Chimia 51 (1997) 935–940
© Neue Schweizerische Chemische Gesellschaft
ISSN 0009–4293

The Fate of Trace Pollutants in Natural Waters – Lakes as 'Real-World Test Tubes'

Stephan R. Müller[a])*, **Bernhard Wehrli**[b]), **Alfred Wüest**[c]), **Hanbin Xue**[b]), and **Laura Sigg**[b])

Abstract. Lakes play an important role as ecosystems and drinking-water supplies, but they are also ideal 'real-world test tubes' for studying the fate and behavior of trace pollutants in natural waters. The trace metals Cu, Zn, and Cd and the organic herbicide atrazine are used to illustrate the combined approach of field measurements and mathematical modeling to assess the behavior of pollutants in natural waters. In contrast to fast flowing waters (*i.e.*, rivers), lakes act as integrators of pollutant inputs from surface waters of the respective catchment area, thus being regional indicators of human activities.

Introduction

Protection of lakes ranks high among the political priorities in Switzerland. Beside their value as aquatic ecosystems, lakes play an important role for recreation and tourism, as drinking-water reservoirs, for fisheries, and, last but not least, they are aesthetic elements of our landscape. For environmental scientists, lakes are also very appealing for studying the biogeochemistry of natural and man-made chemicals under natural conditions. Furthermore, since lakes have clear boundaries and, in contrast to rivers, they act as integrators of contaminant inputs, they are also very well-suited for assessing human activities in the catchment area. Whereas in the past the excessive nutrient input – leading to eutrophication and subsequent degradation of the water quality – was of major concern [1][2], today the continuous input of inorganic and organic trace pollutants into surface waters has become of increasing importance.

In this article, the approaches taken at EAWAG to evaluate the input and dynamic behavior of trace pollutants in lakes are addressed. First, the different processes acting on pollutants in lakes (*Fig. 1*) are reviewed and a brief overview of the (mathematical) models developed for describing quantitatively the combined effect of the various transport and transformation processes on the distribution and residence time of a given chemical is given. This general approach is then illustrated by two examples. The first example demonstrates how biological processes influence the speciation and thus the bioavailability as well as the residence time of the trace metals Cu, Zn, and Cd in the water column. In the second example, a study focusing on the evaluation of the inputs and persistence of one of the most widely used herbicides in agriculture, *i.e.*, atrazine, in different lakes is presented.

Transport and Transformation of Pollutants: From Processes to Models

Physical Processes. The most simple model balancing the mass of a pollutant in a lake is the continuously stirred tank reactor. The input-output analysis of a mixed reactor model (including river input, rain fall, gas exchange, outflow and sedimentation) can already yield considerable insight into the behavior of a given pollutant [3]. The rate of elimination by flushing is given by $k_w = Q/V$ [a^{-1}], where Q is the average outflow and V is the lake volume. Typical flushing rates of Swiss lakes range from 7 a^{-1} and 0.07 a^{-1} (corresponding to hydraulic residence time of the water of 0.15 to 15 years, respectively). Since elimination by flushing is im-

