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## From Molecules to Ecosystems: Topics, Challenges, and Players in Environmental Chemistry

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Abstract. This article is meant to be appetizer and introduction to this special issue of CHIMIA on 'Chemistry at EAWAG'. Two major topics presently challenge environmental chemistry, not only at EAWAG: The human impact on global and regional biogeochemical cycles and the pollution of the environment by anthropogenic chemicals. In order to tackle the various tasks associated with these problems, environmental chemists have to build bridges between the molecular scope of laboratory experiments and the systems approach of comprehensive field and modeling studies. This requires the ability to collaborate with other disciplines and to combine their knowledge with a profound understanding of chemistry. Some consequences of these requirements for research and education in environmental chemistry are also addressed in this article.

#### Introducing Environmental Chemistry

Global change. Green chemistry. THE ENVIRONMENT. Sustainability... There is no lack of buzzwords these days. 'Environmental Chemistry' is a scientific response to the public perception that the relationship between chemistry and the environment is a difficult one. However, as a science, environmental chemistry has its own agenda. In this article, we present a synoptic overview of scientific questions, achievements, available tools, unresolved problems, and future opportunities of this rather young branch of chemistry. Such a brief overview of a whole scientific field is, of course, always limited by the personal optics and bias of the authors. In the following, we use two different cameras to zoom into the field of environmental chemistry. We start with a little sketch of the big issue how humans influence global and regional geochemical cycles by releasing compounds such as CO<sub>2</sub> and NH<sub>4</sub>+ into the environment. Then we discuss the challenge to assess the environmental impacts of synthetic chemicals. When considering that globally, over 30000000 t of synthetic chemicals are produced each year and that more than 100000 different compounds are in daily use, it should come to no surprise that this topic plays a prominent role in the chemical research conducted at the Swiss Federal Institute for Environmental Science and Technology (EAWAG). We will argue that, in order to tackle all these problems, it is an important job of environmental chemists to build bridges between the molecular approaches of laboratory experiments and the systems approach of multidisciplinary field studies. This job description has influenced significantly the teaching of environmental chemistry at the university level. Environmental chemists at EAWAG are actively involved in teaching their young science to students from different fields, in particular, to students of environmental sciences at the Swiss Federal Institute of Technology in Zürich (ETHZ). We hope that in the future this new generation of scientists will help to strengthen the dialog between chemical companies and the chemistry of the environment.

In the other articles of this special issue of CHIMIA, the researchers of EAWAG present an overview of their own chemical research representing some typical 'bands' in the spectrum of contemporary environmental chemistry. In our following discussion, we will refer to these articles hoping to provide a somewhat larger context for the various topics.

# Geochemical Cycles – a Little Sketch of Big Issues

Let us first have a look at some of the big problems concerning the handling of matter in industrialized societies. In order to analyze material fluxes it is useful to consider different environmental compartments such as the hydrosphere, atmosphere, geosphere, and biosphere. The 'anthroposphere' consists of the human societies and their physical infrastructure. Fig. *I* exemplifies some typical interactions between man and the environmental compartments. Fossil fuel is mobilized from the geosphere,  $CO_2$  accumulates in the atmosphere and is repartitioned between the oceans and the biosphere. Nitrogen fertilizer is produced from N2, after application to soils it is taken up by the biosphere and washed out to the oceans. Metals accumulate mainly in the anthroposphere with minor fractions leaching into the environment. Fig. 2 shows characteristic trends for the global use of resources over the last 50 years [1].

