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Fate of Fluorescent Whitening Agents in the River Glatt

THOMAS POIGER,[†]
FRANZ GÜNTER KARI,[‡] AND
WALTER GIGER*

Swiss Federal Institute for Environmental Science and Technology (EAWAG) CH-8600 Dübendorf, Switzerland

With the use of computer simulation (AQUASIM), the dynamic behavior of the two fluorescent whitening agents (FWAs) that are currently used in laundry detergents in Switzerland (DSBP, a distyrylbiphenyl, and DAS 1, a diaminostilbene) has been evaluated quantitatively for the River Glatt, a small highly polluted stream in Switzerland. The one-dimensional simulation was based on independently determined photolysis and sorption rate constants, and measured FWA concentrations at the beginning of the studied river section and in two major tributaries (effluents of sewage treatment plants). Concentrations of FWAs were 0.4−1.2 μg/L in river water and 2.9−5.7 μg/L in sewage, respectively, with very little diurnal variation. Direct photolysis and partitioning between aqueous phase and sediment and macrophytes were identified as the most important processes affecting the fate of DSBP and DAS 1 in the river. Simulation of FWA concentrations with photolysis as the only process yielded concentration traces with minima during daytime and maxima at night, which contradicted the observed uniform concentrations. By taking sediment/water exchange into account, good agreement between measured and modeled FWA concentrations was achieved. The observed removal of FWAs during transport (12 h residence time) was 31% and 12% for DSBP and DAS 1, respectively, corresponding to half-lives of 0.9 and 2.7 d, respectively, under cloudless summer skies.

Introduction

Fluorescent whitening agents (FWAs) used in detergents are moderately water-soluble organic compounds with a high affinity for cellulosic material. When adsorbed to textiles, their strong blue fluorescence eliminates the yellowish cast of white fabrics and makes them look whiter. The two most used detergent FWAs are DSBP, a distyrylbiphenyl FWA, and DAS 1, a diaminostilbene FWA (Figure 1). Worldwide consumption of DSBP and DAS 1 are estimated at 3000 and 14 000 t/yr in 1990 (*1*). Consumption in Switzerland (1992) was approximately 89 t/yr, corresponding to 0.1% of the laundry detergents consumed (*2*). Although FWAs are added to detergents to attach to the washed goods, they also remain in the washing liquor to some extent and are discharged with the wastewater.

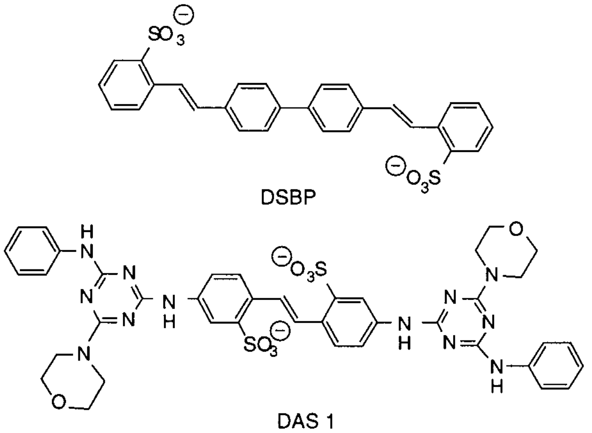

FIGURE 1. Structures of the two studied FWAs. Full names: DSBP, 4,4′-bis(2-sulfostyryl)biphenyl; DAS 1, 4,4′-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2′-disulfonate.

During sewage treatment, DSBP and DAS 1 are removed from wastewater with average efficiencies of 50 and 90%, respectively (*1*). This removal is caused exclusively by adsorption to sewage sludge, whereas biodegradation of FWAs was not observed in either the aerobic biological stage or in the anaerobic sludge treatment. Concentrations of DSBP and DAS 1 in the effluents of four sewage treatment plants were in the range of 2−9 μg/L (*1*). A monitoring study conducted at several Swiss rivers showed that DSBP and DAS 1 were present at concentrations of 0.001−1 μg/L. Concentrations varied greatly between small, highly polluted and large, less polluted rivers. Mass loadings of FWAs generally correlated well with the population discharging to the particular watershed, with the exception of two FWA production sites, where mass loadings were 4−18 times higher than predicted by the population density (*3*). The FWA concentrations found in surface waters were always well below the predicted no-effect concentrations (PNEC) of 100 μg/L (*4*).

FWAs strongly absorb UV light with a maximum absorbance at 350 nm and can then undergo fluorescence, reversible isomerization from (*E*)- to the corresponding (*Z*)-stilbene, and photodegradation. The isomerization process is also referred to as photofading (*5*) since the (*Z*)-isomers do not fluoresce. Photolysis of FWAs is much slower than isomerization. However, the photochemical half-lives of FWAs are still appreciably short to affect FWAs in surface waters (Table 1). Although the photolysis quantum yields of DSBP and DAS 1 are almost identical, DSBP degrades four times faster than DAS 1. This is due to the greater absorbance of the (*E*)/(*Z*)-isomer mixture of DSBP present in natural waters. Photolysis mainly leads to aldehydes formed upon cleavage of the stilbene groups and to alcohols from the addition of water to the stilbene double bond (*6*).

