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Eawag News

Anthropogenic micropollutants in water: impacts – risks – measures

Editorial

Rik Eggen, molecular biologist, Deputy Director of Eawag.

Chemicals are ubiquitous

More than 47 million substances – natural and synthetic, organic and inorganic – are currently listed in the American Chemical Society's Chemical Abstracts Service (CAS) Registry. To appreciate the significance of this vast total, one needs to be aware that over the past 7 years more than 11,000 substances have been added to the list every day. In 2002, when Eawag last devoted its Info Day to the issue of micropollutants, the CAS Registry only contained around 18 million substances. Equally striking is the increase in the global production of chemicals from 1 million tonnes per year in 1930 to over 300 million tonnes today. The total of 140,000 chemical products registered for sale in Switzerland since 1969 seems almost harmless by comparison.

Chemicals are thus an integral part of our daily lives. They are used, for example, as industrial chemicals, as pesticides and biocides, as human and veterinary medicines, in cleaning and personal care products, and as flame retardants in furniture and computers. Among the most recent developments are nanoparticles, which are already to be found in over 800 products – a rapidly growing market. Despite the differences in their properties, many of these chemical substances have one thing in common: sooner or later, they end up in surface waters.

While research has previously tended to focus on the effects of individual substances under controlled laboratory conditions, we are now aware that the situation in natural waters is much more complex. These new challenges are being actively addressed by Eawag researchers. A few examples:

► In many cases, concentrations of contaminants in surface waters fluctuate sharply; here, Eawag is developing powerful models designed to provide realistic toxicity predictions without the need for additional experiments.

► Micropollutants generally occur as an unknown mixture with long-term effects, which are not only difficult to detect but subject to additional stress factors such as ultraviolet radiation, temperature and pathogens. To assess the risks of multiple stressors, Eawag is testing a method which allows altered protein expression patterns to be identified in organisms.

► The effects of nanoparticles are largely unknown; initial studies by Eawag have now shown how they enter and how they can affect the environment.

However, as well as conducting research, Eawag is committed to translating new findings into practice. In partnership with authorities and industry, it is developing approaches and technologies that can be used to prevent or reduce releases and impacts of micropollutants. The establishment of the Centre for Applied Ecotoxicology, with its headquarters at Eawag, marks another step in the direction of combining research with the concrete requirements of practitioners.

Fortunately, only a fraction of the 47 million substances listed in the CAS registry are actually used, and there remains an enormous potential for new substances – by which I mean not only additional pollutants, but also more readily degradable substances lacking toxic side effects.

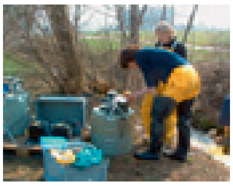
Cover photo: Eawag researcher Ilona Szivak of the Environmental Toxicology department at the experimental channels which are used to study the effects of risk factors such as contaminants and ultraviolet radiation on algal biofilms. (Photo: Ruedi Keller, Zurich)

Content

In focus: Anthropogenic micropollutants

4 **New challenges in the assessment of chemicals**
Chemicals – in textiles, detergents, medicines, sunscreens, canned products and insect sprays – are part and parcel of our daily lives. But while they may be indispensable, the widespread use of these substances calls for constant, critical evaluation.

8 **Dynamics of biocide and pesticide input**



Biocides and pesticides are used to control harmful organisms in agriculture and in urban areas. How do the substances find their way into natural waters? And is agriculture really the main source of water pollution?

12 **Effects of fluctuating contaminant concentrations**

Is it true that "the dose makes the poison"? And how long does it take for exposed organisms to recover? To answer these questions, Eawag is developing toxicokinetic/toxicodynamic models.

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15 **Transformation products – relevant risk factors?**
Chemical substances in the environment are often transformed into products which are more stable and more readily water-soluble than the parent compound. What risks do these transformation products pose?

19 **Interaction of multiple stressors**
Aquatic organisms are exposed to a mixture of chemicals and are also affected by other stressors such as temperature, ultraviolet radiation, parasites and pathogens.

22 **Effects of engineered nanoparticles**

As nanoparticles are already widely used, it was only too likely that they would end up in the environment and produce toxic effects. This has now been demonstrated for the first time by Eawag studies.

25 **Eliminating micropollutants: wastewater treatment methods**
In many cases, micropollutants are only partly eliminated at wastewater treatment plants. How can the plants be upgraded to improve elimination performance? A task for modern process engineering.

28 **Eliminating micropollutants: efficiency assessment**

The elimination of micropollutants at wastewater treatment plants requires additional treatment steps – but what chemical and biological indicators are suitable for assessing their effectiveness?

31 **Evaluation of surface waters in Switzerland and Europe**
Micropollutants pose growing challenges for water protection both nationally and internationally. As part of the FOEN's "MicroPoll Strategy" project, an evaluation concept is currently being elaborated.

Miscellaneous

In focus:
Anthropogenic micropollutants

Kristin Schirmer,
biologist and head of the
Environmental Toxicology
department.

New challenges in the assessment of chemicals

Chemicals – in textiles, detergents, medicines, sunscreens, canned products and insect sprays – are an integral, often indispensable, part of our daily lives. Even so, the widespread use of these substances calls for constant, critical evaluation.

Thousands of chemicals play an important role in our daily activities (Fig. 1). They allow new technologies to be developed and help us to maintain our health and improve our quality of life. As a result of widespread use, these substances also enter the environment, although in many cases this is unintentional, certain agents, such as pesticides, are deliberately released into the environment. A significant pathway for the input and spread of chemicals is water – for example, when substances are washed out by rainwater or transported by wastewater (see the article by Irene Wittmer on p. 8). Many everyday and industrial chemicals have already been detected in surface waters, in groundwater and in some cases also in drinking water [1].

Water thus bears the imprint of human activities. However, many substances are only to be found at trace levels, e.g. 1 g in a volume of 100 million water pails, which is equivalent to approx. 1 ng per litre. On account of the low concentrations, these substances are known as micropollutants – as opposed to macropollutants, which occur in concentrations several orders of magnitude higher. Macropollutants are, however, much less numerous, and their effects on the environment have been comparatively well studied [2]. A case in point is phosphate: increased input of this nutrient in surface waters promotes the growth of primary producers such as cyanobacteria and green algae. This may lead to oxygen depletion due to microbial degradation of the algal biomass, or to the release of algal toxins. By contrast, little is known as yet about the possible impacts of micropollutants on aquatic organisms and ecosystems. This is because, given the low concentrations present, any effects on organisms, if they do occur, will only develop over time – insidiously – and are therefore difficult to detect or predict.

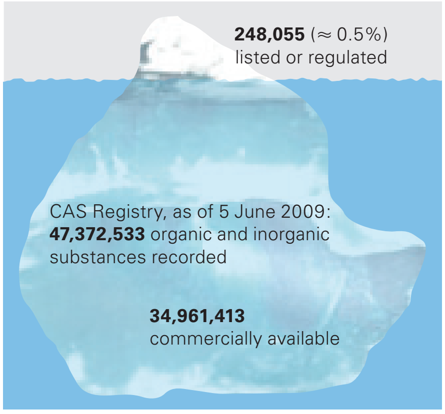

Fig. 1: The roughly 250,000 substances listed or regulated are only the tip of the iceberg. CAS = Chemical Abstracts Service.

Cause and effect: successful contraception. The difficulty of establishing a causal link between a micropollutant and a change in an ecosystem is shown by the example of estrogenic substances. These compounds act in a similar way to the female sex hormone estradiol and are thus able to disrupt the endocrine system in animals. The list of estrogenic substances widely found in natural waters includes not only the synthetic estrogen ethinyl estradiol, which is used as an oral contraceptive, but also bisphenol A, which is added to various plastics as a softening agent.

After numerous laboratory studies around the world had demonstrated that estrogenic substances impair reproduction in fish, Canadian and US researchers embarked on an unusual field experiment. For three years in succession, they spiked an experimental lake in northern Ontario with ethinyl estradiol [3]. A collapse in the fish population was indeed observed (Fig. 2), while fish in the control lake continued to develop normally. This study supports the thesis that estrogenic substances can have long-term effects on populations in an ecosystem. At the same time, the observations do not automatically prove that such reproductive disorders – which also affect fish in some Swiss waters – are generally attributable to chemicals with estrogenic activity. Reproduction may be influenced by a variety of other factors such as food or temperature, acting alone or in combination with micropollutants. Accordingly, the possible effects of a substance within an ecosystem must be considered, not in isolation, but in the context of the relevant influences and factors. If such interactions are to be extrapolated to other situations, it is necessary to identify the underlying mechanisms of action. This is one of the key challenges for research in environmental toxicology.

Hallmarks of substances of concern. Persistence, potential for bioaccumulation, biological activity – are by no means new characteristics for substances posing a potential environmental risk. It was these properties that led to the declaration of a worldwide ban on the production and use of polychlorinated biphenyls (PCBs) under the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2001. PCBs were first manufactured in 1929, and they were initially popular precisely because of their unique stability. For example, their thermal stability made electrical transformers and condensers safer to use. In addition, like many other chlorinated compounds, PCBs are only degraded very slowly in the environment. They accumulate in tissue such as body fat or breast milk and cause biological effects that may only become apparent years after exposure. These include skin disorders (e. g. chloracne) and weakening of the immune system. PCBs are also suspected of acting as endocrine disruptors in humans and animals.

A number of newer substances exhibit at least some properties similar to those of traditional POPs – e. g. the synthetic polycyclic musk fragrance galaxolide, which is a persistent compound. It has been shown that galaxolide concentrations at various depths in Lake Erie sediments are strongly correlated with annual perfume consumption in the United States (Fig. 3) [4]. Moreover, galaxolide is fat-soluble and hence bioaccumulative, as confirmed by its presence in breast milk and also in marine organisms. Lastly, galaxolide is biologically active: it inhibits the activity of efflux pumps, which normally transport toxic substances out of cells [5]. It remains to be determined whether this effect also increases the sensitivity of organisms to other micropollutants.

New challenge: pseudo-persistent substances. The example of galaxolide shows that we can certainly have recourse to knowledge of traditional POPs in assessing novel chemicals. Nonetheless, there is a serious gap in our knowledge: unlike traditional POPs, many of the newer substances are polar (hence readily soluble in water), ionizable and contain numerous functional groups. In addition, they are used in various physical forms – e. g. in solution or as nanoparticles. This gives the substances new properties, which in turn may affect their environmental fate and toxic potential (see the article by Renata Behra on p. 22).

In contrast to traditional POPs, many of the micropollutants currently detectable at relatively constant concentrations in natural waters are readily degradable, either biologically or physico-chemically. The fact that they often remain widely distributed is due to constant releases into the environment and incomplete elimination at wastewater treatment plants. To a certain extent, input is at least balanced by degradation. Because these chemicals are constantly present despite their short half-life, they have been described as "pseudo-persistent". However, not all substances that are degradable are also pseudo-persistent. Depending on how they are used, environmental releases may vary markedly, e. g. as a result of the seasonal application of pesticides (see the article by Roman Ashauer on p. 12). The interplay of input and degradation thus raises new questions for environmental scientists: what are the dynamics of release, distribution and elimination? Do micropollutants need to be removed from wastewater or drinking water, and is this technically possible? What transformation products arise from micropollutants (see the

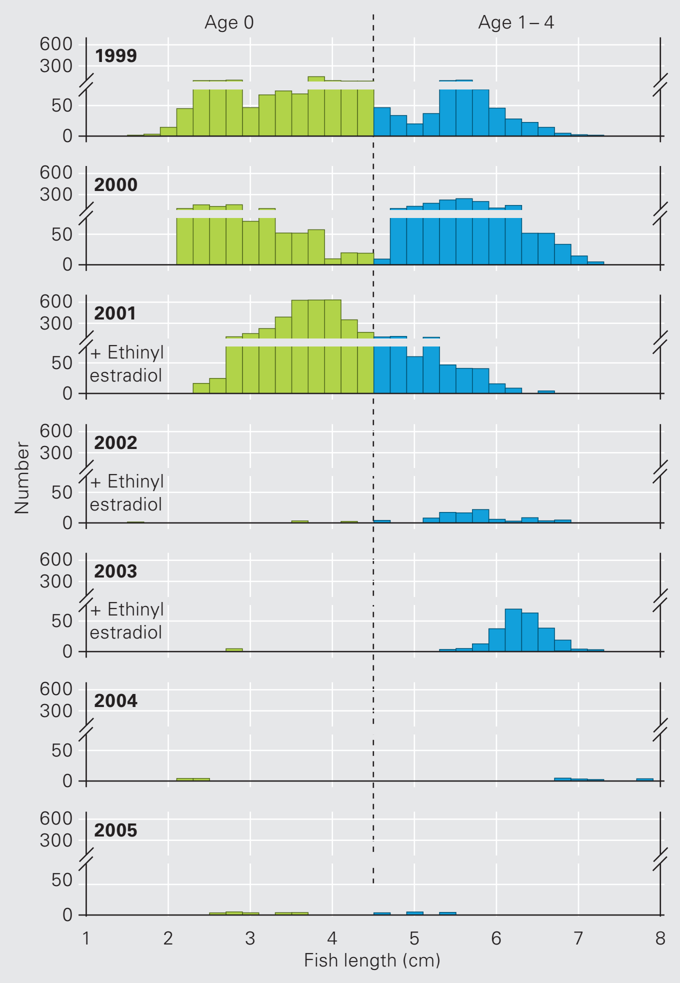

Fig. 2: Collapse of a population of fathead minnows in a Canadian lake after the addition of minute amounts of ethinyl estradiol in 2001–2003.

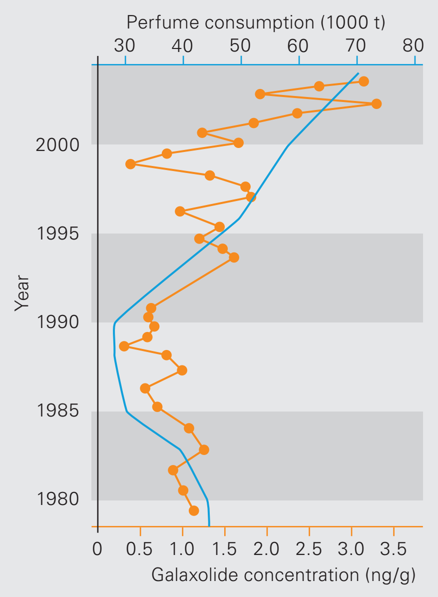

Fig. 3: Galaxolide concentrations (orange) measured in sediments of Lake Erie in North America correlate well with the annual consumption of perfumes in the United States (blue).

Even when we take our morning shower, we leave our mark on the water we use.

article by Kathrin Fenner on p. 15), and can these products and their properties be predicted on the basis of chemical structure? Could transformation products, in turn, be persistent and of toxicological relevance?

New challenge: biologically active compounds. Another property casts a new light on the environmental risk assessment of chemicals: innumerable substances are deliberately designed to be biologically active. At present, the main classes are pharmaceuticals, biocides and pesticides. In future, they could also include nanoparticles – if, for example, they are specifically designed to overcome tissue barriers, such as the blood-brain barrier. Given their high level of biological activity, these substances (alone or in mixtures) can give rise to effects without accumulating in the tissues of organisms. A good example of this is the synthetic estrogen contained in contraceptives. The question thus arises whether these agents' biological target molecules (e.g. enzymes and hormone receptors) are also present in aquatic organisms, and to what extent this entails a potential risk. It also needs to be investigated whether such compounds can produce other effects, "side effects", not associated with the primary biological target.

New challenge: multiple stressors. Bearing in mind the wide variety of factors involved, another challenge arises: chemicals in the environment need to be considered in conjunction with other influences. Firstly, they occur in mixtures and, secondly, they act on organisms in combination with other stressors, such as ultraviolet radiation or pathogens (see the article by Marc Suter on p. 19). So how do chemicals act in mixtures or in combination with other factors? And how do these interactions affect aquatic organisms, populations and communities? To what extent are they able to adapt to the various stressors?

Given the long list of questions, it is clear that we cannot possibly identify every conceivable interaction between synthetic substances and the aquatic environment. Rather, our task as researchers is to work out mechanistically based, generalizable relationships between the properties of substances and their distribution and effects in the environment, in order to develop strategies for reducing risks to a minimum. In this context, precautionary evaluations in the chemicals authorization process are just as important as assessment of the risks of anthropogenic micropollutants in the environment and potential measures for reducing input to natural waters.

The need for integrated approaches. To meet the challenges posed by anthropogenic micropollutants, natural scientists, engineers and social scientists are working closely together at Eawag. This is the case not only for precautionary risk assessment, e.g. with regard to the environmental fate and toxicity of novel synthetic nanoparticles, but also for evaluation of the risks of widespread micropollutants such as biocides and pharmaceuticals.

For example, chemists are developing analytical methods that make it possible to quantify substances occurring in very low concentrations even in complex environmental samples. However, analyses of this kind are concerned only with selected individual substances, so that some of the micropollutants which are present will always remain undetected. In contrast, organisms and also molecular or biochemical tests can indicate the effects of substance mixtures as a whole. By combining chemical and biological analyses, it becomes possible to assign biological effects to specific chemicals or groups of chemicals. This in turn provides decision support for engineers seeking to develop methods for the removal of micropollutants from wastewater or drinking water (see the article by Christian Abegglen on p. 25). Retrospectively, with the aid of the chemical and biological analyses, it is also possible to investigate whether the proposed methods are in fact able to minimize the chemical load, and whether this is actually associated with a reduction in biological activity or toxicity (see the article by Juliane Hollender on p. 28). Social-scientific studies carried out by Eawag researchers – e.g. on the handling of medicines in hospitals – are another key component of efforts to understand the spread of anthropogenic micropollutants and to identify ways of reducing input and hence risks to a minimum.

But close cooperation is required not only within Eawag, if viable approaches are to be developed for the management of (potential) micropollutants. Ultimately, the scientific findings also need to be translated into approaches that are applicable in practice. While the Environmental Toxicology department at Eawag is mainly engaged in basic research, the new, federally mandated Swiss Centre for Applied Ecotoxicology aims in particular to further develop promising ecotoxicological assessment methods so that they can be implemented for environmental monitoring by cantonal authorities and other users (see the article on p. 38). In addition, Eawag scientists act as consultants to operators of wastewater treatment plants and are supporting the Federal Office for the Environment in the development of plans for evaluating and protecting Swiss waters with regard to micropollutants (see the article by Michael Schärer on p. 31).

