw conclusions about when the individual layers of a lake were last in contact with the atmosphere.

The time that's elapsed since then is called the "water age".

That's right. But you still can't argue on the basis of the water age, even though that would be much more intuitive. Instead, you have to rely on the concentrations, because with those, in contrast to water age, the effects of mixing are linear. In other words, if I mix equal volumes of water containing different concentrations, I ob-



Christian Holzner collecting samples: the study on the mixing behaviour of Lake Lugano was part of his doctoral thesis.

tain a liquid with a mean concentration. But if I combine 5-year-old SF₆ water with 1-year-old SF₆ water, that certainly doesn't yield a 3-year-old mixture. So you have to be very careful when you talk about water age.

Now that concentrations have evened out in Lake Lugano, will mixing occur more frequently in the future?

Clearly, Lake Lugano is now functioning quite differently than it did over the past 30–40 years. Complete mixing has produced major changes in the ecological structure of the lake, and vertical water transport has become possible. Of course, I don't know what the mixing behaviour of Lake Lugano was like prior to eutrophication, but I suspect that mixing occurred sporadically, every few years. And I think a similar rhythm will now be re-established.

You've developed a predictive model, haven't you?

Yes, we've used the model to study mixing behaviour under various climate scenarios. We'll only find out whether the predictions are correct a few decades from now.

And what effects is climate change expected to have?

Some scientists assume that the mixing of our lakes will decline in the future as a result of a warming climate. The same argument is always used: the surface water warms up, the density gradient is increased as a result, and mixing of the lake is reduced. That's true but it only applies to the transitional period from the present to a future state.

And when we've arrived in the future?

Then the temperature difference in the lake between summer and winter is likely to be as great as it is today, albeit under a generally warmer regime. Because the deep water will also be warmer – with a temperature of, say, 7°C rather than around 4°C in our latitudes today – I think it's quite conceivable that lakes in future will be better mixed than they are today. The reason is that a small change in temperature at 7°C increases density much more than at 4°C, and the water will immediately sink.

Are you saying that warming of the climate will have positive effects on the mixing behaviour of lakes?

No, that's not an argument you can use. The real question is whether it's natural for complete mixing to occur more frequently. But you can't judge the condition of a lake by the mixing behaviour alone. Rather, it depends on the totality of processes occurring in the lake.

What is the future direction of your research on Lake Lugano? Are any more tracer campaigns planned?

Not at the moment, but I think it would be a good time to start planning because long-term time series are very useful. As the behaviour of Lake Lugano is now quite different than in recent decades, it would make sense to monitor how it develops.

One final question: What is Christian Holzner, the lead author of the study, doing now?

After completing his PhD thesis at Eawag, he went to the Federal Office of Energy. There, the question is how Switzerland can meet its energy requirements in the future. Christian is analysing the technical, economic and political factors which influence the security of Switzerland's domestic and foreign energy supplies. ○ ○ ○

Rolf Kipfer was interviewed by Martina Bauchrowitz

Holzner C.P., Aeschbach-Hertig W., Simona M., Veronesi M., Imboden D.M., Kipfer R. (2009) Exceptional mixing events in meromictic Lake Lugano (Switzerland/Italy), studied using environmental tracers. *Limnology & Oceanography* 54, 1113–1124.

Decentralized systems – future model for wastewater treatment?

In Switzerland, decentralized systems currently play an insignificant role, being used only in remote areas beyond the reach of public sewers. But under what conditions could they be a viable option in this country and other parts of the developed world? And how do researchers and practitioners view the prospects for these systems in developing countries?

What would we do if we had to build Switzerland's wastewater disposal system again, starting from scratch? This question was discussed by experts from the spheres of research and practice at a workshop organized by Eawag over 10 years ago. Max Maurer, head of the Urban Water Management department, recalls: "At that time, we all agreed we would opt for the same type of centralized system. But that was mainly because it was the only system we were familiar with, not because it was the best possible solution." Since then, quite a lot has happened in this field, and Eawag is increasingly also exploring alternative – especially decentralized – systems.

These activities are being pursued at different levels, ranging from conceptual and economic studies, through the develop-

ment and piloting of robust new methods, to the practical implementation of decentralized systems, particularly (at present) in developing countries. A wide variety of aspects are being studied in detail: methods for urine source separation and treatment, nutrient recovery and fertilizer production, and wastewater recycling (small-scale household treatment systems), as well as new models for cost-benefit analysis, taking account of planning uncertainties such as population development, water availability and climate change. But what concrete progress has been made by researchers? What do practitioners think of decentralized approaches? And what added value do decentralized systems actually offer over centralized systems? These questions have been widely discussed among water professionals.

Abwasserverband Altenrhein



Are there any alternatives to centralized wastewater treatment plants?

Water availability. Over the last decade, significant technological advances have been made in the area of decentralized wastewater treatment systems, which in the past tended to be dismissed as inefficient. These developments have largely been driven by concerns about water availability, as it is difficult to operate a sewer network with a centralized treatment plant if water is scarce. This is mainly due to the fact that relatively large amounts of water are needed to transport solids (faeces, toilet paper). For this reason, says Tove Larsen (head of the “Future Concepts” working group in the Urban Water Management department), new concepts in wastewater treatment from a global perspective are increasingly shaped by the issue of water scarcity. Other key factors, she adds, are climate change and the rapid growth of the world’s population. This is demonstrated by the concrete problems already facing Australia, the US, Canada and Asia (see the world map on p. 20).

Water reuse. As in Switzerland, centralized wastewater treatment plants (WWTPs) play a key role in the west of the US, for example. However, as Richard Luthy (Professor of Civil and Environmental Engineering at Stanford University in California) explains, there is one major difference: in Switzerland only about 5% of available water reserves are used, whereas the Western US essentially uses all the available resources: “So for us, water reuse is very important.” The problem is that centralized WWTPs are usually not only far away, but also in low-lying areas, because sewage is drained by gravity. This means that if water is to be reused, it has to be pumped uphill again – an energy-intensive process. Luthy – who spent a few weeks on sabbatical at Eawag at the end of 2009 – is convinced that this problem could be addressed via decentralized wastewater treatment systems. He will be pursuing this approach in a major research project which he intends to launch in California.

Professor Peter Wilderer (TU Munich Emeritus of Excellence), a winner of the prestigious Stockholm Water Prize, also considers the repeated use of water obtained from natural sources to be the major advantage offered by decentralized systems. But in his view, it will be difficult to gain acceptance for these systems in developing countries unless Germany, Switzerland and other industrialized countries lead the way. “So first of all,” he concludes, “there need to have more pilot projects in this part of the world.”

Compact treatment systems. “I’m still dreaming of a robust system that you could put in the basement, like a washing machine, in which wastewater streams would be effectively treated and nutrient cycles would be closed as far as possible,” says Martin Würsten, President of the Swiss Water Association (VSA) and Director of the Canton Solothurn Environment Office. All in all, he adds, although considerable progress has already been made, systems of this kind are not yet mature and still at the pilot stage.

Nutrient recycling. “If we consistently segregate wastewater streams and treat nutrient-rich urine, for example, separately, then we can manage nitrogen and phosphorus quite specifically,” says Tove Larsen, who led the cross-cutting Eawag project on urine source separation (Novaquatis), which was completed in 2007. Nitrogen causes many problems, Larsen explains, particularly through the eutrophication of inland and coastal waters. But one should also remember its effects in the greenhouse gas nitrous oxide (N_2O , laughing gas), which arises, for example, as a by-product of denitrification – the conversion of nitrate (NO_3^-) to molecular nitrogen (N_2). It is therefore important to develop sustainable decentralized systems for nitrogen treatment which do not cause N_2O emissions. This would be possible either if gas scrubbing was incorporated in the method, or if the nitrogen,

Showering with wastewater

In a new pilot study – a joint project initiated by Empa, also involving Zurich University of the Arts (ZHdK) and the University of Applied Sciences Northwestern Switzerland (FHNW) – Eawag is tackling the question of water recycling in a practical way. A living and working module (“Self”) has been designed which is self-sufficient in energy and water consumption. In this prototype, Eawag has incorporated both rainwater filtration and wastewater recycling: grey water treated in a membrane bioreactor can be reused for showering, dish-washing and toilet-flushing. Although at present black water is removed from the internal water cycle, separate drainage and treatment of urine and faeces is conceivable at a later stage of the project.



Futuristic: the “Self” living module is independent of external water and energy supplies.

Testing a small-scale treatment system

Over the past 3 years, Eawag process engineers have gained initial experience with a small-scale treatment system (membrane bioreactor) installed in a Swiss single-family home. Both Christian Abegglen, who oversaw the project as part of his doctoral thesis, and the members of the household are satisfied with the results overall. Abegglen concludes that, while there have been some glitches, a decentralized system of this kind can now provide treatment performance comparable to a centralized wastewater treatment plant. This is true despite the fact that such systems have to meet tougher requirements than large-scale plants. These include greater peak loads (early-morning personal hygiene) and longer under-capacity periods (holidays), as well as higher concentrations of contaminants (e.g. medicines) and toxic substances (e.g. cleaning agents).