### **Oxidizing Fossil Fuels**

The evaluation of environmental consequences of fossil-fuel combustion ranks high on the political agenda and belongs to the most visible research topics in environmental science. The anthroposphere acts as a 'catalyst' which accelerates the oxidation of the vast reservoirs of gas, oil, and coal stored in geological formations (*Fig. 2, a*). At the present emission rate of

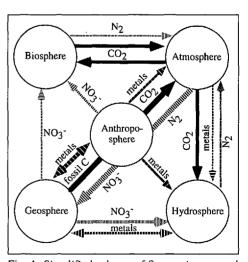


Fig. 1. Simplified scheme of five environmental compartements with major fluxes caused by burning of fossil fuels, production of nitrogen fertilizer, and mining of metals

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1 t of C per capita and year, the known oil and coal reserves would last about 30 and 300 years, respectively. If emissions remain unchanged, the oxidation of these carbon reservoirs could increase the atmospheric CO<sub>2</sub> concentration over the next few centuries by a factor of 3-6 [2].

Through several international research initiatives the scientific community has embarked on the project to closely monitor the outcome of this 'global experiment' which is driven by anthropogenic CO<sub>2</sub> emissions. The reconstruction of atmospheric  $p_{CO_2}$  in the past is crucial to evaluate the anthropogenic changes. Ice cores from Greenland and Antarctica revealed strong correlations in the time series of  $p_{CO_2}$  and reconstructed temperature variations during the past 180000 years [3]. Researchers at EAWAG are involved in the effort to decipher these environmental archives by reconstructing the intensity of solar radiation from the <sup>10</sup>Be record [4]. The ice-core studies have revealed that the atmospheric concentrations of trace gases such as CO<sub>2</sub> and CH<sub>4</sub> have increased by factors of 1.3 and 2.5, respectively, since preindustrial times.

At present, the estimated global  $CO_2$ emission of 7.1 Gt C yr<sup>-1</sup> leads to an observed atmospheric  $CO_2$  increase of 3.2 Gt C yr<sup>-1</sup> and an estimated uptake by the oceans of 2 Gt C yr<sup>-1</sup>. There is an intense search under way for the 'missing' 1.9 Gt. Some of the discrepancy may be accounted for by increased  $CO_2$  uptake of temperate forests due to inadvertent fertilization with nitrogen compounds from  $NO_x$  and NH<sub>3</sub> emissions [5]. On a global scale, the carbon emissions from the deforestation in the tropics seems to be partially compensated by forest regrowth on the northern hemisphere.

#### **Producing Crops**

The Haber-Bosch process has helped to increase agricultural output significantly. World grain yield per hectare increased from 1 t in 1950 to 2.5 t in 1990. Grain consumption is 300 kg per capita and year corresponding to ca. 150 kg carbon [1]. With world population continuing to grow, this average number is declining since 1984. Today, 5% of the terrestrial biosphere is used for grain production. For several reasons such as soil degradation and expansion of urban areas the available grainland area is shrinking. More efficient use of fertilizers and pesticides and innovative agricultural techniques could help to maintain food security.

High productivity in agriculture is often in conflict with the goal to prevent algal blooms in lakes, ponds, and coastal seas. Over the last decades, researchers at EAWAG have analyzed the response of aquatic ecosystems to increasing nutrient loads and developed strategies against fertilization (the so-called eutrophication) of the Swiss lakes [6].

On a global average, a total of 20 kg of fertilizer is consumed per capita and year (see *Fig. 2, c* for the recent trend). In the industrialized world, the excessive use of nitrogen fertilizers together with  $NO_x$ emissions from the combustion of fossil fuel fertilizes terrestrial and aquatic ecosystems leading to soil acidification, loss of plant biodiversity, and intense algal blooms in the coastal seas. On a global scale, anthropogenic nitrogen fixation has reached ca. 145 Mt N yr<sup>-1</sup> and is close to the estimated amount of nitrogen fixed naturally by soil bacteria [5]. It is an open question, whether denitrifying bacteria in anaerobic environments can cope with the anthropogenic nitrate flood. These microorganisms reduce nitrate in soils and sediments to  $N_2$  and trace amounts of  $N_2O[7]$ . Chemists and microbiologists at EAWAG are developing techniques such as microelectrodes and gene probes to analyze the pathways and turnover rates of nitrogen in aquatic systems [8].

