ENVIRONMENTAL CONCENTRATIONS OF BORON, LAS, EDTA, NTA AND TRICLOSAN SIMULATED WITH GREAT-ER IN THE RIVER ITTER

Wind T, Werner U, Jacob M and A Hauk

Journal
Chemosphere

Volume (Number), Pages, Year
54, 1135-1144, 2004

Abstract of paper
A computer simulation of the environmental concentration of some typical consumer-product ingredients was performed using the geo-referenced exposure model GREAT-ER (Geo referenced Regional Environmental Assessment Tool for European Rivers) in the river Itter. Boron and LAS were chosen as typical detergent ingredients along with EDTA, NTA and triclosan as examples of household and cosmetic product ingredients. The simulations were based on consumption figures of the respective chemical in consumer products in the year 2000. For EDTA, the consumption figure used for the calculation had to be extended to commercial products since the EDTA-use in domestic products could not account for the measured concentration alone. The resulting PEC (Predicted Environmental Concentration) for all investigated compounds showed very good accordance to the measured concentrations in the Itter which were monitored in the same year. The concentrations did not deviate more than by a factor of 3. GREAT-ER’s calculated 90th-percentil was never exceeded by the monitoring results thus reflecting a reasonable accuracy.
OCURRENCE OF METHYL TRICLOSAN, A TRANSFORMATION PRODUCT OF THE CBACTREIOCIDE TRICLOSAN IN FISH FROM VARIOUS LAKES IN SWITZERLAND

Balmer ME, Poiger T, Droz C, Romanin K, Bergqvist PA, Müller MD and HR Buser

Abstract of paper

The bactericide triclosan and methyl triclosan, an environmental transformation product thereof, have been previously detected in lakes and a river in Switzerland. Both compounds are emitted via wastewater treatment plants (WWTPs), with methyl triclosan probably being formed by biological methylation. Passive sampling with semipermeable membrane devices (SPMDs) showed the presence of methyl triclosan in some lakes, suggesting some potential for bioaccumulation of the compound. In this study, we report the presence of methyl triclosan in fish (white fish, coregonus sp.; roach, rutilus rutilus) from various lakes in Switzerland receiving inputs from WWTPs. Identification of the compound was based on mass spectral (MS) evidence including MS/MS data. The concentrations of methyl triclosan in the fish were up to 35 ng g\(^{-1}\) on a wet weight basis and up to 365 ng g\(^{-1}\) on a lipid basis with concentrations in a relatively narrow range for fish from the same lake (Thunersee, 4-6 ng g\(^{-1}\); Zürichsee, 32-62 ng g\(^{-1}\); Pfäffikersee, 43-56 ng g\(^{-1}\); Greifensee, 165-365 ng g\(^{-1}\), lipid basis). No methyl triclosan (<1 ng g\(^{-1}\), lipid basis) was detected in fish (lake trout, salmo trutta) from a remote lake in Sweden (Häberstjärnen) and in fish (roach) from a small lake in Switzerland with no input from WWTPs (Hüttnersee, <2->5 ng g\(^{-1}\), lipid basis). The concentrations of methyl triclosan in fish correlated (r\(^2\) = 0.85) with the ratio of population in the watershed to water throughput of the lakes (P/Q ratio), which is considered to be a measure for the domestic burden from WWTPs to a lake. Passive sampling with SPMDs confirmed the presence of methyl triclosan in lakes and a river (Zürichsee and Greifensee; Limmatt) but not in a remote mountain lake (Jörisee) and in Hüttnersee. The bioconcentration factor (BCF) of methyl triclosan estimated from the fish data and SPMD-derived water concentrations was in the order of 1-2.6 \(\times\) 10\(^5\) (lipid basis) and thus in the range of other persistent organic pollutants. SPMDs were found to be reliable for monitoring low concentrations of methyl triclosan in surface water. Methyl triclosan appears to be a suitable...
marker for WWTP-derived lipophilic contaminants in the aquatic environment and fish.
OCCURRENCE OF METHYL TRICLOSAN, A TRANSFORMATION PRODUCT OF THE CBACTREIIOCIDE TRICLOSAN IN FISH FROM VARIOUS LAKES IN SWITZERLAND

Lindström A, Buerge IJ, Poiger T, Bergqvist PA, Müller MD and HR Buser

Journal
ENVIRONMENTAL SCIENCE AND TECHNOLOGY

Volume (Number), Pages, Year
36, 2322-2329, 2002

Abstract of paper
The bactericide triclosan and methyl triclosan, an environmental transformation product thereof, were detected in lakes and in a river in Switzerland at concentrations of up to 74 and 2 ng L\(^{-1}\), respectively. Both compounds were emitted via wastewater treatment plants (WWTPs), with methyl triclosan probably being formed by biological methylation. A regional mass balance for a lake (Greifensee) indicated significant removal of triclosan by processes other than flushing. Laboratory experiments showed that triclosan in the dissociated form was rapidly decomposed in lake water when exposed to sunlight (half-life less than 1 h in August at 47° latitude). Methyl triclosan and nondissociated triclosan, however, were relatively stable toward photodegradation. Modeling these experimental data for the situation of lake Greifensee indicated that photodegradation can account for the elimination of triclosan from the lake and suggested a seasonal dependence of the concentrations (lower in summer, higher in winter), consistent with observed concentrations. Although emissions of methyl triclosan from WWTPs were only \(\approx 2\%\) relative to those of triclosan, its predicted concentration relative to triclosan in the epilimnion of the lake increases to \(30\%\) in summer. Passive sampling with semipermeable membrane devices (SPMDs) indicated the presence of methyl triclosan in lakes with inputs from anthropogenic sources but not in a remote mountain lake. Surprisingly, no parent triclosan was observed in the SPMDs from these lakes. Methyl triclosan appears to be preferentially accumulated in SPMDs under the conditions in these lakes, leading to concentrations comparable to those of persistent chlorinated organic pollutants.
TRICLOSAN IN A SEWAGE TREATMENT PROCESS – BALANCES AND MONITORING DATA

Bester K

Journal
WATER RESEARCH

Volume (Number), Pages, Year
37, 3891-3896, 2003

Abstract of paper
In a German sewage treatment plant that processes 200,000 m³ wastewater per day, the concentration of 2,4,4'-trichloro,2'-hydroxy-phenylether (triclosan) in the in-flowing (~1000 ng l⁻¹) as well as in the out-flowing water (~50 ng l⁻¹) are compared to the concentrations measured in sludge (1200 ng g⁻¹). Considering the mass flow of water and sludge in the respective plant, balances including water and sludge are calculated. Thirty percent of the triclosan is sorbed with weak bonds to the sludge, while some amounts are sorbed as bound residues in the sludge. About 5% is dissolved in the out-flowing water. Thus most of the inflowing material is not recovered as the parent compound but is likely that it is transformed to other metabolites or unrecovered bound residues. These data are compared to the monitoring of sewage sludge of 20 different plants in this region, most of which are smaller, though. The concentrations found in these sludges vary from 1000-8000 ng g⁻¹.