According to Abegglen, further research and innovation is required with regard to phosphorus elimination and energy consumption, which remains significantly higher with a small-scale system than with a large-scale plant. Both of these could be optimized with the aid of electrochemical processes. Kai Udert, a researcher in the Process Engineering department, is currently working on improving the energy balance. To this end, experiments are being conducted in which urinary ammonium is being split into nitrogen and hydrogen, with energy to be recovered from the latter in a fuel cell.

Patrick Lüthy, Imagopress



Not to be underestimated: a pilot treatment system in a Swiss household.

rather than being denitrified, was supplied to the fertilizer industry in a concentrated form – an option currently being studied by Kai Udert, a process engineer at Eawag. The process of nitrification and concentration produces a hygienic fertilizer in the form of ammonium nitrate (ammonium saltpetre). Udert is convinced: “With this process, which could probably be rapidly implemented in practice, numerous problems could be solved at the same time.”

In the case of phosphorus, eutrophication is not the only issue: this is a finite resource, and supplies are likely to be exhausted in around a century. So there is all the more reason to recover this nutrient from urine. The method of choice, which was thoroughly investigated by Eawag in the Novaquatis project, is struvite precipitation. The addition of magnesium to urine leads to the precipitation of struvite (magnesium ammonium phosphate), which can be used directly as a fertilizer.

In principle, then, nutrient recycling methods are ready for application. Moreover, according to Eawag’s calculations, better protection of the environment and natural resources could be achieved with these methods – at around the same cost – than with a centralized WWTP where nutrients are eliminated but not recovered. This would depend, however, on the technologies in question going into mass production.

Existing infrastructure. Controlling inputs of nitrogen and phosphorus to surface waters was one of the main motives for the expansion of WWTPs in Switzerland and many other industrialized

countries in the 1970s. For Peter Hunziker, a member of the VSA Executive Committee and director of an engineering company active in the water management sector, one thing is clear: “Decentralized systems must not be established at the expense of existing centralized infrastructure, thereby driving up costs.” For the higher the design capacity of a process step at a centralized WWTP, the lower the specific costs per inhabitant. In addition, the existing infrastructure still has free capacity to offer, which should be utilized, and even if new challenges arise, e.g. as a result of

Pure sustainability: the urine-based fertilizer struvite.



micropollutants, additional treatment steps can be incorporated inexpensively at centralized plants. However, Hunziker accepts, like many colleagues, that situations may arise in which decentralized systems could increasingly be adopted in Switzerland – for instance, if a planned housing development is not yet connected to the sewer system or when a WWTP reaches the end of its service life. Then, Hunziker says, the costs associated with the various scenarios would need to be precisely calculated.

Planning uncertainties. Calculations of this kind are subject to a whole series of planning uncertainties. One of these is population development. For certain peripheral regions whose future prospects are unclear, decentralized systems could represent an attractive solution. They would prevent investments in infrastructure which subsequently prove unwarranted if inhabitants leave the area as a result of declining economic fortunes. This issue has arisen, for example, in some parts of Germany where the population has decreased by 40–50%. “A centralized system with a large-scale sewer network then becomes costly, without any increase in the value of the service,” says Max Maurer, who is investigating in detail how planning uncertainties should be taken into account.

Maurer is seeking to define criteria which would make it possible to say when centralized or decentralized systems are to be preferred. At the same time, his basic assumption is that decentralized systems essentially offer greater flexibility and the ability to respond more rapidly to the needs of an uncertain future. In other words, he believes the choice of a decentralized system is likely to be more appropriate in the presence of major uncertain-

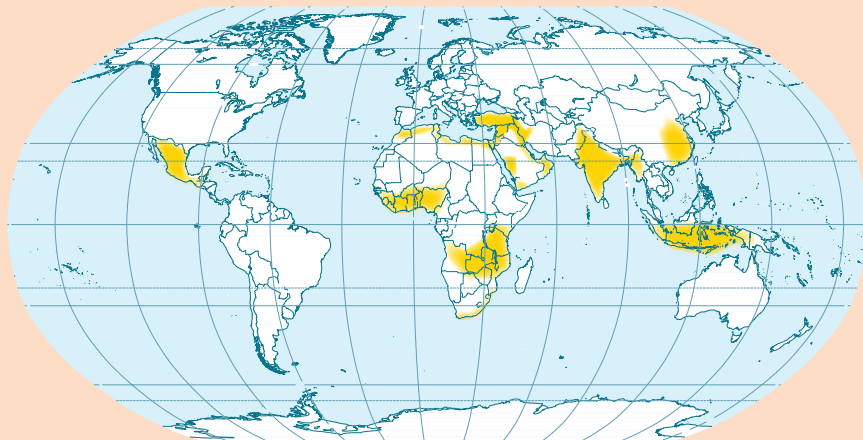
ties. The advantage is that excess capacity is avoided, and further investments can be made as required. In contrast, a centralized system may initially involve lower investments than a decentralized solution, but over a planning horizon of 30–40 years, it may generate higher per capita costs overall. Maurer’s goal is therefore to define comparable costing criteria which take into account both the uncertainty of future developments and the flexibility of the system concerned. As he emphasizes, “Flexibility must be worth something, with a value that can be expressed in Swiss francs.” As well as population trends and economic developments, planning uncertainties also cover aspects such as climate change and changes in the demands placed on wastewater treatment. The aim is ultimately to also apply the comparison of decentralized versus centralized systems to developing countries. In general, these countries are particularly susceptible to planning uncertainties.

Advantages for developing countries. The fact that a decentralized system can be expanded in stages – and financing can be spread out accordingly – is also a significant advantage for developing countries. In addition, the presence of multiple decentralized systems can reduce the risks associated with malfunctions. Christian Zurbrügg, head of the department Water and Sanitation in Developing Countries (Sandec), points out: “In developing countries, systems can stop operating altogether if a spare part is unavailable.” If a centralized plant is affected, this can have a major impact.

But as well as these two advantages, Zurbrügg cites flexibility as the most important feature of decentralized systems: “If you’re in a region, for example, where water is to be reused for irrigation

Decentralized systems: a new industrial sector?

In the On-Site water Treatment technology (OST) project, which involves the Innovation Research in Utility Sectors (Cirus) and Urban Water Management departments, Eawag is carrying out a global analysis of decentralized system concepts. The fundamental questions addressed include: What problems can be tackled more effectively with decentralized rather than centralized solutions? What types of on-site technology are currently available? And how can these technologies be further developed? In addition, the project aims to identify viable paths towards a paradigm shift, as well as markets and players with the potential to create a new industrial sector (e.g. in China, with the participation of German and Swiss companies). Based on this interdisciplinary project, Eawag is also seeking to define future research activities in the field of decentralized systems and to develop an appropriate research strategy.



Decentralized systems would be an option worth considering for regions where the sanitation infrastructure is inadequate and which are also struggling with rapid urbanization and water scarcity (yellow shading).

in agriculture, then the system can be optimized so that pathogens are eliminated but the nutrient content is maintained. If, however, the local surface waters are already eutrophicated, then the nutrients will also need to be removed. And if it's an industrial region with heavily polluted wastewater, then the system can be specifically designed to deal with that." This explains why much of Eawag's work in developing countries involves optimizing processes and systems, and adapting them to different requirements.

Struvite production in Nepal

The site of one Eawag project is Siddhipur, a community on the outskirts of Kathmandu (Nepal) where urine-separating toilets already exist. The inhabitants of this peri-urban area are open to the use of urine as a fertilizer, providing ideal conditions for field-testing a simple decentralized system for struvite precipitation. Experience has demonstrated the effectiveness of the method and the transport system – special bicycles are used to collect the liquid waste from urine-diverting toilets. Eawag is now also studying what can be done with the (still nutrient-rich) liquid left over after struvite precipitation.



Jumbo radishes: Jiban Maharjan, a farmer from Siddhipur, is proud of his urine-fertilized produce.

Master plans. Another important aspect of Eawag's activities in developing countries is providing advice for authorities and helping them to develop sanitation systems. Although in many cases individual decentralized solutions have already been adopted at the household or neighbourhood level, authorities have difficulty in preparing and coordinating master plans. For example, Eawag is currently collaborating with the authorities in Ouagadougou, the capital of Burkina Faso. Here, it has become clear that the large number of existing septic tanks cannot possibly be connected to the centralized system. The question now arising is how they can still be integrated into an overall system.

