Dynamic Behavior of Fluorescent Whitening Agents in Greifensee: Field Measurements Combined with Mathematical Modeling of Sedimentation and Photolysis

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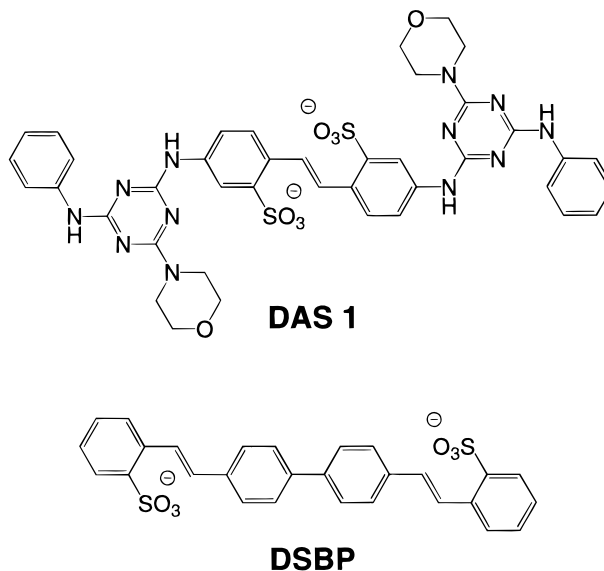
FIGURE 1. Structures of the FWAs included in this study. DAS 1, 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonate; DSBP, 4,4'-bis(2-sulfostyryl)biphenyl.

The dynamic behavior of the two fluorescent whitening agents (FWAs) that are currently used in laundry detergents in Switzerland (DAS 1, a diaminostilbene, and DSBP, a distyrylbiphenyl) has been evaluated quantitatively during 1 year for Greifensee, a small lake in Switzerland, by using a one-box model and simulation software (MASAS) for modeling organic pollutants in lakes. Both the one-box model and the one-dimensional simulation were based on (i) independently evaluated processes affecting the fate of FWAs and (ii) measured FWA concentrations in the lake. The relevant processes were derived from literature data and from measurements in the lake and in its tributaries. Besides loading from tributaries, only photo-degradation (responsible for 53% and 81% of the elimination of DAS 1 and DSBP, respectively), sorption/sedimentation (20% and 9%), and flushing (27% and 10%) were found to be relevant for FWAs in Greifensee. In particular, no evidence was found for other degradation processes such as biodegradation or hydrolysis. During 1 year, concentration depth profiles were measured above the deepest point of the lake in intervals of 4 weeks. The measured FWA concentrations were between 50 and 120 ng L^{-1} (DAS 1) and between 10 and 110 ng L^{-1} (DSBP), with maximum values in the thermocline during summer. Evidence was found that these maximum values originated from subsurface loading occurring in summer at levels of 4–8 m depth. This study is one of the first field validations for photochemical degradation rates measured in the laboratory.

Introduction

Laundry detergents contain several synthetic chemicals and are important potential sources for the pollution of natural waters. They are applied in large amounts and discharged almost quantitatively to municipal and industrial wastewaters. For example, worldwide consumption of a major detergent ingredient, the linear alkylbenzenesulfonates (LAS), reached 2.8×10^6 t per year in 1995 (*1*). It is therefore important to know the behavior and the effects of individual detergent components during sewage treatment and after release to the aquatic environment.

Several studies have been performed to determine the concentrations of specific detergent compounds in various compartments of the aquatic environment. These monitoring studies have provided important information on the occurrence and distribution of detergent-derived chemicals in sewage treatment plants, rivers, and lakes. However, the data collected in such studies rarely provide quantitative information on the various processes that determine the fate of a given compound in the system being considered. Investigations focusing on the determination of in situ rates of transport, mixing, and transformation processes as well as on the quantification of the inputs of specific organic chemicals to natural waters are (for detergent ingredients as well as for other anthropogenic pollutants) still rather scarce. Two recent studies of organic pollutants in surface waters evaluated the dynamic behavior of tetrachloroethene (PER), atrazine, and nitrilotriacetate (NTA) in Greifensee, a small lake in Switzerland (*2, 3*). The main processes affecting the fate of these chemicals in this lake are gas exchange (PER), biodegradation (NTA), and flushing (all three). Another process that might influence the fate of chemicals in natural waters (photodegradation) was studied recently with a similar approach in a river (*4*). In the study presented here, photodegradation has been investigated in a lake together with sorption/sedimentation using fluorescent whitening agents (FWAs, Figure 1) as probe substances. FWAs are degraded photochemically (*5*), and they sorb onto particles. A recent study of FWAs in the benthos of Greifensee (*6*) demonstrates that sorption/sedimentation is relevant in natural systems.

