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Triclosan: Occurrence and Fate of a Widely Used Biocide in the Aquatic Environment: Field Measurements in Wastewater Treatment Plants, Surface Waters, and Lake Sediments

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Triclosan is used as an antimicrobial agent in a wide range of medical and consumer care products. To investigate the occurrence and fate of triclosan in the aquatic environment, analytical methods for the quantification of triclosan in surface water and wastewater, sludge, and sediment were developed. Furthermore, the fate of triclosan in a wastewater treatment plant (biological degradation, 79%; sorption to sludge, 15%; input into the receiving surface water, 6%) was measured during a field study. Despite the high overall removal rate, the concentration in the wastewater effluents were in the range of 42−213 ng/L leading to concentrations of 11−98 ng/L in the receiving rivers. Moreover, a high removal rate of 0.03 d^{-1} for triclosan in the epilimnion of the lake Greifensee was observed. This is due to photochemical degradation. The measured vertical concentration profile of triclosan in a lake sediment core of lake Greifensee reflects its increased use over 30 years. As the measured concentrations in surface waters are in the range of the predicted no effect concentration of 50 ng/L, more measurements and a detailed investigation of the degradation processes are needed.

Introduction

In Europe, ∼350 tons of triclosan (*1*) commercially known as Irgasan DP 300 or Irgacare MP (for structure, see Figure 1) are presently used as an antimicrobial substance in many products. Triclosan is added as a preservative or as an antiseptic agent in medical products such as hand disinfecting soaps, medical skin creams, and dental products. Triclosan has also found a place in many everyday household products, thanks to successful marketing and increasing acceptance and desire for hygiene products by the public. Today, triclosan can be found as an antimicrobial active component in consumer care products such as toothpaste, mouthwash, and soaps, as well as in household cleaners and even in textiles, such as sportswear, bed cloths, shoes, and carpets. Because of its high antimicrobial effectiveness and its easy processibility in solutions and solids, the popularity of triclosan has continuously increased over the last 30 years.

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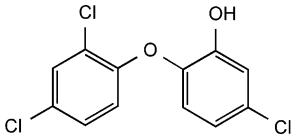

FIGURE 1. Structure of triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol).

The incorporation of triclosan in this vast array of products results in discharge to wastewater treatment plants (WWTPs) and then into surface waters. The major concern of the occurrence of triclosan in surface water is its toxicity to certain algae species, i.e., *Scenedesmus subspicatus*. For this species, a no observed effect concentration (NOEC) of 500 ng/L has been determined (*2*, *3*). Considering the commonly used safety factor of 10, a predicted no effect concentration (PNEC) of 50 ng/L is obtained (*2*). Moreover, some recent findings gave rise to a controversial discussion about a possible bacterial resistance to triclosan, which may result from its property to block lipid biosynthesis by specifically inhibiting the enzyme enoyl-acyl carrier protein reductase (*4*, *5*).

For a simple environmental risk assessment, the PNEC of triclosan can be compared with measured triclosan concentrations. Only a few data are available in the literature on the occurrence of triclosan in the aquatic environment. Triclosan was found in wastewater (0.07−14 000 μg/L) (*6*−*9*), in streams (50−2300 ng/L) (*8*, *10*), in seawater (50−150 ng/L) (*11*), and in sediments (1−35 μg/kg) (*12*). These sporadic measurements are hardly sufficient, even for a simple exposure analysis. For a more established exposure assessment, a better understanding of the processes that determine the fate of triclosan in the environment is required.

Triclosan is a chlorinated phenoxyphenol with a pK_a of 8.1 (*13*). The pH of the surface waters (common range between 7 and 9) has thus a big influence on its speciation and therewith on its fate and behavior. The relatively high octanol−water partition coefficient (log K_{ow} of 5.4) of its protonated form (*13*) can lead to sorption to particles. Moreover, as the dissociated form of triclosan absorbs sunlight (*13*), photodegradation may be a possible elimination process for triclosan in surface water. On the other hand, triclosan is quite stable against hydrolysis (*2*).

Since only a few data on the environmental behavior of triclosan are available in the literature, the aim of this research was to determine the occurrence and fate of Triclosan in wastewater treatment plants, in surface waters (rivers and lakes), and in sediments. Further, only a few analytical methods can be found in the literature mainly based on liquid−liquid extraction as the sample preparation step (*7*, *8*, *10*−*12*, *14*, *15*). Therefore, sensitive and precise analytical methods were developed for the quantification of triclosan in surface waters and wastewater as well as in sediments and sludge. These methods allowed us to carry out mass flux studies in the hydrological catchment area of lake Greifensee in Switzerland (see Figure 2).