Worldwide use of pesticides has increased dramatically since the mid of this century (Fig. 2, d). Initially, adverse effects such as the bioaccumulation of DDT have initialized a hot political debate. Since then progress has been made in the design of less hydrophobic and better degradable pesticides such as atrazine. However, the article of Müller et al. [9] illustrates that chemicals such as atrazine, that have been shown to be degradable in soils, behave conservatively in lakes, *i.e.*, no degradation in the water column can be observed. Recent developments to reduce the pesticide load include the synthesis and use of active chiral compounds instead of racemic mixtures. This approach would minimize the release of ineffective but potentially harmful chemicals into the environment. The article of Kohler et al. [10] reports on efforts at EAWAG to track chiral compounds in the environment and to determine the degradation of enantiomers separately.

#### [Mio. t oil equivalents $yr^{-1}$ ] [Mio. t yr<sup>-1</sup>] 8000 800 Fossil Fuel Steel 6000 600 a) b) total 4000 400 oil 2000 coal 200 gas 0 0 [Mio. t yr<sup>-1</sup>] [Mio. t yr-1] 200 4 c) d) **Total Fertilizer** Formulated Pesticides 3 150 100 2 50 1 0 0 1970 2000 1960 1970 1980 1990 2000 1950 1960 1980 1990 1950

### Fig. 2. Global trends of fossil-fuel consumption and production of steel, total fertilizer and pesticides [1]

#### Mining Metals

Mining of metals provides an example of an anthropogenic process, where the main product (Fe) is stored in the anthroposphere itself. A significant fraction of the 130 kg steel produced per person and year [1] is used to build the infrastructure of industrialized civilizations such as buildings, roads, and vehicles [11]. Fig. 2, b shows the global steel production since 1950. If we integrate the amount of metallic iron produced over the period 1950-95, we obtain 25 Gt, i.e., more than 4 t of iron per person living today. On the other hand, mining of heavy metals such as Zn, Cd, Pb, and Hg has accelerated the natural geochemical cycles by factors close to 3, 7, 25, and 3, respectively [12]. To track the pathways of heavy metals in aquatic systems, information about speciation and partitioning between the aqueous phase, mineral particles, and organic matter is essential. The articles of Müller et al. [9],

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Sigg et al. [13], and Hug et al. [14] illustrate analytical and experimental approaches to identity the pathways of trace metals from the surface waters into the final deposits – the sediments.

#### Improving Resource Efficiency

The trends shown in Fig. 2, a-c illustrate three examples where man is changing the elemental cycles of our planet. However, global emission rates hide dramatic differences between North and South. While carbon emission in 1995 was 5.3 t per capita in the USA, an average person in India had only 0.3 t C at disposition [15]. If we want to reduce the risks associated with imbalanced chemical cvcles, we have, as a first priority, to increase the resource efficiency of the economies in the North. A popular study indicates that an improvement by a factor of four could be achieved in industrialized countries [16]. It is an important challenge for environmental chemistry to support this goal with knowledge and priorities how to restore global and regional chemical cycles.

#### Assessing the Dynamic Behavior of Inorganic and Organic Pollutants in the Environment

When addressing the issue of the contamination of the natural environment by inorganic and organic pollutants, one often tends to (over)emphasize the consequences of spectacular accidents or the problems connected with the remediation of contaminated sites and with hazardous waste management. There is no question that wastewater treatment, waste incineration, landfills, dump sites are important issues. However, of at least equivalent importance is the chronic contamination of the environment due to the daily use of chemicals (e.g., fuel additives, solvents, components of detergents, dyes and varnishes, additives in plastics and textiles, chemicals used for construction, antifouling agents, herbicides, insecticides, fungicides, catalytic converters, battery components, and materials for electronic devices). Many of these chemicals are produced in such large quantities that they may be of concern, even if only a small fraction of the total amount used reaches the environment. A somewhat simplistic but nevertheless quite instructive little calculation shall illustrate this point. In drinking water, in Switzerland, the concentration of a particular chlorinated solvent may not exceed 10  $\mu$ g l<sup>-1</sup>, for total pesticides this limit is  $0.5 \ \mu g \ l^{-1}$ . Hence it