Personal Communication with the Author
- 50% municipal and 50% from a large brewery
- high sludge generation due to high DOC, and high sludge load
- low triclosan inflow concentrations due to dilution from brewery waste water
Abstract of paper
The fate of triclosan in diverse stages of two sewage treatment processes has
been determined. The elimination process differed considerably depending on
the technology applied in the respective sewage treatment plant (STP). The plant
operating with a two-stage biologic (activated sludge) process removed triclosan
more efficiently than the STP with a combination of physical and activated sludge
process. The treatment in the aeration basin was the dominant elimination
mechanism, whereas the final biologic filter was not very effective. The elimina-
tion rates for triclosan were 87% and 95%, respectively. These data were com-
pared with emissions of a multitude of STPs in the river Ruhr catchment area as
well as triclosan and its known transformation product, triclosanmethyl, in the
river. The concentrations of both compounds were between <3 and 10 ng/L in
true surface-water samples for triclosan and between 0.3 and 10 ng/L for tri-
closan-methyl. The STP effluents held higher concentrations (10 to 600 ng/L tri-
closan). The ratio of triclosan to triclosan-methyl did not change significantly
within the longitudinal profile of the river, but diverse STPs discharging to the
river exhibited individual triclosan-to-triclosan-methyl ratios. From the riverine
concentration data, in-river elimination rates and half-life were estimated.
CO-OCCURRENCE OF TRICLOCARBAN AND TRICLOSAN IN U.S. WATER RESOURCES

Halden R and DH Paull

Journal
ENVIRONMENTAL SCIENCE AND TECHNOLOGY

Volume (Number), Pages, Year
39, 1420-1426, 2005

Abstract of paper
Triclocarban, N-(4-chlorophenyl)- N¢-(3,4-dichlorophenyl)-urea, is a polychlorinated phenyl urea pesticide, marketed under the trademark TCC and used primarily as an antibacterial additive in personal care products. Despite its extensive use over several decades, environmental occurrence data on TCC are scarce. This is due in part to a lack of analytical techniques offering the desired sensitivity, selectivity, affordability, and ease of use. This need is addressed here by introducing a liquid chromatography electrospray ionization mass spectrometry (LC/ESI/MS) method allowing for the determination of TCC concentrations in aquatic environments at the ng/L level. TCC was concentrated from aqueous samples by solid-phase extraction, separated from interferences on a C18 column by either isocratic or gradient elution, and detected and identified in negative ESI mode by selectively monitoring the (M - H)- base peak (m/z 313) and its 37Cl-containing isotopes (m/z 315, 317) that served as reference ions. Particulates contained in aquatic samples were extracted and analyzed separately. Accurate quantification was achieved using stable isotopes of TCC and triclosan as internal standards. Addition of 10 mM acetic acid to the mobile phase yielded acetic acid adducts ([M - H + 60]-) that were successfully exploited to boost method sensitivity and selectivity, especially when analyzing challenging environmental matrixes. Method detection limits were matrix dependent, ranging from 3 to 50 ng/L. In 36 grab samples obtained from the Greater Baltimore area, TCC was detected in river water and wastewater at concentrations of up to 5600 and 6750 ng/L, respectively. Raw and finished drinking water did not contain detectable quantities of the pesticide (<3 ng/L). In conclusion, the new LC/ESI/ MS method was applied successfully to collect environmental occurrence data on TCC in U.S. water resources. Study results suggest that the bacteriostat and pesticide is a frequent but currently underreported contaminant whose environmental fate and behavior deserve further scrutiny.
PHOTOCHEMICAL CONVERSION OF TRICLOSAN TO 2,8-DICHLORODIBENZO-P-DIOXIN IN AQUEOUS SOLUTION

Latch DE, Packer JL, Arnold WA and K McNeill

Journal
JOURNAL OF PHOTOCHEMISTRY AND PHOTOBIOLOGY
Short communication

Volume (Number), Pages, Year
158, 63-66, 2003

Abstract of paper
The direct photolysis of triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol), an antimicrobial additive commonly detected in surface waters, is studied. It is found that 2,8-dichlorodibenzo-p-dioxin is produced in both buffered and natural (Mississippi River) water with yields ranging from 1-12% under a variety of conditions. This result indicates that triclosan is likely converted to 2,8-DCDD in sunlight-irradiated surface waters.
AQUEOUS PHOTOCHEMISTRY OF TRICLOSAN: FORMATION OF 2,4-DICHLOROPHENOL, 2,8-DICHLORODIBENZO-p-DIOXIN, AND OLIGOMERIZATION PRODUCTS