Experimental Section

Analysis of Triclosan in Water. All water samples were filtered immediately after collection in the laboratory with high-pressure filtration equipment MD142-5-3 (Schleicher & Schuell) using pure cellulose membrane filters RC55 (pore size 0.45 μm; diameter 142 mm; Schleicher & Schuell) and stored at 4 °C in the dark overnight. The analysis took place the next day. One liter of the filtered water (pH adjusted to 3) was spiked with 10 μL of a 10 ng/μL solution of 5-chloro-

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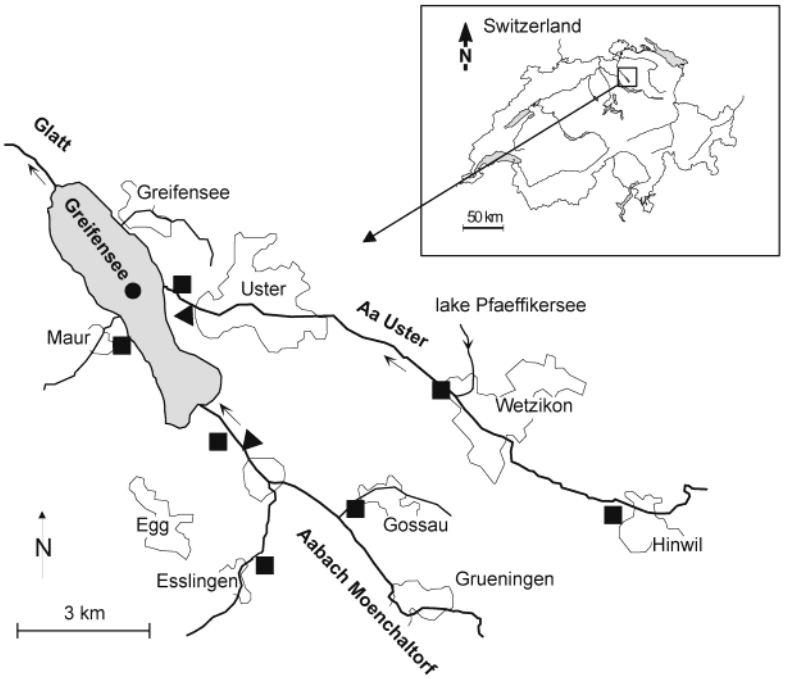

FIGURE 2. Map of lake Greifensee study area with cities and major rivers. The sampling sites are marked as follows: ■ wastewater treatment plants; ▼ rivers; ● lake (deepest point).

(2,4-dichloro-[$^{13}C_6$]-phenoxy)phenol in ethanol as an internal standard ($^{13}C_6$-labeled triclosan was kindly provided from Ciba SC, Basle, Switzerland). The solid-phase extraction of the water samples and the derivatization of the extracts is described by Oellers et al. (*16*). A 2-μL aliquot of the extract was injected splitless in a HRGC8000 (Fisons, England) (injection temperature 250 °C). A 30-m RTX-5MS (0.25-mm i.d.) fused-silica column (Restek, Bad Homburg, Germany) was used with helium as carrier gas (1.5 mL/min). The temperature program was set up as follows: 1 min at 90 °C, first ramp 15 °C/min to 150 °C, 15 min at 150 °C, second ramp 5 °C/min to 200 °C, 5 min at 200 °C, third ramp 15 °C/min to 290 °C, and held at this temperature for 5 min.

Detection was performed with a MD800 mass spectrometer (Fisons Instruments) in the positive electron impact mode (70 eV, 220 °C). For triclosan methyl ether (methyl triclosan), the ions m/z 302 (quantification ion), 304, and 252 and for [$^{13}C_6$]-triclosanmethyl ether, the ions m/z 308 (quantification ion), 310, and 258 were acquired in the single ion monitoring mode (SIM) with a dwell time of 0.1 s by ensuring the correct ion ratios (<20% variation) and retention time. The amount of triclosan in the samples was calculated from eight-point calibration curves generated with spiked (triclosan and [$^{13}C_6$]-triclosan), extracted, and derivatized Nanopure water samples. Blank samples with Nanopure water were regularly analyzed to ensure that the samples were not contaminated with triclosan during the analysis. For recovery experiments, derivatized standard solutions of [$^{13}C_6$]-triclosan and triclosan were prepared in ethyl acetate. The setup of the recovery experiments was the same as described elsewhere (*17*). The derivatization yields were determined with solutions of triclosan methyl ether (kindly provided by Ciba SC, Basle, Switzerland) in ethyl acetate.