FWAs have the potential to extend our knowledge of the behavior of detergent chemicals in surface waters. They are rather reactive (photolysis, sorption). In contrast to most other detergent ingredients, the consumption of FWAs is known relatively precisely, and individual substances can be determined reliably (*7*). Two compounds are currently used as FWAs in Swiss laundry detergents: DAS 1 (a *di*amino-*s*tilbene) and DSBP (a *di*styryl*bi*phenyl). Normally, FWAs make up an average mass of 0.1% of the total detergent. In 1995, a total of 59 t of DAS 1 and DSBP were consumed in Switzerland (*8–10*). Both DAS 1 and DSBP absorb UV light

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TABLE 1. Characteristic Data of Greifensee, the Investigated Lake

volume[a] (m^3)	1.51×10^8
surface area[a] (m^2)	8.49×10^6
max depth[a] (m)	32.6
mean depth[a] (m)	17.8
mean residence time of water[a] (yr)	1.1
mean throughflow of water, Q[a] ($m^3 d^{-1}$)	3.7×10^5
mean epilimnion depth (summer)[a] (m)	5
particulate organic carbon[b] ($g\ m^{-3}$)	0.2–2.7
settling velocity of particles[a] ($m\ d^{-1}$)	0.5–2.5
catchment[a] (km^2)	160
inhabitants in catchment[a]	100 000
typical Eddy diffusion coefficients (K_z)	
thermocline April–June ($cm^2\ s^{-1}$)	0.04–0.07
thermocline July–October ($cm^2\ s^{-1}$)	0.001–0.01
hypolimnion whole year ($cm^2\ s^{-1}$)	0.01–0.1

[a] Ref 2. [b] R. Illi and B. Ribi, EAWAG.

with a maximum at 350 nm with a molar extinction coefficient of 60 000–70 000 $M^{-1}\ cm^{-1}$ (5) and emit blue visible light at a maximum wavelength of 430 nm with a fluorescence quantum yield of 0.3 (DAS 1) and 0.8 (DSBP) (11). This blue fluorescence constitutes the function of FWAs in detergents (whitening the fabrics; 12), and it can also be exploited for their analytical determination. The sulfonate groups increase the water solubility of the otherwise hydrophobic FWAs, and the large carbon structures cause an affinity for cellulose surfaces.

During textile washing, FWAs partly remain in the washing liquor and hence are discharged to sewers for treatment in municipal sewage treatment plants (STPs). FWAs are partly retained on the activated sewage sludge due to adsorption. The nonretained fraction of FWAs, approximately 20% of the consumed FWAs, reaches surface waters (13–15), where FWAs are photodegraded in the photic zone. In samples of Greifensee, e.g., half-lives amount to several hours under summer noon sunlight in the top 1.5 cm (5). Below the photic zone, FWAs can be assumed to be persistent because biodegradation has not been observed (16, 17). Concentrations that have been found in surface waters were always far below the predicted no effect concentrations (PNEC) (18–20).

The goal of this work was to quantitatively evaluate experimental data derived from several field investigations conducted at Greifensee using literature data and computer simulation. In particular, we wanted to evaluate the extent to which photochemical degradation rates determined in laboratory experiments can be used to explain the behavior of chemicals in natural waters.

Experimental Section

Greifensee, the Study Site. Greifensee is a small eutrophic lake located 10 km east of Zurich, Switzerland (Table 1; for a figure, see ref 2). It is a holomictic and dimictic lake with regular overturn in December and March. Regular successions of oxic (winter/spring) and anoxic conditions (summer/fall) are observed in the hypolimnion of the lake. A long-term data set of particulate organic carbon (POC), temperature, oxygen, pH, and global radiation were available (21, 22). Water gauge recordings for the main tributaries Aabach and Aa as well as for the outflow Glatt were received from the Water Pollution Control Agency of Zurich.

The relatively high population density in the catchment of Greifensee causes a significant input of anthropogenic chemicals into the lake. The effluents of seven sewage treatment plants (STPs) are discharged into Greifensee either directly or indirectly via the two major tributaries, Aa and Aabach. The only outflow of the lake is the Glatt River.

Sampling and Chemical Analyses. Between April 1995 and April 1996, a total of 14 vertical sample profiles (13–16 depths) were collected above the deepest point of the lake in intervals of 4 weeks. Concentration profiles at this location were assumed to be representative for the whole lake, because in general, horizontal mixing in Greifensee is fast as compared to elimination processes (2). After collection in a stainless steel sampling bottle (Friedinger, Lucerne, Switzerland), the lake water was transferred immediately into 1-L amber glass bottles and transported to the laboratory, and analysis was started within 2 h. The two main tributaries, Aa and Aabach, were sampled with time-proportional portable samplers (Manning Products, Texas). Based on water gauge recordings, flow-proportional 1-day-averaged samples were obtained and analyzed, thus recording the discharge of four of the STPs. The effluents of the other three STPs (discharging directly into Greifensee) were sampled continuously over 24 h periods using flow-proportional sampling devices. One-day composite samples from both tributaries and STPs were collected on 13 days in 500-mL amber glass bottles, representing different seasons, weekdays, and water discharges. After collection, samples were stored in the dark, transported to the laboratory, and analyzed within 2 days.

