Dioxin Photoproducts of Triclosan and Its Chlorinated Derivatives in Sediment Cores

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Triclosan, a widely used antimicrobial, is known to undergo phototransformation in aqueous solution to form 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD). Two sediment cores from a wastewater-impacted depositional zone of the Mississippi River were analyzed for triclosan by ultra performance liquid chromatography-triple quadrupole mass spectrometry (UPLC-MS-Q^3) and for a suite of polychlorinated dioxins and furans by high resolution gas chromatography−mass spectrometry (HRGC-MS) to provide evidence of this photoreaction in the environment. 2,8-DCDD was detected at levels that trended with the historical use of triclosan since its introduction in the 1960s. Three other dioxin congeners, 2,3,7-TCDD, 1,2,8-TriCDD, and 1,2,3,8-TCDD, which are known photoproducts of chlorinated derivatives of triclosan, were also detected with similar trend profiles. These four congeners comprised the majority of di- through tetra-chlorinated dioxins. The trend profile of these specific dioxin congeners did not correlate with the trend profile of the higher-chlorinated dioxin homologues or any chlorinated furan homologues, suggesting a unique source. These results are fully consistent with the phototransformation of triclosan and its chlorinated derivatives that form during wastewater chlorine disinfection as the source of 2,8-DCDD, 2,3,7-TriCDD, 1,2,8-TriCDD, and 1,2,3,8-TCDD in this aquatic environment. As the levels of triclosan-derived dioxins increased over time and the total level of chlorinated dioxins decreased, the contribution of triclosan-derived dioxins to the total dioxin pool increased to as high as 31% by mass in recent years, indicating that their contribution to total dioxin toxicity may need consideration.

Introduction

The use of triclosan, a topical antimicrobial, has increased dramatically over the past half century as it has been incorporated into ever growing numbers of consumer and medical products. Triclosan was first patented in 1964 (*1*) and shortly thereafter added to medical supplies, soaps, shampoos, and deodorants. In the U.S., it was first added to commercial liquid hand soap in 1987, and by 2001, 76% of commercial liquid handsoaps contained triclosan (*2*). Because 96% of the triclosan used in consumer products is disposed of in residential drains (*3*), large triclosan loads are routinely measured in wastewater treatment plant influents (*4*−*6*). Because of its relatively high hydrophobicity (log K_{ow} = 4.2), triclosan removal efficiencies are greater than 90% in conventional activated sludge wastewater treatment because of sorption to the biosolids (*5*). Triclosan, however, is still frequently detected in wastewater effluents and wastewater-impacted waterways throughout the world (*4*−*9*).

Upon exposure to chlorine, the common wastewater and drinking water disinfectant, triclosan is transformed by chlorination at the *ortho*- and *para*- positions of its phenol ring to form three chlorinated triclosan derivatives (CTDs; Figure 1), 4,5-dichloro-2-(2,4-dichlorophenoxy)phenol (4-Cl-TCS), 5,6-dichloro-2-(2,4-dichlorophenoxy)phenol (6-Cl-TCS), and 4,5,6-trichloro-2-(2,4-dichlorophenoxy)phenol (4,6-Cl-TCS) (*10, 11*). The CTDs have been detected in wastewater influent, effluent, and fish (*4, 12, 13*).

Two important triclosan elimination pathways from surface waters are photolysis and partitioning to settling particles. Photolysis has been shown to be responsible for ∼80% of triclosan loss in the epilimnion of Lake Greifensee, Switzerland (*14*). One of the solar photolysis products of triclosan in water, however, is the chlorinated dioxin, 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD) (*15*−*17*) (Figure 1). Analogous to triclosan, 4-Cl-TCS, 6-Cl-TCS, and 4,6-Cl-TCS photochemically react to form 2,3,7-trichlorodibenzo-*p*-dioxin (2,3,7-TriCDD), 1,2,8-trichlorodibenzo-*p*-dioxin (1,2,8-TriCDD), and 1,2,3,8-tetrachlorodibenzo-*p*-dioxin (1,2,3,8-TCDD), respectively, under solar irradiation (Figure 1) (*15, 18*). The dioxin products from the CTDs are potentially of greater concern than 2,8-DCDD formed directly from triclosan, because dioxin receptor binding/toxicity increases with chlorine substitution in the lateral positions (*19, 20*). Once formed by photolysis, the dioxins could partition to particles that ultimately settle in depositional zones along with triclosan that is removed from the water column by this process.

