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Editors
Diana Hornung (EAWAG),
Patricia J.S. Colberg (USA)

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Title page picture
The development of tadpoles of the domestic green frog *(Rana esculenta)* may be negatively affected by exposure to trace compounds (see article by Fent on page 8). Tadpoles exposed to trace compounds exhibit lower survival rates and take longer to complete metamorphosis. Exposure to environmental chemicals may, in fact, contribute to the disappearance of many amphibian species.

(Photo donated by Prof. H.U. Reyer, University of Zurich)

The Duties and Joys of Continuing Education

Ever more knowledge and know-how are being developed and accumulated worldwide. The portion thereof that can be reasonably comprehended by any one individual becomes vanishingly small. The time needed for the completion of studies grows longer as they become more specialized, while demands on professionals are changing at an ever increasing pace. Our educational system can no longer keep up with these changes and is in need of a fundamental reform.

The partitioning of our lifes into three slices – 25 years of education, 35 years of professional activity, 20 years of retirement – is inadequate. The long-lasting basic education is wearisome and lacks practical relevance by the time it is over. It can neither adapt flexibly enough to newly emerging needs nor provide professionals with an update of their knowledge and expertise. In addition, the vast reservoir of wisdom and experience of senior professionals is left untapped. This state of affairs is absurd from the human and from the economic standpoint. Therefore, the education, professional life, and retirement must be given a modular structure and be better integrated. Continuing education is a key element in this process. I would like to outline some of the experience gained from the EAWAG's program of advanced courses in environmental science and technology for professionals (dubbed PEAK) and to draw some personal conclusions:

- Attending courses is primarily a matter of time constraints and less so one of money.
- The knowledge, experience,and motivation of course participants significantly enhance course discussions.
- Courses combining playful approaches to study with the assessment of individual performance prove to be more efficient than traditional *ex cathedra* lectures.
- The large number and variety of courses offered is confusing and their quality difficult to assess.
- Educational needs are not systematically assessed and communicated.
- Continuing education offered by universities is neither developed nor marketed well enough.

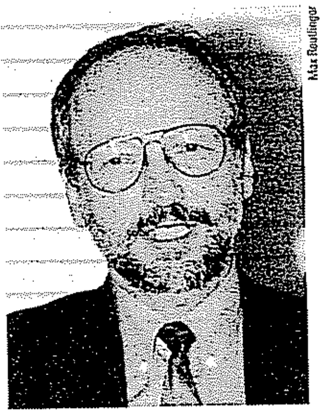
My vision for the future is as follows: Continuing education becomes a duty to schools and universities. The governement's role in this is to help finance continuing education (even possibly to the detriment of basic education), to set educational goals and quality criteria and to ensure the right to continuing education for everyone. Apart from that, the free market is supposed to apply to continuing education and to ensure a high standard in the quality of the offer. Basic and continuing education thus merge into a life-long process, a pleasureable and efficient duty at the same time.

Herbert Güttinger
Staff of the director,
continuing education

Walter Giger

Micropollutants in the Environment

From Environmental Monitoring to Process-oriented Field Studies



Walter Giger

Micropollutants in the environment have been the subject of scientific investigation for some 30 years. But what are the critical pollutants? And how are we to evaluate their compatibility with the environment? Today's analytical methods allow us to predict the environmental behavior of contaminants, but leave us an insufficient basis on which to evaluate their effects on organisms and ecosystems.

Global Elemental Cycles: the Special Case of Carbon

The fate of all chemical elements is controlled by highly interdependent global cycles in which natural biogeochemical processes are linked with anthropogenic mass fluxes (see, e.g., [1]). The cycling of carbon is particularly complex in that it plays a very important role in its oxidized forms (carbonates, carbon dioxide), while in its reduced state, it is the basis for biology. The fundamental principle of life is the transformation of carbon dioxide to biomass via autotrophic primary production. The biochemical cycle is closed when organic matter reverts to carbon dioxide via mineralization, respiration, and photochemical degradation. Upon further transformation, a small fraction of biological material is converted to oil, gas, and coal. Modern industrial processes use many naturally occurring organic compounds, particularly fossil fuels, for energy production and as raw materials in the chemical industry. It is estimated that some 70'000 synthetic organic chemicals are currently in use worldwide.

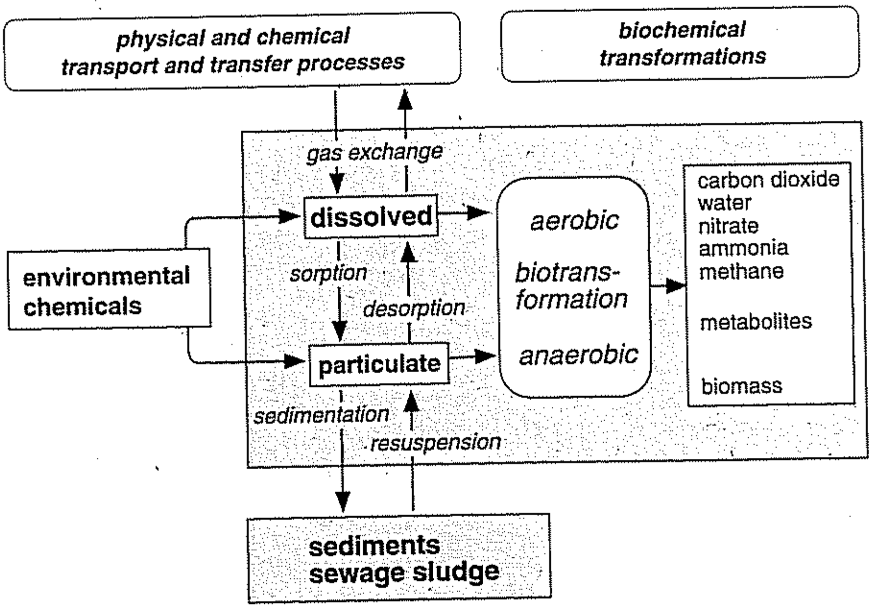


Fig. 1
Chemodynamic processes controlling the environmental behavior of organic chemicals in aquatic and terrestrial ecosystems.

Organic Compounds in the Environment: Trace Compounds and Trace Contaminants

During the mining, manufacturing, transport, storage, use and disposal, a certain fraction of these anthropogenic organic chemicals is released to the environment; at this point, they are called "environmental chemicals" or *Umweltchemikalien*. It is the goal of environmental chemistry to develop a detailed knowledge of their input, distribution, accumulation and transformation. A large number of these synthetic compounds are rapidly reverted to carbon dioxide and other inorganic compounds, either by natural processes or by technologically enhanced degradation. In addition to microbial transformations in aquatic and terrestrial systems, photochemical reactions in the atmosphere return them to inorganic matter or biomass. Problems can arise when these transformations occur very slowly or when such compounds reside in a particular part of an ecosystem for a time, which may result in accumulation. Long residence times increase the potential for damage to plants, animals and ecosystems. In the same sense, increased concentrations due to bio- or geoaccumulation lead to a higher potential for detrimental effects.

Environmental chemical compounds are classified as trace compounds when they are present in very low concentrations (one in a million, mg/kg, mg/l, ppm). Normally, trace compounds account for a very small fraction of the total chemical contamination caused by organic or inorganic compounds. Trace compounds become toxic pollutants based on their toxicological or ecotoxicological behavior on various biological levels, as discussed in the article by Fent [2].

The overriding characteristic which determines the importance of a particular chemical compound in the environment is its rate of degradation. Easily degradable compounds are usually removed from an ecosystem before negative effects occur. Exceptions include accidents involving compounds with high acute toxicity or releases in high quantities. Two examples may suffice as a small selection from a long list of incidents: the pollution of the Rhine after the major fire at Schweizerhalle in November 1986; the accidents involving the insecticide permethrin during 1993–95 and the accidental releases of cyanide-containing wastewaters.

Trace contaminants play a particularly important role in the atmosphere where they are responsible for a wide variety of damaging effects, notably formation of ozone and smog in the troposphere, acid deposition, ozone depletion in the stratosphere, and climate change. Very often, effects are observed only after the original pollutant has been chemically altered or transported over long distances (see p. 51, comment on 1995 Nobel Prize in Chemistry in this issue).

Testing Chemicals for Their Effects on the Environment

In order to evaluate the environmental effects of a chemical compound, one has to first study its environmental behavior or chemodynamics, and then assess possible damaging effects [3]. In this context, ecotoxicology may be considered a separate discipline.

Figure 1 illustrates processes governing the environmental behavior of chemical compounds in aquatic and terrestrial ecosystems. A number of transport and transfer processes, including degradation and transformation, are dominated by microbially mediated reactions occurring under aerobic or anaerobic conditions. In the best case, biotransformation yields end products such as carbon dioxide, water, nitrate or ammonia, methane and biomass. In less favorable situations, metabolites may be formed that are more difficult to degrade. Such compounds are then classified as trace contaminants; nonylphenol is an example. It is toxic and nondegradable under anaerobic conditions; it, therefore, accumulates in the sludge of anaerobic digestors [4].

Thirty Years of Determining Micropollutants in the Environment: Persistent Compounds

About 30 years ago, polychlorinated hydrocarbons (insecticides like DDT) were first documented as trace compounds in environmental samples. A few years later, polychlorinated biphenyls were detected, followed by polychlorinated dibenzodioxins and dibenzofuranes (PCDD and PCDF). These compounds are lipophilic, essentially nonvolatile, extremely diffi-

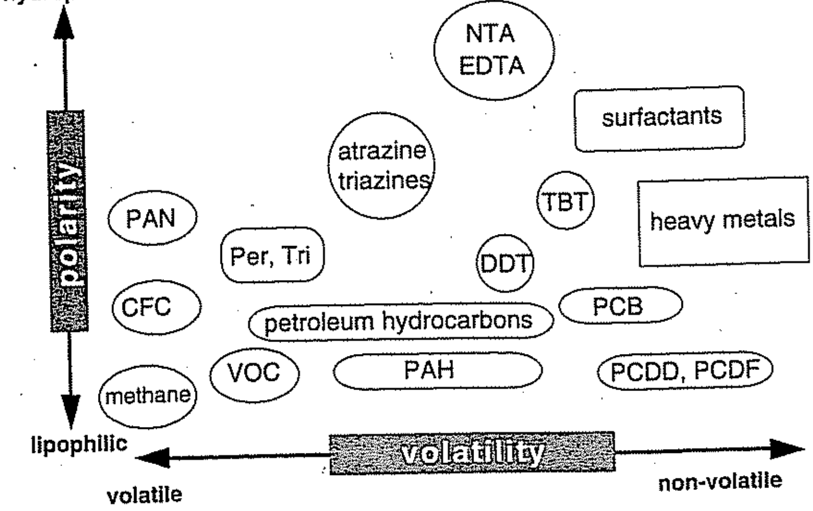


Fig. 2
Organic chemicals in the environment plotted on a polarity-volatility diagram.
CFC = *chlorofluorocarbons (e.g., freon)*
PAN = *peroxyacetylnitrate (a compound in smog)*
VOC = *volatile organic compounds*
Per = *perchloroethylene*
Tri = *trichloroethylene*
PAH = *polycyclic aromatic hydrocarbons*
PCB = *polychlorinated biphenyls*
PCDD = *polychlorinated dibenzodioxins*
PCDF = *polychlorinated dibenzofuranes*
TBT = *tributyltin*
NTA = *nitrilotriacetate*
EDTA = *ethylenediaminetetraacetate*
Surfactants = *surface active compounds, active ingredients in detergents*

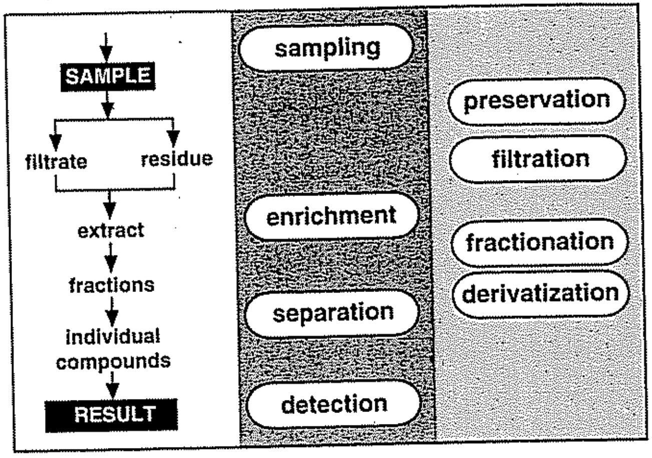


Fig. 3
Procedural steps in environmental analyses of organic and inorganic trace compounds.

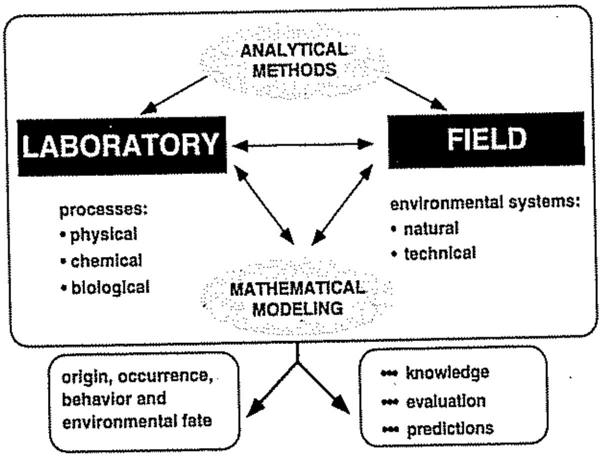


Fig. 4
Working concept for laboratory and field-based investigations on the behavior of environmental chemicals.

cult to degrade and, therefore, tend to accumulate in the biosphere. Heavy metals (Cd, Pb, Hg, Zn and others) are typically not degraded at all and, as a consequence, accumulate in both the geosphere (soils, sediments) and the biosphere.

Environmental chemicals may be plotted in polarity-volatility-diagram (Fig. 2) in which the position along x- and y-axes indicates the relative volatility and polarity of a given compound. The position of a particular compound in this diagram yields a rough approximation of its physicochemical behavior in the environment. Tetrachloro- and trichloroethylene (Per and Tri), both compounds which are extremely difficult to degrade, are very mobile in the hydrosphere and have been found to be a problem in ground water and drinking water supplies. Petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAH) are relatively lipophilic and exhibit moderate to low volatility. Volatile compounds are found in the gas phase and, therefore, of concern primarily in the atmosphere. Two examples of hydrophilic compound classes are found in detergents; namely surfactants and the organic metal chelating agents NTA and EDTA.

Environmental Analytical Chemistry

Significant progress in the study of micropollutants in the environment has been facilitated by the development of powerful analytical methods, i.e., qualitative and quantitative environmental analytical chemistry. Many environmental contaminants may now be quantified in very low concentrations in different types of samples (water, soil, air, biological samples). Typically, environmental samples have a complex matrix, and it takes highly sophisticated methods in order to reliably determine the compounds of interest. In many cases, complex mixtures (isomers, homologs, congeners) have to be analyzed, either because the technical products are of a complex composition initially, or because very similar products are being used. Most methods, specially in the case of organic trace analyses, are still very involved. Environmental measurements in real-time and on location (on-line/in-situ sensors) has not yet become a reality for trace compounds.

At the beginning of every environmental analysis is the sampling procedure, an extremely important step determining success and applicability of the results. Analysis usually involves a multi-step procedure, using enrichment and separation methods before the individual compound(s) of interest can be detected (Fig. 3).

Chemical analysis using gas and liquid chromatographic separation techniques has become routine. A number of directly coupled detection methods are in use today including mass spectrometry.

In addition to the sophisticated analytical methods employed in today's laboratories, efficient sample collection and enrichment techniques are very important. Also important are quality assurance and quality control, guaranteeing that results are accurate and reproducible. Efforts are currently underway to define standard criteria for quality control within the European Community and elsewhere.

From Monitoring to Process-oriented Field Studies

There are two ways to determine the environmental behavior of inorganic or organic compounds: (a) use controlled conditions in a laboratory setting to investigate individual processes relevant to a compound's behavior in the environment or (b) conduct integrated field studies addressing the behavior of the compound in a natural setting or in an engineered system. Both cases require the use of well developed analytical methods and mathematical models (see Fig. 4).

Field studies may be designed according to two different principles. In monitoring studies, compound concentrations may be measured over long periods of time in order to determine its behavior as a function of place and time. This allows evaluation of the effects of regulatory measures [5]. Even monitoring-based projects should be increasingly guided by computer models, as discussed by Müller et al. [6].

Process-oriented, or so-called chemodynamic studies (fate and behavior studies) focus on mass fluxes in systems which are relatively limited in size, but include the dynamic behavior of the system. These kinds of studies yield knowledge about underlying processes and are significantly enhanced when they include mathematical modeling. They are being increasingly used in the evaluation of both engineered processes (e.g., wastewater treatment [7], water treatment) and natural systems [5, 8].

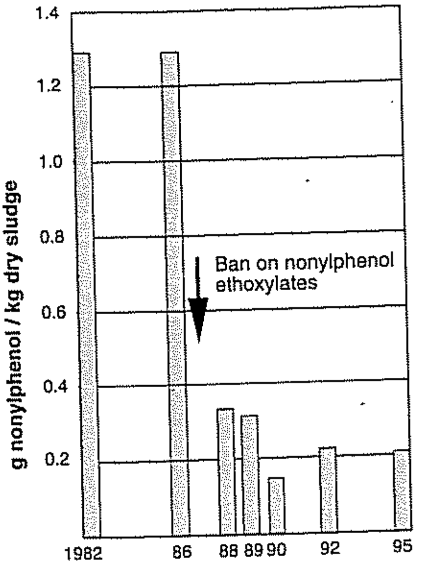


Fig. 5
Nonylphenol concentrations in anaerobic digestor sludge in the Canton of Zürich [5]. The reduction of nonylphenol concentrations in the sludge after 1986 is due to the ban on nonylphenol polyethoxylate use imposed by the Swiss federal ordinance on environmentally dangerous compounds (Stoff-Verordnung).

Case Study of Monitoring Approach: Nonylphenol in Anaerobic Digestor Sludge

During the 1970s and 1980s, nonylphenol polyethoxylates were used in Switzerland in large quantities as nonionic surfactants (i.e., active ingredients in detergents). Studies conducted by EAWAG in wastewater treatment plants of a number of communities revealed that biodegradation of apparently innocuous surfactants leads to the formation of toxic metabolites [4]. Nonylphenol, without the ethoxy group, is a highly toxic compound which accumulates in anaerobic digestor sludge because it is not degraded under anaerobic conditions. In addition to its toxic properties, very recently it has been shown that nonylphenol also exhibits so-called estrogenic effects, meaning that it shows activity similar to the female sexual hormone estradiol [2]; the two compounds are very similar in structure.

In a Swiss ordinance on environmentally dangerous compounds (Stoff-VO), which was issued in 1986, the use of nonylphenyl ethoxylates in fabric detergents was banned. In order to determine the success of this regulatory measure, a sampling program was initiated in 1982 to monitor nonylphenol concentrations in anaerobic digestor sludge in the Canton of Zurich. Results indicate that a significant reduction of nonylphenol concentrations was evident after issuance of the ordinance – from 1.3 g per kg to approximately 0.2 g per kg dry sludge (Fig. 5). Analyses of the sludges revealed the presence of an organic pollutant in significant concentrations, which exhibits toxicity similar to that of the heavy metal cadmium.

This example illustrates how the impact of a regulatory measure may be assessed in the field. The monitoring program was limited to measurements at one critical point in the system, i.e. at the point of accumulation. Results indicate that products containing nonylphenyl-related compounds are still in use. According to industry sources, between 40 and 70 tons are being used annually, mostly in industrial detergents; 3000 tons/yr were used before the regulatory restrictions were imposed. As the numbers indicate, however, nonylphenol-relatives and precursors still find their way into municipal wastewaters.

Case Study of Chemodynamic Approach: NTA and EDTA in the River Glatt

Both of the organic chelating agents nitrilotriacetate (NTA) and ethylenediaminetetraacetate (EDTA) are representative of very water soluble environmental compounds (see Fig. 2). They are used in a variety of applications because of their excellent metal binding behavior. In particular, NTA is used as a phosphate substitute in detergents. In connection with the ban on phosphates in detergents, large-scale monitoring studies on NTA and EDTA were conducted in Switzerland. These studies revealed the very different environmental behaviors of these two relatively similar chemical compounds [5]. While NTA is easily degraded by microorganisms, EDTA is not, though it may be degraded photochemically if it is present in the form of the iron-complex. Monitoring results do not, however, yield any information on the kinetics of the processes governing their environmental behavior. Only measurements in wastewater treatment plants allow certain limited statements to be made about the kinetics of their degradation.

One particular project (dissertation research conducted at EAWAG [8]), was aimed at investigating the kinetics of NTA and EDTA degradation in the River Glatt (Canton Zurich). In this process-oriented study, daily concentration curves for both trace compounds were determined at several locations along the river. The data was interpreted with the help of a mathematical model which incorporated both biological and photochemical degradation.

Figure 6A shows daily concentrations of NTA at monitoring stations near Rümlang, Niederglatt and Rheinsfelden. NTA was eliminated with a half-life of about eight hours, as indicated by simulation calculations. More elaborate calculations, taking into consideration the effects of a biofilm along the river bed, yielded good agreement with the measured NTA concentrations (Fig. 6B). Degradation during the winter months was found to be somewhat slower.

EDTA exhibited a very different behavior. During the winter months, no degradation was observed, as can be seen in data obtraineed from the monitoring station near Niederglatt (Fig. 6C). During the summer months, however, photochemical degradation was clearly evident. It was also discovered that the degradation rate was a function of the percentage of photolabile iron-EDTA and light penetration in the river (Fig. 6D).

Outlook

From the results presented in this article the following conclusions can be drawn:

◎ Even when employing very powerful analytical techniques, only a small fraction of the overall contamination is detected in most situations. The selection of representative and relevant indicator compounds is, therefore, very important.

◎ In order to enhance the knowledge of environmental processes, laboratory and field studies alike should be complemented by mathematical modeling.

◎ An environmental chemical becomes a pollutant only after negative biological and physical effects have been documented. In order to assess the compatibility of a compound with the environment, both its environmental behavior and detrimental effects must be evaluated.

The current challenge in environmental sciences is to supplement the relatively advanced understanding of the environmental fate of compounds with information on their ecotoxicology. The ultimate goal is to give regulatory bodies concerned with environmental protection a better basis for making decisions on the environmental compatibility of chemicals.

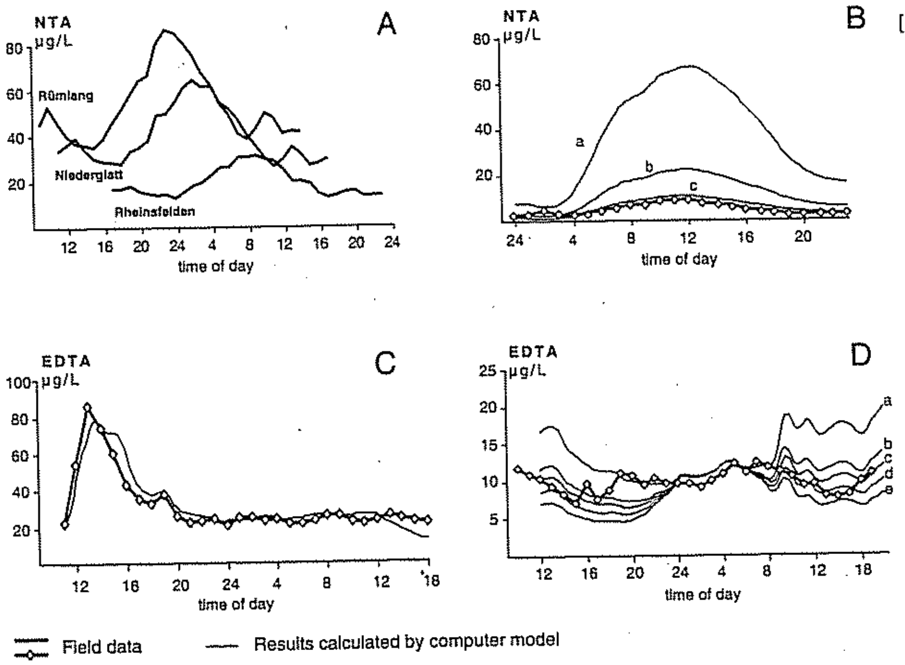


Fig. 6
Measured and calculated daily concentration curves for NTA and EDTA in the River Glatt (Canton Zurich, according to [8]).
A: NTA-concentrations along the River Glatt, with monitoring stations at Rümlang, Niederglatt and Rheinsfelden. The graphs demonstrate a half-life for NTA degradation of about 8 h.
B, C and D: Comparison of measured concentrations with model calculations.
B: NTA concentrations at Rheinsfelden compared to model calculations assuming different degradation rates in the biofilm along the river bed (a: no degradation; b and c: increasing degradation rates).
C: EDTA concentrations at Niederglatt compared to calculations assuming no degradation.
D: EDTA concentrations at Rümlang compared to values calculated for different percentages of iron-EDTA complexes which is photodegradable (photolabile EDTA; percentages: a = 0, b = 30, c = 40, d = 50, e = 60).

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[1] Stumm, W. (1971): Einfache Modelle im Umweltschutz: Der Mensch und die hydrogeochemischen Kreisläufe. Vom Wasser, *38*, 1–16.

[2] Fent, K. (1996): Effects of Micropollutants. EAWAG news, *40 E*, 8–12.

[3] Weber, A. und H. Barben (1984): Beurteilung ökologisch relevanter Daten neuer organischer Chemikalien. CHIMIA, *12*, 443–456.

[4] • Giger, W. (1989): Organische Verunreinigungen im Klärschlamm: Herkunft und Verhalten in der Umwelt. Mitteilungen der EAWAG, *28*, 8–11.
- Giger, W., P.H. Brunner, M. Ahel, J. McEvoy, A. Marcomini und C. Schaffner (1987): Organische Waschmittelinhaltsstoffe und deren Abbauprodukte in Abwasser und Klärschlamm. Gas – Wasser – Abwasser, *3*, 111–122.

[5] Giger, W., C. Schaffner, F.G. Kari, H. Ponusz, P. Reichert und O. Wanner (1991): Auftreten und Verhalten von NTA und EDTA in schweizerischen Flüssen. Mitteilungen der EAWAG, *32 D*, 27–31.

[6] Müller, S., M. Ulrich and R. Schwarzenbach (1996): Optimized Monitoring of Contaminants: Atrazine as an Example. EAWAG news, *40 E*, 36–39.

[7] Siegrist, H.R. (1995): Behavior of Trace Compounds During Sewage Treatment. EAWAG news, *40E*, 13–18.

[8] • Kari, F.G. (1994): Umweltverhalten von Ethylendiamintetraacetat (EDTA) unter spezieller Berücksichtigung des photochemischen Abbaus. Dissertation ETHZ Nr. 10698.
- Kari, F.G. and W. Giger (1995): Modeling the photochemical degradation of ethylenediaminetetraacetate (EDTA) in the Glatt. Environ. Sci. Technol., *29*, 2814–2827.

Karl Fent

Effects of Micropollutants

Diana Hartung

Karl Fent

Micropollutants exert chronic effects on living organisms at all biological levels. The focus on chronic effects in ecotoxicology research must be intensified.

Chronic Effects Largely Unknown

Some 70'000 synthetic compounds are in use worldwide and enter water bodies – sometimes in trace quantities and sometimes in large amounts. Generally, they do not adversely affect organisms; surprises, however, always occur. Acute effects are important, but the more subtle damage caused by low levels of exposure over long periods of time are of special concern.

There are three properties of micropollutants that may be classified as critical:

- high biological activity with correspondingly high (chronic) toxicity
- high persistence and mobility in the environment
- a tendency towards bioaccumulation with corresponding concentration in the food chain.

Usually micropollutants possess several of these properties. They may affect all biological levels; that is, from the molecular level to the ecosystem level.

Most cases of environmental damage caused by trace elements are not predictable and have only been recognized through the appearance of damage. This has been the case for DDT, PCBs, organotin compounds, acidification of surface waters or recent cases of forest damage. In general, the chronic effects of chemicals on ecosystems are not yet well known; any investigations have been perfunctory until now. Ecotoxicology aims to better understand the impact of micropollutants in order to prevent the damage they can cause. Several negative effects of micropollutants are described below.

The Importance of Environmental Chemistry

Environmental chemistry is an important basis for understanding the toxic impacts on ecosystems. Due to advanced trace analysis techniques, the concentrations of micropollutants can be measured and possible effects on organisms can be evaluated. The adverse effects of tributyltin (TBT) in the late 1970s were elucidated only because the methods of trace analysis had become available.

Chemical Speciation and Bioavailability

Very few conclusions about possible detrimental effects can be drawn simply from measuring concentrations

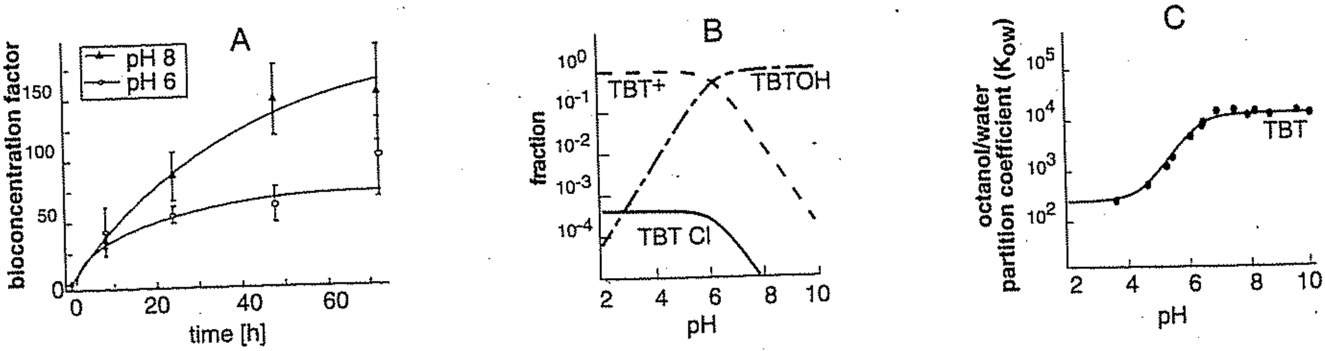


Fig. 1
A: Bioconcentration of tributyltin chloride (TBTCl) in Daphnia magna at pH 6 and pH 8 (after [2]).
B: Chemical speciation in 1 mM chloride.
C: Octanol/water partition coefficient from pH 2 to 10 (after [3]) explain the observed differences in bioconcentration. The lipophilic TBTOH species predominates at pH 8 and is assimilated more easily than the cationic form which is predominant at pH 6.

Level	Effect	Site of effect (organism)	Micropollutants
Molecules	mutations, cancer	liver tumors (fish)	PAH
	inhibition of enzymes	cytochrome P450 (fish)	OT, HM
		ATP-formation, oxidative phosphorylation	OT, HM
	inhibition of ion channels	nerve cells (fish, arthropods)	pyrethroids
Cell	cytotoxicity	cell membrane	OT, HM, peroxide, radicals
Organism	organ damage	necroses	various
	growth and development	metamorphosis in amphibians	OT
	altered behavior	search for food, predator evasion	OT
	immunotoxicity	impaired immune response (fish, mammals)	OT, HM, PCB, dibenzodioxins
	neurotoxicity	nervous system	pyrethroids, carbamates, organophosphates
	physiological effects	metabolic disorders (hormones, enzymes)	various
	reproduction	estrogenic effects (fish, reptiles, birds, mammals)	alkylphenols, DDT etc.
		androgenic effects (molluscs)	tributyltin
		early developmental stages in fish	OT, HM
		thinning of egg shells (birds)	DDT
Population,	distribution of ages and sizes	plankton, invertebrates and vertebrates (fish)	various pesticides, HM, acid
Community			various
Ecosystem	composition and density of species	lakes and lotic systems	various

Table 1
Examples of toxic effects of micropollutants on various biological levels in aquatic ecosystems.
PAH = polycyclic aromatic hydrocarbons/petroleum-derived compounds; OT = organotin; HM = heavy metals.

of chemicals in the environment as toxicity depends entirely on that fraction of a substance that is biologically available. Bioavailability depends both on environmental factors (e.g., the amount of dissolved organic carbon) and on the speciation of the compound or element. The importance of these parameters is illustrated in the following example. The toxic effect of TBT is significantly higher at pH 8 than at pH 6 (see Fig. 1A). At higher pH levels, 16 out of 70 Daphnia die and at pH 6 only five die if they are exposed to 4.5 µg/l of TBT over 3 days. How can this be explained? For the assimilation of foreign substances, the charge (ionization) is important, apart from the size of the molecule. In general, ions are not lipid soluble and thus cannot freely diffuse across the cell membrane.