The FWAs were extracted from samples of 200 mL (lake water) and 50 mL (rivers and STPs) by solid-phase extraction (C18 Empore disks; Varian, Harbor City, CA). After separation by reversed-phase HPLC (column: Hypersil ODS, 3 μm, 100 mm × 2.1 mm i.d. with precolumn; Hewlett-Packard), individual FWAs were irradiated in the column eluent with a UV lamp (254 nm, 5 s) and detected with fluorescence (excitation, 350 nm; emission, 430 nm; Hewlett-Packard, 1046A). Recovery rates were 87–88%, and standard deviations ($n = 8$) were 1–12%. Both DAS 1 and DSBP could be determined down to concentrations of 3 ng L^{-1} (7).

Cylindrical sedimentation traps (78 cm length and 9 cm diameter; 23) were exposed mid-lake at 10 and 30 m depth during the whole investigation period (April 1995–April 1996). The particulate material in the traps was collected every 4 weeks and was subsequently freeze-dried, extracted in methanol, and analyzed by HPLC (same procedure as for aqueous samples).

Chemicals. FWAs for calibration, all present as E- or E,E-isomers and technical grade as well as the internal standard (technical grade), were obtained as sodium salts from Ciba-Geigy AG (Basel, Switzerland) with purities of 97% (DAS 1) and 90% (DSBP). 4,4′-Bis(5-ethyl-3-sulfobenzofur-2-yl)-biphenyl, a research compound, was used as an internal standard. This compound has not been applied as a FWA and therefore does not appear in environmental samples but shows fluorescence in the same wavelength region as the FWAs. Ammonium acetate (analytical grade) was purchased from Merck ABS AG (Basel, Switzerland). Tetrabutylammonium hydrogen sulfate (TBA) was purchased from Fluka AG (Buchs, Switzerland). All solvents (HPLC grade) were purchased from FEROSA (Barcelona, Spain) and were used as received.

Mathematical Simulation Model. The measured data were evaluated using the computer software MASAS (24) (*M*odeling of *A*nthropogenic *S*ubstances in *A*quatic *S*ystems), which allows the construction of mathematical models for describing the dynamic behavior of chemicals in lakes. The lake was described by a vertical, one-dimensional model of 32 boxes that assumed complete mixing within every box and within the epilimnion. However, near point sources (e.g., inflows of streams or STPs), pollutant concentrations may have been somewhat higher; these parts of the lake were not the focus of this study. In contrast, vertical mixing below the epilimnion was explicitly described as a turbulent diffusion process with time- and depth-dependent diffusion coefficients. These coefficients (Table 1) were computed

TABLE 2. One-Box Model for Greifensee

	DAS 1				DSBP			
	min	max	av	contribution[b] (%)	min	max	av	contribution[b] (%)
loading from inflow (g d^{-1})[a]	67	239	114		97	313	156	
95% conf int (g d^{-1})		±27				±32		
outflow (River Glatt) (g d^{-1})[a]	12	69	29	27	4	36	16	10
sedimentation (g d^{-1})[a]	4	65	21	20	4	75	14	9
photodegradation (g d^{-1})[a]	9	98	56	53	34	231	129	81
total FWA in the lake (kg)	10.1	15.3	12.7		6.6	10.8	8.6	
change within one period (g d^{-1})	−76	+52	0		−72	+54	−5	

[a] Individual values for every period were used for the one-box model and for the computer simulation (minimum and maximum given as examples). The average is given only for information and was not used for calculations. [b] Contribution to total FWA reduction averaged over the whole year (April 1995−April 1996).
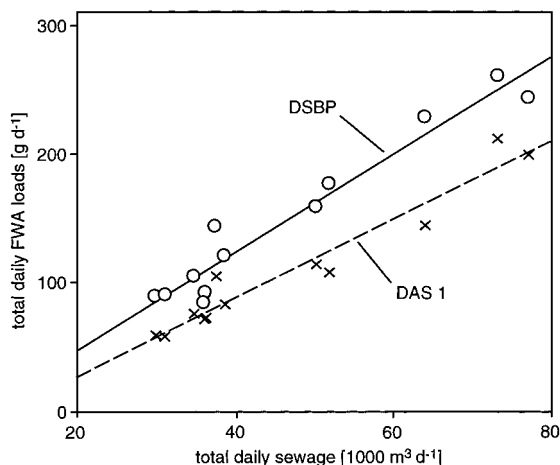

