

Partitioning, Persistence, and Accumulation in Digested Sludge of the Topical Antiseptic Triclocarban during Wastewater Treatment

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The topical antiseptic agent triclocarban (TCC) is a common additive in many antimicrobial household consumables, including soaps and other personal care products. Long-term usage of the mass-produced compound and a lack of understanding of its fate during sewage treatment motivated the present mass balance analysis conducted at a typical U.S. activated sludge wastewater treatment plant featuring a design capacity of 680 million liters per day. Using automated samplers and grab sampling, the mass of TCC contained in influent, effluent, and digested sludge was monitored by isotope dilution liquid chromatography (tandem) mass spectrometry. The average mass of TCC (mean \pm standard deviation) entering and exiting the plant in influent ($6.1 \pm 2.0 \mu\text{g/L}$) and effluent ($0.17 \pm 0.03 \mu\text{g/L}$) was 3737 ± 694 and $127 \pm 6 \text{ g/d}$, respectively, indicating an aqueous-phase removal efficiency of $97 \pm 1\%$. Tertiary treatment by chlorination and sand filtration provided no detectable benefit to the overall removal. Due to strong sorption of TCC to wastewater particulate matter ($78 \pm 11\%$ sorbed), the majority of the TCC mass was sequestered into sludge in the primary and secondary clarifiers of the plant. Anaerobic digestion for 19 days did not promote TCC transformation, resulting in an accumulation of the antiseptic compound in dewatered, digested municipal sludge to levels of $51 \pm 15 \text{ mg/kg}$ dry weight ($2815 \pm 917 \text{ g/d}$). In addition to the biocide mass passing through the plant contained in the effluent ($3 \pm 1\%$), $76 \pm 30\%$ of the TCC input entering the plant underwent no net transformation and instead partitioned into and accumulated in municipal sludge. Based on the rate of beneficial reuse of sludge produced by this facility (95%), which exceeds the national average (63%), study results suggest that approximately three-quarters of the mass of TCC disposed of by consumers in the sewershed of the plant ultimately is released into the environment by application of municipal sludge (biosolids) on land used in part for agriculture.

Introduction

A growing body of literature suggests that pharmaceuticals and personal care products (PPCPs) are not completely removed during wastewater treatment (1, 2). Whereas much

attention has been focused on PPCPs passing through conventional wastewater treatment plants (WWTPs) and becoming detectable in effluent-receiving streams (3), few studies have explored the partitioning of compounds into municipal wastewater residuals and their subsequent fate during sludge treatment (1, 4, 5). This lack of information is due in part to the difficulty of accurately detecting and quantifying PPCPs in the challenging analytical matrix of municipal sludge. Previously, our laboratory employed isotope dilution gradient liquid chromatography with electrospray ionization mass spectrometry (6) to perform a preliminary analysis of the behavior of PPCPs in a large activated sludge WWTP (5). Following development of a more selective method using triple quadrupole tandem mass spectrometry (7), this novel tool was applied to conduct a mass balance for a specific PPCP whose environmental fate has long been neglected (4).

Triclocarban (TCC; *N*-(4-chlorophenyl)-*N'*-3,4-dichlorophenylurea) is employed extensively as a topical antiseptic additive in personal care products. Since 1957, this diaryl urea compound has been added to antimicrobial soap, cosmetics, and other personal care products at levels of 0.5–5% (w/w) for its germicidal properties (8). At an estimated production volume of $0.5\text{--}1.0 \times 10^6$ pounds per year ($2.27\text{--}4.74 \times 10^5 \text{ kg/y}$), TCC is classified as a high production volume (HPV) chemical requiring an environmental risk assessment by the U.S. Environmental Protection Agency (EPA) (8). Triclocarban has a low water solubility of 2.0–4.6 mg/L at 20 °C and a high logarithmic octanol/water partitioning coefficient ($\log K_{OW}$) of 4.9 (4), indicating a significant potential for sorption. The trichlorinated aromatic structure of TCC suggests potential resistance to both chemical and biological transformation processes. The environmental half-life (DT50) of TCC is estimated at 120 and 540 days in soil and sediment, respectively (4). A limited number of studies focusing on the toxicity of TCC have shown the diaryl urea compound to impair mammalian reproduction by causing decreased birth weight and to reduce survival in rats (9). In humans, exposure to TCC has been associated with methemoglobinemia (10–12). Environmental transformation of TCC (2) can result in the formation of chlorinated anilines, which are hematotoxic and carcinogenic (13).