Speciation

The species of a molecule is defined as its existing form as a result of many balance reactions. The form of a molecule, be it dissolved, adsorbed or bound either in a complex or another form, influences its assimilation in organisms and its behavior in the environment. The speciation of TBT in the aqueous phase is primarily determined by the pH level [3]. At acid pH levels, TBT is primarily present in the form of charged cations (TBT^+); at increased pH levels (pH >7), neutral tributyltin hydroxide (TBTOH) is formed (Fig. 1). At pH 6, about 60–75% of TBT is present in its cationic form (TBT^+), while at pH 8, it is found almost exclusively as neutral TBTOH. As suggested by the octanol/water partition coefficient, the latter form is significantly more lipophilic than the cationic form (Fig. 1). Thus, the bioconcentration at pH 8 is enhanced, compared to that at pH 6 (Fig. 1A). The increased mortality is, therefore, a result of increased bioavailability and the bioconcentration of the TBTOH species. Furthermore, this experiment shows that toxicity depends on the concentration within the organism or in a critical organ (body burden).

Toxic Effects at All Biological Levels

Two main factors govern the toxicity of micropollutants: (1) dosage and (2) sensitivity. One consequence of differences among species is that different organisms may be damaged to various degrees, depending on the substance(s) to which they are exposed. The modes of toxic action is also of importance. These factors must always be kept in mind when attempting to understand the effects of chemicals on ecosystems. As shown in Table 1, the impact of trace substances on living organisms occurs at all biological levels.

Molecular and Biochemical Effects

Trace compounds can damage essential molecules and vital cell structures. The inhibition of enzymes is one effect environmentally significant chemicals may have on living organisms at the molecular level. For example, inhibition of the cytochrome P450 enzyme, which plays an important role in the detoxification of foreign substances [4], is described below. Relatively high concentrations of organotin compounds such as TBT and triphenyltin (TPT) destroy these enzymes in the liver of fish (Fig. 2). As these enzymes are also required for other essential metabolic processes and for the formation of steroid hormones, their destruction has additional consequences to the organism.

Over 70 marine snail species have suffered chronic damage in aquatic ecosystems worldwide from traces (a few ng/l) of tributyltin. These trace concentrations have an androgenic effect on female snails, which develop a penis and become sterile. In polluted coastal areas, whole populations of snails have suffered such damage. In addition to the increased incidence of

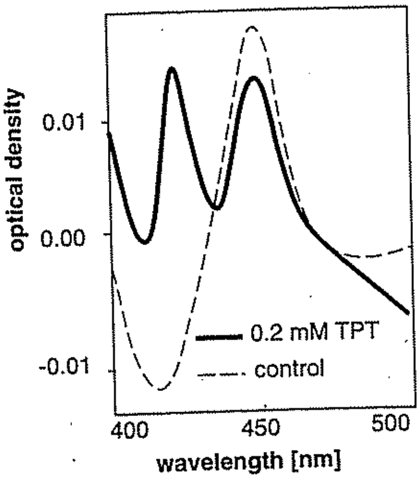


Fig. 2
Destruction of cytochrome P450 in the liver of fish by triphenyltin (0.2 mM). The degradation product is present in the form of cytochrome P420 (after [4]).

masculinized snails, there are few if any juvenile snails left in the population. This effect can be traced back to the inhibition of cytochrome P450-dependent monooxygenases in the snails, as we postulated in our research [4] and which is corroborated by the most recent studies on marine snails [5]. Affected female snails contain an increased amount of the male sex hormone testosterone. The latter accumulates in the snails because it can no longer be converted into estrogen. The cytochrome P450-dependent enzyme aromatase which catalyzes this conversion is inhibited by TBT [5]. As these effects can also be observed in freshwater snails, the concentrations currently found in boat harbors and in rivers are still ecotoxicologically relevant [1].

Cell Toxicity

Damage to the cell does not have adverse consequences for unicellular organisms only. Particularly susceptible are cells which carry out basic vital functions in an organism or those which cannot be replaced (e.g., nerve cells). The liver of higher organisms performs a key role in general metabolism and in the detoxification of foreign substances. The effects on hepatocytes of fish can be investigated by in vitro cultivation of the cells.

As they do in the liver itself, these cultivated cells perform important metabolic functions. Our research indicates that the damage caused to the cell membrane or to the mitochondria can be assessed relatively quickly and reliably using biochemical reactions. The toxicity of approximately 50 different organic micropollutants (e.g., organotin compounds, chloro-, nitro- and alkylphenols, sulfonic acids) clearly indicates a dependence on the dose and is correlated to the acute toxicity in fish (Fig. 3). Using such in vitro assays, the acute toxicity for fish can be estimated and the potential for damage can be assessed from environmental samples. Such new cell systems can be utilized in assessing newly developed chemicals and in testing environmental samples.

Effects on the Organism

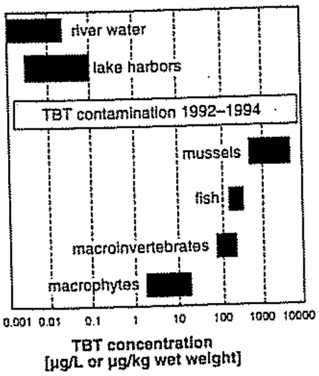
Trace compounds mainly have subtle effects on vital functions. Major chronic effects on aquatic organisms mainly concern their growth, development and reproduction as well as damage to important organs such as gills and the nervous and immune systems. Damage to early life stages are of general importance, especially in fish and amphibians. About 80% of the contaminants investigated have the strongest impact during this stage in their development. The most critical phase is usually the early larval stage.

A brief exposure to TBT in concentrations found in boat harbors (0.8 µg/l) cause histological damage to skin, eyes, muscles and kidneys [6] *(Reference to picture shown in article of Zehnder: see page 40).* Observed alterations in the eyes of such larvae (cataracts) are accompanied by a reduction in eyesight. The search for food and evasion of predators is, thereby, impaired in such larvae, reducing their chances of survival.

Similar alterations in these tissues as well as behavioral changes are also caused by triphenyltin (TPT), a fungicide used in cultivating vegetables (e.g., potatoes, celery, sugar beets). The exposure of fish larvae or of tadpoles of indigenous frogs (Rana lessonae and Rana esculenta) which spawn in natural waters contaminated by such pesticides causes behavioral alterations

Organotins...

... are among the most toxic compounds known to aquatic organisms. Tributyltin (TBT) is chronically toxic in trace concentrations of but a few billionths of a gram per liter (ng/l) for the most sensitive organisms such as oysters (deformations of the shell, inhibition of reproduction) and aquatic snails (androgenic effects). TBT is also very toxic to fish; a few µg/l can be lethal.



This compound is used as a biocide in antifouling paint for the submerged parts of ship hulls and in several other materials. As a result of severe damages in oyster beds and on marine coastlines, these paints have been banned in many western countries. The retail sale of such paints has been banned in Switzerland since July 1990. To date, they are still being used on large ships and their use is increasing in Southeast Asia. The contamination of harbors in Switzerland dropped after the sales ban, but levels in harbors (1994: up to 110 ng/l) and rivers (1992: up to 30 ng/l) are still high enough to be detrimental to susceptible organisms [1].

Recent sources are, apart from the use of remaining stocks of antifouling paints containing TBT, wood protection chemicals. These compounds can also be found in sewage sludge in concentrations of about 1–10 mg/kg (dry weight), the same level as seven years ago.

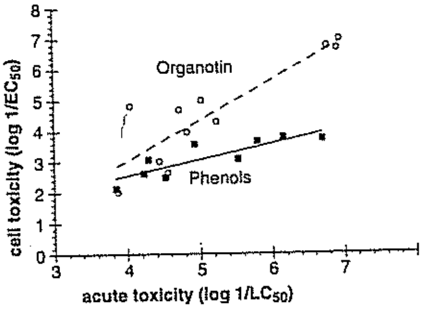


Fig. 3
Significant correlation between cell toxicity (in vitro) and acute toxicity in fish. The EC_{50} value represents the concentration at which half of the cells become damaged. The LC_{50} value corresponds to the lethal concentration for 50% of the fish.

detrimental to survival. Reduction of swimming and feeding activities result in retarded development of the larvae, having negative consequences for survival. Exposure of tadpoles for one month to 0.8 and 1.9 µg/l TPT causes mortality, reduced growth and strongly retarded metamorphosis [7]. Exposure for three months delayed metamorphosis by up to 17 days, which has deleterious effects on the adult stage. There are also variations in the sensitivity of genetically differing frog species and clones. Frogs with a wide distribution and which can also be found in deteriorated environments *(Rana esculenta)* exhibit the least sensitivity to TPT. The species which is restricted to natural habitats *(Rana lessonae)*, however, shows greater impairment.

Reproduction: Micropollutants Affecting Hormonal System

Substances which negatively affect reproduction also have significant effects on the level of populations and ecosystems and are thus of primary ecotoxicological importance. The problems centering around micropollutants which affect the hormonal system have suddenly become urgent, as serious effects have been observed in fish over the past few years. Degradation products of nonionic tensids/surfactants (alkylphenolpolyethoxylate) were unexpectedly discovered to possess weak estrogenic activity (causing femininization). Recent studies in England have shown that femininization occurred in fish downstream from sewage treatment plants: male fish were shown to contain vitellogenin, a protein in egg yolk, which is only produced under the influence of the female sex hormone (ß-estradiol), i.e., normally only produced in females [8]. This effect can be traced back to several micropollutants (Table 2). The significant substances here are those having estrogenic effects: nonylphenol (NP), octylphenol (OP) and other degradation products of nonionic surfactants which enter the surface waters via sewage treatment plant effluents [9, 10]. Their effects are, however, 10^4–10^6 times weaker than that of the female sex hormone ß-estradiol [11]. Additional micropollutants also show weak estrogenic effects (Table 2).

Chemicals with estrogenic effects influence the hormonal system either directly by binding to the estrogen receptor of the cell or indirectly by affecting other components of the system by upsetting the hormonal balance. Known compounds with direct effects are nonylphenol, octylphenol, o, p'-DDT and kepone.

The nonylphenol concentrations measured in Switzerland and England are ecotoxicologically relevant (Fig. 4). Their levels are within the concentrations known to cause the production of vitellogenin in fish. Possible estrogenic effects on fish can, therefore, not be dismissed in waters heavily contaminated with wastewater, being especially significant in summer at low water levels and at a high proportional level of wastewater in running waters. Taking into account the importance of these effects, work on this problem must be intensified, as such effects have been observed in common micropollutants. Experimental work and field studies are needed in order to develop systems with which the estrogenic effects of chemicals may be detected.

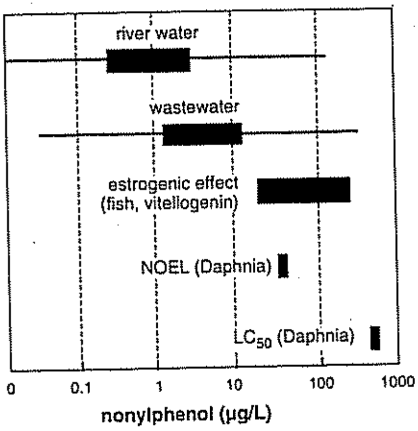


Fig. 4
Concentration of nonylphenol in wastewater and contaminated rivers in Switzerland [9, 10] and England as well as its effects on fish and Daphnia. Averages (thick bar) and concentration ranges (thin line) are depicted. Estrogenic effects occur in concentrations found in wastewater. The acute effect usually shown (LC_{50} value), as depicted for Daphnia, is much higher, however. The concentration at which no effects can be observed (NOEL, no observed effect level, i.e., the concentration at which effects cannot yet be observed) is lower, however.

Practical Consequences

Empirical evidence on the negative effects of micropollutants suggests that assessing their chronic effects is practically impossible using the currently available testing methods. Practical improvements should include both im-

Trace compound	Application or source
nonylphenol	industrial cleaning agent detergent: degradation product of APE[1]
octylphenol	industrial cleaning agent detergent: degradation product of APE
nonyl- and octylphenol ethoxylate	degradation product of APE
nonyl- and octylphenol carboxylic acid	degradation product of APE
synthetic estrogens (estradiols)	contraceptive pill
butylbenzol phthalate, dibutyl phthalate	softeners in plastics
bisphenol A	softeners in plastics

Table 2
Some of the known estrogenic micropollutants in the effluents of sewage treatment plants;
[1]APE = alkylphenol polyethoxylates.

proved methods for assessing the contamination of organisms and the development of reliable testing systems.

Biomarkers as Indicators of Contamination

Biochemical alterations in organisms are viable biomarkers for the detection and assessment of contaminations and damages to organisms caused by chronic concentrations of pollutants. Biomarkers react very sensitively to certain micropollutants and express the biochemical reactions of the organisms to stress. Hence they can serve as early-warning systems. Their high effectivity in assessing contamination is due to the fact that they can determine the decisive bioavailable fraction of the chemicals. Biomarkers can supplement chemical analytical methods, for they measure the reaction of the organism to contamination.

A review of approximately 80 field studies shows that the induction of cytochrome P450-dependent monooxygenases (P450) is closely correlated to contamination with PCBs, petrochemicals and other chlorinated compounds including those from paper mills (Fig. 5). In 90% of the studies, the contamination can be related to an increase in these enzymes, and in a fourth of the cases, it can be correlated to the degree of contamination. This biomarker reaction is linked to the toxic effects (e.g., disturbed hormonal balance), pointing to the toxic effects of the chemical contamination. Analytical methods alone can identify the substances, but their ecotoxicological significance remains unclear.

The Development of New Testing Systems for Chronic Ecotoxicity

Our high standard of living has bestowed a chemical legacy on our planet. The ecotoxicological testing of substances, however, has not kept up with the pace of their development and use. Permits for new compounds are almost solely given on the basis of tests for acute toxicity; reproduction studies on Daphnia lasting 14–21 days is usually all that is required. Furthermore, "old" compounds need not be tested. As data on acute toxicity do not allow direct conclusions to be drawn as to chronic toxicity, the assessment of the latter becomes ever more urgent for new compounds being produced in large quantities. As the unexpected chronic effects of organotin compounds and nonylphenol imply, the available testing methods must be improved. The development of new systems for detecting both acute and chronic effects on key vital functions such as reproduction have to be intensified. To this end, new biochemical techniques using cell systems can be useful. For example, the estrogenic effect of chemicals can be shown by using fish hepatocytes. The acute toxicity to fish can also be detected using cell lines. In order to assess chronic effects, sensitive biochemical assays (receptor binding, induction of cytochrome P450 and stress proteins, reporter genes) must be developed or made use of to a larger extent.

Additional efforts in research on the development of new systems should result in the increased application of reliable testing methods so that possible chronic effects on ecosystems can be detected as soon as the chemicals are developed. On the other hand, the fact that communities and ecosystems can become impaired indirectly through chronic effects also has to be taken into consideration. Ecotoxicology aims to discover and understand the effects chemicals have on various biological levels in the light of their environmental chemistry and fate in the environment. This endeavour can only be successful if the basic ecotoxicological mechanisms involved can be discovered and understood.

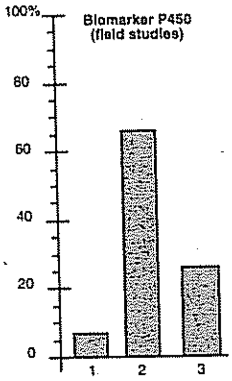


Fig. 5
Biomarker cytochrome P450 as indicator for the contamination of fish with certain micropollutants (PCB, PAHs, chlorinated dibenzodioxins and furans, micropollutants in wastewater from paper mills). In over 90% of the approx. 80 investigations, the increase of the cytochrome P450 enzyme is correlated to the contamination.

- *1 = not significant, no connection between P450 and contamination;*
- *2 = significant, increased P450 levels in connection with contamination;*
- *3 = correlation, statistically proven correlation between P450 and contamination.*

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[1] Fent, K. and J. Hunn, *Organotins in freshwater harbors and rivers: temporal distribution, annual trends and fate.* Envir. Toxicol. Chem., 1995. *14*, p. 1123–1132.

[2] Fent, K. and P.W. Looser, *Bioaccumulation and bioavailability of tributyltin chloride: influence of pH and humic acids.* Wat. Res., 1995. *29*, p. 1631–1637.

[3] Weidenhaupt, A.N.J., *Trialkylzinnverbindungen: Speziierung im Oktanol/Wasser System. Sorption an Mineraloberflächen.* 1995, Dissertation ETH Zürich, Nr. 10'940.

[4] Fent, K. and T.D. Bucheli, *Inhibition of hepatic microsomal monooxygenase system by organotins in vitro in freshwater fish.* Aquat. Toxicol., 1994. *28*, p. 107–126.

[5] Oehlmann, J., *Imposex bei Muriciden (Gastropoda, Prosobranchia). Eine ökotoxikologische Untersuchung zu TBT-Effekten.* 1994, Dissertation Universität Münster, Deutschland.

[6] Fent, K. and W. Meier, *Tributyltin-induced effects on early life stages of minnows Phoxinus phoxinus.* Arch. Environ. Contam. Toxicol., 1992. *22*, p. 428–438.

[7] Fioramonti, E., R.D. Semlitsch, H.U. Reyer, and K. Fent, *Long-term effects of triphenyltin and pH on survival, body mass and time to metamorphosis of tadpoles of Rana lessonae and Rana esculenta.* Appl. Ecol., 1996 (submitted).

[8] Purdom, C.E., et al., *Estrogenic effects of effluents from sewage treatment works.* Chem. Ecol., 1994. *8*, p. 275–285.

[9] Giger, W., P.H. Brunner, and C. Schaffner, *4-Nonylphenol in sewage sludge: Accumulation of toxic metabolites from nonionic surfactants.* Science, 1984. *225*, p. 623–625.

[10] Ahel, M., W. Giger, and M. Koch, *Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment I. Occurrence and transformation in sewage treatment.* Wat. Res., 1994. *28*, p. 1131–1142.

[11] Jobling, S. and J.P. Sumpter, *Detergent components in sewage effluent are weakly oestrogenic to fish: An in vitro study using rainbow trout (Oncorhynchus mykiss) hepatocytes.* Aquatic Toxicol., 1993. *27*, p. 361–372.

Hansruedi Siegrist

Behavior of Trace Compounds During Sewage Treatment

The behavior of a trace compound during sewage treatment can be described using a mathematical model as long as gas exchange, sorption, aerobic and anaerobic degradation of the compound and the operating conditions in the sewage treatment plant are known. Hydrophilic compounds must be aerobically degradable, whereas lipophilic compounds require anaerobic degradation, as they become sorbed to particles and enter the digester directly after primary clarification. Most volatile compounds escape by way of aeration at the biological treatment stage and should exert no adverse effects on the atmosphere.

Diana Hornung

Hansruedi Siegrist

Introduction

Before an organic or inorganic compound is produced and used in large quantities, thereby entering the environment, its physical, chemical and biological properties must first be determined. This is especially true for compounds that are directly applied to water itself such as detergents and other cleaning agents. The behavior of the compounds during sewage treatment is mainly determined by the following three processes:

- gas exchange with the atmosphere
- sorption to the suspended solids and to the formed biomass
- aerobic and anaerobic biodegradation.

Depending on the treatment stage and the properties of the compounds, the influence of these three processes differs markedly. A sewage treatment plant with mechanical treatment (screening, grit removal and primary clarification), biological treatment (nitrification in an activated sludge system) and sludge treatment (digestion and dewatering) will serve as our model plant. The excess sludge (secondary sludge) is led back into the inflow of the grit removal tank or to the primary clarifier and is then thickened with primary sludge (Fig. 1). Relevant to the environment are the treated wastewater, the exhaust gases from aeration and the sludge which is often used as fertilizer in agricultural soils. In the following description of the material fluxes, the residual solids from screening (usually burned) and grit removal (brought to a disposal site) are omitted from consideration.

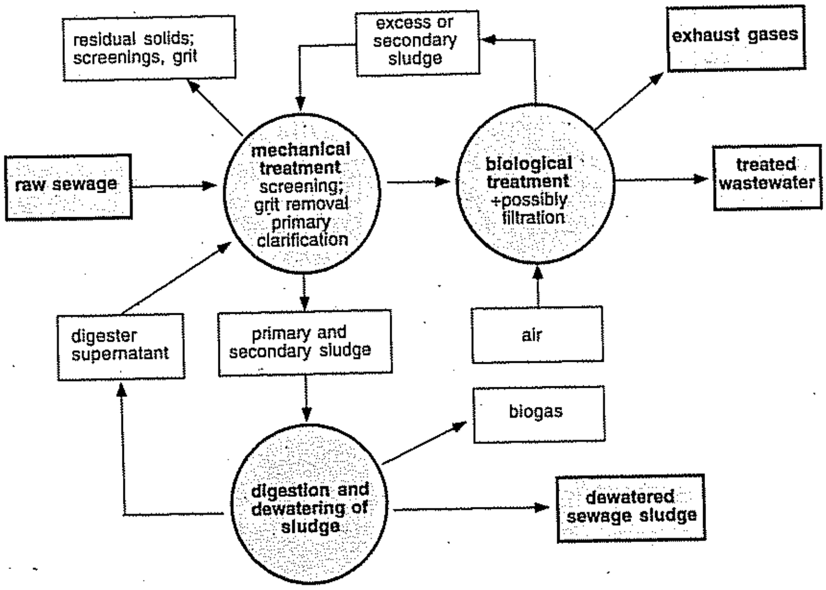

Fig. 1
Schematic diagram of a sewage treatment plant illustrating both mechanical and biological stages, including anaerobic digestion and dewatering of sludge.

The Properties of Trace Compounds

Air/Water Partitioning (Gas Exchange)

Air/water partitioning of a gas is important for the stripping of a compound during biological treatment

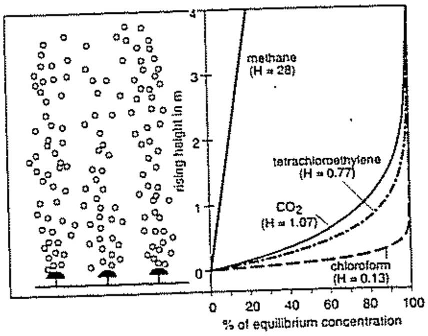

Fig. 2
Enrichment of a volatile compound in a rising gas bubble during fine-bubble aeration ($d_{bubble} \approx$ 3 mm), assuming that the concentration in the aqueous phase is the same throughout the total depth of the tank (equilibrium concentration $Sg = H \cdot Sw$, $T = 20$ °C).

and aerated grit removal. At thermodynamic equilibrium, the distribution between gaseous and aqueous phases may be described by Henry's Law:

$$S_{g,i}/S_{w,i} = H_i \qquad [m_W^3\ m_G^{-3}]$$

where H_i = dimensionless Henry's Law constant for the substance i (Henry's Law constants for several important compounds are given in [1, 2] and Stumm and Morgan, Aquatic Chemistry, 3rd Ed.).

$S_{g,i}$, $S_{w,i}$ = concentration of a substance in the gaseous and the aqueous phase [$g_i\ m^{-3}$].

The less volatile a compound, the smaller its Henry's Law constant and the faster the compound in a rising air bubble attains equilibrium with the dissolved compound in the aqueous phase (Fig. 2). During fine-scale aeration of an activated sludge system, CO_2 attains 95% of its equilibrium concentration after rising only three meters [1]. For compounds almost attaining their saturation equilibrium in the rising gas bubble ($H < 2$), the mass flow F_{gas} of the gas being stripped is proportional to the injected amount of air Q_g, H and its dissolved concentration S_w:

$$F_{gas,i} = Q_G \cdot S_{w,i} \cdot H_i \qquad [g_i\ d^{-1}]$$

For $H < 0.5$, the above relation can also be used for the aerated grit chamber.

Solid/Water Distribution (Sorption)

The distribution of a compound between its solid phase (suspended matter: particles and evolved biomass) and the aqueous phase is significant to the behavior and biodegradation of a compound during sewage treatment. The transfer of a compound from the aqueous to solid phase is called sorption; the opposite process is desorption. Nonpolar compounds are lipophilic and absorbed to a large extent by the solid organic phase. Polar and ionized compounds are hydrophilic and remain mostly in the aqueous phase.

Most compounds which possess long nonpolar carbon chains, such as the amphiphilic, surface-active tensides/surfactants, are adsorbed to solids in spite of their polar or charged groups (e.g., linear alkylbenzenesulfonates (LAS), secondary alkylsulfonates (SAS), quarternary amines, alkylphenols). Ions can be bound through adsorption, precipitation and ion exchange, the latter two processes being of secondary importance in the treatment of domestic sewage. The cationic heavy metal ions adsorb to the negatively charged surfaces of the inorganic particles and to the biomass.

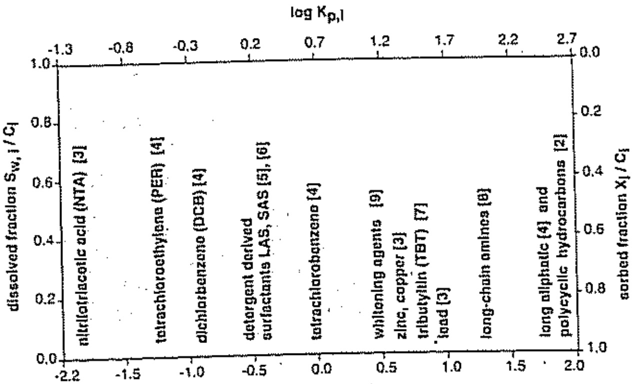

Fig. 3
Dissolved and sorbed fractions of a compound as a function of the product of the distribution coefficient of sorption $K_{p,i}$ and the concentration of suspended matter $X_{ss,in} = 0.2\ kg_{ss}\ m^{-3}$ in the influent of a domestic sewage treatment plant.

The higher the sorbed fraction of a compound, the more efficiently it is removed in the mechanical stage of treatment. Compounds which mainly reside in the aqueous phase enter the biological treatment stage directly.

In the equations below the dissolved substances are labelled S, sorbed substances X and the total concentration abbreviated with C and always pertain to m^3 of water volume. We may assume an approximately linear sorption for trace compounds:

$$X_i = K_{p,i} \cdot S_{w,i} \cdot X_{SS} \qquad [g_i\ m^{-3}]$$

$K_{p,i}$ = solid/water distribution coefficient of the compound i [$m^3\ kg_{ss}^{-1}$] ($K_{p,i}$ can be estimated from the octanol/water distribution coefficient K_{ow} [2] or be determined through sorption experiments).

X_{ss} = concentration of the suspended solids (related to the influent) [$kg_{ss}\ m^{-3}$]

X_i = sorbed concentration of the compound i (related to the influent)

The dissolved proportion of substance i can be calculated from the following equation:

$$\frac{S_{w,i}}{C_i} = \frac{S_{w,i}}{S_{w,i} + X_i} = \frac{1}{1 + K_{p,i} \cdot X_{ss}}$$

At a concentration of suspended solids amounting to $X_{ss,in} = 0.2\ kg_{ss}\ m^{-3}$ influent, over 50% of the compound is adsorbed to particles at $K_{p,i} > 5$ or ($K_{p,i} \cdot X_{ss,in} > 1$), respectively (Fig. 3).

The chlorinated volatile aliphatic and aromatic hydrocarbons attain sorption equilibrium after less than 30 minutes [4]. This process takes approximately 1–2 hours for larger molecules such as optical whitening agents (derivatives of stilbenes and biphenyls) [9]. We can assume, therefore, that both the primary and excess sludge are in equilibrium with the aqueous phase in primary and secondary clarification. If the excess sludge is recycled to the influent of the grit removal tank and then thickened together with the primary sludge in the primary clarifier, the sorption equilibrium between the mixed sludge and primary effluent can nearly be attained through intensive mixing in the grit removal tank. This equilibrium cannot, however, be reached when the excess sludge is directly led to preclarification.

Biodegradability

The biodegradability of a compound depends on the redox state of the water and the average washout rate (dilution rate = D_x) of bacteria in the system. The lower the washout rate, i.e., the longer the residence time (solid retention time SRT = $1/D_x$), the more diversified the biomass becomes; degradation of normally nondegradable compounds becomes possible.

In the biological stage of treatment, aerobic and denitrifying conditions prevail with biomass residence times of SRT = 4–15 days. During digestion of sludge, anaerobic conditions predominate with high hydraulic residence times (20–40 days).

Biodegradation is usually described by Monod kinetics. If the maximal growth rate of the bacteria breaking down a trace compound is significantly higher than the rate at which the activated sludge is washed out, $\mu_{max} >> D_x = 1/SRT$, biodegradation may be described using first-order kinetics:

$$r_{deg,\,i} = -k_i \cdot S_{w,i} \cdot X_{ss} \qquad [g_i\ m^{-3}\ d^{-1}]$$

k_i = 1st order degradation constant for the substance i [$m^3\ kg_{ss}^{-1}\ d^{-1}$] (must be determined through tests carried out under the same conditions as found in the sewage treatment plant).

X_{ss} = biomass [$kg_{ss}\ m^{-3}$]

When calculating values for the intermediate products of degradation, both their rate of production from the original compound and their subsequent rate of degradation must be considered. Only the degradation of a single compound is described below.

The kinetics of biodegradation are dependent to a great extent on the adaptation of the bacteria to the compound they are to remove. If a compound occurs irregularly or develops irregularly in the plant (with interruptions of weeks), its biodegradation may be incomplete, even though it is completely degraded when present in continuous supplies (Fig. 4).

The Monod constant (concentration at which the degradation of a compound occurs at half the maximal rate) depends on the experimental conditions at which the bacteria grow. Lower Monod constants have been observed for the degradation of NTA [3] as well as for nitrification at decreasing concentrations of the compound in the reactor. This means that those bacteria whose enzyme systems possess the highest affinity to the compound become naturally selected. The reaction constant k_i increases with a decreasing Monod constant. In order to determine the kinetics of degradation then, conditions must be used that are similar to those found in the sewage treatment plant (i.e., solid retention time, temperature, concentration range, composition of the wastewater).

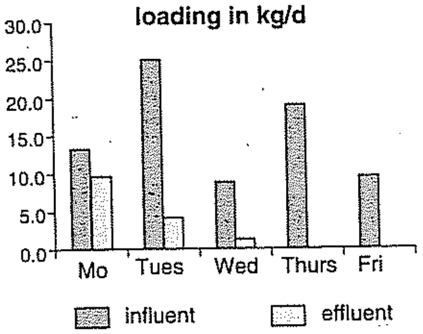

Fig. 4
Adaptation in the degradation of 3-nitrobenzenesulfonic acids (oxidation agent used in the textile industry) in the two-stage nitrifying sewage treatment plant in Herisau after a 4 week interruption in production by the textile industry [10]. The adaptation occurred within a few days. Batch experiments demonstrated that the doubling time of maximal degradation rate is less than 1.5 days.

A Simple Model of a Sewage Treatment Plant

Using the following simplified model, the flux of trace compounds is estimated. The three stages of mechanical and biological treatment and sludge treatment are discussed separately. As they are connected to one another by way of recirculation flow (Fig. 1), a subsequent iterative procedure is needed for determining the single contributions of each stage to the flux. In order to calculate the flux, the operational conditions given in Table 1 must be known.

Mechanical Treatment

Under stationary conditions, the loads of the influent, the excess sludge and the digester supernatant are equal to the load in the primary effluent, the mixed sludge (primary and excess sludge) and the exhaust gas of the grit removal system:

$$Q_{in} \cdot C_{in,i} + Q_{es} \cdot C_{es,i} + Q_{ds} \cdot C_{ds,i}$$
$$= Q_{pe} \cdot C_{pe,i} + Q_{ms} \cdot C_{ms,i} + Q_{g,gr} \cdot C_{g,i}$$

We can assume that practically no sludge enters the preclarification tank by way of the digester supernatant. The lipohilic compound loads in the digester, supernatant which enter the digester by way of the mixed sludge are,

Parameter	Symbol	Range	Used	Dimension
temperature	T	10–20	15	°C
production of primary sludge	$X_{ss,ps}$	0.1–0.15	0.12	$kg_{ss}\ m_{influent}^{-3}$
production of excess sludge	$X_{ss,es}$	0.1–0.15	0.12	$kg_{ss}\ m_{influent}^{-3}$
production of mixed sludge	$X_{ss,ms}$	0.2–0.3	0.24	$kg_{ss}\ m_{influent}^{-3}$
production of digested sludge	$X_{ss,ds}$	0.15–0.2	0.17	$kg_{ss}\ m_{influent}^{-3}$
solid retention time in activ. sl. sys.	SRT	4–15	10	d
residence time in digester	θ_h	20–40	30	d
suspended matter in the influent	$X_{ss,in}$	0.2–0.3	0.22	$kg_{ss}\ m_{influent}^{-3}$
suspended matter in prim. effluent	$X_{ss,pe}$	0.1–0.15	0.10	$kg_{ss}\ m_{influent}^{-3}$
suspended matter in sec. effluent	$X_{ss,se}$	0.01–0.02	0.01	$kg_{ss}\ m_{influent}^{-3}$
air consumption in aeration	$q_{g,as}$	5–10	8	$m_g^3\ m_{influent}^{-3}$
air consumption in grit removal tank	$q_{g,gr}$	0.5	0.5	$m_g^3\ m_{influent}^{-3}$

Table 1
Operational conditions of a domestic sewage treatment plant as basis for calculating the flux of a trace substance. The range is given for dry weather based on an amount of 0.33 m^3 of wastewater per day.

therefore, small and not considered here. Furthermore, the currents in the digester supernatant in excess, mixed and digested sludge are also not relevant as they only amount to a few percent of the inflow; hence $Q_{in} = Q_{pe} = Q$. For the excess, mixed and digested sludge, only the amount of compound sorbed to the particles is taken into account. The concentration of the sorbed substances in the excess sludge is assumed to be in equilibrium with their dissolved concentrations in the secondary effluent (S_{se}), and the sorbed concentrations of the compounds in the mixed sludge in equilibrium with their concentrations in the primary effluent. Furthermore, the dissolved concentration in the grit removal system seems to approximate the dissolved concentration in the primary effluent, S_{pe}. With respect to the influent Q:

$$S_{in,i} \cdot (1+X_{ss,in} \cdot K_{p,i})+X_{ss,es} \cdot S_{se,i} \cdot K_{p,i} =$$
$$= S_{pe,i} \cdot (1+X_{ss,pe} \cdot K_{p,i})+X_{ss,ms} \cdot S_{pe,i} \cdot K_{p,i}+$$
$$q_{g,gr} \cdot H_i \cdot S_{pe,i}$$

and $S_{in,i}$, $S_{pe,i}$, $S_{se,i}$ = dissolved conc. of i in the influent, the primary and secondary effluent.