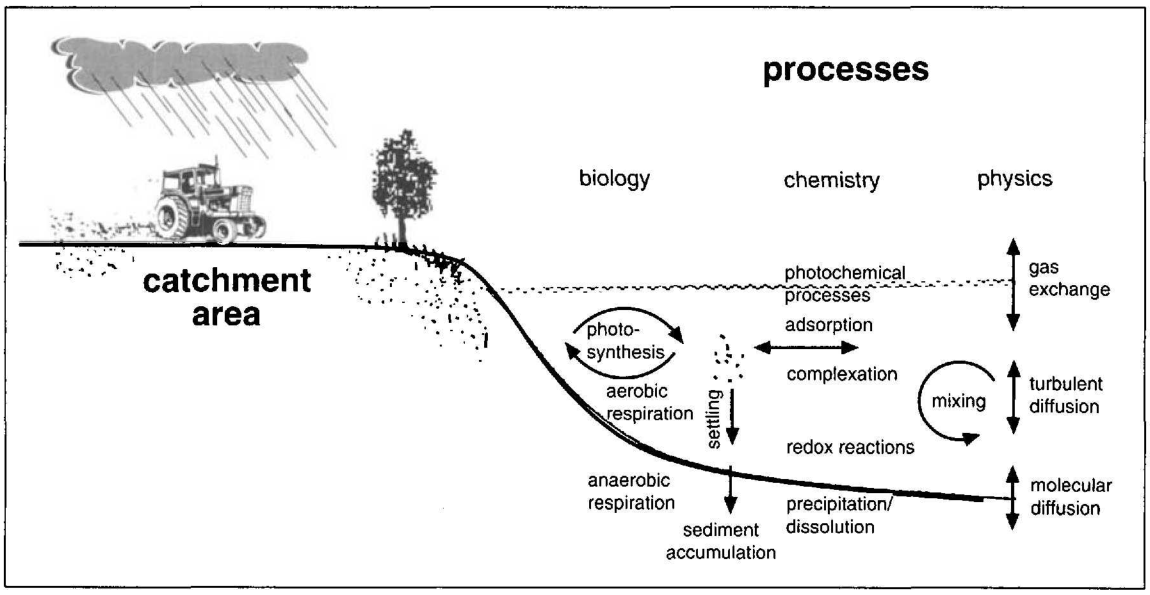

Fig. 1. *Schematic illustration of the different processes in lakes*

Correspondence: Dr. S.R. Müller
[a]) Chemistry Department
[b]) Biogeochemistry Department
[c]) Environmental Physics Department
Swiss Federal Institute for Environmental Science and Technology (EAWAG)
Überlandstrasse 133
CH-8600 Dübendorf
Tel.: +41 1 823 54 60, Fax: +41 1 823 54 71
E-Mail: stephan.mueller@eawag.ch

portant for all compounds (dissolved and particulate species), this rate constant defines the intrinsic timescale of the system.

For volatile compounds (such as volatile organic pollutants and trace elements forming volatile species, *e.g.*, As or Hg), gas exchange has to be included. The rate constant for this process is given by $k_g = \beta/h$ [d^{-1}], where β is the piston velocity of the exchange and h is the depth of the surface water volume, which stays in contact with the atmosphere. For a typical value of $\beta \approx$ 0.5 m d^{-1} and a 5-m thick surface layer, the residence time of such a species would be *ca.* 10d (k_g = 0.1 d^{-1}). The modeling of volatile organic compounds and gases which are part of the biological cycles (such as O_2 and CO_2) requires also a careful parameter estimation for gas exchange. Furthermore, for less volatile species, more sophisticated models have to be applied.

Most time of the year, lakes are vertically stratified: The surface acts as a heat collector for solar radiation and as a consequence, during summer, the surface layer reaches temperatures of more than 20°, whereas the deep layers stay cool at typically 4–5°. This leads to strong density stratification and decoupling of the surface water (epilimnion) from the deep water (hypolimnion). Consequently, vertical mixing is weak during summer, and the surface and deep water masses can be regarded as separated layers (boxes). In winter, the combined action of surface cooling and wind leads to basin-scale vertical water exchange. In contrast to the vertical stratification, lakes are usually well-mixed horizontally. Describing the lake by using a mixed reactor in winter and two mixed, but separated, reactors in summer offers the most simple of the vertically structured models. For detailed studies, affecting the fate of a pollutant within the vertical structure of the water column, the more appropriate one-dimensional (1-D) vertical model should be applied. This includes the vertical rates of exchange within the water column – usually quantified by diffusivity – which can be derived from vertical profiles of tracers such as temperature [4].

The lake internal, ***biological processes*** such as photosynthesis and respiration strongly influence the chemical conditions such as pH and redox potential as well as the particle type and concentration in lake water. Large O_2 oversaturation can occur in the surface layer. However, typically 10–30% of the biological production settle in the form of particles to the lake bottom where a large fraction of this organic material is mineralized by microorganisms. Oxic respiration depletes dissolved oxygen, and reductive conditions are commonly encountered in the hypolimnion of stratified lakes. Reductive transformations of pollutants may occur under these conditions [5]. However, during the intense mixing of the water column in winter, oxygen-depleted water is brought in contact with the atmosphere and gas exchange reloads the oxygen reservoir of the lake.

Particles from the epilimnion can act as a 'conveyor belt' and transport associated pollutants into the hypolimnion. Various sorption processes play a role for the binding of metals and of organic pollutants to particles [6]. Gravity drives the sedimentation of particles from river input, photosynthetically produced biomass (algae, plankton), and calcite crystals. During this process, reductive dissolution of iron and manganese oxides and the reoxidation of Fe^{2+} and Mn^{2+} in the water column may produce an additional source of particles in the deep water [7]. The sedimentation of a pollutant out of a well-mixed box can be described by the characteristic rate constant, k_s, which is defined as $k_s = v_s * (1 – f_l)/h$ where v_s is the average particle settling velocity, $(1 – f_l)$ is the fraction of the compound in particulate form, and h is the depth of the box. Pollutants, however, may be released at the sediment surface or they may accumulate in the final storage – the lake sediments. Therefore, the processes at the sediment-water interface play a key role in the modeling of pollutants such as heavy metals which strongly adsorb to particles [8].

We can now combine the lakes physical and biological processes with the ***pollutant-specific processes***. Beside flushing, gas exchange, and sedimentation, pollutants in the water column of lakes can be eliminated by chemical transformations (*e.g.*, hydrolysis, direct and indirect photolysis) or by microbial transformations. For low pollutant concentrations typically encountered in lake waters, all processes can be expressed as first-order or pseudo-first-order reactions which can directly be compared to k_w, k_g, and k_s. Such rates can often be estimated by simple 'back-of-the-envelope' calculations based on literature data and on theoretical considerations (for details see [9][10]).