"Safe disposal of human excreta in urban areas of developing countries is one of the weak points," admits Jon Lane, Executive Director of the Water Supply & Sanitation Collaborative Council, a UN-mandated organization based in Geneva. Lane sees a need

for research particularly with regard to community toilet facilities in slums – in terms of both basic approach and technology. Good-quality, objective research results are required as an aid to decision-making for politicians. In his view, Eawag is one of the few independent research institutions worldwide that can provide the necessary scientific expertise.

Paradigm shift. According to figures recently published by the Federal Office for the Environment (FOEN), the replacement value of Switzerland's water supply and wastewater disposal infrastructure amounts to CHF 220 billion, or almost CHF 30000 per inhabitant. The conveyance system alone accounts for 90 % of this total. Therefore, for Eawag researcher Max Maurer, the first major paradigm shift would be towards solutions providing an alternative to the existing conveyance system. This would then entail a second key step, namely the consistent separation of wastewater streams (urine, faeces, grey water). Tove Larsen comments: "Today, unlike just a few years ago, I'd be surprised if source separation and decentralized solutions did not at least begin to become established in Switzerland and other industrialized countries." "Even so," Max Maurer adds, "the aim of current research is not to push decentralized systems as the only true solution. Instead, we want to find out in which situations a centralized or decentralized approach is optimal and sustainable." And there is general agreement among researchers and practitioners that systemic changes in urban water management should be effected over a period of decades, so that existing capital investments are safeguarded.



Martina Bauchrowitz

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Saskia Zimmermann, environmental scientist and doctoral student in the Water Resources and Drinking Water department.

Co-authors: Yunho Lee, Urs von Gunten

Removing micropollutants and phosphate with ferrate

Alongside ozone, ferrate has emerged as a new option for enhanced wastewater treatment at municipal treatment plants. Both substances oxidize anthropogenic organic micropollutants. Ferrate offers the additional advantage of removing phosphate – by precipitation – at the same time. But what doses of ferrate are required? And is the use of ferrate cost-effective? We report here on initial experience from the Eawag laboratory.

As treated wastewater still contains traces of pharmaceuticals, personal care products and household chemicals, it contributes substantially to water pollution. Since the possibilities for reducing consumption of these products are limited, attention is currently focused on how micropollutants can be eliminated from treated effluents [1]. One strategy involves the addition of a third treatment step at conventional wastewater treatment plants (WWTPs). In this additional step, micropollutants could be removed by oxidation processes. Thanks to the experience accumulated at Eawag over several years in the field of ozonation, it was possible for a large-scale pilot project to be carried out at the Regensdorf WWTP, where ozone was used as an oxidant [2].

A substance representing a potential alternative to ozone is ferrate $[\text{Fe}(\text{VI})\text{O}_4]^{2-}$ – an oxidant and disinfectant containing iron in the +VI oxidation state. Ferrate is particularly attractive because – unlike ozone – it serves not only as an oxidant but also as a precipitant: first, in the form of Fe(VI), it acts as an oxidant, being reduced to Fe(III) in the process. Fe(III), which has already been used for many years in wastewater treatment to precipitate phosphate, is thus a useful, non-toxic decomposition product of ferrate. Another advantage of ferrate is that – as far as is known – no unwanted by-products arise during the oxidation process.

Research on the possible application of ferrate in wastewater treatment began only recently. Eawag has now investigated the

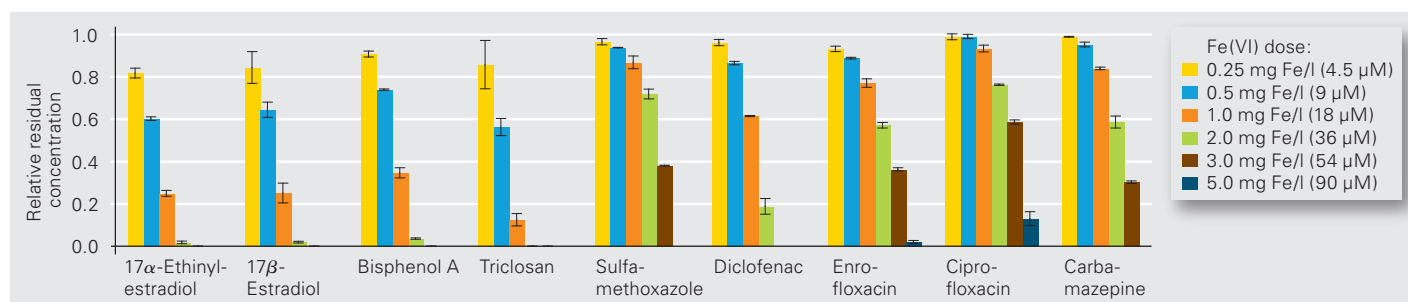
potential of ferrate to oxidize a wide variety of micropollutants in wastewater – also in comparison with ozone – and sought to establish what doses of ferrate are required to remove phosphate from wastewater by precipitation.

Removal of reactive micropollutants from wastewater. The aim of our study was to analyse directly in wastewater the oxidation of as wide a range of micropollutants as possible, with different properties. In a similar manner to ozone, ferrate also attacks electron-rich moieties in the molecules of micropollutants. These include, in particular:

- ▶ phenols, contained for example in the endocrine disruptors 17α -ethinylestradiol, 17β -estradiol, bisphenol A and the biocide triclosan;
- ▶ amines, found for example in the antibiotics sulfamethoxazole, enrofloxacin, ciprofloxacin and in the analgesic and anti-inflammatory agent diclofenac;
- ▶ alkenes (compounds containing double bonds), found for example in the antiepileptic drug carbamazepine.

As Fig. 1 shows, a ferrate dose of around 2 mg Fe/I is sufficient for complete oxidation of substances with phenolic moieties. However, amines and alkenes are only fully oxidized by a ferrate dose of around 5 mg Fe/I; overall, they are thus less reactive than phenols [3, 4]. In addition, it is known from the literature

Fig. 1: Relative residual concentration of a wide range of micropollutants containing electron-rich moieties in treated wastewater from the Dübendorf WWTP as a function of the ferrate dose.



that ferrate also reacts with other electron-rich moieties such as sulfides and thiols, but this was not investigated in our project.

In the absence of such electron-rich moieties, however, substantially higher doses of ferrate are needed: for example, 15 mg Fe/l was required to achieve 40% oxidation of the lipid-lowering agent bezafibrate and the contrast medium iopromide, and only 10% oxidation was achieved with the same dose in the case of the analgesic and anti-inflammatory drug ibuprofen [3] (Fig. 2).

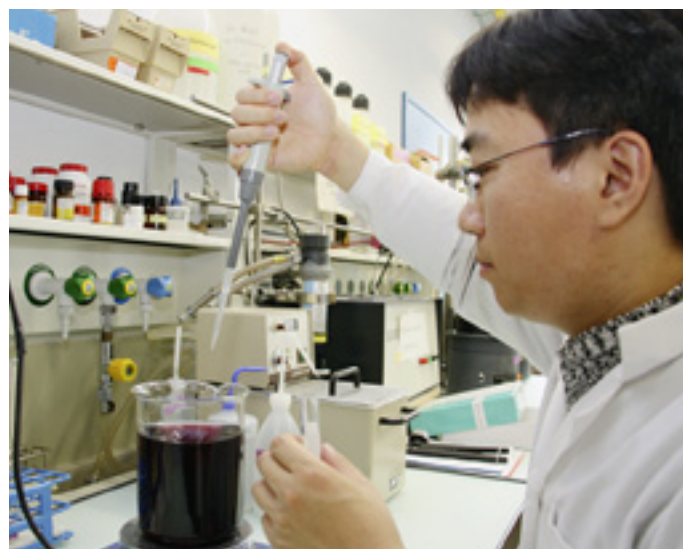
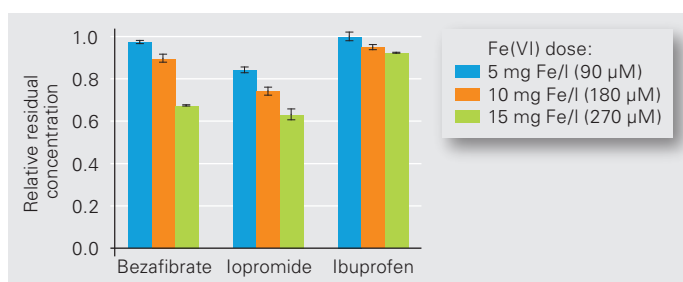
Less efficient than ozone for oxidation of micropollutants.

In recent years, various studies have confirmed that ozone is an effective agent for the oxidation of micropollutants in wastewater. For this reason, it is particularly interesting to compare the two substances as oxidants for wastewater treatment. Figure 3 provides an overview of the oxidation of selected micropollutants containing electron-rich moieties as a function of the dose of ferrate or ozone. Only one of the compounds studied, 17 α -ethinylestradiol, was oxidized roughly equally efficiently by both oxidants. In this case, a dose of 20 μ M (~1 mg/l) ferrate or ozone was sufficient to ensure complete oxidation. All other micropollutants analysed were oxidized less efficiently by ferrate than by ozone. To achieve complete oxidation, about three times more ferrate than ozone was required – e.g. 53 μ M (= 3 mg/l) ferrate versus 20 μ M (= 1 mg/l) ozone for the oxidation of diclofenac [3].