LATCH DE, PACKER JL, STENDER BL, VANOVERBEKE J, ARNOLD WA, and K MCNEILL

Journal
ENVIRONMENTAL TOXICOLOGY AND CHEMISTRY

Volume (Number), Pages, Year
24, 517-525, 2005

Abstract of paper
The photochemical fate of the antimicrobial agent triclosan is presented. Experiments performed in both natural and buffered deionized water show that triclosan rapidly photodegrades by direct photolysis ($t_{1/2} = 5$ h, pH 8, noon summer sunlight, 45°N latitude). Both 2,8-dichlorodibenzo-p-dioxin (2,8-DCDD) and 2,4-dichlorophenol (2,4-DCP) are produced. The 2,8-DCDD and 2,4-DCP also are photolabile and, thus, are intermediates. The yields for 2,8-DCDD and 2,4-DCP ranged from 3 to 12% depending on the conditions employed. When triclosan is photolyzed in the presence of Suwannee River (GA, USA) fulvic acid, a portion of the initial mass is recovered as insoluble material. Based on experiments in which the formation of insoluble material was monitored with photolysis time, it is postulated that photolysis in natural waters leads to some of the triclosan being coupled to humic matter. Triclosan also reacts rapidly with both singlet oxygen ($k_{\text{rxn}} = 1.07 \pm 0.03 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in water of pH 10) and hydroxyl radical ($k_{\text{OH}} = 5.4 \pm 0.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Indirect photolysis pathways, however, are not expected to be important because of low steady-state concentrations of reactive oxygen species in natural waters and the efficiency of the direct photolysis of triclosan.
Abstract of paper
Pharmaceuticals are a class of emerging contaminants whose fate in the wastewater treatment process has received increasing attention in past years. Acidic pharmaceuticals (ibuprofen, naproxen, mefenamic acid, ketoprofen, and diclofenac), caffeine, and the antibacterial triclosan were quantified at four different steps of wastewater treatment from urban wastewater treatment plants. The compounds were extracted from wastewater samples on Waters Oasis hydrophilic-lipophilic balance solid-phase extraction columns, silylated, and analyzed by gas chromatography-mass spectrometry. For the chemicals studied it was found that the majority of the influent load was removed during secondary treatment (51-99%), yielding expected surface water concentrations of 13 to 56 ng/L.

Specific triclosan findings

<table>
<thead>
<tr>
<th>WWTP</th>
<th>Sample</th>
<th>Triclosan (µg/L)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>3.0</td>
</tr>
<tr>
<td></td>
<td>Primary sludge</td>
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</tr>
<tr>
<td></td>
<td>Secondary sludge</td>
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</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>0.072</td>
</tr>
<tr>
<td>2</td>
<td>influent</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>Primary sludge</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Secondary sludge</td>
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</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>0.047</td>
</tr>
<tr>
<td>3</td>
<td>influent</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>Primary sludge</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>Secondary sludge</td>
<td>0.065</td>
</tr>
</tbody>
</table>
Effluent 0.028
This shows a elimination rate of 95.1; 97 and 97.6 % respectively.
FATE AND EFFECTS OF TRICLOSAN IN ACTIVATED SLUDGE

Federle T W; Kaiser S K and Nuck B A

Journal
ENVIRONMENTAL TOXICOLOGY & CHEMISTRY

Volume (Number), Pages, Year
21, 1330-1337, 2002

Abstract of paper
Triclosan, 5-chloro-2(2,4dichlorophenoxy)phenol, is a widely used antimicrobial agent. To understand its fate during sewage treatment, the biodegradation and removal of triclosan (TCS) was determined in activated sludge. In addition, its effects on treatment processes were assessed. Fate was determined by examining the biodegradation and removal of $^{14}$C (2,4 dichlorophenoxy) TCS in laboratory batch mineralization experiments and bench-top continuous activated sludge systems (CAS). In batch experiments with unacclimated sludge, TCS was mineralized to $^{14}$CO$_2$, but the total yield varied as a function of test concentration. Systems that were redosed with TCS exhibited more extensive and faster mineralization indicating that adaptation was a critical factor determining the rate and extent of biodegradation. In a CAS study in which the influent level of TCS was incrementally increased from 40 ug/L to 2000 ug/L, removal of parent exceeded 98.5% and removal of total radioactivity (parent and metabolites) exceeded 85%. Between 1.5 and 4.5% of TCS in the influent was sorbed to the wasted solids, while >94% underwent primary biodegradation and 81-92% was mineralized to CO$_2$ or incorporated in biomass. Increasing levels of TCS in the influent had no adverse effects on any wastewater treatment process including COD, BOD and ammonia removal. In a subsequent experiment, a CAS, acclimated to 35 ug/L TCS, received two separate 4-hour shock loads of 750 ug/L TCS. Neither removal of TCS or treatment processes exhibited significant adverse effects. An additional CAS study was conducted to examine the removal of a low level (10 ug/L) of TCS. Removal of parent equaled 94.7%, and biodegradation remained the dominant removal mechanism. A subsequent series of CAS experiments examined removal at four influent concentrations (7.5, 11, 20 and 50 ug/L) of TCS and demonstrated that removal of parent ranged from 98.2 to 99.3 and was independent of concentration. While TCS removal across all experiments appeared unrelated to influent concentration, removal was significantly correlated ($r^2 = 0.87$) with COD removal indicating that TCS removal was related to overall treatment efficiency of specific CAS units. In conclusion, the experiments show that TCS is extensively biodegraded and removed in activated sludge systems and will not adversely affect sewage treatment processes at levels expected in

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household and manufacturing wastewaters.
Ref. No. 11