To describe quantitatively and dynamically the physical, biological, and compound-specific processes, different tools for the numerical modeling have been developed at EAWAG. CHEMSEE is a versatile program for the general modeling of concentration profiles based on a discrete 1-D transport-reaction model [11]. MASAS has been optimized to predict the fate of organic pollutants in different lake systems [12]. It contains a database of lake parameters and compound-specific information. AQUASIM [13][14], on the other hand, is a modular simulation package allowing different aquatic systems to be combined and coupled. It includes modules for batch reactors, river sections, or a water column of a lake [15].

The assessment of the fate and behavior of pollutants in lakes will be illustrated in the following by two case studies on the *sedimentation and bioavailability of trace metals* and the *quantification of the input and dynamic behavior of atrazine.*

Sedimentation and Bioavailability of the Trace Metals Cu, Zn, and Cd in Lakes

The most important elimination processes of Cu, Zn, and Cd from the lake water column are sedimentation and flushing. To predict concentrations of metals it is therefore important to analyze the relative rates of sedimentation and of flushing. As a prerequisite of sedimentation, the trace metals have to be bound to the settling particles. The extent of binding to particles depends on chemical factors such as the affinity of metals for the surfaces of the particles, the speciation of metals in solution, and the pH. The following investigation was focused on the quantitative description of the sorption/sedimentation process, the evaluation of the bioavailability, and the establishment of a mass balance for these trace metals in different lakes.

The settling particles in an eutrophic lake such as Greifensee consist, as mentioned above, to a large extend of autochtonous material with large fractions of organic matter (settling plankton biomass), calcium carbonate as well as manganese and iron oxides [16]. Manganese and iron oxides precipitate in the lake when anoxic water containing dissolved Mn^{2+} and Fe^{2+} comes into contact with oxygenated water [16]. These freshly precipitated Mn and Fe oxides typically exhibit large surfaces with numerous surface sites, to which trace metals may be bound.

Binding of metals to plankton comprises uptake into the cells, as well as binding to surfaces. Essential elements are taken up in typical concentrations, according to the necessary amounts for the cells and to their availability in lake water, which is linked to the speciation. The correlations between the content of various elements in the settling particles in Greifensee as well as between their sedimentation rates, indicate that organic matter, on one hand, and manganese oxide, on the other hand, are of particular importance for the sedimentation of the trace metals copper and zinc [16][17]. Large variations of the sedimentation rate are observed over the year for Zn, with a maximum during summer. The maximum sedimentation of Zn in summer coincides with the maximum sedimentation rate of organic C and P, whereas during lake overturn, high Zn sedimentation rates occur together with the sedimentation of manganese oxides.

A mass balance using field measurements for Zn in Greifensee based on measurements in the settling particles and in the water column, revealed that *ca.* 87% of the Zn inputs were retained in the sediments (*Fig. 2*). The riverine input shown in *Fig. 2* was estimated from the mass-balance calculation and was found to be in a similar range as Zn concentrations in comparable rivers. Preliminary model calculations to simulate the temporal and spatial variations of Zn in the water column, performed with CHEMSEE [11], indicated that the available data were insufficient to validate such a model. A better identification of the particles to which Zn is bound (biological particles, $CaCO_3$, aluminum silicates from soils, Fe and Mn oxides, *etc.*) and a quantification of the sedimentation fluxes of these particles would be needed to simulate the Zn sedimentation.

Depending on the sedimentation rate and on the extent of binding of metals to the settling particles, the metal concentrations in the water column of lakes are kept at low levels in spite of significant inputs. The metals accumulate almost quantitatively in the sediments.

With regard to the bioavailability and the toxic effects of trace metals, the key parameters are, however, not their total concentrations, but their chemical speciation and especially the concentration of free aqua ions. The essential elements Cu and Zn are toxic only at elevated concentrations, whereas the nonessential element Cd has mostly toxic effects. The free ion concentrations of Cu, Zn, and Cd are generally regulated by organic complexes in lakes. Therefore, phytoplankton may exert a feedback control on metal speciation in solution by releasing organic ligands. We studied the speciation of Cu, Zn, and Cd in various lakes to examine these interactions.