The photolysis rate constants determined in the laboratory were successfully applied in a comprehensive study of the fate of FWAs in Greifensee, a small eutrophic lake in Switzerland (*7*). In this study field investigations on inputs and vertical concentration profiles of FWAs in the lake were combined with computer modeling using the independently determined photolysis rate constants as well as solid/water partitioning coefficients. Averaged over a whole year in Greifensee, 80 and 50% of DSBP and DAS 1, respectively, were removed by direct photolysis and another 10 and 27%, respectively, were removed by sorption/sedimentation (*7*).

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* Corresponding author telephone: +41-1-823 54 75 Fax: +41-1-823 50 28; e-mail: giger@eawag.ch.

[†] Present address: Department of Plant Protection Chemistry, Swiss Federal Research Station, CH-8820 Wädenswil.

[‡] Present address: Basler & Hofmann Consulting Engineers Ltd., CH-8029 Zurich, Switzerland.

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TABLE 1. Kinetic Parameters for Fluorescence, Photoisomerization, and Photodegradation of FWAs[a]

	DSBP	DAS 1	ref
ϕ_f	0.82	0.33	(*17, 18*)
$\alpha_{E,Z}$	20/80	85/15	(*6*)
$\phi_{E,iso}$	0.069	0.29	(*18*)
$\phi_{Z,iso}$	0.48	0.36	(*18*)
ϕ_{deg}	0.00012	0.00010	(*6*)
$t_{1/2\,(min)}$	87	278	(*6*)

[a] Abbreviations: ϕ_f, fluorescence quantum yield (only (*E*)-isomer); $\alpha_{E,Z}$, isomer ratio [*Z*]/[*E*] under photostationary conditions in summer noon sunlight; $\phi_{E,iso}$, $\phi_{Z,iso}$, isomerization quantum yields for the (*E*)-, and (*Z*)-isomers; ϕ_{deg}, photodegradation quantum yield; $t_{1/2}$, half-life in the top 15 mm of Greifensee water under summer noon sunlight.

Comparison of the amount of FWAs discharged with sewage effluent and the amount of FWAs present in rivers indicates that some removal occurs (*1, 3*). From the work summarized above it is conceivable that photolysis affects the fate of FWAs in rivers. Sorption is also likely to be involved in the fate of FWAs in rivers. This is confirmed by measurements of FWA concentrations in river sediments at Rümlang where 5.2 and 3.3 mg/kg, respectively, of DSBP and DAS 1 were found (*8*). Apparent solid−water distribution ratios, K_d, determined with this sediment were 190 L/kg for both FWAs assuming E/Z ratios found in surface waters (*9*). In another study with suspended solids in a lake, a log K_d for both FWAs of 3.9 ±0.2 was reported (*7*). This rather large difference of more than a factor of 10 may be in part explained by the difference in organic content, which was 11% in the river sediment and up to 39% in the lake sediment. FWAs potentially also adsorb to macrophytes which are abundant in the River Glatt. However, no data of FWA concentrations in macrophytes is available.

Other processes, such as biodegradation or gas exchange are not expected to occur. With respect to biodegradation, FWAs can be assumed to be persistent. Biodegradation was not observed during sewage treatment (*10*) and in a laboratory study conducted with five different FWAs, biodegradation in river water did not occur over a period of 30 days (*11*). The FWAs investigated here are ionic compounds with relatively high molecular weight and are thus unlikely to volatilize to a significant extent.

The goal of the work presented here was to determine whether removal of detergent FWAs occurs during transport in rivers and to determine the extent of this removal. Of particular interest was whether the ready photodegradability of FWAs determined in the laboratory can be extended to the real river situation. To this end, a field study was conducted at the River Glatt, a small stream in Switzerland. The experimental data was quantitatively evaluated using computer simulation, taking into account only processes that are known to be relevant in other systems and using input values in reliable ranges. The results of this investigation should allow the fate of the two mostly used detergent FWAs in natural waters to be assessed.

Experimental Section

Description of the Watershed. The field investigation was conducted at the River Glatt (Switzerland) which originates at the outlet of Greifensee and is a tributary to the River Rhine. The flow distance from source to mouth is 36 km. In 1992, the average water discharge at a gauge in Rheinsfelden was about 7.5 $m^3\ s^{-1}$; the water residence time within the river is 15−20 h depending on flow velocity. The river bed slope ranges from 1 to 7 % resulting in an average flow velocity of approximately 0.5 $m\ s^{-1}$. The bank is lined with trees to a certain extent so that the light conditions in the water column range from shadow to full exposure to sunlight.

The River Glatt receives water from several small tributaries of which the most important are the Chriesbach, the Leutschenbach, and the Fischbach. The Glatt Valley is a densely populated area intensively used for agricultural and industrial purposes. Several sewage treatment plants, STPs (Fällanden, 1.4 km downstream; Dübendorf, 6.3; Zurich−Glatt, 9.8; Opfikon, 12; Niederglatt, 22.3; Bülach, 25.4; Glattfelden, 33.2) discharge wastewater into the River Glatt. At low discharge up to 30% of the water at the river mouth consists of treated sewage (*12*).

