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TRICLOCARBAN, TRICLOSAN, POLYBROMINATED DIPHENYL ETHERS, AND 4-NONYLPHENOL IN BIOSOLIDS AND IN SOIL RECEIVING 33-YEAR BIOSOLIDS APPLICATION

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Abstract—Land application of biosolids is a common practice throughout the world. However, concerns continue to be raised about the safety of this practice, because biosolids may contain trace levels of organic contaminants. The present study evaluated the levels of triclocarban (TCC), triclosan (TCS), 4-nonylphenol (4-NP), and polybrominated diphenyl ethers (PBDEs) in biosolids from 16 wastewater treatment plants and in soils from field plots receiving annual applications of biosolids for 33 years. All of the four contaminants evaluated were detected in most of the biosolids at concentrations ranging from hundreds of μg/kg to over 1,000 mg/kg (dry wt basis). They were detected at μg/kg levels in the biosolids-amended soil, but their concentrations decreased sharply with increasing soil depth for 4-NP, PBDEs, and TCC, indicating limited soil leaching of those compounds. However, potential leaching of TCS in the biosolids-amended soils was observed. The levels of all four compounds in the surface soil increased with increasing biosolids application rate. Compared with the estimated 33-year cumulative input to the soil during the 33-year consecutive biosolids application, most of the PBDEs and a small percentage of 4-NP, TCC, and TCS remained in the top 120-cm soil layer. These observations suggest slow degradation of PBDEs but rapid transformation of 4-NP, TCC, and TCS in the biosolids-amended soils. Environ. Toxicol. Chem. 2010;29:597–605. © 2009 SETAC

Keywords—Biosolids Land application Fate Pharmaceuticals and personal care products Persistence

INTRODUCTION

Farmland application is considered to be the most sensible and cost-effective biosolids management option for many municipalities, and it provides tremendous savings in fertilizer costs to the farmers [1,2]. It is estimated that biosolids production in the United States could reach 8.2 million dry mg/year by 2010, 70% of which would be land applied [3]. However, concerns over the biosolids land application practice remain, because the biosolids may contain detectable levels of various anthropogenic chemicals that could enter the wastewater stream via domestic and industrial sources [4,5].

In recent years, a group of anthropogenic chemicals classified as pharmaceutical and personal care products (PPCPs) has received a lot of media attention, mainly as a result of frequent detection of these chemicals in biosolids [6–8] and their potential negative impacts on various organisms [9–11]. Each year, large quantities of PPCPs are consumed in the United States and worldwide. In 2006, the United States and Canada alone accounted for approximately half of the worldwide sales of pharmaceuticals [12] (http://www.efpia.eu/Content/Default.asp?PageID=608). A large amount of PPCPs used by humans eventually ends up in wastewater via excretion with urine and feces as parent compounds, conjugated compounds, or metabolites and through washing or direct disposal [13]. During the wastewater treatment process, some PPCPs tend to partition into biosolids because of their high affinity for organic-matter-rich biosolids [14–16].

The federal regulations that govern the land application of biosolids have limits on nutrients, metals, and pathogen contents in biosolids [17]. However, there are no regulatory limits on the contents of anthropogenic organic chemicals, because there has been insufficient evidence suggesting significant human health risk associated with organic contaminants in biosolids. It is suspected that land application of biosolids containing traces of PPCPs may provide a potential route through which these contaminants may enter the environment [7]. To date, little is known about the environmental impact of PPCPs and their fate in biosolids and biosolids-amended soils.

Since the 1960s, triclocarban (TCC) and triclosan (TCS) have been added as antibacterial agents to many consumer products such as hand soaps, toothpastes, creams, etc. [18,19] (http://www.epa.gov/HPV/pubs/summaries/tricloca/c14186tp.pdf). Nonylphenol polyethoxylates, parent compounds of 4-nonylphenol (4-NP), have been in use for more than 40 years as detergents, emulsifiers, wetting agents, and dispersing agents in many household and industrial products [20]. In the early 1970s, the increasing use of inflammable materials such as plastics in electrical equipment such as personal computers or synthetic fibers in sofas and curtains led to the widespread use of polybrominated diphenyl ethers (PBDEs) as flame retardants [21]. The basic chemical characteristics and common use of these

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All Supplemental Data may be found in the online version of this article.

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compounds can be found in Supplemental Data, Table S1. All of these compounds have been frequently detected in biosolids worldwide [7,14,22–24].