FIGURE 2. Correlation of the total daily sewage in the catchment of Greifensee and the total daily FWA loads measured at the outlets of three STPs and the two tributaries discharging FWAs into Greifensee. Lines show the linear correlations: DAS 1 (crosses, dashed line) = $3.05Q - 33.3$ ($r^2 = 0.94$); DSBP (circles, solid line) = $3.82Q - 28.2$ ($r^2 = 0.95$). 95% confidence intervals: ± 27 (DAS 1), ± 32 (DSBP).

from independently measured temperature profiles by the heat budget method (25). For lake throughflow, outflow data were used. A more thorough description of MASAS is given in ref 24.

Results and Discussion

This study is based on a research concept with three parts, as reflected in the text below: First, every relevant process was evaluated independently. In particular, reliable parameters were determined for FWA boundary fluxes (input from STP effluents, elimination by flushing, sorption/sedimentation, and gas exchange) and for the degradation of FWAs. Second, FWA concentration profiles were measured in the lake during 1 year. Third, the mathematical model was set up based on the two previous steps.

Evaluation of Boundary Fluxes: Loading and Elimination by Flushing and Sorption/Sedimentation. To assess the loading of FWAs into Greifensee for every day of the year investigated, total daily loads were measured on 13 days (sum of the three STPs and two tributaries discharging to Greifensee; measurements in two smaller tributaries showed no measurable FWA concentrations). These total daily loads were correlated with the total daily sewage (sum of the water that was treated in all STPs of the catchment) (Figure 2). The correlation determined by linear regression showed good linearity with correlation coefficients of 0.94 and 0.95 for DAS 1 and DSBP, respectively. This indicates that the FWA mass in sewage is reduced more efficiently during sewage

treatment when less water is treated (based on the assumption that the daily FWA mass discharged to STPs is constant). This observation can be explained as FWAs are eliminated from sewage treated in STPs exclusively by sorption onto sewage sludge (13). Sludge is diluted during rainy periods, which leads—in combination with the constant sorption coefficient—to higher loads in the effluent. The correlation equations were assumed to be representative for the entire investigated year since samples were collected on all days of the week, in all seasons, and under dry as well as rainy conditions. Calculated loadings ranged from 67 to 239 g d^{-1} (average 114 g d^{-1}) and from 97 to 313 g d^{-1} (average 156 g d^{-1}) for DAS 1 and DSBP, respectively. Confidence intervals estimated with the standard deviation were ± 27 g d^{-1} (DAS 1) and ± 32 g d^{-1} (DSBP) (Table 2). The values obtained by this procedure were directly used in the model.

Three boundary fluxes may eliminate FWAs out of a lake, namely, flushing, sorption/sedimentation, and gas exchange. Flushing and sorption/sedimentation were evaluated with measurements in the lake. The product of the average FWA concentration in the top 5 m of the lake and the actual outflow of River Glatt was used as elimination by flushing providing values between 12 and 69 g d^{-1} for DAS 1 (average 29 g d^{-1}) and between 4 and 36 g d^{-1} for DSBP (average 16 g d^{-1}). The FWAs collected in the two sediment traps (10 and 30 m) were used to estimate the sedimentation of FWAs above and below 10 m, respectively. These values were between 4 and 65 g d^{-1} for DAS 1 (average 21 g d^{-1}) and between 4 and 75 g d^{-1} for DSBP (average 14 g d^{-1}). The opposite flux, from the sediment into the water, was neglected as the FWA concentrations were more or less constant in the hypolimnion throughout the year. The third possible boundary flux, gas exchange, is predicted to be rather unimportant as the FWAs investigated have great molecular weights (>500) and are present in aqueous solutions primarily as anions. A comparison of the boundary fluxes (Table 2) shows that a degradation of FWAs in Greifensee is occurring because the measured concentrations are not increasing as expected from the boundary fluxes only. A simple one-box model was therefore established to estimate possible degradation processes.