MEASUREMENT OF TRICLOSAN IN WASTEWATER TREATMENT SYSTEMS

McAvoy D C; Schatowitz B; Jacob M; Hauk A and Eckhoff W S

Journal
ENVIRONMENTAL TOXICOLOGY & CHEMISTRY

Volume (Number), Pages, Year
21, 1323-1329, 2002

Abstract of paper
The objective of this study was to investigate the fate and removal of triclosan (TCS: 2,4,4'-trichloro-2'-hydroxy-diphenyl-ether), an antimicrobial agent used in a variety of household and personal care products, in wastewater treatment systems. This objective was accomplished by monitoring the environmental concentrations of TCS, higher chlorinated derivatives of TCS (Tetra II: 2, 3', 4, 4'-tetrachloro-2'-hydroxydiphenylether; Tetra III: 2, 4, 4'; 5'-tetrachloro-2'-hydroxydiphenylether; Penta: 2, 3', 4, 4', 5'-pentachloro-2'-hydroxydiphenylether), and a potential biotransformation byproduct of TCS (TCS-OMe: 2, 4, 4'-trichloro-2'-methoxydiphenylether) during wastewater treatment. These analytes were isolated from wastewater using a C18 solid-phase extraction (SPE) column and from sludge with supercritical fluid CO₂. Once the analytes were isolated, they were derivatized to form trimethylsilyl ethers prior to quantitation by GC/MS. Recovery of TCS from laboratory spiked wastewater samples ranged from 79 to 88% for influent, 36 to 87% for final effluent, and 70 to 109% for primary sludge. Field concentrations of TCS in influent wastewater ranged from 3.8 to 16.6 ng/L and for final effluent ranged from 0.2 to 2.7 ng/L. Removal of TCS by activated sludge treatment was approximately 96%, whereas removal by trickling filter treatment ranged from 58 to 86%. The higher chlorinated Tetra-II, Tetra-III, and Penta closans were below quantitation in all of the final effluent samples, except for one sampling event. Digested sludge concentrations of TCS ranged from 0.5 to 15.6 μg/g (dry weight), where the lower value was from an aerobic digestion process and the highest value from an anaerobic digestion process. These results suggest that TCS is readily biodegradable under aerobic conditions, but not under anaerobic conditions. The higher chlorinated closans were near or below the limit of quantitation in all of the digested sludge samples. Based on results from this study the chlorinated analogues and biotransformation byproduct of TCS are expected to be very low in receiving waters and sludge amended soils.
Abstract of paper
The concentrations and removal of triclosan, an antibacterial ingredient in consumer products, were measured at advanced trickling filter (TF) and activated sludge (AS) wastewater treatment plants (WWTPs) in the River Aire basin in the UK in September, 2000. Additionally, the in-stream removal of triclosan was measured directly in the stream receiving the treated effluent from the TF plant, using a fluorescent dye tracer to determine the water plug travel times. The in-stream removal of the truly dissolved and un-ionized (i.e. bioavailable) fraction of the compound was measured using semipermeable membrane devices (SPMDs) deployed at various distances downstream from the WWTP discharge point. The estimated removal rates were used in the GREAT-ER (Geography-Referenced Regional Exposure Assessment Tool for European Rivers) model to predict the site-specific distribution of triclosan concentrations in the Aire basin as well as to calculate regional concentrations. High WWTP (~95%) and in-stream (0.21-0.33 h⁻¹) removal rates of triclosan confirm that this chemical is degraded and rapidly eliminated from the aquatic environment.
TRICLOSAN – OCCURRENCE AND FATE OF A WIDELY USED BIOCIDE IN THE AQUATIC ENVIRONMENT: FIELD MEASUREMENTS IN WASTE WATER TREATMENT PLANTS, SURFACE WATERS AND LAKE SEDIMENTS

Singer H; Müller S; Tixier C and Pillonel L

Journal
ENVIRONMENTAL SCIENCE AND TECHNOLOGY

Volume (Number), Pages, Year
36, 4998-5004, 2002

Abstract of paper
Due to its wide range of use in medical and consumer care products, the biocide triclosan reaches waste water treatment plants, surface waters and sediments. We have developed analytical methods for the quantification of triclosan in surface water and wastewater, sludge and sediment. Furthermore, we have followed triclosan fate in a wastewater treatment plant (biological degradation: 79%; sorption to sludge: 15%; input into the receiving surface water: 6%). Despite the high overall removal rate, the concentration in the waste water effluents were in the range of 42 to 213 ng/L leading to concentrations of 11 to 98 ng/L in the receiving rivers. Moreover, quite a high removal rate of 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 is reflecting its increased use since 30 years. As the measured concentrations in surface waters are in the range of the predicted no effect concentration (PNEC) of 50 ng/L, more measurements and a detailed investigation of the degradation processes are needed.

Additional remarks from the submitter
For more detailed quantification of the triclosan removal rates in the lake reference is made to Tixier et al., 2002 (Ref. No. 11).
A FIELD STUDY OF TRICLOSAN LOSS RATES IN RIVER WATER (CIBOLO CREEK, TX)

Morrall D; McAvoy D; Schatowitz B; Inauen J; Jacob M; Hauk A and Eckhoff W

Journal
CHEMOSPHERE

Volume (Number), Pages, Year
54, 653-660, 2004

Abstract of paper
Triclosan is an anti-microbial agent used in down-the-drain consumer products. Following sewage treatment some of the triclosan will enter receiving waters. This study was designed to determine the die-away rate of triclosan released into a river as part of the sewage treatment plant effluent matrix. The study was conducted in Cibolo Creek, a moderate sized stream (discharge ~0.1 m$^3$/s) located in South Central Texas. Triclosan was analyzed from samples collected upstream of the sewage treatment plant, the sewage treatment plant effluent, and the river downstream from the effluent discharge. The first-order loss rate of parent triclosan from the water column was calculated from measured data ($0.06 \ h^{-1}$) and this rate corresponded to a 76% reduction in triclosan over an 8 km river reach below the discharge. Mathematical modeling indicated that sorption and settling accounted for approximately 19% of total triclosan loss over 8 km. When removing sorption and settling, the remaining amount of triclosan had an estimated first-order loss rate of $0.25 \ h^{-1}$. This loss rate was presumably due to other processes such as biodegradation and photolysis. These data show that loss of parent triclosan from the water column is rapid. Additional data are needed to fully document loss mechanisms.
PHOTOTRANSFORMATION OF TRICLOSAN IN SURFACE WATER: A RELEVANT ELIMINATION PROCESS FOR THIS WIDELY USED BIOCODE – LABORATORY STUDIES, FIELD MEASUREMENTS AND MODELLING