A few reports based on short-term laboratory and field studies of the transformation of PPCPs in biosolids and biosolid-amended soils, predicting half-lives of several PPCPs ranging from less than one month to a few years [25–27], are available in the literature. However, information is scarce concerning concentrations of PPCPs in soils receiving continuous and long-term application of biosolids. Therefore, the present study evaluated concentrations of 4-NP, PBDEs, TCC, and TCS in biosolids from 16 wastewater treatment plants (WWTPs) in the United States and in soil samples from long-term field plots that have received annual applications of biosolids for 33 years. The present study is the first investigation reporting levels of 4-NP, PBDEs, TCC, and TCS in a soil profile after a history of long-term biosolids application.

MATERIALS AND METHODS

The occurrence of 4-NP, selective congeners of PBDEs (PBDE-47, -99, -100, -153, and -154), TCS, and TCC was evaluated in fresh biosolids and composted biosolids collected from 16 WWTPs in the United States. Detailed information about these WWTPs can be found in Supplememtal Data, Table S2. Several subsamples of biosolids were collected immediately after the dewatering step, i.e., after the belt press or centrifugation. In the WWTPs that compost their biosolids, subsamples of biosolids were collected from different depths within a compost pile. The subsamples were composited on site immediately after collection and were placed in precleaned wide-mouth borosilicate jars. The samples were placed in a cooler on ice, transported to the laboratory, and stored at −20°C.

The long-term field plots were established in 1973 by the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC) on a calcareous mine spoil (pH 7.8, bulk density 1.91 mg/m^3) at a land reclamation site located in Fulton County, Illinois (see Supplemental Data, Fig. S1). The plot dimensions were 4.6 by 12.2 m, and treatments consisting of a control (receiving no biosolids) and anaerobically digested primary and waste-activated biosolids were applied annually at 16.8, 33.6, and 67.2 mg biosolids/ha (dry wt). Inorganic fertilizers were applied annually as N–P–K (336–224–112 kg/ha) to the control plots and 112 kg K/ha to the biosolids-amended plots. Corn (*Zea mays* L.) was planted in each plot and manually harvested every year. Data on the metal uptake by corn from these plots were used in the risk assessments conducted by the U.S. Environmental Protection Agency (U.S. EPA) to develop the Part 503 biosolids regulations. At the end of 2005, when the soil samples were collected from these field plots for the present study, the cumulative biosolids loadings were 0, 554.5, 1,109, and 2,218 mg biosolids/ha (dry wt). The experimental design was a randomized block of four treatments and four replications. Additional details about the field plots are given elsewhere [28].

It is noteworthy that the long-term plots with cumulative loadings of 554.5 to 2,218 bg dry biosolids/ha represent the worst-case scenario, and it would take over 100 years of continuous annual applications of biosolids to reach this high cumulative loading at the U.S. EPA-recommended agronomic rate of biosolids application, which generally ranges from 16 to 20 mg dry biosolids/ha.

In 2005, four soil cores (0–120 cm) were randomly collected from each plot. Each core was divided into four depth increments (0–15 cm, 15–30 cm, 30–60 cm, and 60–120 cm), and soil samples for the corresponding depths were combined and thoroughly mixed on site to obtain composite soil samples of each depth interval for each plot. Care was taken to prevent cross-contamination among sites by thoroughly rinsing the soil sampler and mixing apparatus. The composite soil samples were placed in wide-mouth prerinsed borosilicate glass jars. The samples were placed in a cooler on ice, transported to the laboratory, and stored at −20°C.

Sample extraction, clean-up, and analysis

For 4-NP and PBDEs, 2 g of freeze-dried and ground soil or biosolids was extracted using methylene chloride (CH_2Cl_2) on an accelerated solvent extraction (ASE) system (ASE 200; Dionex). An appropriate amount of hydromatix was mixed with the samples to compensate for the extra space in the ASE extraction cell. The ASE extraction conditions were as follows: two extraction cycles, pressure 1,500 psi, temperature 100°C, heat 5 min, static 20 min, 100% flush, purge 120 s. Approximately 35 ml of extract was recovered after the ASE extraction. Each extract was concentrated to a final volume of approximately 1 ml and then cleaned up by passing it through a deactivated silica gel column. After the clean-up, the column was eluted first with 30 ml hexane (fraction containing PBDEs) and then with 20 ml 20% acetone/hexane (fraction containing 4-NP). Each elution fraction was collected and concentrated down to exactly 2 ml for quantitative analysis of PBDEs with gas chromatograph with electron capture detector (GC/ECD) and for quantitative analysis of 4-NP with gas chromatograph with mass spectrophotometer detector (GC/MS). Gas chromatography/mass spectrometry was used for confirmation of PBDEs. Further analytical details are given in Supplemental Data, Table S3.