Lower reactivity offset by higher stability. In subsequent studies of the kinetics of oxidation reactions, the rate constants (k values) for the reactions of the micropollutants analysed were found to be three to four orders of magnitude lower for ferrate than for ozone [3]. In fact, on the basis of the preceding experiments, we would have expected the values here to be considerably higher. So how is it to be explained that ferrate is, nonetheless, not much less efficient than ozone in the oxidation of micropollutants?

To understand this, the stability of each of the oxidants in wastewater needs to be taken into account. Ferrate is consumed less rapidly by other components of wastewater and by self-decay than is the case for ozone. For example, it took more than 30 minutes for a ferrate dose of 40–45 μ M to be completely consumed in a secondary effluent from the Regensdorf WWTP – at pH 8 and with a DOC (dissolved organic carbon) concentration of 5 mg/l.

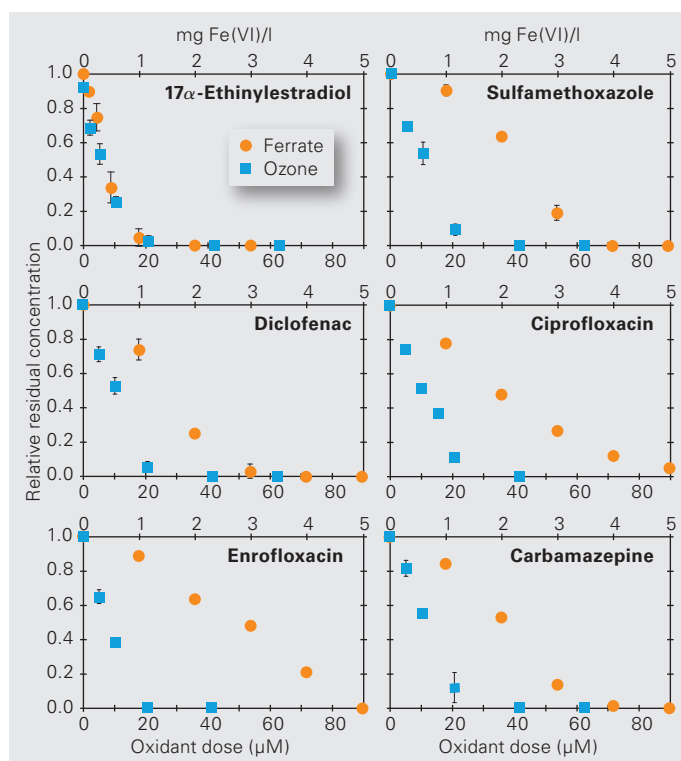
Fig. 2: Relative residual concentration of selected micropollutants lacking electron-rich moieties in treated wastewater from the Dübendorf WWTP as a function of the ferrate dose.



Postdoctoral fellow Yunho Lee measures the Fe(VI) concentration of a test solution.

By contrast, the same dose of ozone was consumed in only 5 minutes. Ferrate is thus present over a longer period and attains a higher exposure value (concentration \times time), thereby largely compensating for its lower reactivity with micropollutants [3]. Our tests also indicated that ferrate should be added to the secondary

Fig. 3: Relative residual concentration of selected micropollutants in treated wastewater from the Dübendorf WWTP after oxidation by ferrate (orange circles) or ozone (blue squares) as a function of the oxidant dose.



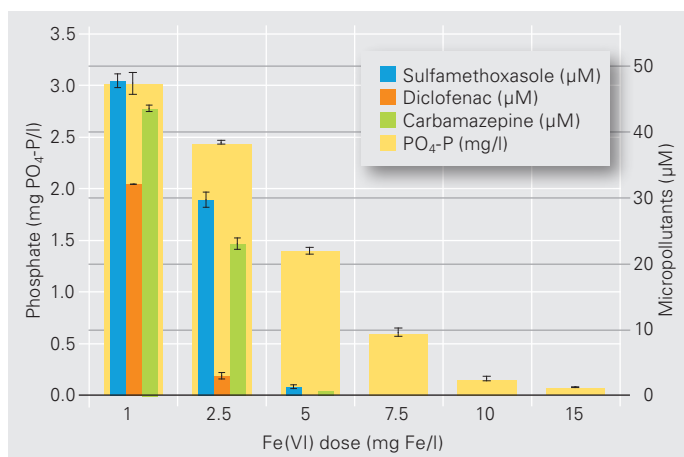


Fig. 4: Oxidation of selected micropollutants and simultaneous phosphate precipitation in treated wastewater from the Dübendorf WWTP as a function of the ferrate dose.

effluent, rather than to wastewater entering the biological treatment step, since here it would be too rapidly consumed as a result of the activated sludge and high DOC concentrations.

Phosphate in wastewater precipitated by the decomposition product Fe(III).

In the course of the oxidation of micropollutants and other wastewater constituents, and as a result of self-decay, ferrate [Fe(VI)] is reduced to Fe(III). Fe(III), in turn, has long been used in wastewater treatment for chemical precipitation of phosphate. We wished to determine how much ferrate needs to be added in order to allow phosphate to be removed from wastewater at the same time. In our laboratory tests, we experimented with a phosphate content of 3.5 mg PO₄-P/l, which represents a realistically high concentration of phosphate in a WWTP influent.

In fact, a ferrate dose of 7.5 mg Fe/l is sufficient to reduce the phosphate concentration to below 0.8 mg PO₄-P/l – in accordance with the regulations on wastewater discharges to receiving waters in Switzerland (Fig. 4). This corresponds to approx. 80 % precipitation. The three reactive micropollutants sulfamethoxazole, diclofenac and carbamazepine were almost completely oxidized by a ferrate dose of 5 mg Fe/l. Thus, the ferrate doses required for complete oxidation of reactive micropollutants are lower than those required for phosphate precipitation [3].

Ferrate: a worthwhile option. Overall, our studies showed that ferrate is well suited for the oxidation of micropollutants in wastewater. Although it is somewhat less efficient than ozone in oxidizing micropollutants, it offers the additional advantage of eliminating phosphate. The ferrate doses required for phosphate precipitation are higher than those needed for complete oxidation of reactive micropollutants. It could therefore make sense, in terms of the operating costs of a WWTP, to use ferrate to ensure complete oxidation of reactive micropollutants, while achieving a degree of phosphate precipitation in the process. The remaining phosphate could then be precipitated using Fe(III) or Fe(II), in line with existing practice.

Questions now arise regarding the production and storage of ferrate. As the substance decomposes in contact with water, it cannot be transported or stored in an aqueous solution. In powdered form, ferrate has to be stored in airtight containers to protect it from humidity. Ideally, therefore, it would need to be continuously produced *in situ* (e.g. with the aid of an electrochemical cell) and then added to wastewater. However, preparation of a mixture using powdered ferrate at the WWTP is also conceivable. Treatment plants already performing chemical phosphate precipitation with solutions of Fe(II) and Fe(III) could then also use existing pumps and mixing systems for the application of ferrate.

At present, the use of ferrate is more expensive than the application of ozone. While ozone production costs amount to CHF 1–2 per kilogram, ferrate costs around CHF 18 per kilogram (comparison based on the molecular weight of ozone and ferrate in K₂FeO₄). However, experience has shown that manufacturing costs for chemicals fall dramatically as soon as large-scale production begins. A comprehensive analysis of the costs for ferrate would also have to take into account both the savings arising from simultaneous phosphate removal and the lower investment costs required for the necessary infrastructure, compared with ozone (use of existing feed systems for phosphate precipitation with iron). ○ ○ ○

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Assessment of chemicals: fish cells as an alternative to whole fish



Katrin Tanneberger, food chemist and postdoc in the Environmental Toxicology department. Co-authors: Christina Otto, Kristin Schirmer

Every year, hundreds of thousands of fish die in toxicology tests worldwide. Among the possible alternatives being explored by Eawag, fish cells are particularly promising. However, the toxic effects of chemicals are generally less marked in fish cells than in whole fish. Here, we explain the reasons for this – and discuss how fish cell-based assays can be optimized.