We hypothesized that triclosan and the wastewater-produced CTDs could serve as an important, yet unrecognized, source for polychlorinated dioxins in the environment. As a first step in testing this hypothesis, we sought to examine the congener-specific temporal trends of chlorinated dioxins and compare them to the temporal trend of triclosan. To accomplish this, two sediment cores were collected from the dominant depositional zone of the Mississippi River (Lake Pepin; Supporting Information, Figure S1) downstream of several wastewater treatment plant outfalls serving a major metropolitan area (Minneapolis/St. Paul, MN). There are no

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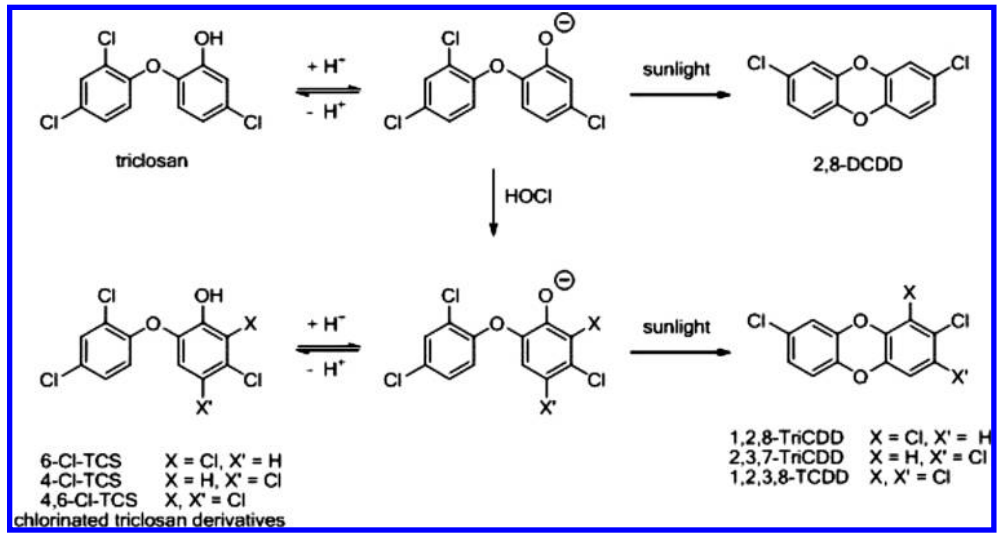

FIGURE 1. Previously established chlorination and photochemical transformations of triclosan leading to polychlorinated dibenzo-*p*-dioxins.

other depositional zones between Minneapolis/St. Paul and Lake Pepin where sediment dating can be performed and where contaminants (such as triclosan and dioxins) would be expected to accumulate. These cores were dated, sectioned, and analyzed for triclosan and its dioxin photoproducts as well as incineration-derived polychlorodibenzo-*p*-dioxin and polychlorodibenzofuran (PCDD/F) homologues.

Experimental Section

Sediment Core Collection. Two sediment cores were obtained from Lake Pepin (Minnesota, U.S.A.) in June, 2008. The first core (I.3; 80 cm sediment depth) was collected 6 km from the inflow of Lake Pepin (44°33′18.391″ N, 92°22′56.082″ W), while the second core (V.4; 76 cm depth) was collected 4 km from its outflow (44°26′04.267″ N, 92°09′30.685″ W). The cores were dated by stratigraphic correlation of whole-core magnetic susceptibility, as measured on a Geotek Multi-Sensor Core Logger (MSCL), with previously dated cores collected from the same locations in 1996. The original chronology was derived from a synthesis of ^{210}Pb, ^{137}Cs, and AMS−^{14}C dating and stratigraphic markers based on pollen analysis and loss-on-ignition, as described in Engstrom et al. (*21*). Core I.3 extended back to only 1986 owing to the high sediment accumulation rates at the head of Lake Pepin, while core V.4 dated to 1940 at its base. Core I.3 was sectioned into 10 slices of 4 to 10 cm depth, and core V.4 was divided into 9 slices of 8 to 10 cm depth. Each section was homogenized, and the moisture content was determined gravimetrically after drying a subsample in an oven at 110 °C.