For TCC and TCS, 3 g of freeze-dried soil or biosolids sample was weighed into a 25-ml beaker. In the soil samples, the target compounds were extracted three times with 7 ml acetone and 15-min sonication intervals (Bransonic 52, 50/60 Hz; Branson Ultrasonics). In the biosolids samples, the target compounds were extracted four times using 10 ml acetone and 15-min sonication intervals. After each sonication, the sample was centrifuged at 3,500 *g* for 10 min, and the supernatant was decanted into the same vial. The final supernatant was evaporated to complete dryness using a turbo evaporator and then redissolved in 1.5 ml and 50 ml acetonitrile for the soil and biosolids samples, respectively. The final solution was filtered with a Millex Millipore filter (0.45 μm, PTFE, 13 mm) and transferred to a 1.5-ml glass vial for analysis of the target compounds with a liquid chromatograph with mass spectrophotometer detector (LC/MS). Further analytical details are given in Supplemental Data, Table S4.

Laboratory blank samples were extracted and analyzed using the above-described methods. No laboratory cross-contamination in the blank samples was observed. The recovery rates for PBDEs, 4-NP, TCC, and TCS spiked in clean soil samples were 98% ± 5%, 101% ± 3%, 92% ± 2%, and 111% ± 2%, respectively. The recovery rates for PBDEs, 4-NP, TCC, and TCS spiked in clean biosolids samples were 95% ± 4%, 98% ± 5%, 92% ± 2%, and 126% ± 6%, respectively. The limit of quantitation (LOQ) for each analyte was determined based on the standard deviation of the detector's response (SD) and the slope of the calibration curve (S) according to the formula: LOQ = 10(SD/S) (CFR Part 136, Appendix B, 1993). The SD was determined based on the standard deviation of the responses from seven standard solutions with the same lowest concentration of the calibration curve for the target analyte. The slope of the calibration curve was determined by the responses of standard solutions with seven different concentrations. The LOQ values for PBDEs, 4-NP, TCC, and TCS in soils were 0.5, 10, 0.5, and 0.5 μg/kg, respectively. The LOQ values for PBDEs, 4-NP, TCC, and TCS in biosolids were 5, 40, 8, and 12.5 μg/kg, respectively.

Although previous investigations have shown that PBDE-209 tends to be dominant in biosolids [29], congeners PBDE-47, PBDE-99, PBDE-100, PBDE-153, and PBDE-154, which are more toxic than PBDE-209 [30], have frequently been detected as the dominant PBDE congeners in biological samples worldwide [29,31]. Therefore, the present study's investigation of biosolids and biosolids-amended soils focused on congeners PBDE-47, PBDE-99, PBDE-100, PBDE-153, and PBDE-154 only.

Nonmeteric multidimensional scaling, a nonparametric method, was used to provide graphic ordination of the relative contribution of the four analytes to the total analyte pool. Matrix dissimilarity was measured using the Sorenson distance measure. Analysis was conducted using the software package PC-ORD v. 4.0 (MJM Software) and following the recommendations of McCune and Mefford [32].

RESULTS AND DISCUSSION

Occurrence of TCC, TCS, PBDEs, and 4-NP in biosolids

Both TCC and TCS were detected in a majority of the fresh biosolids and composted biosolids samples investigated in the present study (data listed in Supplemental Data, Table S2). Triclocarban was detected at levels above its analytical detection limit in all but one biosolids samples. The TCC concentrations in biosolids ranged from 0.23 to 80 mg/kg (dry wt). The median TCC concentrations in aerobically and anaerobically digested biosolids were similar (Fig. 1). Triclosan was detected at above the detection limit in 20 of the 23 samples of biosolids