One-Box Model: Evaluation of Degradation Rates. Photodegradation of FWAs in natural waters has been observed by Kramer (26), who reported degradation rates for the upper 2 m box of Greifensee, measured with filtered water and based on the assumption of cloudless days and complete mixing within the box considered. To evaluate daily photodegradation rates for the investigated period, these maximum rates had to be reduced on account of clouds, reflection at the air−water interface, and particles in the water. The daily flux of photons (400−800 nm) reaching the earth near Greifensee was used as a measure for the clouds. Therefore, the photodegradation rates reported by Kramer et al. for
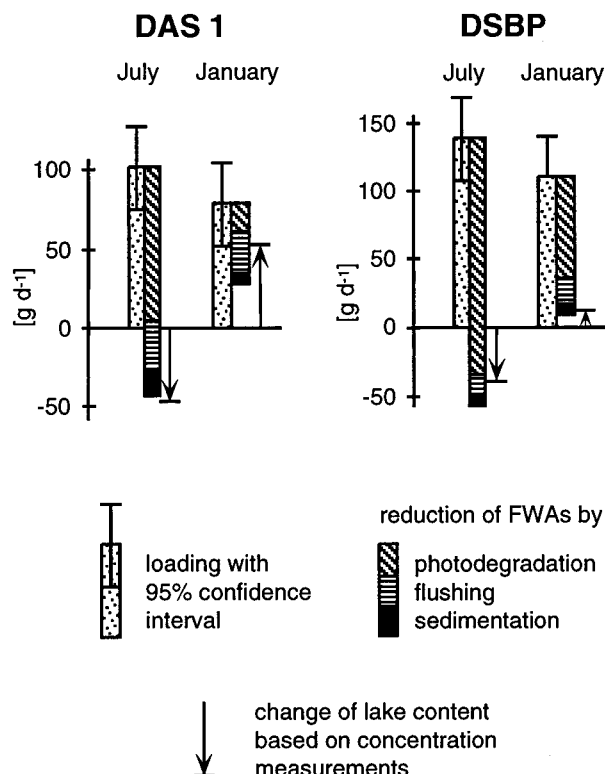
DAS 1

July   January

DSBP

July   January

loading with
95% confidence
interval

reduction of FWAs by

photodegradation
flushing
sedimentation

change of lake content
based on concentration
measurements

FIGURE 3. One-box model for DAS 1 (left) and DSBP (right). The model was established for 13 periods of 4 weeks and is shown for the two periods in July 1995 and January 1996.

May 15 were attributed to May 22, 1995, the day with the biggest flux of photons during the investigation, assuming this day to be cloudless. The photodegradation rates for all other days were calculated proportionally to the respective photon fluxes on the basis of the rates of May 22. The new rates were subsequently reduced by a factor corresponding

to the fraction of light reflected at the air−water interface (6%, constant throughout the year; 27) and by a factor corresponding to attenuation by particles in the water. This factor was estimated by calculating the reduction of visible light from the lake surface to 1 m depth. On May 30, 1995, this reduction was smallest and completely attributed to dissolved organic matter (assumption: no particles in the lake after the precipitation of lime occurring in May). The additional reduction of visible light on the other days throughout the year was attributed to particles in the water (reduction of 5−29%). By the help of these converted photodegradation rates and the FWA mass in the top 2 m box of Greifensee (estimated from concentration measurements above the deepest point of the lake), the amount of FWAs degraded photochemically was calculated for every 4-week period of the investigation. The values were between 9 and 98 g d^{-1} (average 56 g d^{-1}) for DAS 1 and between 34 and 231 g d^{-1} (average 129 g d^{-1}) for DSBP.

Besides photodegradation, other degradation processes may occur in Greifensee, namely, biodegradation or hydrolyses, although they are expected to be negligible as they have not been observed to date (16, 17). Nevertheless, the data evaluated above allows for the development of a simple one-box model, comparing the change of total FWA mass in the lake with the sum of all processes affecting FWA concentrations. With this one-box model, it is possible to estimate whether degradation processes other than photodegradation have to be considered for Greifensee. This comparison was made for 13 periods of 4 weeks each between April 3, 1995, and April 2, 1996. For 10 out of the 13 periods, for each DAS 1 and DSBP the difference between measured and modeled mass change in the lake is smaller than the confidence intervals estimated for the FWA loading into the lake (as examples, the results for July and January are shown in Figure 3). Only during two periods (DAS 1, December and February; DSBP, June and December) the FWA mass increased too strongly in the one-box model, thus giving evidence for an additional degradation process. Nevertheless, biodegradation and hydrolysis can be expected to be
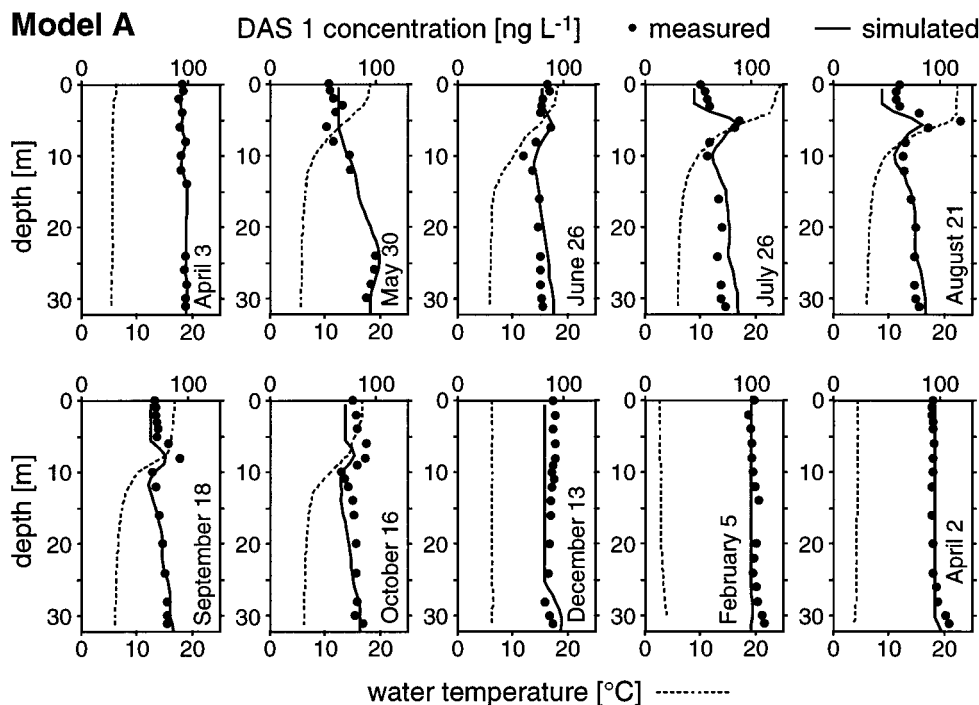
Model A   DAS 1 concentration [ng L^{-1}]   • measured   — simulated