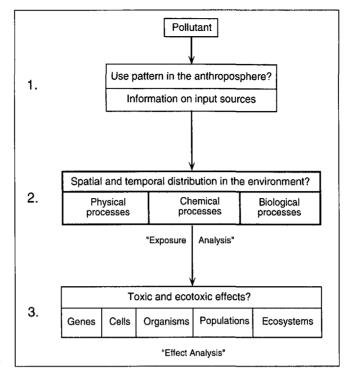


Fig. 3. Three major tasks in the assessment of a chemical pollutant in the environment

would only take 10 t of a chlorinated solvent and 0.5 t of pesticides, respectively, to 'spoil' an annual supply of (drinking) water ( $10^9 \text{ m}^3$ , 80% spring and groundwater, 20% lake water). The annual consumption of chlorinated solvents is, however, several 10000 t, that of pesticides over, 2000 t! It is therefore not surprising that because of the presence of minor pollutants treatment costs for drinking water are increasing.

A major present and future task encompasses identification and possibly replacement of those widely used chemicals that may pose hazards to human health as well as to natural ecosystems. Furthermore, new chemicals must be designed to be 'environmentally compatible'. All of these tasks require knowledge of 1) the use patterns of a given chemical in the anthroposphere, 2) the processes that govern its transport, distribution, and transformations in the environment, and 3) its effects on organisms (including man), communities, and whole ecosystems (Fig. 3). In the following we will focus primarily on the second topic, which represents a central focus of chemical research at EAWAG since the analysis of the fate of a chemical in the environment is a prerequisite for a proper assessment of adverse effects. At present, there are considerable efforts at EAWAG to expand its research to more effect-oriented topics. Major emphasis is placed on the uptake of pollutants by aquatic organisms and on the molecular mechanisms of toxic effects. Some general aspects and specific topics concerning this rather new area of research which requires a close collaboration between chemist,

biologists, and toxicologists are discussed in the article of *Escher et al.* [17].

#### Processes Determining the Distribution and Fate of Pollutants in the Environment

As is illustrated in Fig. 4 for a lake system, a chemical pollutant that is introduced into the environment (e.g., into air, soil, surface water) is subject to various transport, mixing, transfer, and transformation processes. Advective, dispersive, and diffusive transport phenomena distribute a chemical within a given environmental compartment. Transfer processes exchange chemicals between compartments or different phases (e.g., gas exchange across the air-water interface, partitioning between water and solids, bioaccumulation). A variety of homogeneous and heterogeneous chemical, photochemical, and biological reactions may transform chemical compounds. Obviously, each of these processes itself is determined both by the specific properties and reactivities of the chemical as well as by various and varying environmental factors such as pH, temperature, or redox potential. If we consider the tremendous complexity of natural systems, environmental chemists face a tough job to provide any scientifically sound qualitative and quantitative assessment of the environmental dynamics of a given chemical pollutant. They can only succeed if a significant part of their activity is devoted to fundamental studies on chemical processes in natural systems. Buffle et al. [18] have recently discussed this point and emphasized that the scope of environmental chemistry is, of course, not limited to pollutants.

#### Playgrounds and Challenges for Environmental Chemists

In the early days of environmental chemistry -i.e., in the early 70s to mid 80s - the field was dominated by analytical chemists who, due to tremendous development in analytical chemistry at that time, were able to monitor environmental concentrations of a large number of inorganic and, particularly, organic pollutants. Although such monitoring studies were, of course, very important with respect to the documentation of an environmental problem, the vast amount of data collected rarely provided quantitative information on the pertinent processes that determined the environmental behavior of the chemicals considered. This was recognized in the early 80s (see e.g., [19]), and research aimed at the development of general concepts for describing pollutant behavior in the environment has since, also at EAWAG, grown significantly.