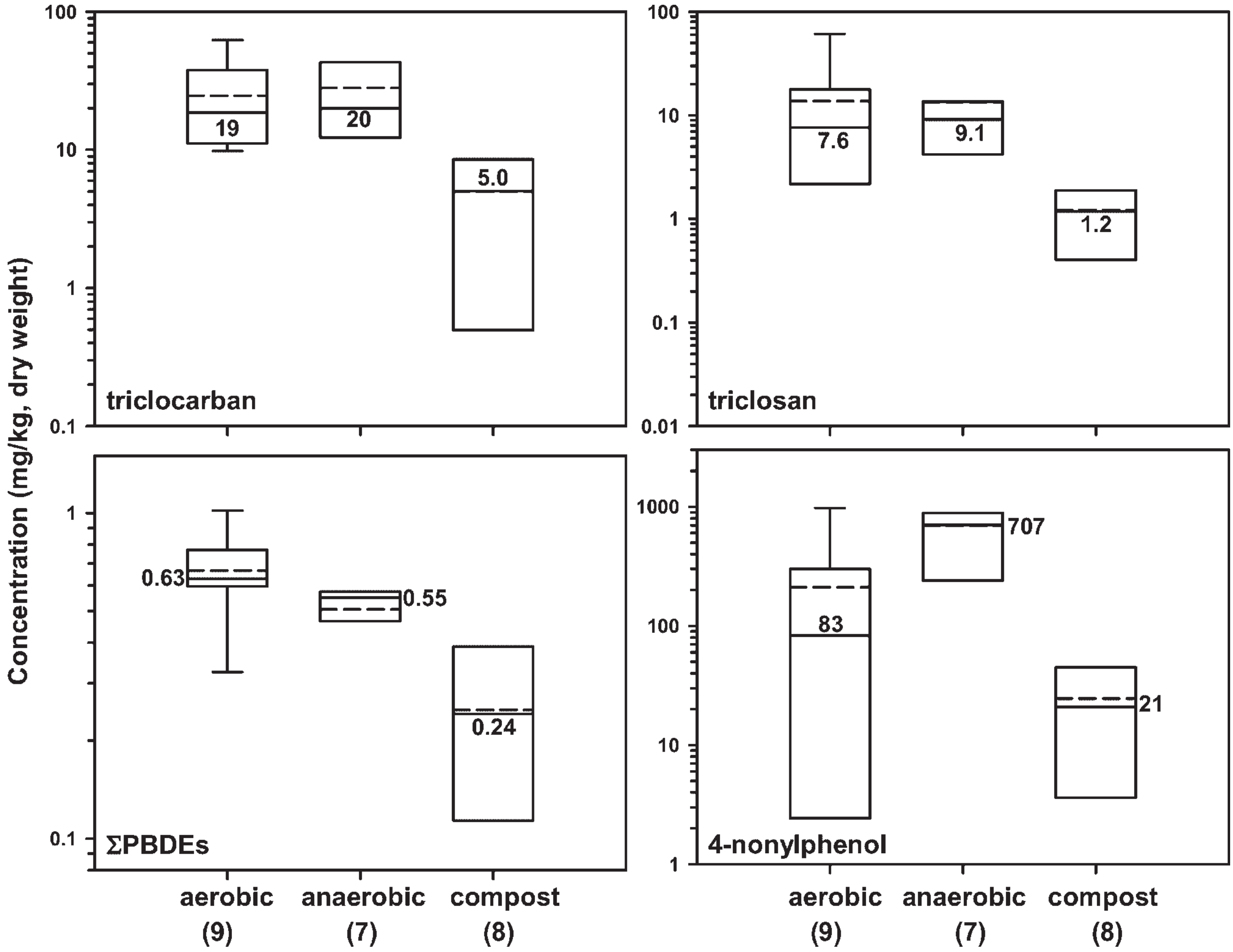

Fig. 1. Box plot (log) concentrations of triclocarban (TCC), triclosan (TCS), total polybrominated diphenyl ethers (ΣPBDEs), and 4-nonylphenol (4-NP) in aerobically and anaerobically digested biosolids and compost samples. The numbers of samples tested in each group are given in parentheses under the *x* axis. Dashed lines indicate average values. The solid line within each box (with values marked inside or next to each box), the lower and upper boundaries, and the error bars below and above the box mark the 50th (median), the 25th and 75th, and the 10th and 90th percentiles, respectively.

analyzed, with concentrations ranging from 0.33 to 61 mg/kg (dry wt). The median concentrations of TCS in aerobically and anaerobically digested biosolids were also similar (Fig. 1). In a previous investigation, Kinney et al. [8] analyzed nine samples of biosolids from seven U.S. states and reported TCS levels ranging from 1.2 to 33 mg/kg (dry wt). Recently, Ying and Kookana [33] reported concentrations of TCS in biosolids from 19 WWTPs in Australia that were comparable to TCS concentrations observed in the present study. Analysis of biosolids produced at four Canadian WWTPs showed that concentrations of TCC and TCS ranged from 2.2 to 6.0 mg/kg and 0.62 to 11.6 mg/kg, respectively [24].

All five congeners of PBDEs (PBDE-47, -99, -100, -153, and -154) evaluated were detected in the biosolids analyzed in the present study (Fig. 1). Concentrations of ΣPBDEs (sum of PBDE-47, -99, -100, -153, and -154 congeners) in the 23 samples of biosolids analyzed ranged from 0.071 to 1.02 mg/kg (dry wt). The median ΣPBDE concentration in anaerobically digested biosolids was slightly lower (0.55 mg/kg vs. 0.63 mg/kg) than the median concentration observed in aerobically digested biosolids. The ΣPBDE concentrations reported in biosolids from elsewhere in the United States and Canada ranged from 0.5 to 3.5 mg/kg [23], which were higher than the levels observed in this investigation, because those investigations included congener PBDE-209. The distribution patterns of PBDE congeners in aerobically and anaerobically digested biosolids and composted biosolids were similar (Supplemental Data, Fig. S2). The relative abundance of PBDE congeners followed the order PBDE-47 > PBDE-99 > PBDE-100 > PBDE-153 and PBDE-154. Similar distribution patterns for these five congeners of PBDEs were reported for biosolids investigated by other researchers [23]. It is worthwhile to mention here that PBDEs are ubiquitous in the environment, and their concentrations in household dust were reported to be much higher than the levels generally observed in biosolids. Rudel et al. [34] reported that the sum of BDE-47, BDE-99, and BDE-100 in household dust samples collected from 89 homes on Cape Cod, Massachusetts, USA, ranged from less than the detection limit to 35.8 mg/kg, with a median concentration of 0.3 mg/kg.