Sampling Program. The field study was conducted in summer, when the sunlight intensity is highest and effects due to photolysis are more likely observable. Samples were taken at two sites in the river and in effluents of two sewage treatment plants. Sampling sites for the river were at Rümlang (13.2 km, downstream) and Rheinsfelden (35.2 km, just before entering into the River Rhine). Wastewater effluent samples were taken from the STP at Niederglatt (22.3 km) and Bülach (25.4 km). The STP Glattfelden serves only a very small population and was therefore not included in the field study. The locations of the sampling sites are given in Figure 1. The effluents of the STPs at Niederglatt and Bülach were included since they deliver significant loads of FWAs into the river. To allow application of a one-dimensional river model, it was necessary that the effluents of the STPs be homogeneously mixed within the river cross section at the downstream river sampling site. For the station Rümlang this was secured by measurement of a cross section concentration profile (data not shown).

The samples from the river sites were 1-h composite samples (1 grab sample per 10-min interval). They were taken in the middle of the river using time-proportional portable samplers (portable priority contaminant samplers, no. 4900, Manning Products, TX) and comprised time periods of at least 24 h. The STP effluent samples were 2-h composite samples from time-proportional sampling devices and were also taken at least during 24 h. After collection, the composite samples were transferred to 250-mL opaque PE bottles containing 2.5 mL of formaldehyde (37%), transported to the laboratory, and stored at 4 °C until analysis.

Chemical Analysis. Wastewater (40 mL) and river water (100 mL) samples were analyzed by solid-phase extraction using C_{18} bonded-phase silica Empore disks followed by reversed-phase high-performance liquid chromatography and postcolumn UV irradiation fluorescence detection as described by Poiger and co-workers (*1*). The precision of the method indicated by the relative standard deviation (RSD) for DSBP and DAS 1 were ±1% and ±5% for sewage effluent, and ±2% and ±3% for river water, respectively. Recoveries for DSBP and DAS 1 were 93−96% ad 84−91%, respectively. Method detection limits of 0.03 μg/L (DAS 1) and 0.003 μg/L (DSBP) were well below the FWA concentrations found in Glatt river water. Photolysis products of DSBP and DAS 1 could, however, not be observed in river water using this method, because the products do not flourescence nearly as strongly as the parent compounds.

Tracer Experiments for Calibration of River Hydraulics. To be able to model the transport of FWAs in the River Glatt, it was necessary to obtain some information about the basic hydraulic conditions in the river during the field investigations. Besides the discharge volume and the river bed slope, the hydraulic conditions are mainly affected by the shape and roughness of the wetted perimeter and growth of macrophytes, both of which exert great influence on the mean flow velocity. Therefore, during the field investigation, a tracer experiment was conducted in the River Glatt to evaluate the way in which artificial, dissolved tracers expanded after injection into the river. The fluorescent dyes rhodamine B and fluorescine were used as artificial tracers. Thirty grams of tracer material were dissolved in 20 L of river water and

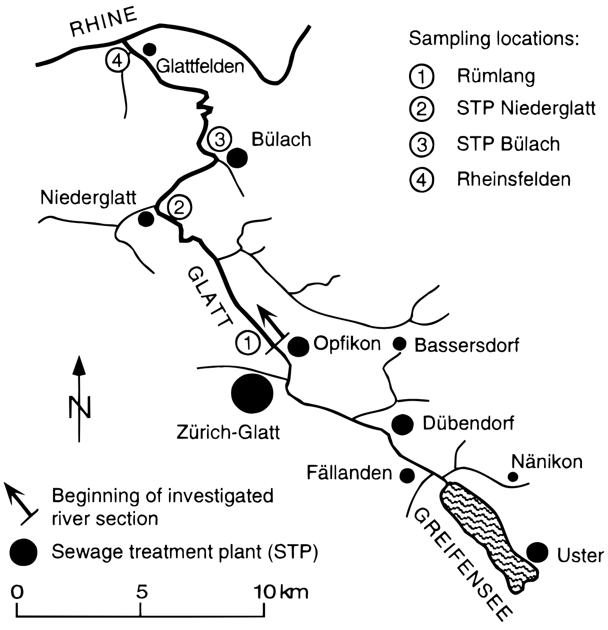

FIGURE 2. Map of the Glatt valley watershed, Switzerland. Shown are the sewage treatment plants (STPs) which discharge into the River Glatt and the sampling locations. The size of the dot representing a particular STP is proportional to its corresponding water discharge.

then introduced upstream of the sampling site at Rümlang (Figure 2). Since we scheduled concentration measurements at relatively short distances from the point of release, the tracer substance was released over the entire river cross section. For the continuous measurement of the tracer break-through curves at several locations, we used an in situ fluorometer equipped with suitable light filters. Because fluorescine is relatively quickly degraded by sunlight the tracer experiment was conducted very early in the morning. The locations for tracer measurement were chosen in a way so that no overlap of the break-through curves occurred. The printer output of the fluorometer was digitized and fed into the river transport model.

Discharge Data. The water discharges in the river and from the STPs are important variables for calculation of substance concentrations with the river transport model. Relevant discharge data from the water gauges at Rümlang and Rheinsfelden were supplied by the Swiss Hydrological Service in Bern, the water volumes discharged from the STPs were available by fixed water gauge recordings. The water gauge recordings were digitized and served as input into the river transport model.