Anthropogenic micropollutants: everybody's responsibility. Micropollutants are ubiquitous in the aquatic environment, and their presence is largely a result of our lifestyle. They can even yield forensic information – for example, the concentrations of cocaine and its main urinary metabolite measured in Italian surface waters revealed that consumption in the community was much greater than had been indicated by official surveys [6]. Water quality is thus influenced by everyone. The approaches developed at Eawag help to improve our understanding of the relationships between the structure, environmental fate and effects of pollutants on organisms in water and are designed to identify risks for aquatic ecosystems and to show how such risks can be minimized.

This also includes the development of technologies for removing pollutants from municipal wastewater and from raw drinking water. However, despite intensive research, major uncertainties remain. Interactions between chemicals and the environment are complex, and elimination technologies at wastewater treatment plants are costly, especially when the aim is to remove substances present in low concentrations. This makes it important to analyse all the stages in the life cycle of a chemical [7]. The most direct way of reducing risks would be to synthesize chemicals in such a way that they are environmentally acceptable, i.e. rapidly and fully degradable. However, the property of being readily degradable is often in opposition to the properties originally desired – e.g. the stability of a pharmaceutical passing through the stomach, which enables it to reach the target organs intact. We therefore require additional approaches for avoiding the input of chemicals into the environment as far as possible. These include greater awareness on the part of consumers in handling the chemicals contained in everyday products – from use to disposal or possibly even recycling. This is an issue that concerns all of us. ○○○

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Dynamics of biocide and pesticide input

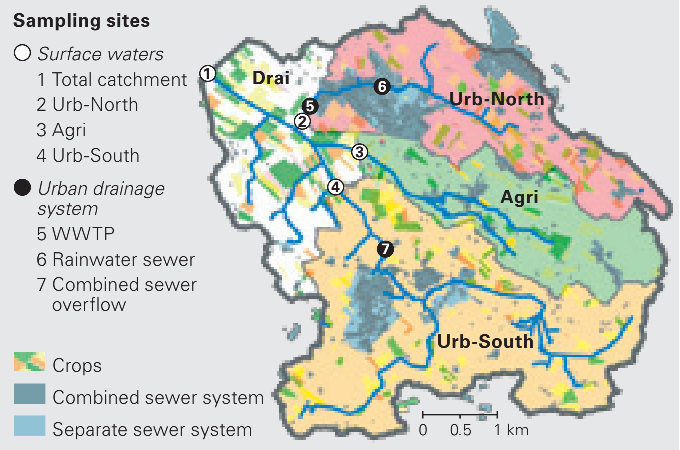
Biocides and pesticides are used to control harmful organisms in agriculture and in urban areas. But how do these substances ultimately find their way into natural waters? And is agriculture in fact the main source of water pollution? These questions are being investigated by Eawag researchers in various projects.

Irene Wittmer, environmental scientist and doctoral student in the Environmental Chemistry department.
Co-author: Michael Burkhardt

Agriculture was long regarded as the main source of pesticide input to surface waters. Accordingly, the agricultural use of pesticides is clearly regulated, and people who work with these substances require a licence to do so. When Switzerland's agricultural policy was reshaped around 15 years ago, one of the goals defined was a 50 % reduction in pesticide input. Although pesticide use declined by 25–30 % from 1992 to 2004 [1], agricultural pesticides still contribute to water pollution, despite all the regulations in force.

Input of biocides and pesticides from urban areas. At the same time, initial studies carried out at the end of the 1990s indicated that pesticides, such as the herbicide mecoprop, can also originate from urban areas [2]. In some cases, pesticides are chemically identical to biocides used in urban areas (see Box). On the basis of sales figures, however, it was assumed that the quantities of biocides and pesticides used in urban areas are much lower than in the agricultural sector. The fact that this underestimated the amounts actually used was demonstrated when estimates of consumption were first published in 2007. At approx. 2000 tonnes per year, the level of biocide use in urban areas of Switzerland (excluding alcohol- and chlorine-based disinfectants) [3] is roughly comparable to agriculture, where around 1300 tonnes of pesticides are applied [4]. Eawag is therefore studying in detail the contributions of urban and agricultural sources of water pollution.

Fig. 1: Overview of the study area and the seven sampling sites.
Urb = urban land use, Agri = mainly agricultural use, Drai = drained area.
Degree of urban land use: Agri < Drai < Urb-South < Urb-North.



Amounts of pesticides used. In a large-scale project, biocide and pesticide flows are to be assessed in a selected study area. The catchment, covering a total area of 25 km^2, is close to the Greifensee. It comprises 470 hectares of farmland, as well as two communes (12,000 inhabitants) sharing a wastewater treatment plant (WWTP). The area was divided into four subcatchments (Fig. 1) – one with mainly urban (Urb-North) and one with agricultural land use (Agri) and two with mixed use (Urb-South, Drai). During major rain events in 2007, numerous water samples were collected at four sampling sites in watercourses and three sites in the urban drainage system (WWTP outlet, combined sewer overflow, rainwater sewer). The samples were analysed for a series of biocides and pesticides (see Table on p. 10).

First, however, we conducted surveys on the amounts of pesticides used: almost all the farmers (95 %) and a manageable number of urban households (60 of 1800) were surveyed in the study area. It was found that isoproturon was the pesticide most used for agricultural purposes (107 kg applied), followed by glyphosate, atrazine and terbuthylazine (74, 64 and 42 kg). Four other substances (mecoprop, mesotrione, sulcotrione and diazinon) were used in quantities between 2 and 13 kg.

Pesticides were used in 80 % of the households surveyed, largely to protect roses from insects. In addition, 20 % of the respondents reported that – in spite of a legal prohibition (of which they were unaware) – they also used pesticides on driveways. Surprisingly, in the 60 households, 45 different agents were used, including three of the substances covered by our study – mecoprop, diazinon and glyphosate. Our extrapolation indicated that urban areas are thus not to be neglected as a source of pesticides. As yet, we cannot draw any conclusions concerning the use of biocides; this will first need to be roughly estimated on the basis of consumption figures and product information.

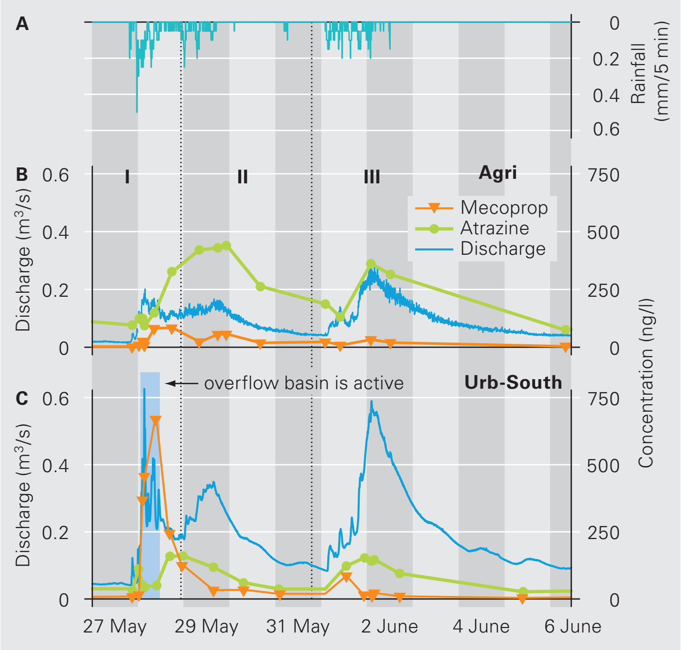


Fig. 2: Concentrations of mecoprop and atrazine measured in two watercourses during rain events between 27 May and 6 June 2007. Rainfall is shown (A), as well as data from the sampling sites in the predominantly agricultural subcatchment Agri (B) and the mainly urban subcatchment Urb-South (C).

Biocides and pesticides transported by rainwater. Pesticides and biocides used outdoors can be washed out and transported into surface waters by rainwater. The example selected here – rain events that occurred at the end of May/beginning of June (Fig. 2A) – illustrates the different concentration dynamics of substances released from an urban and an agricultural area. Curves are shown for atrazine (a substance used exclusively in the agricultural area) and mecoprop (mainly used in the urban area; see Table). These rain events coincided with the agricultural application period for atrazine. The following conclusions can be drawn:

▶ The discharge dynamics differ markedly for the Agri and Urb-South subcatchments (blue curves in Fig. 2B + C). In the agricultural area, the three peak discharges caused by the rainfall are considerably lower, as water is absorbed and subsequently released by the unsealed soils. In the urban area, by contrast, water runs off the sealed surfaces (roads, paved areas, roofs) without any delay. Some of this runoff drains directly into receiving waters via rainwater sewers, while the remainder enters the combined sewer system and reaches the WWTP via overflow basins. In the case of very heavy rainfall, however, excess water is discharged from the combined sewer overflow tanks directly into the stream. This was the case for the first peak discharge in the Urb-South subcatchment (Fig. 2C).

▶ Atrazine concentrations rise as stream discharge increases (green curves in Fig. 2B + C). This applies not only for the agricultural area but also, albeit to a lesser extent, for the mixed-use Urb-South area.

▶ In the urban receiving waters, concentrations of mecoprop (orange curve in Fig. 2C) rise sharply in association with the overspill from the combined sewer overflow basin. Thereafter, the overflow is no longer active and mecoprop concentrations remain low during the two subsequent peak discharges. In the agricultural area, meanwhile, mecoprop concentrations in the stream are only slightly increased during all three phases (Fig. 2B). This is presumably also due to losses from the small number of settled areas in the subcatchment. Similar concentration dynamics were observed for the biocides carbendazim and diuron, also typically used in urban areas.

For rain events in general, therefore, it can be said that increased contamination of natural waters with agricultural pesticides usually occurs during the application season, whereas substances with biocidal and pesticidal effects can enter waters from urban areas throughout the year (cf. Fig. 3A + B). Apart from this rainfall-related input, however, there are constant losses from urban areas and temporary increases in concentrations from agricultural sources. For example, we measured elevated diazinon concentrations in WWTP effluents all year round (> 50 ng/l), and on several occasions, we observed massive increases in pesticide concentrations (up to 20,000 ng/l atrazine), most likely attributable to inappropriate handling or disposal.

Urban areas: a significant contribution to water pollution. As well as studying concentration dynamics, the composition of loads can be assessed in order to determine the relative importance of agricultural and urban sources for the occurrence of substances in natural waters. In the case of the rain event at the end of May, the two agriculturally influenced subcatchments play an important role in the composition of the atrazine load, while the combined sewer overflow and the WWTP (dark brown and dark blue areas in Fig. 3A) contribute virtually nothing to this load. In contrast, the predominantly urban subcatchment contributes decisively to the

Biocides and pesticides

Biocides and pesticides are used to control unwanted organisms. Put simply, while pesticides serve to protect plants, biocides are used for all other types of application (protecting walls and facades, preserving wood, controlling household pests, etc.; see Table). The approval of active substances is regulated by the Biocidal Products Ordinance (VBP) and the Plant Protection Products Ordinance (PSMV). Biocides and pesticides enter natural waters via various pathways. In agricultural areas, pesticides enter watercourses from fields via surface runoff or drainage flows and as a result of inappropriate handling or disposal of spray mixtures. Substances used in urban areas enter surface waters via sewer systems.

mecoprop load observed during the same event. The WWTP and the combined sewer overflow account for up to 25 % of the total load. Measurements of the two substances in the autumn indicate that the atrazine load is extremely low, while the mecoprop load remains high. In addition, the mecoprop load exhibits the same pattern as in the spring. This shows that the sources of mecoprop remain more or less constant. It is not yet clear, however, whether this input is attributable to urban applications (gardening season from May until the end of September) or to constant losses from flat roofs and foundation sealing membranes.

Flat roofs: a possible source of mecoprop. The fact that mecoprop is indeed released from flat roofs is demonstrated by another Eawag study. The herbicide is used to prevent root penetration in bitumen sheets (roofing felt) on flat roofs. A large proportion of the mecoprop is leached out in roof runoff. As several million square metres of flat roofs sealed with bitumen membranes are constructed in Switzerland each year, it is not surprising that mecoprop is ultimately also found in numerous surface waters. It enters these waters either directly via rainwater sewers or in "treated" wastewater – the elimination of mecoprop at WWTPs is only 10 – 30 %.

Our studies have now shown that, with two more modern root protection agents based on the ethyl hexyl ester (Herbitect®) and the octyl ester of mecoprop (Preventol®B5), hydrolysis and leaching are reduced, compared with the traditional product based on the polyglycol ester (Preventol®B2) (Fig. 4). Leaching behaviour is also influenced by the composition of bitumen sheets – the content and quality of bitumen, polymer and mineral filler: in products with a higher bitumen content, leaching was reduced by another 50 %. In recent years, the concentrations of mecoprop added to bitumen have already been reduced by about half. A further reduction would only be possible if efficacy was still assured, but there is uncertainty as to where the threshold for efficacy lies.

Educating consumers and modifying chemical compositions to minimize losses. Our findings clearly demonstrate that both agricultural and urban applications of biocides and pesticides lead to water pollution. But how can such losses be minimized in the future? One option is to improve the management of biocides and

Applications of the various biocides and pesticides studied. The levels of importance assigned to the individual substances are based on the concentrations measured in the study area (Fig. 1).

🟩 important agricultural 🟢 less important agricultural 🟧 important urban 🟠 less important urban ☐ not detected

		Urban: constant	Urban: seasonal	Agricultural: seasonal
		Biocide	**Pesticide**	**Pesticide**
Agricultural	Sulcotrione			☐ Chinese silver grass, maize
	Mesotrione			🟢 Maize
	Atrazine			🟩 Maize[1]
	Terbuthylazine			🟩 Pomaceous fruit, maize
Urban and agricultural	Isoproturon	☐ Facades, preservatives, etc.		🟩 Cereals
	Glyphosate		🟧 Lawns, railway lines, roadsides, etc.	🟩 Fallows, fruit, meadows, pastures
	Mecoprop	🟧 Flat roofs[2], foundation sealing membranes	🟧 Gardens, lawns, driveways[3], roadsides, etc.	🟢 Cereals, Chinese silver grass, fruit, meadows, pastures
	Diazinon	🟠 Unknown sources, flea collars[4]	🟧 Roses, fruit, ornamentals, gardens	🟢 Fruit, sugar beet, rape, vegetables, cut flowers
	Diuron	🟧 Facades, preservatives, etc.		☐ Fruit, asparagus, bushes, vines
	Carbendazim	🟧 Fungicides for bathrooms, facades, etc.		☐ Fruit, vegetables, rape, potatoes, sunflowers
Urban	Terbutryn	🟧 Fungicides for bathrooms, facades, etc.		
	Irgarol	🟠 Antifouling coatings, facades, etc.		
	IPBC	☐ Preservatives, wood protection products, etc.		
	Isothiazolinone	☐ Preservatives, facades, etc.		

[1] The sale of atrazine has been prohibited since December 2008. However, farmers are allowed to use up existing stocks until December 2011.

[2] Although mecoprop is not legally classified as a biocide, it can be considered equivalent in terms of its effects.

[3] Although this type of application is illegal, it was confirmed in our survey.

[4] In flea control products, diazinon is neither a biocide nor a pesticide, but a veterinary medicine..

pesticides. There is great potential here, especially with regard to the use of pesticides in urban areas, since many consumers are not familiar with the proper use of these agents – or aware of existing prohibitions. However, there is also room for improved management of pesticides in the agricultural sector, even though training and information are available. But it will be more difficult to minimize diffuse losses from agricultural sources. Often, these losses may even derive from a small proportion of the total field area [5]. For this reason, an Eawag project is currently seeking to identify those agricultural areas where the risk of losses is particularly high.

Another way of reducing losses is to improve the chemical composition of products. In the case of mecoprop in bitumen sheets, this has already been done. "At source" measures are required in applications of this kind, where water pollution cannot be effectively reduced by conventional treatment processes since most of the runoff does not even reach the WWTP. Last year, after three decades in which only Preventol®B2 was used in bitumen sheets, the three main manufacturers modified their formulations to include Herbitect® and Preventol®B5 in the light of our findings. According to recent recommendations issued by the Federal Office for the Environment (FOEN) on mecoprop in bitumen roofing sheets, roof runoff should be infiltrated through a microbially active soil layer to avoid contamination [6]. In addition, the manufacturers and the FOEN recommend that root-resistant sheets should only be used on genuine green roofs; they are not generally required on gravel-covered or bare roofs. Over the long term, all these measures combined could prevent 96 – 98 % of mecoprop leaching, thus leading to a reduction in water pollution. ○ ○ ○

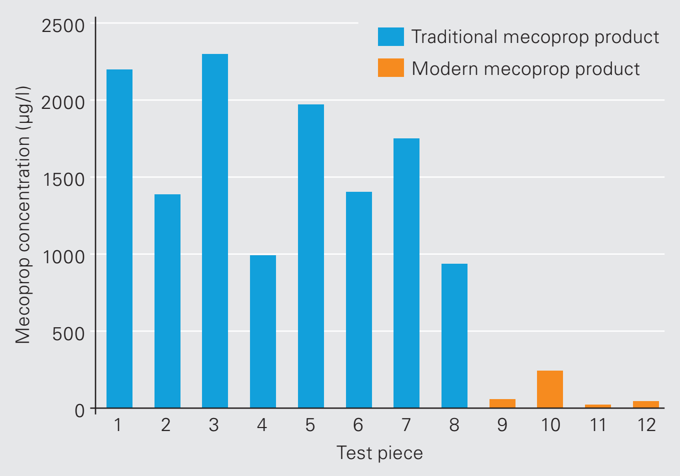
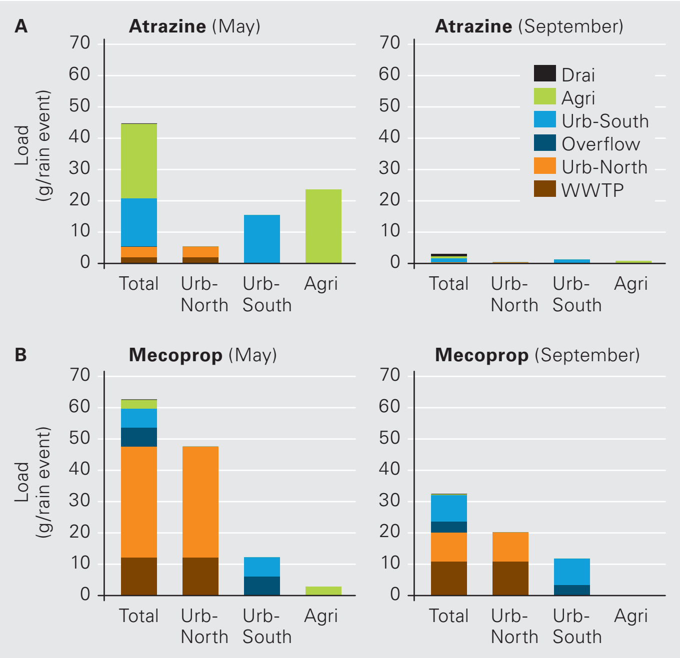


Fig. 4: Leaching of mecoprop from bitumen sheets.