The concentrations of 4-NP in 18 of 23 biosolids evaluated were found to be above the detection limit, with concentrations ranging from 4.85 to 1,380 mg/kg (dry wt; Fig. 1). As expected, the anaerobically digested biosolids had a higher median 4-NP concentration than that observed in the aerobically digested biosolids. The concentration of 4-NP in composted biosolids was significantly lower than the levels found in anaerobically and aerobically digested biosolids. Similar trends in 4-NP concentrations were reported by Giger et al. [22]. La Guardia et al. [6] tested 11 biosolids and compost samples from four U.S. states and reported that 4-NP concentrations in biosolids ranged from 5.4 to 887 mg/kg. Rudel et al. [34] reported that the levels of 4-NP in household dust samples collected from 118 homes on Cape Cod, Massachusetts, USA, ranged from 2.6 to 8.7 mg/kg. Currently, in the United States, there are no regulatory limits on 4-NP levels in land-applied biosolids. However, the European Union has recently imposed a numeric limit of 50 mg/kg for 4-NP in land-applied biosolids, which is much lower than the levels generally detected in biosolids throughout the United States.

The median concentrations of 4-NP, TCC, TCS, and ΣPBDEs in composted biosolids were significantly lower than the median concentrations of these compounds in the uncomposted (both anaerobically and aerobically digested) biosolids evaluated in the present study (Fig. 1). The process of composting usually incorporates biodegradable material (e.g., wood chips, grass clippings). In the present study, the calculations of TCC, TCS, 4-N,P and PBDEs concentrations in the composted biosolids did not compensate for the bulk material added, because detailed information on the bulk material added to the biosolids was lacking. Figure 2 shows significantly different percentage reduction rates for TCC, TCS, ΣPBDEs, and 4-NP in the biosolids compared with the composted biosolids within a WWTP. These results indicate that the lower concentration values of these compounds in the composted samples are due to their degradation during the composting process in addition to dilution with bulk material in biosolids. Similar reduction rates would be observed for all target compounds if dilution were the only contributing factor to their lower levels in composted biosolids compared with the uncomposted fresh biosolids. Previous research by Das and Xia [35] demonstrated that composting biosolids mixed with wood shaving at a dry weight percentage ratio of 43:57 removed 80% of the total 4-NP within 2 weeks. The data in Figure 2 also suggest that degradation efficiency during composting varied among the WWTPs investigated, ranging from 31 to 100% for the four target compounds. These observations suggest that composting could be used as an option for reducing the levels of these compounds in land-applied biosolids, if necessary.

The multivariate analysis data shown in Figure 3 clearly demonstrate the impact of the size of treatment facility/population on the concentrations of TCC, TCS, ΣPBDEs, and 4-NP in biosolids. Two distinct clusters were observed based on the populations served by the WWTPs. The WWTPs that serve populations between 125,000 and 2,200,000 customers tend to have higher 4-NP levels but slightly lower TCC levels in the biosolids compared with the WWTPs that serve smaller populations (25,000–70,000). The levels of TCS and ΣPBDEs in the biosolids did not contribute significantly to the variances on both axes in Figure 3. Within each of the two clusters shown in Figure 3, no obvious trend was observed regarding the levels of the four target analytes and the wastewater treatment processes.

Concentrations in biosolids-amended soils

The pH values and organic C contents in soil from different depths are listed in Supplemental Data, Table S5. The concentrations of TCC, TCS, ΣPBDEs, and 4-NP in the soil profile (0–120 cm depth) are presented in Figure 4. The concentrations of these compounds in the surface soil layer (0–15 cm) increased with increasing cumulative loadings of biosolids. However, this difference with cumulative loadings became less significant in soil samples below 30 cm depth. The soil concentrations of all the four contaminants evaluated decreased sharply within the top 30-cm depth and leveled off in deeper layer. The differences in soil concentrations of these compounds among various cumulative loadings of biosolids were more pronounced in the top 0- to 15-cm soil layer, and they were less pronounced in the 15- to 30-cm soil layer (Fig. 4). It should be noted that, at the levels of cumulative loadings of biosolids investigated in the