The solid/water distribution coefficient of the substance i $K_{p,i}$ is assumed to be equal for all suspended matter. The concentration of dissolved i in the primary effluent is dependent on processes in the biological stage because of excess sludge recycling, which means:

$$S_{pe,i} = \frac{S_{in,i} \cdot (1+X_{ss,in} \cdot K_{p,i})+S_{se,i} \cdot X_{ss,es} \cdot K_{p,i}}{1+K_{p,i} \cdot (X_{ss,pe}+X_{ss,ms})+H_i \cdot q_{g,gr}}$$

pe = primary effluent
se = secondary effluent

Biological Treatment

In the stationary condition, the influent load (primary effluent) is equal to that of the secondary effluent, the excess sludge, the gas issuing from aeration and biodegradation:

$$Q_{pe} \cdot C_{pe,i} = Q_{se} \cdot C_{se,i} + Q_{es} \cdot C_{es,i} + H_i \cdot Q_{g,as} \cdot S_{as,i}$$
$$+ k_{as,i} \cdot S_{as,i} \cdot X_{ss,as} \cdot V_{as}$$

In a completely mixed reactor, the dissolved concentration in the activated sludge system is equal to that in the secondary effluent, $S_{as,i} \approx S_{se,i}$; the total amount of activated sludge corresponds to that which is produced during the solid retention time (SRT); $X_{ss,as} \cdot V_{as} = SRT \cdot Q \cdot (X_{ss,es} + X_{ss,se})$. For the excess sludge, only the sorbed amount is taken into consideration. With respect to the influent:

$$S_{pe,i} \cdot (1+X_{ss,pe} \cdot K_{p,i}) = S_{se,i} \cdot (1+X_{ss,se} \cdot K_{p,i})$$
$$+X_{ss,es} \cdot S_{se,i} \cdot K_{p,i}+H_i \cdot q_{g,as} \cdot S_{se,i}$$
$$+k_{as,i} \cdot S_{se,i} \cdot SRT \cdot (X_{ss,es}+X_{ss,se})$$

and for the concentration in the secondary effluent:

$$S_{se,i} = [S_{pe,i} \cdot (1+X_{ss,pe} \cdot K_{p,i})]/$$
$$[1+X_{ss,se} \cdot K_{p,i} +X_{ss,es} \cdot K_{p,i}$$
$$+H_i \cdot q_{g,as}+k_{as,i} \cdot SRT \cdot (X_{ss,es}+X_{ss,se})]$$

$k_{as,i}$ = 1st order degradation constant of the substance i in the activated sludge system [$m^3\ kg_{ss}^{-1}\ d^{-1}$].

Sludge Treatment

Under stationary conditions, the influent load from primary clarification (mixed sludge consisting of primary and excess sludge) equals the load sorbed to the digested sludge and anaerobic degradation. The sorbed amount of the substance in the digested sludge is assumed to be in equilibrium with the dissolved concentration in the digester supernatant $S_{di,i}$. The flux of the digester supernatant and of the dissolved fractions being negligible, we obtain:

$$Q \cdot X_{ss,ms} \cdot S_{pe,i} \cdot K_{p,i} = Q \cdot X_{ss,ds} \cdot S_{di,i} \cdot K_{p,i}$$
$$+k_{di,i} \cdot S_{di,i} \cdot X_{ss,di} \cdot V_{di}$$

The entire amount of digested sludge in the digester is the amount produced during a certain hydraulic residence time: $X_{ss,di} \cdot V_{di} = \theta_h \cdot X_{ss,ds} \cdot Q$

$$S_{di,i} = \frac{S_{pe,i} \cdot X_{ss,ms} \cdot K_{p,i}}{X_{ss,ds} \cdot K_{p,i}+k_{di,i} \cdot \theta_h \cdot X_{ss,ds}}$$

$k_{di,i}$ = 1st order degradation constant of the substance i in the digester [$m^3\ kg_{ss}^{-1}\ d^{-1}$]

Through recirculation of the excess sludge, the processes in both the mechanical and biological treatment systems are interdependent. The three equations for determining the dissolved concentrations in the primary and secondary effluents as well as the digester have to be calculated, e.g., by using an iterative procedure with the help of a spreadsheet [11]. The sorbed concentrations of the substances and their total fluxes can subsequently be determined from their dissolved concentrations.

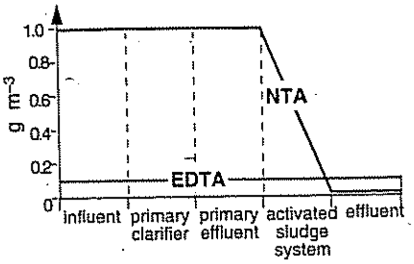

Fig. 5
Concentration profiles of NTA and EDTA in a domestic sewage treatment plant.

The Behavior of Trace Substances

The flux and behavior of some of the compounds found in a domestic sewage treatment plant, currently under investigatation at the EAWAG, are discussed below, using the operational conditions shown in Table 1.

Hydrophilic Compounds

The microbial degradation of the complexing agents NTA (nitrilotriacetic acid, a substitute for polyphosphate in detergents) and EDTA (ethylenediaminetetraacetate) has been investigated intensively over the past several years. NTA is easily biodegradable under aerobic conditions, whereas EDTA is not. Its sorption to particles is less than 1%. Average concentrations in influent are approximately 1 g NTA m^{-3} and 0.1 g EDTA m^{-3}, respectively. The degradation constant for NTA is calculated using experimentally derived data from [3]:

$k_{as,NTA} = 40\ m^3\ kg_{ss}^{-1}\ d^{-1}$.

Since sorption to solids is negligible, the removal efficiency η_{NTA} can be calculated for the entire plant using the following approximation formula:

$$\eta_{NTA} = 1-\frac{S_{se,NTA}}{S_{in,NTA}} = 1-\frac{1}{1+k_{as,NTA} \cdot X_{ss,es} \cdot SRT}$$
$$= 1-\frac{1}{1+40 \cdot 0.12 \cdot 10} = 0.98$$

Because EDTA is persistent, its load in the secondary effluent is five times higher than that of NTA (Fig. 5). Apart from naturally occurring complexing agents among the degradation products, the dissolved fraction of heavy metals is dependent on EDTA. In most of the domestic sewage treatment plants investigated to date, NTA-removal efficiencies of over 95% were observed for a solid retention time of more than four days.

Volatile Compounds

When studying the behavior of volatile compounds, the degree to which oxygen can be utilized, i.e., the efficiency of bubble aeration, is of major importance. The poorer the utilization of oxygen, the more air has to be injected into the system and the higher the stripping capacity of the aeration. Under normal operating conditions, a utilization of 8–15% of the oxygen from air may be assumed. For oxygen consumption rates of 120 g O_2 m^{-3} for the degradation of organic matter and an additional 120 g O_2 m^{-3} for nitrification, the oxygen content of the air being 300 g O_2 m^{-3}, the amount of 5–10 m^3 air per m^3 influent is needed. In order to generate mixing in the grit removal tank, approximately 0.5 m^3 air m^{-3} influent are required. The degree to which volatile compounds are removed in the grit removal tank may be substantial, in spite of the relatively small air flow compared to the activated sludge system, as their dissolved concentration is significantly higher in mechanical than in biological treatment (Fig. 6).

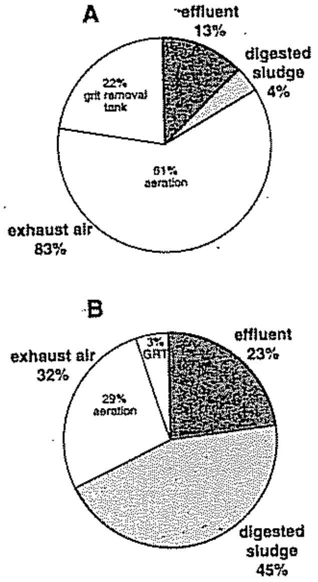

Fig. 6
Calculated behavior of
A) tetrachloroethylene
$H = 0.6, K_p = 0.23\ m^3\ kg_{ss}^{-1}$
B) tetrachlorobenzene
$H = 0.16, K_p = 4.2\ m^3\ kg_{ss}^{-1}$
according to the parameters of the model.

Tetrachloroethylene (solvent, melting point = 251 °C) and tetrachlorobenzene (solid, melting point = 329 °C) are discussed below as examples (Fig. 6). Both compounds are only minimally degradable. Under anaerobic conditions, some biodegradation of tetrachloroethylene has been observed, but only after a long adaptation time. Tetrachloroethylene is slightly volatile, sorbs weakly to solids and is stripped to over 80%. Tetrachlorobenzene is semi-volatile and is removed through sorption (45%) and stripping (32%; Fig. 6). This is the case for dewatered and liquid sludge; the sorbed fraction evaporates when the sludge is dried.

In a tank with plug flow, the efficiency of stripping is enhanced and the effluent load is decreased in comparison to a completely stirred reactor, e.g., the tetrachloroethylene load decreases from 13% to 5% (model calculation with a cascade of 3 reactors). This result may also be obtained when comparing calculated and measured data with those from a large sewage treatment plant in Chicago (Table 2). Differences with respect to the calculated values for trichloroethylene can probably be explained through variations in the load throughout the day, as averages from grab samples instead of 24h composite samples were used for the comparison.

Lipophilic and Amphiphilic (Surface-Active) Compounds

The tensides or surfactants used in detergents, LAS (linear alkylbenzenesulfonates) [5] and SAS (secondary alkylsulfonates) [6], sorb to a substantial degree to solids despite their negatively charged sulfonate group. Both compounds are degradable under aerobic conditions; under anaerobic conditions, they are biologically inert, their behavior being about the same in the sewage treatment plant (Fig. 7). In order to calculate the flux of LAS, the solid/water distribution coefficient from [11] (K_p = 1.66 m^3 kg_{ss}^{-1}) was used. The first order reaction constant for the aerobic degradation was estimated using the observations from the sewage treatment plant (ARA) Werdhölzli [5], (k_{as} = 40 m^3 kg_{ss}^{-1} d^{-1}). The LAS sorbed to the mixed sludge (26% of the influent load) entered the digester wherein no further degradation took place under anaerobic conditions.

compound	H 20°C [–]	K_F $\frac{m_W^3}{kg_{ss}}$	K_{OW} $\frac{m_W^3}{m_{Octanol}^3}$	S_{so}/S_{po} calculated completely mixed	 calculated cascade of 3 reactors	 measured
chloroform	0.13	0.06	93	0.59	0.50	0.54
trichloroethylene	0.41	0.12	240	0.31	0.19	0.10
tetrachloroethylene	0.77	0.23	760	0.19	0.08	0.13

Table 2
Comparison of calculated and measured data on three volatile chlorinated C2 hydrocarbons in the influent and effluent of a large sewage treatment plant in Chicago ($q_g = 5.3\ m_g^3\ m^{-3}$ influent, $X_{ss,es}$ = 0.09 kg_{ss} m^3 influent) [12].

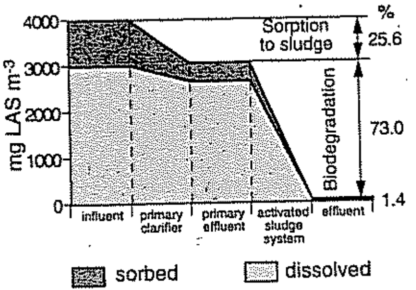

Fig. 7
Calculation of the flux of LAS (K_p = 1.66 m^3 kg_{ss}^{-1}, $k_{ss,LAS}$ = 40 m^3 kg_{ss}^{-1} d^{-1}).

A consumption of 6500 t/a (1990) of LAS results in an influent load of 1.4 g $d^{-1}cap^{-1}$ (13 million population equivalents), or 4 g LAS m^{-3}, respectively. According to model calculations, this equals 6 g LAS kg_{ss}^{-1} in digested sludge. In various plants in the Canton of Zurich, levels in the range of 5.6±1.6 g LAS kg_{ss}^{-1} have been reported [13].

About 90% of the influent load of the lipophilic tributyltin, which is not degraded under either aerobic or anaerobic conditions, is removed by sorption and remains in the digested sludge ($K_P \approx 30$ m^3 kg_{ss}^{-1}) [7]. The more lipophilic a compound, the more important is its biodegradablilty under anaerobic conditions because of the utilization of the digested sludge as fertilizer in agriculture. Strongly lipophilic compounds (long-chain aliphatic and polycyclic hydrocarbons) are also still mainly bound to filterable matter after secondary clarification. A filtration stage would thus reduce the effluent load considerably.

Heavy Metals

Heavy metals adsorb to particles as a result of electrostatic interactions between cationic metal ions and the negatively charged surfaces of inorganic particles (oxide surfaces) and the biomass. The dissolved fraction depends on the synthetic complexing agents present in the water, such as EDTA, and on naturally occurring complexing degradation products such as amino acids, and humic and fulvic acids [14]. Dissolved copper is bound so strongly to natural complexing agents that an artificially effected increase in the concentration of NTA in the effluent of the sewage treatment plant of Zurich-Glatt did not result in an increase in copper in the effluent [3]. Measurements in the activated sludge system of the Zurich Glatt treatment plant obtained values of $K_p \approx 20$ m^3 kg_{ss}^{-1} for zinc and copper and $K_p \approx 40$ m^3 kg_{ss}^{-1} for lead, which adsorbs more strongly to particles [3]. According to calculations using the model, removal efficiencies amounting to 80% for zinc and copper and 90% for lead were achieved. The removal efficiencies from published data are slightly lower, 60–90% [15], probably because the excess sludge led back into primary clarification did not have enough time to reach equilibrium with the concentration in the primary effluent. In addition, the concentration of suspended matter in the secondary effluent was often significantly higher than assumed by the model.

Practical Consequences for the Quality of Waste Water

In order to be able to evaluate the behavior of a trace compound during the course of sewage treatment, its Henry's Law and sorption constants and its potential for aerobic and anaerobic degradation must be known. Assuming that sewage sludge will still be applied in agriculture in the future the following has to be recommended for trace compounds found in the wastewater:

- Hydrophilic compounds enter the biological stage directly and so must be easily degradable under aerobic conditions.
- A part of the lipophilic and surface-active compounds enter the anaerobic sludge treatment directly by way of primary clarification through sorption to particles; hence they should be easily degradable, both aerobically and anaerobically.
- Most of the volatile compounds, such as the short-chain halogenated aliphatic hydrocarbons are stripped off in the biological stage and in the aerated grit removal tank and hence should have no negative effects on the atmosphere. Less volatile compounds also have to be easily degradable both aerobically and anaerobically.
- About 60–90% of the heavy metals sorb to the sewage sludge. The fraction entering natural waters (10–40%) is, however, not negligible. Although heavy metal load has been reduced strongly, zinc and copper may cause problems for the application of sewage sludge in agriculture in the future because their input into the soil is higher than their output. Heavy metal concentration in wastewater should therefore be reduced further.

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[1] Siegrist H. und Boller M. (1995): Manuskript Gasaustausch, In: Systemanalyse und Reaktortechnik, PEAK A3, EAWAG.

[2] Schwarzenbach R., Gschwend P., and Imboden D. (1993): Environmental organic chemistry, John Wiley & Sons, New York.

[3] Alder A., Siegrist H., Gujer W. and Giger W. (1990): Behaviour of NTA and EDTA in biological wastewater treatment, Wat Res., *24*, 733–742.

[4] Matter Ch. (1979): Sorptions- und Stoffaustauschprozesse refraktärer organischer Leitsubstanzen in einer Belebungsanlage, Dissertation ETHZ Nr. 6403.

[5] Siegrist H., Alder A., Brunner P. and Giger W. (1989): Pathway analysis of selected organic chemicals from sewage to agricultural soil. In: *Sewage sludge treatment and use* (Eds.: Dirkzwager A.H. and Hermite P.L.), Elsevier applied science, London.

[6] Field A.J., Field T.M., Poiger T., Siegrist H. and Giger W. (1995): Fate of secondary alkane sulfonate surfactants during municipal wastewater treatment, Wat. Res., *29*, 1301–1307.

[7] Fent K. und Müller M.D. (1991): Occurance of organotins in municipal wastewater and sewage sludge and behaviour in a treatment plant, Env. Sci. and Tech., *25*, 489–493.

[8] Matthijs E., Gerike P., Klotz H., Kooijman J.G.A., Korber H.G. and Waters J. (1992): Removal and mass balance of the cationic fabric softener Di(hydrogenated)tallowdimethylammoniumchloride in activated sludge treatment plants, AIS/CESIO internal report.

[9] Poiger T. (1994): Behaviour and fate of detergent-derived fluorescent whitening agents in sewage treatment, Dissertation ETHZ Nr. 10'832.

[10] Altenbach B. (1995): Determination of Benzene- and Naphtalenesulfonates in wastewater and their behavior in sewage treatment, Dissertation ETHZ, Nr. 10'832.

[11] Struijs J., Stoltenkamp J. and van de Meent D. (1991): A spreadsheet-based box model to predict the fate of xenobiotics in a municipal wastewater treatment plant, Wat. Res., *25*, 891–900.

[12] Namkung E. and Rittmann B. (1987): Estimating volatile organic compound emissions from publicly owned treatment works, J. Wat. Poll. Contr. Fed., *59*, 670–678.

[13] Giger W., Alder A., Brunner P., Marcomini A. and Siegrist H. (1989): Behaviour of LAS in sewage and sludge treatment and in sludge treated soil, Tenside Deterg., *26*, 95–99.

[14] Xue H., Oestreich A., Kistler D. und Sigg L. (1995): In welcher Form liegt Kupfer in verschiedenen Gewässern vor?, EAWAG news, *39D*, 13–16.

[15] Chassot G. (1995): Recencement et évaluation du métabolisme anthropique sur la base des boues d'épuration, Diss. ETHZ, Nr. 11'155.

Hasan Belevi

Trace Elements Provide Insight into Solid Waste Combustion Processes

In Switzerland's municipal solid waste incinerators (MSWIs), exhaust gas quality has consistently improved over the past 20 years due to various technical advances and the expansion of gas cleaning systems. The problems in the industry have thus shifted away from the quality of the gas produced to the quality of the solid residues that result from the process.

Hasan Belevi

Material Fluxs in Municipal Solid Waste Incinerators

About 80% of all municipal solid waste in Switzerland is thermally treated in MSWIs. In addition to carbon, the most abundant element, municipal solid waste contains almost all other elements on the periodic table in at least trace quantities. Complex chemical reactions take place during the combustion process. As a result, some elements are deposited in the bottom ash. The majority of the others enter the flue gas and are distributed between the gas cleaning residues and the exhaust gas.

The distribution of waste constituents among the various products of an MSWI may be determined by material flux analysis [1–3], as was recently performed on the MSWI located in St. Gallen. Figure 1 summarizes the various chemical and physical treatment processes occurring in the plant. The quantities of all substances entering and leaving the system are measured. In this case, municipal solid waste was collected from households and commercial concerns and burned during the sampling.

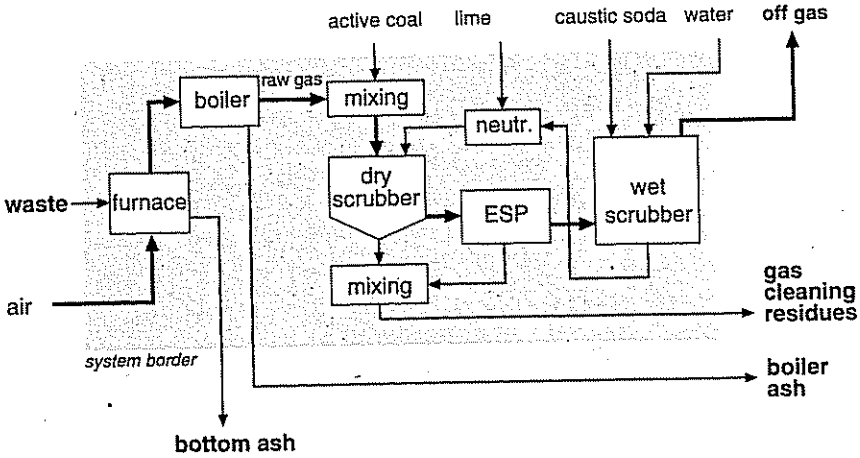

Fig. 1
System analysis of the St. Gallen municipal solid waste incinerator.

Figure 2 shows the conversion of the waste to the four types of products. About 75% of the waste is converted to exhaust gas. Each ton of waste produces 230 kg of bottom ash, 21 kg of gas cleaning residues, and 3 kg of boiler ash. The quality of these products is determined by the chemical and physical properties of the municipal solid waste and the process engineering parameters at each processing stage in the MSWI.

Figure 3 shows the proportional distribution of six elements in the products. The lithophile elements phosphorus (P) and copper (Cu) are transferred to the bottom ash, while cadmium (Cd) and antimony (Sb) mainly enter the flue gas and become concentrated in the gas cleaning residues. Zinc (Zn) and lead (Pb) are transferred to both the bottom ash and gas cleaning residues.

Elemental Composition of Municipal Solid Waste

The composition of municipal solid waste may be calculated from the material fluxs and product composition.

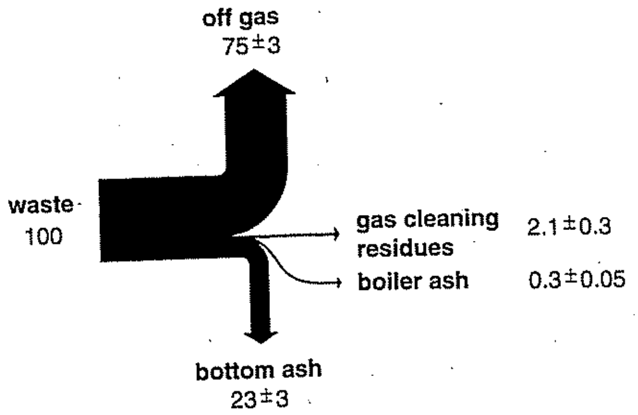

Fig. 2
Conversion of waste to various product types in the St. Gallen MSWI. All values are expressed as wt%.

Figure 4 shows the water content and elemental composition of municipal solid waste treated in the St. Gallen MSWI. The water content of the waste is approximately 25 wt%. The carbon content of the municipal solid waste (37 wt%) is relatively high compared with values found in the literature. This may be due to the commercial waste this burn contained which on average has higher carbon concentrations than municipal solid wastes. About 20 wt% of the waste consists of oxygen and about 4 wt% of hydrogen, which are present in the waste in forms other than water. The lithophile elements silicon, iron, calcium and aluminum together account for about 10 wt%. The remaining 4 wt% of the waste consists of the other elements.

Product Quality

Table 1 compares the elemental composition of the bottom ash and gas cleaning residues with the concentrations in rocks and ores. The element contents of the bottom ash are one to two orders of magnitude higher than in rocks (mercury is an exception); however, they are much lower than the contents of ores. The bottom ash has no relevance as an ore. On the other hand, if it is landfilled or used as a road-building material, it has an increased environmental hazard potential due to the accumulation of the trace elements.

The gas cleaning residues contain the heavy metals Zn and Pb in almost the same concentrations as ores. This makes them potential resources which could be segregated and recycled. Landfilling without first reducing the high concentrations of trace elements is unacceptable.

For environmentally sound waste management, the distribution of elements between the products should be optimized. The concentration of trace elements in the bottom ash should be reduced, but increased in the other residues. Specific control of product quality clearly requires a better understanding of the chemical and physical processes which take place in thermal treatment plants.

Influence of Input and Process Engineering on Product Quality

To better understand those processes which influence the distribution of elements in the products, additional laboratory-scale experiments were conducted. Figure 5 serves to illustrate the complexity of the processes involved. The transfer of Zn to the gaseous phase of artificial mixtures is shown for two temperatures (500 °C and 900 °C) as a function of temperature and residence time. In addition to quartz as the main constituent, the first mixture contained 0.29 mol of zinc chloride, 0.06 mol of zinc oxide and 0.15 mol of zinc metal per kg. In the second mixture, a bottom ash sample was added in place of the quartz but was otherwise identical to mixture 1. The transfer of elemental Zn to the gas phase was determined at a constant air feed rate.

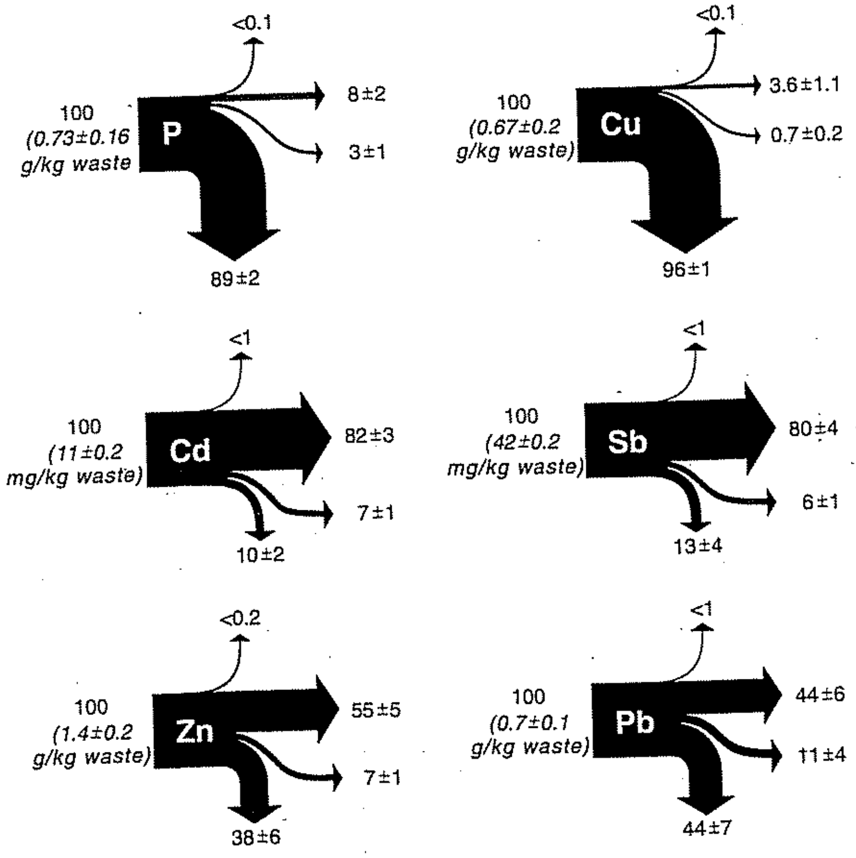

Fig. 3
Distribution of elements among the various products in the St. Gallen MSWI.

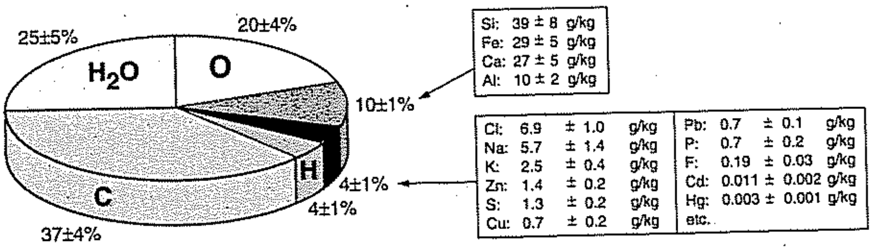

Fig. 4
Composition of municipal solid waste treated in the St. Gallen MSWI.

In the case of the first mixture treated at 500 °C, 0.17 mol/kg of Zn were transferred to the gas phase in less than one hour. In the case of the second mixture, which contained bottom ash instead of quartz, no Zn was transferred to the gas phase at the lower temperature. In the case of the first mixture treated at 900 °C, approximately 0.25 mol/kg Zn was transferred to the gas phase within a few minutes. In the case of the quartz-free mixture treated at the higher temperature, 0.1 mol/kg Zn was transferred to the gaseous phase after 15 minutes and 0.15 mol/kg after 4 hours. These results suggest that the matrix plays a major role in trace metal transfer to the gaseous phase during thermal treatment.

Unfortunately it is not possible to conduct similar experiments in MSWIs, as poor product qualities due to parameter modifications are unacceptable; however, other experiments can be performed by burning various types of waste. This was, in fact, done in the St. Gallen incinerator. Figure 6 shows the transfer coefficients of Zn and Pb during combustion of domestic municipal solid waste and of mixed municipal solid waste (domestic municipal solid waste and similar commercial waste). The calorific value of the mixed municipal solid waste is higher than that of the domestic municipal solid waste due to its higher content of plastics, paper and wood.

The coefficient of Zn transfer to the bottom ash was significantly higher for the domestic municipal solid waste than for the mixed municipal solid waste. The cause may lie in the differing composition of the two types of waste. Formation of Zn chlorides and Zn oxides in the furnace may be influenced by this different matrix, which may cause a different distribution of Zn between the flue gas and the bottom ash. The concentrations of Zn in the bottom ash, however, are approximately identical in both experiments (3.0±0.6 and 2.8±0.3 g/kg). The reasons for this are (1) the concentration in the mixed municipal solid waste is higher than the concentration in the domestic municipal solid waste and (2) a higher percentage of the Zn enters the bottom ash during combustion of domestic municipal solid waste than during combustion of mixed municipal solid waste. The concentrations in the gas cleaning residues, however, differ significantly (22±1 g/kg and 36±2 g/kg). Lead exhibits the same behavior.

The temperatures measured in the combustion chamber are the same in both cases, as the temperature in the incinerator is controlled so as to achieve good burnout; however, the different distributions of Zn and Pb are reason to suspect that the temperature distributions on the grate are not identical. The matrix may also play a role here.

Another way of carrying out field tests is to study various plants. Figure 7 shows the distribution of Pb between the various residues of the Oftringen MSWI. In this plant, approximately 7.5 t/h of municipal solid waste are combusted in a grate kiln and some 2.7 t/h of sewage sludge with a dry

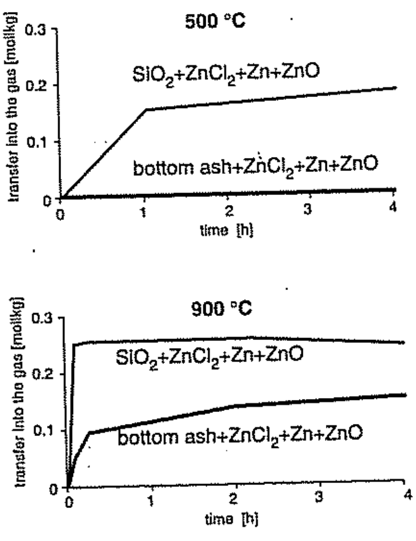

Fig. 5
Transfer of Zn to the gaseous phase in laboratory experiments conducted at two temperatures.

Element	Content [g/kg]			
	Bottom ash[1]	Gas cleaning residues[1]	Volcanic rocks[2]	Ores (raw materials)[2]
Zn	2.8	36	0.07	40
Pb	1.6	14	0.015	20
Cu	2.3	1.1	0.03	10
Cd	0.006	0.4	0.0002	4
Hg	0.0002	0.1	0.00008	2

[1] Average composition of over 20 samples
[2] Average composition of over 100 samples [4]

Table 1
Concentrations of some elements in bottom ash, gas cleaning residues, volcanic rocks and ores.

solids content of 25% are burned in a rotary kiln. Hot gases from the combustion chamber of the grate kiln are fed counter-current into the rotary kiln. The exhaust gases from sludge combustion are, in turn, fed into the combustion chamber of the grate kiln.

Roughly 99% of the Pb input comes from the municipal solid waste. This is because the Pb concentrations in the sewage sludge are one order of magnitude lower, and the material fluxs are also much smaller. Some 54% of the Pb goes into the bottom ash and 43% into the boiler ash and precipitator dust. The balance ends up in the sewage sludge ash.

The Pb input to the rotary kiln from sewage sludge is smaller than its output to the sewage sludge ash. The Pb concentration in the sewage sludge ash is 2–5 times higher than expected. There is clearly an additional source of Pb to the rotary kiln via the flue gas from the grate kiln. This phenomenon indicates that, at temperatures of 800–900 °C in the grate kiln, substances with relatively high vapor pressures enter the flue gas. When they come into contact with the sludge in the rotary kiln, a portion may be transferred to the sewage sludge ash.