Fig. 3: Comparison of loads of atrazine (A) and mecoprop (B) measured at six different sampling sites (cf. Fig. 1) during rain events in May (60 mm rainfall) and in September (35 mm rainfall).



We are grateful to our colleagues – Hans-Peter Bader, Markus Boller, Ruth Scheidegger, Heinz Singer, Christian Stamm and Steffen Zuleeg (all at Eawag), and Regula Haag, Sivotha Hean and Peter Schmid (all at Empa). Financial support was provided by the Federal Office for the Environment (FOEN) and the Canton Zurich Office for Waste, Water, Energy and Air (AWEL).

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Effects of fluctuating contaminant concentrations

Is it true that "the dose makes the poison"? How long does it take for exposed organisms to recover? What are the effects of sequential exposure to contaminants? These are some of the questions we are trying to answer with the aid of toxicokinetic/toxicodynamic models and experiments.

Traditionally, toxic effects of contaminants have mainly been measured and assessed on the basis of concentrations in the environment or in the test medium. Toxicity is described in terms of the concentrations at which 50 % of test organisms (e.g. fish or freshwater amphipods) show a response (effective concentration/EC_{50}) or die (lethal concentration/LC_{50}). However, little attention is paid to the period of exposure producing these effects. The duration of ecotoxicology tests is often determined in an arbitrary way: for example, one of the most important tests – the acute fish toxicity test – runs for four days, so it can be conveniently carried out in the course of a working week. For these historical reasons, there are hardly any instruments or methods in ecotoxicology and chemical risk assessment that take temporal aspects (dynamics) into account.

Nonetheless, advances in environmental monitoring, chemical analysis and modelling of the environmental behaviour of chemicals mean that, increasingly, exposure to contaminants is no longer simply described by a single concentration, but by concentration time series. Concentrations are of course not constant over time but can fluctuate widely, with repeated peak exposures occurring, for example, at wastewater treatment plant outlets and following heavy rainfall in agricultural areas (e.g. after the application of pesticides) or on urban surfaces (e.g. leaching and runoff from facades and roads). Eawag therefore aims to develop theoretical concepts, experimental approaches and mathematical models allowing explicit characterization of the time course of toxic effects. One particular priority is the development of toxicokinetic/toxicodynamic (TKTD) models [1–4].

Eawag technician Anita Hintermeister monitoring an experiment that involved exposure of *Gammarus pulex*.

Toxicokinetics: what the organism does with the substance – toxicodynamics: what the substance does to the organism. TKTD models comprise mathematical equations that describe two key aspects of how a toxic substance interacts with a test organism: firstly, the toxicokinetic component, which deals with various processes from uptake through metabolism to elimination and, secondly, the toxicodynamic component, which is concerned with when toxic effects occur and how potent they are.

Thus, in contrast to classical EC_{50} or LC_{50} values, which merely provide a snapshot, TKTD models cover the entire time course of the processes associated with toxic action. To do so, however, the model must first be parameterized – i.e. a series of model parameters need to be determined experimentally in advance. In the case of our Threshold Damage Model (TDM), these are: the uptake and elimination rate constants, the damage and recovery rate constants, and the threshold above which damage to the organism is sufficient for toxic effects to become visible. These parameters depend on physicochemical properties and modes of action, and they are specific to each compound and test organism. At Eawag, we use the freshwater amphipod *Gammarus pulex* as a model organism. The TDM is, however, applicable for different modes of action with different rates of recovery, while most other models designed for this purpose are special cases of the TDM which are only applicable with certain restrictions, i.e. only for particular modes of action [4]. A universal model of this kind represents a major advance, providing an improved framework for carrying out mechanistic ecotoxicology on a quantitative basis.

Significance of timing, as well as dose, for toxicity of multiple exposures. With pesticide contamination in particular, recur-

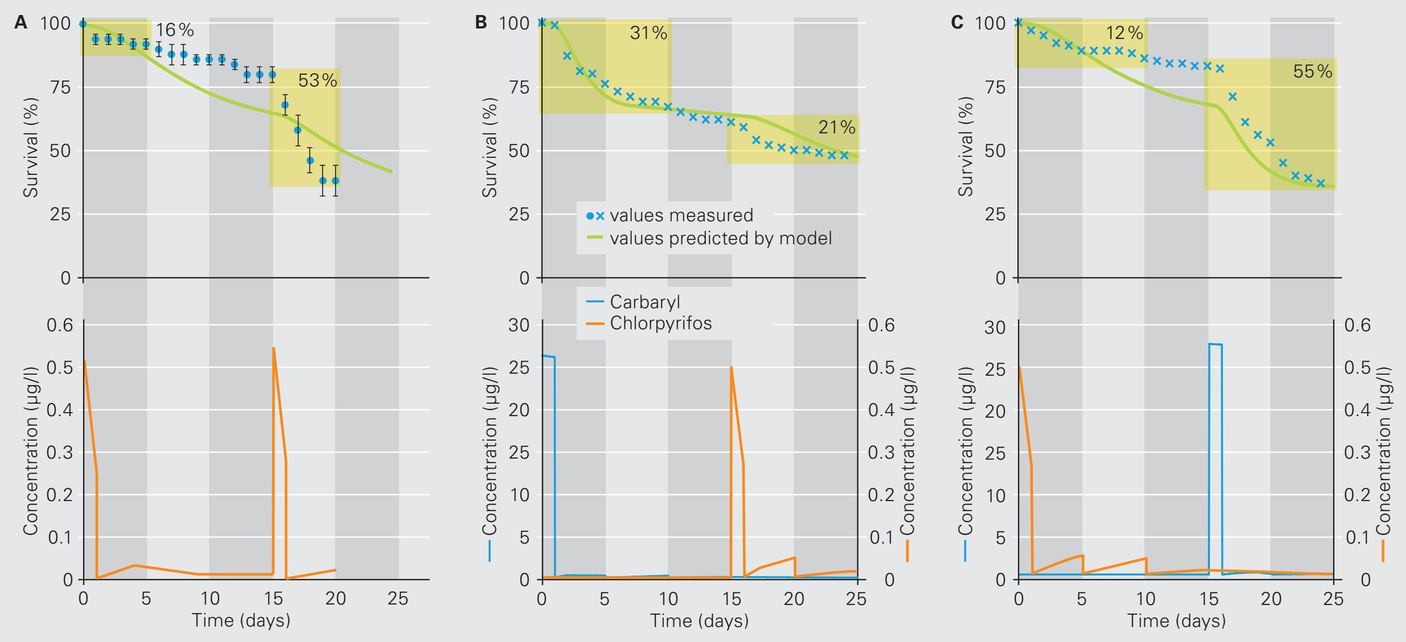


Fig. 1: Survival of *Gammarus pulex* (top) exposed to fluctuating concentrations of contaminants (bottom). A: Repeated exposure to the pesticide chlorpyrifos, with an interval of 14 days between pulses. B and C: Exposure to the pesticides chlorpyrifos and carbaryl in different sequences, with intervals of 14 days between pulses. Yellow boxes = Percentage of organisms dying.

rent peaks are to be expected in surface waters. For this reason, we chose this group of substances for our first experiments. In Switzerland, specific concentration limits are currently being elaborated for each pesticide – the acute (AQC) and the chronic quality criterion (CQC) (bottom of Fig. 2) [5]. Unlike the AQC, it is permissible for the CQC to be exceeded in natural waters. However, it has yet to be established scientifically how often such exceedences may occur, and at what intervals. The values to be specified for intervals between exposures and transgression of the CQC will depend on how rapidly an organism can recover from a previous exposure to a contaminant – and our TKTD models can be used to answer such concrete questions.

Our experiments show, for example, that delayed toxicity may occur if the recovery period between two equally intense pesticide exposures is not sufficiently long (Fig. 1A). Even if the *Gammarus* had enough time – here, 14 days – to eliminate the pesticide from the first exposure, their physiological condition may not yet have returned to the normal range. The second exposure is then more toxic than the first. In the case of chlorpyrifos, about 16 % of the organisms died after the first contact with the pesticide, and another 53 % after the second exposure. This means that the toxicity is determined not only by the dose, but also by the timing of the application in relation to previous exposures to the same [3] or different stressors [2].

Sensitivity affected by the sequence of exposures. An important role is also played by the sequence of exposures to different contaminants. This is illustrated by the example of the pesticides chlorpyrifos and carbaryl, as shown in Fig. 1B and C. When the *Gammarus* were exposed first to carbaryl and then, 14 days later, to chlorpyrifos, the death rates were 31 % and 21 % respectively (Fig. 1B). When the order was reversed, 12 % of the organisms died after exposure to chlorpyrifos and 55 % after exposure to carbaryl (Fig. 1C). Thus, the mortality associated with carbaryl is 31 % in one case and 55 % in the other, although the organisms were exposed to the same dose in both cases. The increased toxicity is caused by the previous exposure to chlorpyrifos, even though this occurred 14 days earlier. This suggests that the organisms had not recovered sufficiently. The difference between the death rates associated with chlorpyrifos (12 % or 21 %) is less marked, indicating that the organisms were able to recover more rapidly from the previous exposure to carbaryl.

The toxicity of a substance thus also depends on the situation with regard to earlier exposures. Overall, this means that the toxic potential of a substance will be greater if organisms have been damaged by previous exposure to a contaminant (either the same or a different one).

Our experiments also showed that the measured values are in close agreement with the results predicted by the model (Fig. 1). In future, it will therefore be possible not only to predict realistic toxicities for fluctuating contaminant concentrations using the model alone, but also to include directly in the simulation the safety factors (e.g. 100-fold factor) that are required in risk assessment (Fig. 2).

Ongoing experimental studies and future potential. After our work on pesticides, we are currently seeking to extend the TKTD model to a larger number of substances with different properties

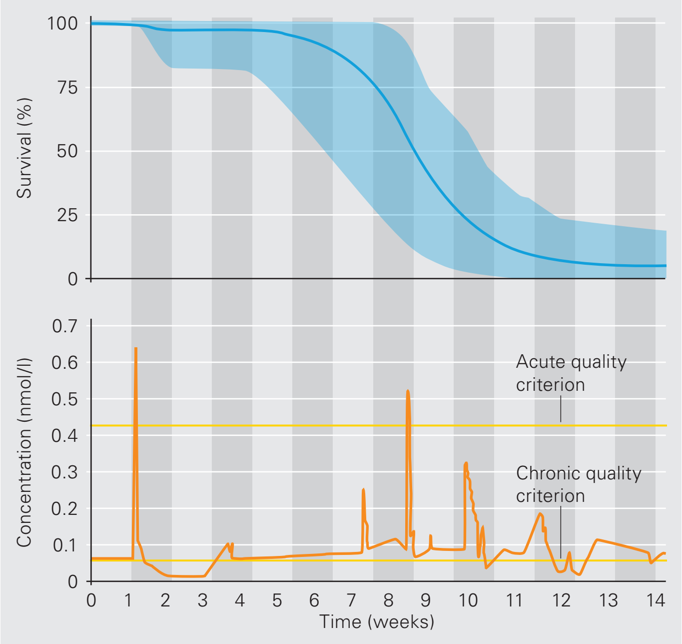
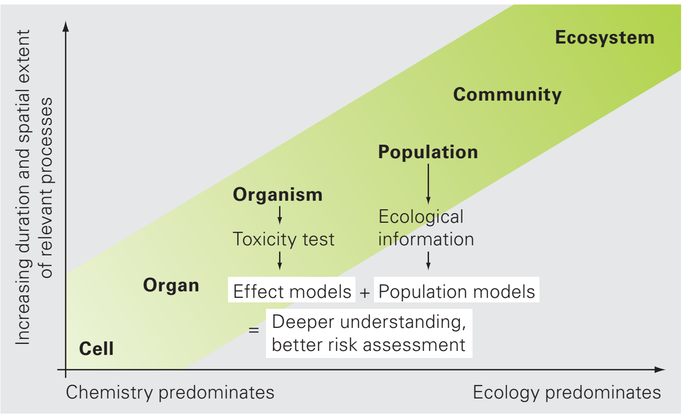


Fig. 2: Typical contaminant concentration profile in a stream (bottom) and the associated survival probabilities (blue band, top) simulated using the TKTD model. To obtain the model input, the concentrations are multiplied by a safety factor.

and modes of action. We are studying the hypothesis that certain toxicodynamic parameters, such as the recovery rate, depend on the mode of action. If this were the case, these parameters could be derived from the modes of action, or conversely, the mode of action from the parameters. As well as broadening the foundations of ecotoxicology, such relationships would also be helpful in estimating the environmental toxicity of numerous chemicals without the need for additional experiments. This would be very useful, e.g. in connection with REACH, the European Union's new chemicals regulation. As the TKTD models explicitly simulate time courses and processes, we also hope to gain a better understanding of how short-term and long-term toxicity values are related – so-called acute-to-chronic ratios (ACRs). These ratios are an important element in the determination of safety factors for risk assessment. As well as improving risk assessment, a better understanding of ACRs would reveal how they relate to the recovery time of organisms. In cooperation with Wageningen University (the Netherlands), we intend to use TKTD models to explain how observed differences in sensitivity between different aquatic organisms are attributable to species-specific characteristics.

In order to include in chemical risk assessment not only processes occurring at the individual level but also the ecology of aquatic organisms, we are also seeking to integrate TKTD models into population models (Fig. 3). This should make it possible to analyse the relative contributions of the recovery of aquatic organisms at various levels of biological organization and, on this basis, to formulate appropriate protection measures. ○ ○ ○

Fig. 3: Integration of mechanistic effect models (e.g. TKTD models) and ecological information described by population models. As different processes (biochemical vs ecological) predominate at different scales, a combination of different models provides a more comprehensive understanding and an improved risk assessment of chemicals.



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Transformation products – relevant risk factors?

Chemical substances can be transformed in the environment into products that are more stable, more readily water-soluble and even, in certain cases, more toxic than the parent compound. Eawag is developing methods that will allow the risk of these transformation products to be better assessed.

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The degradation of a chemical substance in the environment does not always lead to rapid and complete mineralization. Instead, in the course of the degradation process, relatively stable transformation products may be formed. This is the case in particular for many active substances – such as pesticides, pharmaceuticals and biocides – which have relatively complex molecular structures that are only gradually degraded. This is confirmed by extensive measurements of stable pesticide transformation products in surface and ground waters in the US [1], but also by findings in Switzerland [2].

Detecting unknown transformation products

For most conceivable transformation products, no chemical standards are available. Normally, however, such reference standards are required to allow a compound in an environmental sample to be unequivocally identified. We therefore developed a detection method that provides sufficient information to enable a measured signal to be confidently assigned to a possible structure. In high-resolution mass spectrometry, compounds are detected on the basis of their exact mass, which is determined with such a high degree of accuracy that only a small number of molecular formulae having precisely this mass are even conceivable. However, further evidence is needed to confirm that a measured signal actually corresponds to the postulated transformation product. In our method, we therefore introduced two additional parameters alongside high-resolution mass spectrometry: the liquid chromatography retention time, which is a measure of the polarity of the compound, and fragment spectra from tandem mass spectrometry, which provide further information on the molecular structure.

The structure of transformation products is often very similar to that of the parent compound. However, they are usually somewhat more polar and enter natural waters more easily on account of their greater solubility. Generally speaking, toxicity is only rarely increased as a result of these structural changes, and similar or lower toxicity than the parent compound would normally be expected. This means that the stable transformation products of polar compounds such as pesticides, pharmaceuticals and biocides not only contribute to chemical water pollution but also, in combination with the parent compound, may lead to increased overall toxicity in the aquatic environment.

These points would need to be taken into account both in the assessment of chemical water quality – e. g. in the context of the EU Water Framework Directive – and in prospective chemical risk assessment. However, no clear requirements are specified in the relevant EU regulations, except in the case of the authorization of pesticides. Accordingly, we have only a fragmentary knowledge of what transformation products we should expect to find in our water resources, and to what extent they contribute to overall chemical pollution.

Within the KoMet project (combined modelling and measurement approach for the identification of relevant transformation products in water resources), we have therefore developed a toolbox of methods to address this problem. KoMet is part of the MicroPoll strategy initiated by the Federal Office for the Environment (FOEN).

Can the formation of possible transformation products be predicted? Transformation products are formed in the environment in many different ways. In addition to chemical processes such as hydrolysis, redox reactions or photolysis, microbial, enzyme-catalysed degradation plays an important role. Compounds of aquatic relevance in particular, which usually enter the environment via the soil or a wastewater treatment plant, are frequently degraded by bacteria and/or fungi in these compartments.

In a joint project involving the University of Minnesota and the Technical University of Munich, we are therefore developing a computerized expert system [3] that can predict typical products of microbial degradation. The system relies on biotransformation rules, defined on the basis of experimentally studied biodegradation pathways. These rules recognize existing structural units in the compound and simulate the formation of transformation products. However, the multiplicity of applicable rules rapidly generates numerous predicted products – including some that have never been observed for a given chemical. In order to restrict the number of predicted transformation products, we defined a series of higher-level rules that determine priorities among the various applicable rules.

For example, without rule priorities, the expert system predicts 12 products for atenolol, a beta blocker used to slow the heart rate (Fig. 1). However, when the higher-level rules are applied, only 6 possible products remain. One product in particular is found experimentally – atenololic acid, which is formed by enzyme-catalysed hydrolysis. For 47 other pharmaceuticals and pesticides, it was likewise possible to reduce the number of predicted products by an average of 16 % without known products being lost in the process [4].