Analysis of Triclosan in Sludge and Sediments. One-gram aliquots of the freeze-dried and homogenized sludge or sediment sample were weighted into 2-mL stainless steel extraction cells and spiked with 10 μL of a 10 ng/μL [$^{13}C_6$]-triclosan solution in ethanol. After complete mixing with quartz sand, an accelerated solvent extraction (ASE) was carried out in three cycles, each with 2 mL of dichloromethane for 5 min at 100 °C and 103 bar, in a Dionex ASE 200 device equipped with a solvent controller (Sunnyvale, CA). To remove polar impurities, the combined extracts were reduced under a nitrogen stream to ~2 mL, percolated through a conditioned silica column (2 g of silica gel 60 in a 3-mL cartridge, deactivated with 5% water and conditioned with 2 mL of dichloromethane) and rinsed with 2 mL of dichloromethane. The evaporation of the extract, the derivatization procedure, and the conditions for the chromatographic separation were the same as for the water samples.

The derivatized sediment extracts were analyzed with a ThermoQuest (Austin, TX) gas chromatograph TraceGC2000 coupled with an ion trap mass detector GCQ (positive electron impact ionization mode, 70 eV, 220 °C). The selectivity was increased by MS/MS experiments (parent ion m/z 302 and 308 of triclosan and [$^{13}C_6$]-triclosan methyl ether, respectively; ion isolation time of 8 ms; maximum ion injection time of 25 ms). The product ions were scanned (m/z 150−310) after a collision-induced dissociation with argon, at an excitation voltage of 1.5 V for 15 ms at a q value of 0.45 (the q value refers to the resonance voltage). The single reaction monitoring (SRM) transitions m/z $302^+ \rightarrow 252^+$ and $308^+ \rightarrow 258^+$ were used for the quantification and the transitions m/z $302^+ \rightarrow 232^+$ and $308^+ \rightarrow 238^+$ for the confirmation. The calibration curve was produced by using derivatized standard solutions in ethyl acetate. Blank samples with pure quartz sand were processed to show that no triclosan carry-overs took place. Different recovery experiments were done by spiking lake Greifensee sediment from 1960 to 1961 with 100 ng/g triclosan i) before extraction, ii) before the cleaning step with silica gel and iii) before the derivatization with diazomethane. For each recovery experiment, three replicate analyses were carried out.

Description of Field Sites and the Sampling Procedure. Wastewater Treatment Plants. Figure 2 gives an overview of the 130-km^2 study area in which ~90 000 people live (the catchment area of lake Pfäffikon is excluded). The treatment in all seven WWTPs (see squares in Figure 2) consists of three steps: mechanical clarification, biological treatment (nitrification), and flocculation filtration. Note that the effluent is not disinfected by any further treatment such as chlorination. In two WWTPs (Gossau and Wetzikon), biological treatment

TABLE 1. Concentration and Load of Dissolved Triclosan in Weekly Flow-Proportional Effluent Samples (June 7−13, 1999) of All WWTPs in the Catchment Area of Lake Greifensee

WWTP site	inhabitants serviced	sewage flow, m^3/day	treated effluent: concn of dissolved triclosan, ng/L	treated effluent: load of dissolved triclosan, g/day	treated effluent: per capita output load, mg/day per 1000 persons
Uster[a]	34000	29390	103	3.0	90
Wetzikon	17500	15150	213	3.2	180
Egg	11200	8190	58	0.5	40
Gossau	10500	8 010	42	0.3	30
Hinwil	8900	11110	123	1.4	150
Maur[a]	4500	5480	173	1.0	210
Moenchaltorf[a]	3100	1940	103	0.2	60
total	89700	88080		9.6	

[a] Directly discharging into lake Greifensee.

is supplemented with an anoxic zone for denitrification. In failure-free operation, all WWTPs remove at least 85% of influent *chemical oxygen demand* (COD) and at least 95% of the influent *biological oxygen demand* (BOD). The detailed characteristics of the WWTPs are summarized in Table 1 and ref *18*. As almost everywhere in Switzerland, the sewer system is equipped with combined sewer overflows (CSOs). Due to strong variations in the storm magnitude threshold of the more than 100 CSOs in the catchment area, the amount of overflowing sewage water during stormwater events is unknown.

From June 7 to June 13, 1999, from all seven WWTP 72-h flow-proportional composite samples were collected from the effluent. The samples were kept cool inside the sampler at 4 °C. Every third day, the samples were transported to the laboratory and mixed to get weekly flow-proportional composite samples for each WWTP.

From August 16 to October 22 1999, weekly flow-proportional effluent samples were collected in the same way for the WWTPs of Uster, Maur, and Moenchaltorf (directly discharging in the epilimnion of lake Greifensee).