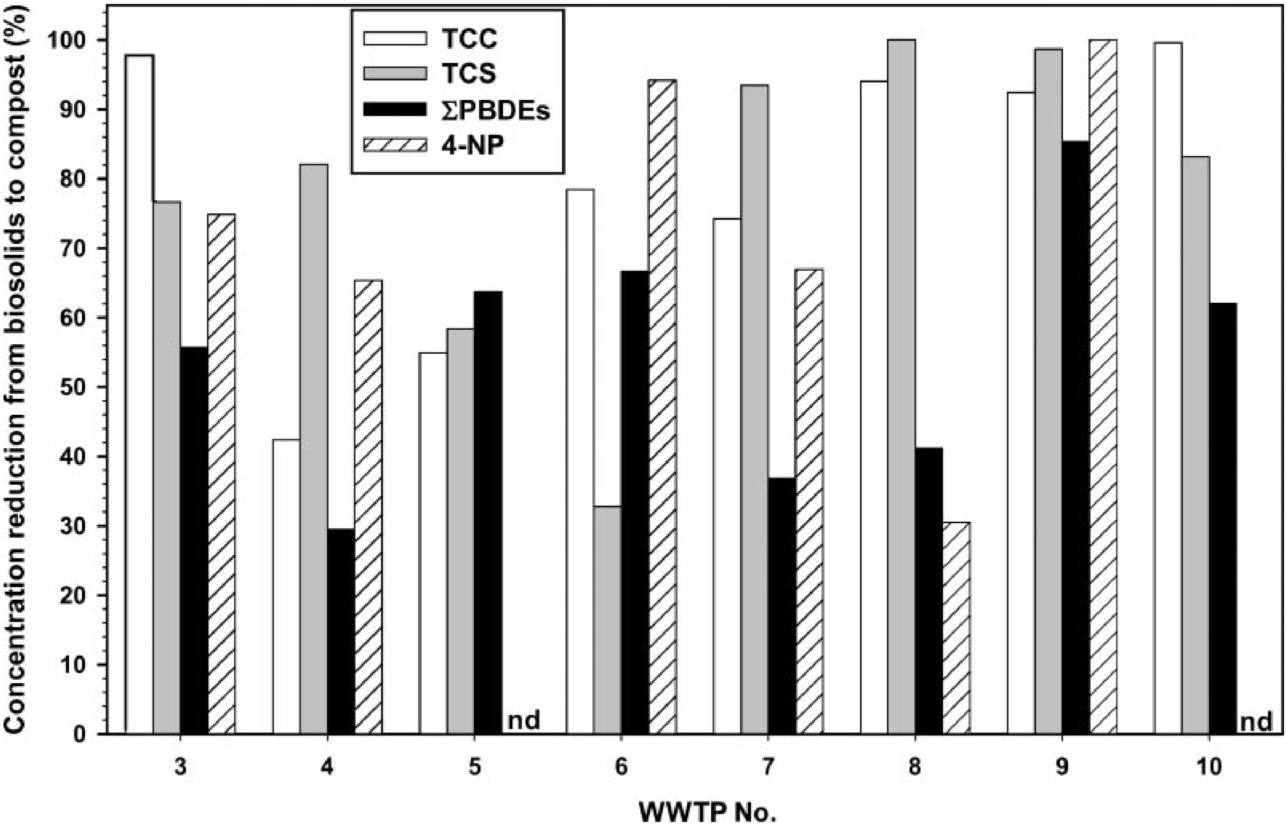

Fig. 2. Percentage reduction of triclocarban (TCC), triclosan (TCS), total polybrominated diphenyl ethers (ΣPBDEs), and 4-nonylphenol (4-NP) in biosolids compared with composted biosolids from the same waste water treatment plant (WWTP). nd = Below the detection limit in both biosolids and compost samples.

present study, approximately the top 0 to 15 cm of soil is composed predominantly of the biosolids material. At the highest cumulative loadings of 2,218 mg dry biosolids/ha, the levels of TCC, TCS, ΣPBDEs, and 4-NP in the 0- to 15-cm soil samples were 1,251, 52, 658, and 8,834 μg/kg dry soil, respectively. However, the soil concentrations of TCC, TCS, ΣPBDEs, and 4-NP at the 15- to 30-cm layer sharply decreased to 371, 25, 105, and 1,840 μg/kg, respectively, and the concentrations at the 60- to 120-cm depth decreased further to 23, 19, 4.2, and 68 μg/kg, respectively. Similar trends were observed in the other plots with cumulative loadings of 554.5 and 1,109 mg dry biosolids/ha (Fig. 4).