Tracking down transformation products. The predictions of the expert system can now be used to search specifically for possible transformation products, either in a biodegradation experiment in the laboratory or in an environmental sample. As a general rule, the methods of trace analysis can only be applied when one knows what one is looking for. Also required are reference standards – pure forms of the target compounds which are used to calibrate the analytical procedure, so that a target compound can actually be identified in an environmental sample. Typically, however, no reference standards are available for predicted transformation products. To get round this problem, we developed an analytical method based on high-resolution mass spectrometry – a relatively new technique – which does not require the use of reference standards (see Box on p. 15). With this method, for three pharmaceutical substances studied, we have already identified four previously unknown transformation products, which – as predicted by the expert system – were formed in biodegradation experiments carried out in reactors containing sewage sludge (Fig. 2).

Non-negligible amounts in surface waters. Even more crucial, however, than the question of what transformation products are formed in laboratory experiments, is what products actually occur in water resources – and in what quantities. To investigate this, we also applied our combined method. For a total of 52 pesticides, biocides and pharmaceuticals used in significant quantities in Switzerland, and representing different chemical classes, a list of approximately 1800 possible transformation products was generated using the expert system. Of these candidates, 19 were actually detected in 6 representative samples from medium-sized Swiss watercourses. As regards the pesticides, these included not only several well-known and frequently observed transformation products (desethylatrazine or metolachlor ethanesulfonic acid) but also various pesticide transformation products that had previously only been detected in laboratory studies and rarely or never in environmental samples (products of the fungicide azoxystrobin and of the herbicides chloridazon, metamitron and metribuzin). In the case of pharmaceuticals, the transformation products found were generally known human metabolites. It is, however, possible that some of these also partly arise as a result of biodegradation in wastewater treatment plants, since they are also predicted as microbial products. Another 10 transformation products – though not directly identified by our method since they were present in relatively low concentrations – could nonetheless be detected because reference standards were available for these products.

Overall, our study shows that, in Swiss surface waters, transformation products do not occur with unexpected frequency or in very high concentrations. However, for around half of the active

Fig. 1: Transformation products predicted by the expert system for the beta blocker atenolol. The main environmental transformation product, atenololic acid, is highlighted in orange.

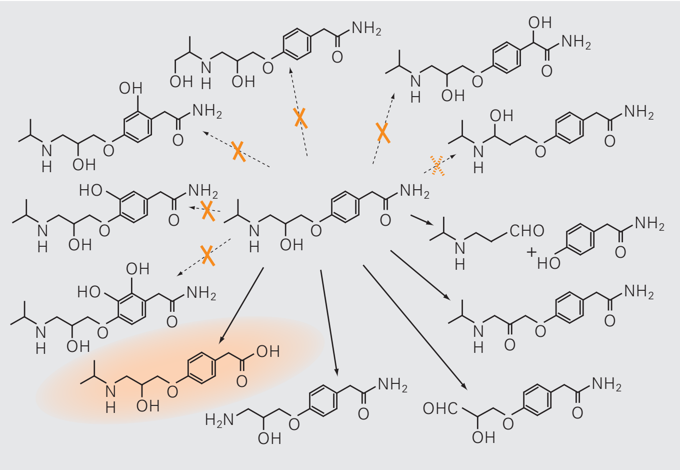
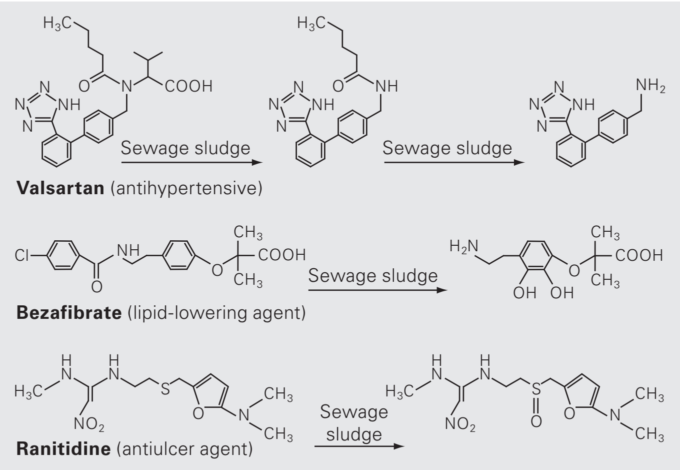
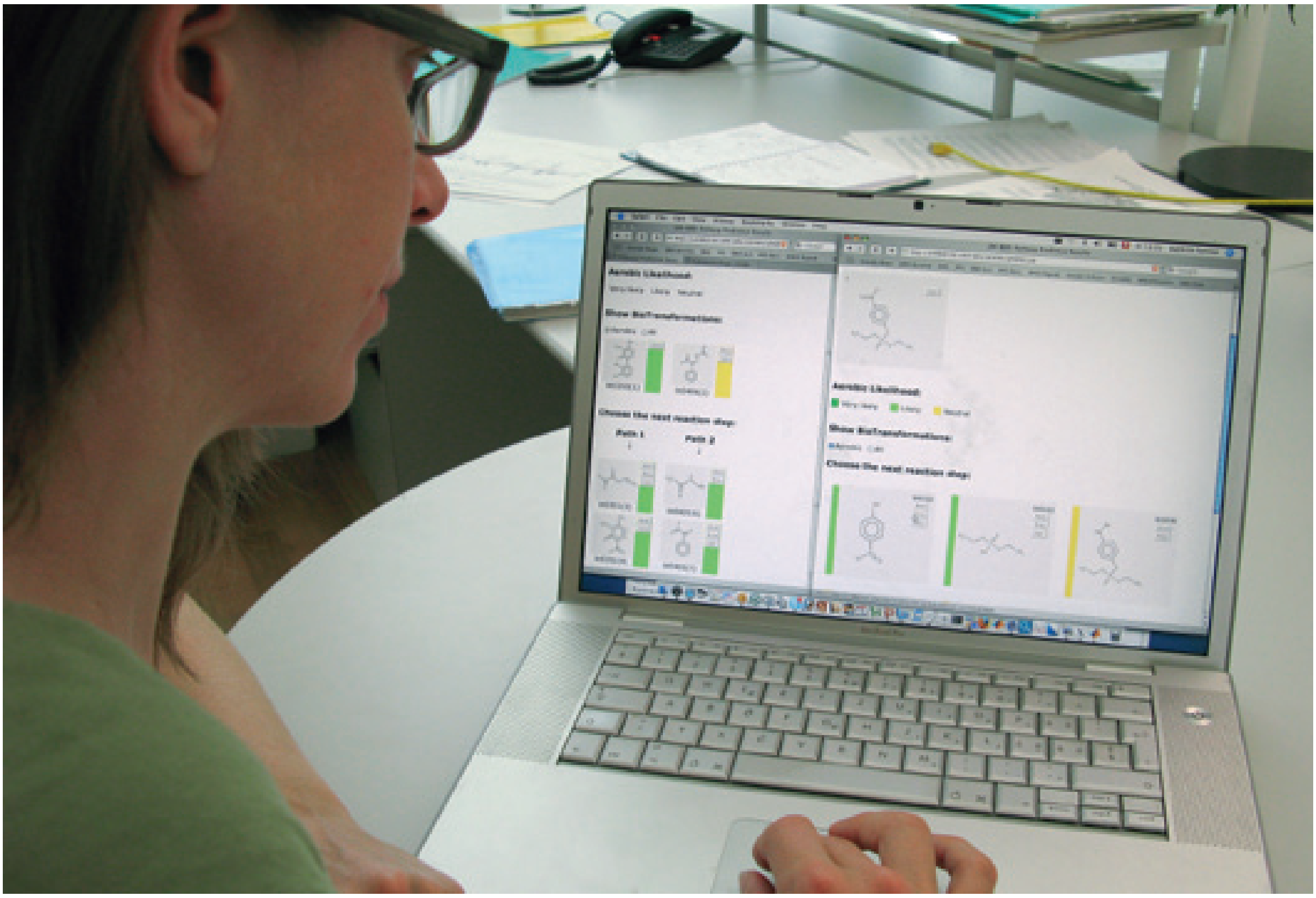


Fig. 2: Four newly discovered transformation products of pharmaceuticals, which were initially predicted by the expert system and then actually detected in degradation experiments.





Prediction of transformation products using a computerized expert system.

substances studied, one or two transformation products were found, which must therefore be relatively stable and mobile. Transformation products are thus not negligible as additional contaminants in water resources, but they most probably do not represent a problem of unsuspected proportions.

A relevant contribution to overall toxicity? It is often argued that transformation products are only really relevant if their toxicity is equal to or greater than that of the parent compound. This is only the case for about 30 % of the transformation products from 37 pesticides for which data on the relative toxicity of transformation products and parent pesticides was compiled [5]. However, as the transformation products generally occur in a mixture with the parent compound and at least in some cases have the same mode of action, their contribution to the overall effect cannot be neglected.

In the part of our project dealing with toxic effects, we are therefore investigating how knowledge about the effects of the parent compound can be used to estimate the toxicity of transformation products. Many parent compounds exert what is known as specific toxicity on particular organisms (e. g. interaction with enzymes or reactions with DNA or proteins). This means that their toxicity is higher than the minimum (baseline) toxicity which every chemical substance exerts by accumulating in the cell membrane of an organism and disrupting its function. The baseline toxicity of a compound is associated with its lipophilicity (degree of solubility in fats) and can be readily estimated on the basis of its structure. The toxicity of transformation products can be expected to lie between baseline toxicity and the specific toxicity of the parent compound. On the basis of the lipophilicity of the transformation products, it is thus possible to delimit a range of possible effective concentrations, expressed as the EC_{50} (concentration at which a response is observed in 50 % of the study population).

The procedure is illustrated here by the example of the herbicide diuron and two of its main transformation products – DCPMU and DCPU (Fig. 3A). As a herbicide, diuron is specifically effective against algae, and the risk assessment was therefore carried out for this organism. From the spring to the autumn of 2008, we determined the concentrations of diuron and its transformation products during major rain events in a tributary of Lake Murten (La Petite Glâne). It was shown that, during one of the later events in September, the transformation products evidently contributed

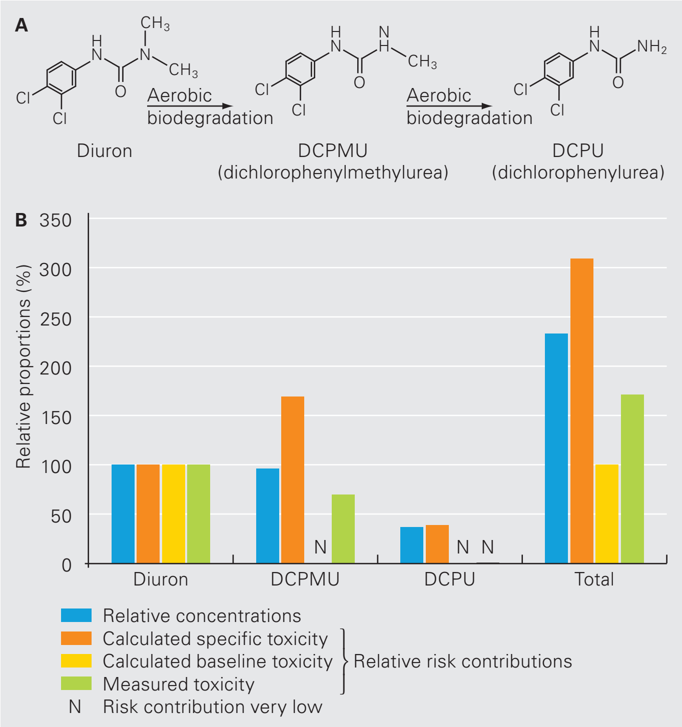


Fig. 3: (A) Formation of the transformation products DCPMU and DCPU by microbial degradation of the pesticide diuron. (B) Measured concentrations and predicted and observed risk contributions of diuron, DCPMU and DCPU during a late-summer rain event. The values for DCPMU and DCPU are scaled to those for diuron (= 100 %).

more than 50 % to the total concentration (blue bars in Fig. 3B). Their contribution to the risk can now be estimated via the quotient of the measured concentration and the predicted EC_{50}. We thus calculated that, if the two transformation products are taken into account in the risk assessment, a 210 % higher risk is to be expected (orange bars), on the assumption that they also act as specific inhibitors of photosynthesis. However, if the transformation products lose their specific activity and only exert baseline toxicity, the risk would not be significantly increased (yellow bars). To test the plausibility of these maximum and baseline estimates, we also charted the risk contribution using EC_{50} values determined experimentally by our group, which revealed a 70 % increase in the risk contribution (green bars). This example thus demonstrates that transformation products potentially relevant to the environmental risk can be reliably identified with the aid of our method, and that, in individual cases, transformation products may indeed substantially increase the overall risk.

Taking transformation products into account in chemicals assessment. Overall, our studies indicated that transformation products of pesticides, biocides and pharmaceuticals do not occur with unexpected frequency or in very high concentrations in Swiss surface waters. Even so, for around half of the compounds studied, one or two products were found, which – as shown by the example of diuron – may well contribute to an increase in chemical-related effects in water resources. Measures to reduce input of transformation products are difficult to adopt, as these products are of course formed only when the parent compound is degraded (as desired). In addition, they often exhibit higher mobility than the parent compound and are thus distributed relatively efficiently in surface and ground waters. It would therefore appear to be all the more important to take transformation products into account in the assessment of chemicals. While this is already the case for pesticides, such requirements and specific procedures have yet to be included in the assessment of industrial chemicals and pharmaceuticals. A key prerequisite for this is that models for the prediction of transformation products and for estimation of their environmental concentrations and effects should be further developed for implementation in practice.

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Co-authors: Renata Behra, Rik Eggen, Beat Fischer, Enrique Navarro and Holger Nestler

Interaction of multiple stressors

In natural waters, organisms are exposed to a mixture of chemicals and are also affected by other stressors such as temperature, ultraviolet radiation, parasites and pathogens. At Eawag, the risks associated with multiple stressors are being assessed using various methods, including analysis of altered protein expression patterns.

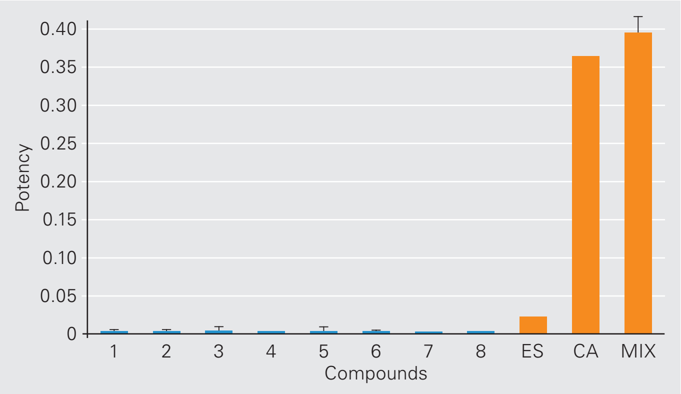
Aquatic organisms are adversely affected by a wide variety of chemical, physical and biological stressors, such as contaminants, increased temperature and ultraviolet radiation levels, parasites and pathogens. To date, the combined effects of all these stressors – with the possible exception of toxicity caused by chemical mixtures – have not been taken into account in risk assessment, which may lead to underestimation of the toxic effects of chemicals. For this reason, Eawag is currently developing methods that should help to improve risk assessment for multiple stressors.

Effect summation *versus* concentration addition. Classical toxicity tests determine the effects of high concentrations of individual substances on cell systems or model organisms under controlled laboratory conditions. The aim is generally to establish the concentration at which a response is observed in 50 % of the organisms (EC_{50}). For an environmental risk assessment, the EC_{50} is then extrapolated to the ecological level, i. e. the field system. Unfortunately, however, the situation encountered in the field is quite different. As a rule, we find lower concentrations of individual substances, but a large number of chemicals. In addition, this chronic exposure is not evenly distributed and constant, but subject to spatial and temporal variation. In order to assess such complex systems, one needs to understand how the individual chemicals act and what mixture effects are to be expected.

Figure 1 shows the estrogenicity of eight environmental hormones at low concentrations in a bioassay [1]. For each individual substance, the effect lies just above the detection limit and can be considered unproblematic. The potency remains low when the effects of the individual compounds are added together (effect summation, ES in Fig. 1). However, if a mixture is tested containing these eight substances in the same concentrations as before, the response observed is significantly higher than is predicted by effect summation (MIX in Fig. 1). This can be explained by the concept of concentration addition, i. e. the chemicals in combination act as a single substance. The effects of the mixture can therefore be calculated if the relative potency of the individual substances in the bioassay and their concentrations determined by chemical analysis are known (CA in Fig. 1). However, concentration addition is only applicable if all the components of a mixture have the same mode of action – in this case, activation of the estrogen receptor. If the various components have dissimilar modes of action, they have to be assessed individually, as their effects are independent of each other. The concepts of concentration addition and independent action have been little used in risk assessment to date.

Is dose addition also seen with multiple stressors? Exposure to chemicals is accompanied by other stressors, which will doubtless become even more important in the future on account of climatic and environmental changes – e. g. rising temperatures and increased exposure to ultraviolet radiation. As an example of the interplay of different factors, we can consider the production and toxic effects of reactive oxygen species (ROS) in photosynthetic organisms. These include free radicals such as the superoxide anion and the hydroxyl radical, excited singlet oxygen, and mo-

Fig. 1: The effects of eight estrogenic compounds (1–8) were determined individually. If these individual effects are added together, the resultant effect (ES = effect summation) is considerably lower than that observed when a mixture of the eight substances (MIX) is analysed in a bioassay. By contrast, the assumption of concentration addition (CA) yields an effect of similar potency (modified from [1]).