Computer Software. The model simulations for the FWA transport in the River Glatt were performed using AQUASIM (*13*), a tool for simulation and data analysis of aquatic systems. The river section compartment of AQUASIM allows the solution of the St. Venant differential equations for one-dimensional river hydraulics. The river bed's geometry (including drops), the discharge at the upstream end of the river section to be modeled, lateral tributaries, and diffuse inflows have to be provided by the user. The user can specify any type of reactions for the transported substances. The program does not provide a sophisticated way of dealing with river sediment. Processes such as solids transport, settling, resuspension, and burial have to be defined by the user. For this study, given the limited amount of information regarding sorption (see below), a rather simple approach was taken to model the exchange between sediment and water column by introduction of a dynamic surface state variable for the concentration of sediment-bound FWAs which is not transported with the water flow.

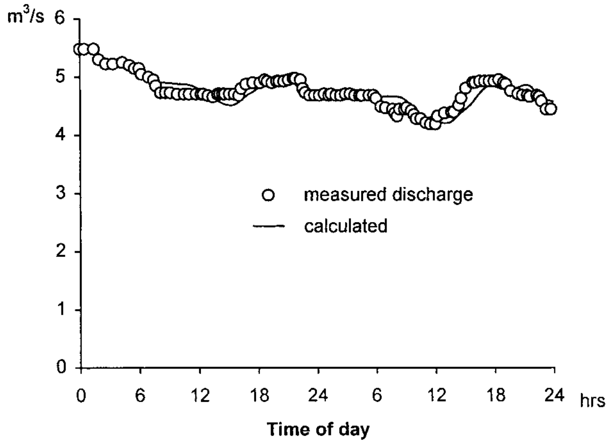

FIGURE 3. Measured and modeled water discharge of the River Glatt at Rheinsfelden.

For the simulation, the river was divided into 11 physically reasonable reaches. The river hydraulics were calibrated using the tracer experiment for defining the friction slope according to Darcy–Weisbach using the break-through curves of a dye tracer at several stations along the Glatt. The friction coefficents for the 11 reaches were adjusted until the measured break-through corresponded to the one predicted by the model. As can be seen in Figure 2 many small tributaries and effluents from STPs flow into the River Glatt. Neglecting infiltration into groundwater and evaporation, the discharge *Q* should increase with flow distance. Besides the river inflow at Rümlang (starting point of model calculations), only the effluent discharges of the STPs Niederglatt and Bülach were taken as main tributaries. To compensate for the small deviation between the measured discharge and the model predictions at Rheinsfelden (<15%) we defined a hypothetical diffuse lateral inflow *q* which was varied within the model until the water balance at this station was equalized. A comparison of measured and modeled water discharge at Rheinsfelden is given in Figure 3.

For computing theoretical photochemical half-lives of FWAs in the River Glatt we used the computer program GCSOLAR which has been described in detail by Zepp and Cline (*14*). Briefly, the program calculates the amount of light available for photolysis as a function of date, time, lattitude, and altitude. Data about the photochemical reaction quantum yield and the molar extinction coefficient of the substance, as well as the light attenuation coefficient of the water body and the geographical location have to be supplied to the model. Using this information, the program then provides rate constants as a function of date, time, and water depth. Although GCSOLAR ignores light-scattering effects in water bodies, its applicability for predicting the photochemical degradation of FWAs has already been shown (*7*). The output of GCSOLAR was incorporated into AQUASIM for specifying the photochemical degradation kinetics.

Results and Discussion

FWA Concentrations in Wastewaters and River Water. The concentrations of DSBP and DAS 1 in the effluents of the STPs at Niederglatt and Bülach were very similar, ranging from 2.9 to 5.7 μg/L with very little diurnal variation (Figure 4A). Whereas the DAS 1 concentrations in effluents of the two STPs are practically identical (3.1–4.2 μg/L), DSBP concentrations in Bülach are almost twice as high as those in Niederglatt. That means that either a large discharger of DSBP (such as a commercial laundry facility) is present in the area connected to the Bülach STP or that the two STPs differ in their efficiency with respect to DSBP removal. Averaged over the investigation period the two STPs together

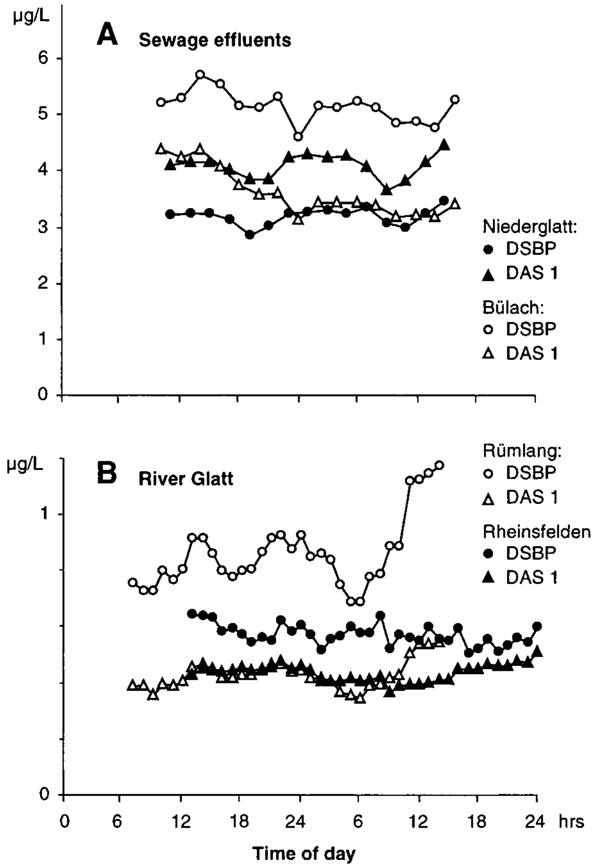

FIGURE 4. Measured FWA concentrations in sewage effluents (A) and river water (B).

deliver an average load of 2.9 g/h each of DSBP and DAS 1 to the river.