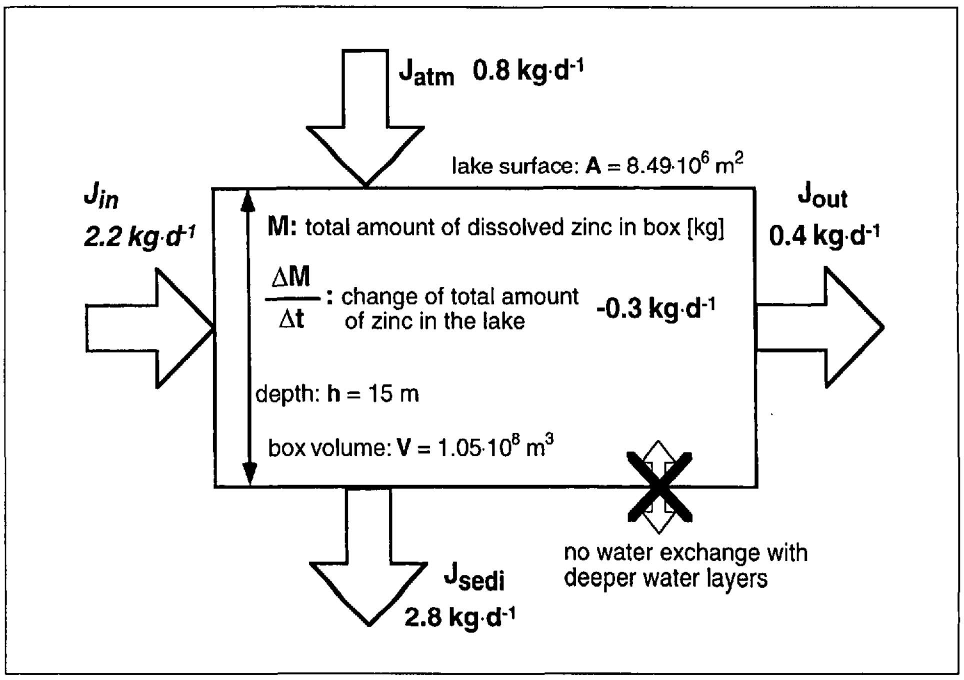

Fig. 2. *Mass balance of Zn in the epilimnion of Greifensee.* The fluxes to the sediments, in the effluent, and from the atmosphere are calculated from measured data; the flux into the lake is evaluated from the mass balance. *Ca.* 87 % of Zn is retained in the sediments (adapted from [17]).

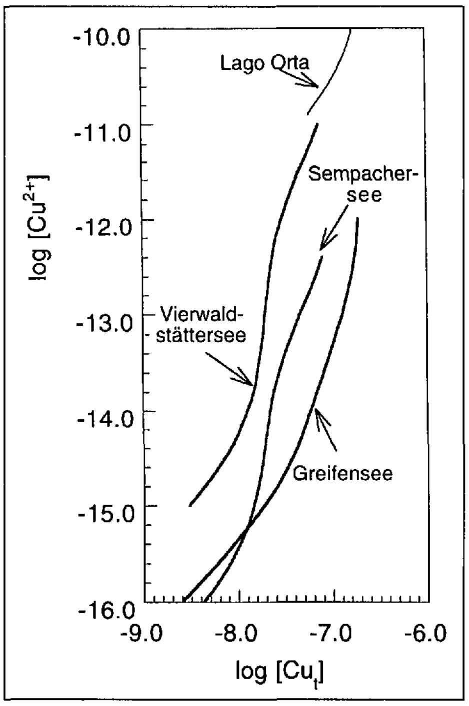

Fig. 3. *Titration of lake-water samples with Cu: Concentration of free aqua Cu^{2+} ions* vs. *total Cu.* The extent of complexation of Cu is larger in eutrophic lakes (Greifensee, Sempachersee) than in the oligotrophic Vierwaldstättersee and in Lake Orta with metal pollution and lower pH.

Sensitive techniques of ligand exchange and voltammetry have been developed to determine the free ion concentrations and the organic complexation of Cu, Zn, and Cd in lake waters. These techniques are based on ligand-exchange equilibria between an added well-characterized ligand and the natural ligands in a water sample. Following sample equilibration, the metal complexes formed with the added ligand are measured by voltammetry. The free metal ionic concentrations and complexation parameters are determined from equilibrium calculations [18–20].

In the eutrophic Greifensee, more than 99% of dissolved Cu ($[Cu_{total}]/[Cu^{2+}] = 10^6–10^7$), 98% of dissolved Cd, and *ca.* 50% of dissolved Zn exist in strong organic complexed form in the epilimnion; the free metal concentrations are very low with pCu (–log $[Cu^{2+}]$) = 14–16, pZn = 8.6–9.5, and pCd = 12. On the average, the conditional stability constants of the strong organic ligands were in the range of log K = 14.6 for Cu, 9.0 for Zn, and 10.2 for Cd (pH *ca.* 8), with available ligand concentrations of 54 nM for Cu and Zn, 6 nM for Cd in the euphotic zone of Greifensee.

The links between the complexation of the trace metals and the biological processes, mostly the growth of phytoplankton, are indicated by several observations.

Table. *Characteristic First-Order Rate Constants for the Elimination of Atrazine from the Epilimnion of Greifensee from Literature Data and Simple Calculations* (see Text and [9])

Elimination by	$[d^{-1}]$
Flushing (k_w)	0.009
Sedimentation (k_s)	<0.001
Gas exchange (k_g)	<<0.001
Chemical transformation	~0.001
Photochemical transformation	
direct photolysis	<0.001
indirect photolysis	<0.002
Biological transformation	?

The comparison between various lakes shows stronger complexation of Cu in the more eutrophic lakes (*Fig. 3*). In the eutrophic Greifensee, the complexation of Cu by strong organic ligands exhibits seasonal variations, which are parallel to the biological productivity [18]. Cd complexation in the eutrophic lake is also stronger than in the oligotrophic lake. Therefore, the strong natural ligands, presumably of recent biological origin, play an important role in controlling the metal speciation.