Triclosan Analysis. Single wet samples with a mass corresponding to ∼10 g dry weight from each core section were spiked with 500 ng of $^{13}C_{12}$-triclosan as an isotope dilution internal standard for the analysis of triclosan. A single unspiked blank sample of clean sand was processed and analyzed to ensure that there was no triclosan contamination. Two clean sand recovery standards were spiked with 500 ng of $^{13}C_{12}$-triclosan and 500 ng of triclosan to measure the relative recovery of unlabeled triclosan. The samples were Soxhlet extracted into methanol for 16−18 h. The extracts were concentrated to ∼5 mL and centrifuged for 10 min at 5,000 rev/min to remove particulate matter. The supernatant was then transferred to a new vial by gastight syringe, and its exact volume was recorded. From each supernatant, 1.00 mL was dissolved in 25 mL of water (adjusted to pH 4 with H_2SO_4/NaOH) via sonication for 10 min. These solutions were then solid-phase extracted according to a modified version of the method described by Vanderford and Snyder (*22*). Waters Oasis HLB 6 cc/200 mg cartridges on a Restek 12-port vacuum manifold were preconditioned with sequential 5 mL aliquots of MTBE, methanol, and water. The samples were loaded and run under vacuum at ∼2 mL/min. The cartridges were then washed (3 × 5 mL 50:50 methanol:water (v/v)), dried under vacuum for 25 min, and eluted into graduated glass centrifuge tubes with 5 mL of methanol followed by 5 mL of 90:10 MTBE/methanol (v/v). The SPE extracts were concentrated under nitrogen to <500 μL and quantitatively loaded onto silica columns conditioned with ethyl acetate for further cleanup. Silica columns were prepared by packing 6 cc disposable syringes with a plug of glass wool, a thin layer of sand, 2.00 g of silica gel (Sorbent Technologies Premium Rf, 60 Å, 40−75 μm or Sorbent Technologies Standard grade, 60 Å, 32−63 μm) in a slurry of ethyl acetate, and a thin upper layer of sand. The columns were eluted by gravity with 10 mL of ethyl acetate. The eluants were concentrated under nitrogen and solvent exchanged to a final volume of ∼100 μL in 50:50 acetonitrile/water (v/v). Eight calibration standards were prepared in 50:50 acetonitrile/water (v/v) with triclosan concentrations ranging from 2.50 to 2,500 μg/L and a constant concentration of $^{13}C_{12}$-triclosan internal standard (125 μg/L).

Triclosan analysis of processed samples and calibration standards was carried out using a Waters NanoAcquity ultra performance liquid chromatograph (UPLC) equipped with a Finnigan TSQ Quantum Ultra triple quadrupole mass spectrometer (MS-Q^3). Sample injections of 8 μL were made onto a Phenomenex Synergi MAX-RP column (150 × 0.5 mm, 4 μm, 80 Å) using a binary gradient of 15 mM ammonium acetate buffer (A) and acetonitrile (B) at a constant flow rate of 10 μL/min. The gradient began at 50% B, ramped up linearly to 100% B at 20 min, ramped linearly down to 50% B at 23 min, and held at 50% B until 35 min to allow for re-equilibration. The LC effluent was diverted to waste during the first 10 min and last 10 min of the run when triclosan was not eluting to prevent contamination of the ionization source. Negative mode electrospray ionization was used. Single reaction monitoring (SRM) of the precursor ion (deprotonated triclosan; m/z 287) to chloride ($^{35}Cl^-$; m/z 35) transition was carried out for triclosan quantification at a collision voltage of 12 V. For identity confirmation, a second SRM transition from 289 to $^{37}Cl^-$ (m/z 37) was also monitored. The SRM transition from 299 to $^{35}Cl^-$ (m/z 35) was used for the quantification of the isotope dilution standard, $^{13}C_{12}$-triclosan. ESI-MS-Q^3 parameters were set as follows: spray