water temperature [°C] ----------

FIGURE 4. Vertical DAS 1 concentration profiles (dots, scale at the top of graph) and temperature (dotted lines, scale at the bottom of graph) measured above the deepest point of Greifensee in 1995/1996. Solid lines: computer simulation with fitted sedimentation velocities (starting April 3, 1995), model A with depth loading.
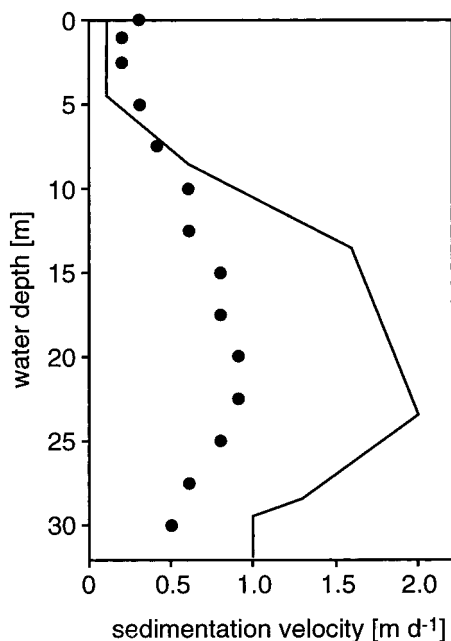
FIGURE 5. Sedimentation velocities of particles in Greifensee (July). Dots: calculated assuming a constant particle flux. Base of the calculations: measured POC in the water column and measured sedimentation rates from sedimentation traps. Line: corrected with a correction factor in order to achieve the measured depth profiles with the computer simulation, model A.

faster in summer than in winter. Since no evidence can be found for these processes in May, July, and August, the observed differences are probably due to other factors. It is remarkable that the differences are observed in periods with heavy rains only. Therefore, it may be possible that the input of FWAs into Greifensee is overestimated in our model during heavy rains. We can imagine two reasons for this. First, the correlation between the sewage treated and the FWA input into Greifensee may only be linear up to a certain discharge of sewage. Second, a part of the FWAs discharged into Greifensee may not origin from STPs but from sewage sludge that was previously applied to farm fields. Rain may then wash out the FWAs from the fields and discharge them into Greifensee via the rivers. These two cases would lead to an overestimation of the FWA input into Greifensee.

No explanation can be given for two cases where the FWA mass decreased too strongly in the one-box model (DAS 1, August; DSBP, March). In these cases, our model seems to be simplified too much, neglecting processes that are not known to us. However, the general agreement of simulation results with the observations in the lake indicate that our assumptions are correct for the major part of the year investigated. The field validation of photodegradation rates is especially remarkable and indicates that biodegradation and hydrolysis are negligible in Greifensee. Concerning the velocity of photodegradation, it is interesting to note that the DAS 1 mass in the whole lake is reduced by 2−24% within 28 days (DSBP, 11−61%). Both DAS 1 and DSBP are therefore not readily photodegradable in Greifensee following the definition about degradability given by an EC directive (28). Note that this statement is somewhat arbitrary, as the EC directive does not specify the "aquatic environment". If only the photic zone of Greifensee is considered as aquatic zone, as was done by Kaschig et al. (29), DAS 1 (in spring and summer) and DSBP (throughout the year) are readily photodegradable. However, we think it is more appropriate to define the whole lake as aquatic environment.