#### Molecular Approaches

Fig. 5 depicts in a very general way the 'playgrounds' on which environmental chemists can be found today. As is indicated and already mentioned above, a quantitative assessment of the inputs, the distribution and the fate of a pollutant in the environment, hinges on the ability to quantify all pertinent processes as well as their interplay in a given system. This requires a profound understanding of the molecular interactions that govern a given process. Hence, environmental science raises important questions which can be handled with good basic chemical research [18]. Pragmatic theoretical and experimental approaches and statistical descriptions of chemical interactions are often useful to describe the interactions between natural 'reactants' and anthropogenic compounds. Some illustrative examples of such more basic process-oriented work at EAWAG are discussed in the articles dealing with homogeneous and heterogeneous oxidation [20] and reduction [21] reactions, with the microbial degradation of chiral organic compounds [10], and with the sorption of pollutants to natural surfaces [13]. In this context, the use of spectroscopic techniques was quite successful to characterize solid-liquid interactions on environmentally relevant surfaces [13] [14]. These examples show that environmental chemists have to cope with many different aspects of chemistry, and that cooperation with specialists in the various fields of chemistry is a necessity, a fact that has unfortunately still not yet been fully recognized.

#### **Comprehensive Field Studies**

Understanding molecular interactions represents, however, only one part of the 'playgrounds' of environmental chemistry. The other and even more challenging part is the transfer of the concepts and data derived from theory and laboratory experiments to the macroscopic world. Any quantitative assessment of the dynamic

an be handled sin, a water-treatment plant) requires, on research [18]. the one hand, knowledge from various other disciplines including a.o. environmental physics, environmental microbiology, hydrology, (hydro)geology, or environmental engineering and, on the other hand, it relies on the ability to conduct comprehensive field studies. Obviously, only field studies provide the final clues to how things really are. Only with field studies information on fluxes, *in situ* trans-

be obtained

Physical or chemical tracers are extremely helpful to quantify the actual characteristic transport and mixing processes of an environmental compartment. The article of *Hofer et al.* [22] illustrates some typical tracer techniques used at EAWAG to characterize the hydraulic transport properties of aquifers and landfills or the reactivity of subsurface minerals in redox reactions.

formation rates, and long-term trends can

behavior of chemicals in a natural or tech-

nical system (e.g., a river reach, a lake, an

aquifer, a soil compartment, an ocean ba-

Due to the increasing emissions of some chemicals illustrated in *Fig.* 2 it is often difficult to extrapolate the conditions of an undisturbed natural system. A special type of field studies is, therefore, concerned with the analysis of environmental archives such as ice cores [3][4], tree rings, or laminated lake sediments. This approach allows one to reconstruct the precise dynamics of environmental changes in the past.

#### Analytical Chemistry

Considering the great variety and complexity of questions to be answered in field and laboratory studies, it is obvious that almost all areas of analytical chemistry are challenged. In many cases, established methods have to be further developed in order to meet the requirements for a particular type of investigation. At EAWAG, the scope of 'analytical challenges' encompasses a.o. the continuous monitoring of inorganic species in natural and wastewaters (see Pacini et al. [23]), the application of micro-electrodes for the measurements of concentration gradients at the sediment/water interface and in biofilms [8], the characterization of solids and solid surfaces and their interactions with chemical species using spectroscopic and other methods [13][14], the speciation and quantification of trace metals [9], and the identification and quantification of organic micropollutants (see Suter et al. [24]) in environmental samples. It is a major task to develop very accurate and precise methods that allow to quantify a particular