For a detailed mass flux investigation in the Gossau WWTP, additional samples from the outlet of the primary and secondary sedimentation were drawn for the time period from June 7 to June 13. With the aid of a scoop, 15 L of sludge was taken from the activated sludge tank of the Gossau WWTP and then transported in a glass bottle to the laboratory. The centrifuged solid was immediately freeze-dried.

Rivers. From August 16 to October 22, 1999, the two main tributaries Aa Uster and Aabach Moenchaltorf (see Figure 2) were sampled with portable samplers (Manning Products). Flow monitoring stations of the governmental authorities were used to get 72-h flow-proportional composite samples. The samplers were equipped with glass bottles and Teflon suction lines. The samples were picked up every third day and combined for the both rivers separately to weekly flow-proportional composite samples in the laboratory.

It must be pointed out that the sorption potential of the samplers and the degradation during storage were checked by a test with spiked river and effluent water (triclosan spike level 300 ng/L). No triclosan sorption took place in the sampling equipment (data not shown). The triclosan degradation was less than 10% both in the river and in the WWTP installations during the maximum storage time of 3 days in the field (see Figure S1 in the Supporting Information).

Lake Greifensee. Greifensee is a small eutrophic lake with regular deep-mixing over winter (from December to March) and a mean water residence time of 408 days. Its detailed hydraulics and morphology have already been described in detail before (*19*). The main data are summarized in Table S1 (see Supporting Information).

On August 16 and October 22, 1999, water samples were collected above the deepest point of the lake (filled circle in Figure 2), at seven depths, with a stainless steel sampling bottle (Friedinger, Lucerne, Switzerland). Vertical concentration profiles at this location were assumed to be representative for the whole lake due to the fast horizontal mixing compared to the slow vertical one (*20*).

A sediment core was taken in autumn 1998 in the middle of the lake (filled circle in Figure 2) with the help of a remote-controlled freeze corer (for a detailed description see ref *21*). The sediment core was cut into annual layers, which could be easily identified by their oxic and anoxic color structure. As an additional dating method for the annual layers, the ^{137}Cs signal from Chernobyl 1986 and atomic bomb tests from 1963 were used (for method details, see ref *22*). The sediment layers were freeze-dried in a high-vacuum equipment. The samples were kept at −20 °C in the dark. In 1999, two-year bulk samples were analyzed in order to get a sediment depth profile representing a time range of 1960−1993.

Results and Discussion

Performance of the Analytical Method for Surface Water and Wastewater. The analytical method for water samples consists of the four steps, filtration, enrichment, derivatization, and GC/MS analysis, which were all optimized. Several filter materials were tested (at concentration levels of 20 and 100 ng/L). The membrane filters made of regenerated cellulose caused negligible loss of triclosan (absolute recovery, >92%), whereas the polyamide filters caused an almost total holdback of the dissolved triclosan (absolute recovery ~3%). Solid-phase enrichment using Oasis cartridges yielded high absolute recoveries of triclosan in distilled water (89 ± 3%), lake water (82 ± 1%), and wastewater effluent (91 ± 2%).

The maximum reaction yields for the derivatization with diazomethane were reached with an addition of 10 vol % methanol. The maximum yield was reached at 30 min (distilled water, 85 ± 9%; lake water, 74 ± 6%; and wastewater effluent, 58 ± 8%).

The relative recoveries of triclosan from lake water and wastewater effluent, using [$^{13}C_6$]-triclosan as an internal standard, resulted in 105% (±6%) over the whole method (filtration, enrichment, derivatization, separation, and quantification). The limit of quantification (LOQ, signal-to-noise ratio, 1:10) in lake water and wastewater were 1 and 5 ng/L, respectively. The relative standard deviation (RSD) of the results for 10 identical lake water samples (Greifensee) was 5% at a level of 11 ng/L. The RSD of the results for 10 identical WWTP samples (Maur WWTP) was 6% at an average concentration of 400 ng/L. The calibration generated with extracted spiked Nanopure water proved to be linear (correlation coefficient, $r^2 > 0.999$) within the range of 1−500 ng/L. The chromatogram of a lake water sample illustrates the performance of the analytical method (see left plot of Figure S2 in the Supporting Information).

Methyl triclosan is a potential biotransformation product of triclosan. Due to the analytical procedure used, the measured triclosan corresponds to the sum of triclosan and methyl triclosan. However, by splitting the extract before the derivatization step, methyl triclosan could be determined in the underivatized fraction. The concentration of methyl triclosan analyzed in some lake water (epi- and hypolimnion) and river water samples was found to be ~0.5 ng/L, which is already below the LOQ. In some randomly selected WWTP effluent samples, methyl triclosan concentrations were always below the LOQ of 5 ng/L (all values were somewhat above the limit of detection of 2 ng/L). These data for methyl triclosan correlate well with the published data of Lindström et al. (*8*). Due to the low concentrations and low fraction of methyl triclosan compared to triclosan, methyl triclosan can be considered to be negligible, and therefore, in the following discussion the sum of triclosan and methyl triclosan is always presented.