The only peer-reviewed study on the degradation of TCC during wastewater treatment dates from 1975. In this laboratory study, 20% of the initial mass of TCC was degraded over a period of 10 weeks in fresh activated sludge, and removal rates were as high as 97% under optimized conditions (2). Extensive sorption (>90%) of TCC to particles of activated sludge was observed but the study left unanswered the question of how these laboratory observations translate to real world situations (2). In 1991, TCC was found in the effluent of two WWTPs in New Jersey at concentrations of 2 and $6 \mu\text{g/L}$ (14), demonstrating incomplete removal during wastewater processing. Non-peer-reviewed studies on the removal of TCC during wastewater treatment showed influent and effluent concentrations ranging from 0.4 to $50 \mu\text{g/L}$ and 0.08 to $12 \mu\text{g/L}$, respectively, suggesting an aqueous-phase removal efficiency range of 65–97% during wastewater treatment (8).

In the present study, we performed a mass balance of TCC during full-scale wastewater treatment by tracking the compound in both the liquid phase (i.e., influent and effluent) and the solid phase (i.e., municipal sludge) using isotope dilution liquid chromatography electrospray ionization mass spectrometry (LC/ESI/MS) and tandem mass spectrometry (MS/MS).

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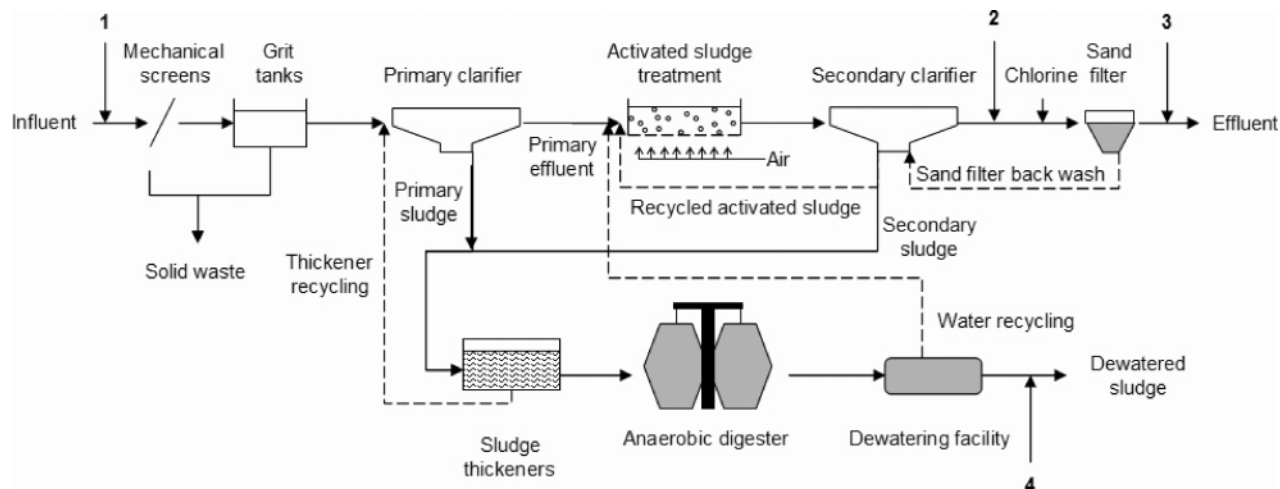


FIGURE 1. Flow diagram showing the process train for wastewater and sludge handling in the full-scale activated sludge treatment plant studied. Numbers indicate the four sampling locations used.

Experimental Section

Chemicals. Triclocarban (CAS No. 101-20-2) was obtained from Sigma-Aldrich (Milwaukee, WI). Cambridge Isotope Laboratories Inc. (Andover, MA) carried out the custom synthesis of carbon-13 labeled TCC uniformly labeled in the *p*-chlorophenyl ring ($^{13}\text{C}_6\text{-TCC}$; 99%) and kindly provided deuterated TCC (TCC- d_7 ; 99%) as a gift. All solvents of HPLC grade were purchased from Fisher Scientific (Pittsburgh, PA). All other chemicals were obtained at the highest purity available from Sigma-Aldrich (Milwaukee, WI).