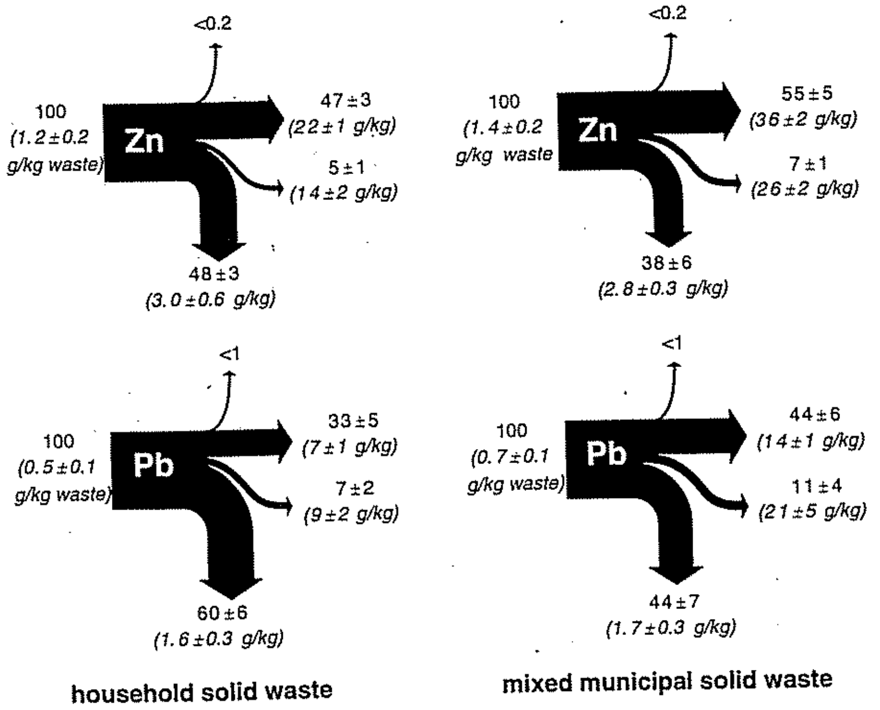

Fig. 6
Distribution of Zn and Pb among the products. Values are expressed in both wt% and concentrations (in brackets) for two different types of waste.

Conclusions

Numerous chemical elements are present in municipal solid waste in trace concentrations. During thermal waste treatment, their quantities in the bottom ash should, if possible, be reduced and accumulated in other residues in an effort to both to recover and reuse them and to reduce the environmental hazard potential of the bottom ash.

Studies on the behavior of trace elements in thermal waste treatment plants suggest that the quality of the product residues depends on both the characteristics of the waste and on various aspects of the process engineering. Such studies are useful in making environmental assessments of MSWIs and for achieving better control of residue quality.

Finally, I would like to make the following predictions:

- In the future, the MSWI of today will give way to "product-oriented thermal/chemical waste treatment plants" in which the distribution of elements among the products will be specifically controlled.
- Processes in these plants will be optimized, taking into account the characteristics of the inputs (concentrations of main constituents, concentrations of trace elements, etc.) and the behavior such substances during treatment.

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[1] Brunner P.H. & H. Moench (1986): «The Flux of metals through municipal solid waste incinerators», Waste Management and Research, S. 105–119.

[2] Baccini P., P.H. Brunner, H. Belevi, G. Henseler, W. Obrist und H.P. Diener (1987): «Einführung in die Methodik der Stoffflussanalyse», EAWAG-Seminar, 16. August, Zürich.

[3] Belevi H. (1993), «Was können Stoffflussstudien bei der Bewertung der thermischen Abfallbehandlung leisten?», VDI Berichte Nr. 1033. S. 261–275.

[4] Smith, D.G. (1981), «The cambridge encyclopedia of earth sciences», Cambridge university press, New York.

[5] Wedephol, K.H. (1971), «Geochemistry». Holt, Rineharr, Winston Inc., New York.

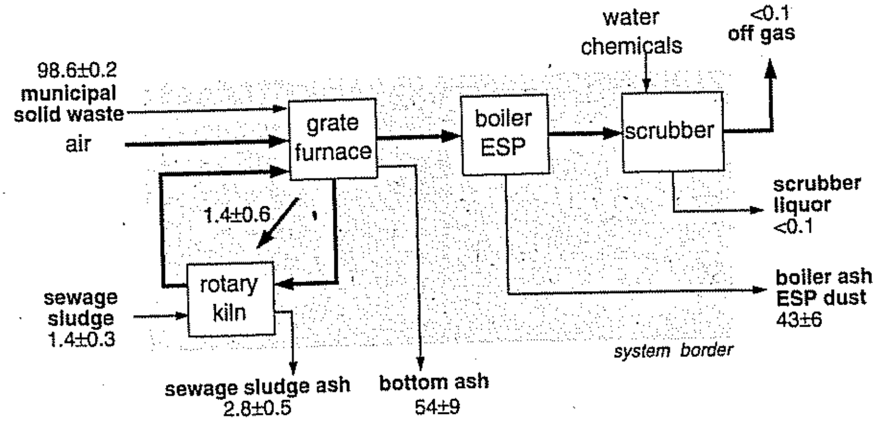

Fig. 7
Distribution of Pb (in wt%) for the Oftringen MSWI.

Thomas Egli and Matthias Bally

How is the Microbial Degradation of Trace Compounds Regulated?


Diana Hornung

Thomas Egli

Microbial biodegradation of trace compounds in sewage treatment plants and in natural waters is always accompanied by the presence of naturally occurring carbon compounds which result from the decomposition of plant and animal material. The ratio of natural available compounds to trace compounds is an important factor in the regulation of the enzymes which effect the degradation of trace compounds.

What do Heterotrophic Microorganisms Feed on?

As their nutritional basis, heterotrophic microorganisms make use of cell material which other organisms have built up. Being decomposers, they fulfill a central function in the global carbon cycle: they oxidize (mineralize) the CO_2 fixed by green plants and algae back to carbon dioxide and thus complete the natural carbon cycle (Fig. 1). Many of these organisms possess proteins (enzymes), which also allow them to utilize organic chemicals, even if they are synthetic, as nutrients; that is, to transport them into the cell, break them down and use them for their growth. For this reason, the mineralization of many organic chemicals which are spilled into the environment depends on biodegradation by heterotrophic microorganisms.

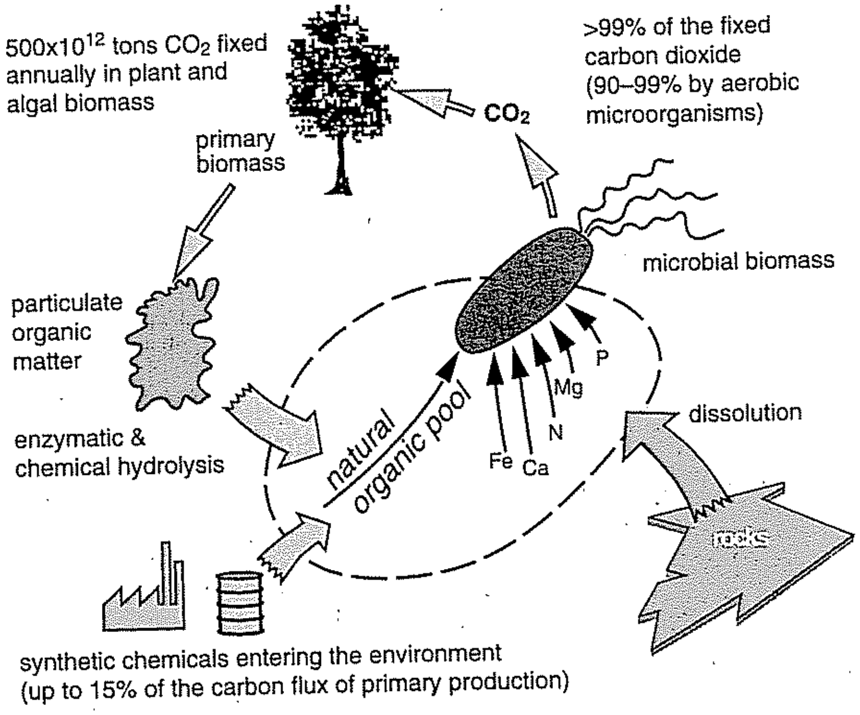

Fig. 1
The importance of heterotrophic microorganisms in the global carbon cycle and in the degradation of persistent synthetic organic chemicals found in the environment.

Carbon Compounds Only Available in Limited Amounts

Naturally occurring carbon compounds can be found in the environment mainly in the form of particulate organic material (POM) originating from decomposing plant and animal cells. This material, consisting of various high molecular weight compounds, cannot directly be utilized as a substrate by microorganisms. It must first be broken down into its chemical constituents through chemical or enzymatic processes. The concentrations of natural nutrients available for the growth of microorganisms such as sugars or amino acids are very low in all ecosystems [1]. Their concentrations are mostly in the range of a few micrograms per liter (see Table 1). Such low concentrations of bioavailable carbon compounds are, on the one hand, due to the slow hydrolysis rates of POM;

	Concentration (µg / L)
Total dissolved organic carbon (DOC)	500 – 10'000
Organic carbon available to microorganisms	approx. 1-5% of the dissolved carbon
Bound sugars	10 – 1000[a]
Total free sugars	10 – 100[a]
Total fatty acids	1 – 100[a]
Bound amino acids	10 – 100[a]
Total free amino acids	1 – 20[a]
Total aromatic compounds	1 – 5000[a]
Urea	1 – 100[a]
Free glucose	1 – 50[a]
Free fructose	1 – 20[a]
Free glutamate	0.5 – 5[a]
Alkylated anilines	1 – 10[b]
Chlorinated anilines	0.1 – 5[b]
NTA	0.1 – 10[c]
Linear alkylbenzenesulfonate	1 – 30[d]

[a] ocean-/freshwater [1]

[b] Rhine river water [Meijers I.A.P. (1987) 5. Dechema Fachgespräche Umweltschutz]

[c] riverwater [Houriet J.P. (1990) BUWAL-Bulletin 3/90, 18–39]

[d] riverwater [Waters J. & Feijtel T.E.J. (1995) Chemosphere 30: 1939–1956]

Table 1
Concentrations of natural organic compounds and of several organic chemicals found in the environment and which are used as a basic source of nutrition by heterotrophic microorganisms in different aquatic systems. "Bound" means that these compounds are found in polymeric form. As a rule, the lower limit is given by the concentrations found in oligotrophic marine systems; the upper limit by those in eutrophic freshwater systems.

on the other hand, they are a result of a continuous consumption due to the capability of microorganisms to assimilate such substances into the cell using efficient transport systems at very low concentrations. Both of these factors have led to the situation that in most ecosystems the bioavailability of carbon compounds is probably the main limiting factor for the growth of heterotrophic microorganisms [2] (see also contribution by Bosma and Harms on bioavailability, p. 28ff).

Compared to natural occurring carbon compounds available in surface waters, the concentrations of synthetic chemicals found in the environment are mostly one to two orders of magnitude lower. Concentrations of these chemicals found in the raw wastewater of domestic sewage plants are usually somewhat higher, yet this mainly applies to compounds which are being used in large quantities, such as substances used in detergents, the concentrations of which are occasionally rising to over one milligram per liter for a very short time.

Simultaneous Degradation of Trace Compounds and Natural Substrates

Many observations suggest that at the extremely low nutrient concentrations found in sewage treatment plants and natural waters, microorganisms do not restrict themselves to only one of the many carbon compounds which are present for their growth, but that they assimilate and utilize many different compounds simultaneously as nutrients [3]. Even synthetic organic chemicals found in the environment are in most cases probably degraded together with naturally occurring compounds. Trace compounds are estimated to make up less than 1% of the total carbon used for a microorganism's growth.

Regulation of Degradation Enzymes

In laboratory studies using pure cultures of microorganisms which degrade synthetic organic chemicals found in the environment it was observed that the regulation of the formation of degrading enzymes depends on a twofold regulation:

- On the one hand, they are not produced in the absence of the chemical – or at most in very small quantities. If such a substance comes close to a microorganism, the respective degradation enzymes have to be produced first (induced).
- On the other hand, their production is influenced by the availability of naturally occurring nutrients (mainly carbon compounds such as glucose from the degradation of cellulose from plants); if such easily degradable nutrients are available in excess amounts they may inhibit the production of degradation enzymes for persistent organic chemicals in the environment.

Most studies, however, are restricted to the growth of these microorganisms on single substrates at high concentrations. Information on the regulation of degradation enzymes during growth at conditions found in the environment is practically nonexistent. The question arises then as to whether microorganisms ever produce the enzymes needed for degradation of trace substances under growth conditions found in sewage treatment plants. Does the presence of natural carbon compounds inhibit the production of these enzymes? These questions have been asked in our laboratory for one chemical found in the environment, the complexing agent nitrilotriacetic acid (NTA). Experiments were conducted using pure cultures of an NTA-degrading bacterium and in sewage treatment plants.

The Degradation of Nitrilotriacetic Acid (NTA)

NTA-degrading bacteria were isolated from the environment; many were found to belong to a new genus of bacteria *(Chelatobacter heintzii)* [4]. These bacteria enjoy a wide distribution in nature, and there is evidence that they contribute to a large extent to the degradation of NTA in sewage treatment plants and in surface waters [5,6]. The enzymes responsible for the degradation of NTA in *Ch. heintzii* were isolated and described; an O_2-dependent NTA-monooxygenase (NTA-MO) was found to be the key enzyme [4].

Assuming that NTA is not being degraded alone but simultaneously with carbon compounds of natural origin, *Ch. heintzii* was grown in a carbon-limited continuous culture at a constantly low growth rate and fed with various mixtures of glucose plus NTA. The influence that composition of the glucose/NTA mixture had on the degradation of NTA and the production of the NTA-MO was recorded [7].

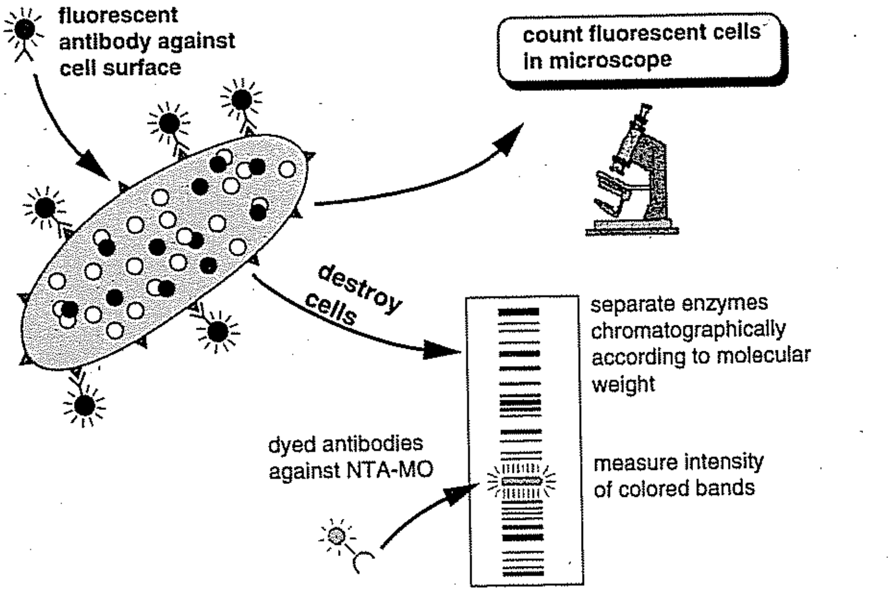

Fig. 2
Immunological methods applied in detecting and quantifying NTA-degrading microorganisms (especially the genus Chelatobacter) and the key enzyme for the degradation of NTA, NTA-monooxygenase (NTA-MO).

If the bacteria were grown on glucose only, the production of NTA-MO was inhibited, and the measured activity of the enzyme fell to near the detection limit. If mixtures of NTA plus glucose were provided, the bacteria always utilized both NTA and glucose, regardless of the glucose concentration. When grown on mixtures in which the fraction of NTA was less than 1% of total carbon, no significant increase in the production of NTA-MO was observed, although the bacteria were able to degrade the small amounts of NTA provided (Fig. 2). If the culture was fed a mixture composed, for example, of 260 µg NTA-C/l plus 727 mg of glucose-C/l (0.036% NTA-C/99.964% glucose-C), then NTA was degraded to an equilibrium concentration of 12 µg NTA-C/l. NTA degradation in mixtures containing less than 1% NTA-C is probably due to a low basic level of the NTA enzymes. If the bacteria received NTA/glucose mixtures with more than 1–3% NTA-C, then a marked increase in NTA-MO was always observed. The extent of the activity of the NTA-MO in this case was clearly dependent on the composition of the substrate mixture (Fig. 2).

Behavior of NTA-Degraders in Sewage Treatment

From the observations mentioned above, the question arises whether or not NTA-degrading bacteria behave in the same way in sewage treatment plants or in their natural environments; that is, are NTA-degrading bacteria present in large amounts in sewage sludge because they mainly feed on substrates other than NTA and consequently only degrade NTA on the side? Conversely, are only a small number of bacteria found in sewage sludge specialized to degradation of NTA and thus have induced their NTA enzymes completely?

Both the number of NTA-degrading bacteria in sewage sludge as well as the presence of NTA-MO were investigated in two sewage treatment plants, ARA Glatt and ARA Säntis. The main difference between the plants is in the composition of their wastewater. In order to determine the number of NTA-degrading bacteria and to quantify the amount of NTA-MO, antibodies with color markers were used – one of which binds specifically to the surface of the *Chelatobacter* cell, each one of the other two being specific to one of the two subunits of the NTA-MO enzyme (see description of the methods in Fig. 2).

The results obtained correspond to previous studies in other sewage treatment plants [5], the fraction of NTA-degrading bacteria in the sludge of the domestic sewage plant ARA Glatt being in the range of several percent. NTA clearly accounted for less than 1% of the total dissolved carbon in this plant. Despite the presence of such cells and the almost 99% efficiency of NTA degradation, the presence of the NTA-MO enzyme could not be detected (Table 2).

In contrast, the plant on the Säntis (a mountain) was run by three restaurants which all use a dishwashing detergent containing a high proportion of NTA. The fraction of NTA in the total dissolved carbon of the wastewater was in the range of 5–10%. Although in this plant the proportion of antibody-positive bacteria, amount-

	ARA Glatt	**ARA Säntis**
NTA-C: DOC	0.06%	6.9%
Number of NTA-degraders	$1 \cdot 10^7$ pro ml SS	$3.2 \cdot 10^7$ pro ml SS
Fraction of NTA-degraders intotal population	4.2%	0.9%
NTA-MO, cA	n.d.	0.045 mg/g SS
NTA-MO, cB	n.d.	0.007 mg/g SS
NTA-degradation efficiency	98.9%	99.9%

Table 2
Quantification of NTA-degrading microorganisms and NTA monooxygenase (NTA-MO) in the sewage sludge of both sewage treatment plants (ARA) Glatt and Säntis using antibodies.

NTA-C = carbon from NTA; DOC = dissolved organic carbon; n.d. = not detectable. Detection limit for NTA-MO components cA and cB was 0.0005 mg protein/g dried sewage sludge (SS). The total number of cells in the sewage sludge was determined by using the acridine orange method. Data from [6].

ing to 1% of the entire population, was slightly lower than in the ARA Glatt, the presence of NTA-MO could be detected in the sludge. Obviously these results have to be interpreted with caution; for example, it has not been verified whether the number of immunopositive cells is a good estimate of the total number of NTA-degrading bacteria or whether all of the NTA-degrading bacteria present in the plant degrade NTA using NTA-MO (discussed in [3]). The results nevertheless suggest that regulation of the production of NTA-degrading enzymes is an important factor in sewage treatment plants and that the degradation of NTA most probably occurs through regulation of the production of NTA-degrading enzymes rather than by enrichment of the NTA-degrading bacterial population.

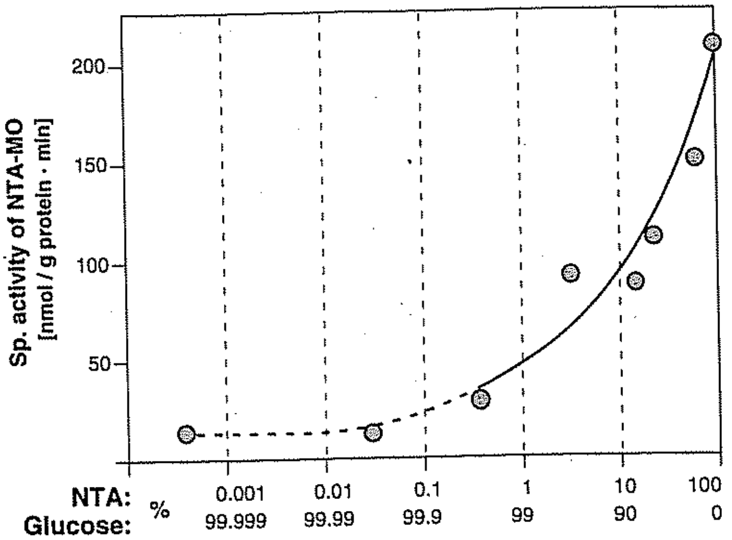

Fig. 3
Production of NTA-MO during the growth of Ch. heintzii (ATCC 29600) in a carbon-limited chemostat culture using mixtures of NTA plus glucose in various concentrations. The rate of dilution was kept constant at D = 0.06 h^{-1}. Data from [7].

The Induction of NTA-Degrading Enzymes

The fact that NTA-degrading microorganisms can be found in most sewage treatment plants and surface waters but that their NTA-degrading enzymes are not induced begs the question as to how the induction of NTA-degrading enzymes occurs with time. Are these bacteria able to react to the presence of NTA within a few minutes or do they need days before they are able to synthesize the appropriate enzymes?

Laboratory experiments using pure cultures of *Ch. heintzii* were carried out in order to answer this question [6, 8]. The temporal course of the production of NTA-degrading enzymes was analyzed during transition from glucose to NTA as the nutrient medium. In these experiments, NTA-degrading enzymes were detected in the bacterial cells within minutes using a simple test. The cells were harvested, washed and their respiratory activity was measured with an oxygen probe in the presence of NTA. In this test, induced cells showed an enhanced rate of oxygen uptake in the presence of NTA, whereas non-induced cells did not show any increase in the uptake of oxygen. The results from this simple method could be corroborated by determining the NTA-MO activity and by the immunological quantification of NTA-MO [6].

First, *Ch. heintzii* was grown in continuous culture with glucose as their sole source of carbon at a constant rate of dilution. Under such conditions, the cells do not produce any NTA-degrading enzymes (see Fig. 3) and an NTA-stimulated enhanced rate of oxygen uptake could not be detected. If glucose was then entirely replaced by NTA in the influent nutrient medium (while retaining the rate of dilution), the cells were unable to utilize NTA for a longer period of time; only after over 20 hours did the NTA-stimulated enhanced rate of oxygen uptake indicate an increased production of NTA enzymes (Fig. 4).

Since such abrupt changes in the availability of nutrients are rare in sewage treatment plants and since other easily degradable carbon sources are always present apart from NTA, the experiment was repeated. The new influent medium contained a mixture of glucose and NTA. The results shown in Fig. 4 suggest that an increased proportion of glucose in the mixture drastically reduces induction time. These results show clearly that the availability of additional, easily degradable carbon compounds do not necessarily inhibit the production of enzymes degrading a pollutant, but that they may support their production (under the condition that they are not present in excessive concentrations). They probably provide the energy needed by the microbial cells to produce new enzymes under such transitional conditions.

Based on these results, we can expect that the production of NTA-degrading enzymes can occur relatively quickly in a sewage treatment plant and that the presence of alternative carbon sources seem to have a supporting and accelerating influence on the dynamic course of the enzyme induction process.

Conclusions and Practical Applications

Simple laboratory experiments on NTA-degrading bacteria have shown that microorganisms degrade this environmental pollutant in sewage treatment plants and in ecosystems simultaneously with naturally occurring carbon compounds and that production of NTA-degrading enzymes depends mainly on the relationship between the amount of NTA and other available compounds. The fact that NTA is usually found in very low concentrations and provides only a small proportion of the carbon necessary for microbial growth leads to minimal formation of NTA-degrading enzymes. Preliminary investigations in sewage treatment plants have also shown that information on the regulation of NTA degradation enzymes gathered from pure culture experiments can probably also be applied to this complex situation; hence, the degradation of NTA occurs primarily through the activity of "uninduced" cells (i.e., cells with a very low basic level of NTA enzymes) which are ubiquitously present in quite large numbers in sewage sludge and also in rivers and lakes [5,6]. This assumption seems not only to apply to NTA but also to the degradation of other trace compounds, as similar behavior patterns has also be observed in microorganisms which degrade methylene chloride, p-toluene sulfonate (A. Tien and T. Egli, unpublished) and methanol [3].

Such regulation patterns could provide practical information on the dynamics of degradation processes in ecosystems and sewage treatment plants based on inducible enzyme systems. We suppose that "uninduced" cells can only produce a delayed reaction to a sudden input of NTA, whereas partly induced cells should be capable of reacting relatively quickly to a pulse of NTA. This statement is supported by observations made on model sewage treatment plants which were supplied with various mixtures of NTA plus synthetic wastewater [6].

The use of specific mixtures of easily degradable carbon sources together with chemicals could be used to either maintaining steady state degradation or to specifically stimulate the degradation of environmentally problematic chemicals in industrial sewage treatment plants. Also the stimulation of specific degradation efficiencies in mixed microbial populations ~~for use~~ in cleaning contaminated soils is conceivable and work in this direction has already been done [9]. A further application of this knowledge can be imagined in the standardized "ready biodegradability" tests currently in use for organic chemicals. To date these tests are mainly based on the use of the tested chemical as the sole substrate, provided as the carbon source for a mixed population of microorganisms. The results presented here suggest that the use of specific mixtures of substrates could result in a reduction in the adaptation times for the degradation of otherwise "recalcitrant" chemicals.

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[1] Münster U. (1993): Concentrations and fluxes of organic carbon substrates in the aquatic environment. Antonie van Leeuwenhoek *63*, 243–264.

[2] Morita R. Y. (1993): Bioavailability of energy and the starvation state. In: Starvation in Bacteria (S. Kjelleberg, ed.), Plenum Press, New York, pp. 1–23.

[3] Egli T. (1995): The ecological and physiological significance of the growth of heterotrophic microorganisms with mixtures of substrates. Adv. Microb. Ecol. *14*, 305–386.

[4] Egli T. (1994): Biochemistry and physiology of the degradation of nitrilotriacetic acid and other metal complexing agents. In: Biochemistry of Microbial Degradation (C. Ratledge, ed.), Kluwer Academic Publishers, Dordrecht, pp. 179–195.

[5] Wilberg E., El-Banna T., Auling G., and Egli T. (1993): Serological studies on nitrilotriacetic acid (NTA)-utilising bacteria: Distribution of *Chelatobacter heintzii* and *Chelatococcus asaccharovorans* in sewage treatment plants and aquatic ecosystems. Syst. Appl. Microbiol. *16*, 147–152.

[6] Bally M. (1994): Physiology and Ecology of Nitrilotriacetate Degrading Bacteria in Pure Culture, Activated Sludge and Surface Waters. Dissertation Nr. 10'821, ETH Zürich.

[7] Bally M., Wilberg E., Kühni M., and Egli T. (1994): Growth and enzyme synthesis in the nitrilotriacetic acid (NTA) degrading *Chelatobacter heintzii* ATCC 29600. Microbiol. *140*, 1927–1936.

[8] Bally M. und Egli T. (1995): Dynamics of substrate consumption and enzyme synthesis in *Chelatobacter heintzii* during growth in carbon-limited continuous culture with different mixtures of glucose and nitrilotriacetate (NTA). Appl. Environ. Microbiol. (in press).

[9] Rittmann B.E., Seagren E., Wrenn B.A., Valocchi A.J., Ray C. und Raskin L. (1994): In Situ Bioremediation, 2nd ed., Noyes Publications, Park Ridge, New Jersey, USA.

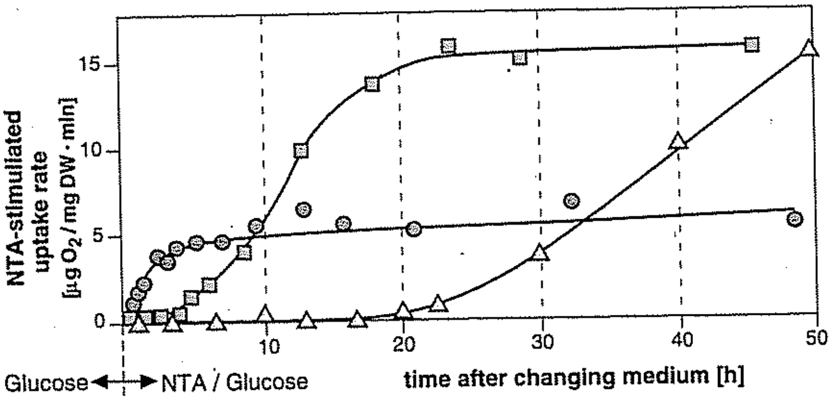

Fig. 4

Dynamics of NTA-MO production in cells of Ch. heintzii *(ATCC 29600) grown on glucose (measured as oxygen assimilation rate stimulated by NTA) after addition of NTA (△) or mixtures of glucose and NTA (▣ = 50% glucose/50% NTA; ◎ = 90% glucose/10% NTA). Before that, the bacteria were grown in a carbon-limited chemostat with glucose provided as the sole carbon source at* $D \doteq 0.06\ h^{-1}$. *The dilution rate was kept constant during the entire experiment at* $D = 0.06\ h^{-1}$. *Data from [6, 8].*

Tom Bosma and Hauke Harms

Bioavailability of Organic Pollutants

Tom Bosma

A number of organic chemicals which leach into ground water from heavily polluted soils may be eliminated. To achieve their removal, however, the bioavailability of a pollutant must be maximized. Solubility, sorption and mass transfer together influence the rate of biodegradation of environmental contaminants.

The mass production of synthetic organic compounds and their use in all areas of human life has led to widespread contamination of practically every compartment of the biosphere. Industrial chemicals are released due to accidents and improper land disposal. They enter the environment because of carelessness during transportation, storage and use. A number of compounds, among them pesticides, are deliberately introduced into the environment in large quantities. Global pollution by low concentrations of many of these chemicals was first detected in the 1960s. More recently, public concern has been aroused by the knowledge that toxic organic chemicals may leach from polluted soils into ground water and endanger drinking water supplies. Many countries have already developed programs for cleaning up contaminated sites, many of which give preference to biological approaches, as they have little apparent effect on soil structure and are particularly cost effective. One problem with using biological techniques, however, is the limited amenability of many pollutants to biodegradation.

The purpose of this article is to consider the bioavailability of organic pollutants from the point of view of a bacterium who wishes to use environmental contaminants as a food source. Such an organism asks two questions: (1) how can I ingest of the chemical and (2) how can I digest it?

A fundamental prerequisite for the biotransformation of any chemical is the existence of microorganisms that either possess the biochemical abilities needed for degradation or are able to acquire such capabilities through genetic exchange with other microorganisms. It is also important for the overall biochemical reaction to be thermodynamically favorable; that is, to supply the microorganism with energy for its efforts. The goal of a biological clean-up operation then must be to maximize the bioavailability of a pollutant, i.e., the flow of the chemical to the bacterium.

A certain degree of contaminant flow in the direction of a bacterium is caused by the organism itself (see Fig. 1). As a result of its degradation activity, the bacterium decreases the concentration of a chemical at the cell surface and effectively forms a concen-

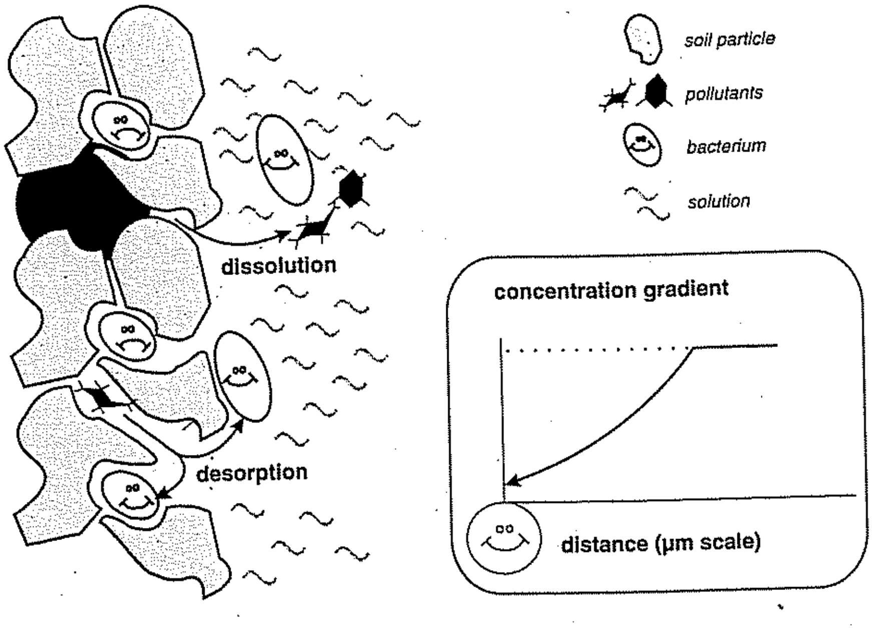

Fig. 1
Schematic illustration of a bacterium in soil or ground water (left) and the pollutant gradient caused by its degradation activity (right).

tration gradient [1]. Another driving force ensuring contaminant movement is the permeability of the soil matrix to the pollutant. The role of each of these factors in determining bioavailability will be examined in detail below.