Tixier C; Singer H P; Canonica S and Müller S R

Abstract of paper
The phototransformation of the widely used biocide triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) was quantified for surface waters using artificial UV light and sunlight irradiation. The pH of surface waters, commonly ranging from 7 to 9, determines the speciation of triclosan (pKₐ = 8.1) and therefore its absorption of sunlight. Direct phototransformation of the anionic form with a quantum yield of 0.31 (laboratory conditions at 313 nm) was identified as the dominant photochemical degradation pathway of triclosan. Combining the photochemical parameters with actual meteorological data and field measurements allowed us to validate a model describing the behavior of triclosan in the water column of a Swiss lake (lake Greifensee). From August to October 1999, direct phototransformation accounted for 80% of the observed total elimination of triclosan from the lake. The remaining major sink for triclosan was the loss in the outflow. Thus, during the summer season, direct phototransformation appears to be a major elimination pathway of triclosan in this lake. Based on absorption spectra and quantum yield data, the phototransformation half-lives of triclosan were calculated under various environmental conditions typical for surface waters. Daily-averaged half-lives were found to vary from about 2 to 2'000 days, depending on latitude and time of year. We showed that, for correct exposure data and an improved risk assessment of triclosan in surface water, information has to be collected about the different factors affecting the occurrence and also the elimination processes of triclosan in surface water.
Triclosan (TCS) is an antimicrobial agent used in a variety of consumer products. To determine the fate of TCS that escapes the sewage treatment process, 14C-TCS (1.7 ppb) was added to multiple sources of river water amended with sewage. River water was collected from the Ohio River, Great Miami River, Little Miami River, Whitewater River and East Fork of the Little Miami River. TCS degradation was observed with river water from every source. Half-lives ranged from 2.5 to 3.6 days. In all test systems, a non-polar intermediate (which is presumably methyl-TCS) appeared concurrent with the disappearance of TCS. This metabolite accounted for up to 15 percent of the total and subsequently decreased in concentration.

Additional remarks from the submitter
Excerpts from the key findings:
Biodegradation rates were similar in all river waters, indicating that effluent was the major source of degraders. Rates of parent loss and mineralization were similar, consistent with little accumulation of metabolites.
A non-polar metabolite, presumably Me-TCS, was formed in all river waters. Although not persistent, its disappearance rate was slower than that of parent TCS. The formation of significant Me-TCS in this study, compared to other studies in activated sludge and raw sewage, suggests Me-TCS formation is favored by a high ratio of TCS to microbial biomass, which saturates the degradation process. Thus, Me-TCS is likely formed by a secondary pathway, which is likely gratuitous or a detoxificaton process and whose importance is situationally defined.
LABORATORY EVALUATION OF TRICLOSAN BIODEGRADATION IN WASTEWATER AND RIVER WATER RECEIVING UNTREATED SEWAGE

Schwab E L and Federle T W

Abstract of paper
Triclosan (TCS) is a chlorinated aromatic compound with antimicrobial applications. Biodegradation of TCS was examined in wastewater and wastewater diluted into river water to simulate an untreated discharge scenario. Radiolabeled TCS was dosed in a realistic concentration (<10 ppb), and disappearance of the material was monitored by LSC and Rad-TLC. TCS loss was also benchmarked against COD and NH3 removal. Degradation was evaluated at different levels of dissolved oxygen. TCS degradation occurred at similar rates in both raw wastewater and wastewater diluted into river water and was faster than NH3 loss. In systems respiked with sewage and TCS (simulating a second discharge of waste into a polluted stream), the biodegradation rates of TCS, COD and ammonia were faster than those in clean water systems receiving sewage for the first time.

Additional remarks from the submitter
Excerpts from the key findings:
Triclosan (TCS) is not likely to be persistent in untreated discharge situations. It was extensively mineralized to CO2 and only a single transient polar metabolite was observed.
The rate of TCS biodegradation was faster than or similar to that of BOD (COD) and much faster than that for NH3, indicating that TCS levels will be greatly reduced once a receiving stream recovers from conventional pollutants.
Abstract of paper
To provide the first nationwide reconnaissance of the occurrence of pharmaceuticals, hormones, and other organic wastewater contaminants (OWCs) in water resources, the U.S. Geological Survey used five newly developed analytical methods to measure concentrations of 95 OWCs in water samples from a network of 139 streams across 30 states during 1999 and 2000. The selection of sampling sites was biased toward streams susceptible to contamination (i.e. downstream of intense urbanization and livestock production). OWCs were prevalent during this study, being found in 80% of the streams sampled. The compounds detected represent a wide range of residential, industrial, and agricultural origins and uses with 82 of the 95 OWCs being found during this study. The most frequently detected compounds were coprostanol (fecal steroid), cholesterol (plant and animal steroid), N,N-diethyltoluamide (insect repellant), caffeine (stimulant), triclosan (antimicrobial disinfectant), tri(2-chloroethyl)phosphate (fire retardant), and 4-nonylphenol (nonionic detergent metabolite). Measured concentrations for this study were generally low and rarely exceeded drinking-water guidelines, drinking-water health advisories, or aquatic-life criteria. Many compounds, however, do not have such guidelines established. The detection of multiple OWCs was common for this study, with a median of seven and as many as 38 OWCs being found in a given water sample. Little is known about the potential interactive effects (such as synergistic or antagonistic toxicity) that may occur from complex mixtures of OWCs in the environment. In addition, results of this study demonstrate the importance of obtaining data on metabolites to fully understand not only the fate and transport of OWCs in the hydrologic system but also their ultimate overall effect on the human health and the environment.
Triclosan was detected in 49 of 85 water samples. The median concentration was 0.04 μg/l, the median concentration of the detects only was 0.14 μg/l, the maximum concentration was 2.3 μg/l. The sampling sites were a mix of urban and agricultural sites, and were generally sites that had problems of one reason or another in the past. Triclosan is not further discussed.
Triclosan, (known chemically as 5-Chloro-2-(2,4-Dichlorophenoxy) Phenol or 2,4,4'-Trichloro-2'-hydroxydiphenylether) has been in commercial use as a preservative in a variety of consumer and commercial products, from deodorants and toothpaste to laundry detergents and medical devices. As the range of products containing triclosan and the total worldwide use of the germicide has increased, so too has the interest in understanding which environmental compartments this material will enter and its possible effects. The products containing triclosan are designed to be disposed of either down the drain (as in the case of toothpaste or hospital, industrial, and home use antimicrobial cleaners) or to sanitary landfills (as with packaging materials). Triclosan could reach the terrestrial environment directly from sanitary landfills and through the use of onsite septic systems or indirectly through the practice of applying sewage sludge to land through the disposal of gray water on soil. Since triclosan is a chemical that can find applications under either the Environmental Protection Agency or the Food and Drug Administration, studies have been run with different protocols for different federal offices. It should similarly be noted that these unpublished studies were run over a period of years, that they were run in different laboratories, and that some were run in another country. Consequently, in this case, studies will be reviewed that deal primarily with the terrestrial fate and effects of triclosan. These studies include data from soil biodegradation, sorption, and terrestrial toxicity studies on earthworms, fowl, plants and bacteria.
Ref. No. 20

STUDY
TRICLOSAI - DETERMINATION OF AEROBIC BIODEGRADATION IN SOIL

Author: Christensen K P
Institute: Springborn Laboratories, Inc., 790 Main Street, Wareham, Massachusetts 02571, USA

Method: US FDA Technical assistance document, section 3.12 / GLP

Year: 1994
Test System: Three soil types were inoculated with activated sludge obtained from an industrial sewage treatment plant receiving triclosan in the waste stream. The biodegradation potential of triclosan in soil was determined by the carbon dioxide evolution method.