Performance of the Analytical Method for Sludge and Sediments. ASE was chosen for the extraction of triclosan from freeze-dried and homogenized sludges and sediments. Besides a number of solvents and solvent mixtures with different polarity (from acetonitrile to toluol), all relevant extraction conditions (temperature, pressure, solvent volume, and number of extraction cycles) were evaluated. The best absolute extraction yields of 99% (±2%) were obtained at 100 °C, 103 bar, and after a triple extraction with 2 mL of dichloromethane. An absolute recovery of 95% (±3%) was obtained for the cleanup step of the dichloromethane extract on silica gel (deactivated with 5% water), and a derivatization yield of 58% (±5%) was achieved after addition of 10 vol % methanol. The relative triclosan recovery for the whole method (referring to the internal [$^{13}C_6$]-triclosan) was 100% (±3%). The LOQ for lake sediment was 5 ng/g dry matter. The sediment analysis (Greifensee, 1988/1989) showed a good precision ($n = 3$) with an average concentration of 37 ± 4.4 ng/g (dry matter). The method performance is illustrated by the chromatogram of a lake Greifensee sediment sample from 1988 to 1989 (see right plot of Figure S2 in the Supporting Information).

Since the organic carbon−water partition constant (K_{oc}) of 4.0×10^4 L/kg for methyl triclosan (see ref *8*) is about the same as for triclosan (see below), the fraction of methyl triclosan can be estimated to be about the same as in water samples. This means that the presented values of the sum of triclosan and methyl triclosan for sludge and sediment contains in average ~5% methyl triclosan, what is confirmed by measurements of methyl triclosan in activated sludge by McAvoy et al. (*7*).

Occurrence and Fate of Triclosan in a Wastewater Treatment Plant. The occurrence and fate of triclosan, i.e., its degradation and its sorption to sludge, were quantified under real world conditions in the Gossau WWTP during one week (sampling see Experimental Section). The wastewater cleaning procedure in this WWTP consists of four steps: mechanical treatment, activated sludge treatment with a preceding denitrification step, and phosphate precipitation with filtration in the effluent (see Figure 3). In a grab sample from the activated sludge tank, a concentration of 580 ng/g (dry matter) and of 35 ng/L was found for adsorbed (c_s) and dissolved triclosan (c_w), respectively. These measurements allowed us to determine an organic carbon−water partition constant (K_{oc}) of 4.7×10^4 L/kg, using the following equation

$$c_s = K_{oc} c_w f_{oc} (1 + 10^{(pH - pK_a)})^{-1} \quad (1)$$

and considering an organic carbon content fraction (f_{oc}) of the sludge particles of 0.4 and a measured pH of 7.3.

Average dissolved concentration of triclosan in the weekly flow-proportional composite samples ranged from 520 ng/L in the primary clarified effluent to 45 ng/L in the secondary effluent. From the measured dissolved triclosan, the calculated adsorbed triclosan (based on the measured K_{oc} value, see above), and the measured water flow, we were able to determine the total mass flux of triclosan in this WWTP. Over the one-week survey, 79% of triclosan was biologically degraded and 15% was removed with the excess sludge (see Figure 3). This observed high biological degradation, which could be a complete mineralization to CO_2, a primary biotransformation (see ref *23*), or both, and this strong sorption to sludge of triclosan in the Gossau WWTP are in accordance with the results of other activated sludge treatment plants (see ref *7*). However, despite the high standard of this WWTP and its high removal performance, 6% of the triclosan entering the plant left in the effluent (after the filtration stage) at a concentration of 42 ng/L.

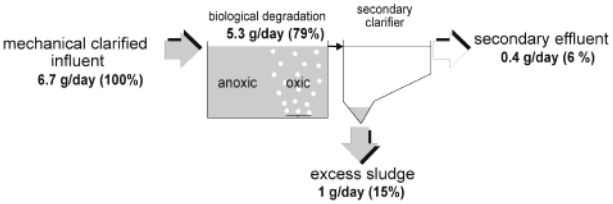

FIGURE 3. Mass flow of triclosan (dissolved and undissolved) for the biological treatment step in the wastewater treatment plant of Gossau. Note: Due to the chosen sampling points, triclosan removal during the primary mechanical treatment and the filtration of the secondary effluent is unknown.