Phytoplankton influences thus the cycles of trace elements in various manners. The presence of strong ligands binding Cu, Zn, and Cd appears to be linked with the phytoplankton productivity. The sedimentation of organic matter contributes to the transport of trace metals to the sediments. The primary productivity and the subsequent decomposition processes of organic matter affect the redox conditions, and thus the cycling of the redox sensitive elements iron and manganese, which in turn influence the sedimentation of other trace metals [16][17][21]. However, to be able to model quantitatively the behavior of trace metals in lakes, the role of the strong organic ligands with regard to the uptake and adsorption of metals needs to be better understood.

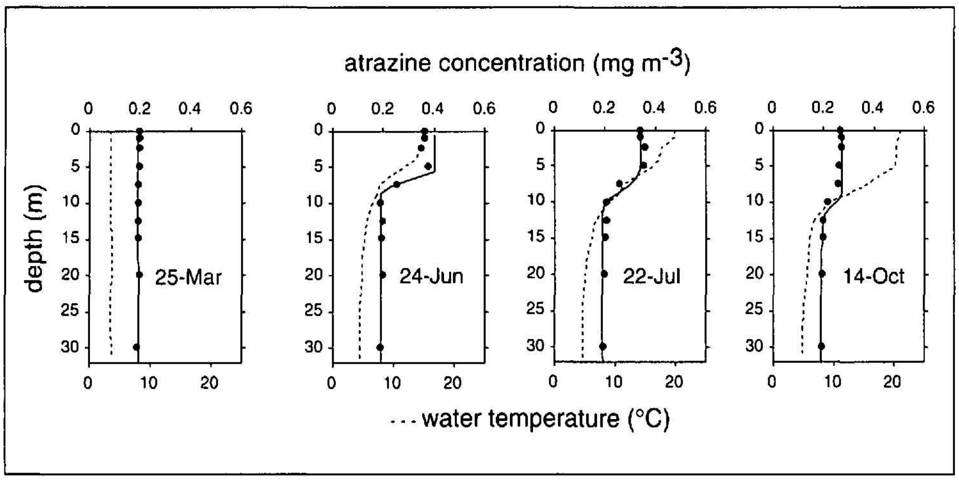

Fig. 4. *Selected vertical atrazine concentration profiles* (dots) *and water temperature* (dotted lines) *measured above the deepest point in Greifensee in 1991.* Solid lines: Computer simulation (for details see text and [9]).

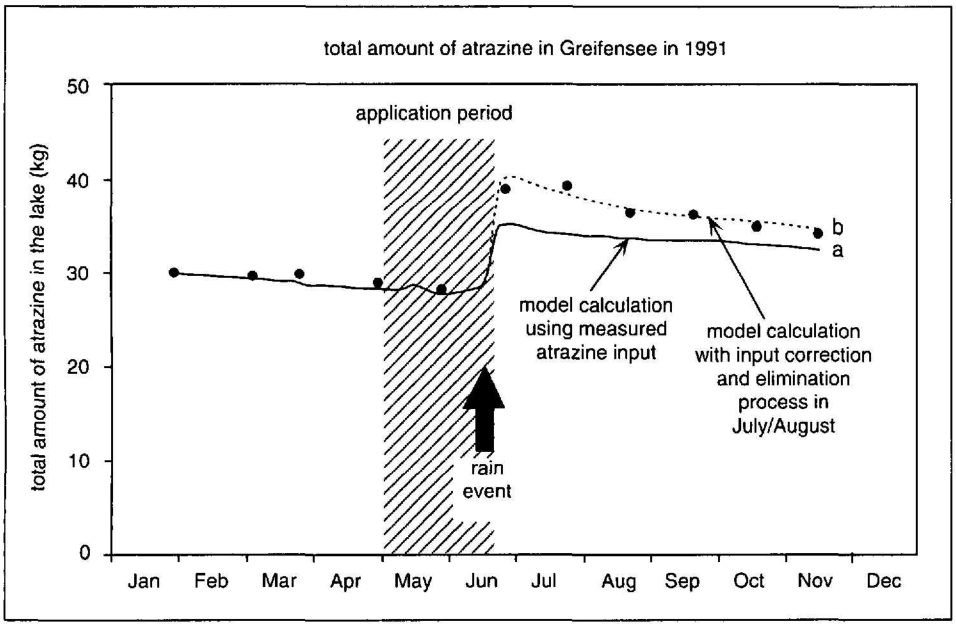

Fig. 5. *Time course of the experimental and modeled total amount of atrazine in Greifensee over the study period (1991).* The dots indicate the experimental values calculated from the measured profiles. *Line a* represents the model calculation using the experimental input function and assuming conservative behavior of atrazine in the lake; *line b* represents the model calculation with input correction and *in situ* elimination during the months of July and August. The atrazine-application period is marked with the shadowed bar.