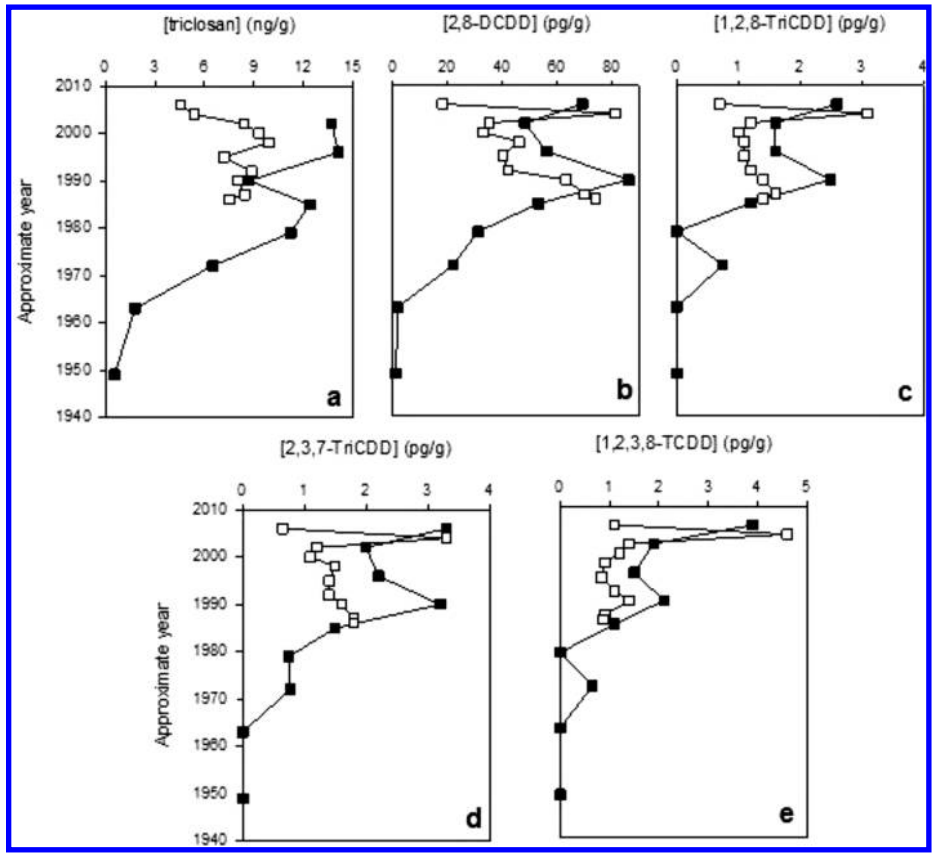

FIGURE 2. Profiles of triclosan and triclosan-derived dioxins in two sediment cores. Concentrations as a function of time (depth) for a, triclosan; b, 2,8-DCDD; c, 1,2,8-TriCDD; d, 2,3,7-TriCDD; and e, 1,2,3,8-TCDD for sediment cores I.3 (open symbols) and V.4 (closed symbols) collected from Lake Pepin. Approximate dates represent the midpoint of each core section. Note different units and scales on the *x*-axes. Analytical errors are quantified in the Supporting Information.

voltage 3,500 V, nitrogen sheath gas pressure 40, capillary temperature 250 °C, capillary offset −35 V, argon collision gas pressure 1.0 mTorr, tube lens 140 V, dwell time 150 ms per SRM transition. Instrument blanks (pure 50:50 acetonitrile:water (v/v)) were analyzed approximately every 10 samples to ensure that no contamination due to carry-over between samples occurred.

Samples were quantified from an eight-point external calibration curve constructed by plotting the ratio of analyte signal to isotopically labeled internal standard signal versus the analyte concentration. The reporting limit established required the ratio of analyte signal to isotopically labeled internal standard signal for a sample to be greater than that of the lowest calibration standard. The raw analyte signal also had to be greater than 10 times the analyte signal observed in the laboratory blank.

Dioxin and Furan Analysis. An approximately 10 g dry weight sample of each homogenized core section was spiked with 19 $^{13}C_{12}$-labeled di- through octa-CDD/F isomers as isotope dilution internal standards and analyzed following a version of U.S. EPA Method 1613B (*23*), expanded to analyze for di- and tri-CDD/Fs, as outlined below. Method blank and laboratory spike samples were prepared with the extraction batch to demonstrate freedom from laboratory contamination and to provide precision and accuracy information for the analysis. Each sample was extracted with toluene for 16−18 h using a Soxhlet/Dean−Stark apparatus. The extracts were spiked with $^{37}Cl_4$-2,3,7,8-TeCDD as a cleanup standard, concentrated, and washed by shaking with concentrated sulfuric acid. Each extract was then eluted through a multilayer silica column (2 g neutral silica, 4 g acidic silica, and 2 g basic silica) with hexane. Each eluate was added to a 4 g activated aluminum oxide column (Ecochrom Super 1) and eluted with 60:40 dichloromethane/hexane (v/v). Each eluate was then solvent exchanged into hexane and added to a column containing approximately 0.5 g of 18% activated carbon on Celite. Potentially interfering compounds were washed through each column in the forward direction and then the analytes were eluted off the column with 20 mL of toluene in the reverse direction. The toluene was then concentrated, spiked with $^{13}C_{12}$-labeled PCDD/F recovery standards, and concentrated to a final volume of 40 μL.

In addition to the U.S. EPA Method 1613 calibration set, a secondary calibration standard set was prepared from individual di- and tri-CDD/Fs at the same levels as the tetrachlorinated standards from the Method 1613 calibration set. Aliquots of these two calibration standard sets were combined to prepare a five-point calibration set containing di- through octa-CDD/Fs at concentrations ranging from 0.25 to 1000 pg/μL.

High-resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) analysis was performed using a Waters Autospec Ultima high resolution mass spectrometer operated in selected ion recording mode (positive electron impact, > 10,000 resolution, 32 eV, 280 °C). The acquisition windows were set to include all tetra- through octa-CDD/F isomers and selected di- and tri-CDD/F isomers. Selected sample extracts were analyzed using expanded acquisition windows, and it was verified that other non-target di- and tri-CDD/F isomers were not present at significant levels (estimated at <10% of targeted di- and tri-CDDs).