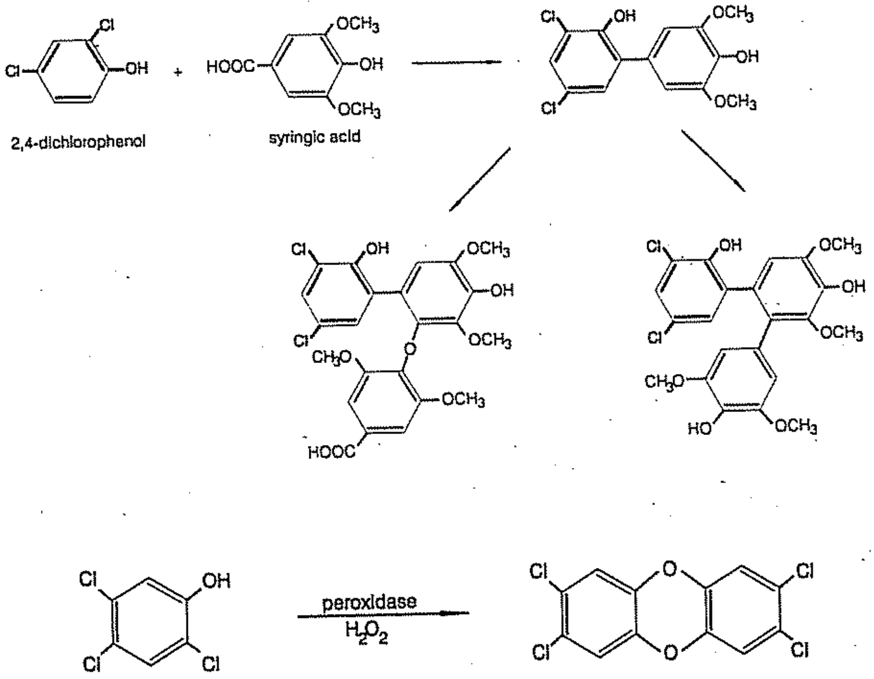

Fig. 2
Binding of pollutants to humus (above) and formation of polychlorinated dioxins (below).

The Concentration Gradient

Formation of Bound Residues and Dissolution Kinetics

The concentration gradient established between the ground water and bacterial cell surface may be influenced by factors other than bacterial degradation. Incorporation of pollutants into organic material and precipitation of sparingly soluble compounds leads, for instance, to a lower gradient and consequently to reduced pollutant flow [2]. Some organics like phenols, benzoic acids and anilines so closely resemble natural compounds that they may become incorporated into humus-like structures (Fig. 2). This process, which is called *coupling*, is catalyzed by soil minerals (clays and iron oxides) or by enzymes (peroxidase, phenol monooxygenase) and results in a decrease in dissolved contaminant concentrations. Such structure lose any biological or chemical activity. There are, in fact, proposals to use the formation of humus-bound organic residues as a remediation technique. The danger exists, however, that under some circumstances particulate organic matter may become mobile leading to dispersion of the pollutant. It has also been shown that coupling reactions do not always result in detoxification, but may lead to the formation of more toxic compounds such as polychlorinated dioxins und dibenzofurans (Fig. 2).

Hydrophobic chemicals are generally unevenly distributed in soil and tend to accumulate into lumps or to form droplets. Pollutants are in many cases also disposed of in pure liquid or solid form. Coal tar, accumulated in former town gas production sites, is an extreme form of such contamination. These types of contamination can only be eliminated by bacteria after they have dissolved in the ground water and passed through the soil matrix. Dissolution kinetics, therefore, greatly influence the flow of contaminants. One somewhat controversial possibility is the use of surface-active compounds to facilitate the dissolution process.

Lowering of the Pollutant Concentration at the Cell Surface

The uptake and degradation of a chemical by a bacterium leads to a decrease in its concentration at the cell surface which, in turn, effectively increases the flow of pollutant to the bacterium [2]. As mentioned previously, a prerequisite for pollutant degradation is the existence of the appropriate information in the microorganisms' genome and its expression. Suitable degradation routes can only be created if the overall reaction yields energy-assisted and if the highest energy barrier can be overcome by enzymes during the course of the reaction. The next section describes mechanisms which lead to the acquisition of such genetic information and discusses energy-related aspects of biodegradation.

Acquisition of Genetic Information

Degradation of an organic compound requires the activity of various enzymes. The recalcitrance of certain environmental contaminants to microbial degradation may, therefore, be due to a lack of the genetic information required to synthesize such enzymes. The acquisition of a working degradation route for a given anthropogenic compound may reside in the metabolic abilities present in a habitat being expressed in a single bacterium [3]. In such a case, in addition to the transmission of genetic information from one microorganism to another, small changes in the enzymes themselves may also be needed; these are accomplished by mutations. Such evolutionary phenomena are held responsible for the long time that microorganisms often take to adapt to the degradation of environmental chemicals.

The addition of laboratory-grown bacterial cultures which are already specialized in degradation of the pollutant in question can significantly

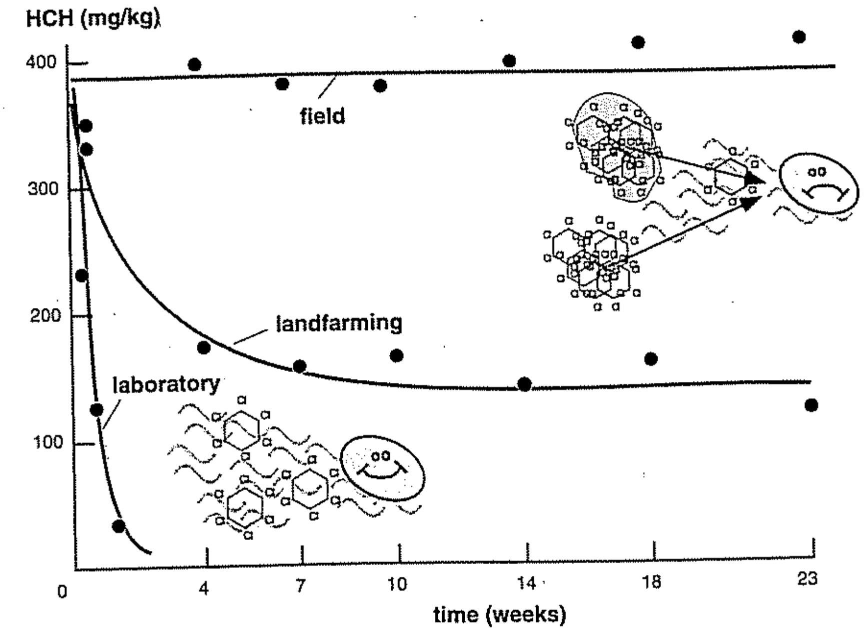

Fig. 3
Biodegradation of α-hexachlorocyclohexane (HCH) in soil at various concentrations (mg/kg).

reduce the period of adaptation. Even if these organisms cannot themselves live in polluted soils, the genetic information introduced can still be available to the microorganisms that are better adapted to the site. The genes introduced can both be actively transmitted to established organisms and taken up by them in the form of free DNA.

Energy-related Considerations

The biodegradability of a compound depends on the thermodynamics of the overall reaction and on the kinetics of the rate-determining step of the enzymatic degradation route, which often is the one which requires the highest activation energy for initiation. Biological mineralization of most organic pollutants is thermodynamically favourable under both aerobic and anaerobic conditions as indicated by negative values for the Gibbs free energy (ΔG). For instance, the process of reductive dehalogenation is an energy-supplying process when coupled with oxidation of an organic substrate. So there are no obvious thermodynamic reasons for the lack of degradation of some pollutants in soil. For instance, no reductive dechlorination of monochlorobenzene has been found in environmental samples, even though there is no significant difference in thermodynamic terms between this reaction and reductions of more highly chlorinated benzenes which take place at a higher rate [2]. It is the particularly high energy barrier of the first reaction which causes the stability of chlorobenzenes to increase as the number of chlorine atoms decreases.

Soil Permeability

Influence of Mass Transfer on the Rate of Degradation

Bacteria and contaminants are unevenly distributed in the environment; therefore, the transport of the pollutant to the bacterium may largely determine the rate of degradation (Fig. 1). Spatial separation has various causes: the pollutant may have collected in organic particles that are inaccessible to bacteria or may have entered the soil in solid form or as a liquid. In addition, the dissolved concentrations in the vicinity of such localized contamination may be so high that bacteria cannot survive. A number of pollutants appear to be inaccessible to bacteria under such conditions. This is especially true at sites which have been polluted for a long time.

For instance, no degradation of α-hexachlorocyclohexane (HCH) could be found in soils which had been contaminated with this chemical for 40 years (see Fig. 3: top line "Field"). Nor could degradation be stimulated by adding nutrients or oxygen. In contrast, mixing the soil by landfarming, thus shortening the average distance between the pollutant and the microorganisms which were present in the soil, led to immediate degradation of HCH. The rates of degradation in laboratory tests were even higher (Fig. 3), and there was a positive correlation with the intensity of mixing [4].

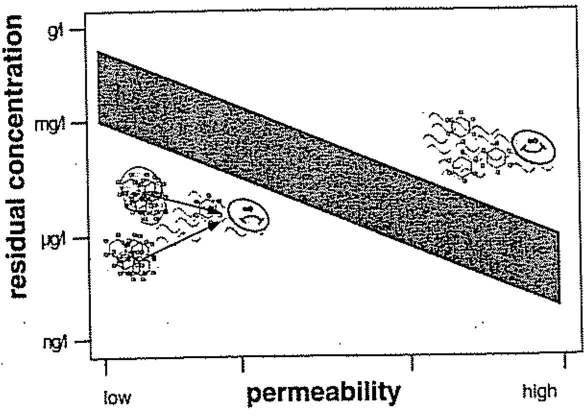

Fig. 4
Residual concentration of an organic pollutant as a function of soil permeability.

Influence of Mass Transfer on the Residual Concentration

The occurrence of relatively high residual pollutant concentrations can also be explained by limited mass transfer. As illustrated in Fig. 4, residual concentrations are inversely proportional to soil permeability. Improving the mobility of pollutants consequently leads not only to an increase in the rates of degradation but also to a decrease in residual concentrations.

Conclusions

Once microorganisms have acquired the ability to degrade an organic contaminant, mass transfer becomes the rate-determining step in a clean-up operation. At present, mixing soil is the only way to accelerate the biotransformation process. The example of HCH suggests that the intensity of mixing required for clean-up that also meets legal requirements is very high and can only be achieved in special reactors. This applies to the majority of sites that are contaminated with organic compounds.

Another strategy is certainly conceivable; namely, to treat the relatively easily degradable, more mobile portion of the pollutant *in situ* in a relatively short time and leave the immobile portion which has less potential for harm. Pollutants which are slowly released from this portion would simply need to remain under observation so as to enable further clean-up operations to be carried out if necessary. To achieve change, however, serious attempts should be made to organize activities in such a way that the possibility of soil pollution is minimized and renewed contamination, should it occur, is immediately remediated.

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[1] Harms H. and Zehnder A.J.B. (1994): Influence of substrate diffusion on degradation of dibenzofuran and 3-chlorodibenzofuran, Appl. Environ. Microbiol., *60*, 2736–2745.

[2] Bosma T.N.P. (1994): Simulation of subsurface biotransformation, Ph.D. Thesis, Wageningen, The Netherlands.

[3] van der Meer J.R., de Vos W.M., Harayama, S., and Zehnder A.J.B. (1992): Molecular mechanisms of genetic adaptation to xenobiotic compounds, Microbiol. Rev., *56*, 677–694.

[4] Rijnaarts H.H.M., Bachman A., Jumelet J.C., and Zehnder A.J.B. (1990): Effect of desorption and intraparticle mass transfer on the aerobic mineralization of a-hexachlorocyclohexane in a contaminated calcareous soil, Environ. Sci. Technol., *24*, 1349–1354.

Books

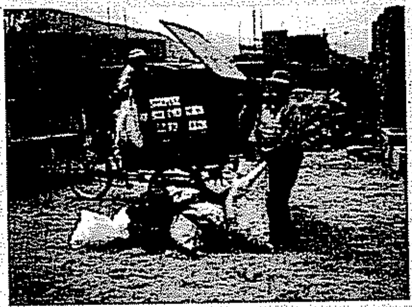
Ambühl, H. (Red.): Limnologische Berichte Donau 1994, Band II: Gast- und Übersichtsreferate der 30. Arbeitstagung der Int. Arbeitsgemeinschaft Donauforschung in Zuoz – Engadin, Schweiz 1994. EAWAG, Dübendorf und Generalsekretariat der IAD, Wien 1995, 321 Seiten. ISBN 3-906484-12-2.

Müller, D., Oehler, D., Baccini, P.: Regionale Bewirtschaftung von Biomasse. Eine stoffliche und energetische Beurteilung der Nutzung von Agrarflächen mit Energiepflanzen. (Teil des Projektes «Energiegras und Feldholz» des Bundesamtes für Energiewirtschaft), EAWAG, Forschungsabteilung Stoffhaushalt und Entsorgungstechnik; ETH[Z], Lehrstuhl für Stoffhaushalt und Entsorgungstechnik. vdf – Hochschulverlag AG an der ETH Zürich 1995, 111 pp. ISBN 3-7281-2213-0.

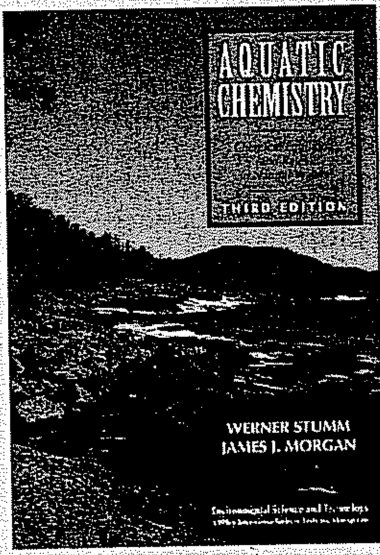
Lerman, A., Imboden, D., Gat, J. (Eds.): Physics and Chemistry of Lakes. 2nd. Ed. Springer-Verlag, Berlin 1995, 240 pp. ISBN 3-540-57891-9. [Fr. 123.–]

Stumm, W., Morgan, J.J.: Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters. A Wiley-Interscience Publication. J. Wiley & Sons, New York 1996, 3rd Ed., XVI + 1022 pp. ISBN 0-471-51184-6; paperback: 0-471-51185-4.

Pfammatter, R., Schertenleib, R.: Non-Governmental Refuse Collection in Low-Income Urban Areas – Lessons Learned from Selected Schemes in Asia, Africa and Latin America, SANDEC Report No 1/96, Duebendorf, Switzerland (1996).



Manual refuse collection by a small private enterprise in a peri-urban area of Lima, Peru. This new SANDEC publication deals with refuse collection schemes in low-income urban areas which are operated at community level either by community organisations or small private enterprises. It summarises the lessons learned from a review of selected schemes in Asia, Africa and Latin America, and assesses the basic conditions for increased service coverage in peri-urban areas of tropical cities.



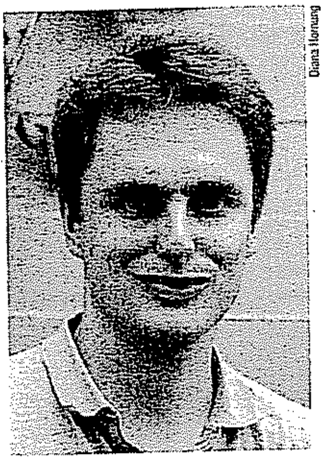
"Aquatic Chemistry"

Werner Stumm, EAWAG, Switzerland and James J. Morgan, California Institute of Technology. Now fully updated and expanded, this Third Edition of a bestselling, upper-level text provides students of environmental science, engineering, and chemistry with an understanding of the concepts, techniques, and applications of aquatic chemistry in natural waters. Covering general principles – chemical thermodynamics and kinetics, acids and bases, atmosphere-water interactions, precipitation and dissolution – the book stresses a quantitative treatment of the processes which determine the composition of natural waters.

Martin Mengis and Reto von Schulthess

Nitrous Oxide Emissions from Sewage Treatment Plants and Lakes

Microorganisms which oxidize and reduce nitrogen compounds in sewage treatment plants and lakes produce nitrous oxide (N_2O) as an intermediary product. N_2O is a greenhouse gas, contributing to the deterioration of the ozone layer in the stratosphere. In this study, N_2O emissions from lakes and sewage treatment plants were estimated. Practical consequences for water protection strategies are discussed.


Diana Hornung

Martin Mengis

Problems with Nitrogen in Water Protection and Conservation

Swiss lakes and rivers are increasingly becoming polluted with nitrogen-containing compounds [1]:

- Every year about 66'000 tons (t) of nitrogen (N) are flushed and leached from soils into natural waters. This N originates from the concentrated application of nitrogen fertilizer in intensive agriculture and from nitrogen oxides (NO_x) which enter the atmosphere via combustion processes (i.e., motorized vehicles and industry). The simultaneous effect of both processes results in a diffuse fertilization of soils with N.
- An additional 41'000 t of N enter the hydrosphere from treated effluents leaving sewage treatment plants as well as from untreated wastewater.

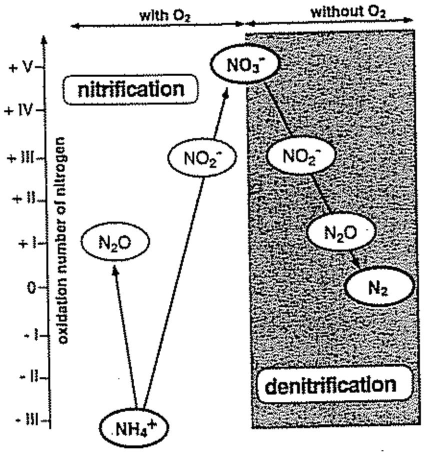


Fig. 1
Microbial nitrogen conversions that occur in sewage treatment plants. These also occur naturally in lakes and their sediments. The compounds in bold print are the initial and end products of both processes. The intermediate compounds only occur as trace compounds.

The natural input of N into bodies of water has been increased six-fold as a result of anthropogenic influences.

- The nitrogen content of most lakes and streams in Switzerland is increasing continuously and has already doubled in lakes in the past 15–30 years [2].
- Nitrate (NO_3^-) is one of the most common pollutants in Swiss groundwater.
- Switzerland exports about 81'000 t of N annually into the North Sea through the outflowing Rhine. As nitrogen limits the growth of algae in the North Sea's coastal waters, Switzerland clearly shares responsibility for the progressive eutrophication of the North Sea.

Nitrogen Removal from Lakes and Sewage Treatment Plants

The anthropogenic nitrogen pollution of lakes results in a shift in the composition of algal populations. The primary production remains unchanged, however, as it is limited by the availability of phosphorus. This is why increased nitrogen input does not lead to eutrophication of the lakes. Swiss lakes are able to remove some 26'000 t of nitrogen annually by two main pro-

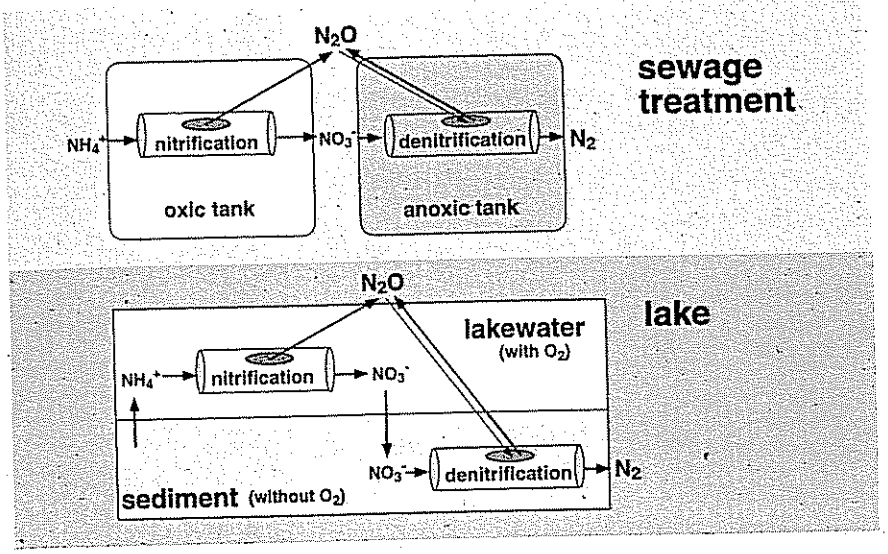


Fig. 2
N_2O production in lakes and sewage treatment plants which can lead to atmospheric emissions. The formation of N_2O through the processes of nitrification and denitrification is shown as leaks in a pipe. Denitrification may also be a sink for N_2O, whereby N_2O is reduced to N_2.

cesses: (1) by deposition in sediments; and (2) by release of elemental nitrogen (N_2) and nitrous oxide (N_2O) to the atmosphere, both of which are produced by microorganisms.

Measures are needed in the areas of agriculture and motorized traffic in order to reduce the nitrogen input to surface and ground waters in the future. Currently, the larger sewage treatment plants in Switzerland are being extended to include an additional treatment stage. In order to remove the nitrogen from the wastewater, specific microbial processes are being applied – the same ones that occur naturally in lakes and which produce gaseous nitrogen compounds (see Fig. 1).

Ammonium (NH_4^+) is formed in wastewater, especially from uric acid in human excrement. In lakes, NH_4^+ is set free during the decomposition of algal biomass. One group of microorganisms, the nitrifying bacteria, oxidize NH_4^+ with oxygen (O_2) to nitrate (NO_3^-). In doing so, they gain chemical energy. A second group, the denitrifying bacteria, reduce NO_3^- to N_2. This process occurs in the absence of O_2 because NO_3^- replaces O_2 as the oxidizing agent in the degradation of carbon compounds. Nitrite (NO_2^-) and nitrous oxide (N_2O) are two of the intermediary by-products of both microbial processes.

As nitrification and denitrification take place at different O_2 concentrations, they are temporally and spatially separated both in sewage treatment plants and in lakes. In sewage treatment plants, they often occur in two different tanks – in the aerated nitrification tank and in the non-aerated denitrification tank (Fig. 2). In lakes, the two processes occur in biofilms at the sediment-water interface. N_2O and N_2 can escape from sewage treatment plants and lakes into the atmosphere; in this way, nitrogen is eliminated from the water.

Sources of N_2O and Impact on the Atmosphere

Even though N_2O is not toxic to humans and is a naturally occurring trace gas in the atmosphere, N_2O emissions from sewage treatment plants and lakes have unwanted consequences. After carbon dioxide (CO_2) and methane (CH_4), N_2O is the third most important greenhouse gas in the earth's atmosphere and contributes to the destruction of the ozone layer in the stratosphere [3]. The concentration of N_2O in the atmosphere has been increasing steadily for several decades. The current rate of increase is 0.2–0.3% annually. The reason for this observable global increase is most likely due to acceleration of the nitrogen cycle through human activity.

According to the current state of research, N_2O is mainly produced during microbial nitrogen conversion processes in soils and bodies of water. Reliable scientific data on N_2O emissions from aquatic systems, especially from lakes, wetlands and sewage treatment plants, however, are scarce. This was the impetus for two recent doctoral research studies at the EAWAG. The primary objectives of the first project were to estimate N_2O emissions from sewage treatment plants with integrated nitrogen elimination and to identify potentially critical operational scenarios. The objective of the second project was to determine N_2O emissions from lakes in order to be able to estimate their role in the global increase of atmospheric N_2O.

N_2O Emissions in Sewage Treatment Plants

Development of a Working Model and Reactor Experiments

In order to quantitatively describe N_2O production, a mathematical model was developed [4, 5]. In this model, the most important intermediate steps of nitrification and denitrification were defined. In order to assess both the unknown kinetic parameters of each step and the dependence of N_2O emissions on various operational conditions, the operation of a sewage plant was simulated in laboratory experiments. The mathematical model was calibrated with the results of these measurements.

Conclusions from Laboratory Experiments

Figure 3 shows N_2O production from denitrifying bacteria in the reactor as calculated by the model according to the O_2 and NO_2^- concentrations. The calculation illustrates the significance of O_2 and NO_2^- to N_2O emissions. The maximum N_2O emission is at 1.5 g m^{-3} O_2 and 10 g N m^{-3} NO_2^-. Transferring the calculated emission values to a sewage treatment plant should only be made with caution since the emission is dependent on the conditions selected for the reactor and nitrification was not taken into

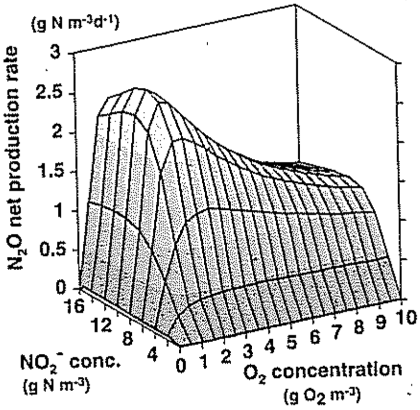


Fig. 3
Rate of N_2O *production in a laboratory reactor with respect to* O_2 *and* NO_2^- *concentrations as calculated by a mathematical model.*

account for the calculation. Nevertheless, basic rules for minimal N_2O emissions during the nitrogen removal process can be postulated:

- NO_2^- concentrations over 2 g N m^{-3} should be avoided in the aerated tanks as they lead to increased N_2O emissions.
- In non-aerated tanks O_2 concentrations below 0.25 g m^{-3} result in minimal N_2O emissions, although the NO_2^- concentration is relatively high.

Testing the Model with Measurements in a Sewage Treatment Plant

In order to test whether the developed model may be applied to sewage treatment plants, it was tested with measurements from the sewage treatment plant at Opfikon in the Canton of Zürich. This sewage treatment plant has been expanded in recent years to include a nitrogen elimination stage. The NO_3^-, NO_2^- and N_2O concentrations in the aerated and non-aerated tanks of the sewage treatment plant were periodically determined. As an example, Fig. 4 shows the diurnal patterns of both the measured and calculated N_2O concentrations in the aerated tank. Between 0800 and 1000 hours, digester supernatant from the sewage sludge treatment was diverted into the influent tank. This addition of digester supernatant caused an increase in the NH_4^+ concentration. The intense nitrification of NH_4^+ and denitrification of NO_3^- released NO_2^- and N_2O. The dynamics and the order of magnitude of the NO_3^-, NO_2^- and N_2O concentrations could all be simulated satisfactorily using the mathematical model, suggesting that it may be useful in estimating N_2O emissions from sewage treatment plants.

Quantification of the N_2O Emissions of Sewage Treatment Plants

After calibrating the model's parameters with the laboratory reactor and testing the model with a large-scale plant, estimates of N_2O emissions from Swiss sewage treatment plants can now be made. The calculated N_2O emissions from the Opfikon sewage treatment plant have been extrapolated for total nitrogen turnover in Swiss sewage treatment plants. A total of about 0.2–0.7‰ of the influent nitrogen content of a communal sewage treatment plant is released into the atmosphere. Although this estimate has been greatly simplified, an annual amount of 9–30 t N of N_2O emissions from Swiss sewage treatment plants can be expected.

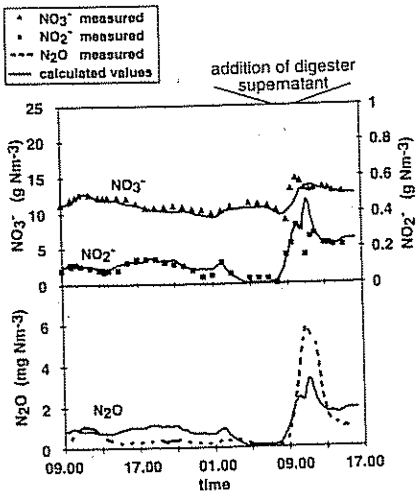


Fig. 4
Experiments conducted in the sewage treatment plant of Opfikon: denitrification and nitrification under aerobic conditions in the nitrification zone. Calculated concentrations (lines) of NO_3^-, NO_2^- *and* N_2O *correlate well with the measurements (▲, ■, - - -). The addition of digester supernatant caused the* NH_4^+ *concentration to increase. The intense nitrification of* NH_4^+ *and denitrification of* NO_3^- *caused the release of* NO_2^- *and* N_2O*.*

N_2O Emissions in Lakes

Are Lakes Sources or Sinks of N_2O ?

Because the same microbial nitrogen conversion processes occur in lakes as in sewage treatment plants, natural aquatic sytems can likewise release N_2O into the atmosphere. Current research postulates that lakes and seas are not only sources of N_2O but may also be sinks [6]. The reason for this is that denitrifying bacteria reduce N_2O to N_2 in the oxygen-free (anoxic) deep waters (Fig. 2). In order to test this hypothesis, concentration profiles of N_2O with depth were made in Lakes Alpnach, Rot and Zug. At the time of sampling, the deepest waters contained no oxygen.

Lakes Alpnach, Rot and Zug: Sources of N_2O

In all of the measurements made in the anoxic deep water zones, a N_2O undersaturation (compared to equilibrium N_2O concentrations in the atmosphere) was found. In spite of this apparent consumption of N_2O in the deep water layers, the surface waters of the investigated lakes were always oversaturated with N_2O. In the layers containing oxygen, more N_2O was being produced than was being consumed in the deep waters. Despite differences in nutrient levels and oxygen status, all of the lakes emit N_2O to the atmosphere. These results contradict the hypothesis that lakes with oxygen-free deep waters may serve as sinks for atmospheric N_2O.

Annual Profile of N_2O Concentrations: Lake Baldegg

As soon as a lake stratifies, the N_2O concentration at depth increases by a factor of 6 within a few months (Fig. 5). Lake Baldegg was a source of atmospheric N_2O during the entire investigation period, the surface water always being oversaturated with N_2O.

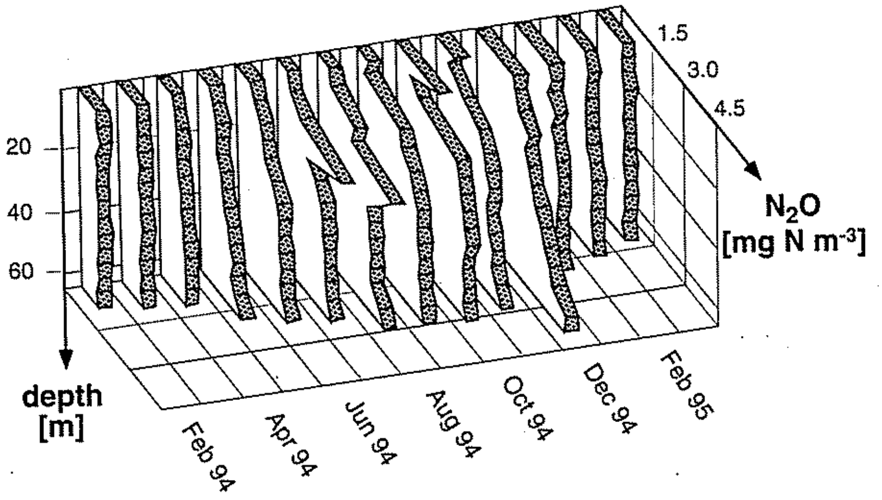


Fig. 5
N_2O in the water column of Lake Baldegg. In summer, N_2O accumulates in the deep water layers. In winter, N_2O emissions into the atmosphere are the highest, as deep waters containing high N_2O concentrations mix with surface waters.

In the winter, deep water with high N_2O concentrations wells up and is mixed with the surface water. For this reason, N_2O emissions from Lake Baldegg increase markedly and lead to a reduction in N_2O concentrations within the lake.

Since the highest N_2O concentrations were measured in the vicinity of the sediment surface, fine-scale gas measurements were carried out directly at the surface of the sediment. Maximum N_2O concentrations were directly detected at the sediment surface (Fig. 6). The maximum concentration suggests that N_2O is being produced at the sediment-water interface in the Lake Baldegg. This N_2O is constantly diffusing into the deep water layer and into the sediment. Estimates have suggested that N_2O production at the sediment surface is sufficient to explain the observed accumulation in the deep water layer during summer stagnation in the lake [7].

An Estimate of N_2O Emissions from Lakes

On the basis of our results, we can as yet only roughly estimate the range of N_2O emissions from Swiss lakes. Switzerland's lakes release approximately 40–400 t of nitrogen into the atmosphere per year. We intend to perform measurements in all major Swiss lakes in order to verify these estimates. Compared to nitrogen removal in lakes, N_2O emissions are negligible.