Input and Dynamic Behavior of Atrazine in Lakes

The widespread use of pesticides, in particular of herbicides, in agriculture requires an evaluation of the impact of such biologically active compounds on surface water quality. In 1959, *Ciba* has marketed the herbicide atrazine which is still one of the most widely used herbicides worldwide. The mobility of atrazine, its persistence, and the large amounts applied, *e.g.*, on corn fields and along railroads, lead to considerable concern about contamination of drinking and surface water in the late 70s. Atrazine concentrations above the drinking-water limit of 0.1 µg/l were the reason for restricting (Switzerland) or even banning (Germany) its application in the late 80s early 90s in several countries. In the following example, atrazine is used as a model compound to assess the input and behavior of a contaminant in lakes. It further represents an excellent case for evaluating the effects of herbicide-application restrictions on surface water quality.

In contrast to fast flowing rivers, lakes are integrators of pollutant inputs to surface waters from soil runoff in the respective catchment area. Therefore, lakes can be used to quantify the input of atrazine to surface waters. However, as discussed earlier, the processes affecting its fate in a lake (transport and transformation processes) must be known or experimentally determined.

In order to get an idea of the relative importance of the various processes affecting atrazine in the water column of Greifensee (*i.e.*, elimination by flushing, gas exchange, sorption and sedimentation/resuspension, chemical, photochemical, and biological transformation), it is helpful to perform some simple calculations to estimate the various elimination rates as introduced in the first section of this article. Because in lakes, some of the

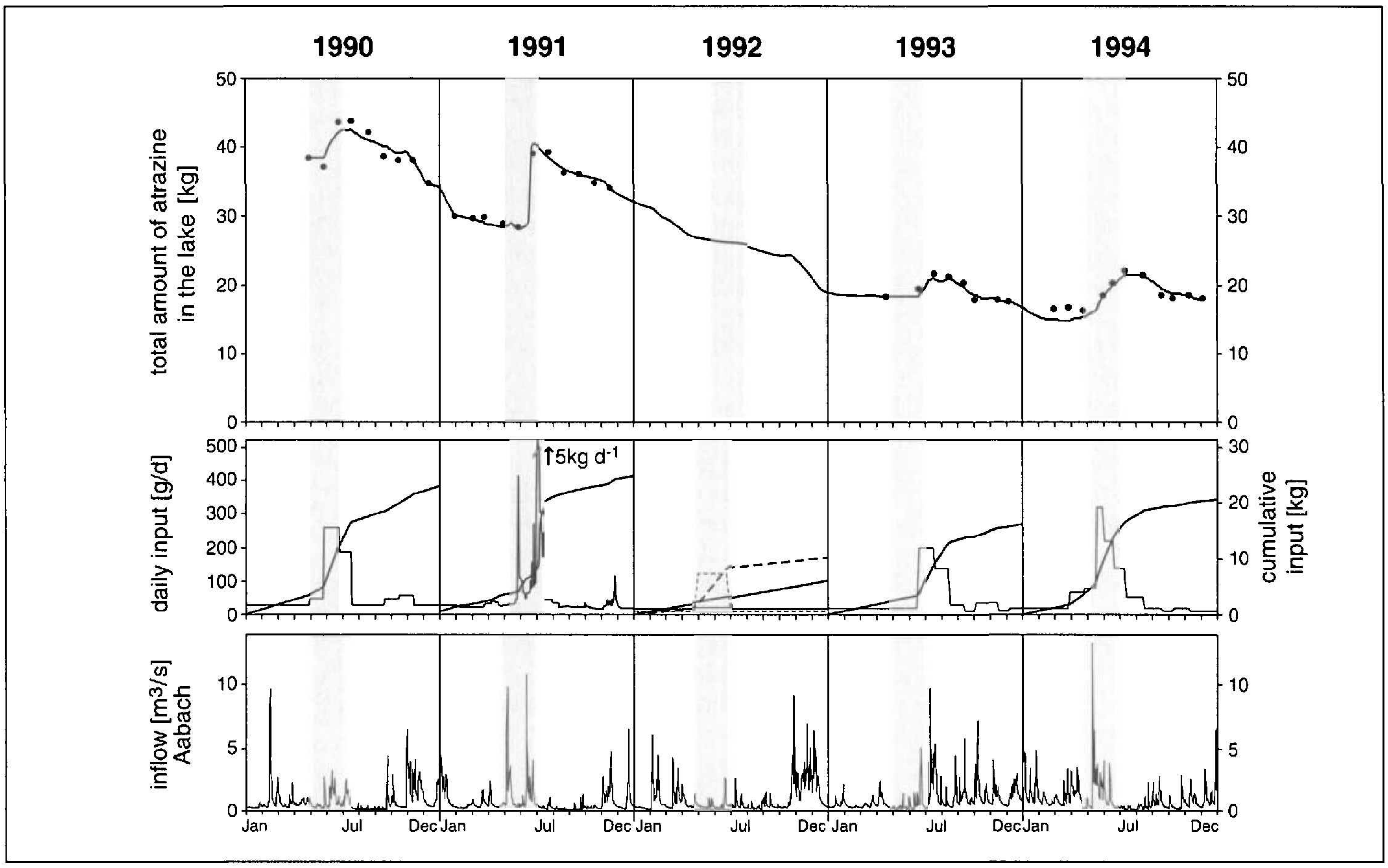

Fig. 6. Top: *Time course of the total atrazine amount in Greifensee for the period 1990–1994.* Dots: Measured values (calculated from the concentration profiles and the corresponding water volumes). The solid line represents the results of the computer simulation (for details see text and [22]). Middle: *1990, 1993, and 1994: Calculated daily input* (thin solid line), *calculated cumulative input* (thick solid line); *1991: measured input, see* [9]; *1992: no measurements, only simulation scenario.* Bottom: *Waterflow in the main tributary Aabach.* The atrazine-application period is marked with the shadowed bar.