Exposure: 64 days
Test concentration: 200 μg per kilogram of soil
Substances: 14C-radiolabelled triclosan, 94.8 % radiochemical purity

Analytical Monitoring: yes

Summary:
After 64 days of testing, carbon dioxide evolution, primary biodegradation and half-life in soils are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Soil type</th>
<th>Arkansas</th>
<th>Kansas</th>
<th>Wisconsin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>silt loam</td>
<td>loam</td>
<td>sandy loam</td>
<td></td>
</tr>
<tr>
<td>Mean cumulative 14CO₂– evolution rate</td>
<td>20.1 %</td>
<td>11.9 %</td>
<td>13.6</td>
<td></td>
</tr>
<tr>
<td>Primary biodegradation of triclosan</td>
<td>77.3 %</td>
<td>79.3 %</td>
<td>93.1 %</td>
<td></td>
</tr>
<tr>
<td>Calculated half-life of triclosan</td>
<td>35.2 days</td>
<td>29.1 days</td>
<td>17.4 days</td>
<td></td>
</tr>
</tbody>
</table>

The result of this study indicated that triclosan undergoes both, primary biodegradation and complete mineralization under the conditions tested.

The ability of the microbes in all three soil types to degrade the reference material, glucose, was poor (42.8-50.5%). The fact that triclosan was degraded may be viewed as an indication of the relatively easy biodegradation of the compound.
AQUATIC TOXICITY OF TRICLOSAN (5-chloro-2-(2,4-dichlorophenoxy)phenol)

Orvos DR; Versteeg D; Inauen J; Capdevielle M; Rothenstein A and Cunningham V

Journal
ENVIRONMENTAL TOXICOLOGY & CHEMISTRY

Volume (Number), Pages, Year
21, 1338-1349, 2002

Abstract of paper
The aquatic toxicity of triclosan, a chlorinated biphenyl ether used as an antimicrobial in consumer products, was studied using activated sludge microorganisms, algae, invertebrates, and fish. Triclosan, a compound used for inhibiting microbial growth, was not toxic to wastewater microorganisms at concentrations less than aqueous solubility. The 48-h Daphnia magna EC50 was 390 µg/L and the 96-h LC50 values for Pimephales promelas and Lepomis macrochirus were 260 and 370 µg/L, respectively. Using an early life-stage toxicity test with Oncorhynchus mykiss, a no observed effect concentration and lowest observed effect concentration of 34.1 µg/L and 71.3 µg/L, respectively, were determined. During a 96-h Scenedesmus study, the 96-h biomass EC50 was 1.4 µg/L and the 96-h no observed effect concentration was 0.69 µg/L. Other algae and Lemna were also investigated. Bioconcentration was assessed using Danio rerio. The average triclosan accumulation factor over the 5-week test period was 4157 at 3 µg/L and 2532 at 30 µg/L. Algae were determined to be the most susceptible organisms. Toxicity of a triclosan-containing wastewater secondary effluent to P. promelas and Ceriodaphnia was evaluated and no observed differences in toxicity between control and triclosan-treated laboratory units were detected. The neutral form of triclosan was determined to be associated with toxic effects. Ionization and sorption will mitigate those effects in the aquatic compartment.
VARIATION OF ACCUMULATION AND CLEARANCE OF THE PREDIOXIN 5-CHLORO-2-(2,4-DICHLOROPHENOXY)-PHENOL (IRGASAN DP 300, TRICLOSAN) WITH THE PH OF WATER

Schettgen C; Schmidt A and Butte W

Journal ORGANOHALOGEN COMPOUNDS

Volume (Number), Pages, Year
43, 49-52, 1999

Abstract of paper
(Abstract from literature search) Bioconcentration experiments for triclosan were performed with zebra fishes at pH 6, 7, 8 and 9. The water contained 35-50 µg/L of triclosan. After 250 days the fish were brought into water containing no triclosan. During the accumulation phase of 250 days the uptake of triclosan by the fishes was monitored, and during the clearance phase the concentration of triclosan in the fishes as well as in the water was measured. The uptake as well as the clearance rate depended from the pH value, and with increasing pH values the rate constants for uptake and clearance of triclosan by zebra fish decreased.

Additional remarks from the submitter
The following bioconcentration factors (BCF) and rate constants for uptake (k1) and clearance (k2) of triclosan in dependence on the pH of water are reported:

<table>
<thead>
<tr>
<th>pH</th>
<th>BCF</th>
<th>k1 (h⁻¹)</th>
<th>k2 (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>8700</td>
<td>356</td>
<td>0.0410</td>
</tr>
<tr>
<td>7</td>
<td>8150</td>
<td>288</td>
<td>0.0354</td>
</tr>
<tr>
<td>8</td>
<td>6350</td>
<td>262</td>
<td>0.0413</td>
</tr>
<tr>
<td>9</td>
<td>3700</td>
<td>129</td>
<td>0.0347</td>
</tr>
</tbody>
</table>