It has been estimated that, over the next 10 years, 54 million vertebrates will be required for toxicological testing of chemicals to comply with EU legislation on the Registration, Evaluation and Authorisation of Chemical substances (REACH) [1]. Since June 2007, under these new regulations, all substances placed on the European market in quantities of more than one tonne per year have been required to be tested for risks to human health and the environment. In the environmental risk assessment of chemicals, the group of animals used most frequently is fish, with toxicity generally being determined on the basis of mortality (OECD Test Guideline 203, acute toxicity to fish). The drawbacks of this method are not only the need for fish to be killed, but also the fact that such tests do not provide evidence of the modes of action of the substances studied, or detect chronic effects. In a project known

as “CELLsens” (Development of a strategy to predict acute fish lethality using fish cell lines and fish embryos), Eawag is therefore exploring possible alternatives to the fish toxicity test. One promising option – alongside computer-based prediction models and zebrafish embryo tests – is the use of fish cells (see Box).

The problem: fish cells are less sensitive than whole fish in toxicity tests. Despite the considerable potential of this approach, the use of fish cells is not yet included in any legally prescribed tests. Numerous studies have shown that there is a good correlation between cell toxicity and acute fish toxicity, specifically with regard to relative sensitivity, i.e. the ranking of effects from non-toxic to highly toxic. However, when the correspondence is considered in absolute terms, fish cells prove to

Development of a cell line

Cell lines are derived from organs and tissues of various fish species. First, primary cell cultures are prepared. If these primary cultures can be successfully reproduced, a cell line is obtained. Compared with mammalian cell lines (e.g. those derived from mice or humans), fish cell lines offer a significant advantage: in most cases, these cell lines are permanent or “immortalized”, i.e. they can divide and reproduce indefinitely. In fish cells, the process of immortalization occurs spontaneously, although the causes of this phenomenon have yet to be fully elucidated.

Animals are only required for the generation of a cell line; ideally, this will involve a single creature. Once the cell line has been established, no further animals are needed.

Cultivation of fish cells under sterile conditions.



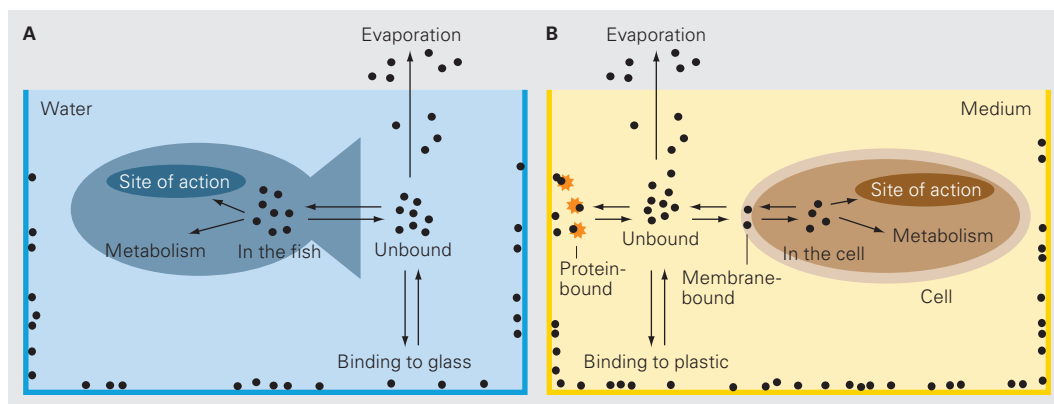


Fig. 1: In the fish test (A) and in the cell-based assay (B), the distribution of the chemical depends on a number of factors, all of which – in competition with each other – influence the fraction that can penetrate the animal or cell and produce toxic effects. In the present case, sorption of the chemical to proteins can be neglected, since our exposure medium (L15/ex) does not contain any proteins.

be about ten times less sensitive than whole fish [2]. This means that, in cell tests, higher concentrations of chemicals are needed to produce the same toxic effect. The discrepancy between whole fish and fish cell tests is attributed in particular to the lower bioavailability of substances – i.e. the fraction freely available to cells [2]. For although the distribution paths are essentially the same in fish and in cells (Fig. 1), conventional, microplate-type cell culture systems promote losses, e.g. through sorption of substances to the walls of sample wells. Thus, the surface available for sorption in relation to the volume of the test unit is considerably greater in a microplate than in an aquarium: for example, a 10 l aquarium measuring 20x20x25 cm has a surface-to-volume ratio of 280 cm²/l, whereas a unit in a 24-well microplate 1.6 cm in diameter and 1.7 cm deep has a surface-to-volume ratio of approx. 10,000 cm²/l.

We are currently seeking ways of optimizing the test system and have focused on, for example, the physico-chemical properties of substances, the exposure medium and the dosing method (Fig. 1). In the CEIISens project, we are working with a total of 60 organic compounds – selected as representative of many others – which differ in their modes of toxic action, physico-chemical properties (e.g. volatility and lipophilicity) and degree of toxicity (low to high) [3].

Extent of sorption and evaporation attributable to physico-chemical properties of substances. Processes such as sorption and evaporation are dependent on the physico-chemical properties of substances. The more lipophilic the test compound is, the more it will bind both to the walls of the test wells – especially when these are made of plastic – and to proteins present in the culture medium. The volatility of a substance can be described by the Henry's law constant. The greater the value of this constant, the higher the volatility of the compound. Both of these factors – lipophilicity and volatility – thus reduce the availability of chemicals, thereby leading to lower sensitivity of the test system.

To date, these properties of substances have rarely been taken into account in *in vitro* studies. However, this can readily be done by determining the free concentration of the substance in the medium. Using a mathematical model, we demonstrated that

the absolute sensitivity of the cell test can be markedly increased by adjusting the toxicity values for the lipophilicity and volatility of test substances [4]. This adjustment yields absolute sensitivity values that are comparable for cells and fish.

Less is more: our experience with a minimal medium. Many components of culture media, such as serum, vitamins or antioxidants, have a protective effect on cells. Unlike human cell lines, the fish cell lines used at Eawag are capable of surviving in a minimal medium (L15/ex) developed by our group, which contains only physiological salts, galactose and sodium pyruvate [5]. This medium – now available commercially – is based on the commonly used culture medium L-15. L15/ex has already been shown to have a sensitizing effect on fish cells [6].

Direct versus indirect dosing. In a further study, we showed that the toxicity of chemicals also depends on the dosing method, particularly when dimethyl sulfoxide (DMSO) is used as a solvent [7]. Test compounds can be introduced either directly or indirectly. With direct dosing, a highly concentrated stock solution is pipetted straight into the exposure medium onto the cells. With indirect dosing, in contrast, a chemical solution previously diluted with L15/ex is added to the medium (Fig. 2A). The two dosing methods would not actually have been expected to affect the toxicity of chemicals. But, as can be seen from the example of 1,2-dichlorobenzene (DCB) in Fig. 2B, the opposite is true. It is striking that the dose-response curve is shifted considerably to the left after direct dosing, as compared with indirect dosing. With direct dosing, the EC₅₀ (i.e. the concentration causing death in 50 % of the cells) is 5 times lower. In seeking to explain this effect, we focused on the interior of the cell.

What can we learn from internal concentrations? DMSO has a permeabilizing action – i.e. it renders cell membranes more permeable, thereby making it easier for test substances to penetrate the cell. In the case of indirect dosing, a homogeneous mixture of L15/ex, DMSO and DCB is applied to the cells; with direct dosing, however, a film consisting of DMSO and DCB forms directly on the cells. Is it possible that the formation of this film promotes the

uptake of the test compound into the cells? To test this hypothesis, we measured internal concentrations of DCB immediately after dosing; after all, it is not the external but the internal concentrations of a substance in a cell that are responsible for its toxicity. After direct dosing, the quantity of DCB entering cells was indeed found to be significantly larger than after indirect dosing.

In ecotoxicology, the concept of lethal body burden is used to describe the whole-body concentration of a chemical required to produce a lethal effect. This concentration is expressed in millimoles per kilogram wet weight. McCarty et al. [8] calculated that the lethal body burden of chemicals with a narcotic mode of action such as DCB is between 2 and 8 mmol/kg in fish. We extended this concept to fish cells. For the RTgill-W1 cells used in our study, we calculated a lethal body burden of 6 mmol DCB per kilogram with direct dosing, and about 4 mmol/kg with indirect dosing. Thus, when internal lethal concentrations are taken into account, the differences in sensitivity between direct and indirect dosing are eliminated, and the toxic effects measured are independent of the dosing procedure.