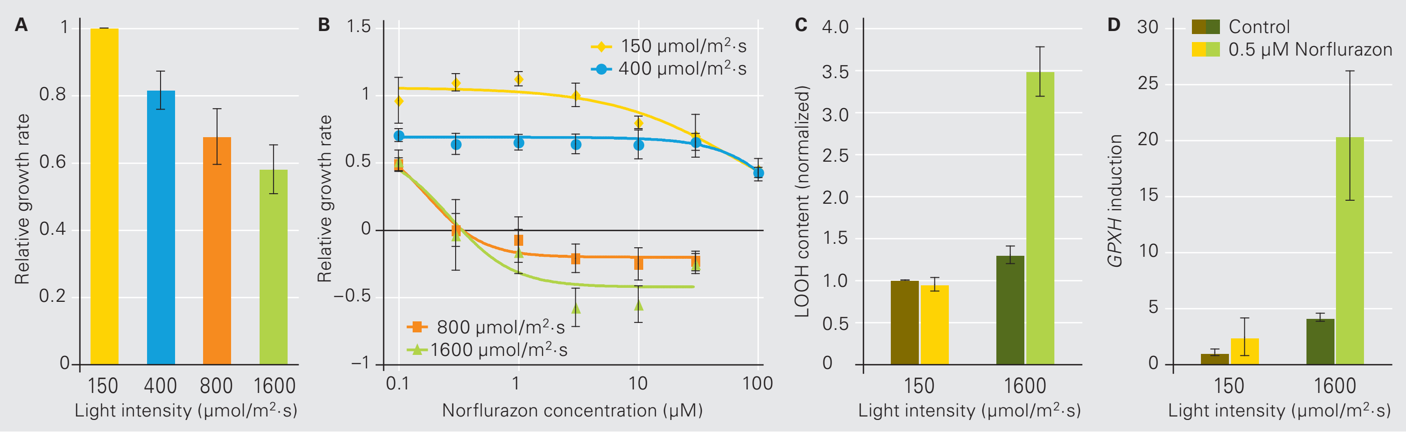
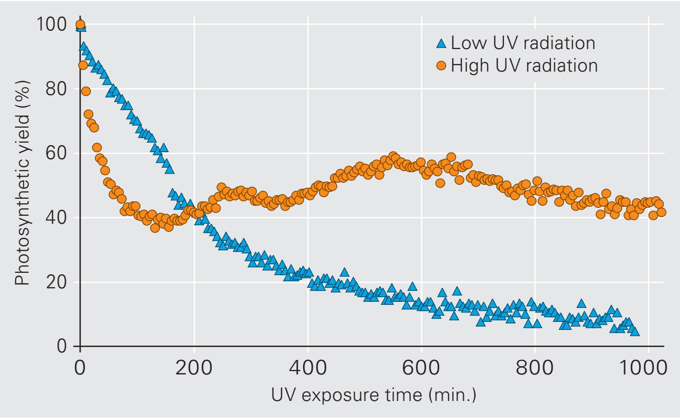


Fig. 2: (A) Effects of increasing light intensity on growth rate. (B) Effects of increasing light intensity and norflurazon concentration on growth rate. Growth rate 1 = cells grow normally; growth rate 0 = cells survive, but do not reproduce; negative growth rates = cells die. (C and D) Effects of high light intensity and norflurazon concentration on production of lipid peroxides (LOOH) and induction of the glutathione peroxidase homologous gene *(GPXH)* [2].

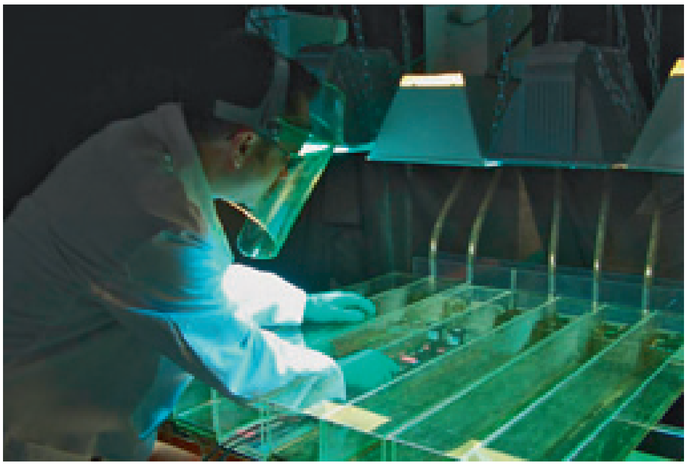
lecular oxidants such as hydrogen peroxide and ozone. They are produced in plants and algae in response both to contaminants and to physical stressors (e.g. ultraviolet radiation), and even in normal conditions, they are formed under high light intensities. In cells, the ROS not only reduce enzyme activity but also induce the formation of harmful lipid peroxides in the membranes – effects which may even lead to cell death. To protect themselves, plants have developed defence mechanisms. Firstly, they produce lipid-soluble carotenoids and tocopherols which dissipate excess energy, thereby inhibiting the generation of ROS. In addition, there are water-soluble antioxidants such as vitamin C and glutathione, which act as reducing agents, inactivating ROS either directly or as peroxidase cofactors. The two key questions arising are: What happens when plants experience additional stress, e.g. due to herbicides? And does the principle of dose addition still apply?

Figure 2 illustrates the influence of light in combination with the herbicide norflurazon on the green alga *Chlamydomonas reinhardtii* [2]. Norflurazon blocks the carotenoid biosynthesis, thus limiting the cell's ability to prevent increased generation of ROS. In Figure 2A, the first point to note is that at a high light intensity the algal growth rate is reduced to 50 %. This is due to the increasing concentration of ROS in the cell. When exposed to norflurazon as an additional stressor (Fig. 2B), the algae grow even more slowly, stop growing altogether, or may even die. At a high light intensity, even 0.5 µM norflurazon induces the production of lipid peroxides (LOOH, Fig. 2C), which impair membrane integrity. By contrast, under non-stressful light conditions, no effects on growth or LOOH production are observed at this concentration (Fig. 2B and C). Under high light intensity and in the presence of norflurazon, the ROS activate the glutathione peroxidase homologous gene *(GPXH)* (Fig. 2D), which serves as a biomarker for oxidative stress. Glutathione peroxidase helps to protect the membranes by reducing the production of lipid peroxides. Our findings thus indicate that only the combination of the two stressors produces a marked response – in a similar manner to concentration addition for chemical mixtures – and that the effects caused by multiple stressors can only be understood if the underlying modes of action are known.

Fig. 3: Photosynthetic yield of algal communities (periphyton) acclimatized for 71 days to high- or low-intensity ultraviolet radiation [3].



Acclimatization of periphyton to high-intensity ultraviolet radiation. If organisms or communities are acclimatized to a stressor, their behaviour when exposed to a second stressor with the same mode of action is different from that of non-acclimatized organisms or communities. Figure 3 offers a good example of tolerance acquired through exposure to ultraviolet radiation [3]. Periphyton, an algal community growing on a solid surface, was acclimatized to ultraviolet radiation of high intensity (high-elevation conditions) or low intensity (conditions typical of lowlands). After 71 days' acclimatization, the periphyton communities were then exposed to an even higher dose than is received in high mountain areas. It was found that in non-acclimatized periphyton the photosynthetic yield fell to below 10 %, while in the periphyton acclimatized to high-intensity ultraviolet radiation it initially declined and then stabilized at 40 – 50 %. Although all the species



Eawag researcher Enrique Navarro at the Plexiglas channels in which sessile algal communities (periphyton) are exposed to ultraviolet radiation.

in this periphyton community showed acclimatization to the higher level of exposure, not all were equally effective. The most sensitive species are eliminated and the resultant community as a whole shows higher tolerance.

Even more interesting is the finding that the algal community adapted to high ultraviolet radiation and is also more tolerant to cadmium. This is because cadmium also produces oxidative stress, which causes less damage in a community that is accustomed to ultraviolet radiation, as the defence mechanisms have already been activated. This result is likewise only explicable if one knows that ultraviolet radiation and cadmium have similar modes of action on the algal community.

Effects at protein level. Growth rate or photosynthetic yield are physiological endpoints which describe the overall state of an organism or a community, but allow little to be concluded about the underlying molecular mechanisms. For this purpose, it is more useful to analyse gene expressions and the resulting protein cascades or the metabolites formed. Unlike classical physiological endpoints, these methods permit a global analysis of the system, providing information on all the changes occurring in the cell and indicating modes of action. Using DNA microarrays, the effects of multiple stressors can thus be directly linked with expression profiles of thousands of genes, offering insights into the complex signalling pathways and defence strategies of an exposed organism. Global analyses of this kind have only been possible since methods became available which can generate vast amounts of data in a very short time.

Global analyses are now also possible at the protein level. Here, too, expression profiles from treated and untreated samples are compared in order to identify proteins that respond specifically to single or multiple stressors. For protein separation, as well as conventional two-dimensional gel electrophoresis, increasing use is being made of two-dimensional liquid chromatography coupled with mass spectrometry. The essential difference is that the extracted proteins are enzymatically digested prior to chromatographic separation and the amino acid sequence is determined by mass spectrometry.

In an experiment to determine protein expression, we treated the green alga *Chlamydomonas reinhardtii* with the herbicide paraquat. We showed that, together with many other proteins, significantly more superoxide dismutase was to be found in the paraquat-treated sample than in the untreated algae. This example illustrates how analysis of protein expression can provide information on the mode of action, as paraquat diverts electrons from photosystem I to oxygen, leading to the formation of superoxide. As well as superoxide dismutase, other proteins were identified which play a role in coping with stress – e.g. the thioredoxin-dependent peroxidase, or photosystem II components (D1 and D2 proteins). Global analysis of protein expression is thus a powerful tool for investigating modes of action and for identifying proteins that can serve as biomarkers of exposure.

Following the herbicide and ultraviolet radiation experiments, we now intend to analyse protein expression patterns after exposure to multiple stressors, in the hope of gaining deeper insights into toxicity mechanisms and the resulting stress response. This improved understanding, in combination with marker proteins indicating exposure to multiple stressors, will provide the basis for a more comprehensive risk assessment for water resources. ○ ○ ○

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Renata Behra, biochemist and head of the Algal Communities and Populations group in the Environmental Toxicology department.
Co-authors: Ralf Kägi, Enrique Navarro, Michael Burkhardt, Laura Sigg

Effects of engineered nanoparticles

As nanoparticles are already widely used, it was only too likely that they would ultimately find their way into the environment. This has now been demonstrated for the first time by Eawag studies – which also show how engineered nanoparticles can exert toxic effects on aquatic organisms.

Nanoparticles are found in increasing numbers of products, making it all the more likely that they will also be released into the aquatic environment. This may occur in the course of production, use or disposal, either directly (e. g. as a result of accidents) or via wastewater. Although the proportion of engineered nanoparticles in the environment remains low, compared with natural particles [1], there is still a need to assess the environmental risks. This calls not only for analytical systems to permit quantification but also for information on input pathways, amounts, and the fate and toxicity of engineered nanoparticles in natural waters. Initial studies describing the adverse effects of nanoparticles on aquatic organisms have now been published; overall, however, knowledge in this area is largely lacking. The situation is complicated by the existence of a very broad spectrum of engineered nanoparticles, differing in their chemical, physical and morphological properties (see Box "Engineered nanoparticles"). But precisely these properties need to be taken into account in efforts to understand how nanoparticles act on organisms, since they influence the bioavailability of particles and the mechanisms of toxicity. Eawag is therefore currently carrying out studies on the release and toxicity of engineered nanoparticles, and developing analytical methods for their characterization and detection in aquatic systems.

Titanium dioxide nanoparticles released from facades. It took almost 100 years for the detrimental effects of particles of a different type – asbestos fibres – to be finally recognized. Today, asbestos is banned in Switzerland, the EU and many other countries. To avoid a similar scenario arising with nanoparticles, it is essential to assess at an early stage the extent to which these particles are released. It is now generally agreed that nanoparticles do end up in the environment sooner or later, but this has not been specifically shown to date. However, such data are indispensable if we are to be able to predict future concentrations of nanoparticles in various environmental compartments (air, water, soil).

In an initial case study, the leaching of whitening pigments from facades was therefore investigated [3]. These engineered particles of titanium dioxide (TiO_2) are of various sizes, which can be described by a Gaussian distribution. On average, the TiO_2 particles measure about 150 nm (based on the total number), but approx. 10 % fall into the nanoparticle category (< 100 nm). Thanks to their spherical shape, the whitening pigments can be readily distinguished from natural (geogenic) TiO_2 particles. In the study, facades, facade runoff and urban stormwater runoff (discharged into receiving waters) were analysed for engineered TiO_2 nanoparticles. Figure 1A shows a new facade, in which indi-

Engineered nanoparticles

Engineered nanoparticles are nanotechnologically produced solid particles with a diameter of 100 nm or less (1 nanometre = a millionth of a millimetre), which take a wide variety of forms. They may consist of metals or metal oxides (inorganic, e. g. silver or titanium dioxide nanoparticles) or of carbon (organic nanoparticles). They can vary in shape (tubes, spheres, disks, fibres) and surface properties (untreated or chemically modified). Depending on the conditions, they can occur as individual particles or as aggregates in suspension. The artificial particles exhibit novel mechanical, electronic, chemical or optical properties, which are due to their high surface-to-volume ratio and make them ideally suited for various scientific, medical, industrial and commercial applications. Over 800 nanotech products are already available on the market. These include, for example, water-repellent textiles, ultraviolet-absorbing sunscreens, and antibacterial cosmetics, deodorants and toothpastes, as well as paints and varnishes that give surfaces a self-cleaning, antimicrobial or scratch-resistant coating. One of the most widely used nanomaterials is silver [2]. Often, however, it is not known whether products contain silver in the form of a salt (e. g. silver nitrate or silver chloride) or as engineered silver nanoparticles.

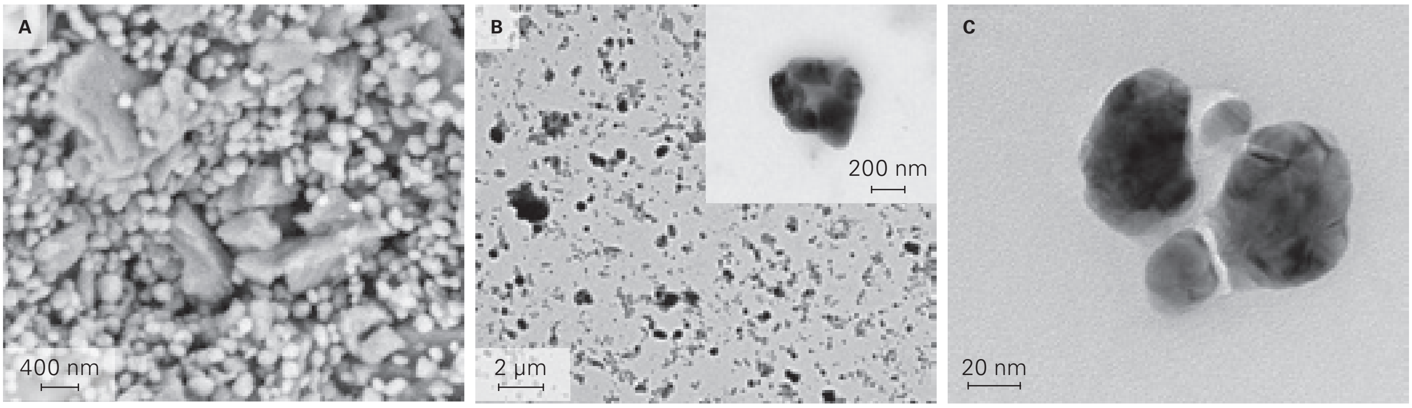

Fig. 1: Titanium dioxide nanoparticles in a facade (A), in facade runoff (B) and in urban stormwater runoff discharged into receiving waters (C).

vidual TiO_2 particles are clearly recognizable as bright spots. Very similar particles were also found in the facade runoff (Fig. 1B). Particles of the same size and shape were likewise detected in the urban runoff (Fig. 1C), which suggests that they mainly originate from the facades. From an (eco-)toxicological viewpoint, whitening pigments do not raise significant concerns, but they are well-suited as a model substance for evaluating the transport of nanoparticles from urban areas to the aquatic environment. It can be assumed that other nanoparticles will behave in a similar way to TiO_2 particles.

Silver nanoparticles from facades also found in water. Far more critical, in terms of ecotoxicology, is the case of engineered silver nanoparticles (see Box "Ecotoxicity of silver"), which are also used, for example, in facade paints. Engineered silver nanoparticles consist of metallic, uncharged silver atoms, although the particle surfaces may also be modified by inorganic or organic substances. As a result, they obtain a positive or negative charge, which prevents aggregation of the particles. The leaching of engineered silver nanoparticles from a facade was initially investigated in a simulation chamber, in which the facade was exposed to rain and sunlight under controlled conditions. Microscopic analysis of the facade runoff indicated that silver nanoparticles 5–10 nm in size are indeed leached from the facade. Alongside the chamber experiments, the same paint on a model house was exposed to natural weathering. Interestingly, the initial results show that silver nanoparticles are released from the model house in even larger quantities – even though the conditions in the simulation chamber are considerably harsher and much more water was used. It is thus clear that silver nanoparticles, like TiO_2 particles, can enter natural waters. But what are the effects of silver nanoparticles in the aquatic environment?

Toxicity of silver nanoparticles partly due to silver ions. Another case study was carried out to investigate the effects of engineered silver nanoparticles on the photoengineered activity of the model green alga *Chlamydomonas reinhardtii* [4]. For this purpose, we used a suspension of metallic, carbonate-coated silver particles with an average size of 25 nm (Fig. 2). Because the metallic silver particles are produced from silver ions (Ag^+), a small residue of silver ions (in our case around 1 %) is always present in suspensions of this kind. In our ecotoxicology experiments, we aimed to find out whether the particle suspension has toxic effects on photosynthesis and, if so, whether the toxicity is caused by the silver ions (see Box "Ecotoxicity of silver") or by the nanoparticles themselves.

The algae were exposed to the suspension of silver nanoparticles for 1 or 2 hours. In addition, to compare the effects of the particles directly with those of silver ions, experiments were performed with a silver nitrate solution. It was found that algal photosynthesis is increasingly inhibited as total silver concentrations rise, and that silver nitrate is more toxic than the silver

Ecotoxicity of silver

Silver (Ag) has long been known to have antimicrobial effects: in the 19th century the metal was already used as an antibiotic, and it was recognized even earlier that drinking water keeps better in silver vessels. The use of silver as a disinfectant is based on the fact that it is toxic to a broad spectrum of bacteria and has relatively low toxicity to humans. For various aquatic organisms, silver is also among the most toxic metals. It is persistent and at relatively high concentrations in water, it can accumulate both in sediments and in organisms. As for other metals, the toxicity of silver is dependent on the bioavailability of silver ions (Ag^+), which is influenced in turn by the chemical composition of the experimental medium, or water. The toxic effects of silver ions can be reduced by the presence of complexing agents, but at the same time the toxicity of silver is essentially based precisely on its strong affinity for sulfhydryl, amino and phosphate groups, which leads in organisms to the formation of complexes with various biomolecules.

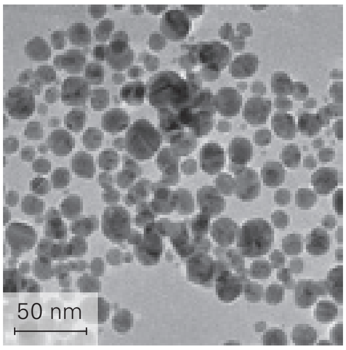

Fig. 2: Transmission electron micrograph of the engineered silver nanoparticles used in our study.