Virtually no diurnal variation was observed with the FWA concentrations in the River Glatt at either of the two sampling points (Figure 4B). Concentrations in river water were only 8–10 times smaller than in sewage effluent, underlining the remarkably high load of the river Glatt with treated wastewater. With average loads of 11.6 g/h DSBP and 5.8 g/h DAS 1, the river itself delivers 75% of the FWAs to the investigated river section. The concentration of DSBP in Rheinsfelden is about two-thirds of that in Rümlang, while DAS 1 concentrations are practically identical at both sites. This comparison gives a first indication that the two compounds behave differently during transport in the River Glatt.

Rate constants for direct photolysis of DAS 1 and DSBP were calculated using the program GCSOLAR, on the basis of UV absorption spectra and photolysis quantum yields published by Kramer and co-workers (*6*). To calculate the effect of light attenuation by dissolved organic matter in the river, GCSOLAR also requires the input of the absorbance spectrum of the river water, which was recorded for several samples collected at different times during the field study. The time and depth dependence of the photolysis rate constants were separated as shown in Figure 5. The surface photolysis rates as a function of daytime plot along a Gaussian-shaped curve with a maximum at noon (Figure 5A). The photolysis rate rapidly decreases with depth; this behavior is the same for both FWAs (Figure 5B). For the simulation of photodegradation in AQUASIM, the photolysis rate was expressed by

$$-\frac{\mathrm{d}[\mathrm{FWA}]}{\mathrm{d}t} = k_{\mathrm{time}}k_{\mathrm{depth}}[\mathrm{FWA}]$$

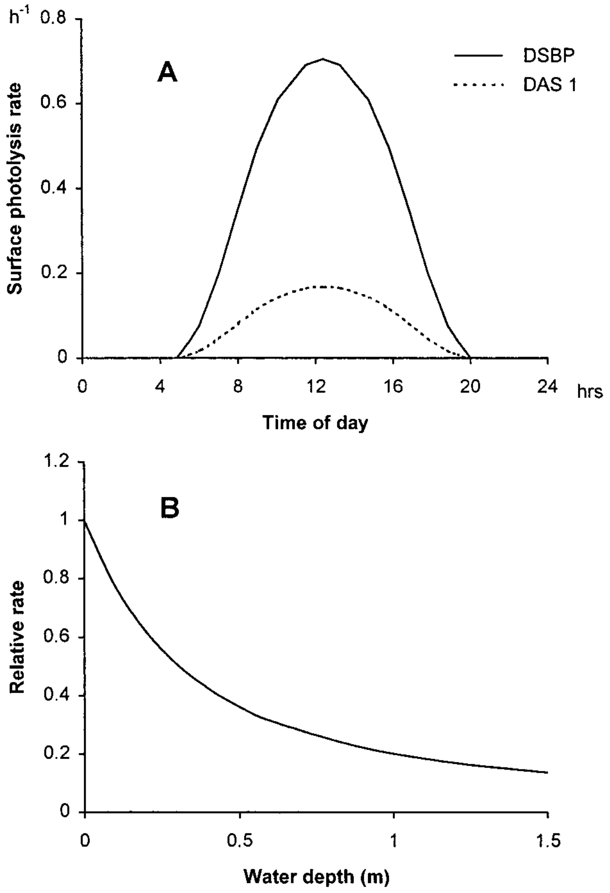

FIGURE 5. Photolysis rates of FWAs in Glatt river water at the surface (A) and integrated over the depth of the water body, relative to the surface rate (B).

where k_{time} and k_{depth} are the time- and depth-dependent terms of the rate constant, which were supplied to the program as two separate lists of data pairs.

For natural waters, it is very difficult to quantify the amount of light that is actually available within the water column. Light is reduced by clouds and overcast conditions, by suspended material and shading effects caused by river macrophytes and by trees that line the river bank. The meteorological conditions during the field study were characterized by cloudless skies so that light attenuation by overcast skies was not a concern. However, the nutrients discharged by the many sewage treatment plants lining the river lead to a dense growth of macrophytes. Additionally, the river is lined by trees at many places. Thus, conventional light measurements within the water body would have failed to yield attenuation data for the whole river section. To account for these difficulties, time- and space-integrated light availability in the River Glatt was determined in situ by release of a pulse of photolabile iron(III) ethylenediaminetetraacetate complex ($\mathrm{Fe^{III}}$–EDTA) (*12*). This complex is approximately 10 times more rapidly photodegraded than DSBP. By observation of the $\mathrm{Fe^{III}}$–EDTA pulse at several locations along the River Glatt and comparison of the measured concentration profiles to calculated profiles it was found that photodegradation is much slower than expected and thus only approximately 15% of the light is available for photolysis within the water column.