Method Evaluation and Performance. Trace amounts of triclosan were detected in the clean sand method blank and in the instrument blank samples. These levels were at least 10 times below the reporting limit, which was established to be 0.3 ng/g. The triclosan signal for every sediment sample

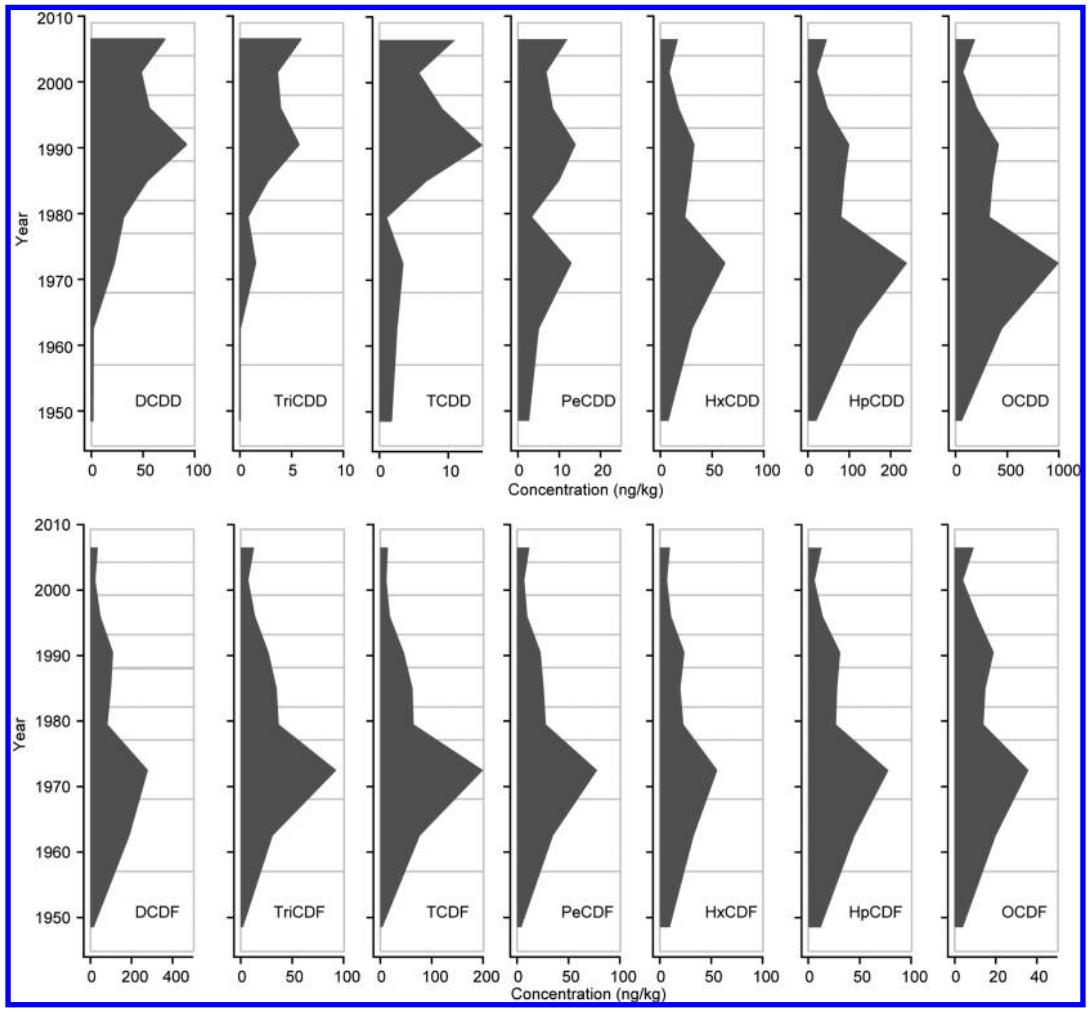

FIGURE 3. Temporal trends of all PCDD and PCDF homologue groups in core V.4. Di-, tri-, and tetrachlorodibenzo-*p*-dioxin homologues include the contributions of the specific congeners derived from triclosan. The concentration values for each core section are plotted in the center of the date range of each core section. The core section date ranges are represented by the boxes in the background of each plot.

was at least 10 times greater than the triclosan signal in the method blank, and in most cases, several orders of magnitude greater. Because of the heavy matrix and high amount of ion suppression in the mass spectrometry analysis, low absolute recoveries of $^{13}C_{12}$-triclosan were obtained (22 ± 18%, n = 9 for core V.4 and 10 ± 9% n = 8 for core I.3). The isotope dilution methodology, however, was expected to correct for these losses, as demonstrated by the high relative recoveries of spiked triclosan in the laboratory spike samples (95 ± 3%, n = 2). Additional information about the triclosan method performance is provided in the Supporting Information, Table S1.