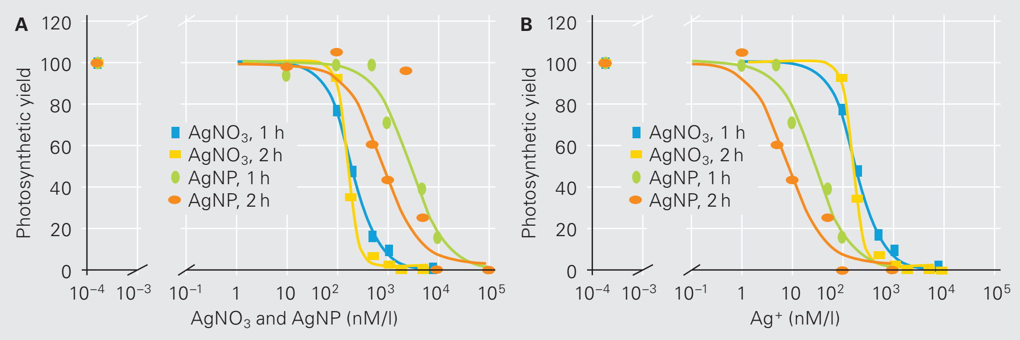

Fig. 3: Toxic effects of silver nanoparticles (NP) and a silver nitrate solution on photosynthetic activity in the green alga *Chlamydomonas reinhardtii* plotted as a function of the total (= metallic + ionic) silver concentration (A) and the silver ion concentration alone (B).

nanoparticles (Fig. 3A). To separate the effects of the particles from those of the silver ions, the experiments were repeated in the presence of cysteine. This amino acid forms strong complexes with silver ions, so that the ions are subsequently no longer available to the algae. In this case, the toxic effects of the silver nanoparticle suspension were completely abolished in the presence of an excess of cysteine – i. e. the toxicity of the particle suspension must be based on the effects of the silver ions.

Surprisingly, if the toxicity of the nanoparticles and silver nitrate is plotted as a function of the silver ion concentration (Fig. 3B), it becomes apparent that silver nanoparticles are more toxic than silver nitrate. However, this effect cannot be wholly explained by the silver ions present in the particle suspension, as the concentration is too low. Other processes must also be involved. One logical explanation is that, through contact with the algae, the silver nanoparticles release larger quantities of silver ions. As we studied toxicity solely in terms of photosynthetic activity, we cannot exclude the possibility that nanoparticles also enter the algae, triggering additional toxic mechanisms. We are currently investigating this hypothesis, and provisional findings indicate that silver nanoparticles are indeed taken up by algal cells.

Research under real conditions: the experimental house used to determine the release of nanoparticles from facades.

Environmental releases of nanoparticles to be avoided! Our findings confirm that nanoparticles are released into the environment, and that the associated ecotoxicological risks are not to be underestimated. This applies not only for aquatic but also for terrestrial systems. Further studies are required, also covering other nanomaterials. In addition, standard methods need to be developed for the detection of nanoparticles and for the assessment of toxicity (cf. the article on the Ecotox Centre on p. 38).

Manufacturers should commit themselves to sensible use of nanoparticles. It is also important to educate consumers – firstly, through consistent labelling (at present, the composition of products is frequently unclear) and specific instructions on handling, and also by informing consumer associations about potential health and environmental risks. The priority goal should be to prevent nanoparticles spreading in the environment.

We are grateful to our Eawag colleagues N. Odzak, F. Piccapietra, I. Szivak and B. Wagner.

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Eliminating micropollutants: wastewater treatment methods

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In many cases, micropollutants are only partly eliminated at wastewater treatment plants. The remaining fraction, together with any transformation products, enters receiving waters with the treated effluents. What options can modern process engineering offer to improve elimination performance?

In recent years, organic micropollutants such as pharmaceutical residues or hormones have been detected in various lakes and rivers in Switzerland [1]. They mainly enter surface waters via domestic wastewater and – not surprisingly – wastewater treatment plant (WWTP) effluents have been identified as the main source of these substances. This is because existing treatment plants were not designed to eliminate substances of this kind, but to reduce input of solids, organic material and nutrients. Even so, modern treatment plants remove a large proportion of micropollutants, either by means of sorption to activated sludge or by biological degradation/transformation [2]. However, residual contamination with pharmaceuticals, hormones or other micropollutants can still cause problems in aquatic ecosystems. One way of minimizing input of organic micropollutants to surface waters is to integrate an additional treatment step at WWTPs.

What options are available? An additional process that can be used to upgrade treatment plants needs to meet various requirements:

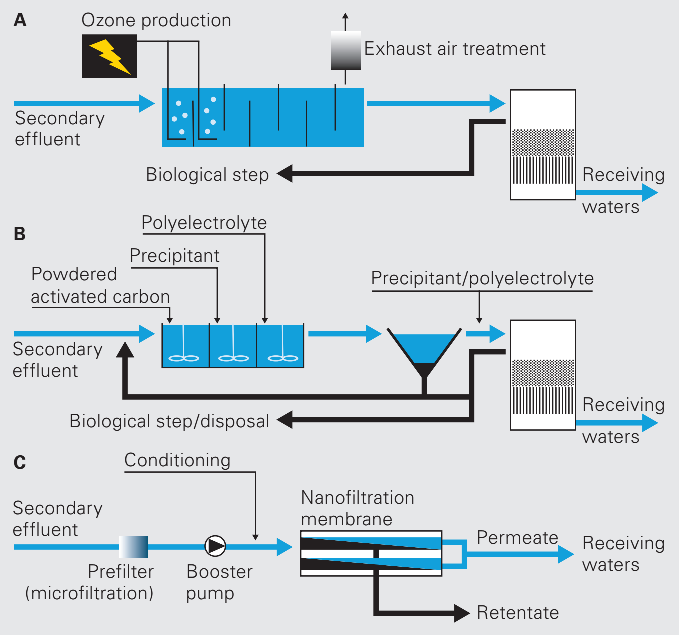
- Broad spectrum of action: it must be possible for a wide range of problematic substances to be largely eliminated.
- No problematic by-products: the formation of toxic or otherwise problematic products in the additional step must be avoided.
- Ease of use: it must be straightforward to operate and should not call for specialist staff.
- Cost/benefit ratio: the use of resources (materials, energy, staff, costs) must be reasonable and provide appropriate benefits.

In fact, a number of existing methods make it possible to eliminate micropollutants effectively. Some of these are already used in the treatment of drinking water, although the requirements differ markedly in the case of wastewater treatment:

- Background contamination: the concentration of organic substances in treated wastewater is around 5–50 times higher than in drinking water. Micropollutants account for less than 1 % of this total – i.e. more than 99 % consists of "harmless", natural substances. At the same time, these natural substances influence the effectiveness of the methods under consideration, thus often leading to reduced efficiency and increased costs.
- Inflow variation: both the volumes of wastewater to be treated and the composition can vary significantly (by a factor of 10). The process in question has to be able to respond appropriately to such fluctuations.

When all these aspects are taken into account, three methods emerge as suitable candidates for advanced wastewater treatment – ozonation, powdered activated carbon adsorption and "dense membrane" technologies (especially nanofiltration).

Fig. 1: Schematic flow charts for the ozonation (A), powdered activated carbon adsorption (B) and nanofiltration (C) processes. Other options are available (in particular for activated carbon).



These methods are being investigated more closely, from different perspectives, in various departments of Eawag.

Ozonation: feasible at a large scale. As part of the "MicroPoll strategy" project, Eawag has been closely involved in studying large-scale ozonation of treated wastewater at the Regensdorf plant [3]. Ozone has a strong oxidizing action – i. e. many substances are attacked and transformed by this agent. Since ozone is highly unstable, it has to be generated at the site of application – in an energy–intensive process – from dry air or from liquid oxygen. It is added in gaseous form to the wastewater stream, and sufficient time must then be available for it to react with the wastewater constituents (Fig. 1A). The amount of ozone required depends on various parameters, such as the level of background dissolved organic matter and wastewater pH and alkalinity, as well as the desired elimination performance (see the article by Juliane Hollender on p. 28). The concentration of many organic micropollutants is substantially reduced even with relatively low doses of ozone (see Fig. 1 on p. 29).

One problem with ozonation is that in general the target compounds are not fully mineralized, but merely transformed, and so even more harmful substances may be produced as a result. Accordingly, experience at Regensdorf indicated that after ozonation an additional step is required – e. g. sand filtration – to break down reactive oxidation products.

However, as well as removing micropollutants, ozone reduces not only the microbial count but also odour, colour and foam. Because ozone is a potent irritant, safety measures are also required to protect staff in the event of malfunctions. In the Regensdorf pilot study, however, it was shown that the application of ozonation at a WWTP is technically and operationally feasible. At the same time, it is associated with increases of around 10 – 20 % in both energy consumption and costs, although these figures depend on various factors, including the size of the plant (cf. Table).

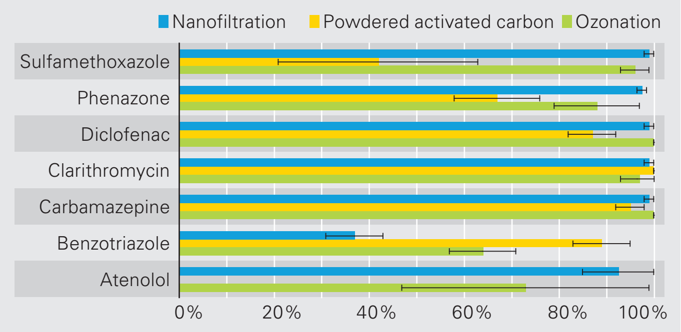


Fig. 2: Elimination rates for selected micropollutants with the three processes. The data, collected by Eawag, are applicable for the following operating conditions: ozonation – dose 0.6 g O_3 per gram dissolved organic carbon (Regensdorf); powdered activated carbon – dose 10 mg PAC per litre (Eawag pilot plant); nanofiltration – Dow Filmtec NF90 membrane operated at 5 bar (Eawag pilot plant).

Powdered activated carbon adsorption: effective, but slow. Treatment with powdered activated carbon (PAC) is being studied – also as part of the "MicroPoll strategy" project – in small-scale pilot plants at Eawag. In this process, PAC (particle diameter 10 – 50 µm) is added to the wastewater. Thanks to the huge surface area (1000 m^2/g) and other specific chemical properties (e. g. charge, arrangement of molecules), many substances adsorb onto the particles. Activated carbon adsorption is a highly promising method for the removal of numerous micropollutants (Fig. 2): elimination rates of more than 80 % are achieved for many (but not all) substances in treated wastewater with a dose of 10 – 20 mg PAC per litre. In contrast to ozonation, activated carbon adsorption is a slow process. For many substances, equilibrium concentrations are only attained after several hours. One way of accelerating and optimizing the adsorption process is to circulate the carbon so that – as with activated sludge – it remains in the system longer than the water (Fig. 1B). The general difficulty with PAC treatment lies in separating the carbon from the water. Various options are available: it can be done either via sedimentation, which necessitates the use of precipitants, or via (membrane) filtration, which requires additional energy. With sedimentation, a downstream sand filter is needed to retain carbon that has not been removed. The used carbon is then incinerated, and the sorbed organic substances are thus completely mineralized.

Another way of improving the effectiveness of activated carbon adsorption would be to recycle the carbon to the biological step of the treatment plant. As activated carbon is normally only used after the biological step – i. e. when concentrations of contaminants are already very low – its surface is only partly loaded and its full purification potential is not effectively exploited. When carbon is recycled to the biological step, where contaminant concentrations are higher, additional loading occurs. This approach is currently being investigated at Eawag, but it is not yet clear whether activated carbon will adversely affect degradation proc-

Overview of energy consumption and costs for downstream ozonation or PAC adsorption. The values include sand filtration except otherwise noted. Primary energy represents total energy consumption, including production and transport of the agents required (oxygen, PAC). The costs are given for small (< 15,000 PE = population equivalents) and large (> 100,000 PE) wastewater treatment plants (WWTP) and comprise investment and operating costs [4].

	Unit	**Ozonation**	**PAC**
Additional energy consumption WWTP (without sand filtration)	kWh/m^3	0.05–0.15	< 0.005
Additional energy consumption WWTP	kWh/m^3	0.1–0.2	0.05
Increase in energy consumption WWTP	%	20–50	10–20
Primary energy	kWh/m^3	0.3–0.5	0.4–0.7
Costs small WWTP < 15,000 PE	CHF/m^3	0.32–0.36*	0.42–0.47*
Costs small WWTP < 15,000 PE	CHF/PE/a	32–36	42–47
Costs large WWTP > 100,000 PE	CHF/m^3	0.09–0.11*	0.15 – 0.20
Costs large WWTP > 100,000 PE	CHF/PE/a	10 – 15	15 – 20

*Average wastewater volume per PE: 100 m^3 per year.

esses in activated sludge and whether a significant benefit can be achieved. With this set-up, the carbon would be continuously removed from the system with the activated sludge.

The additional energy required for activated carbon adsorption at the treatment plant is low. However, as the production of activated carbon is highly energy-intensive, primary energy consumption is higher than with ozonation (Table). The costs are also estimated to be slightly higher than for ozonation and are largely dependent on the costs of powdered activated carbon (likely to rise sharply in the future).

Dense membranes: an option for water-stressed areas. Dense membranes (as used in nanofiltration and reverse osmosis) are made of a material that is much more permeable to water than to dissolved substances, while particles are fully retained. At an operating pressure of 5–40 bar, relatively pure water can thus be obtained from feed water rich in dissolved substances and particles (Fig. 1C). After biological treatment, the wastewater generally has to be prefiltered (microfiltration) and the pressure boosted before it passes through the filter modules. The water is circulated several times so as to increase the flow rate across the membrane, wash away deposits and thus slow down the formation of a cake layer. Depending on the composition of the wastewater and the type of membrane, conditioning – i.e. the addition of chemicals – will also be needed to prevent precipitation and membrane fouling. Even so, membranes will require regular chemical cleaning.

The concentrate held back by the membrane is known as the retentate, while the treated water is known as the permeate. The yield, i.e. the permeate/wastewater ratio, typically lies between 75 % and 80 %. Consequently, between 20 % and 25 % of the wastewater – in the form of contaminated retentate – has to be further treated and disposed of. In addition, both the energy requirements (due to the high operating pressure) and the costs are substantially higher than with ozonation or PAC adsorption. The energy required is estimated at 1–2 kWh/m^3. Given the energy and cost considerations and the lack of disposal options for the retentate, dense membrane technologies do not appear to be suitable for municipal wastewater treatment in Switzerland. However, in areas of water scarcity, where drinking water is to be prepared directly or indirectly from treated wastewater, these technologies – especially nanofiltration – are certainly an option to be considered.

Additional treatment steps: important, but not sufficient. If input of organic micropollutants from municipal wastewater to surface waters are to be reduced in Switzerland, ozonation and PAC adsorption are particularly suitable options. They make it possible to remove a substantial proportion of these contaminants. While ozonation performs somewhat better in terms of costs, the micropollutants are merely transformed rather than being fully retained. With the PAC process, the substances end up bound to the surface of the carbon. The residual carbon (together with the residual sludge) then has to be dewatered, dried and incinerated. With regard to energy consumption, the two methods are comparable, although in the case of ozonation the energy requirement mainly arises at the treatment plant itself, whereas large amounts of energy are required for the production of powdered activated carbon. In the current state of knowledge, the two processes are thus about equally well suited.

However, treatment plants are not the only sources of micropollutants from urban drainage systems. These substances also enter natural waters via surface runoff, combined sewer overflows or leaking sewers. Input pathways also include agriculture, industrial emissions and other diffuse sources (see the article by Irene Wittmer on p. 8). Input of micropollutants to surface waters can be substantially reduced, but not wholly eliminated, by means of additional treatment steps at WWTPs. The problem of micropollutants in Swiss waters, therefore, cannot be solved – even if it is considerably alleviated – merely by adopting end-of-pipe measures. At-source measures (e.g. replacement of critical chemicals, reduced consumption) should continue to be pursued as the top priority.

We are grateful to Marc Böhler and Bettina Sterkele (Process Engineering) and to Michael Schärer (FOEN).

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Eliminating micropollutants: efficiency assessment

Various ways of upgrading wastewater treatment plants so as to enhance the elimination of micropollutants are currently being considered. But what chemical and biological indicators can be used to evaluate the effectiveness of additional treatment steps?

To eliminate micropollutants at wastewater treatment plants (WWTPs), it is not sufficient merely to install appropriate systems (see the article by Christian Abegglen on p. 25) – their effectiveness and any shortcomings need to be assessed in order to optimize the processes. In the case of WWTPs, it is necessary to define chemical and biological measurement methods that can be used to evaluate the efficiency of the additional treatment steps. To date, individual substances or selected biological effects have been measured in a relatively arbitrary manner. Our aim, therefore, was to propose a set of general, cost-efficient methods of evaluation providing meaningful results for future assessments of treatment performance. Our work was carried out as part of a pilot study on ozonation with subsequent sand filtration at the Wüeri WWTP in Regensdorf [1]. At the same time, our study was designed to estimate the elimination efficiency of the additional ozonation step.

Parameters determined in the ozonation pilot study at the Wüeri WWTP in Regensdorf.

Parameters	Test substances/assays	Function/indicator substances/toxicity endpoints
General WWTP parameters	Chemical and biological oxygen demand, undissolved substances, DOC, nitrogen species	WTTP characterization
Micropollutants	▶ 53 substances with continuous input	Pharmaceuticals, biocides
	▶ Biologically active substances	Estrogens (estrone)
	▶ Additional 180 substances	Broad spectrum
	▶ Reaction products of ozonation	Nitrosamines, bromate
Toxicity (mode of action-based assays)	▶ Bioluminescence assay	Non-specific toxicity
	▶ Combined algal assay	Non-specific (growth inhibition) and specific (photosynthesis inhibition) toxicity
	▶ Yeast estrogen screen	Estrogenic effects
	▶ Acetylcholinesterase inhibition	Neurotoxic effects
	▶ umuC assay	Genotoxic effects

Broad range of parameters. In defining the parameters to be assessed, the approach we adopted was to start with a broad range of measurements and then narrow these down for future assessments on the basis of the experience accumulated (Table). As well as general WWTP parameters, therefore, we determined firstly the concentrations of a wide variety of micropollutants, e.g. pharmaceuticals and biocides, which enter the WWTP continuously in wastewater and whose loads are influenced by the newly installed treatment processes. We also investigated the formation of two known by-products of ozonation – nitrosamines and bromate. Secondly, we used various bioassays to determine the general and specific toxicity of the micropollutants contained in the water [2–3]. This makes it possible not only to gain an impression of how overall contamination with micropollutants is reduced, but also to identify specific, particularly problematic effects, such as estrogenicity, neurotoxicity and genotoxicity.