Wastewater Treatment Plant. Sampling was conducted at a large U.S. activated sludge WWTP located on the East Coast. The plant is designed to treat about 680 million liters per day of wastewater from 1.3 million residents in an urban area in the Mid-Atlantic region. The sewershed is approximately 363 km² and the raw wastewater produced is primarily of domestic origin with minor amounts contributed by industrial flow (1.9%). The treatment train comprises pretreatment, and primary, secondary, and tertiary treatment (Figure 1). Following removal of larger objects from wastewater during pretreatment using mechanical screens, raw sewage enters a set of primary clarifiers that overflow into the activated sludge tanks of the secondary treatment stage. The hydraulic residence time of aerobic biological treatment is between 8 and 10 h. During tertiary treatment, effluent of the secondary clarifiers is chlorinated and passed through sand filters prior to discharge. Primary and secondary sludges are blended and anaerobically digested at 35–37 °C for an average period of 19 days. Dewatering of the digests yields finished solids in the form of digested, dewatered sludge. Typical 5-day biochemical oxygen demand (BOD) values for plant influent and effluent were 138 and 2.1 mg/L, respectively, indicating an average BOD removal efficiency of 98.5%. Total suspended solids (TSS) concentrations in influent and effluent during the sampling period were 112 and 2.0 mg/L, respectively, yielding an average TSS removal efficiency of 98.2%.

Sample Collection. Samples of influent (200 mL) and effluent (1000 mL) were collected in the spring of 2004 at the locations indicated in Figure 1 using an ISCO 6712 portable automated sampler (ISCO Inc; Lincoln, NE) programmed to obtain hourly samples over a 24-h time period. Additionally, 24-hour composite samples (hourly aliquots) of influent were collected over a 7-day period in March 2004. Grab samples of dewatered, digested sludge also were collected using 500 mL I-Chem polyethylene bottles (Fisher Scientific; Pittsburgh, PA). Samples were placed on ice and shipped to the laboratory. Upon arrival, they were immediately aliquotted,

fortified with isotope-labeled TCC- d_7 surrogate standard to allow for recovery correction, and stored at –20 °C. Influent, effluent, and sludge samples were spiked at 3, 0.1, and 200 µg/L, respectively. Additional information on the sampling strategy can be found in the Supporting Information (SI).

Sample Preparation and Analysis. Influent and effluent samples were analyzed along with blanks and quality control samples by isotope dilution LC/ESI/MS using previously reported procedures (6) with slight modifications (SI). Sludge samples (10 mL) were dried at 70 °C and homogenized; 200-mg fractions were mixed with Ottawa sand (EMD Chemicals; Gibbstown, NJ) free of TCC contamination, filled into 5-mL extraction cells made from stainless steel, and extracted with acetone using an accelerated solvent extraction (ASE) unit (Dionex ASE 200, Dionex; Sunnyvale, CA). The extractions were carried out in one cycle at 1500 psi and 100 °C for 5 min. Finally, the cell was flushed with greater than one pore volume of fresh solvent (60% cell volume). Concentrated extracts were processed and analyzed as described elsewhere (6). Measured concentrations of TCC were confirmed by analysis of aliquots of the diluted organic extracts (80% methanol) by isotope dilution isocratic LC negative electrospray ionization MS/MS using a Quantum Ultra triple quadrupole tandem mass spectrometer (Thermo Electron; San Jose, CA) as described in detail elsewhere (7). Results of spiking experiments performed to assess the appropriateness and recovery of these techniques are provided in the Supporting Information.