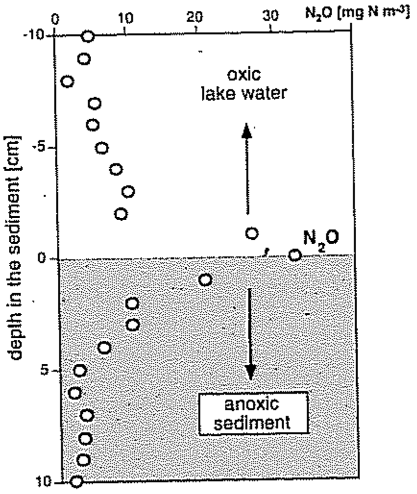


Fig. 6
N_2O at the sediment-water interface of Lake Baldegg (July, 1994). N_2O is produced at the sediment surface. It diffuses into the anoxic sediment (where it is reduced) and into the oxic deep water where it accumulates (arrows indicate the direction of diffusion).

Conclusions

- The planned introduction of nitrogen removal in Swiss sewage treatment plants will not lead to significant increases in N_2O emissions to the atmosphere. N_2O emissions from sewage treatment plants account for less than 1% of total emissions in Switzerland. Neither construction nor operational measures are needed to reduce N_2O emissions from sewage treatment plants.
- As lakes remove nitrogen quite effectively, they can counteract the over-fertilization of Swiss waters with nitrogen. Nevertheless, it is possible that increasing nitrogen pollution could lead to increased N_2O emissions from lakes. To date, N_2O emissions from lakes amount to less than 3% of the total N_2O emissions in Switzerland.
- The impact of various sources of nitrous oxide on a global scale is still controversial. It is, however, regarded as certain that the rate of global N_2O emissions is increasing as a consequence of anthropogenic activity.

Source	N_2O-emission [t N / Jahr]	fraction [%]
sewage treatment	9–30	<1
lakes	40–400	<3
motor traffic	2700	17
agriculture	13'400	82
Total	16'000–17'000	100

Table 1
Estimate of the various proportional amounts of N_2O sources in Switzerland (data from [4] and [8]).

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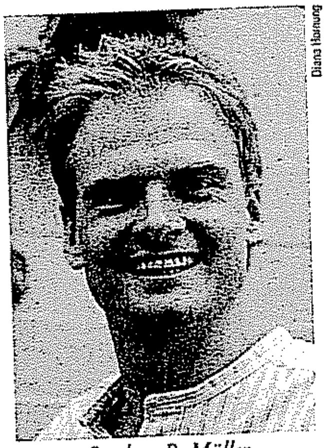
[1] BUWAL 1993: Der Stickstoffhaushalt in der Schweiz. Konsequenzen für Gewässerschutz und Umweltentwicklung. Schriftenreihe Umwelt, *209*.
[2] EAWAG 1990: Stickstoff in Wasser und Luft – Implikationen für den Gewässerschutz, EAWAG news, *30*.
[3] IPPC (Intergovernmental Panel on Climate Change) 1990: Climate Change, the IPCC scientific assessment. Cambridge University Press.
[4] Schulthess von, R. 1994: Die Emission von Lachgas (N_2O) in denitrifizierenden Belebungsanlagen, Diss. ETH Nr. 10'790.
[5] Schulthess von, R. und Gujer, W. 1994: Emission von Lachgas in denitrifizierenden Belebtschlammanlagen, Gas Wasser Abwasser, *9*, 731–739.
[6] Knowles, R., Lean, D.R.S. and Chan, Y.K. 1981: Nitrous oxide concentrations in lakes: variations with depth and time. Limnol. Oceanogr. 26(5): 855–866.
[7] Mengis, M., Gächter, R. and Wehrli, B. 1996: Nitrous oxide emissions to the atmosphere from an artificially oxygenated lake, Limnol. Oceanogr., 41 (3): 548–553.
[8] Grud, A. und Fuhrer, J. 1995 : Treibhausgasemissionen der schweizerischen Landwirtschaft, Agrarforschung 2 (6), 217–220.

**Stephan R. Müller, Markus M. Ulrich,
Michael Berg and René P. Schwarzenbach**

Optimized Monitoring of Contaminants: Atrazine as an Example


Diana Hartung

Stephan R. Müller

Environmental contaminants can be efficiently monitored if the crucial transport properties and transformation behaviors have been described quantitatively. This study demonstrates how an optimal monitoring program can be designed with the help of well targeted field studies and mathematical modeling. The herbicide atrazine and its metabolites in lake water serve as an example.

Literature Data, Field Studies and Model Development

The water quality of many surface waters in Switzerland is being monitored by elaborate monitoring programs, including continuous monitoring, periodic spot checks and individual studies. In light of the high cost of such programs, the ecological and economical optimization of these monitoring functions will receive increasingly more scrutiny in the near future. To this end, well-targeted field studies and mathematical modeling can make significant contributions.

The first step in the process is the quantitative description of the environmental behavior of a target compound. In the case of a lake, this includes its input into, mixing and transport within the lake, and chemical and biological degradation. These processes determine the spatial and temporal distribution of a compound within the lake. In general, an iterative approach is used which can be summarized as follows:

- A hypothesis about the environmental behavior of a compound is formed based on literature data.
- A detailed field study is undertaken to quantify the dominant processes affecting its behavior.
- The relevant processes are incorporated into a computer model.
- The model is tested by additional measurements in the field.
- The model, in conjunction with representative measurements, becomes

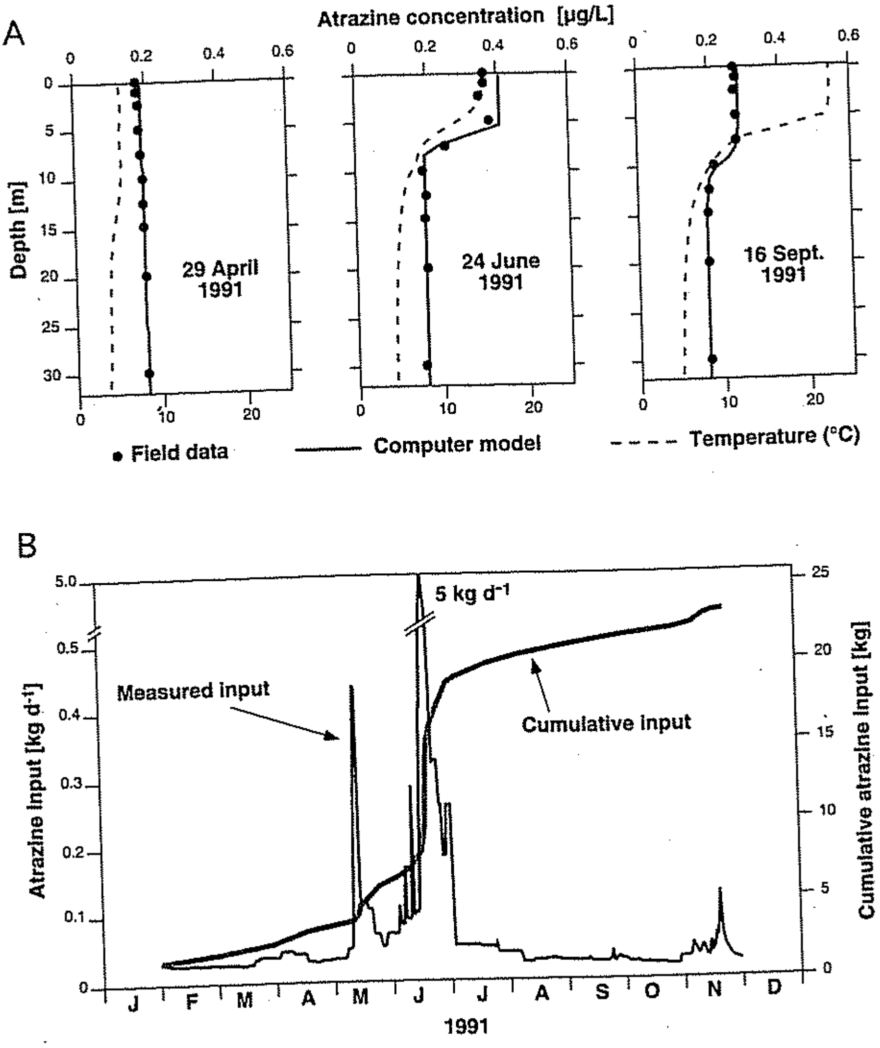


Fig. 1
Intensive field study in Greifensee in 1991.
A: Representative concentration profiles; B: Measured atrazine input.

the primary tool employed in the monitoring process.

The model makes predictions and, without much additional effort, may be adapted to situations dealing with similar surface waters and other compounds.

The study described here demonstrates how the general approach described above translates into definite steps. The herbicide atrazine serves as an example. First, the uses of atrazine and our current understanding of its fate in the environment is reviewed. Next, a detailed field study (Greifensee, 1991) and subsequent model development and validation (additional monitoring in the same lake and inclusion of data from different lakes) is discussed. The following section deals with degradation products of atrazine. In conclusion, an optimized monitoring program is presented, together with a discussion which critically evaluates the costs and the benefits of using this approach.

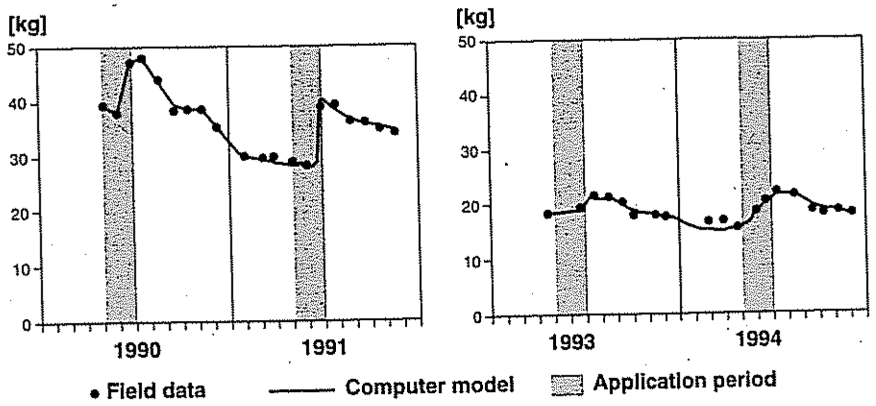


Fig. 2
Total amount of atrazine in Greifensee in 1990–91 and 1993–94.

Atrazine as a Model Compound

Atrazine is one of the most important herbicides in use worldwide. In Switzerland, about 120 tons of atrazine were used in 1989. For comparison, in the United States' corn belt (a large portion of its watershed drained by the Mississippi River) atrazine is applied at a rate of about 20'000 tons per year. Since the early 1980's, atrazine has been detected in many drinking water supplies in concentrations significantly above the tolerance level for pesticides (0.1 µg/l). Since 1989, the use of atrazine in Switzerland has been severely restricted with only about 60 tons per year applied in recent years. Currently, it may only be used on corn, at a rate of 1 kg/hectare, and may not be applied after June 30.

There are many ways atrazine is introduced into the environment. During its application, for example, atrazine is released into the atmosphere by evaporation from the spray being applied to the crop. Once it has been applied, it is released into the atmosphere through evaporation from the plant and soil surface, into lakes and streams through surface runoff, and into ground water by surface runoff percolating though soils.

In a lake, the fate of atrazine is controlled by a number of transport and transformation processes. On the basis of available literature data, the following hypotheses can be formulated: lake inlets introduce atrazine into the surface layers of a lake (epilimnion). The intput is highest during the application period. Within the lake, several mixing processes occur. During the time when the lake is stratified (approximately April through December), atrazine is evenly distributed throughout the epilimnion within just a few days. Atrazine is continuously being exported from the lake via the outlet. A small portion of atrazine is transported to the hypolimnion by the much slower vertical mixing of water. The winter circulation (ca. January through March) distributes atrazine evenly throughout the lake.

In addition to the transport processes described above, a number of mechanisms are expected to reduce the amount of atrazine in the water column, namely chemical and biological degradation, gas exchange with the atmosphere, sorption to particles, sedimentation, and incorporation into sediments. The rates of chemical hydrolysis, gas exchange and sedimentation can be estimated from the physico-chemical properties of a compound (rate constant of hydrolysis, Henry's Law constant and sorption coefficients) and system parameters such as pH of the lake water, wind velocities and particle concentrations. In the case of atrazine, contributions from all processes within the lake can be ignored since they total less than 1% of the amount of atrazine that is lost via the lake outlet. Indirect photochemical and biological degradation, as well as total atrazine input to the lake, cannot be estimated with sufficient accuracy from existing literature data and must be determined from field studies.

Intensive Field Study and Model Development: Atrazine in Greifensee [1]

In 1991, the concentration profile for atrazine was determined at the deepest point in Greifensee on a monthly basis (see Fig. 1, top panels). Since moderately reactive compounds are rapidly and evenly distributed within individual layers of a relatively small lake by horizontal mixing processes, it was possible to restrict sampling to one location, the site of greatest depth. Atrazine input to Greifensee from the main tributaries (Aa and Aabach) as well as from several smaller tributaries – a parameter critical to the development of a reliable model – was determined quantitatively by an intensive sampling program (see Fig. 1, bottom panel).

The simulation software package «MASAS» was used to construct the mathematical model [2]. With the help of this software, the various processes (input, output, mixing, degradation) were integrated into a dynamic, one-dimensional vertical model. This enabled us to calculate simulated

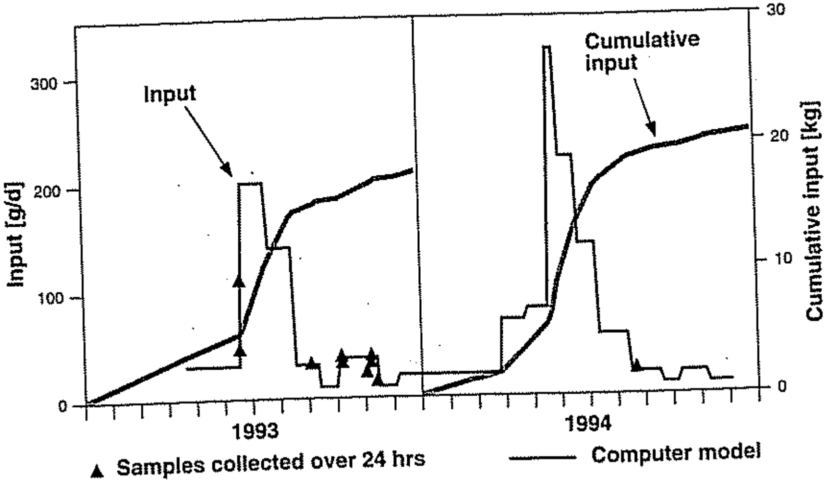


Fig. 3
Model validation I: Measured and modeled atrazine input to Greifensee in 1993–94.

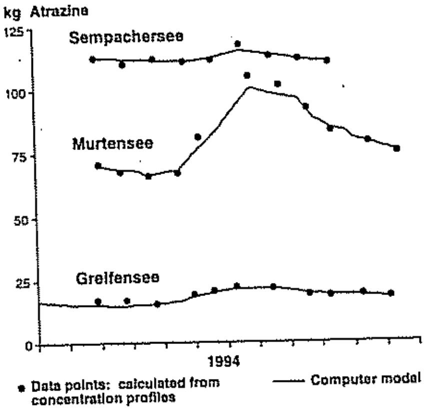


Fig. 4
Model validation II: Total amount of atrazine in Greifensee, Murtensee and Sempachersee (1994).

concentration profiles and total lake content (Fig. 2) and to compare them with corresponding measurements in the field.

There is clearly good agreement between field measurements and model calculations based on the following processes:

- Water mixing within the lake
- Distinctly seasonal input of atrazine
- Conservative behavior of atrazine in the water column (exception: small degree of degradation in July and August due to indirect photochemical or biological degradation).

Our mathematical model was successful, therefore, in quantitatively describing the dynamics of atrazine behavior in Greifensee.

Model Validation

The model developed was tested and validated on the basis of field data collected in Greifensee (1990 and 1993–94) and in Murtensee and Sempachersee (1994; characteristic parameters are compiled in Table 1). The sampling program was significantly reduced for this part of the study. In particular, atrazine input was determined by spot-samples in Greifensee (in the form of several 24-hour bulked samples in the tributaries to Greifensee) and not at all in Murtensee and Sempachersee. Fig. 2 shows the total mass of atrazine in Greifensee calculated on the basis of the measured concentration profiles for 1990–91 and 1993–94, and the simulation results, respectively. The 1991 values of atrazine input to Greifensee were actual measurements, while input values were obtained from the model calculations for 1993–94. These values were in good agreement with spot samples (see Fig. 3). We could, therefore, confirm the validity of the mathematical model developed for Greifensee [3]. The overall decrease of atrazine in the lake between 1990 and 1994 is apparent and may be explained by the limitations imposed on atrazine usage during that period. Application of the model to Murtensee and Sempachersee provided additional confirmation of its validity, as may be seen in Fig. 4. Again, input values were calculated by the model.

Expansion of the Model: Degradation Products of Atrazine

Atrazine can be microbially degraded in soils. The main products are desethylatrazine, deisopropylatrazine and hydroxyatrazine. In order to apply the model to these degradation products, it was necessary to make predictions about the processes governing their behavior in a lake. Based on the physical-chemical properties of these compounds, it is again expected that the dominant processes will be total input and a small degree of loss due to degradation during the summer months.

The three metabolites were monitored as part of the 1994 field study [3, 4]. They were introduced to the lake with a slight delay relative to atrazine. This was expected since they are formed only after atrazine has been applied to the soil. Preliminary model calculations show that all three compounds behave very much like atrazine. This expansion of the model demonstrates that after a labor-intensive development phase, the model may be applied to similar compounds with very little additional effort.

Optimization of the Monitoring Program

The computer model allows us to design a more efficient monitoring program for triazines. In the case of

	Greifensee	Murtensee	Sempachersee
Volume [10^6 m^3]	151	530	639
Maximum depth [m]	32	45	85
Average residence time [yr]	1.1	1.2	15.4
Land cultivated for corn in watershed [ha]	1000	3800	330
Total atrazine input in 1994 (model) [kg]	21	72	8
Percentage of atrazine reaching lake [%] (Assumption: 1 kg atrazine used per ha of corn)	2.1	1.9	2.3

Table 1
Characteristics of the three lakes studied.

atrazine, the most critical factor in predicting concentrations in the lake is the input during the early summer, during or shortly after application of atrazine in corn fields. The highest concentrations are observed immediately after this input period. The remaining processes (loss from lake via effluent, background input during periods outside of the application period, distribution within the lake) which determine the spatial and temporal distribution of atrazine within the lake can be simulated with sufficient accuracy on the basis of easily accessible field measurements (effluent concentrations, water temperature) and model calculations. The mass of atrazine reaching the lake during the application period does not have to be measured in order to predict whether lake concentrations will exceed water quality criteria. The lake acts as an "integrator"; it is, therefore, sufficient to determine one concentration profile after the period of atrazine application. The temporal and spatial variation of atrazine concentrations for the rest of the year may be simulated by the computer model. This reduced monitoring program, in conjunction with the computer model, yields the following information: (1) maximum concentration of pollutant in the lake; (2) total mass of the pollutant in lake; (3) annual input; and (4) long-term trends.

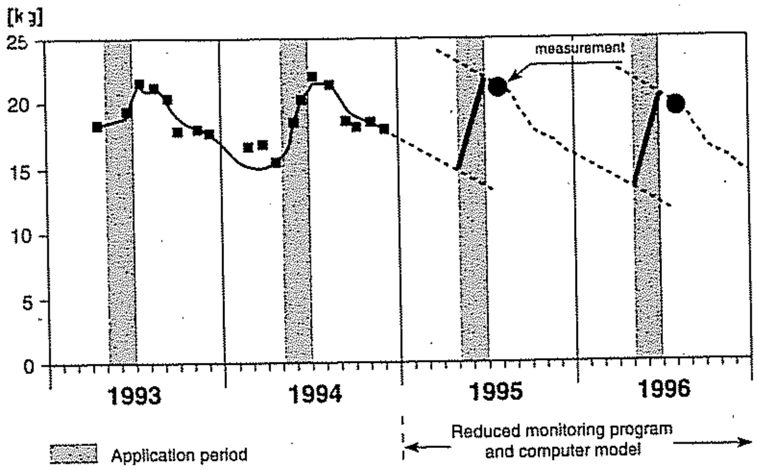


Fig. 5
Application of computer model: atrazine in Greifensee 1993–96.
■ *Data points*
—— *Computer model 1993–1994*
-- *Extrapolation of total amount in lake, calculated by the computer model, based on data from monitoring program.*
/ *Increase in total amount during study period, calculated as difference between model projections for two consecutive years.*
● *Proposed sampling program for 1995–96.*

Fig. 5 demonstrates the combination of a reduced monitoring program with a computer model for 1995 and 1996. The solid circle represents the total mass of atrazine in the lake, which was determined from the concentration profiles taken at the end of July. The subsequent behavior of atrazine is calculated by the computer model (dotted line). The increase in the total mass of atrazine in the lake, due to input during the application period in early summer, can be calculated as the difference between calculated total mass for the current and the previous year. The computer model allows us to address questions which go beyond the main purpose of the monitoring program. For example, the effect of restrictions in atrazine application can be evaluated, and projections about the effects of additional restrictions may be made.

Conclusions: Cost and Benefits

The effort made for quantification of the dominant processes, the conducting of an intensive field study and the development of a computer model was considerable and amounted to at least one person year (PY). Validation of the model with a multi-year monitoring program and transfer to other lakes was limited to a few sampling events and analyses of concentration profiles and selected influent samples. Taking advantage of previously established knowledge, this phase required much less effort (approx. ¼ PY). Model expansion to include atrazine metabolites required a moderate effort, which mainly consisted of the development of appropriate analytical techniques and the simultaneous monitoring of atrazine and its metabolites (approx. ½ PY) [4].

The optimized and computer-assisted monitoring program is reduced to one sampling event per year; therefore, it is possible to analyze all of the samples in a single batch, and the results can immediately be evaluated using the computer model. It is possible that the computer model be modified and expanded to include other compounds which are relevant in the environment including additional pesticides. The initially high investment in terms of person-power pays off in the long run by reducing monitoring costs and, at the same time, providing a better understanding of the behavior of pollutants in the environment.

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[1] Ulrich M. M., S.R. Müller, H. P. Singer, D.M. Imboden, R.P. Schwarzenbach (1994): Input and dynamic behavior of the organic pollutants tetrachloroethene, atrazine, and NTA in a lake: a study combining mathematical modeling and field measurements, *Environ. Sci. Technol. 28,* 1674–1685.

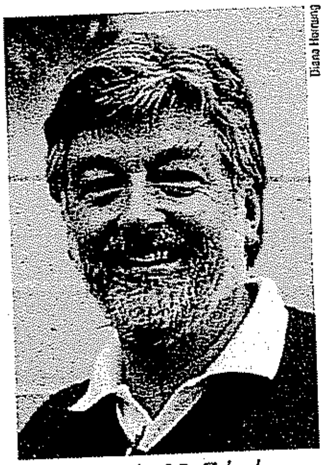
[2] Ulrich M.M., D.M. Imboden, R.P. Schwarzenbach (1995): MASAS – a user-friendly simulation tool for modeling the fate of anthropogenic substances in lakes, *Environ. Software.* Vol. *10,* No. 3, pp. 177–198.

[3] Müller S.R., M.M. Ulrich, M. Berg, R.P. Schwarzenbach: Triazines and their metabolites in Swiss lakes: input and dynamic behavior (in preparation).

[4] Berg, M., S.R. Müller, R.P. Schwarzenbach (1995): Simultaneous determination of triazines including atrazine and their major metabolites hydroxyatrazine, desethylatrazine, and deisopropylatrazine in natural waters. *Anal. Chem. 34,* 1860–1865.

Alexander J.B. Zehnder

Fazit


Diana Hornung

Alexander J.B. Zehnder

The ever increasing use of synthetic chemicals in our daily lives leads to a greater probability of introducing them into the environment. While dramatic impacts have been demonstrated for a few of these compounds, the long-term effects of the vast majority are still unknown. Science, industry and regulatory agencies are challenged to protect the biosphere and humankind against the potential detrimental effects of these trace compounds.

Relevance of Trace Compounds

In most cases, trace compounds are not detected by organisms since they are present in only very low concentrations and are most often taken up inadvertently through food, water and air. Some trace chemicals (e.g., pesticides, solvents) accumulate in the food chain. Impacted organisms are weakened, their reproductive cycle is disturbed, and/or they die. The dramatic reduction in raptor populations as a result of DDT accumulation was the first clear warning of the presence and potentially deleterious effects of trace chemicals. DDT, and especially its metabolite DDE, interfere with neurohormonal mechanisms and prevent sufficient calcification of eggs, resulting in the birds inadvertently crushing their eggs. In another example, the massive die-off of seals in the North Sea in 1987 was probably the result of bioaccumulation of pesticides and chlorinated hydrocarbons. Elevated concentrations of these compounds in their tissues and organs weakened their immune systems and made them more susceptible to viral infections. It was, in fact, not possible to dispose of dead animals by "normal"means since the high concentrations of toxic chemicals in their carcasses classified them as hazardous wastes. The reduction of sperm counts in human males, which has been well documented in Europe, may also be a consequence of greater exposure to trace organic chemicals.

A few short-lived trace compounds in the atmosphere may cause local air quality problems, while more long-lived compounds can result in global changes. Examples of such short-lived molecules include NO_x (see article by Mengis and von Schulthess) and hydrocarbons; chlorofluorocarbons (CFCs) and nitrous oxide (N_2O) in constrast, are long-lived substances. All of these compounds are known to affect the global ozone cycle. Short-lived compounds increase ozone levels in the troposphere, while long-lived compounds deplete the protective ozone layer in the stratosphere. Carbon dioxide and methane are trace compounds, as well. They are classified as "greenhouse gases" and contribute to global climate change.

Trace chemicals released by humankind are also beginning to affect the dynamic equilibrium between the biosphere and geosphere. This interaction has direct effects on the so-called "anthroposphere" – the environment

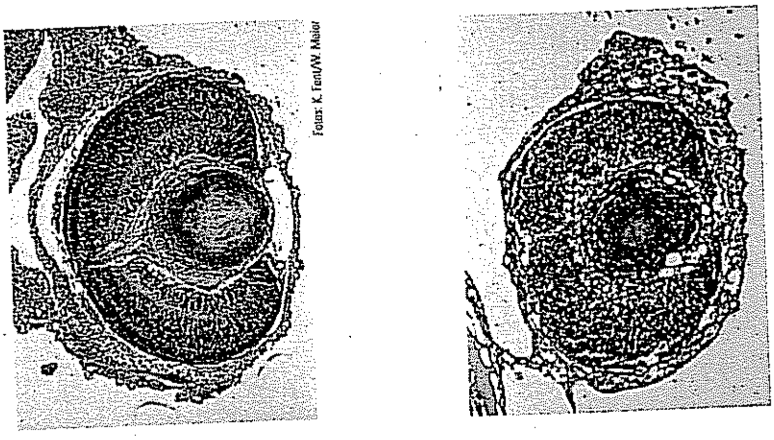

Fotos: K. Fent/W. Meier

Fig. 1
Tributyltin (TBT), used in antifouling paints for boats, and triphenyltin, which is used in agriculture (see article by Fent) cause damage in different tissues in the eyes of minnows larvae when present in concentrations of 0.8-4.5 micrograms/l (left: normal; right: damaged). In addition to the formation of necroses in various tissues, note the increased number of vacuoles and the effect on the pigment layer in the posterior part of the eye (left, in both pictures).

created by humankind. It is, therefore, extremely important to monitor trace chemicals, both quantitatively and qualitatively, as well as document their fate and effects in the environment. This knowledge will allow us to develop strategies to better control the distribution of trace chemicals in an effort to protect Earth's ecosystems and preserve them for future generations.

What Do We Need to Know?

In order to be able to better understand and predict the effects of trace chemicals in the environment, we need better information on their reactivity. Analytical chemistry is the basis for the quantitative determination of trace chemicals. The fate of a particular compound in the environment is determined by processes on the molecular level as well as by parameters describing the system as a whole. The behavior of a compound and its effects on an organism not only depend on its total concentration, but also on its speciation (the chemical form in which the compound is present). Heavy metals, for example, can occur in a number of redox states; they may be complexed, adsorbed or present as a low-solubility salt. Organic compounds may exist as free phase, dissolved, adsorbed, or absorbed in another complex organic phase. Each species of a particular compound behaves differently and has different effects. Our knowledge of the speciation and concentrations of individual species is rudimentary at best. We clearly need to develop quantitative *in situ* measurements in order to reliably predict the fate of compounds in the environment.

Apart from analytical chemistry, we also need information on the fundamental mechanisms of toxicity. Acute toxicity has been well documented in a large number of studies, most often manifested as visible symptoms (e.g., death, malformations; Fig. 1). What is missing is information on molecular-level mechanisms, especially with respect to the chronic effects of chemicals which reduce an organism's ability to adapt and compete. In the long run, such "handicaps" of organisms or populations can have devastating effects on whole ecosystems.

State of the Art

Contributions in this issue should give the reader a broad view on the current state of environmental research as well as serve to illustrate how fundamental science can be applied to understand practical problems. Quantitative analytical chemical methods to detect a broad selection of trace compounds is now available (article by Giger), and basic models describing their behavior have been developed (article by Müller et al.). Methods are available for *in situ* measurements of some species in atmospheric and aquatic systems, but not in ground waters or soils. The fate of trace compounds has been investigated on a large-scale, leaving our understanding of the physical, chemical and biological processes on the molecular level in a rather primitive state (article by Bosma and Harms).

Similar statements can be made about the ecotoxicology of trace compounds. Ecotoxicology and environmental chemistry have progressed relatively well, while on the molecular or mechanistic levels, our knowledge base has major gaps which will need to be closed in the future.

Future Developments

It is probably safe to assume that "classical" analytical methods for sample preparation and laboratory analysis will be improved dramatically over the next few years, although no fundamental changes in these methods is to be expected in the near future. In addition to these *ex situ* methods, we have to develop methods which will allow us to assess processes where they occur, i.e., from the atomic to the microscopic level. Ultimately, processes at these levels are responsible for the behavior of a system on the macroscopic scale. In addition, they form the basis for any modeling approach describing the environmental fate of trace compounds.

In the 1980s, electronic sensors (electrodes) were developed at a rapid pace. Their miniaturization enabled us to determine concentration gradients of many inorganic solutes with a resolution of a few microns. The recent combination of microelectrodes with enzyme systems yields sensors with much broader applications, even extending to organic compounds (Table 1).

Only very recently have sensors been developed which allow species-specific *in situ* measurements. We can now distinguish between chemical and biological sensors, although both rely on so-called "reporter" systems. Chemical sensors typically use molecules whose reactivity in the environment is well known and which show sufficient selectivity. Their behavior yields direct information on the chemical make-up and composition of an environmental compartment. From the behavior of such sensors extrapolations can be made on the fate of other compounds or compound groups. Furfurylalcohol represents one of the few well documented reporter systems. This alcohol selectively reacts with singlet oxygen ($^1O_2$). A sensor using furfurylalcohol can directly quantify concentrations and follow reactions.

Biological sensors, on the other hand, work on the basis of reporter genes whose activity can be detected as luminescence or fluorescence. In the case of luminescence, the luciferase gene of the bacterium *Vibrio fischeri* is used, while fluorescence is obtained from the gene responsible for an autofluorescence protein in the jelly fish *Aequorea victoria*. These genes are incorporated into specific bacteria or cultivated cells of higher organisms which are able to transform specific compounds. The incorporation occurs immediately behind the genes responsible for the initial steps in the transformation of a chemical. When the genetically modified bacterium is exposed to the target compound, the transformation path is activated,

Method	Based on	Current technology	Comments
Microelectrodes	Electrochemical Sensors	Applicable to all ions and molecules which can be measured with commercially available electrodes Currently used in practical applications	• Commercially available • On-line measurements • No extraction required • High stability
Biosensors	Combination of electrodes and enzyme systems in one electrical circuit	Available for a few compounds (mostly organic compounds) Development primarily for medical applications Miniaturized to the level of a micro-biosensor only in selected cases	• Large number of sensors under development • On-line measurements • No extraction required • Variable stability
Chemical probes	Specific reactivity of certain molecules used as reporter system	Only very few molecules known; e.g., furfurylalcohol for the detection of singlet oxygen	
Biological probes	Reporter genes for bioluminescence or fluorescent proteins	Some examples in laboratory applications Field applications only in their infancy	• On-line measurements • Genetically modified bacteria • In principle stable

Table 1
In situ *Detection Methods.*

together with the reporter gene, allowing a direct optical quantification of transformation activity. Depending on the system, biological sensors can detect individual compounds or groups of closely related compounds. In addition, such sensors may yield information on the bioavailability of trace compounds in the environment. The first successful field studies in soils are currently underway in the USA, where a luminescence reporter system for naphthalene is being tested.