most important processes occur at or near the surface (*e.g.*, gas exchange, direct and indirect photolysis), the epilimnion is the most obvious compartment to be used for preliminary calculations. The pseudo-first-order rate constants compiled for atrazine in the epilimnion of Greifensee (see *Table*) show that flushing is, besides possible biodegradation, the by far most important elimination process (for details see [9]). *In situ* rates for microbial transformation in the water column of lakes are not available for atrazine, and the extrapolation of biotransformation rates determined in laboratory systems to the conditions prevailing in the field is extremely difficult. Nonetheless, results of laboratory degradation studies using natural waters imply that atrazine would be transformed rather slowly. In summary, atrazine can be expected to be quite persistent in the water column of the lake, however, its seasonal input variation and its *in situ* fate in the 'test tube' lake have to be assessed using field measurements and mathematical modeling.

To evaluate and quantify the various processes, it is crucial to establish a mass balance. To this end, the atrazine input (data not shown) and the atrazine concentrations at various depths in the lake have been measured (see *Fig. 4*), taking the vertical stratification into account. The total atrazine amount in the lake was calculated from the concentration profiles and the corresponding water volumes (see dots in *Fig. 5*). As is evident, a significant input of atrazine occurred after the atrazine-application period in April/May (see *Figs. 4* and *5*), which was caused by several rain events (surface runoff and/or drainage channels).

Quantitatively, the fate of atrazine has been assessed by combining the measured atrazine input with a 1-D vertical transport model using the simulation tool MASAS [9][12] (see first section of this article), and assuming a conservative behavior of atrazine in the water column, *i.e.*, no elimination other than flushing. The solid line in *Fig. 5* represents the simulation result: As can be seen, the total amount of atrazine measured in the lake before the application/rain event is well represented by this (conservative) model (January to May). To match the experimentally determined total atrazine amount in the lake in July and August, however, an additional input during the rain event (which was clearly underestimated) and an additional elimination process with a rate constant of *ca.* 0.003 d^{-1} (one third of k_w) in the epilimnion in July/August had to be introduced (see solid line in *Fig. 4* and dotted line in *Fig. 5*, model b). Obviously, it is very difficult to determine *experimentally* the input of a compound that is primarily introduced into a lake by runoff during rain events, even with an extensive sampling effort. On the other hand, the combination of measurements in the lake with modeling yields very accurate source/input functions. This study clearly shows that atrazine was quite persistent in the water column of Greifensee. Further, the fact that atrazine has only been applied to corn fields since 1989 allowed close estimates of the total amounts used in the catchment area (1590 kg) and showed that *ca.* 1.8% of the atrazine applied in 1991 has been transported into the lake.

In 1994, Murtensee and Sempachersee were included in the investigations to evaluate to what extent the results obtained for atrazine in Greifensee in 1991 (persistence and input fraction) could be extended to other lakes and/or to other years. In addition, a long-term study in Greifensee (1990 to 1994) was conducted in order to evaluate the effects of weather conditions (particularly rainfall) and application restrictions on the total atrazine input into the lake. These studies are discussed in detail in [22]. In the following, a few important results are summarized.

First, the 'fate and behavior model of atrazine in Greifensee' assuming only elimination by flushing and some additional elimination in July/August in the epilimnion could be applied successfully to the vertical concentration-profile measurements taken in Murtensee and Sempachersee, allowing the atrazine input to be quantified: Despite the quite different catchment areas and hydraulic properties of the three lakes, the atrazine input fractions were very similar in the same year (2% ± 0.1%). The long-term study in Greifensee using the same input-quantification approach (see *Fig. 6*), however, revealed that, over several years, the annual input varied between 0.5% (very dry weather) and 2% (very wet weather) of the total amount applied. A good correlation was found between the input (expressed as percentage of the total atrazine applied, which includes, *e.g.*, the reduced application rate in 1994) and the amount of precipitation during and right after the application period (expressed as percentage of the average water flow in the main tributary).

Furthermore, the input of the primary atrazine metabolites, desethylatrazine, deisopropylatrazine, and hydroxyatrazine, as well as other triazine herbicides could be quantified in the three lakes using the same model. However, for this study a new, sensitive and precise analytical method had to be developed [23]. Note, that the precision and accuracy of the analytical method is decisive for the quantification of the compound behavior [24].

Presently, the approach developed for evaluating the input and behavior of atrazine and various other pesticides is used to investigate the effects of the Swiss agricultural policy measures (*e.g.*, direct payments to the farmers) on the input of pesticides into surface waters.