Mass Balance Calculations. Mass balances for primary plus secondary treatment and for combined primary, secondary, and tertiary treatment were calculated using the following equation:

$$W_{\text{trans}} = (Q_{\text{inf}} \times C_{\text{inf}}) - (Q_{\text{eff}} \times C_{\text{eff}}) - (TS_{\text{dig}} \times Q_{\text{dig}} \times C_{\text{dig}}) - W_{\text{vol}} \quad (1)$$

where W_{trans} = mass input lost to transformation or otherwise unaccounted for (g/d); Q_{inf} = flow rate of influent (L/d); C_{inf} = concentration of TCC in influent (g/L); Q_{eff} = flow rate of treatment effluent (L/d); C_{eff} = concentration of TCC in treatment effluent (g/L); TS_{dig} = fraction of total solids in digested sludge; Q_{dig} = flow rate of digested sludge (L/d); C_{dig} = concentration of TCC in digested sludge (g/L); and W_{vol} = mass loss by volatilization (g/d).

Results

TCC Mass Loading in Influent. To investigate the variability in TCC loading over the course of a day, mass input estimates were obtained based on influent concentrations and hourly

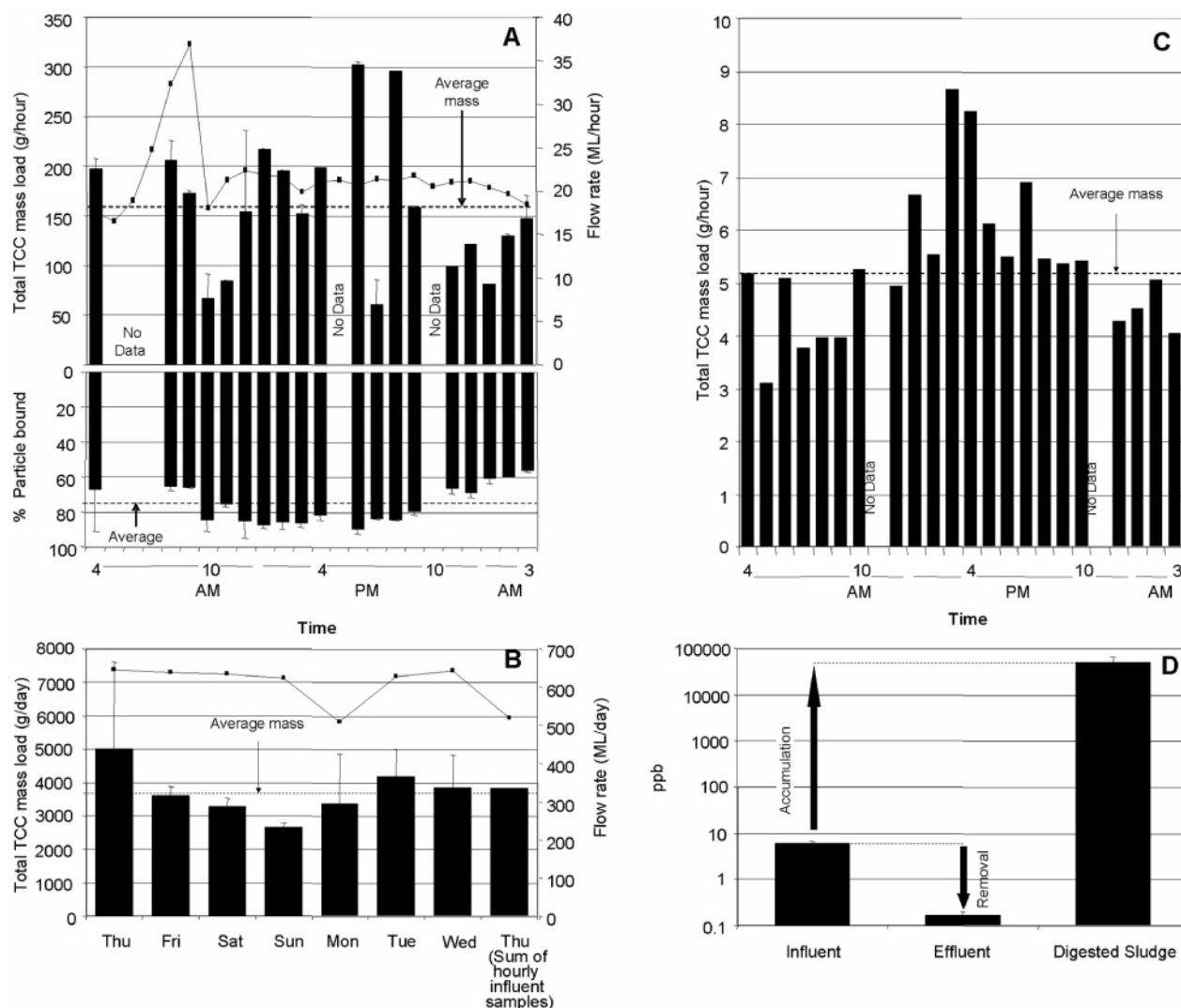


FIGURE 2. Mass estimates, flow rates, and fate of TCC during full-scale activated sludge wastewater treatment. Substantial fluctuations of TCC mass in influent were observed over a 24-h time period (A; upper panel). Flow rates peaked in the morning hours of the day of sampling due in part to a heavy rainfall event (3.5 cm). Chemical analysis of aqueous and particulate fractions of raw wastewater showed that $76 \pm 11\%$ of the mass of TCC was sorbed to particles (A; lower panel). When analyzing 24-hour composite influent samples collected over the course of a week, fluctuations in TCC loading were observed to be less pronounced (B). The hourly mass of TCC passing through the plant in tertiary effluent also showed some fluctuation and averaged 5.3 g/h (C). The mass of TCC found in liquid and solid samples (expressed in units of $\text{ppb}_{w/w}$ and $\text{ppb}_{w/wr}$, respectively) demonstrated that elimination of TCC from the aqueous phase during the treatment process resulted in an accumulation of the compound in digested sludge (D). Error bars indicate the higher of two independent experimental measurements (A) or the standard deviation of 3 or more measurements for each observation reported (B, D); see SI for further information.