For the dioxin and furan analysis, the absolute recoveries of the isotopically labeled PCDD/F internal standards in the sample extracts ranged from 23−114%. Information for each internal standard is compiled in Supporting Information, Table S2. All of the labeled standard recoveries obtained were within the target ranges specified in U.S. EPA Method 1613. Because the quantification of the native analytes was based on isotope dilution methodology, the data were automatically corrected for variation in recovery and accurate values were obtained. Laboratory samples (sand) fortified with native standards exhibited relative recoveries of 92−123% with relative percent differences of 1.0 to 12.0% (n=2) after isotope dilution-correction, confirming the accuracy and precision of the method. No di- through tetra-CDD/F isomers were detected in the laboratory method blank. Selected penta- through hepta-CDD/F isomers, however, were detected in the blank at levels well below the calibration range of the method. For OCDD/F, levels <1 pg/g were detected in the blank. The concentrations determined for the sediment samples were all at least 10 times higher than the levels detected in the method blank. Additional quality assurance data for the dioxin method is provided in the Supporting Information, Table S3.

Results and Discussion

Triclosan was detected in the sediment cores with an upward-vertical concentration profile, reflecting the increasing use of triclosan since the 1960s (Figure 2a). A similar result was seen in Lake Greifensee (Switzerland) (*9*) and in estuaries in the U.S. (*24*). Corresponding with the increase in triclosan levels from 1963−2008 (Figure 2a), the concentration profile of 2,8-DCDD, the known photoproduct of triclosan, revealed a substantial increase over the same period in sediment core V.4 (Figure 2b). Similar levels of 2,8-DCDD and triclosan were also observed for core I.3 (Figure 2a,b), though temporal trends could not be discerned, for this core did not date back as far as V.4. Concentrations of 2,3,7-TriCDD, 1,2,8-TriCDD, and 1,2,3,8-TCDD, the known photoproducts of the chlorinated derivatives of triclosan, also increased over time in core V.4 with similar levels in I.3 (Figure 2c−e). These trends are markedly different than those observed for higher chlorinated dioxin homologue groups and the PCDF homologues, which peaked in concentration in the 1970s and have been decreasing since then (Figure 3).

While concentrations generally trend upward for triclosan and the triclosan-derived dioxins in core V.4, a peak in the concentration of the triclosan-derived dioxin congeners was observed in the section dated from 1988−1993 followed by a dip in the late 1990s. This decrease was observed for all dioxin and furan homologues (not just the triclosan-derived dioxins; see Figure 3), and thus, is unlikely to reflect specific source or loss processes of the specific congeners derived from triclosan. There was a major flood in the region in 1993 and the 1990s were a period of high flows and high sediment flux to Lake Pepin, which may explain this decrease (*25*). In core I.3, a peak in the concentrations of these congeners was observed in the section dated from 2003−2005 followed by a large decrease in the subsequent section. Again, this same pattern was observed for each dioxin and furan homologue and likely does not reflect specific source or loss processes.

In all sections of cores I.3 and V.4, 2,8-DCDD comprised at least 90% of the total DCDD congener concentration (Σ[DCDD]), and in most core sections, 2,8-DCDD was the only DCDD congener detected. Likewise, 2,3,7-TriCDD and 1,2,8-TriCDD together made up at least 90% of Σ[TriCDD] and in most sections were the only TriCDD congeners detected. Various TCDD congeners were detected throughout core V.4, but 1,2,3,8-TCDD was not detected in the deepest sections. 1,2,3,8-TCDD, however, comprised an increasing fraction of Σ[TCDD] over time, reaching 37% and 35% of Σ[TCDD] in the uppermost sections of core I.3 and V.4, respectively. Additionally, the ratio of the sum of the TriCDD and TCDD triclosan-derived congener concentrations to the 2,8-DCDD concentration in core sections of I.3 and V.4 ranged from 0.02−0.14. This ratio is comparable to the ratio of their putative photochemical precursors, that is, Σ[CTDs]:[triclosan], observed in previous analyses of wastewater treatment plant effluents (0.01, 0.16, 0.07) (*4*), measured in the effluent of the major plant that discharges into the Mississippi River upstream of Lake Pepin (0.17) (*26*), and found as methylated analogues in carp of a wastewater treatment plant drainage outlet (0.03) (*12*).