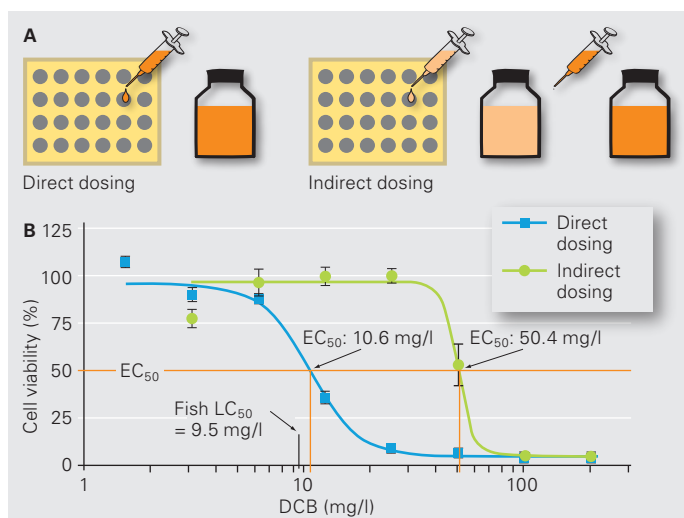
Nonetheless, even though with direct dosing it is possible to obtain comparable sensitivity between whole fish and fish cells without determining the unbound and internal concentrations, we recommend that chemicals should be applied indirectly to cells. Indirect dosing reflects the natural exposure conditions of fish in water and is thus the more realistic scenario. In addition, only this method can prevent individual cells from being exposed to much higher concentrations of chemicals than others. However, to give an accurate account of the sensitivity of fish cells, toxicity data should always be based on the actual internal concentration.

Fish cells: an alternative to whole fish in toxicity tests. With optimized test conditions, fish cells thus represent a promising test system for the assessment of chemical risks and in particular

the implementation of the REACH regulations. A further aspect of the CEIISens project is the selection of new endpoints for toxicity tests, since lethality is only one possible – and not even a particularly sensitive – endpoint; moreover, it does not permit any conclusions concerning the mode of toxic action of chemicals. For this reason, we are looking (among other things) for suitable marker genes which, on the basis of activity patterns, provide an indication of why substances are toxic to cells. The new fish cell-based toxicity test will consequently help not only to reduce the number of animal experiments but also to analyse in detail the modes of action and chronic effects of chemicals. ○○○

The CEIISens project, launched in December 2006, is funded by the European Chemical Industry Council (CEFIC) and the UK Department for Environment, Food and Rural Affairs (Defra).

Fig. 2: (A) Schematic illustration of direct and indirect dosing. (B) The location of the dose-response curves and thus also the EC₅₀ values for 1,2-dichlorobenzene DCB depend on the dosing procedure.



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From source to sink: flame retardants

Since the mid-1970s, global production of flame retardants has risen from zero to several hundred thousand tonnes per year. Although these substances reduce the flammability of many different products containing plastics or synthetic materials (e. g. computers, cars and textiles), they also raise environmental concerns. We have studied the spread of flame retardants all the way from production to disposal.

One television a day catches fire in Switzerland, and this figure would probably be far higher if television sets were not treated with flame retardants. But while the benefits of these substances are recognized, some members of this group of chemicals are known to pose risks to human health and the environment. For example, brominated flame retardants (see Box) – used in electrical and electronic equipment – are persistent and bioaccumulative and may also have endocrine-disrupting effects [1]. These substances have been detected in surface waters, the atmosphere and remote areas (including polar regions), and they have also been found in animals [2, 3].

But what quantities of these substances are released from everyday products into the various environmental compartments?

Did you know that you sit on brominated flame retardants every day?



Ruth Scheidegger, scientist in the “Material Fluxes in the Anthroposphere” section of the System Analysis, Integrated Assessment and Modelling department. Co-authors: Hans-Peter Bader, Leo Morf (formerly GEO Partner AG, now Canton Zurich Office for Waste, Water, Energy and Air/AWEL)

Answers to this question are required in order to plan measures whereby diffuse emissions of brominated flame retardants can be limited. Using a method known as dynamic substance flow analysis, we have therefore studied the pathways taken by brominated flame retardants from source to sink.

Considering the complete history of flame retardants. The distribution pathways of brominated flame retardants have already been studied with the aid of traditional substance flow analysis both in Denmark [4] and in Switzerland (at the request of the Federal Office for the Environment/FOEN) [5]. However, this method merely provides a picture of the situation at a given point in time; in other words, it cannot take into account the long residence times of flame retardants in certain applications or, consequently, future substance flows. Consider, for example, the life cycle of a sofa: here, brominated flame retardants are either directly incorporated into or applied to the surface of the materials used in the production process. The finished piece of furniture, including the flame retardants, then makes its way via the retail

What are flame retardants?

Flame retardants are substances used to reduce or inhibit the flammability of combustible materials.

The roughly 200 widely used flame retardants can be divided into four groups according to their chemical composition: inorganic (e. g. $\text{Al}(\text{OH})_3$), halogenated (e. g. polybrominated diphenyl ether), organophosphate (e. g. trichloroethyl phosphate) and nitrogen-based flame retardants (e. g. melamine).

Worldwide, several hundred thousand tonnes of brominated flame retardants are used per year, particularly in plastic casings of electrical and electronic devices, circuit boards, polystyrene foams and textiles.

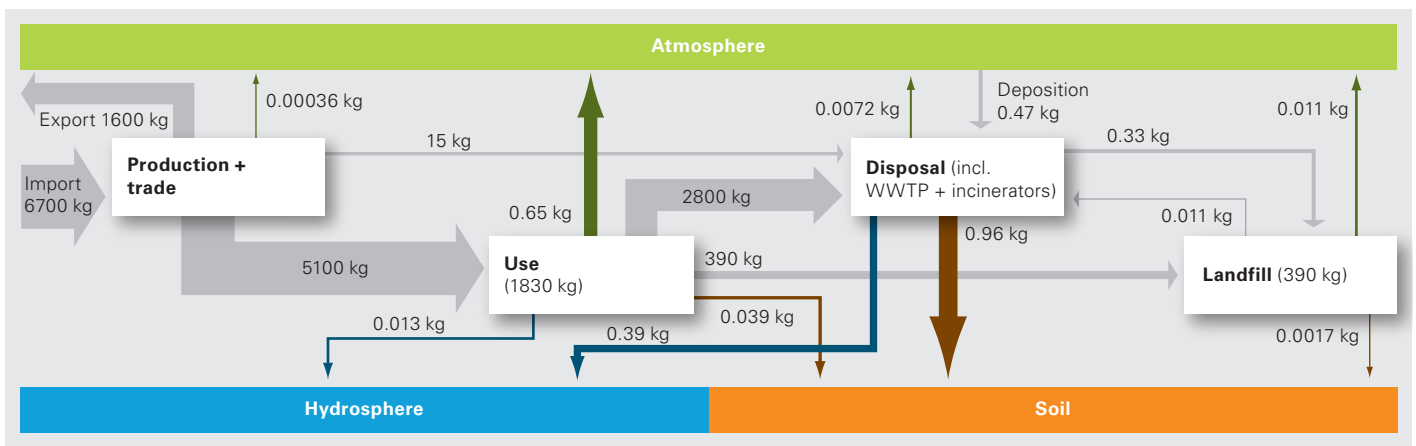


Fig. 1: Flows and changes in stocks of hexabromocyclododecane (HBCD) in textiles in 2000. Arrows for all flows under 1 kg (and for all flows over 1 kg) are drawn in proportion to each other. WWTP = wastewater treatment plants.

trade to our living room, where it is used for a number of years or decades before being disposed of or recycled. One of the key requirements, therefore, is to assess how long, on average, goods remain in “intermediate storage” – in this case, how long the sofa remains in the living room. In order to take the complete history of products into account in the analysis, we developed a dynamic substance flow analysis model in collaboration with the engineering consultancy GEO Partner AG Resource Management [6,7]. This provides a full description of the pathways of flame retardants throughout their life cycle, from production through use to disposal (Fig. 1). The model also takes into consideration the proportions of products containing flame retardants which are recycled or incinerated and which ultimately end up in landfills or at wastewater treatment plants. The model takes into account the fact that, in the past, some of the products disposed of were directly landfilled. At the same time, it calculates the flame retardant emissions entering the various environmental compartments – the atmosphere (gaseous and particulate emissions), hydrosphere (in solute form, as a result of processes such as cleaning – e.g. when sofa covers are washed) and soil (particulate emissions). An additional strength of the model is that it also estimates uncertainties for individual substance flows and stocks.

	2000	Scenario: “Business as usual”		Scenario: Substance ban	
		2010	2020	2010	2020
Year	2000	2010	2020	2010	2020
Stocks in use (kg)	40200	58000	63000	24000	240
Stocks in landfill (kg)	4200	5100	5700	5100	5400
Cumulative input to hydrosphere (kg)	6.6	10.4	14.7	9.7	10.6
Cumulative input to atmosphere (kg)	6.9	15.0	24.7	13	14
Cumulative input to soil (kg)	19.0	23.0	24.3	22.6	23

Stocks of HBCD in use or in landfill and cumulative inputs to environmental compartments.

What data are included in the model? The data to be fed into the model are often difficult to obtain. For example, measurements of flame retardant concentrations in products, environmental compartments or waste are rarely if ever available. Our only option, therefore, was to investigate in detail data on the use of products containing flame retardants (in particular, consumption and application patterns) and the flame retardant content of these products. In addition, we estimated emission factors for the production, use and end-of-life phases. The uncertainty associated with these values is partly due to the fact that emission flows from the production and end-of-life phases are strongly dependent on the specific technologies used, and production and waste management processes are being continuously refined. Other important sources of data were the two substance flow analyses mentioned above [4, 5], recent literature on flame retardants, and discussions with experts.