flow rates. The average hourly mass of TCC entering the plant was 160 ± 69 g/h (mean \pm SD). Significant variability was observed over the course of a weekday (Figure 2A) caused, at least in part, by a heavy rainfall event that led to increased flow due to infiltration of rainwater into the leaky infrastructure of the separate sewer system. Hourly extremes of 61 and 303 g/h were observed. On average, $76 \pm 11\%$ of TCC mass in influent was sorbed to particles (range 51–92%) (Figure 2A; lower panel). Daily fluctuations, determined via analysis of 24-h composite samples collected on 7 consecutive days (Figure 2B), were less pronounced, as indicated by an average TCC mass of 3737 ± 694 g/d (mean \pm SD), and daily extremes of 2664 and 5022 g/d.

TCC Mass Output in Effluent. The mass output of TCC in tertiary effluent was determined to equal 5.3 ± 1.3 g/h (mean \pm SD), with extremes of 3.1 and 8.7 g/h. On average, 127 ± 6 g/d of TCC were found to pass through the plant (Figure 2C). Twenty-four hour samples of secondary effluent, obtained in hourly increments upstream of chlorination and filtration processes, were analyzed to compare the overall

aqueous-phase removal efficiencies of secondary and tertiary wastewater treatment using non-filtered samples (total concentration). At 151 ± 48 g/d (mean \pm SD), the calculated TCC mass output in secondary effluent was comparable to that in tertiary effluent (127 ± 6 g/d).

TCC Mass Output in Sludge. To complete the mass balance, the amount of TCC retained in dewatered, digested sludge was determined in 3 composite samples representative of the sampling period. These samples were analyzed repeatedly by LC/MS ($n = 15$) and LC/MS/MS ($n = 6$). In addition, spiking experiments were carried out using the very same samples to ensure that TCC could be extracted and quantified with confidence and reproducibly in this matrix (SI). The mean concentration of the antimicrobial in dewatered sludge was 51 ± 15 mg/kg on a dry weight basis, yielding an estimated mass output of 2815 ± 917 g/d.