Levels of TCC, TCS, ΣPBDEs, and 4-NP were 744, 21, 28, and 246 μg/kg, respectively, in the surface soil (0 to 15 cm) of the control plots (Fig. 4). Insofar as no biosolids were ever applied to the control plots and there was no field and laboratory cross-contamination during sampling and sample analysis, the occurrence of these compounds in these plots could be attributed partially to potential cross-contamination from the biosolids plots over the years. Cross-contamination could occur during biosolids application, plowing, and planting operations, because there were no buffer areas to separate the control plots from the biosolids plots. In addition, atmospheric deposition might also have contributed to the detection of these compounds in the control plots. In North America, atmospheric concentrations of PBDEs have been detected ranging from 5 pg/m^3 near Lake Superior, to 22 pg/m^3 in Toronto, and to approximately 52 pg/m^3 in Chicago [36]. Alkylphenols have been detected at concentrations ranging from 0.13 to 81 ng/m^3 in the Lower Hudson River Estuary [37]. Although information on the atmospheric concentrations of TCC and TCS was not available, it is likely that these compounds may occur in the atmosphere at detectable levels because of their widespread use and frequent detection in environmental matrices such as biosolids and water [24]. The partitioning behavior (air/particle) for TCC and TCS is expected to be similar to that of PBDEs and 4-NP, because these compounds have identical vapor pressures. Furthermore, a previous investigation also reported detection of trace levels of total dioxins in the same control plots [38]. These results are consistent with the previous reports and suggest that atmospheric deposition could be one of loading pathways of organic contaminants to soils [39–41].

The levels of 4-NP in biosolids were not monitored and reported in the literature until the mid-1980s [22], for PBDEs until the early 1990s [42], and for TCC and TCS until the early 2000s [43]. Sufficient information that somewhat reflects the North America temporal concentration changes in biosolids during the time period when the long-term biosolids application project was conducted was found only for 4-NP (Supplemental Data, Fig. S3). The reported concentration ranges for 4-NP in biosolids for most of the years between 1984 and 2005 were similar, at levels below 1,500 mg/kg (dry wt). Although there is a lack of historical monitoring data on levels of PBDEs, TCC, and TCS in biosolids, research has shown their similar close association with biosolids [6–8]. It is reasonable to assume that those compounds have a concentration trend similar to 4-NP in biosolids during the last 20 years of this experiment (between 1985 and 2005), because all of those compounds have been in