The accumulation phase was followed by a clearance phase at the same pH values. During the clearance phase the concentration gradient results in a depuration of triclosan from fish into the water. As the blood pH of fish (ca 7.4) is independent of the pH of the surrounding water, clearance rates are always identical. In the full report, half life’s for elimination of 16.8 – 19.9 hours are reported.
Bioconcentration factors (BCF) are important parameters to assess the environmental fate of chemicals. In this report we describe the determination of BCF for triclosan, a trichlorophenoxy phenol, for some dissociating herbicides like Dichlorprop, MCPA, Mecoprop, Triclopyr and Picloram as well as for selected pyrethroids like Cyfluthrin, Cypermethrin, Deltamethrin and Permethrin. It was shown that BCF and rate constants for the uptake of triclosan are decreasing with an increasing pH of the test water. The BCF for the herbicides evaluated are all below 10, confirming data already reported for herbicides of similar structure. Thus, for these compounds there is no tendency to bioaccumulate. Furthermore, there was no correlation between BCF and n-octanol/water partition coefficients or dissociation constants. BCF of pyrethroids were between 860 and 2200. For the analysis of pyrethroid metabolites a gas chromatographic method using daughter-ion mass spectrometry for detection was established. The detection limit of this method was 1 mg/kg, but metabolites could not be detected in fish during the bioaccumulation experiments. The high toxicity of pyrethroids for fish was approved; LC50-values were between 1 and 5 mg/l. To evaluate physiological effects in fish, produced by pyrethroids, EROD activities in preparations of trout liver were measured. No increase in activity could be detected, but there was a tendency to lower values. We think this to result from the high toxicity of pyrethroids that could have impaired this enzyme system.

Additional remarks from the submitter
The triclosan related results of this report are summarised in:

Schettgen C et al.; VARIATION OF ACCUMULATION AND CLEARANCE OF THE PREDIOXIN 5-CHLORO-2-(2,4-DICHLOROPHENOXY)-PHENOL (IR-GASAN DP 300, TRICLOSAN) WITH THE PH OF WATER.

ORGANOHALOGEN COMPOUNDS 43, p 49-52, 1999
BIOAKKUMULATION VON TRICLOSAN BEI VERSCHIEDENEN pH-WERTEN DES WASSERS UND DER PYRETHROIDE CYFLUTHRIN, CYPERMETHRIN, DELTAMETHRIN UND PERMETHRIN

Schettgen C

Journal
OLDENBURG UNIVERSITY, DISSERTATION

Volume (Number), Pages, Year
126 p, 2000

Abstract of the report
The bioconcentration factor (BCF) and the kinetics of the accumulation and elimination of 5-chloro-2-(2,4-dichlorophenoxy)-phenol (triclosan) in zebra fish was determined with different pH-values of the water. It could be shown, that in contradiction to discoveries raised sooner both the kinetic of accumulation and the BCF value of triclosan depend on the pH-value of the water, the kinetic of the elimination was independent of the pH-value of the water. For the pyrethroids Cyfluthrin, Cypermethrin, Deltamethrin and Permethrin, very lipophilic substances used as insecticides, BCF values were determined on juvenile rainbow trout on a flow-through system, BCF values between 860 and 2200 were observed, referring to the fat content of fish 27000 to 64000. Simultaneously LC50 values were determined and the effect on oxidases of the liver examined. Metabolites of pyrethroids had no influence on the measured bioaccumulation since their concentration under the test conditions were below the detection limit.

Additional remarks from the submitter
The triclosan related results of this report are summarised in:

Schettgen C et al.; VARIATION OF ACCUMULATION AND CLEARANCE OF THE PREDIOXIN 5-CHLORO-2-(2,4-DICHLOROPHENOXY)-PHENOL (IRGASAN DP 300, TRICLOSAN) WITH THE PH OF WATER.

ORGANOHALOGEN COMPOUNDS 43, p 49-52, 1999
Ref. No. 25

TRICLOSAN, A COMMONLY USED BACTERICIDE FOUND IN HUMAN MILK AND IN THE AQUATIC ENVIRONMENT IN SWEDEN

Adolfsson-Erici M; Pettersson M; Parkkonen J and Sturve J

Journal
CHEMOSPHERE

Volume (Number), Pages, Year
46, 1485-1489, 2002

Abstract of paper
High levels of the commonly used, effective bactericide triclosan were found in three out of five randomly selected human milk samples. It was also found in the bile of fish exposed to municipal wastewater and in wild living fish from the receiving waters of the three wastewater treatment plants.

Additional data in the paper
The following levels of triclosan in fish bile samples were reported in this paper:

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Distance from discharge</th>
<th>Triclosan concentration in fish bile, mg/kg fresh weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wild living roach</td>
<td>2.5 km from Grabo STP</td>
<td>4.4</td>
</tr>
<tr>
<td>Wild living eelpout</td>
<td>1.0 km from Ryaverken STP</td>
<td>0.63 – 0.90</td>
</tr>
<tr>
<td>Wild living eelpout</td>
<td>2.5 km from Ryaverken STP</td>
<td>0.24 – 0.37</td>
</tr>
<tr>
<td>Wild living perch</td>
<td>2.5 km from Henriksdal STP</td>
<td>0.44</td>
</tr>
<tr>
<td>Rainbow trout in cages</td>
<td>0 – 2 km from Grabo STP</td>
<td>47 – 17</td>
</tr>
<tr>
<td>Rainbow trout in tanks with treated wastewater</td>
<td>-</td>
<td>59 – 120</td>
</tr>
</tbody>
</table>

The detection of low levels of triclosan in parts of the excretion organs of wild living fish does not necessarily indicate a build-up of triclosan in other organs and in the edible parts of the fish.
STUDY
TRICLOSAN: TOXICITY MITIGATION BY HUMIC ACID DURING A 96-HOUR TOXICITY TEST WITH THE FRESHWATER ALGAE (SCENEDESMUS SUB-SPICATUS)

Author: Drottar K R and Krueger H O
Institute: Wildlife International Ltd. Easton, Maryland 21601, USA
Method: US EPA, Series 850, Guidelines OPPTS 850.1085 and 850.5400 / GLP
Year: 1999
Species: Scenedesmus subspicatus
Exposure: 96 hours
Substance: Triclosan, >99 % purity (Sample 42218)
Analytical Monitoring: yes

Summary:

Toxicity of triclosan to Scenedesmus subspicatus in μg/L:

<table>
<thead>
<tr>
<th></th>
<th>Without humic acid</th>
<th>With 20 mg/L humic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>96-h EC50</td>
<td>1.6 μg/L</td>
<td>3.5 μg/L</td>
</tr>
<tr>
<td>NOAEC</td>
<td>0.74 μg/L</td>
<td>2.4 μg/L</td>
</tr>
</tbody>
</table>

Humic acid appeared to mitigate the toxicity of triclosan by a factor of approximately three. Algal cells resumed normal growth after eight days during the recovery period. Consequently, the effects upon algal growth were considered to be algistatic, rather than algicidal.
STUDY
ACUTE TOXICITY (LC50) STUDY OF TRICLOSAN (Code FAT 80'023/Q)
TO EARTHWORM

Author: Wuethrich V
Institute: RCC Umweltchemie AG, CH-4452 Itingen, Switzerland


Year: 1990
Species: Earthworm, Eisenia foetida foetida.
Exposure: 14 days
Test concentrations: 64, 128, 256, 513, 1026 mg per kilogram of soil (dry weight)
Substance: Triclosan, 99.5 % purity

Analytical Monitoring: no

Summary: Based on mortality data, triclosan proved to be non-toxic to earthworms up to a concentration in soil (dry weight basis) of 1026 mg/kg. No abnormal symptoms were detected in live worms.