Fate of TCC in the WWTP. The fate of TCC in the tertiary treatment plant is shown in Figure 3. Only $3 \pm 1\%$ (average 127 ± 6 g/d) of the total daily TCC mass input (average 3737 ± 694 g/d) passed through the plant into effluent-receiving

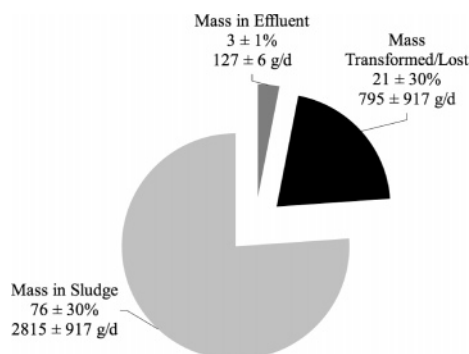


FIGURE 3. Fate of TCC in the activated sludge wastewater treatment plant. The mass balance presented considers all wastewater and sludge processing steps performed, i.e., pretreatment, primary, secondary, and tertiary treatment of wastewater, as well as digestion and dewatering of wastewater residuals. Only about 21% of the TCC mass input was observed to undergo transformation. The majority of the load accumulated in sludge ($76 \pm 30\%$) and a small fraction passed through the plant ($3 \pm 1\%$).

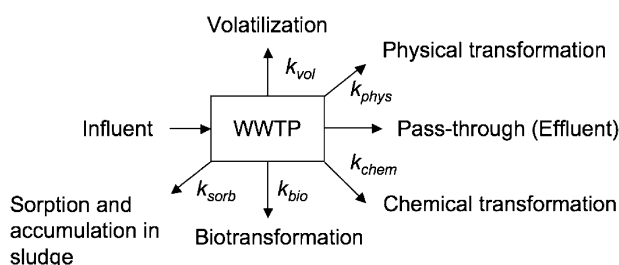


FIGURE 4. TCC can undergo various fates during processing in wastewater treatment plants (WWTPs). The primary route observed in this study was via sorption of the compound to sludge, followed by persistence and accumulation in this matrix despite additional treatment of this material.

surface waters (Table 1). Despite the excellent overall removal of TCC from the aqueous phase ($97 \pm 1\%$), the majority of the TCC load ($76 \pm 30\%$; average 2815 ± 917 g/day) persisted during the treatment process and accumulated in dewatered sludge. The input fraction lost, presumably by biological transformation, or unaccounted for reached $21 \pm 30\%$ (average 795 ± 917 g/d). Primary and secondary wastewater treatment alone provided a TCC removal efficiency of 96%, similar to the overall aqueous-phase removal efficiency of the tertiary plant, as determined via analysis of non-filtered samples.

Discussion

Fate of TCC during Wastewater Treatment. TCC can have various fates during wastewater treatment (Figure 4). Since only about 3% of the TCC mass entering the plant was detectable in the effluent, the remaining mass must have undergone one or a combination of the following five processes: volatilization, chemical transformation, physical transformation, aerobic or anaerobic biotransformation, or sorption to inorganic particles and microorganisms that were removed from the aqueous stream and incorporated into municipal sludge. The volatilization term in eq 1 was ruled to be negligible based on TCC's low vapor pressure (6.67×10^{-5} Torr at 25°C), high boiling point ($344 \pm 37^\circ\text{C}$ at 760 Torr), and strong sorption potential (K_{OC} of 31 700; all values estimated using quantitative structure activity relationship models (4)).

Although the experimental approach did not allow for distinguishing among physical, chemical, and biological transformation, the latter was assumed to be the most

TABLE 1. Fate of the Antiseptic Compound Triclocarban during Full-Scale Activated Sludge Wastewater Treatment

treatment process/matrix considered	mass estimate
average influent mass; $n = 6^b(\text{g/d}) \pm \text{SD}^a$	3,737 \pm 694
average tertiary effluent mass; $n = 22 (\text{g/d}) \pm \text{SD}^a$	127 \pm 6
average secondary effluent mass; $n = 24 (\text{g/d}) \pm \text{SD}^a$	151 \pm 48
average concentration in digested sludge; $n = 3^b(\text{mg/kg dry weight}) \pm \text{SD}$	51 \pm 15
estimated annual mass entering the plant (kg/a)	1,360

^a Average mass \pm standard deviation (SD). ^b Composite samples (see SI for further information).