Triclosan Concentrations in the Effluents of Seven WWTPs and in the Two Receiving Rivers. To evaluate the range of the triclosan concentrations in different WWTP effluents and to quantify the input of triclosan into surface water on a regional scale, WWTP effluent samples were collected from all WWTPs in the catchment area of lake Greifensee (for details see the Experimental Section, Figure 2, and Table 1). All seven WWTPs have similar BOD or COD removal efficiency. Moreover, the filtration stage leads to a suspended solid concentration of ~10 mg/L in all effluent samples. Therefore, the transport of triclosan by particles can be calculated as ~10% for all WWTPs (see eq 1, and assuming similar pH and f_{oc} as for Gossau WWTP). Thus, in the samples, only the dissolved fraction of triclosan was analyzed. The concentration of triclosan in the effluents entering the rivers ranged between 42 and 213 ng/L and the corresponding triclosan loads were between 0.2 and 3.2 g/day. Assuming that private households were the only sources of triclosan, the output load by the treated effluents corresponded to 30−210 mg of triclosan/1000 inhabitants per day (see Table 1).

Figure 4 shows the time course of triclosan concentration in the rivers Aa Uster and Aabach Moenchaltorf from August 16 and October 22, 1999. Despite a rather constant triclosan concentration in the outflow of the WWTPs (see Figure 5), the triclosan concentration in the river Aa Uster (see Figure 4) increased by a factor of 5 during high-water events (first week of October). This increase may be due to the discharge of untreated wastewater from the sewer system into the river by CSOs during rain events. For the river Aabach Mönchaltorf, the impact of untreated wastewater through stormwater overflow systems is smaller than for the river Aa Uster. A rather constant triclosan concentration of ~20 ng/L was observed in this river during the whole field study. According to these results, triclosan concentrations measured in surface water sometimes exceeded the PNEC of 50 ng/L. Therefore, a more detailed risk assessment is needed (see discussion below).

Fate of Triclosan in the Lake Greifensee. The fate of triclosan in surface water was determined by establishing a

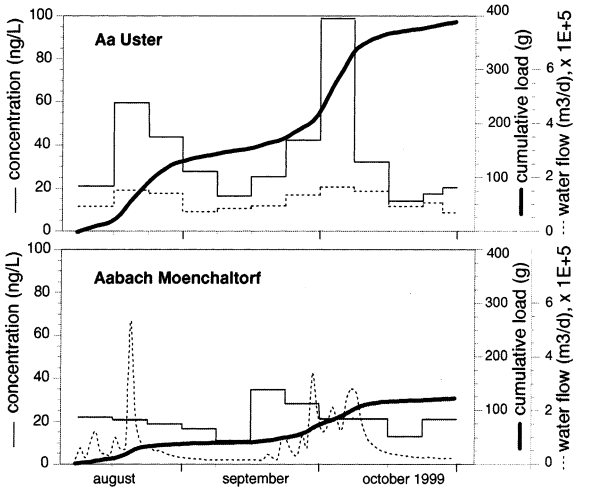

FIGURE 4. Time course of the measured dissolved triclosan concentration (thin line), the corresponding cumulative triclosan load (thick line), and the water flow (broken line) in the main tributaries during the study period from August 16 to October 22, 1999. Note: for the water flow of Aa Uster, only average weekly values were available.

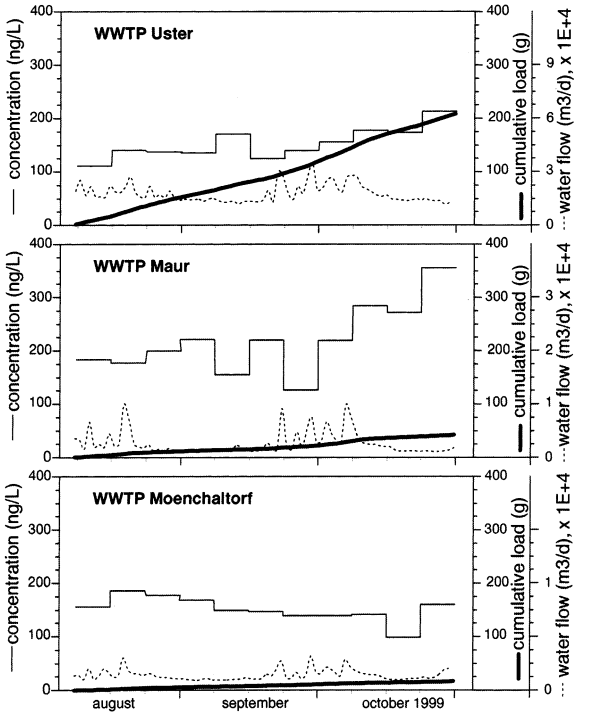

FIGURE 5. Time course of the measured dissolved triclosan concentration (thin line), the corresponding cumulative triclosan load (thick line), and the water flow (broken line) in the wastewater treatment plants, which discharge directly into the lake from August 16 to October 22, 1999.