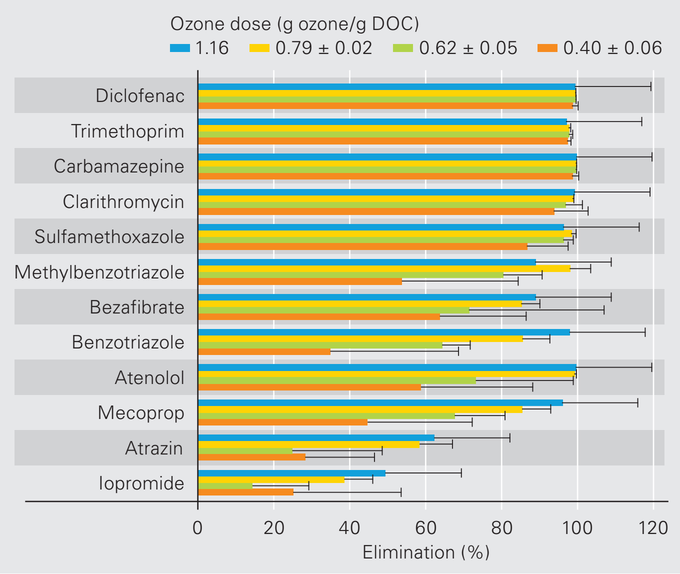
Reduction of micropollutants in the Furtbach due to ozonation. Initially, we studied a total of 53 indicator substances. On account of their polarity, these are mainly found in the aqueous phase, they are highly persistent in the WWTP and in some cases they have been shown to be biologically active. Substances were selected which are oxidized by ozone at different rates, owing to their different functional groups. The degree of oxidation depends on the reactivity of a substance with ozone and on the ozone dose (Fig. 1) which is available for oxidation and does not react with other constituents of wastewater. As well as ozone itself, continuously generated OH radicals play an important role as oxidizing agents. They are less specific oxidants than ozone and generally exhibit very high rate constants for reactions with micropollutants. Accordingly, in spite of their short lifetime and low concentrations, they can contribute markedly to the oxidation of a micropollutant. This applies in particular to micropollutants that lack a high degree of reactivity with the highly selective ozone.

The intermediate ozone dose (0.6 g O_3 per gram dissolved organic carbon (DOC)) leads to a significant reduction in the number of substances detected above the limit of quantification in the WWTP effluent. Only 16 of the 53 substances studied were found in concentrations of more than 15 ng/l. In the case of substances which are more recalcitrant to ozone (e. g. mecoprop, benzotriazole and atenolol), concentrations were clearly reduced. The antibiotics investigated were eliminated completely, but contrast agents only partly. After the biological step, estrogens only occur in concentrations below 6 ng/l and were completely eliminated with the intermediate ozone dose (detection limit 0.1–2.5 ng/l). This is in agreement with the ecotoxicological analysis based on the yeast estrogen screen (YES), which indicates a substantial reduction of estrogenic activity (see below).

In order to gain an overview of the behaviour of an even broader spectrum of micropollutants during ozonation, screening – using high-resolution mass spectrometry – was expanded to cover approximately 180 additional substances. The range of compounds studied comprises of pesticides, pesticide transformation products, biocides, anticorrosive agents, pharmaceuticals and their metabolites, and food additives – all substances that are used in relatively large quantities in Switzerland or the EU and thus potentially to be found in the environment.

Of the 180 substances, 25 were detected in concentrations of more than 15 ng/l in the secondary effluent, but most of these were effectively eliminated in the course of ozonation with the intermediate ozone dose. Among the substances less well removed were the artificial sweetener sucralose and the antiepileptic drug levetiracetam.

Fig. 1: Influence of ozone dose on the elimination of selected persistent micropollutants in the ozonation step.



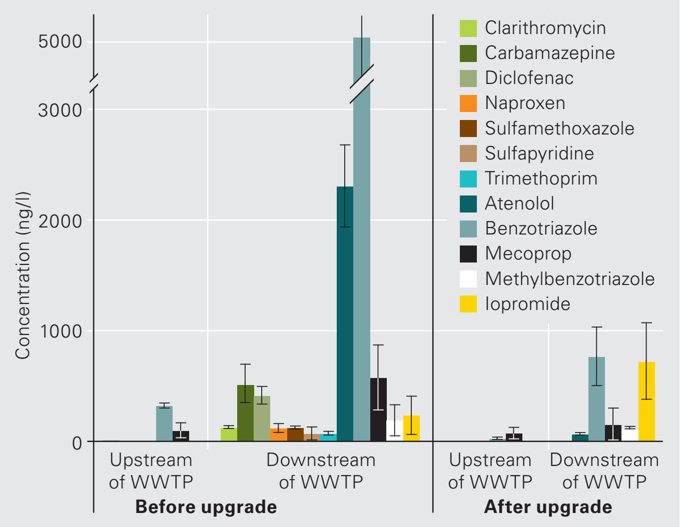


Fig. 2: Comparison of dry-weather water quality in the Furtbach upstream and downstream of the WWTP before and after installation of the ozonation system. The dose applied in the ozonation step was 0.62 ± 0.05 g ozone per gram DOC.

The additional treatment step thus substantially improves water quality in the Furtbach stream (Fig. 2). As a result of ozonation, input of micropollutants to the Furtbach from the WWTP are reduced by 70 %. The total reduction in input of micropollutants to the stream amounts to 27 kg per year, with benzotriazole accounting for 7.5 kg, atenolol 2.6 kg, diclofenac 2.4 kg, mecoprop 1.3 kg and carbamazepine 1.1 kg.

Nitrosamines and bromate: problematic by-products of ozonation? It is known that, during the ozonation process, carcinogenic nitrosamines can be formed from organic nitrogen compounds, and bromate from bromide. For this reason, concentrations of eight nitroso compounds over time were studied at the WWTP. Of the nitrosamines measured, three were not found above the detection limit of approx. 1 ng/l, while the rest were detected in the low nanogram-per-litre range. Significant quantities of NDMA (5–15 ng/l) are formed during ozonation, but on average 50 % is eliminated again in the subsequent sand filtration step.

As yet, no generally accepted limits exist for nitrosamines in surface, ground or drinking water. Based on toxicology data, the concentration of NDMA in drinking water associated with a lifetime cancer risk of one in one million is 0.7 ng/l (EPA, IRIS database). At the same time, however, depending on food composition, significant amounts of nitrosamines can also be formed in the body and excreted in urine [4].

Concentrations of bromide in wastewater at the Wüeri treatment plant were found to be typical of municipal wastewater – under dry weather conditions, ≤30 µg/l after the ozone step. Samples collected at various points in the ozone reactor showed that even with an ozone dose of 1.2 g O_3 per gram DOC the limit of 10 µg/l specified for bromate in drinking water is not exceeded.

In conclusion, it can be said that both nitrosamines and bromate are formed during the ozonation of municipal waste-

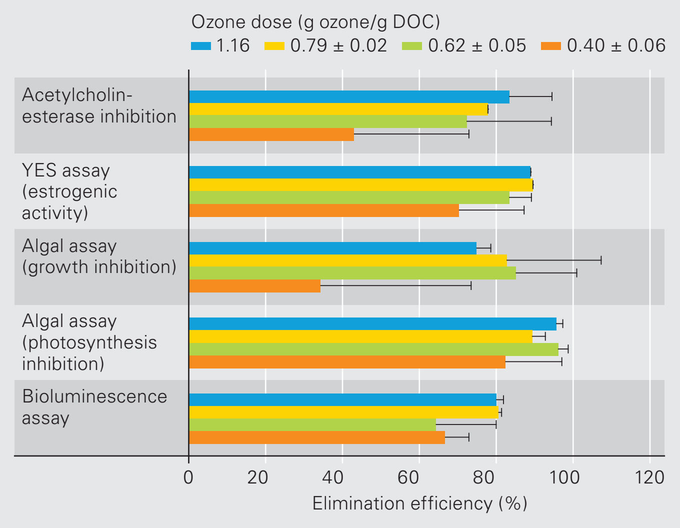


Fig. 3: Elimination efficiency of ozonation (including sand filtration), as determined by various mode of action-based test systems.

water. However, the concentrations of these problematic products are very low and thus do not raise any concerns; nonetheless, they should be assessed again for wastewater of different composition.

Toxicity reduced by ozonation. The fact that ozonation including sand filtration improves the treatment performance of the WWTP is also demonstrated by the toxicity tests (Fig. 3) [2–3]. As the ozone dose increases, the toxicity of the water studied is reduced. Thus, with the bioluminescence and the algal growth inhibition tests, non-specific toxicity was found to decrease by 40 – 80 %. In addition, specific toxic effects are also reduced: inhibition of photosynthesis (combined algal assay) – as induced by atrazine, for example – is reduced by 70 – 90 %, and neurotoxicity (acetylcholinesterase inhibition) – caused by insecticides such as diazinon – decreases by 60 – 80 %.

Before ozonation, the YES assay indicates concentrations of over 1 ng/l estradiol equivalents in water – a level proposed as a mode of action and bioassay-based limit for estrogenicity. Ozonation reduced the estrogenic effects by more than 95 %, which correlates well with the results of trace analysis. It would even be worth considering whether costly trace analysis for estrogenic substances cannot be replaced by a sensitive and inexpensive bioassay procedure.

All the samples from the primary clarifier showed marked genotoxicity, although the samples had to be highly concentrated. While this effect is already reduced in the biological step, it only disappears almost completely after ozonation. This also shows that ozonation does not lead to the formation of significant amounts of genotoxic substances.

As well as these test batteries focusing on micropollutants, the University of Frankfurt carried out tests involving aquatic organisms as part of the EU project Neptune. In rainbow trout and annelids, adverse effects on development, reproduction and biomass production were observed after ozonation; however, these disappeared after subsequent sand filtration. Ozonation should therefore always be followed by a sand filtration step as an additional barrier [1].

Future evaluation: trace analysis for selected substances combined with toxicity tests. The installation of the ozonation system enhanced the reduction of organic micropollutant concentrations and effects in WWTP effluents. Even an ozone dose of 0.6 g O_3 per gram DOC (approx. 3 mg/l) increased the elimination efficiency of the WWTP for the broad range of substances investigated by an average of 40 – 50 %. As a result, toxicity detected with the aid of bioassays was also reduced.

While screening for more than 200 substances was worthwhile and relevant in the context of this research project, it would generally be too costly for monitoring purposes. Based on consumption data, the properties of micropollutants and their behaviour in the various WWTP treatment steps, a subset of six substances was selected for integration into future assessment efforts – i. e. carbamazepine, diclofenac, sulfamethoxazole, benzotriazole, mecoprop and estrone. These substances are particularly suitable for the evaluation of additional measures such as ozonation and powdered activated carbon adsorption.

Although the results of trace analysis often correlated well with less costly mode of action-based bioassays, chemical analysis remains indispensable. It makes it possible to calculate reductions in pollutant loads – values that could subsequently be relevant for the specification of legal requirements. To gain a better overall evaluation and ensure that substances with significant effects are not overlooked, selected bioassays should be used in combination with trace analysis for the assessment of effectiveness. ○ ○ ○

We are grateful to C. Abegglen, N. Bramaz, S. Zimmermann, C. Götz, S. Koepke, M. Krauss, C. McArdell, C. Ort, H. Siegrist, H. Singer, R. Schöneberger, M. Suter, U. von Gunten (Eawag) and to M. Schärer (FOEN) for the fruitful cooperation in the MicroPoll project.

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Evaluation of surface waters in Switzerland and Europe

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Micropollutants pose growing challenges for water protection both nationally and internationally. As part of the FOEN's "MicroPoll Strategy" project, the contamination of surface waters was analysed. Based on the findings of this study, an evaluation concept is currently being elaborated in Switzerland, taking account of ongoing developments in the European Union.

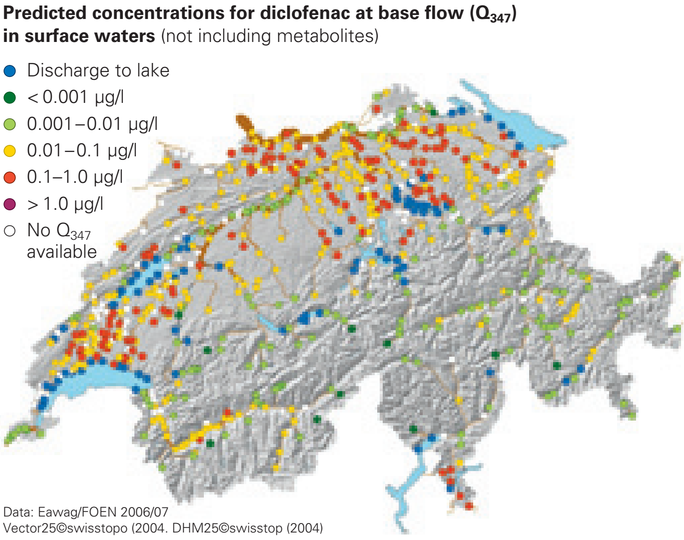
Input of organic micropollutants such as endocrine disruptors, biocides and pharmaceuticals via urban drainage systems is an emerging challenge for water protection. The widespread detection of such pollutants in surface waters suggests that, in its current form, existing legislation concerning the supply and use of substances is insufficient and is only suitable for regulating individual compounds and groups of compounds. In addition, certain agents (e. g. medicines) are indispensable or can hardly be prohibited. In future, it is likely that the number of substances used in products will increase further, and that the quantities of medicines and personal care products consumed will rise as a result of the ageing population. The question thus arises how urban wastewater management can be optimized to ensure long-term protection of natural waters. In order to define appropriate, targeted measures for improving wastewater management, suitable methods of evaluating surface waters are required. To this end, various efforts are under way both in Switzerland and in Europe.

Analysis of the situation. No systematic overview exists on the input, the occurrence or the behaviour of organic micropollutants in Swiss surface waters. As part of the FOEN "MicroPoll Strategy" project, an analysis of the current situation was therefore carried out, focusing on organic micropollutants from wastewater treatment plants (for more information on the project, see [1]). An overview of the presence of micropollutants in surface waters provides an important basis for the assessment of possible risks and for the definition of measures.

To this end, a database was established, incorporating the results of various measurement campaigns conducted by cantonal water protection agencies, research institutes and other institutions. This collection of data showed that a large number of organic micropollutants can be detected in the nanogram- to microgram-per-litre range in Swiss surface waters. The database currently contains a total of over 13,000 measurements of micropollutants. In particular, the substances concerned are persistent and relatively mobile in water, and mainly belong to the following groups: corrosion inhibitors, endocrine disruptors, plant protection products, biocides and pharmaceuticals. Many of these substances are not included in international lists drawn up under the EU Water Framework Directive (e. g. priority substances) or compiled by international water protection commissions. They can thus be classified as emerging pollutants.

Despite the large number of measurements recorded, the database provides only a temporally and geographically limited picture of the contamination situation. Systematic long-term monitoring would be required at numerous surface water sites, which is not currently available for organic micropollutants. Therefore, an additional model-based analysis was carried out in order

Fig. 1: Risk potential in Swiss surface waters illustrated by the example of the anti-inflammatory agent diclofenac. The relevant water quality criterion (based on ecotoxicity) is 0.1 µg per litre [2].



Data: Eawag/FOEN 2006/07
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to permit a reliable and rapid nationwide evaluation of Swiss surface waters. A mass flux model was developed [3], which can be verified using the available measurement data. Predicted concentrations in rivers were calculated for various substances, such as the anti-inflammatory agent diclofenac (Fig. 1). It is apparent that in small and medium-sized watercourses of the Swiss Plateau – especially when discharged effluents are not sufficiently diluted – predicted concentrations can reach a level that can lead to adverse effects on aquatic organisms. Similar findings were also described for natural and synthetic estrogens in National Research Programme (NRP) 50 "Endocrine Disruptors" [4]. The results of the model calculations were confirmed by the measured data in the database and by an additional measurement campaign in Swiss rivers.

Furthermore, it was also possible to illustrate the accumulation of persistent compounds from municipal wastewater in receiving waters with the mass flux model. Via bank infiltration, such substances may enter groundwater used as a drinking water resource. Although the concentrations of micropollutants in drinking water resources do not currently pose a risk to public health, there is a need to consider measures for reasons of precautionary consumer protection. As Europe's "water tower", Switzerland also has a special responsibility towards downstream riparian states. Every day, micropollutants are "exported" to neighbouring countries in treated wastewater (Fig. 2).

The analysis of the current situation shows that there is a need to optimize urban drainage systems in the Swiss Plateau region. Through centralized measures to reduce loads and improve water quality (e.g. via ozonation or activated carbon filtration) at selected wastewater treatment plants (WWTPs), it would be possible to eliminate a large proportion of micropollutants.

Development of a concept for the evaluation of surface waters. Based on the situation analysis, an ongoing task of the FOEN is the preparation of a list of organic micropollutants of Swiss relevance to serve as a basis for future evaluation of the quality of surface waters. In the elaboration of this list, consideration is given as far as possible to sales and consumption statistics, knowledge of the relevant input pathways and dynamics, measurement data from Swiss surface waters, and data on the behaviour and toxicity of substances in the aquatic environment. However, because much of this information is often unavailable, a relatively simple methodology was adopted for the categorization and selection of compounds [5]: as a first step, a list was compiled consisting of 260 substances which in the light of current knowledge are potentially of concern for Swiss surface waters. It includes substances that are widely detected in high or problematic concentrations or need to be taken into account in view of international obligations.

As a second step, because mobile and persistent compounds are particularly problematic, the substances on the list were assessed in relation to the following aspects:

- For which of these substances is a relevant proportion (at least 10 %) to be found in water?
- How rapidly are these substances degraded in water?