important of the three processes. In general, phototransformation is not a significant removal mechanism for chemicals during sewage treatment due to the high turbidity of wastewater and a deep tank geometry that discourages interactions between chemicals and sunlight. Other physical and chemical transformation processes were not expected to occur to an appreciable degree because TCC, unless subjected simultaneously to extremes of both temperature and pH (18), is known to be very stable and resistant to hydrolysis in ambient conditions. Biotransformation including complete microbially mediated mineralization had been identified in an earlier study as a likely process of TCC removal during activated sludge treatment; however, the extent to which this process is effective during full-scale treatment had not been explored previously (2). Activated sludge wastewater treatment facilities are designed for optimal biotransformation activity by providing a high density of active microorganisms, a variety of carbon and energy sources at low concentrations that may promote co-metabolism of recalcitrant contaminants, and a milieu of anoxic and oxic zones favoring both anaerobic and aerobic microbial metabolism. Despite these enhanced conditions, no more than $21 \pm 30\%$ of the total mass of TCC was actually biotransformed, lost, or otherwise unaccounted for. Confirmation of biotransformation theoretically can be accomplished by monitoring of the anticipated major TCC metabolites, 4-chloroaniline and 3,4-dichloroaniline. However, their diagnostic value is limited because both compounds have additional sources. In this study, the analytical techniques used precluded the detection of chloroanilines.

Sorption to sludge was demonstrated to be the principal fate of TCC during conventional wastewater treatment. The occurrence and extent of the sorption process was consistent with previous reports. In simulated activated sludge biodegradation experiments, 90% of TCC had been observed to sorb to particles (2). Sorption also is an important process in natural waters, where the mass of the antimicrobial associated with particulates is on the order of $72 \pm 10\%$ (6). Due to its strong affinity to particles ($76 \pm 11\%$ sorbed in raw sewage), a significant fraction of the TCC mass entering the plant was removed, but not transformed, in the primary clarifiers. The remaining mass entered the activated sludge units but did not undergo much transformation either. Data confirming this process were collected previously at the study location, where total TCC concentrations in slurries from the primary and secondary clarifier were observed to exceed $300 \mu\text{g/L}$ (4). Biodegradation may have been limited in part because the TCC mass removed in the primary clarifiers never reached the activated sludge tanks where biotransformation rates were expected to be the greatest due to 8–10 h of aerobic microbial contact time. From studies on triclosan (1), a structurally related antimicrobial compound (4), it is known

TABLE 2. Aqueous-Phase Removal Efficiency of Triclocarban in the Study Plant and in Other Facilities for Which Non-Peer-Reviewed Data Are Available in the Gray Literature (8)

treatment plant	influent ($\mu\text{g/L}$)	effluent ($\mu\text{g/L}$)	aqueous-phase removal efficiency ^a (%)
Activated Sludge			
this study	6.1 ± 2.0 ($n = 6$)	0.17 ± 0.03 ($n = 22$)	97 ± 1 ($n = 9$)
Main Street Pensacola, FL	42	6	88
Polk Run	14.5	0.54	96
Trickling Filters			
Dayton, OH	15 ($n = 6$)	5 ($n = 6$)	65 ($n = 3$)
Northeast Pensacola, FL	27	2	93
Montclair Pensacola, FL	50	12	76
Stretfort Plant, UK	0.4	0.08	81
Glendale, OH	16.3	4.82	70

^a Experimentally defined in this study as the total concentration of analyte in unfiltered, liquid samples.

that trichlorinated binuclear aromatic antimicrobials are biotransformed more effectively in aerobic conditions.

High residual concentrations of TCC in digested and dewatered sludge suggest a pronounced resistance of the compound to anaerobic degradation. One potential anaerobic biotransformation route of TCC is the reductive dechlorination to congeners of reduced chlorine content. Reductive dechlorination is an important mechanism for the biotransformation of many polychlorinated, aromatic pollutants, including polychlorinated biphenyls (PCBs), dioxins, and benzenes (19). The process is mediated by obligate anaerobes that gain energy by using the otherwise persistent chloroaromatics as electron acceptors (19). The digesters at the plant are operated in continuous flow mode with an average sludge retention time of 19 days, which favors the enrichment of obligate anaerobic organisms. However, these organisms either were not present in sufficient quantities or unable to transform TCC to an appreciable degree. Accumulation in sludge of other halogenated aromatics has been observed previously. Reported concentrations of dioxins (20), polychlorinated biphenyls (PCBs) (21), polybrominated diphenyl ethers (PBDEs) (22), and triclosan (23) were as high as, respectively, 0.083 mg TEQ/kg (toxic equivalents), 0.074, 1.44, and 55 mg/kg dry weight in sludge. Thus, the mean concentration of TCC found in sludge in this study (51 ± 15 mg/kg, respectively) was comparatively higher than those of other pollutants known to persist and accumulate in sludge.