Seasonal Variation of Measured FWAs in Greifensee. Figure 4 shows typical vertical concentration profiles of DAS 1 (dots) determined above the deepest point in Greifensee. As indicated by the temperature profiles (dotted lines), the lake was stratified between May and November, followed by complete overturn in winter. In winter, with less sunlight and less particles in the lake, total FWA concentrations generally increased. In summer, DAS 1 concentrations exhibit a maximum in the thermocline, whereas concentrations in the epilimnion and in the hypolimnion are distinctly lower. These findings are consistent with the assumption that DAS 1 is eliminated from the water column primarily by two processes, photodegradation in the epilimnion and sorption/sedimentation. We formulated two hypotheses about the origin of these peaks: (i) They are a consequence of subsurface loading of the FWAs (model A). Subsurface loading has been observed for another detergent component, NTA (2). In such a situation, a part of the water discharged to the lake surface through tributaries and STPs is transported immediately to the depth with the corresponding temperature (and density). During the summer, this theoretical intrusion depth is 4−8 m from the lake surface. During winter, the temperature in the lake is always smaller than in the tributaries, thus giving no evidence for a subsurface loading. (ii) A second possibility is that the peaks in the thermocline are caused by particle dynamics (model B) because part of the sinking particles are dissolved in the thermocline, thus transporting FWAs from the epilimnion to the thermocline.

32-Box Model: Computer Simulation. Two simulation models were established and calibrated with DAS 1, model A with subsurface loading and model B without subsurface loading. Subsequently, the models were adapted to DSBP to test their validity. Only substance specific values such as
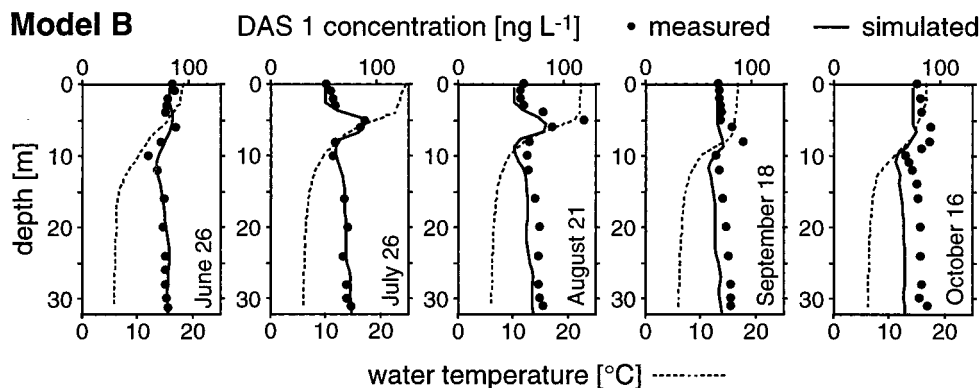

FIGURE 6. Vertical DAS 1 concentration profiles (dots, scale at the top of graph) and temperature (dotted lines, scale at the bottom of graph) measured above the deepest point of Greifensee in 1995. Solid lines: computer simulation with fitted sedimentation velocities (starting April 3, 1995), model B with all loading at the lake surface.
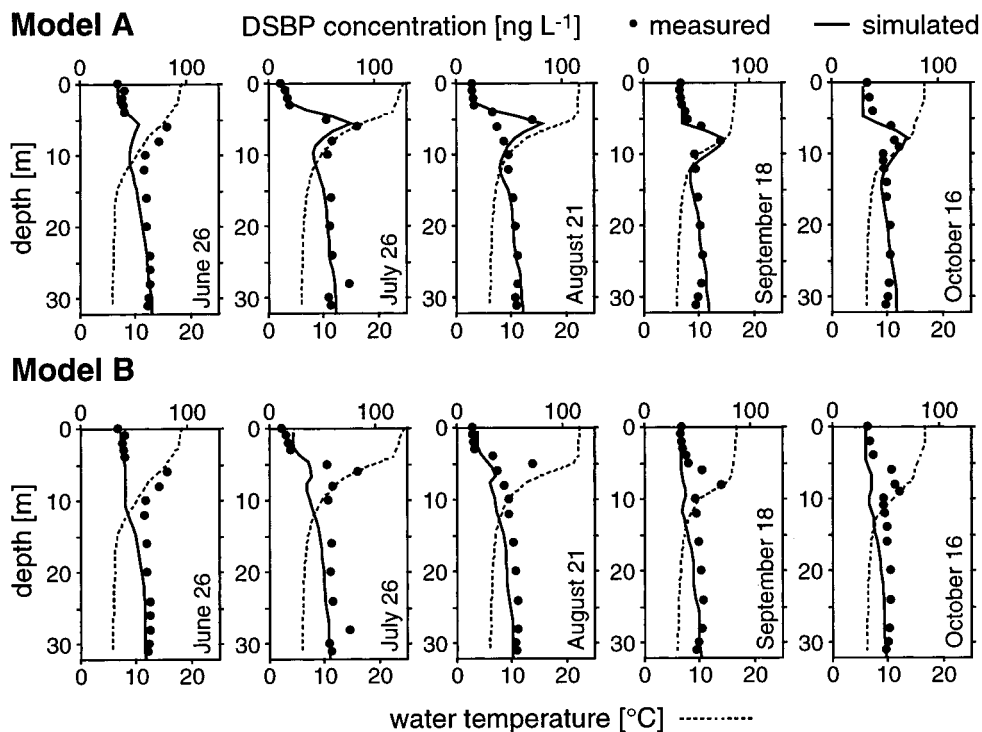
Model A