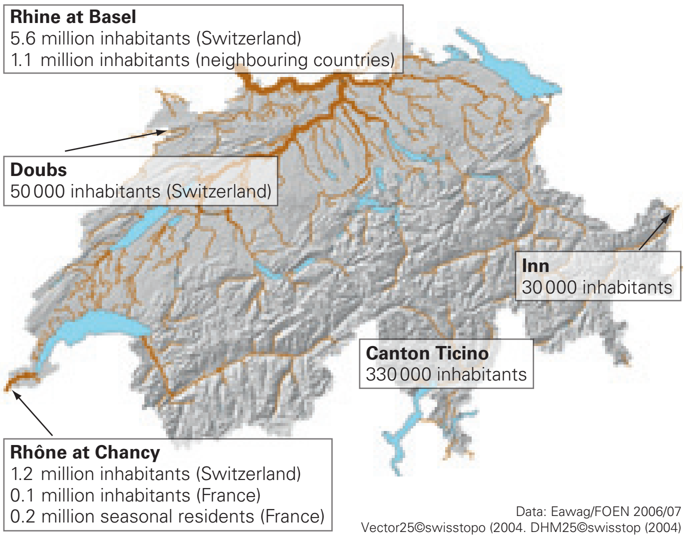

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Fig. 2: The problem of loads exemplified by "wastewater exports" from Switzerland. The brown lines represent wastewater volumes in Swiss rivers: the thicker the line, the greater the volume.

For example, given the current state of technology at municipal WWTPs, readily degradable and strongly sorbing substances are eliminated from wastewater. Substances with these properties are not considered relevant for surface waters, although individual groups of substances may be locally problematic (e.g. local contamination of sediments with strongly sorbing substances due to inadequately dimensioned combined sewer overflows).

Discharge of treated wastewater into a watercourse. In small streams, with inadequate dilution, organic micropollutants can have adverse impacts on plants and animals.

Alongside the substance list, an evaluation and monitoring concept is being developed which is not only guided by current developments in the EU but also takes local conditions into account. A key point here is input dynamics. It is easy to measure persistent, mobile substances, such as pharmaceutical active ingredients, which are continuously released into surface waters in proportion to the size of the population served by a WWTP. In contrast, substances with a complex input dynamic are only temporarily or periodically transported into waters and are therefore much more difficult to capture – e.g. when biocides are leached from facades during rain events. In addition, the aim is to develop appropriate quantitative water quality requirements based on ecotoxicity.

International context. In contrast to Swiss legislation, the EU Water Framework Directive expressly calls for evaluation of chemical status of water bodies based on priority substances. Environmental quality standards (EQS) are applicable throughout the EU for these substances. In addition, in assessing the ecological status of surface waters, EU member states are required to specify EQSs for river basin-specific pollutants. EU member states have to establish monitoring programmes for surface waters and demonstrate that the EQSs are met or that measures taken will lead to compliance. The FOEN aims to keep abreast of relevant EU activities and to ensure the best possible exchange of information.

Switzerland is a member of various international water protection commissions:

- International Commission for the Protection of the Rhine (ICPR).
- International Commission for the Protection of Lake Constance (IGKB).
- International Commission for the Protection of Lake Geneva (CIPEL).
- Joint Commission for the Protection of Italian-Swiss Waters against Pollution (CIPAIS).
- Commission for the Protection of the Marine Environment of the North-East Atlantic (OSPAR).

The agreements between the riparian states aim to improve the quality of these transboundary waters. For example, the ICPR has defined a number of relevant substances for which concentrations in the Rhine are to be reduced below certain target levels. These substances are covered by the programmes operated by the various Rhine monitoring stations. Moreover, under the Rhine warning and alarm system, a broad spectrum of additional substances are subject to continuous monitoring. The ICPR is also developing a strategy on the management of organic micropollutants for the Rhine basin [6].

In the CIPEL, as in the IGKB, measurement programmes are carried out to detect organic micropollutants. Samples from Lake Geneva and Lake Constance are periodically analysed for a relatively comprehensive list of organic micropollutants. The CIPEL supplements its monitoring activities with modelling and also provides for measurements in tributaries – an approach which allows relevant sources and input pathways to be determined fairly reliably. The IGKB pursues a similar strategy of lake and tributary monitoring and is currently also examining mass flux assessment methods.

Seeking comprehensive solutions. The issue of anthropogenic organic micropollutants in surface waters is internationally recognized. At present, no systematic overview is available of the consumption, the emissions, the environmental fate and the toxicity of micropollutants relevant to surface waters. However, there is clear evidence of adverse impacts on the aquatic environment. This suggests, firstly, the need for action to reduce input of problematic micropollutants, such as measures to optimize municipal wastewater treatment. At the same time, there is a need for a plan to evaluate and detect organic micropollutants in surface waters. A plan of this kind is currently being elaborated for Switzerland, giving due consideration to ongoing efforts to elaborate and implement the EU Water Framework Directive. In addition, the FOEN is cooperating with different partners with a view to including organic micropollutants in future monitoring programmes for Swiss surface waters, developing a strategy for the management of micropollutants from diffuse sources, and identifying appropriate tracers for assessing the elimination performance of municipal WWTPs. ○○○

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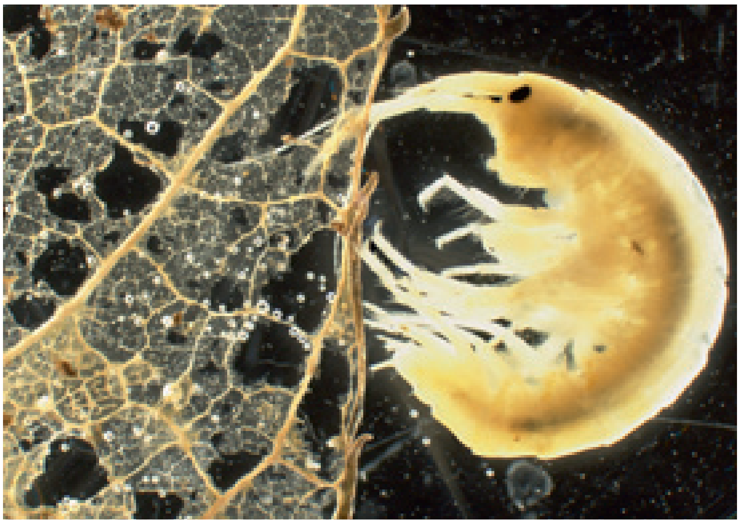
The Swiss Ecotox Centre – reaching out to practitioners

Nanoparticles, endocrine disruptors, cocktails of pollutants – risks for human health and the environment are increasingly widespread. Against this backdrop, the new, federally funded Swiss Centre for Applied Ecotoxicology became officially operational in the autumn of 2008. Among the institution's aims are the development of an integrated ecotoxicological test system.

The situation in natural waters is becoming ever more complex: chemically diverse pollutant cocktails, in combination with other abiotic and biotic stress factors, act on aquatic organisms, thereby affecting the functioning of entire ecosystems. This is the case even though legislation calls for tighter regulation of environmental monitoring and chemicals assessment, and policymakers are seeking to define appropriate measures for water pollution control. But it will only be possible to establish direct causal links, and thus make decisive progress on water protection, with an integrated ecotoxicological test system – simultaneously assessing a variety of modes of action at different biological levels. It goes without saying that a test system of this kind will also need to be sensitive, easy to handle and inexpensive. So with the development of its "Multisens" platform, the Ecotox Centre has set itself a difficult task.

Multisens platform for integrated assessment of surface waters. The basic idea is that the Multisens platform should have a modular structure: with the aid of a series of physicochemical and biological tests, water quality is to be assessed at various levels, ranging from the molecular to the ecosystem. The organism chosen to serve as a model is the freshwater shrimp (*Gammarus* spp.), and therefore the key element of Multisens is the "GamTox" module. This is to be used to analyse the toxicity of pollutants and pollutant mixtures for gammarids themselves, their food sources (leaf litter) and their predators (e.g. fish). The goal is to assess different stages of the food chain and effects on ecosystem processes at the same time. Multisens is rounded off by ecotoxicological laboratory tests. However, the individual elements of Multisens are mainly designed for use in the field – e.g. in surface waters. The prospects of success for these ideas are already demonstrated by numerous studies based on gammarids. The Ecotox Centre has recently summarized the results of these studies in a review article [1] and is currently conducting initial experiments in-house.



Fallen leaves are the main food source for freshwater shrimps *(Gammarus* spp.).

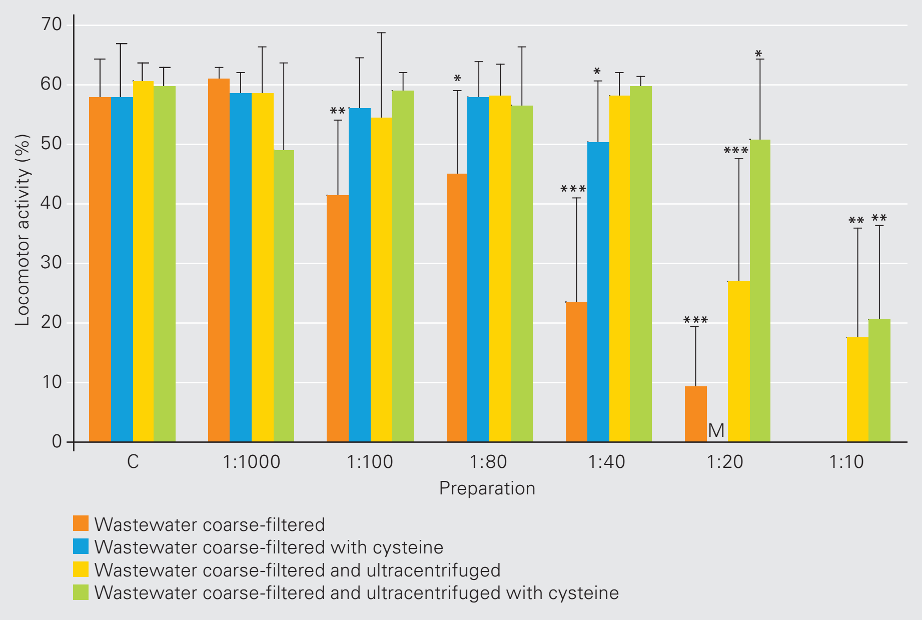
Gammarids – sensitive aquatic organisms. As part of the FOEN's "MicroPoll Strategy" project (see the article by Michael Schärer on p. 31), the Ecotox Centre not only plans to validate various tests for endocrine-disrupting effects [2], but also intends to develop tests involving specific aquatic organisms – in particular, gammarids. There is evidence to suggest that the freshwater shrimp may be a valuable indicator species for water quality: accordingly, in cooperation with Eawag's Aquatic Ecology department, the Ecotox Centre deployed standardized leaf packs upstream and downstream of the outlet of the Regensdorf wastewater treatment plant in the Furtbach. After three weeks in the stream, the communities of aquatic invertebrates established in the leaf packs were analysed. Whereas gammarids predominated above the outlet, blackfly and snails were dominant below the point where treated effluent was discharged – despite the lack of differences in key standard water chemistry parameters. Further studies will, however, be required to determine whether the shift in species composition is in fact attributable to pollutant stress.

***In situ* tests possible with gammarids.** But what characteristics can be used to detect toxic effects in gammarids? The Ecotox Centre is experimenting with a biomonitor system: individual organisms are placed in water-filled (flow-through) sensor chambers, and simple but vital changes in behaviour patterns (e. g. increases or decreases in locomotion or ventilation) are recorded in the form of electric signals. Such changes could be triggered, for example, by exposure to contaminants. In a preliminary experiment – conducted jointly with the Aquatic Ecology department – gammarids were exposed to the antibiotic sulfamethoxazole. In contrast to the control group, both locomotor and ventilatory activity was altered in gammarids after exposure to this substance. These encouraging initial results will now need to be followed by further studies investigating the suitability of these behavioural changes as indicators of exposure to contaminants.

Gammarid locomotion impaired by laundry wastewater. After this preliminary work, gammarids were used in an initial applied research project. This study – in which Eawag's Urban Water Management and Process Engineering departments are involved as well as the Ecotox Centre – concerns wastewater from a laundry. Among the ingredients added to the detergent used at the laundry – because of its disinfectant effects – is particulate silver chloride (see also the article by Renata Behra on p. 22). Compared with other bioassays, the most sensitive response to the contaminated wastewater was observed in gammarids. The organisms' locomotor activity was significantly restricted by the wastewater in dilutions of up to 1:100 (Figure). However, if the wastewater is treated with cysteine (an agent forming complexes with metals including silver) or subjected to ultracentrifugation (to remove particulate metal ions) or a combination of ultracentrifugation and cysteine treatment (to prevent redissolution of metals), significant effects only occur up to the much lower dilution of 1:20. Although these experiments have not established whether the effects are indeed induced by the silver chloride, there is no doubt that toxicity can be markedly reduced by eliminating the metals and the particulate silver chloride from the wastewater. Overall, therefore, the results obtained with gammarids are fairly promising. The next step is to elaborate additional ecotoxicity endpoints at different levels and integrate these into the Multisens platform. ○ ○ ○

Martina Bauchrowitz

Locomotor activity of *Gammarus fossarum* after 24-hour exposure to untreated and treated laundry wastewater at various dilutions with stream water (n = 5–9). M = missing data point; bars missing for the 1:10 dilution due to mortality. C = control (water from the organisms' stream of origin). Asterisks indicate significant differences from controls (* = $p < 0.05$; ** = $p < 0.001$; *** = $p < 0.0001$).



An ecotoxicology hub

With the establishment of the Ecotox Centre just under a year ago, Switzerland now has an independent institution dedicated to applied ecotoxicology, jointly supported by Eawag (aquatic aspects) and the Federal Institute of Technology Lausanne (EPFL, terrestrial aspects). The synergies arising for the institutions concerned are obvious: while Eawag and the EPFL mainly focus on basic research in ecotoxicology, the Ecotox Centre aims to develop existing test methods for chemical risk assessment so that they can be applied in practice. Other Ecotox Centre activities include consultancy and education, as well as committee work and the development of networks in ecotoxicology. The Centre prepares expert reports [1, 2] and undertakes contract research, e. g. for the federal authorities, cantonal agencies and the private sector.

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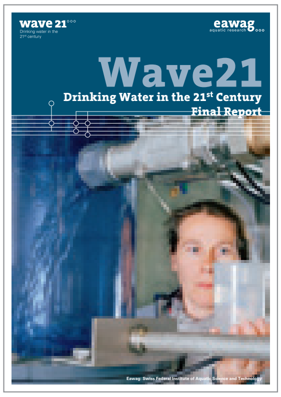
In Brief

Drinking Water in the 21st Century



In the cross-cutting project Wave21, Eawag carried out research on future methods of drinking water treatment with a variety of private-sector and water utility partners. The Final Report – "Wave21: Drinking Water in the 21st Century" – has now been published. The integrated project focused on supplies sourced from surface waters, and in particular on the relationship between raw water parameters and individual treatment steps. Over the next 20 years, extensive innovations will be required in drinking water treatment across Europe. Quality requirements will become increasingly stringent (EU Drinking Water Directive and US EPA standards). At the same time, innovative treatment technologies are available, and there is a growing demand for more effective treatment methods. In addition, increasing numbers of plants require renovation and restructuring. The 70-page Final Report concentrates on the situation in Switzerland. It is accessible under www.eawag.ch/medien/bulletin/20090806/wave_final_report.pdf.

Top research from Eawag

Each month, top publications in selected fields of research are listed by ScienceWatch, the Thomson Reuters science trend tracking service. Among the topics featured in April 2009 was arsenic water pollution. In the period of 2003–2008, 4 of the 24 core papers in this field came from Eawag. The top-ranked paper, with 203 citations, was an article which appeared in "Environmental Science & Technology" in 2003, co-authored by Eawag Director Janet Hering (then based at Caltech).

- Dixit & Hering 2003: Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. Environmental Science & Technology *37,* 4182–4189.
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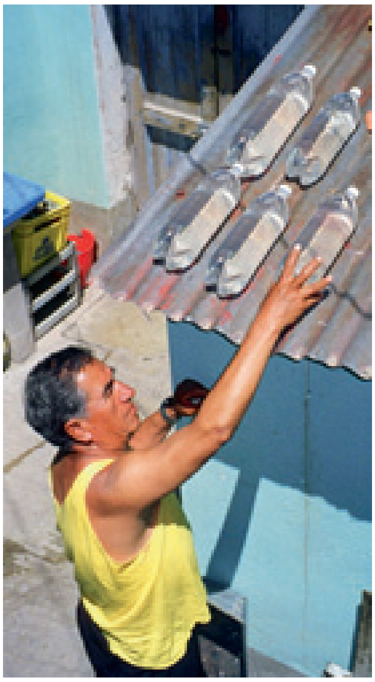
- Winkel et al. 2008: Predicting groundwater arsenic contamination in Southeast Asia from surface parameters. Nature Geoscience *1,* 536–542.

http://bit.ly/SciWatch-Arsenic

Promoting Sodis effectively

A recent study [1] carried out in Bolivia has attracted substantial media attention for its unfavourable findings on the Sodis (solar disinfection) process, in which water is disinfected by placing it in PET bottles and exposing it to sunlight. The study reports that the incidence of diarrhoeal diseases was not significantly decreased in an intervention group as compared with a control group.



This finding is important. But it must be interpreted with great caution. Clearly, the results do not undermine the technical soundness of the Sodis process. The key point is that the intervention group in Bolivia included only a small number of Sodis users and mostly non-users. The proportion of Sodis-treated water consumed was probably less than 14 % [1]. Consequently, as pointed out by the authors of the Bolivian study, the reason for the non-significant results was the failure of the intervention group to adopt the Sodis method and use it in a consistent manner. In other words, the issue is one of compliance, not of technology.

About 4,500 children die of diarrhoea every day. An estimated 3 million people in 30 countries are currently using Sodis to reduce the risk of waterborne disease, often with great success. In one such study, the incidence of cholera during an epidemic in Kenya was 88 % lower among Sodis users than among non-users [2]. This indicates that the consistent application of Sodis has immense potential to reduce diarrhoeal illnesses and protect lives, particularly during epidemics. In this light, it would be fatal to stop promotion of Sodis in developing countries. On the contrary, as the Bolivian study shows, increased effort is needed by all partners to improve acceptance and proper use of the Sodis technology. A major focus of Eawag and the Sodis Reference Center therefore is on assessing effective diffusion strategies and promoting consistent use of the Sodis methodology in different cultural and social contexts.

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[2] Conroy et al. (2001): Solar disinfection of drinking water protects against cholera in children under 6 years of age. Arch. Dis. Child. Oct. *85 (4),* 293–295.

www.sodis.ch