Conclusions

The examples presented here illustrate how field measurements in lakes, laboratory studies, and mathematical modeling can be combined to understand and predict the behavior of pollutants in lakes as well as their interactions with the biogeochemical cycles. The same concepts have already been applied to other pollutants, such as tetrachloroethene (PER), nitrilotriacetate (NTA), and fluorescent whitening agents [9][25][26], for which different elimination processes are important. Gas exchange is most significant for PER, a volatile compound, whereas NTA is mostly biodegraded in the water column. The fluorescent whitening agents are subject to photochemical degradation and sedimentation [25][26]. For each of these pollutants, careful field studies in lakes under well-understood conditions allowed a verification and a quantification of their behavior. The field observations in the lakes, used as 'real-world test tubes', may be compared to predictions based on chemical properties of pollutants and on laboratory studies of the chemical and biological transformations affecting them. From the comparison between predictions and 'real world' observations, gaps in the present knowledge are identified, and predictions about the future fate of pollutants can be revised and refined.

Received: October 16, 1997

---

[1] R. Gächter, D. Imboden, H. Bührer, P. Stadelmann, *Schweiz. Z. Hydrol.* **1983**, *45*, 246.
[2] B. Wehrli, A. Wüest, 'Zehn Jahre Seenbelüftung: Erfahrungen und Optionen', EAWAG Schriftenreihe 9, 1996.
[3] W. Stumm, Ed., 'Chemical Processes in Lakes', Wiley-Interscience, New York, 1985.
[4] D.M. Imboden, A. Wüest, in 'Physics and Chemistry of Lakes', Eds. A. Lerman, D.M. Imboden and J.R. Gat, Springer, New York and Heidelberg, 1995.
[5] R.P. Schwarzenbach, W. Angst, C. Holliger, S.J. Hug, J. Klausen, *Chimia* **1997**, *51*, 908.
[6] L. Sigg, K.-U. Goss, S. Haderlein, H. Harms, S.J. Hug, C. Ludwig, *Chimia* **1997**, *51*, 893.
[7] B. Wehrli, G. Friedl, A. Manceau, in 'Aquatic Chemistry: Interfacial and Interspecies Processes', Eds. C. P. Huang, C. R. O'Melia, and J. J. Morgan, ACS Advances in Chemistry, Ser. 244, Washington, 1995.
[8] G. Furrer, B. Wehrli, *Geochim. Cosmochim. Acta* **1996**, *60*, 2333.
[9] M.M. Ulrich, S.R. Müller, H.P. Singer, D.M. Imboden, R.P. Schwarzenbach, *Environ. Sci. Technol.* **1994**, *28*, 1674.
[10] R.P. Schwarzenbach, D.M. Imboden, P.M. Gschwend, in 'Environmental Organic Chemistry', Wiley, New York, 1993.
[11] M. Ulrich, Dissertation ETH, No. 9632, Zürich, 1991.
[12] M.M. Ulrich, D.M. Imboden, R.P. Schwarzenbach, *Environ. Software* **1995**, *10*, 177.
[13] P. Reichert: *Water Sci. Technol.* **1994**, *30*, 21.
[14] P. Reichert, Concepts underlying a computer program for the identification and simulation of aquatic systems, Version 2, EAWAG, 1996.
[15] G. Goudsmit, P. Reichert, A. Wüest, in 'Hydroinformatics '96', Ed. A. Müller, Balkema, Rotterdam, 1996.
[16] L. Sigg, A. Kuhn, H.-B. Xue, E. Kiefer, D. Kistler, in 'Aquatic Chemistry', Eds. C.R. O'Melia, C.P. Huang, and J.J. Morgan, ACS Advances in Chemistry, Ser. 244, Washington, 1995.
[17] L. Sigg, D. Kistler, M. Ulrich, *Aquatic Geochemistry* **1996**, *1*, 313.
[18] H.-B. Xue, L. Sigg, *Limnol. Oceanogr.* **1993**, *38*, 1200.
[19] H.-B. Xue, L. Sigg, *Anal. Chim. Acta* **1994**, *284*, 505.
[20] H.-B. Xue, D. Kistler, L. Sigg, *Limnol. Oceanogr.* **1995**, *40*, 1142.
[21] H. Xue, R. Gächter, L. Sigg, *Aquatic Sciences* **1997**, *59*, 176.
[22] S.R. Müller, M. Berg, M.M. Ulrich, R.P. Schwarzenbach, *Environ. Sci. Technol.* **1997**, *31*, 2104.
[23] M. Berg, S.R. Müller, R.P. Schwarzenbach, *Anal. Chem.* **1995**, *34*, 1860.
[24] S.R. Müller, *Chimia* **1997**, *51*, 753.
[25] J.M.A. Stoll, M.M. Ulrich, W. Giger, *Environ. Sci. Technol.*, submitted
[26] J.M.A. Stoll, Ph.D. Thesis No. 12355, ETH-Zürich, Switzerland, 1997.