Simulations with Photolysis Only. Partitioning of FWAs between sediment or macrophytes attached to the river bed was initially considered being of minor importance, as the River Glatt is constantly loaded with FWAs and sediment/water exchange should thus be in steady state, which means

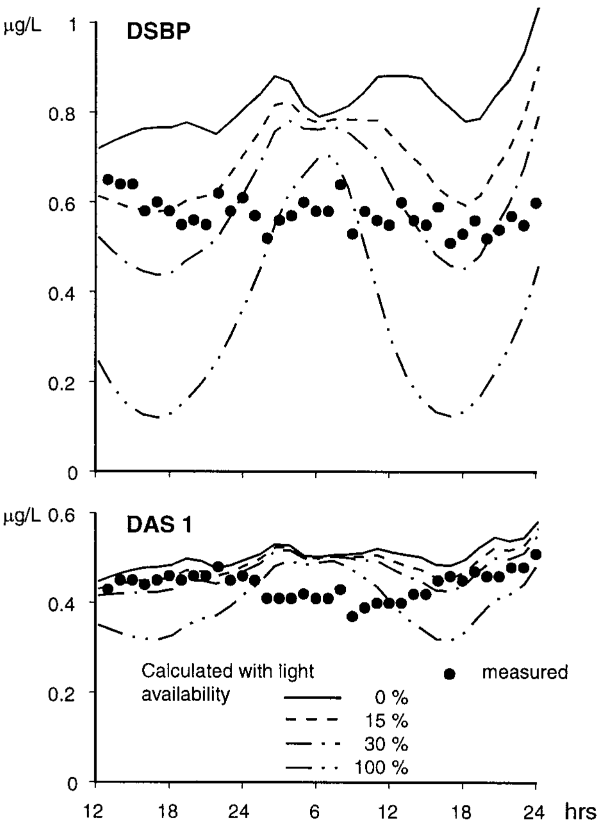

FIGURE 6. Measured and modeled FWA concentrations at Rheinsfelden taking into account only photolysis (no sediment/water exchange). Calculations were performed for different fractions of light available for photodegradation. Annotations: 0%, no photodegradation (conservative model); 30%, 30% light available (70% shading); 100% (no shading).

that the diffusive flux into the sediment equals the diffusive flux out of the sediment. In addition, the River Glatt is a rapidly flowing stream and there is very little sediment accumulation and thus very little potential sequestration of FWAs into the sediments. The sediment is thus considered a pool, rather than a sink for FWAs. Therefore, in a first step sediment/water exchange was not included in the calculations.

Model calculations for DSBP and DAS 1 concentrations at Rheinsfelden (the end of the studied river section) were performed for different percentages of available light (Figure 6). The conservative model (no photodegradation, only transport, dilution, and longitudinal dispersion) is depicted by the solid trace (0%). It clearly shows that some FWA removal has to occur within the river section studied and that the removal of DSBP is much more pronounced than that of DAS 1. This corresponds well with the different photolysis rate constants of the two FWAs (*6*) and is a further indication that photodegradation is the main removal process involved.

The model calculation for the opposite case (100% of the light available for photolysis) obviously underestimates the measured FWA concentrations at Rheinsfelden. As expected, photolysis has a much greater effect on DSBP than on DAS 1. The calculations also show a strong diurnal variation of FWA concentration with minima around noon and maxima at night, which is in contradiction with the measured concentrations. Therefore, another process affecting the environmental behavior must be involved.

Simulation Including Photolysis and Sorption. Small deviations from the steady state between FWA concentrations in the sediment and the water column as produced by the photodegradation of FWAs during the day would lead to a net flux out of the sediment, whereas higher FWA concentrations during the night would lead to a flux into the sediment. To simulate the sediment/water exchange of FWAs with AQUASIM, the following simple kinetic scheme was used:

$$\mathrm{FWA_w} \underset{k_\mathrm{des}}{\overset{k_\mathrm{ads}}{\rightleftarrows}} \mathrm{FWA_s}$$

The following processes were incorporated into AQUASIM:

adsorption:

$$-\frac{\mathrm{d[FWA]_w}}{\mathrm{d}t} = \left(\frac{1}{d_\mathrm{m}}\right)\mathrm{d[FWA]_s}/\mathrm{d}t = k_\mathrm{ads}\mathrm{[FWA]_w}$$

desorption:

$$\frac{\mathrm{d[FWA]_w}}{\mathrm{d}t} = \left(\frac{1}{d_\mathrm{m}}\right)\mathrm{d[FWA]_s}/\mathrm{d}t = \frac{k_\mathrm{des}}{d_\mathrm{m}}\mathrm{[FWA]_s}$$

In the above rate equations $\mathrm{[FWA]_w}$ and $\mathrm{[FWA]_s}$ are the FWA concentrations in the water column and sediment, respectively. The water depth d_m, averaged over the river cross section, was introduced to account for the different units of $\mathrm{[FWA]_w}$ ($\mathrm{mg/m^3}$) and $\mathrm{[FWA]_s}$ ($\mathrm{mg/m^2}$). The rate coefficients for adsorption and desorption, k_ads and k_des of FWAs to Glatt river sediment were determined in batch experiments (*9*). Two types of experiments were performed. In the first experiment, sediment suspended in river water was spiked with a known amount of FWAs and the decrease in $\mathrm{[FWA]_w}$ was observed over time (adsorption experiment). In the second, FWA loaded sediment was added to river water with a very low FWA content and the increase of $\mathrm{[FWA]_w}$ was observed (desorption experiment). The experimental data could be fitted reasonably well with the equation given below, derived for a reversible first-order reaction (*15*):

$$\Delta\mathrm{[FWA]_w} = \Delta\mathrm{[FWA]}_\mathrm{w}^0 \mathrm{e}^{-(k_\mathrm{ads}+k_\mathrm{des})t}$$