Pathways for flame retardants in 2000. Our model was used to study three groups of flame retardants – decabromodiphenyl ether, pentabromodiphenyl ether and hexabromocyclododecane – with each substance class being analysed in four different application areas (electrical and electronic equipment, transport, textiles and construction). The results described below relate to hexabromocyclododecane (HBCD) and its use in furniture and furnishing textiles. In Fig. 1, an overview of flows and changes in stocks is given for 2000.

In total, 6700 kg of HBCD was imported into Switzerland. Of this, around 75% remained in Switzerland, while the rest was re-exported in products. That year, emissions of HBCD to environmental compartments from production, use and disposal/landfill amounted to 2 kg. The snapshot provided by Fig. 1 illustrates the order of magnitude and relative proportions of the various flows but gives no indication of how they change as a function of time.

Substance ban: potential to reduce HBCD inputs to the hydrosphere by around 75%. A deeper understanding can only be gained by considering longer-term trends (Fig. 2). Since the

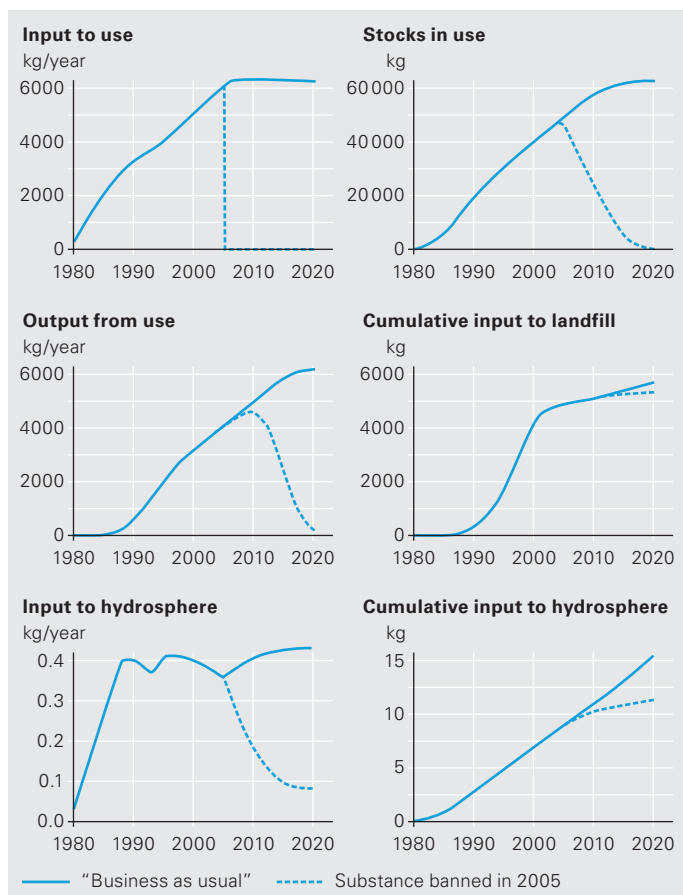


Fig. 2: Input (kg/year) and stocks or cumulative input (kg) of HBCD for the use phase, the landfill process and the hydrosphere compartment. Solid lines: projected trends for HBCD until 2020. Dashed lines: results of modelling based on the assumption that the substance was banned from 2005 onwards.

early 1980s, despite the relatively short service life of 10 years for these products, considerable stocks have accumulated during the use phase (e. g. in buildings) and in landfills. Cumulative inputs to environmental compartments are also growing steadily (see Table). According to the simulations, after a period of 40 years (1980–2020) in Switzerland, approx. 3 % of the HBCD used will have accumulated in landfills and 0.01 % in the hydrosphere.

Now imagine a scenario under which the use of HBCD is banned from 2005 onwards (dashed lines in Fig. 2). Under these conditions, input to the use phase would immediately return to zero. However, even 5–10 years after the introduction of the substance ban, HBCD would still enter the end-of-life phase, since products containing this substance would only be disposed of at the end of their service life. Emissions from production would also be immediately stopped as a result of the ban. In contrast, emissions from the use and disposal phases would show a time delay. In 2020, input to the hydrosphere would be reduced by 75 %. The remaining flows are due to atmospheric deposition of particulate HBCD to soil and leachates from landfills. The curves for the cumulative inputs to landfills and the hydrosphere show only a gradual decline.

HBCD: a substance class of very high concern. Finally, we return to the quantities of HBCD that are expected to accumulate in the hydrosphere from 1980 to 2020. Using our model, we calculated a value of 0.01 % of the total volume of HBCD processed; in other words, over this 40-year period, some 15 kg of HBCD accumulates in Swiss waters. At first glance, this figure may seem low. So can we assume that it raises no environmental concerns? The answer is an emphatic “no”. HBCD is classified as a persistent, bioaccumulative and toxic (PBT) substance by the European Chemicals Agency (ECHA), which is responsible for coordinating the implementation of the new EU chemicals legislation (the REACH Regulation). Indeed, HBCD is highly toxic to aquatic organisms and – on account of its persistence – the substance is known to have the potential to produce adverse impacts on the aquatic environment in the long term. For this reason, HBCD has been included since October 2008 on the list of substances of very high concern which are to be accorded priority in the REACH authorization procedure. However, even if the use of HBCD is soon regulated, we will not be rid of the substance for some time to come. This was demonstrated by our dynamic simulation, which posited a complete ban on the use of the substance from 2005 onwards: although emissions from production decline immediately and those from use and disposal after a certain time lag, any HBCD which has been deposited in sediments and soils remains there indefinitely. ○ ○ ○

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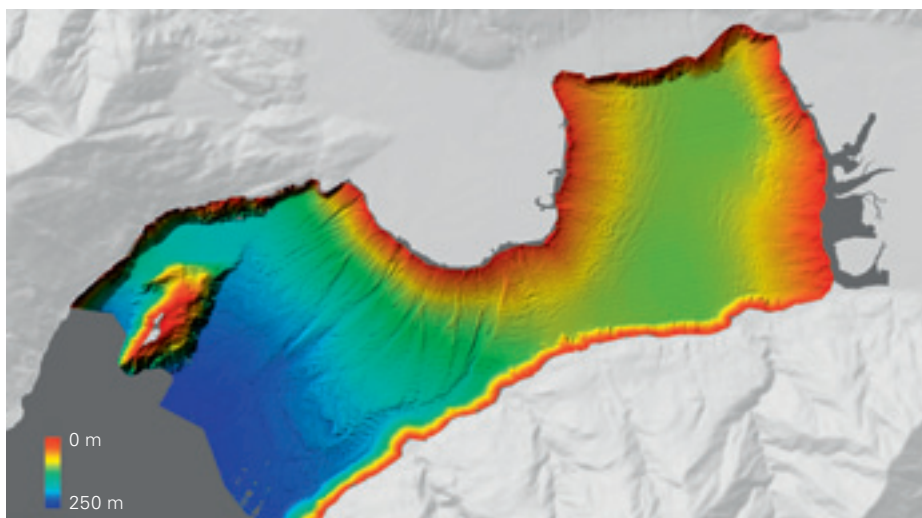
Secrets of the lake floor

After a successful pilot project on Lake Lucerne, Eawag has now started surveying the floor of the Swiss part of Lake Maggiore. Using a sophisticated sonar system, images can now be produced with an unprecedented level of detail. But the computer-generated colour images also pave the way for new research projects.

On a 2-week excursion in May 2009, a team of Eawag scientists aboard the research vessel *Thalassa* criss-crossed the Swiss part of Lake Maggiore, using special sonar equipment to scan the lake floor. This method has been employed for some time by coastal states to produce bathymetric charts of the seabed, but in Switzerland it has only been used in a pilot project on Lakes Lucerne and Geneva. Using modern sonar equipment, it is possible to determine a large number of depth points with each measurement. This data can be processed to produce three-dimensional images of the lake floor with centimetre-scale accuracy. The images now available for Lake Maggiore reveal, for example, underwater cables or – as in the delta of the Verzasca river off Tenero – small craters from which methane is released.

Fascinating insights. Researchers can use these precise records to trace the historical development of the lake. It is striking that while no lake floor channel can now be seen on the slopes of the Maggia delta (where the Maggia now flows into the lake), such channels are visible in the vicinity of former river mouths near Ascona. This allows conclusions to be drawn concerning the frequency and composition of sediment deposits from the Maggia

The bathymetric survey of Lake Maggiore is part of a pilot project involving Eawag and the University of Geneva. It was made possible with technical support from the Geological Survey of Norway and from the University of Ghent in Belgium. Financial support was originally provided by swisstopo (Federal Office of Topography), the Federal Office for the Environment, and the Federal Department of Defence, Civil Protection and Sport.