The development of sensors based on reporter systems is in its infancy, but the potential for analytical applications is enormous. Their use on a routine basis is probably five to ten years away.

Molecular techniques are indispensable when trying to understand the fundamental mechanisms controlling the toxic effects of trace chemicals. Over the past few years, biomarkers have been used as indicators of the level of contamination and severity of damage to organisms (see article by Fent). The use of these biomarkers can be improved by employing molecular techniques. The complex interactions between trace chemicals and organisms must also be investigated. This not only includes the effect of the trace chemicals on the cell or organism, but also the effect of the chemical environment within the cell on the trace compound. Research has only very recently begun to address this question.

Consequences for Science

Science is clearly challenged to broaden our understanding on various levels and to apply its findings to solve practical problems. In the area of analytical chemistry, we need methods to quantitatively detect various species *in situ*. A few such sensor systems usable in complex systems (e.g., soils or ground water) are already available.

The fate of chemical compounds can only be predicted if the reactions of the various species in all environmental compartments are known. This kind of information leads to improved mechanistic models, thereby resulting in improved predictions about the dynamic behavior of trace compounds in the biosphere. Relatively good models are now available for aquatic systems, while the description of ground water and soil systems is only beginning.

Meaningful testing methods to assess the chronic effects of chemicals on ecosystems are practically nonexistent. Ecotoxicological testing is based almost exclusively on acute toxicity. Long-term protection of ecosystems from the deleterious effects of trace contaminants and from chemicals developed in the future is only possible if their impacts are understood on different biological levels and in the context of their chemical behavior in the environment.

Consequences for Regulatory Agencies

In the future, legislative bodies and government agencies must distinguish between chemicals which have already been released into the environment and those that are not yet released. Compounds belonging to the first group should be approached pragmatically, while strict criteria should be formulated for dealing with chemicals in the second group.

In the case of "historically contaminated sites", this means that limits on the total concentration of a trace compound should gradually be replaced by limits on its "effective" concentration. The total concentration of a chemical compound is only conditionally relevant. The effective concentration is that portion of a compound that is bioavailable (Fig. 2). In some cases, this may be equivalent to the total concentration; usually, however, the effective concentration is much smaller than the total concentration. The effective concentration is a function of the properties of the compound and of the composition of a given environment. The concept of effective concentrations would make it possible to base regulations for trace compounds on

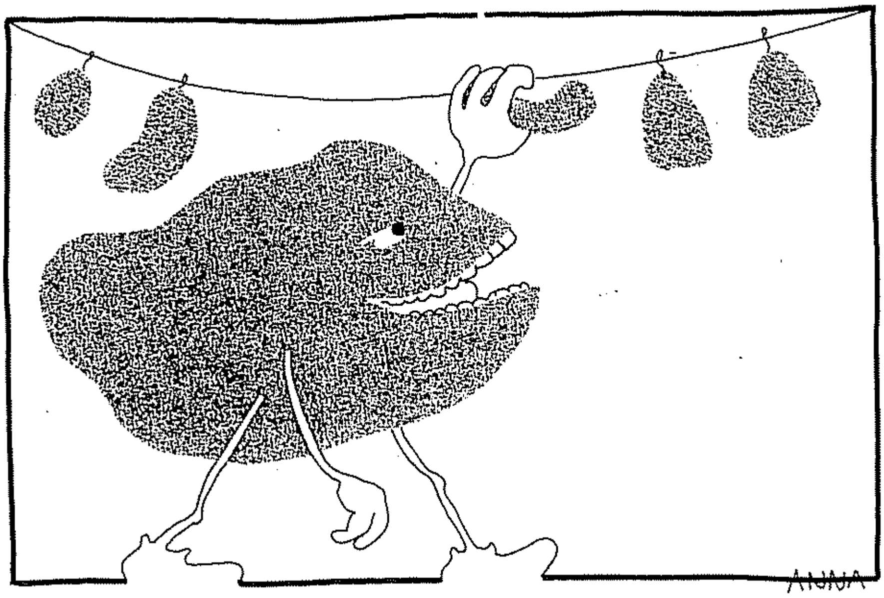


Fig. 2
"Well, let's see what is bioavailable here."

risk and potential damage. In many situations this would lead to a more efficient and economical remediation and cleanup. Quality goals, such as the ones currently being discussed in Switzerland for heavy metals in water, are a pragmatic step towards limits based on effective concentrations.

Stricter criteria must also be developed for compounds that are currently in use. Under no circumstances should we tolerate a compound that has any negative effects on the geosphere, including the atmosphere, biosphere or anthroposphere. The same criteria apply to compounds which may be accidentally released into the environment.

Monitoring programs need to take advantage of the most up-to-date scientific information and should be predictive. Mathematical models may help to extrapolate current observation to the future. Such monitoring programs are both efficient and economical. Monitoring solely for the purpose of data collection will become increasingly more difficult to justify.

Consequences for Industry

Translating the criteria discussed above into consequences for industry leads to the conclusion that chemical and/or biological mineralization continues to be the most important factor in deciding whether a new chemical compound should be used. The time constraints on mineralization depend on the given chemical and physical environment as well as on the specific application. In the atmosphere, for example, a compound is usually eliminated more quickly than in soils or sediments, since mixing and global transport is much faster. Typically, the half-life of a compound released into the atmosphere may be accepted to be on the order of minutes to a few hours. However, half-lives of several days may be acceptable in sediments or soils, depending on the situation.

For compounds that were designed for extended use, such as certain plastics, mineralization criteria are obviously not valid or only partially so. If a compound is designed to be stable and persistent, the technology for reincorporating it into natural cycles must be developed simultaneously. In addition, it is important to prevent release into the environment of additives in composite materials (e.g., plasticizers).

Consequences for EAWAG

EAWAG's involvement in work involving trace compounds will mainly be in the form of scientific research and in targeted campaigns to disseminate new information through publications and courses. Analytical capabilities will be expanded, and the development of sensors and probes will become a high priority. Additionally, in the context of sustainability, EAWAG will devote more resources to the mechanistical understanding of the long-term ecotoxicological effects of trace chemicals. New information will be disseminated to the practice.

Trace Compounds: The Challenge

The ever increasing use of chemicals in our daily lives leads to a higher risk of introducing more of these compounds into the environment. Actively protecting the environment – and ultimately ourselves – from contamination by both old and new trace compounds requires a commitment from all segments of society with respect to handling our resources more carefully. Only a sense of necessity will yield the crucial long-term improvements required to insure that future generations will not only survive, but lead to lives worth living.

In practical terms, the most crucial environmental criterion remains chemical and/or biological degradability. When setting contamination limits, however, effective concentrations should be used instead of total concentrations. This requires, of course, that analytical methods for trace analyses be able to distinguish between different species of a chemical, that the behavior of a compound in a given ecosystem can be modeled and that the toxic effects of a compound (particularly chronic effects) can be correlated to individual chemical species. At the same time, it is of paramount importance to translate this complicated volume of information into regulations that can be respected by both industry and individuals.

David Kinnison

Dimethyl Sulfide in the Marine Atmosphere

David Kinnison

Dr David Kinnison, postdoc at EAWAG in the atmospheric chemistry group 1994–95, studied at King's College London from 1986–1990 where he read chemistry for his bachelor degree and stayed on to take a Master's degree by Research under Dr John Nicholas in gas phase kinetics. After King's he moved to Oxford to study atmospheric chemistry for his D.Phil (PhD) from 1990–94 under Dr Richard Wayne. The main thrust of his work in Oxford was to research the atmospheric fate of CFC replacement compounds, hydrochlorofluorocarbons and hydrofluorocarbons HCFCs and HFCs respectively. His interests cover a wide spectrum of activities in atmospheric chemistry including: the marine atmosphere, degradation of hydrocarbons in the troposphere, formation of acid rain from organics, and photochemical smog formation.

Correspondence to
Dr David Kinnison,
Rose Cottage, Chapel Row, Herstmonceux,
East Sussex, BN27 1RB, England
p. Tel. 0044 1323 832 218
FAX 0044 1323 832 778.

Radicals and Reactions

In general, the gas phase oxidation of organics in the atmosphere is initiated by the hydroxyl radical OH in daylight and by the nitrate radical NO_3 during the night time. For the marine atmosphere, additional radicals have been suggested to be involved including: IO, Cl, Br, ClO, BrO, and HO_2. At first, it was thought that only BrO might be important in the Arctic owing to the relatively high ambient concentration of BrO (10^6 molecule cm^{-3}). Recently, however, it has been suggested that the atmospheric concentration of Cl atoms may be high enough (10^4 molecule cm^{-3}) in the marine troposphere to compete with OH (10^6 molecule cm^{-3}) in the oxidation of organic molecules in the troposphere [3]. A lower concentration of Cl is required because the rate coefficients for the reactions of Cl with hydrocarbons are generally two orders of magnitude greater than the rate coefficients for the reaction of OH with hydrocarbons. Fig. 2 shows possible routes for Cl atom formation in the marine troposphere with the majority of pathways requiring a polluted atmosphere, where the mixing ratio of NO_x (NO and NO_2) is high, 50–500 ppb (as compared to the remote atmosphere where NO_x is about 0.01–0.5 ppb) [4]. Sea-salt aerosols are believed to be the source of Cl and provide the heterogeneous medium for the reactions. The bulk of chlorine in the atmosphere is in the form of HCl which in the gas-phase can react with OH to produce Cl atoms.

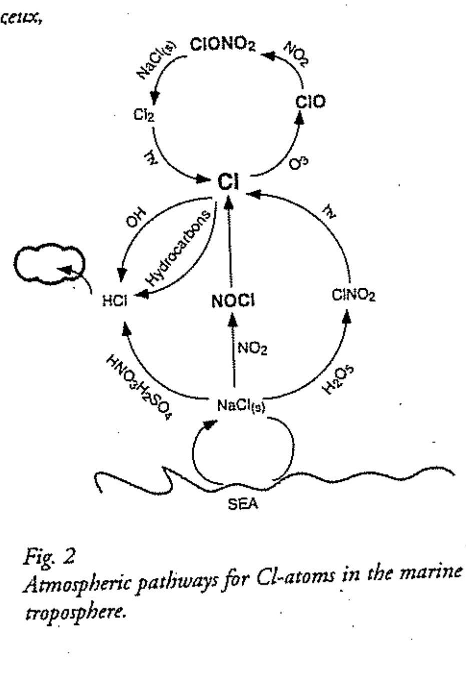


Fig. 2
Atmospheric pathways for Cl-atoms in the marine troposphere.

$$HCl + OH^{\cdot} \rightarrow Cl + H_2O \qquad (1)$$

The reactions of Cl atoms with hydrocarbons are characterized by near zero or small activation energies and high rate coefficients ($10^{-10} - 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}), are exothermic, and can be classified as either abstraction reactions or addition reactions. Thus with alkyl sulfides the Cl atom can either abstract a hydrogen from one of the alkyl branches or add directly to the sulfur to produce an unstable radical intermediate, or adduct,

$$RSR + Cl \rightarrow RSR' + HCl \qquad (2a)$$
$$'RSClR \qquad (2b)$$

The partitioning of reactions (2a) and (2b) is dependent on pressure. It has been shown that at low pressure (1 Torr, 1/760 of an atmosphere) reaction (2a) dominates with a HCl fractional yield of approximately unity while at atmospheric pressure this yield decreases to approximately 0.5 [5]. The products and their fate in the atmosphere are key concerns to atmospheric scientists.

The majority of the DMS atmospheric photooxidation studies undertaken have employed the OH radical as the radical initiator, which is hardly surprising since OH is the most important daytime radical in the atmosphere. Laboratory experiments of the photo-

Background of Dimethyl Sulfide

Dimethyl sulfide, DMS, $(CH_3)_2S$ is a foul smelling gas which is produced naturally in the oceans and plays a important role in climate regulation. DMS is produced in sea water by phytoplankton and is readily released to the atmosphere where it is present in concentrations of approximately 0–1 parts per billion by volume (ppbv). DMS is emitted by phytoplankton both directly and as a breakdown product of dimethylsulfonium propionate which is produced by marine algae in the process of osmoregulation. The global flux of sulfur from DMS from the sea to the atmosphere is roughly 16–50 Tg S y^{-1} which accounts for a large fraction of the total biogenic sulfur emissions (65–125 Tg S y^{-1})[1]. This natural sulfur flux is comparable to the emission of SO_2 from industrial sources, but note that the direct emission of SO_2 from natural sources is small compared to anthropogenic sources. As shown in Fig. 1 once in the marine atmosphere DMS is oxidized eventually into sulfate particles which can act as cloud condensation nuclei, and hence affect the reflectance of clouds (albedo) and therefore the Earth's radiation budget and climate. In the mid eighties the Charlson-Lovelock-Andrea-Warren (CLAW)[2] hypothesis proposed that phytoplankton vary their production of DMS in response to changes in the surface temperature and sunlight, and thus, modulate the planet's climate in a feedback loop. Lovelock in his popular book „Gaia: a new look at life on Earth" has likened the process to that of a thermostat.

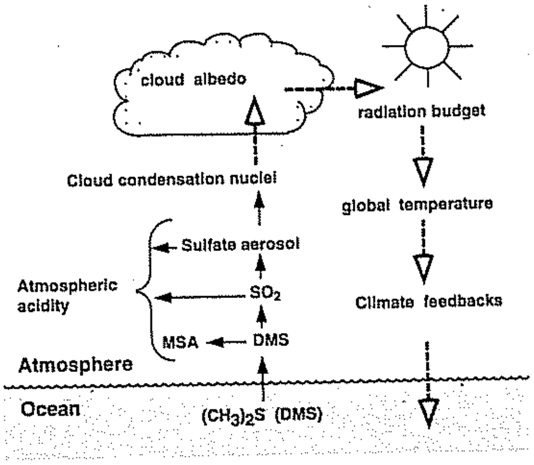


Fig. 1
The air-sea cycle of DMS showing its atmospheric oxidation products and the proposed feedback loop.
MSA: methylsulfonic acid CH_3SO_2OH (Redrawn from Liss P.D., Malin G., and Turner S.M. (1993): Production of DMS by marine phytoplankton in Dimethylsulphide: Oceans, Atmosphere, and Climate, p.p. 1–14, (eds) Restelli G. and Angeletti G. ECSC, EEC, EAEC, Brussels and Luxembourg.)

oxidation of DMS are generally carried out under „simulated" atmospheric conditions, at atmospheric pressure (760 Torr) in an atmosphere of synthetic air containing NO. The OH-DMS photooxidation system is not totally understood, in particular, the mechanism for the formation of methyl sulfonic acid CH_3SO_2OH (MSA). MSA has been routinely measured in the atmosphere and observed as a product in OH/DMS photooxidation laboratory experiments. Field studies suggest that MSA is formed via an addition process but the proposed mechanism of MSA formation via OH addition is dubious. Recently it has been shown that the involvement of the higher oxides (CH_3SO_x) of methyl thiyl radical (CH_3S) seems to be more likely route to MSA [6]. A reaction scheme for the OH/DMS system is shown in Fig. 3.

In view of the possible importance of Cl atom reactions with natural sulfur compounds over the marine atmosphere we have initiated a program of kinetic studies of Cl atoms with DMS and related molecules.

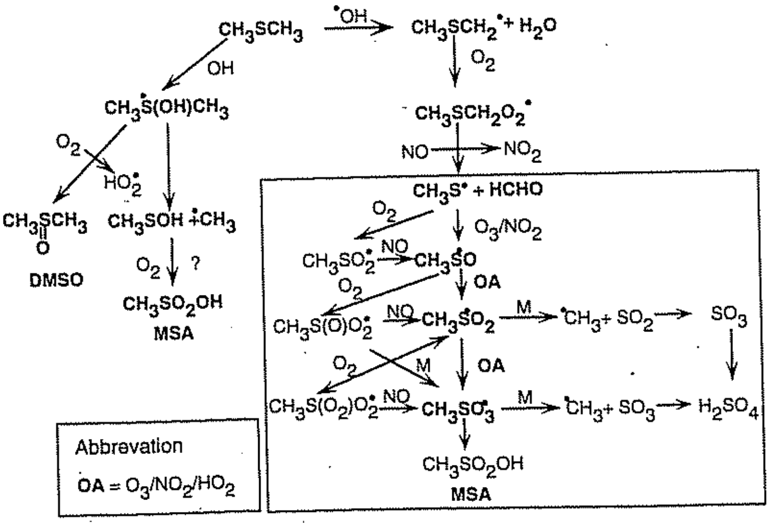


Fig. 3
Atmospheric oxidation of DMS initiated by OH radicals

Kinetic and Mechanistic Studies

We have measured several rate coefficients for the reaction of Cl with alkyl sulfides employing the relative rate method, a competitive technique. A schematic diagram of the apparatus is shown in Fig. 4; it is sometimes referred to as a

„smog chamber“ or „bag reactor“. Vapor samples are prepared in a vacuum system and introduced into the Teflon bag by a flow of either N_2 or synthetic air. The decay of the compound of interest in its reaction with a given radical is measured by gas chromatography relative to a reference compound with a known rate coefficient for its reaction with that radical. Our results have confirmed those of previous studies: the rate coefficients for the reactions of Cl with the alkyl sulfides are high, approaching the gas-kinetic limit; meaning that Cl reacts with the sulfides on almost every collision. Knowledge of the rate coefficients from kinetic studies is useful for product studies, especially when the conditions are varied. For example, measurement of the rate coefficient under O_2-free and -present conditions can provide information about the mechanism of the process. It should be pointed out that the measurement of such kinetic parameters is performed under „ideal conditions“ in our laboratory system and is not truly representative of the atmosphere. The main reason for this approach is to reduce the effects of secondary chemistry on the measurements. For laboratory kinetic studies involving sulfur compounds and their „daughter“ radicals it is imperative to operate under NO_x-free conditions, which is clearly not the case in the atmosphere. Furthermore, we cannot work with the same mixing ratios as found in the atmosphere where sulfur species are in the parts per trillion (ppt) range whereas our analytical sensitivity requires experiments with reactants in the parts per million (ppm) range. An added complication for our system is that alkyl sulfides undergo a rapid dark reaction with Cl_2, the usual source of Cl atoms in laboratory kinetic studies. An alternative source for Cl atoms is provided by the UV photolysis of phosgene, $COCl_2$. We tried to extend the technique to the related group of mercaptans (RSH) some of which are of biogenic origin. We observed a very rapid decay of the mercaptan in the absence of the radical precursor when the chamber was irradiated which was ascribed to the ultraviolet (UVC) photolysis of the mercaptan. An important requirement of the relative rate technique is that the substrate and the reference compound are consumed entirely by the reaction with the selected radical, Cl atoms in our case. Therefore, we could not undertake a relative rate study for the mercaptans. Although the alkyl sulfides do absorb UVC radiation the decay of the sulfides was negligible compared to their reaction with Cl atoms.

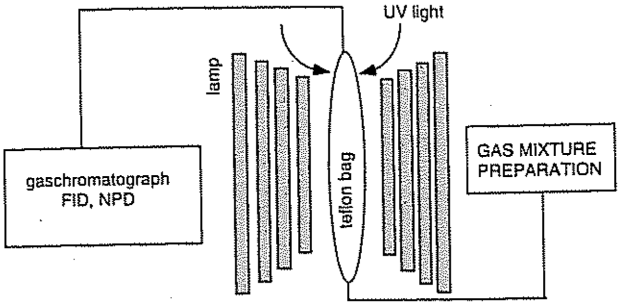


Fig. 4
Apparatus for laboratory kinetic and mechanistic experiments

Fate of DMS + Cl

Our kinetic experiments were carried out as forerunner to product studies. We have been able to show that the overall rate coefficient for reaction of DMS with Cl is clearly enhanced in the presence of O_2. This O_2 effect is best explained by the formation of the adduct, RSClR, in the initial reaction scheme. The overall rate coefficient is enhanced because the adduct reacts with added O_2 and less of the adduct can decay back to the reactants and therefore effectively more substrate, DMS, has been consumed. The O_2 experiments are good evidence for the formation of the adduct and its subsequent reaction with O_2. The products of this reaction have been postulated and a possible reaction mechanism (see Fig. 5) of the Cl/DMS system is in most respects similar to the OH/DMS system.

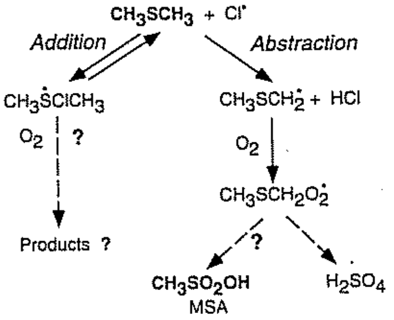


Fig. 5
The proposed reaction scheme for the reaction of DMS with Cl atoms.

The Future

It is evident that additional studies are required to establish the fate of the products of the Cl/DMS system and to elucidate the reaction mechanism. The importance of Cl in the marine atmosphere is still uncertain, and further field studies are needed. Higher concentrations of Cl atoms in the marine atmosphere will decrease the lifetime of hydrocarbons over the sea, and Cl could be equally as effective as the OH radical as one of nature's „atmospheric detergents“.

Studies of the Cl/DMS system will benefit the understanding of the OH/DMS system because the mechanisms intrinsically overlap. In the last two years, researchers

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The courses are based on our own research and experiences and reflect the actual working areas.

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or apply with:
Heidi Gruber, © 01/823 53 93
EAWAG
Überlandstr. 133
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PGC	indicates those courses which can be incorporated into the postgraduate study course
cu	credit units
( )	The second date applies for all those who wish to gain a course certificate with credit units. For other participants, the second part of the coures is optional

3–5 (8–10) July Advanced Course V9/96, PGC, 3 cu	**The Role of Suspended Particles and Sediments Material Fluxes in Streams** Course Directors: Rene Gächter, Jürg Zobrist
26–30 August Applied Course A5b/96, PGC, 3 cu	**Biological Waste Water Treatment Part b: Modeling and Simulation** Course Directors: Willi Gujer, Tove Larsen, Hansruedi Siegrist
2–6 September Applied Course A5c/96, PGC, 3 cu	**Biological Waste Water Treatment Part c: Experimental Field Studies** Course Directors: Willi Gujer, Tove Larsen, Hansruedi Siegrist
10 September Infoday 1996	**Janus – the Two Faces of Phosphorus National Success in Water Problems and Questions of Global Sustainability** Course Directors: Markus Boller, Theresa Buesser
16–20 (23–27) September Advanced Course V10/96, PGC, 5 cu	**Drinking Water Treatment: Removal of Particles** Course Directors: Markus Boller, Mario Snozzi, Urs Von Gunten
1–3 (8–10) October Applied Course A6/96, PGC, 3 cu	**The Problems of Chemical Contamination in Ground Waters** Course Directors: Eduard Hoehn, Peter Huggenberger, Urs Von Gunten
19/20 November Basic Course B4/96, PGC, 1 cu	**Modeling of Natural Systems** Course Directors: Gerrit Goudsmit, Peter Reichert

have identified that the higher oxides of CH_3S radical as essential to the understanding of the photo-oxidation of DMS in the atmosphere. Determining the role of the higher oxides of CH_3S in the marine atmosphere is now a principal objective of atmospheric scientists. Further investigations into the mechanism by end product analysis are intended.

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[1] Restelli G. and Angeletti G.(eds.) Dimethylsulphide: Oceans, Atmosphere, and Climate 1993 ECSC, EEC, EAEC, Brussels and Luxembourg.

[2] Charlson R.J., Lovelock J.E., Andrea M.O., and Warren S.G. (1987) Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature *326*, 655.

[3] Pszenny A.A.P., Keene W.C., Jacob D.J., Fan S., Maben J.R., Zetwo M.P., Springer-Young M., and Galloway J.N. (1993) Evidence of inorganic chlorine gases other than hydrogen chloride in marine surface air. Geophys. Res. Lett. *20*, 699

[4] Seinfeld J.H. Atmospheric Chemistry and Physics of Air Pollution (1986) John Wiley and Sons. New York.

[5] Stickel R.E., Nicovich J.M., Wang S., Zhao Z., and Wine P.H. (1992) Kinetic and mechanistic study of the reaction of atomic chlorine with dimethyl sulfide. J. Phys. Chem. *96*, 9875.

[6] Barone S.B., Turnipseed A.A., and Ravishankara A.R. (1995) Role of adducts in the atmospheric oxidation of dimethyl sulfide. Faraday disc. *100*, 1.

Letter to the Editor to the Guest Commentary by Josef Reicholf (see EAWAG news 39 E, page 8)

Biodiversity is More Than Just Species Diversity

When addressing conservation issues, politicians and ecologists often make reference to the Biodiversity Convention [1], signed by more than 150 countries during the Earth Summmit Conference held in Rio de Janeiro in 1992. This, in turn, has resulted in increased use of the term "biological diversity". Unfortunately, a stale taste lingers after looking more closely at the use of these popular words. In fact, I have the impression that old concepts are simply reappearing in new clothing.

The title of Reichholf's guest commentary promises the reader some fundamental thoughts on the subject. Unfortunately, he interprets the concept of biodiversity in a way that causes more confusion than clarity. Throughout most of his article, biodiversity is assumed to be synonymous with species diversity, the latter being reduced once again to mean species abundance. Admittedly, the author does briefly mention the problems arising from the definitions and implementation of the signed and legally binding convention before stating that species diversity represents the most important aspect of this conservation strategy.

Throughout the entire debate on biodiversity, both in the scientific literature and in the paper on the Earth Summit Conference, there is consensus that roughly three subtopics exist; that is, three hierarchical levels of approaching biodiversity: (1) genetic diversity, (2) species diversity and (3) ecosystem diversity.

The most comprehensive definition of biodiversity with respect to its complexity does not stem from the Earth Summit document but from the Keystone Dialogue:

"Biodiversity is the variety of life and its processes. It includes the *variety* of living organisms, the *genetic differences* among them, the *communities and ecosystems* in which they occur, and the ecological and *evolutionary processes* that keep them functioning, yet ever changing and adapting." [2].

Species diversity

No one disputes the fact that not all of the approaches mentioned above can be treated with equal ease. Species diversity is most certainly the broadest subject, and yet science offers a clearly defined concept of what a species is which, despite several problematic cases, makes the delimitation of organisms into distinct units possible. This has probably contributed to the significance currently being given to species diversity in ecologically-oriented research; several methods and evaluation standards have been developed which are currently accepted for describing species diversity. Such standards are technically simple to use; the ease with which they can be calculated, however, often leads to their inappropriate application and to inaccurate conclusions based on faulty assumptions [3]. Of course, determining the abundance of species is the most practical way of evaluating habitats at this point in time, but does not allow us to automatically conclude that biodiversity is primarily characterized by the number of species.

Genetic diversity

The immense progress made in molecular biology provides increasingly more important input for work on the chemical level, i.e., in genetic diversity. On this level, clearly separable units and preliminary methods for the observation and evaluation of genetic diversity are already available. As these new methods are still being developed, one can almost certainly assume that this field will play an ever larger role. In the future, it may well be possible that the genetic dimension will replace the current focus on species.

The importance of habitat

In contrast to the two levels of information mentioned above – genetic diversity and species diversity, both of whose importance in determining biodiversity is undisputed – the descriptions of *biotopes and ecosystems* cause even more difficulty. The units for assessing the latter have traditionally been applied to plant communities according to the system of Braun and Blanquet (e.g., [4]) which is based on the concept of clearly delimited biotic communities. A description of this kind can usually only be used for small regions, as local abiotic factors result in the development of a number of communities within a region. Furthermore, such a concept involving fixed communities which are naturally separate from one another is not uncontroversial. Consequently, the principles underlying the distribution of plant communities should be tested for their applicability to other groups of species [5].

In spite of such difficulties, new methods for assessing diversity, particularly at the ecosystem level, are unquestionably becoming ever more common and for a number of reasons:

1. As Reichholf states in his article, a large number of species has not yet been described. The conservationist's aim of preserving all living species (i.e., no further species shall become extinct) means that the existence of so-called lesser species and those that seem less attractive must also be insured. Any conservation strategy which encompasses the diversity of biotopes could make a valuable contribution towards this goal [6].
2. Assessing species diversity usually concentrates on a single group of species or, in the best case, on

one *trophic level*, the rest of the organisms in the habitat being largely neglected. As the applicability of the concepts often quoted in this context, namely the keystone, the umbrella*, and the indicator species, is limited, (disregarding for now the basic question about whether these concepts are at all valid), any statement about a habitat resulting from their use will only be based on a *selection of species*. Obviously, the result consists of very biased statements. A single level of evaluation, including the sum of all species diversities, is still missing. It would, for example, be interesting to test whether Reichholf's basic statement based on species diversity (i.e., medium to low trophic levels are linked to high diversity), is also valid for other levels of biodiversity.

3. Assuming that we accept the definition of biodiversity as used above, nature's natural dynamics should also be preserved. The traditional approach to species diversity can not assume to include interactions between the species and their abiotic environment.

4. Even if the concept of habitat diversity can only be described perfunctorily, there is still a need for such overall viewpoints, from the field of practical environmental management to sustainable resource management (e.g., compare to [7]), *keeping in mind that that all hierarchical levels of approach have to be considered depending on the specific conservation problem at hand [8].*

I agree with Reichholf that the concept of biodiversity is difficult to understand. Those countries who have signed the Rio agreement have accepted a challenge; on the level of habitat diversity, preliminary conceptual work is needed before those countries can implement their conservation projects.

The reduction of the *cliché* "biodiversity" to "species diversity" paves the way for confusion; the unsatisfactory use of these terms draws its logical conclusion: either to accept the challenge (i.e., to attempt a better description of the concept of biodiversity), or to resort to use of the old, more clearly defined concept of species diversity. *Adrian Zangger**

(Received 11.8.1995)

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* Umbrella species: those at the end of the food chain, which also require the largest living area.

* Dr. A. Zangger, Hintermann & Weber AG, Consultance in Ecology and Conservation Biology, Hauptstr. 52, CH-4153 Reinach.

[1] Schweizerischer Bundesrat (1994): Übereinkommen der Verienten Nationen über die Biologische Vielfalt, SR 94.040.

[2] Noss, R. F. & A. Y. Cooperrider (1994): Saving Nature's Legacy: Protecting and Restoring Biodiversity. Island Press, Covelo, WA.

[3] Magurran, A. (1988): Ecological Diversity and Its Measurement. Croom Helm, London.

[4] Riecken, U., Ries, U. & Ssymak, A. (1994): Rote Liste der gefährdeten Biotoptypen der Bundesrepublik Deutschland.Schriftenreihe für Landschaftspflege und Naturschutz *41*, 1–184.

[5] World Conservation Monitoring Centre (1992): Global Biodiversity – Status of the Earth's Living Resources. Chapman & Hall, London.

[6] Kaule G. (1991): Arten- und Biotopschutz, Ulmer, Stuttgart.

[7] Kohm, K. A., ed. (1991): Balancing on the Brink of Extinction. Island Press, Covelo, WA.

[8] Noss, R. F. (1990): Indicators for monitoring biodiversity: a hierarchical approach. Conservation Biology *4*, 355–364.

Is Biodiversity Really More than Species Diversity?

Adrian Zangger quite rightfully points to the comprehensive formulation of the term "biodiversity" as it was established at the Earth Summit Conference in Rio (UNCED) and to the debate it has triggered. International conservation and environmental organizations, such as the WWF and the IUCN, use the term in its broader sense. Nevertheless, a rigorous examination of the term results in its reduction to "species diversity" with biotopes and ecosystems being defined by the species contained within them. Indeed, the study of plant communities mentioned by Zangger classifies biotopes on the basis of existing plant species; everyone does the same when investigating a biotope, even when their delimitation may be arbitrary or depend on the formulation of the problem in question.

The concept of ecosystem is a prime example of how a word can become independent, a word which was originally formulated as a research concept in a scientific field and which was then used to mean "a functional unit of nature" or even "a super organism", in order to upgrade the value of an old concept. Its delimitation is so arbitrary that one can just as well speak of the ecosystem of a flower pot as that of a tropical rain forest. In any case, all processes which take place with the participation of living beings and all formations of communities of organisms are based on the existence of species.

It is true that the concept of genetic diversity cannot be comprehensively expressed in all its aspects through current use of the term "species". This is because species is understood to be the potentially "reproductive group of individuals" which can successfully reproduce with one another. A substantial part of genetic diversity may be found within these boundaries; it is the raw material for evolution. In highly developed groups which are largely emancipated from their abiotic environment, such as trees, birds and mammals, genetic diversity lies more or less concealed within the species. The opposite occurs in other groups such as the extremely species-rich insects which have externalized their genetic diversity and are divided finely into different species. Genetic diversity is especially wide within the human species which never could be satisfactorily represented by any one "race" or local population.