In the above equation $\Delta\mathrm{[FWA]_w}$ is the difference between the actual FWA concentration in the water at time t and the concentration at equilibrium. Likewise, $\Delta\mathrm{[FWA]}_\mathrm{w}^0$ is the difference at time zero. From these experiments we obtained the overall sorption rate coefficient $k_\mathrm{sorb} = k_\mathrm{ads} + k_\mathrm{des}$ of 1.2 h^{-1} which was approximately equal for all FWA isomers of DSBP and DAS 1 (data not shown). The individual rate coefficients, k_ads and k_des, can then be derived using the solid/water distribution ratio and the ratio of the amount of solids (M, [kg]) and the volume of water (V, [L]) as

$$K_\mathrm{d}\frac{M}{V} = \frac{k_\mathrm{ads}}{k_\mathrm{des}}$$

Model calculations using $k_\mathrm{ads}/k_\mathrm{des}$ ratios of 1, 10, and 100 with k_ads=1 h^{-1} were performed and an example for a ratio of 10 is shown in Figure 7 for different fractions of light available. As seen in Figure 7, the diurnal variation of FWA concentrations in Rheinsfelden due to photodegradation (Figure 6) is leveled out by sediment/water exchange except for the curve representing 100% light availability. The simulation with a higher $k_\mathrm{ads}/k_\mathrm{des}$ ratio produces curves which are completely flat, whereas in the simulation with a lower ratio the diurnal variation due to photodegradation is only incompletely leveled out (data not shown). For every calculation the initial FWA concentration in the sediments was set so that, on average, no net flux of FWAs to the sediment occurred. Higher $k_\mathrm{ads}/k_\mathrm{des}$ ratios required larger initial sediment concentrations (larger pool). For the cal-

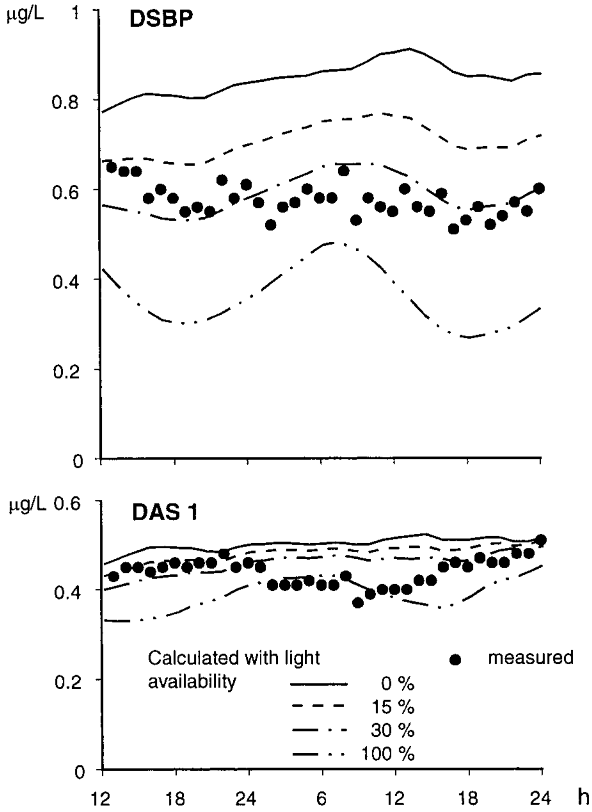

FIGURE 7. Measured and modeled FWA concentrations at Rheinsfelden taking into account photolysis *and* sediment/water exchange. Annotations see Figure 6.

culation shown in Figure 7, sediment concentrations of 1.7–4.3 (DAS 1) and 2.5–6.8 (DSBP) mg/m^2 (water depth 0.4–1.0 m) were used. To relate these surficial concentrations to the concentrations measured in river sediment, the following approximation can be used:

$$[\mathrm{FWA}]_s\ (\mathrm{mg/kg}) = \frac{[\mathrm{FWA}]_s\ (\mathrm{mg/m^2})}{\rho_B 10^3 d_s}$$

Assuming a surficial depth, d_s, of 0.001 m and a bulk dry density, ρ_B, of 0.5 g/cm^3, the surficial concentrations used in the model would be equivalent to 3.4–8.6 and 5.0–13.6 mg/kg DAS 1 and DSBP, respectively, which corresponds well with the measured concentrations of 3.3 and 5.2 mg/kg DAS 1 and DSBP, respectively (*8*).

The best agreement between modeled and measured FWA concentrations (Figure 7) is found when the fraction of light available for photolysis is assumed at 15 (DAS 1) to 30% (DSBP), which is in good agreement with the fraction found in the spike experiment with Fe^{III}–EDTA (*12*).