The floor of the upper part of Lake Maggiore. The Maggia delta can be seen in the middle, with the Isole di Brissago (including the base of the islands) on the left.

river. It is also notable that, unlike the Maggia, the Ticino and Verzasca rivers do not form fan-shaped deltas; instead, their deposits extend westward into the lake along an almost straight line.

Two lakes 1000 years from now? Particularly evident from the new charts is the fact that, sooner or later, the Maggia delta will cut off the uppermost part of the lake. The toe of the delta, which has advanced as far as the foot of the Gambarogno, is already higher than the floor of the eastern part of the lake. It is, however, difficult to say how long it will be before the lake off San Nazzaro is replaced by a river: "That certainly won't happen in the next 500 years," says project leader Flavio Anselmetti, a limnogeologist at Eawag.

New questions. The new images are useful not only in answering questions about the lake's history, but also in making predictions. They also raise new re-

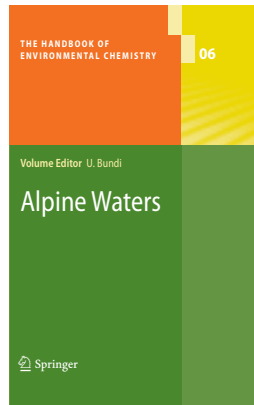
search questions: where deposits lie on steep slopes, could underwater landslides be triggered by a future earthquake, producing a tsunami-like wave? As well as providing a precise topographical picture, do the sonar echoes also indicate the type of sediments found in the lake? In addition, the charts can be used to monitor sediment deposition in lakes, since alterations in the flow regime of streams associated with climate change will also lead to changes in sediment transport and deposits. Initially, the Eawag scientists intend to investigate individual structures even more closely. They are focusing, for example, on the small, round depressions observed in the northern part of the Ticino/Verzasca delta. These pockmarks are a sign of gas seepage in this area. Anselmetti comments: "I don't think the methane gas can be usefully exploited, but the seeps do indicate where the slope could become unstable."



Andri Bryner

Alpine waters

January saw the publication of "Alpine Waters" in the "Handbook of Environmental Chemistry" series. As editors and authors, numerous Eawag scientists have made substantial contributions to this volume. "Alpine Waters" portrays the highly diverse attributes of mountain waters, demonstrates their paramount importance for ecological and social development in mountain regions and indicates both necessary management actions and future challenges regarding sustainable water management. Also considered are downriver reaches and their surrounding lowlands, and, therefore, the relationship between mountain and lowland water issues. The book is addressed to scientists, engineers and graduate students in the fields of environmental sciences, risk assessment and risk controlling, toxicology and ecology, as well as for decision-makers in government, industry and regulatory bodies. ○ ○ ○



Toxic arsenic removed from fields by monsoon floodwaters

As a result of irrigation with arsenic-rich groundwater, this toxic substance can accumulate in paddy soils and – at high concentrations – may ultimately find its way into rice plants. In a study published in *Nature Geoscience*, researchers from Eawag and the ETH Zurich collaborating with scientists from Bangladesh have shown that a certain amount of arsenic is released from soils into floodwaters during the monsoon season. In Bangladesh, irrigation

A villager in his boat crossing paddy fields in the Munshiganj district of Bangladesh. During the monsoon season, many paddies are submerged to a depth of several metres for up to 4 months.



of paddy fields with arsenic-rich water during the dry season adds an estimated 1360 tonnes of arsenic to arable soils per year. Experts are concerned about the possible long-term accumulation of arsenic in paddy soils. Although soil arsenic concentrations are known to decrease in flooded fields over the monsoon season, it has not been clear to date where the arsenic ends up. With analyses of soil porewater and overlying floodwater during the monsoon season in 2006 and 2007, Eawag was able to demonstrate the pathway for arsenic removal. It was shown that arsenic is predominantly mobilized into the soil solution in the uppermost 10 cm of soil, where the greatest accumulation occurs during irrigation; it then enters the overlying floodwater by diffusion and is transported to rivers by the receding floodwaters. Thus, it is estimated that 51–250 mg/m² arsenic is washed out of paddy soils into floodwater and ultimately into the ocean. Each year, 13–62 % of the arsenic added to soils through irrigation is released again via this process. www.eawag.ch/monsoon

New member of Directorate: Jukka Jokela



With the appointment of Jukka Jokela on 1 January 2010, the Eawag Directorate is once again complete. Jokela served as Head of the Aquatic Ecology department at Eawag from 2005 to 2009 and is Professor of Aquatic Ecology at the ETH Zurich. By appointing Jukka Jokela as a member of the Directorate, the ETH Board has underlined its intention to strengthen the interdisciplinary field of ecology and evolution as a focus of aquatic research at Eawag. ○ ○ ○

Measuring rainfall with mobile phone antennas

As rain interferes with radio signals, Eawag researchers have been able to measure rainfall using data supplied by the mobile telecommunications company Orange. The new method offers greater spatial resolution than traditional point measurements provided by rain gauges. In the future, this could be combined with intelligent control systems for sewer networks so as to reduce water pollution in urban areas. Especially in built-up areas, sewer systems are frequently overwhelmed by unexpected rainfall: stormwater is mixed with sewage in pipes, the volume of water exceeds the capacity of retention basins, and the wastewater overflows into local surface waters. Across the year as a whole, the input of harmful substances is relatively low, but short-term peak pollutant levels may be harmful to algae or fish. In addition, the problem will be exacerbated as a result of the increase in heavy rainfall events associated with warming of the climate in Central Europe. Eawag is therefore developing a simulation model that uses data from a mobile phone network to reconstruct rainfall events. This should help to control sewer systems in such a way as to prevent overflows of wastewater. www.eawag.ch/measuringrainfall

In Brief

Eawag Info Day on 22 June 2010

Aquatic biodiversity: a forgotten asset?

The UN has declared 2010 to be the International Year of Biodiversity, and Eawag will be supporting the efforts in this area. At this year's Info Day, to be



held on 22 June, Eawag scientists will present the latest research findings on the subject of aquatic biodiversity. While lakes and rivers only cover 0.3% of the Earth's surface, they are home to 7% of all species – and 40% of all known fish species worldwide. Freshwater bodies thus make a vital contribution to biodiversity. However, this diversity is under threat and measures to preserve it are

urgently required. Species management is often complicated by deficient data, and Eawag is seeking to address this problem through its research and consulting activities. Key topics to be discussed at Info Day include fish biodiversity, genetic diversity and species protection, invasive species, the impacts of climate change, and biodiversity in wastewater treatment www.eawag.ch/infoday

Watt d'Or energy award for Eawag

Energy savings can be achieved through sustainable management of water supplies: this has been demonstrated by the commune of Gordola in Canton Ticino, the winner of the Swiss Federal Office of Energy's prestigious Watt d'Or award in the "Society" category for 2010. Among those who contributed to this success is Eawag, which was involved in a number of research and consulting projects supporting the commune's efforts to implement a modern, sustainable water supply system. Bruno Storni, the member of the Gordola local authority responsible for water supplies, explains: "We could have engaged private consultants to plan certain parts of the system, as we do today with some success. But without Eawag's expertise, the innovative approach, considering both the consumer's and the supplier's perspective, would not have been adopted."



The construction site of the new reservoir, where a drinking water power plant is also being installed.

www.eawag.ch/energyprize

Agenda

Courses

9/10 March, Eawag Kastanienbaum
Electrofishing for trainers (in German)

4/5 May, EPF Lausanne
Introduction to ecotoxicology (in French)

18–20 May, Eawag Kastanienbaum
Fish in Swiss waters (in German)

8/9 June, Eawag Dübendorf
Metals and synthetic metal nanoparticles in the aquatic environment (in German)

15/16 June, Eawag Dübendorf
Environmental chemical analysis: challenges, concepts and methods (in German)

21–25 June, Eawag Dübendorf
Summer School Environmental Systems Analysis

Guided tour

9 March, 17:00, Eawag Dübendorf
Public guided tour of Forum Chriesbach

Conferences

13–18 June, ETH Zürich
GQ10 Groundwater Quality 2010

22 June, ETH Zürich
Eawag Info Day: Aquatic biodiversity – a forgotten asset? (in German)

Groundwater conference GQ 10



GROUNDWATER QUALITY 2010

From 13 to 18 June 2010, an international conference on groundwater quality management is organized by Eawag at the ETH Zurich. It will focus on the management and protection of this vital resource under today's rapidly changing environmental conditions. The conference aims to promote exchanges among researchers, water suppliers, industry and regulators. Supporting the event alongside Eawag are three international bodies – the International Association of Hydrological Sciences, the International Commission on Ground Water and the International Association of Hydrogeologists. www.eawag.ch/gq10