Plant Performance. As suggested previously by a more limited data set (4), the WWTP considered in this work showed an excellent aqueous-phase removal efficiency for TCC, comparable to other plants of similar design. Non-peer-reviewed performance data, provided by the industry to the U.S. EPA as part of the ongoing environmental safety assessment for TCC, indicate that the aqueous-phase removal efficiency of the study plant was the best of all activated sludge treatment facilities investigated (88–97%; Table 2). The mean TCC concentration of 6.1 ± 2.0 $\mu\text{g/L}$ (range 3.5–11.4 $\mu\text{g/L}$) observed in raw sewage at the study location ranked near the low end of TCC levels reported for influent (0.4–50 $\mu\text{g/L}$) (8). From the data presented in Table 2 it can be concluded that the aqueous-phase removal efficiency for TCC differs as a function of treatment type, i.e., activated sludge versus trickling filter treatment. Whereas all activated sludge plants performed at levels of 88% or better, trickling filters (65–93%) showed a wider performance range and frequently were less efficient in removing the antimicrobial from wastewater. Findings of the present study may help to

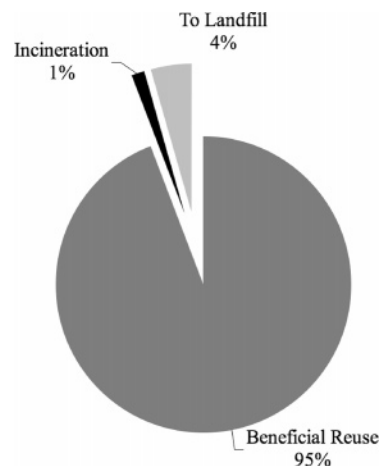


FIGURE 5. Fate of sewage sludge produced in the study plant. The majority of municipal sludge produced was subject to beneficial reuse. Minor amounts were deposited in landfills or incinerated (Source of 2004 data: Maryland Department of the Environment).

explain this performance difference. The observed extensive sorption of TCC to wastewater solids suggests that treatment efficiency should increase with total suspended solids concentration, which is much higher in activated sludge systems than in trickling filters.

Fate of TCC Accumulated in Digested Municipal Sludge.

After the combined treatment of wastewater and wastewater solids, about three-quarters of the initial mass of TCC was still detectable in sludge ($76 \pm 30\%$). This marked persistence of TCC is noteworthy and potentially problematic, given the compound's widespread use, high production volume, and established human toxicity (10–12). Specifically, it implies that approximately three-quarters of the mass of TCC, disposed of by consumers using the topical antiseptic in the sewershed of the plant, ultimately is released into the environment and spread in part on agricultural land. With a recycling rate of 95% (Figure 5), the study location ranks above the national average of 63% reuse of sludge in agriculture and forestry (24).

Considering both the fate of TCC during activated sludge treatment determined in this study, and the per-capita usage rates of TCC in the sewershed calculated here and reported previously (1049 and 1130 mg/person/y, respectively (4)), it must be concluded that more than one metric ton (>1000 kg/y) of TCC is released into the environment in sludge each year from this particular plant alone. To put this finding into perspective, this is equivalent to the total estimated mass of TCC unintentionally released annually nationwide by both sanitary and combined sewer overflows (4). For the United States as a whole, total environmental inputs of TCC from sludge recycling will be relatively higher due to the more than 18 000 treatment facilities that are in operation today. The mechanism of environmental release of TCC identified and quantified in the present study, i.e., via substantial solid phase (sludge) inputs occurring in addition to previously characterized aqueous phase inputs (4), is of potential concern because phenyl urea compounds structurally related to TCC can persist in soil, accumulate in agricultural crops (25), and also may cause secondary contamination of water resources due to surface runoff and vertical leaching in soil.

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Supporting Information Available

Additional information on the study design, sampling strategy, and analytical approaches. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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