simple mass balance over a three-month period using the lake Greifensee as the system boundary (see Figure 6 and ref *19*). The measured input of triclosan into the lake was 720 g (input by the two rivers and the three WWTPs directly discharging into the lake). The total amount of triclosan in the lake, determined from the vertical depth profiles at the beginning and at the end of the study period, decreased from 1450 to 1290 g (or by 160 g). Furthermore, 130 g of triclosan was flushed by the river Glatt. Therefore, an overall elimination/degradation of 750 g of triclosan over this time period can be calculated.

This overall elimination rate of 0.03 d^{-1} for triclosan in the lake water column is the sum of different transport and transformation processes and does not include the flushing rate of 0.006 d^{-1} through the lake outflow. The relative importance of each process can be estimated with simple *back-of-the-envelope* calculations (for details see refs *19* and *24*) based on the physicochemical properties of triclosan and the lake properties (see Table S1 in the Supporting Information). In the following, we will briefly discuss the different processes. Note that the discussion refers to the period from August to October.

Due to the low vapor pressure of 5.4×10^{-4} Pa (*2*) and the stability against strong acids and bases, triclosan elimination through gas exchange or chemical hydrolysis in the lake water can be neglected.

The sedimentation rate constant k_{sed} for triclosan was calculated by assuming sorption equilibrium and a linear sorption isotherm. For the well-mixed epilimnion, a sedimentation rate constant of 0.003 d^{-1} was obtained, considering a mean epilimnion depth of 6.6 m, an average particle settling velocity of 1 m/day, and a particle concentration of 5×10^{-6} kg/L. Furthermore, the sorption active speciation of triclosan was supposed to be the undissociated form. With an average pH of 8.6 in the epilimnion, 24% of the triclosan is undissociated and 98% of the undissociated triclosan is in dissolved form. A sedimentation rate constant k_{sed} of 0.001 d^{-1} was calculated for the hypolimnion. This value corresponds to a third of the sedimentation rate calculated for the epilimnion. The difference comes from the combined effect of a higher hypolimnion depth and a lower pH value of 7.5.

For triclosan photolysis, Spare (*25*) reported a photolysis rate of 1.68×10^{-2} min^{-1}, obtained after irradiation of a triclosan solution in Nanopure water, at pH 7 with artificial sunlight. As a first approximation, this value was taken as the phototransformation rate of triclosan at the surface of the lake. By integrating this value over a well-mixed epilimnion of 6.6-m depth using the GCSOLAR program (*26*), a phototransformation rate of 0.14 d^{-1} could be determined for the epilimnion of lake Greifensee for a clear sky summer day. Including a 50% decrease of the light intensity due to clouds (estimated from global radiation measurements at Swiss Federal Laboratories for Material Testing, Dübendorf, Switzerland), this estimated direct photolysis rate of 0.07 d^{-1} represents the most important degradation process of triclosan in lake Greifensee.

However, this value should be considered cautiously because the calculations were based on a photolysis transformation rate obtained under laboratory conditions using artificial sunlight at pH 7. At this pH, only 7% of triclosan is in its dissociated form and a previous study has shown that only the absorption spectrum of the dissociated form presents an overlap with the sunlight spectrum (*13*)—an essential condition for direct photolysis. With a real pH of 8.6 in the epilimnion, the percentage of the anionic form of triclosan is higher than at pH 7. However, to determine a phototransformation rate in these natural conditions, the reaction quantum yields for both triclosan species (dissociated and nondissociated triclosan) have to be considered, as well as the influence of the dissolved organic matter. Note that we have recently evaluated and quantified these parameters in detailed laboratory and field studies (see Tixier et al. (*27*)).