Two contrasting temporal trends were observed for PCDD/F concentrations in sediment core V.4. The first was best represented by 2,8-DCDD and was characterized by low levels in the earliest core sections and an increase until a peak in the 1988−1993 section. This trend was shared by only three other dioxin congeners: 2,3,7-TriCDD, 1,2,8-TriCDD, and 1,2,3,8-TCDD, and the concentration profile of these three congeners positively correlated with 2,8-DCDD with R^2 values of 0.93, 0.85, and 0.64, respectively (Supporting Information, Figure S2). The second trend type was exemplified by octachlorodibenzo-*p*-dioxin (OCDD), the most abundant dioxin congener in all V.4 sections, and was characterized by a dramatic increase from 1940 until a peak in the early 1970s, followed by a decline over the subsequent decades (Figure 3). This trend type was shared by the hexa- and hepta-CDD homologues and all PCDF homologues (Figure 3), each giving positive linear correlations with OCDD (R^2 values ≥ 0.93; Supporting Information, Figure S2). There was no correlation between the putative triclosan-derived dioxin congeners with the OCDD trend type ($R^2 \leq 0.06$; Supporting Information, Figure S2).

The two disparate trend profiles observed in sediment core V.4 indicate a distinct source for 2,8-DCDD, 2,3,7-TriCDD, 1,2,8-TriCDD, and 1,2,3,8-TCDD from the other PCDD/F homologues, likely the photochemical transformation of triclosan and its chlorinated derivatives in the surface water to which they are discharged. The OCDD trend profile is characteristic of PCDD/F atmospheric deposition in industrialized areas of the U.S. and Europe predominantly from incineration sources (*27*). It usually coincides with PCDD/F homologue patterns dominated by PCDDs, especially the most-highly chlorinated homologues (*27*). An example of this homologue pattern is presented in Figure 4 from the core V.4 section dated from 1968 to 1977.

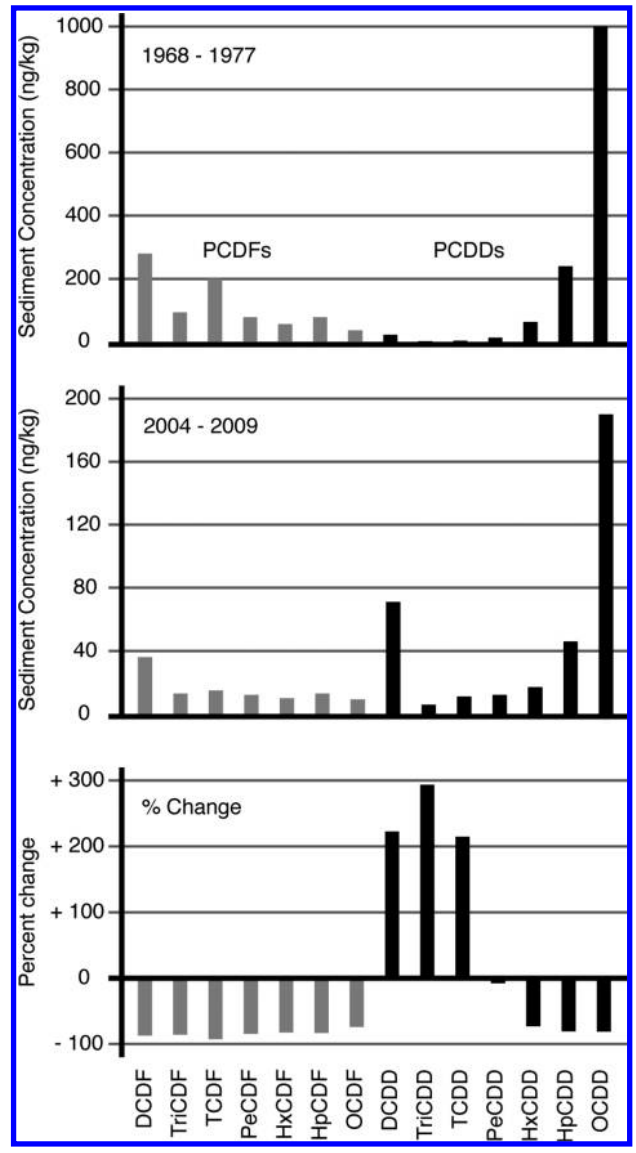

FIGURE 4. Congener distribution profiles from core V.4. The top panel is for 1968−1977 and the middle panel for 2004−2009. For each of these panels, each bar represents the sum of the isomers. The bottom panel shows the percent change between the two time periods.