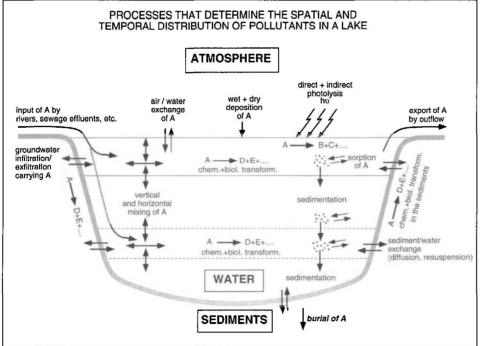


Fig 4. Transport and transformation processes of a pollutant A in a lake

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chemical routinely at the ng l<sup>-1</sup>-level in various different matrices (e.g., natural water, drinking water, wastewater, sediments, soils, sewage sludge, biota). Furthermore, particularly in field studies, the sampling strategy and the sample treatment form an important part of the analytical procedure [23] and require a profound knowledge of the pertinent processes in a given system.

#### Mathematical Models

In general, a proper assessment of the dynamic behavior of a pollutant in a given natural or technical system is possible only by a combination of laboratory experiments, field measurements, and model simulations. Thereby, modeling is used for various purposes like planning of laboratory and field experiments, establishment of mass balances, identification of process, and making predictions. The art of modeling lies in the choice of the 'right' model for a given question. A good modeling strategy is often the result of a close collaboration between environmental chemists and mathematical modelers. Some illustrative examples of this interplay between field measurements and model calculations in natural and technical systems are given in the articles of Müller et al. [9] for lakes and of Alder et al. [25] for sewage treatment plants.

#### **Education in Environmental** Chemistry

As has hopefully become evident from the above discussion, any task involving the assessment of chemicals in the environment requires 1) a broad knowledge of basic chemistry, 2) a profound understanding of the chemical processes and of the factors that govern these processes in the environment, 3) a deep insight into the 'functioning' of a given natural or technical system, and 4) the ability to model the pertinent processes and their interplay in the system considered. Thus, professional education in environmental chemistry has to encompass discipline-oriented as well as system-oriented aspects with a strong emphasis on chemistry (Fig. 6).

Fifteen years ago in Switzerland, most scientists that have entered the field of environmental chemistry came from a classical chemistry background, although environmental chemistry was not and, unfortunately, still is not a major topic in the education of chemists at the university level. Interestingly, at the same time in the US, very few 'pure' chemists became interested in environmental topics and, even

(Mathematical) Analytical Chemistry Mixing and transport Models Laboratory studies Molecular interactions "mechanisms' (compound specific operties and reactivities Individual processes in a given natural system (phase transfer ansformation

Fig. 5. The playground of environmental chemistry. The main goals can be reached by using different tools (left side) and sound scientific knowledge (right side).

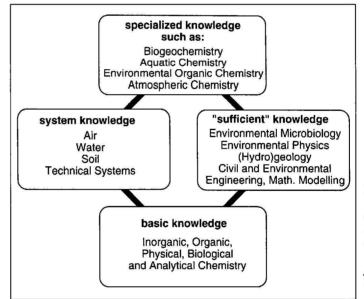
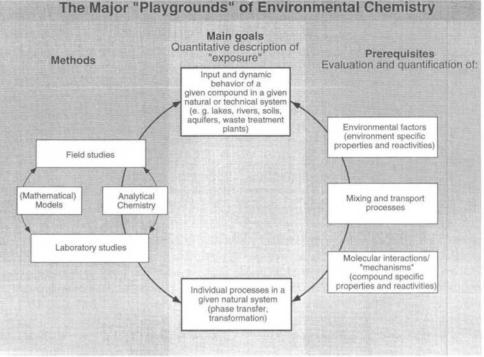