DSBP concentration [ng L⁻¹]   • measured   — simulated

Model B

water temperature [°C] ·········

FIGURE 7. Vertical DSBP concentration profiles (dots, scale at the top of graph) and temperature (dotted lines, scale at the bottom of graph) measured above the deepest point of Greifensee in 1995. Solid lines: computer simulation with fitted sedimentation velocities (starting April 3, 1995); top: model A with depth loading; bottom: model B with all loading at the lake surface. Note the failure of model B, confirming that subsurface loading is required to explain the observed behavior of DSBP.

photodegradation rates or loading were exchanged for the values obtained for DSBP. In that way, an independent control was achieved. As sorption/sedimentation is only responsible for 9−20% of the FWA reduction in Greifensee, this process was roughly estimated. Depth profiles of particulate organic carbon measured in the lake were used together with apparent solid−water distribution ratios (K_d) calculated from FWA concentrations in particles (collected in the sedimentation traps) and in the lake water of the corresponding depth (10 and 30 m) at the end of the collection period (log K_d for both DAS 1 and DSBP, 3.9 ± 0.2). In both models, sorption coefficients of DAS 1 were kept constant. To take into account nonsinking particles, differences in K_d values from one season to another or in different water layers, and different sedimentation velocities, a correction factor was included in the model. Due to constraints of the simulation software used, this factor was included in the sedimentation velocity. As shown in Figure 5 there is a good qualitative agreement with both calculated and adapted sedimentation velocities being highest between 10 and 25 m lake depth. While the quantitative differences are small in the epilimnion, sedimentation velocities had to be increased by a factor of about 2 in the hypolimnion. The same observation was also made by Bloesch and Sturm (*30*), who increased the hypolimnetic particle settling velocity by a mean factor of 3 to 3 m d⁻¹ for a lake model of a lake similar to Greifensee. Subsurface loadings for model A were applied from June to October with increasing depths from 4−6 m to 6−8 m, corresponding to the depths with the same temperature as the tributaries. Best results with the simulation model were obtained by assuming between 10% (June and October) and 40% (July/August) of the total loadings to enter the lake in the mentioned depths. Figures 4 (model A) and 6 (model B) indicate that both models can simulate the measured depth profiles of DAS 1.

To examine the validity of the two models, the same parameters determined for DAS 1 were used to simulate the behavior of the second investigated FWA, DSBP. While model
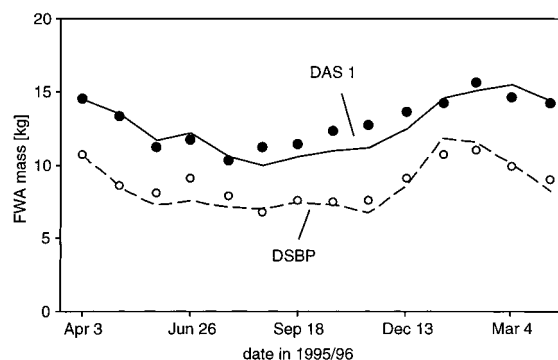

FIGURE 8. Seasonal variation of the total DAS 1 and DSBP mass in Greifensee in 1995/1996; dots represent the measured total mass (black, DAS 1; white, DSBP; calculated from the concentration profiles and the corresponding water volumes); lines represent the results of the computer simulation, model A (solid, DAS 1; dashed, DSBP).

A (with depth loading, Figure 7, top) reproduces the profiles of DSBP very well, model B (without depth loading, Figure 7, bottom) is not able to simulate the behavior of DSBP. Obviously transport by particles alone cannot explain the increase of FWA concentrations in the thermocline. A second process (depth loading) must be involved. In addition to the validation of the model with DSBP, the measured and the modeled seasonal variation of the total FWA amount in the lake were compared, as a control, showing good correspondence for model A (Figure 8). Thus, the photochemical degradation rates measured in the laboratory could be confirmed in our model.

Acknowledgments

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