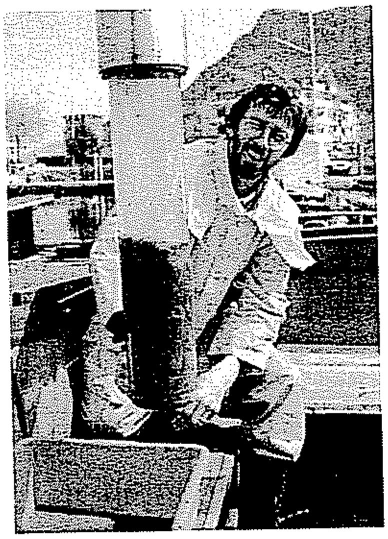
If we intend to preserve the entirety of existing genetic diversity, not a single individual may die – be it human, animal, plant or microbe – as each one is a unique combination of genetic information which will most probably never exist again. As, however, genetic diversity is ever changing in reproductive communities and represents the insurance for their continued existence, the extended approach to the study of biodiversity is again fundamentally reduced to the study of species. The fact that we do not yet know the majority of all organisms, because they lead concealed lives among the wealth of species in tropical rainforests or in the deep ocean, signifies a significant gap in our knowledge base. Such habitats, about which we know very little or, where the species are specifically bound to certain living conditions (stenoecous species), are in need of special "biotope protection". The protection of biotopes and processes are specific forms of species protection, as environmental protection is primarily a form of species protection; namely, for the human species.

Josef H. Reichholf

Habilitations

Upon promotion to professor at the ETH, one obtains the so-called venia legendi; *that is, the right to offer classes of one's own choosing. This is distinctly different from usual teaching requirements, where a given ETH department assigns lecturers specific courses in order to cover the needs of the various curricula. The "habilitation" remains a prerequisite for obtaining a professorship.*

Karl Fent (*1954)...



At work:
Sampling on Lake Lucerne.

... studied zoology and biochemistry at the University of Zürich and obtained his doctorate in 1985 in neurobiology for his work on the orientation capabilities of ants in the Sahara desert. In 1984, he obtained the equivalent of a High School teaching diploma and was a teacher until 1988. He held the position of postdoctoral fellow at the Institute for Toxicology at ETH and the University of Zürich, where he worked with Prof. Zbinden on the toxic effects of chemicals on the human kidney and the toxicity of interferon. At the end of 1987, he joined the EAWAG as a research scientist and started his research on the chemical and toxicological aspects of organotin compounds.

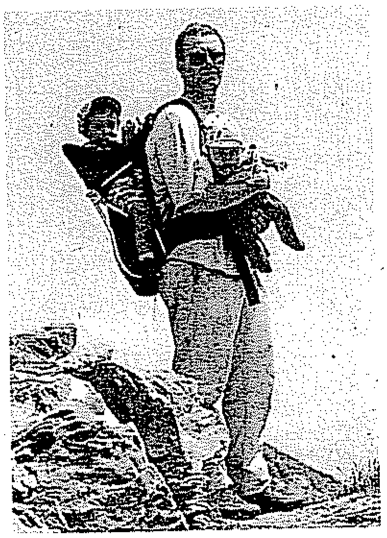
Since 1990, Dr. Fent has held the position of lecturer in Ecotoxicology at the University of Zürich; since 1991, he has held the same post at the ETH-Zürich (Departments XB and VIII). During 1990–1991, he was a visiting scientist at the Woods Hole Oceanographic Institution (USA), where he studied cytochrome P450 in fish and expanded his knowledge on microbial ecology at the Marine Biological Laboratory.

His habilitation dissertation, entitled "Ecotoxicology of Organotin Compounds", has been published in "CRC Reviews in Toxicology". *26*, 1–117 (1996). In his research, Dr. Fent combines concepts of environmental chemistry and toxicology. He is currently investigating the biochemical effects of micropollutants on fish cells as well as developing new concepts for assessing long-term exposure and chronic toxicity.

Dr. Fent was recently offered a position as a professor in Ecotoxicology at the University of Konstanz (Germany), which he declined in order to remain at the EAWAG. He is now leading the group for chemical ecotoxicology in the Department of Chemistry at the EAWAG.

Peter Reichert (*1957)

After obtaining an undergraduate degree in theoretical physics, Peter Reichert obtained his doctorate for work on "Amorphicity as Spatial Chaos" at the University of Basel. He subsequently moved to the Canton of Zürich and since 1985 has been a research scientist in the section for computer and systems sciencies. The focus of his work is in the development of software for the analysis of laboratory and environmental systems, validation of models for technical and natural systems through comparison of model calculations and actual measurements, and improvement of methods for estimating uncertainties in model predictions.

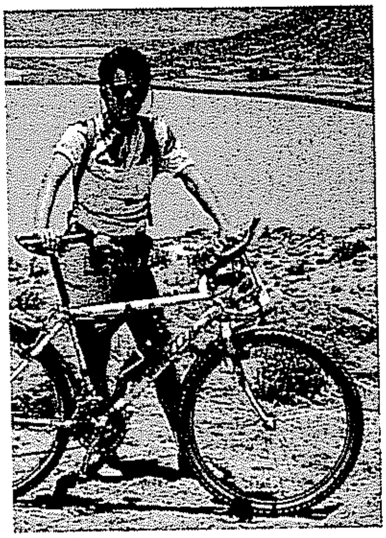


Family time:
With Michael (2 ½ years) and Nora.

Since 1991, Dr. Reichert is lecturer in the Department XB of the ETH-Zürich where he is teaching "Mathematical Modeling of Aquatic Systems". His habilitation dissertation entitled "Concepts Underlying a Computer Program for the Identification and Simulation of Aquatic Systems" has been published as Volume 7 in the series of EAWAG monographs. It discusses the concepts underlying a universally applicable computer program which is capable of simulating aquatic systems and aiding in data analysis. The program is currently being used in many of the projects at EAWAG and at over 50 universities.

Claudia Pahl (*1959)

Claudia Pahl obtained her undergraduate degree in chemistry and molecular biology in Heidelberg. She received her doctorate in 1986 from the Center for Biological Sciences at the University of Basel for her research on non-invasive techniques (in vivo NMR-spectroscopy) for studying the regulation of human metabolism. She subsequently worked for one year as a postdoctoral fellow at Sandoz.



Hobby and recreation (in the Andes).

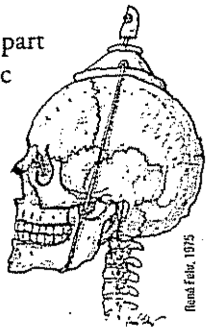
After graduating from the postgraduate course "Municipal Water Supply and Water Protection" at ETHZ-EAWAG in 1988, Dr. Pahl was selected to lead a research group under the chair for environmental physics at the ETH-Zürich in the area of "Mathematical Modeling of Ecosystems". In her current work, she is developing concepts and mathematical models for describing the structure and organization of ecosystems. She is collaborating with human ecologists in developing and applying models describing human ecosystems as complex systems.

Dr. Pahl's habilitation dissertation on theoretical ecology was published in 1995 by John Wiley & Sons: "The Dynamic Nature of Ecosystems, Chaos and Order Entwined" (ISBN 0.471.95570.1, 288 pp.).

Nobel Prize for Chemistry

The awarding of the Nobel Prize for Chemistry to P.W. Crutzen, M.J. Molina and F.S. Rowland marks a clear recognition of the scientific value of environmental science, in general, and of atmospheric chemistry in particular. It has been 20 years since Molina and Rowland first postulated that the presence of trace amounts of synthetic chlorofluorocarbons (CFCs) in the stratosphere can lead to Cl atom catalyzed destruction of the ozone layer.

A significant part of the scientific case against the CFCs, which lead to the Montreal protocol and its amendments, rests on mathematical modelling calculations; this is where there is a connection to work carried out at the EAWAG.



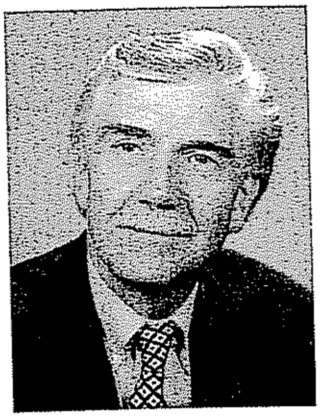
René Fehr, 1975

At the suggestion of Rowland, an international panel of experts in atmospheric kinetics and photochemistry was established in 1977 to provide the data needed by the stratospheric modellers. The IUPAC subcommittee, which at one point included Crutzen, is chaired by Prof. J.A. Kerr who has been at the EAWAG since 1989. It regularly publishes evaluations in the *Journal of Physical and Chemical Reference Data.*

Crutzen's demonstration of nitrous oxide (N_2O) as a compound that contributes to the depletion of stratospheric ozone and the missing N_2O balance has motivated research groups at the EAWAG to quantify the emission of N_2O from denitrifying wastewater treatment plants as well as assess its emission from lakes (e.g., thesis research by R. von Schulthess, in the group of Prof. W. Gujer and M. Mengis, a Ph.D. project at Kastanienbaum in the group of Prof. B. Wehrli).

New focus in limnology

New Professor at the EAWAG



James Ward, born in 1940 in Minneapolis, Minnesota (USA) assumed the professorial chair in aquatic ecology in the Department of Environmental Sciences at the Swiss Federal Institute of Technology in Zürich (ETH) in September 1995. This position (Hydrobiology/Limnology) was previously held for some 25 years by Prof. H. Ambühl and became vacant upon his retirement in 1994. Prof. Ward is also head of the Department of Hydrobiology/Limnology at the EAWAG with its 20-member staff, several doctoral candidates and many temporary employees. Until moving to the EAWAG, Dr. Ward was a professor at Colorado State University in Ft. Collins, Colorado (USA).

Under Prof. Ward's leadership, the department will continue its research and teaching in aquatic ecosystems, focusing on organismic aspects. The planned expansion with new scientists should strengthen research on the ecology of running waters, extend the field of lake ecology to include the littoral zone and introduce a new research area, groundwater ecology, in order to conduct a more comprehensive study of biological communities in aquatic habitats.

Prof. Ward's work has attained international recognition through numerous projects involving the effects of anthropogenic influences on the structure and function of running waters, on the influence of temperature changes on aquatic organisms, on factors determining the spatial and temporal distribution of organisms, on the structure of benthic biological communities and on the groundwater ecology of alluvial systems. Parallel to his extremely wide range of research activities, he has invested much time on lecturing on limnology and on the ecology of running waters. During the course of his successful scientific career, he has been invited as keynote speaker to numerous symposia on four continents.

Prof. Ward has served as president of the North American Benthological Society (1978–88) and on the boards of various other international societies such as the Societas Internationalis Limnologiae, the Ecological Society of America, the Entomological Society of America and the American Society of Limnology and Oceanography (ASLO). He was recently elected to the advisory boards of the Max Planck Institute of Limnology and the Austrian Academy of Science. He is also an editor of the international scientific journal *Regulated Rivers* and has been asked to serve as chief editor of a proposed journal *Groundwater Ecology*

Ward's activities at the EAWAG and ETH

In order to play a key role in the EAWAG's multidisciplinary environmental research, Prof. Ward plans to develop the Limnology Department into an aquatic ecology research center of international stature focusing on both organisms and ecosystems. In addition to the accumulation of new data, the synthesis of scientific concepts and the development of new theories will be fostered. Prof. Ward is convinced that first-class intensive research in Switzerland's waters will not only contribute to solving the country's environmental problems but will also gain international recognition. To this end, effective coordination of diverse projects within comprehensive studies of entire watersheds will play a decisive role. As Ward places special emphasis on the transfer of know-how from research to ecosystem management and on the ecological management of resources, he will thereby ensure that newly-gained theoretical knowledge will be incorporated into practice and that work on concrete environmental problems will be based on a solid theoretical foundation.

Prof. Ward will also place a renewed emphasis on teaching by tightening the organization of existing courses and expanding current subject matter. His teaching in biological and ecological aspects of natural waters will communicate basic concepts, summarize existing knowledge and development trends in the various scientific fields. Laboratory and field courses will familiarize students with modern techniques and analytical methods. The aim of this work is not merely the transfer of knowledge but to ensure a sound understanding of how nature works and to foster environmental ethics.

Peter Bossard

Center of Excellence in Analytical Chemistry of ETH Zurich, CEAC-ETHZ

In June of 1995, ETH-Zürich and the research institutions EAWAG, EMPA and PSI established a Center of Excellence for Analytical Chemistry. Its mission is to coordinate activities of different working groups in the area of analytical chemistry and promote cooperation in education and research.

In order to give participating personnel an opportunity to get to know one another, an informational meeting was held at EAWAG on June 20. More than 70 chemists attended. In introductory remarks, Prof. Ralf Hütter, vice president for research at ETH Zürich, as well as René Schwarzenbach and Alexander Zehnder, both ETH professors residing at EAWAG, applauded the creation of the CEAC-ETHZ and emphasized the importance of collaboration in the field of analytical chemistry. Thirteen additional speakers discussed goals, working concepts and major projects at their respective institutions. More detailed information on a variety of ongoing projects in analytical chemistry was presented in some 30 poster presentations. The day concluded with a panel discussion, which included three representatives from the chemical industry, a leading chemist from a university hospital and a food distributor. The main topic of the discussion was the role of the CEAC in applying research results to "the real world".

One of the first activities of the Center will be the compilation of a directory listing available services in analytical chemistry as well as existing expertise and instrumentation. The directory will also be made available by electronic media. The CEAC-ETHZ is accessible on the World Wide Web under http://beelzebub.ethz.ch/ceac.

The Center of Excellence already has a first success to report. With a grant from the Center for Scientific Culture – World Laboratory, it will be possible to bring senior scientists from developing and Eastern European countries to ETH Zürich, EAWAG, EMPA and PSI, to work in the fields of analytical and environmental chemistry. The program has been named the Wilhelm Simon Scholarship*, in honor of Wilhelm Simon, former professor of organic chemistry at ETH who was internationally renown for his pioneering research and teaching in analytical chemistry. Prof. Simon died in 1992.

Walter Giger

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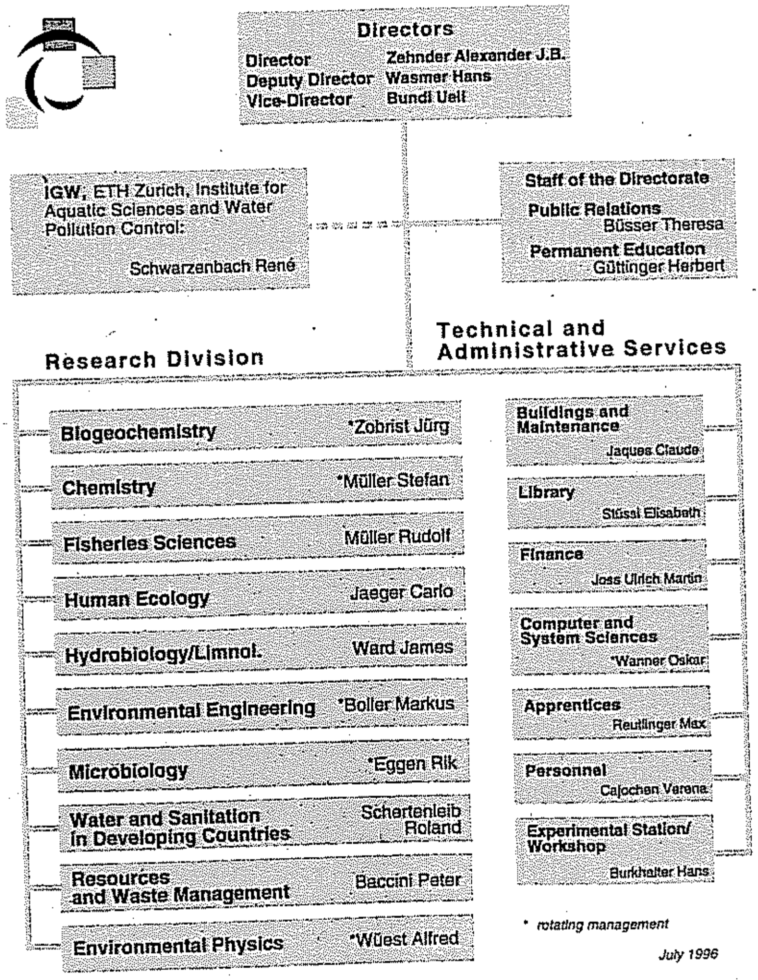
*Send applications to:
World Laboratory Research Center
c/o Professor Renato Zenobi
Analytical Chemistry Group
Laboratory for Organic Chemistry
ETH Zürich
CH-8092 Zürich

EAWAG
Swiss Federal Institute for Environmental Science and Technology



* *rotating management*

July 1996

Dioxin Day Dübendorf

On 9 March 1995, EAWAG hosted a one-day meeting called Dioxin Day Dübendorf, which was organized by EMPA. Eight presentations focused on the analytical chemistry, occurrence, origin and importance of polychlorinated dibenzodioxins and dibenzofuranes. The larger than expected attendance of 120 participants required the audio-video team at EAWAG to set up video conferencing between two different auditoriums.

1995 EAWAG Field Trip

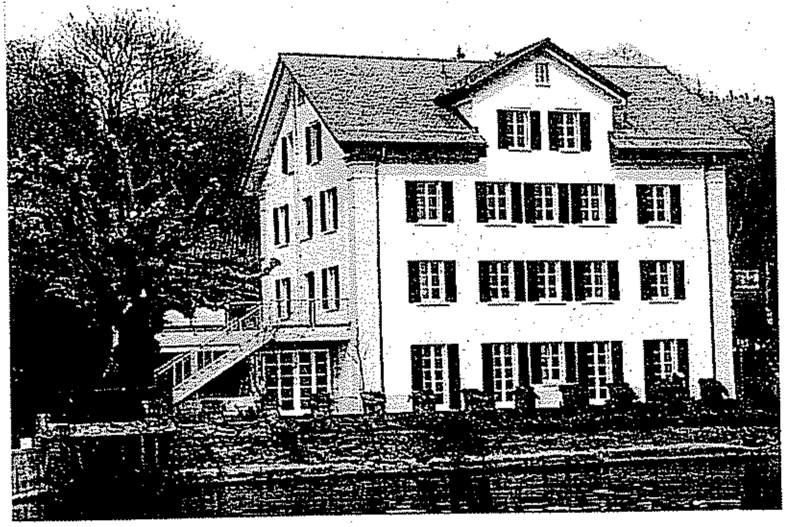
On August 22nd, 1995, the EAWAG field trip was heading to the Töss Valley (Canton of ZH). It was an excellent occasion to become acquainted first-hand with the priority research program called "Sustainable Management of Resources – Water and Anthropogenic Sediments" and to become more familiar with the subject of sustainable use of regional resources.

Accompanied by a slight morning fog, the trip, organized by Walter Wagner, led off by boat to Rapperswil. The SBB then carried the almost 200 participants down the Töss Valley to Rikon. In the lovely sunshine, local government representatives informed the group of their conservation activities for which they received the Swiss Nature Conservation Prize a few years ago. A representative of the H. Bühler AG described the amount of energy that has been gained through the Töss canals, which were built during the time of industrialization. The talks clarified the fact that the principle of sustainability in water protection not only includes protection of nature and landscapes but various aspects of Swiss national heritage as well.

A picnic on the banks of the Töss prepared the large group for a walk along the Töss and into the Linsen Valley. There four working groups from the EAWAG made presentations about current research projects which are being carried out either within the framework of the priority research program or are in some way affiliated with it. The stations, prepared with great care and effort, provided good insight into the research being done and gave everyone the opportunity to actively engage in discussing the various research themes. The relationships between surface waters, ground water, water supply, the morphology of the Töss and the organisms living in it were impressively demonstrated. In the photo, one of the four groups is shown with Dr. H.O. Schiegg, advisor of the Cantonal Department for Water Pollution Control (AGW) of the Canton of ZH, on the subject of the restoration of the Töss to its natural state. At the closing cocktail party on the Rossberg, the participants continued to discuss what they had seen and learned, while at the same time enjoying the more social aspects of the gathering. *Walter Wagner*

New EAWAG Meeting Center in Kastanienbaum (LU)

On 29 March, 1996, Judith Hornberger, from the Department of Federal Buildings, handed over the keys for the newly renovated "Seeheim" in Kastanienbaum to Alexander J. B. Zehnder, the director of EAWAG. The 128-year old building is part of EAWAG's Limnological Research Center. With the renovated "Seeheim", EAWAG now has new teaching facilities, office space and accommodations for visitors to the research center, finally allowing the long planned course and meeting center to become reality. Until recently, the "Seeheim's" original owner occupied two floors of the building. As a part of the renovation, the building was brought up to code, and major improvements with respect to energy conservation were made. Researchers from all over the world use the facility for scientific exchange, some staying only a few days, others for longer periods. The quiet location offers an ideal environment for creative and innovative research.



Can be ordered separately from the EAWAG library (use last page)

Publications

1957 **Bundi, U.:** Vom Umweltschutz zum Umweltmanagement. Schweiz. Ing. & Archit. *113*, H. 13, 318–320 (1995)

1958 **Akeret, B., Stössel, F.:** Vergleichende ökologische Untersuchungen an neun Weihern im Norden des Kantons Zürich. Vjschr. Naturforsch. Ges. Zürich *140*/1, 3–17 (1995).

1959 **Von Schulthess, R., Kühni, M., Gujer, W.:** Release of Nitric and Nitrous Oxides From Denitrifying Activated Sludge. Water Res. *29*, No. 1, 215–226 (1995).

1960 **Kari, F.G., Hilger, S., Canonica, S.:** Determination of the Reaction Quantum Yield for the Photochemical Degradation of Fe(III)-EDTA: Implications for the Environmental Fate of EDTA in Surface Waters. Environ. Sci. & Technol. *29*, 1008–1017 (1995).

1961 **Heijman, C.G., Grieder, E., Holliger, C., Schwarzenbach, R.P.:** Reduction of Nitroaromatic Compounds Coupled to Microbial Iron Reduction in Laboratory Aquifer Columns. Environ. Sci. & Technol. *29*, 775–783 (1995).

1962 **Sigg, L., Kuhn, A., Xue, H., Kiefer, E., Kistler, D.:** Cycles of Trace Elements (Copper and Zinc) in a Eutrophic Lake. Role of Speciation and Sedimentation. In: «Aquatic Chemistry: Interfacial and Interspecies Processes», C.P. Huang, C.R. O'Melia, J.J. Morgan (Eds.). ACS Advances Chemistry Series No. 244. American Chemical Society Washington D.C. 1995, pp. 177–194.

1963 **Xue, H., Sigg, L., Kari, F.G.:** Speciation of EDTA in Natural Waters: Exchange Kinetics of Fe-EDTA in Rivers. Environ. Sci. & Technol. *29*, 59–68 (1995).

1964 **Eberhard, J., Müller, C., Stocker, D.W., Kerr, J.A.:** Isomerization of Alkoxy Radicals Under Atmospheric Conditions. Environ. Sci. & Technol. *29*, 232–241 (1995).

1965 **Johnson, C.A., Brandenberger, S., Baccini, P.:** Acid Neutralizing Capacity of Municipal Wastes Incinerator Bottom Ash. Environ. Sci. & Technol. *29*, 142–147 (1995).

1966 **Boller, M.A., Kavanaugh, M.C.:** Particle Characteristics and Headloss Increase in Granular Media Filtration. Water Res. *29*, 1139–1149 (1995).

1967 **Ventling-Schwank, A.R., Livingstone, D.M.:** Transport and Burial as a Cause of Whitefish (*Coregonus* sp.) Egg Mortality in a Eutrophic Lake. Can. J. Fisheries & Aquatic Sci. *51*, 1908–1919 (1994).

1968 **Meyns, S., Illi, R., Ribi, B.:** Comparison of Chlorophyll-a Analysis by HPLC and Spectrophotometry: Where Do the Differences Come From? Arch. Hydrobiol. *132*, 129–139 (1994).

1969 **Van Veen, H.W., Abee, T., Kortstee, G.J.J., Konings, W.N., Zehnder, A.J.B.:** Substrate Specificity of the Two Phosphate Transport Systems of *Acinetobacter johnsonii* 210A in Relation to Phosphate Speciation in Its Aquatic Environment. J. Biol. Chem. *269*, No. 23, 16212–16216 (1994).

1970 **Semadeni, M., Stocker, D.W., Kerr, J.A.:** The Temperature Dependence of the OH Radical Reactions With Some Aromatic Compounds Under Simulated Tropospheric Conditions. Int. J. Chem. Kinetics *27*, 287–304 (1995).

1971 **Wehrli, B., Friedl, G., Manceau, A.:** Reaction Rates and Products of Manganese Oxidation at the Sediment-Water Interface. In: «Aquatic Chemistry», C.P. Huang et al. (Eds.). Amer. Chem. Soc. Ser. 244, Washington D.C. 1995, pp. 111–134.

1972 **Van der Meer, J.R., Schraa, G., Zehnder, A.J.B.:** Molecular Mechanisms of Adaptation in Soil Bacteria. In: «Adaptation and Selection Mechanisms of Natural and Generically Modified Soil Microorganisms», H. Rogaar, J.D. van Elsas, A.D.L. Akkermans, A.H. van den Heuvel-Pieper (Eds.). The Netherlands Integrated Soil Res. Programme (Vol. 2). Wageningen NL 1995, pp. 49–61.

1973 **Bürgi, H.R.:** Seenplankton und Seensanierung in der Schweiz. In: «Limnologische Berichte Donau 1994» der Int. Arbeitsgem. Donauforschung, Bd. II, H. Ambühl (Hg.), Dübendorf, Wien 1995, S. 71–100 + Summary.

1974 **Kiefer, E.K.E.:** Die Bindung von Kupfer an die Algenarten *Cyclotella cryptica* (Bacillariophyceae) und *Chlamydomonas reinhardtii* (Chlorophyceae). Diss. ETHZ Nr. 10'786, Zürich 1994.

1975 **Perlinger, J.A.:** Reduction of Polyhalogenated Alkanes by Electron Transfer Mediators in Aqueous Solution. Diss. ETHZ No. 10892, Zürich 1994.

1976 **Ambühl, H.:** Die Feinstruktur jüngster Sedimente von Seen verschiedenen Trophiegrades und von Seen in technischer Sanierung. Limnol. Berichte Donau 1994, Bd. II, EAWAG Dübendorf/Int. Arbeitsgem. Donauforschung Wien 1995, S. 101–126.

1977 **Sulzberger, B., Laubscher, H.:** Photochemical Reductive Dissolution of Lepidocrocite. Effect of pH. In: «Aquatic Chemistry: Interfacial and Interspecies Processes», C.P. Huang, C.R. O'Melia, J.J. Morgan, (Eds.). Amer. Chemical Soc. Adv. Chem. Ser. No. 244, Washington D.C. 1995, pp. 279–290.

1978 **Urban, N.R., Verry, E.S., Eisenreich, S.J.:** Retention and Mobility of Cations in a Small Peatland: Trends and Mechanisms. Water Air & Soil Pollution *79*, 201–224 (1995).

1979 **Fent, K.:** Effekte von Umweltschadstoffen auf Fische. In: «Schadstoffe heute im Boden, in Vögeln, in Fischen, in Säugern, im Menschen», M. Schlumpf, W. Lichtensteiger (Hg.). Kind und Umwelt, Bd. 3, Pharmakolog. Inst. der Universität Zürich 1994, S. 67–88.

1980 **Genoni, G.P., Montague, C.L.:** Influence of the Energy Relationships of Trophic Levels and of Elements on Bioaccumulation. Exotoxicol. & Environ. Safety *30*, 203–218 (1995).

1981 **Berg, M., Müller, S.B., Schwarzenbach, R.P.:** Simultaneous Determination of Triazines Including Atrazine and Their Major Metabolites Hydroxyatrazine, Desethylatrazine, and Deisopropylatrazine in Natural Waters. Anal. Chem. *34*, 1860–1865 (1995).

1982 **Jakob, A., Zobrist, J., Davis, J.S., Liechti, P., Sigg, L.:** NADUF – Observation à long terme de l'état physico-chimique des eaux. Gas-Wasser-Abwasser *75*, 378–393 (1995).

1983 **Holliger, C.:** The Anaerobic Microbiology and Biotreatment of Chlorinated Ethenes. Current Biology *5*, 347–351 (1995).

1984 **Field, J.A., Field, T.M., Poiger, T., Siegrist, H., Giger, W.:** Fate of Secondary Alkane Sulfonate Surfactants During Municipal Wastewater Treatment. Water Res. *29*, No. 1301–1307 (1995).

1985 **Fent, K., Looser, P.W.:** Bioaccumulation and Bioavailability of Tributyltin Chloride: Influence of pH and Humic Acids. Water Res. *29*, 1631–1637 (1995).

1986 **Wild, D., Von Schulthess, R., Gujer, W.:** Structured Modelling of Denitrification Intermediates. Water Sci. Tech. *31*, 45–54 (1995).

1987 **Reichert, P., Von Schulthess, R., Wild, D.:** The Use of AQUASIM for Estimating Parameters of Activated Sludge Models. Water Sci. Tech. *31*, 135–147 (1995).

1988 **Siegrist, H., Krebs, P., Bühler, R., Purtschert, I., Röck, C., Rufer, R.:** Denitrification in Secondary Clarifiers. Water Sci. Tech. *31*, 205–214 (1995).

1989 **Gujer, W., Larsen, T.A.:** The Implementation of Biokinetics and Conservation Principles in *ASIM*. Water Sci. Tech. *31*, 257–266 (1995).

1990 **Scheidegger, D.H.:** Bestimmung von Alkoholpolyethoxylaten in Abwasserreinigungsanlagen mittels Gaschromatographie, gekoppelt mit Massenspektrometrie mit chemischer Ionisation. Diss. ETHZ Nr. 11'014, Zürich 1995.

1991 **Friedl, G.:** Die Mineralogie des Mangankreislaufs in eutrophen Seen: Eine Untersuchung mit EXAFS-Spektroskopie. Diss. ETHZ Nr. 10987, Zürich 1995.

1992 **Naegeli, M.W., Hartmann, U., Meyer, E.I., Uehlinger, U.:** POM-Dynamics and Community Respiration in the Sediments of a Floodprone Prealpine River (Necker, Switzerland). Arch. Hydrobiol. *133*, 339–347 (1995).

1993 **Haderlein, S.B., Schwarzenbach, R.P.:** Environmental Processes Influencing the Rate of Abiotic Reduction of Nitroaromatic Compounds in the Subsurface. In: «Biodegradation of Nitroaromatic Compounds», J.C. Spain (Ed.). Plenum Press, New York 1995, pp.199–225.

1994 **Gujer, W., Henze, M., Mino, T., Matsuo, T., Wentzel, M.C., Marais, G. v.R.:** The Activated Sludge Model No. 2: Biological Phosphorus Removal. Water Sci. Tech. *31*, No. 2, 1–11 (1995).

1995 **Krebs, P.:** Success and Shortcomings of Clarifier Modelling. Water Sci. Tech. *31*, No. 2, 181–191 (1995).

1996 **Canonica, S., Hoigné, J.:** Enhanced Oxidation of Methoxy Phenols at Micromar Concentration Photosensitized by Dissolved Natural Organic Material. Chemosphere *30*, 2365–2374 (1995).

1997 **Rijnaarts, H.H.M., Norde, W., Lyklema, J., Zehnder, A.J.B.:** The Isoelectric Point of Bacteria as an Indicator for the Presence of Cell Surface Polymers That Inhibit Adhesion. Colloids & Surfaces B: Biointerfaces *4*, 191–197 (1995).

1998 **Canonica, S., Jans, U., Stemmler, K., Hoigné, J.:** Transformation Kinetics of Phenols in Water: Photosensitization by Dissolved Natural Organic Material and Aromatic Ketones. Environ. Sci. & Technol. *29*, 1822–1831 (1995).

1999 **Altenbach, B., Giger, W.:** Determination of Benzene- and Naphthalenesulfonates in Wastewater by Solid-Phase Extraction With Graphitized Carbon Black and Ion-Pair Liquid Chromatography with UV-Detection. Anal. Chem. *67*, 2325–2333 (1995).

2000 **Van Veen, H.W., Abee, T., Kortstee, G.J.J., Pereira, H., Konings, W.N., Zehnder, A.J.B.:** Generation of a Proton Motive Force by the Excretion of Metal-Phosphate in the Polyphosphate-accumulating *Acinetobacter johnsonii* 210A. J. Biol. Chem. *269*, No. 47, 29509–29514 (1994).

2001 **Henze, M., Gujer, W., Mino, T., Matsuo, T., Wentzel, M.C., Marais, G.v.R.:** Wastewater and Biomass Characterization for the Activated Sludge Model No. 2: Biological Phosphorus Removal. Water Sci. Tech. *31*, No. 2, 13–23 (1995).

2002 **Baumann, U., Güttinger, H., Kasser, U.:** Beurteilung der Umweltbelastung von Reinigungsmitteln. Tenside Surf. Det. *32*, 218–224 (1995).

2003 **Heijman, C.G.:** Reductive Transformation of Nitroaromatic Compounds Under Iron-reducing Conditions. Diss. ETHZ Nr. 11'164, Zürich 1995.

2004 **Siegrist, H., Vogt, D., Wild, D.:** Erzeugung von organischen Substraten durch Frischschlammversäuerung auf Abwasserbehandlungsanlagen. In: «Stickstoffelimination mit oder ohne externe Substrate – Erfahrungen und Überlegungen», 43. Darmstätter Seminar Abwassertechnik. Schrr. WAR 85 , Darmstadt 1995, S. 107–124.

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