The approach taken in this simulation has its limitations in the accuracy of the input parameters, as neither rate constants nor surface concentrations of the FWAs can be measured adequately. To significantly improve the accuracy of this model, the amount of sediment surface participating in the exchange and the FWA concentrations on the sediment surface would have to be measured for different stretches of the river several times during the field study. Despite these limitations, this simulation clearly demonstrates that with reasonable values for the input parameters it is possible to reproduce the observed time course for FWA concentrations in the water column.

Degradability of FWAs in the River Glatt. According to an EC directive (*16*) a compound is considered "readily-biodegradable" if it is degraded by more than 70% within 28 days. If a compound is not biodegradable, it can still be called readily-degradable if there is evidence for another process that leads to the same elimination in the aquatic environment. As outlined in the previous discussion, DSBP and DAS 1 are clearly eliminated from Glatt water by photolysis. Over the course of the field study presented here, on average, 31% and 12% of DSBP and DAS 1, respectively, calculated from the difference between the conservative model and the measured data, were eliminated from the River Glatt. This elimination occurs within a flow distance of 22 km or a residence time of the water of 12 h. The in situ rate constants for elimination of DSBP and DAS 1, calculated from this average removal, were 0.74 and 0.26 d^{-1}, respectively. However, the fast elimination rates were observed during summer at near-perfect conditions for photolysis and should thus be considered to be maximum rates. A similar field study conducted in the winter time most likely would have failed to provide accurate data on the elimination of DSBP and DAS 1 because of the small decrease in concentration due to low sunlight intensity.

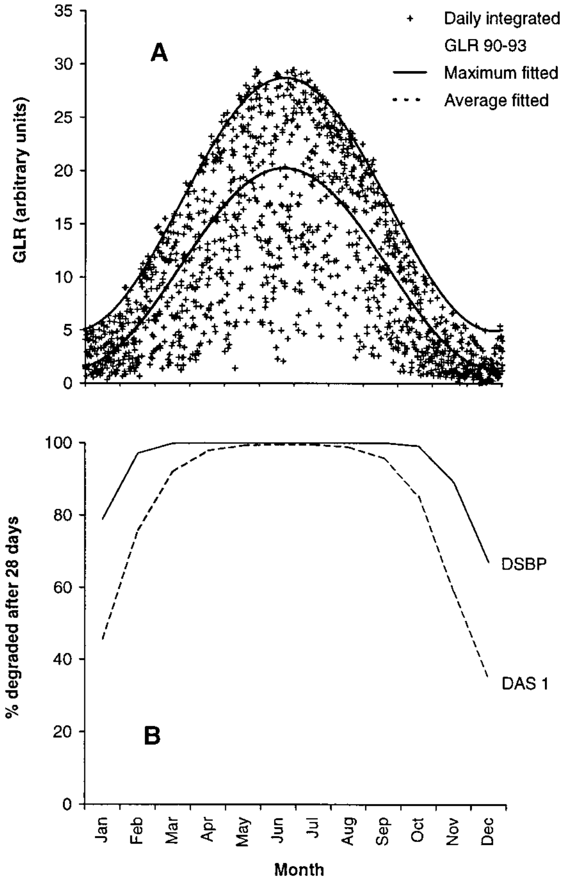

FIGURE 8. Daily integrated global radiation (GLR) for the years 1990–93 with the fitted maximum and average GLR (A) and the fraction of the FWAs degraded in the River Glatt during a residence time of 28 days (B).

The elimination of FWAs can be extrapolated for a full year assuming that all of the removal in the River Glatt is due to photolytical degradation, taking the following factors into account: (i) the seasonal variation of sunlight intensity and (ii) the attenuation of light by overcast skies. An approximation to these two factors can be made by using the data for global radiation measured at a nearby station (Dübendorf, latitude 47.7°). The seasonal variation of light intensity (for cloudless sky) was calculated by fitting a sinus curve to the top 3% of the data points for the years 1989–93 for which consistent and reliable data were available (Figure 8A). The maximum of this curve corresponds to the light conditions encountered during this field study. A second sinus curve, representing the average light conditions, was fitted to all data points. The removal rates observed during this field study were then corrected by the ratio of average available light for a particular day to the maximum light intensity in June and the fraction of FWAs degraded after 28 days were calculated (Figure 8B). These calculations showed that in the River Glatt DSBP is predicted to meet the requirements for ready degradability year round except in December when very little light is available, while DAS 1 is predicted to meet the requirements only from February to October. However, the data in Figure 8 need to be interpreted carefully. Adsorption of FWAs to river sediment and particularly to growing macrophytes (fresh surface) may still provide an additional sink for FWAs in the Glatt river. The contribution of sorption to the overall elimination rate calculated above is, however, expected to be small because of the good agreement between calculated and measured FWA concentration time courses. If sorption indeed had contributed to the elimination, the above extrapolation would overestimate the elimination rate in winter (no growth of macrophytes). It should also be emphasized that the Glatt river is not necessarily an average river with respect to accommodation of photochemical processes. Several factors will increase or decrease photodegradation rates, such as water depth, growth of macrophytes, and concentration of dissolved natural organic matter.

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Note Added in Proof. The forementioned EEC derivative (*16*) calls for complete mineralization. However, the study presented here provides only evidence for primary degradation of DSPB and DAS 1. It should also be noted that for processes other than biodegradation there are currently no standardized test procedures available.

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