Triclosan in the Sediment. Figure 7 shows a vertical concentration profile of triclosan in a sediment core taken in the middle of lake Greifensee. The increasing triclosan concentrations from the early 1960s until the mid-1970s indicates the steadily increased use of triclosan. The decrease of the triclosan concentration observed from the mid-1970s until the early 1980s reflects the introduction of biological wastewater treatment stages in the WWTPs serving the surrounding catchment. However, due to the popularity of

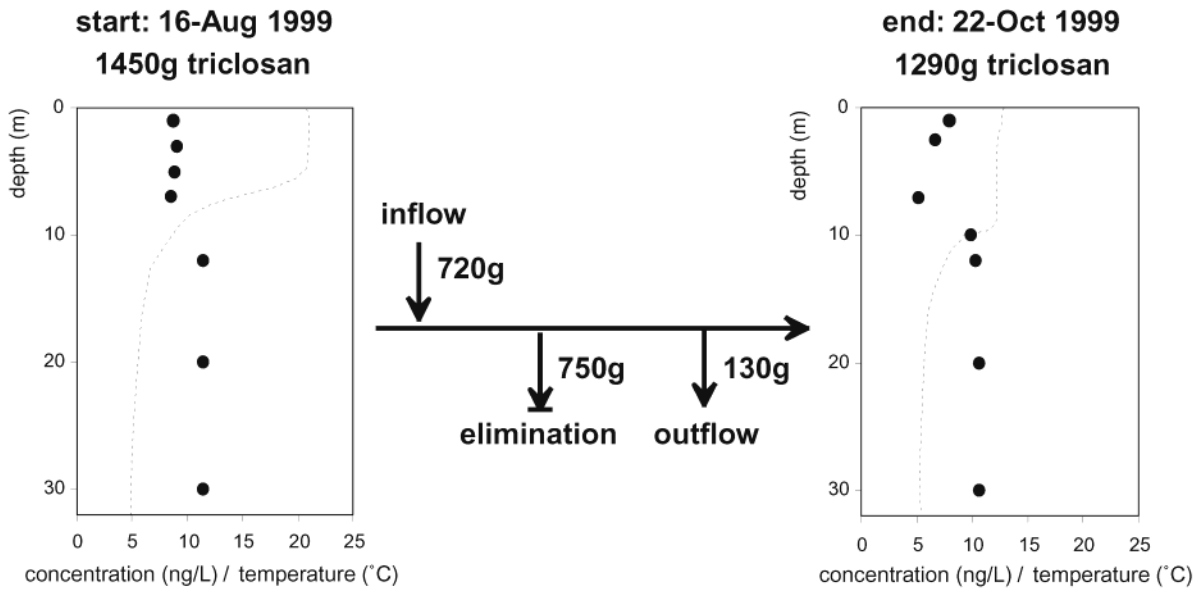

FIGURE 6. Mass balance of dissolved triclosan in lake Greifensee for the field study period from August 16 to October 22, 1999. The amount of degraded triclosan (750 g) was calculated from the sum of measured input (720 g), outflow (130 g), and lake content of triclosan (start, 1450 g; end, 1290 g) as follows: 1450 + 720 − 750 − 130 = 1290 g. The graphs show the vertical concentration profile of triclosan (filled circles) and the water temperature (dashed line) at the beginning and the end of the mass balance period. Note: The lake content of triclosan was calculated from the measured concentration profile and the corresponding lake water volume. The outflowing triclosan load was calculated from the measured water flow of river Glatt and the average triclosan concentration of the epilimnion.

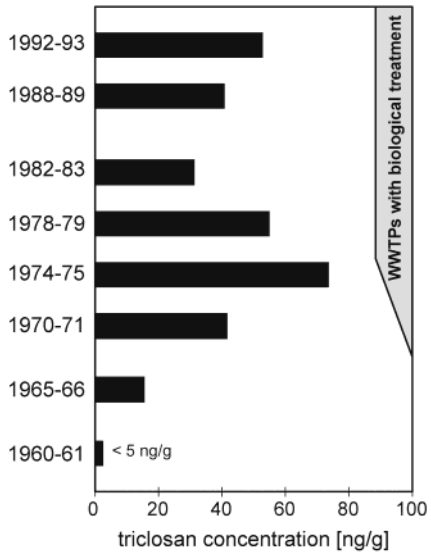

FIGURE 7. Depth profile of triclosan concentration determined in lake Greifensee sediment. The upgrade of the WWTPs in the catchment area with a biological treatment stage is indicated in the graph.

triclosan, the input into the lake sediment continued to increase from the early 1980s until now. This discussion is based on the assumption that triclosan is fairly persistent in the sediment, which has not been verified so far. Nevertheless, the quite high amount of triclosan contained in the 30-year-old sediment layer from 1970 to 1971 showed that triclosan degradation has to be very slow in the sediment.

The measured triclosan concentration of 53 ng/g in the upmost sediment layer is in the same order of magnitude as the triclosan concentration in the sinking particles (125 ng/g—see eq 1, assuming 10 ng/L triclosan in the hypolimnion and a pH of 7.8). The good correlation between the estimated and the measured value confirms the results from the back-of-the-envelope calculations.

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Supporting Information Available

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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