Fig 6. Concept for the education of environmental chemists at ETHZ with the discipline-oriented education in chemistry on the vertical and the broader field of multidisciplinary system studies on the horizontal

today, most of the research and education in environmental chemistry at the top universities take place in geoscience or in environmental science and engineering programs. This clearly indicates that it is possible to enter this field, either from a molecular side or with a more multidisciplinary system-oriented background. With the introduction of the diploma curriculum in environmental natural sciences in 1987 at ETHZ, this multidisciplinary door to environmental chemistry has also been opened in Switzerland. In this curriculum, the first two years consist primarily of a basic training in natural sciences and in mathematics. Afterwards, the students

choose a discipline (e.g., chemistry) and a system (e.g., aquatic systems) in which they specialize and also conduct their practical diploma work. In this part of the curriculum, several chemists located at EAWAG are heavily involved in the teaching, and some textbooks that are widely used in the field of environmental chemistry have been written by some of these people [26]. Fig. 6 shows the topics that students specializing in chemistry are exposed to during their studies. In addition to the natural science education, the 5-year curriculum in environmental natural sciences also includes one semester in practice (e.g., in industry, consulting firms,

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government agencies, *etc.*) as well as a significant exposure to engineering and social sciences. The internet homepage of the department provides detailed information [27].

Today, ten years after the introduction of the curriculum in environmental natural sciences at ETHZ, it can be stated that this initially quite controversial 'experiment' has been very successful. Environmental sciences students specializing in chemistry have completed Ph.D. projects using state-of-the-art molecular approaches. Former diploma and Ph.D. students have demonstrated that they are capable to handle complex chemical systems or to successfully apply their knowledge to practical problems (e.g., in engineering and consulting firms as well as in banks and in insurance companies). Only the chemical industry in Switzerland, in contrast to other chemical companies in Europe, is still reluctant to hire these scientists. We are convinced that the challenge to build a more sustainable chemical industry can only be met with a redesign of many chemical products and processes [28]. 'Responsible care' and 'green chemistry', the worldwide initiatives of the chemical industry, would gain credibility if new actions were based on a collaboration between industrial and environmental chemists. Thus, the highly motivated young people who have decided to get a multidisciplinary education in natural sciences could play a creative role in the chemical industry.

#### **Concluding Remarks**

The question where the 'home base' of environmental chemistry should ideally be located is often raised in science policy. Considering that environmental chemists are torn between molecular interactions and ecosystem dynamics, and that they rely both on an intensive contact with basic chemistry ('to keep the chemistry honest!') as well as on a close collaboration with scientists from other disciplines, it is not obvious whether chemistry departments, environmental science departments, or research institutions provide a more stimulating environment. In Switzerland, all three scenarios exist.

At the universities, environmental chemistry groups are commonly parts of chemistry departments, where they play an important role in developing the more fundamental aspects of environmental chemistry [18]. In the two ETHs, such groups belong primarily to environmental science, geoscience, and engineering departments. The largest group of environmental chemists in Switzerland is located at EAWAG. Here, groups supported by EAWAG and ETH work closely together using the same laboratory and field infrastructure. This situation bears several advantages. First, through the close collaboration of the two institutions, a critical number of environmental chemists from various different chemistry backgrounds work under a common roof. This creates opportunities for larger research projects, particularly those requiring field studies, that could not be carried out by single, isolated groups. Furthermore, the mutual everyday exposure of scientists from various disciplines including natural, engineering, and social sciences makes it possible to tackle environmental problems in a multidisciplinary and thus much more holistic way. Finally, the consulting activities of EAWAG facilitate the transfer of knowledge and ideas between science and the 'real world'.

One of the potential dangers of an interdisciplinary research institution such as EAWAG is the possibility that environmental chemists loose contact to their colleagues in basic chemistry (and vice versa). Considering that environmental chemists depend strongly on the new developments in basic chemistry and that, on the other hand, environmental aspects should become considerably more important in the education of chemists, ways of strengthening these contacts have to be found. It is hoped that this special issue of CHIMIA helps to identify future common interests, and thus to stimulate future collaboration.

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