In contrast to the more highly chlorinated dioxins, 2,8-DCDD, 2,3,7-TriCDD, 1,2,8-TriCDD, and 1,2,3,8-TCDD appear to originate from triclosan, as their temporal trend profiles match historical triclosan use. As shown in Figure 4, the levels of the DCDD, TriCDD, and TCDD homologues increase 200−300% from 1963 to present, consistent with increasing triclosan use. All other PCDF/PCDDs homologues (with the exception of pentachlorodioxins) decrease by 73−93% (Figure 4), consistent with improvements in incineration technologies reducing their emissions. Furthermore, the identity, relative distribution, and predominance of the 2,8-DCDD, 2,3,7-TriCDD, 1,2,8-TriCDD, and 1,2,3,8-TCDD among di-, tri-, and tetra-CDD homologues are fully consistent with the transformation of triclosan by chlorine disinfection and the subsequent photochemical transformation of triclosan and its chlorinated derivatives.

In assigning photochemistry of triclosan and its chlorinated derivatives as the source of these congeners, it is important to account for other potential sources. An alter-

native source could be their presence as trace impurities in formulations of triclosan used in consumer products. 2,8-DCDD has been detected in triclosan at concentrations on the order of 10 ppb, along with other di- and tri-CDD/Fs at the ppb level (*28*) and several 2,3,7,8-substituted dioxin congeners at the low ppt level (*29, 30*). This does not appear to be the source of the dioxins observed in the sediment, because we expect higher removal efficiencies for the more hydrophobic (estimated log K_{ow} values for 2,8-DCDD, 2,3,7-TriCDD, 1,2,8-TriCDD, and 1,2,3,8-TCDD are 5.6, 6.3, 6.3, and 6.9, respectively) (*31*) PCDD impurities than for triclosan during wastewater treatment. Additionally, the TriCDD and TCDD congeners in sediment do not match those reported as impurities in triclosan (*28*−*30*).

Another potential source of these specific di- and tri-CDD congeners is the anaerobic biological reduction of higher chlorinated dioxins within the sediment (*27*). While we cannot rule out this possibility, this source appears unlikely for Lake Pepin because the levels of 2,8-DCDD, 2,3,7-TriCDD, 1,2,8-TriCDD, and 1,2,3,8-TCDD were lowest in the older core sections that had the highest levels of the potential higher-chlorinated precursors and the longest exposure time for anaerobic biotransformation. Conversely, the levels of these di- and trichlorinated congeners were highest in more recent core sections that had lower levels of higher-chlorinated dioxins and less time available for biotransformation. Furthermore, the bioreduction of higher-chlorinated dioxins would be expected to yield a broader suite of di- and trichlorinated congeners than the three predominantly detected in this study.

The levels of triclosan-derived dioxins observed in Lake Pepin indicate that the photochemical reactions of triclosan and its chlorinated derivatives contribute a substantial mass fraction to the total PCDD pool. This finding of traditional persistent organic pollutants (POPs) coming from an unexpected source shares similarities to recent work showing that a polychlorinated biphenyl congener (PCB-11) arises from use of dye and paint pigments (*32*−*34*). In both cases, the specific POPs congener patterns were critical in identifying the sources.

As the level of triclosan-derived dioxins has increased over time while the level of higher-chlorinated dioxins has decreased (Figure 4), the mass contribution of triclosan-derived dioxins rose as high as 29% of the total dioxin pool in core I.3 and 31% in core V.4 (Supporting Information, Figure S3). It is difficult to assess the toxicity implications of this change in the dioxin pool composition, as the specific dioxin congeners derived from triclosan have not been assigned toxic equivalency factors (*35*). This appears to be, in part, because these congeners have not previously been widely detected. The available data indicate the toxicity and receptor binding of these congeners is much weaker than 2,3,7,8-TCDD and perhaps comparable to OCDD (*19, 20, 36*). There is also data that suggests that the mode of toxicity may be different. For example, using recombinant *E. coli* strains to assay for different types of cellular damage, Min et al. (*37*) found that while 2,8-DCDD did not show the wide range of stress response induced by 2,3,7,8-TCDD, it did show general cell toxicity on the order of 1% of 2,3,7,8-TCDD.

Triclosan and its chlorinated derivatives represent a previously unrecognized and increasingly important source of di-, tri-, and tetrachlorinated dibenzo-*p*-dioxins to aquatic systems as recorded by Lake Pepin sediments. A re-examination of dioxin congener patterns in sediments and biota in triclosan-impacted waters may be warranted to assess the need for further toxicological investigation of triclosan-derived dioxins.

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Supporting Information Available

Supplementary Figures S1−S3 (map of Lake Pepin, correlations among dioxin congeners, and percentage of dioxin mass attributable to triclosan-derived dioxins) and Tables S1−S3 (quality assurance data for the analytical methods). This material is available free of charge via the Internet at http://pubs.acs.org.

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