LC50 > 1026 mg/kg
STUDY
FDA SEEDLING GROWTH PHYTOTOXICITY TEST

Author: Schwab D and Heim L C
Institute: ABC Laboratories, Inc., Columbia, Missouri 65202, USA

Method: Based on FDA Technical Assistance Documents (TAD) 4.07 as laid down in the study protocol / GLP

Year: 1997
Species: Cucumber (Cucumis sativus L.)
Exposure: 28 days
Test concentrations: 10, 30, 100, 300 and 1000 μg per kilogram of soil (sandy loam)
Substances: Triclosan, 99.5 % purity
14C-radiolabelled triclosan, 96.1 % radiochemical purity
Analytical Monitoring: yes

Summary:

The NOEC levels for cucumber for all parameters tested in soil were found as:
Percent emergence: >1000 μg per kilogram of soil
Shoot length: >1000 μg per kilogram of soil
Shoot weight: >1000 μg per kilogram of soil
Root weight: >1000 μg per kilogram of soil
Ref. No. 29

STUDY
TRICLOSAN: 14-DAY ACUTE ORAL LD₅₀ STUDY IN MALLARD DUCKS

Author: Pedersen C A and Helsten B R
Institute: Bio-Life Association Ltd., Neillsville, WI 54456, USA
Method: US –EPA FIFRA E No 71-1 / GLP

Year: 1993
Test System: Single oral dose to 19-week-old ducks. A dose group consists of 10 birds, 5 birds per sex.

Exposure: 14 days
Dose: 0, 681, 1470 and 2150 mg/kg
Substance: Triclosan, >99 % purity

Analytical Monitoring: no

Summary:
Acute oral LD₅₀ > 2150 mg/kg

Triclosan is practically non-toxic to mallard ducks.
No mortalities, no abnormal behaviour and no sign of systemic toxicity were recorded.
Gross pathology – No abnormalities.
STUDY
TRICLOSAN: 14-DAY ACUTE ORAL LD₅₀ STUDY IN BOBWHITE QUAIL

Author: Pedersen C A and Helsten B R
Institute: Bio-Life Association Ltd., Neillsville, WI 54456, USA
Method: US –EPA FIFRA E No. 71-1 / GLP
Year: 1993
Test System: Single oral dose to 21-week-old quail. A dose group consists of 10 birds, 5 birds per sex.
Exposure: 14 days
Dose: 0, 147, 316, 464, 681, 1000 and 1470 mg/kg
Substance: Triclosan, >99 % purity
Analytical Monitoring: no

Summary:
Acute oral LD₅₀ = 862 mg/kg
Triclosan is slightly toxic to bobwhite quail. The NOEL was not achieved.
147 mg/kg: diarrhea
316 mg/kg: one mortality
Gross pathology – dark liver; gizzard contents green or yellow; gaseous intestines; dark red gall bladder; legs stretched behind body.
STUDY 
TRICLOSAN: 8-DAY ACUTE DIETARY LC50 STUDY IN BOBWHITE QUAIL 

Author: Pedersen C A and Helsten B R 
Institute: Bio-Life Association Ltd., Neillsville, WI 54456, USA 
Method: US --EPA FIFRA E No 71-2 / GLP 
Year: 1993 
Test System: Dietary, 13-day-old quail. A dose group consists of 10 birds. 

Exposure: 5 day exposure, 3 day recovery period 
Test concentrations: 0, 312, 625, 1250, 2500 and 5000 ppm 
Substance: Triclosan, >99 % purity 

Analytical Monitoring: yes 

Summary: 
LC50 > 5000 ppm 
NOEL = 1250 ppm 
Triclosan is practically non-toxic to bobwhite quail in the acute dietary study. Mortalities at 2500 and 5000 ppm. Depressed body weight and feed consumption, gaseous intestines at 5000 ppm.
AN ECOLOGICAL RISK ASSESSMENT FOR TRICLOSAN IN LOTIC SYSTEMS FOLLOWING DISCHARGE FROM WASTE WATER TREATMENT PLANTS

Reiss R; Mackay N; Habig C and Griffin J

Environmental Toxicology & Chemistry

Volume (Number), Pages, Year
21, 2483-2492, 2002

Abstract of paper
A modeling study was conducted to examine the distribution of concentrations of the antimicrobial triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl ether) in rivers following discharge from wastewater treatment plants (WWTP). Most uses of triclosan are disposed down residential drains, and ultimately reach WWTPs. A modeling analysis was conducted to simulate the discharge of triclosan in WWTP effluents to rivers and calculate the expected concentrations based on characteristics of the reach where the discharge occurred, the estimated concentration of triclosan in the WWTP effluent, and the physicochemical properties of triclosan. A probabilistic exposure assessment was conducted based on data on the characteristics of U.S. reaches receiving wastewater discharges and the physicochemical characteristics of triclosan. A risk assessment was conducted by comparing the estimated concentrations with toxicity endpoint concentrations for species representative of key ecological groups. For fish and invertebrates, neither the acute or chronic risks are of concern, and there are no concerns for vascular aquatic plants. However, certain types of algae are the most sensitive species to triclosan by more than an order of magnitude than other algal or aquatic plant species. For these algae, there is potential for some impact from triclosan near the WWTP discharge during low flow rate periods for some WWTPs with small dilutions.