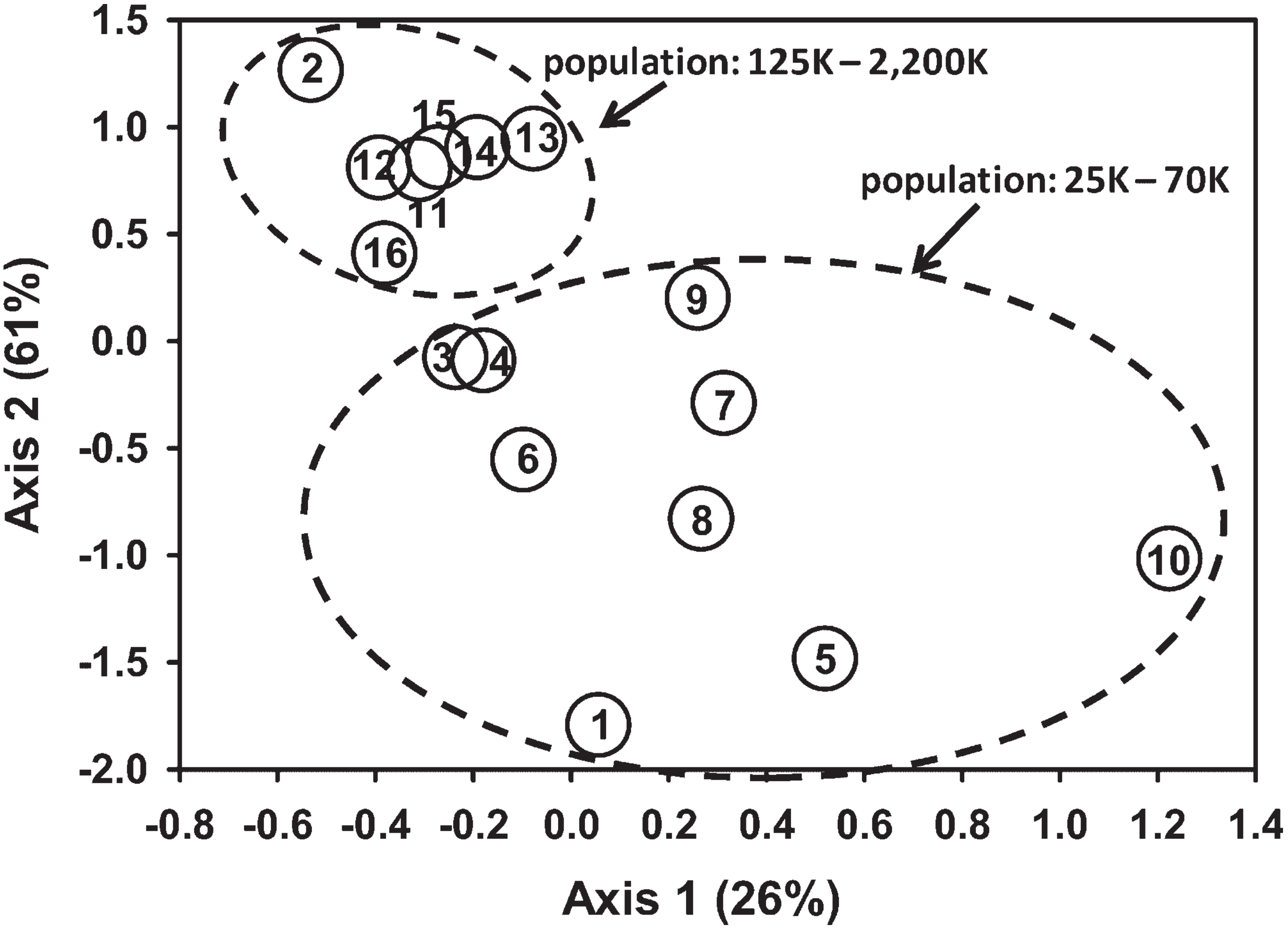

Fig. 3. Multivariate analysis of biosolids based on the levels of the four target analytes. Axis 1 accounts 26% of the variation in the data; axis 2 accounts for 61%. Values of triclocarban contribute the most to the variance along axis 1 ($r^2 = 0.63$, positive correlation). Values of 4-nonylphenol contribute the most to the variance along axis 2 ($r^2 = 0.88$, positive correlation). The numbers in the circles refer to the wastewater treatment plant number listed in Supplemental Data, Table S2.

use as HPV chemicals in many consumer products since their introduction in the late 1960s and early 1970s [18,19]. Based on this assumption, by using the concentrations of each compound detected in the MWRDGC biosolids collected in 2005 (WWTP 14; Supplemental Data, Tables S2), the total mass of each compound applied to the biosolids-amended plots during last 20 consecutive years can be obtained using the equation

$$\text{Mass of a compound applied (kg/ha)} = (20 \times R_{biosolids} \times C_{biosolids})/10^6 \quad (1)$$

where $R_{biosolids}$ is the annual biosolids application rate (kg/ha/y), and the $C_{biosolids}$ values for TCC, TCS, ΣPBDEs, and 4-NP were 24, 4.2, 0.71, and 886 mg/kg (dry wt), respectively.

The mass of each compound remaining in each experimental plot at the time of soil sampling can be calculated using the equation

$$\text{Mass of a compound remaining in soil (kg/ha)} = (D_{soil} \times A_{soil} \times BD_{soil} \times C_{soil})/10^9 \quad (2)$$

where D_{soil} is soil depth (m), A_{soil} is the unit area of soil receiving biosolids (10^4 m^2/ha), and BD_{soil} is the bulk density of the soil (the BD_{soil} values for the 0 to 15 cm surface soils of control plots and plots with 33-year cumulative biosolids loading were 1,910, 1,910, 1,600, and 1,250 kg/m^3 [dry wt basis], respectively; the BD_{soil} value for soils below the 15 cm depth of each treatment plot was 1,910 kg/m^3 [dry wt basis]), and C_{soil} (μg/kg) is the concentration of a target compound in the targeted soil depth of an experimental plot.

As shown in Figure 5, at the end of 33 years of biosolids application, elevated levels of PBDEs in the long-term biosolids plots were evident. By using Equations 1 and 2, the estimated amounts of PBDEs added to the biosolids-amended plots during the last 20 consecutive years were lower than the amounts of PBDEs remained in the top 120-cm soil layer of the plots (Fig. 5). This observation has two implications: 1) persistence and accumulation of substantial amount of PBDEs in biosolids applied to the soils and 2) the amount of PBDEs introduced to the soils via 33-year consecutive biosolids application underestimated persistence of PBDEs in soils receiving biosolids applications for up to 15 years, as reported by other researchers [44]. Figure 5 shows that the 20-consecutive-year estimated input of 4-NP, TCC, and TCS to the experimental plots was 30 to 50, two to nine, and four to 12 times higher, respectively, than the amount of those compounds that remained in the top 120-cm soil layer after 33 years of biosolids application. The large discrepancy between the estimated 20-year cumulative input and the amount remaining in the soil for the three compounds may be due to their dissipation over time or their

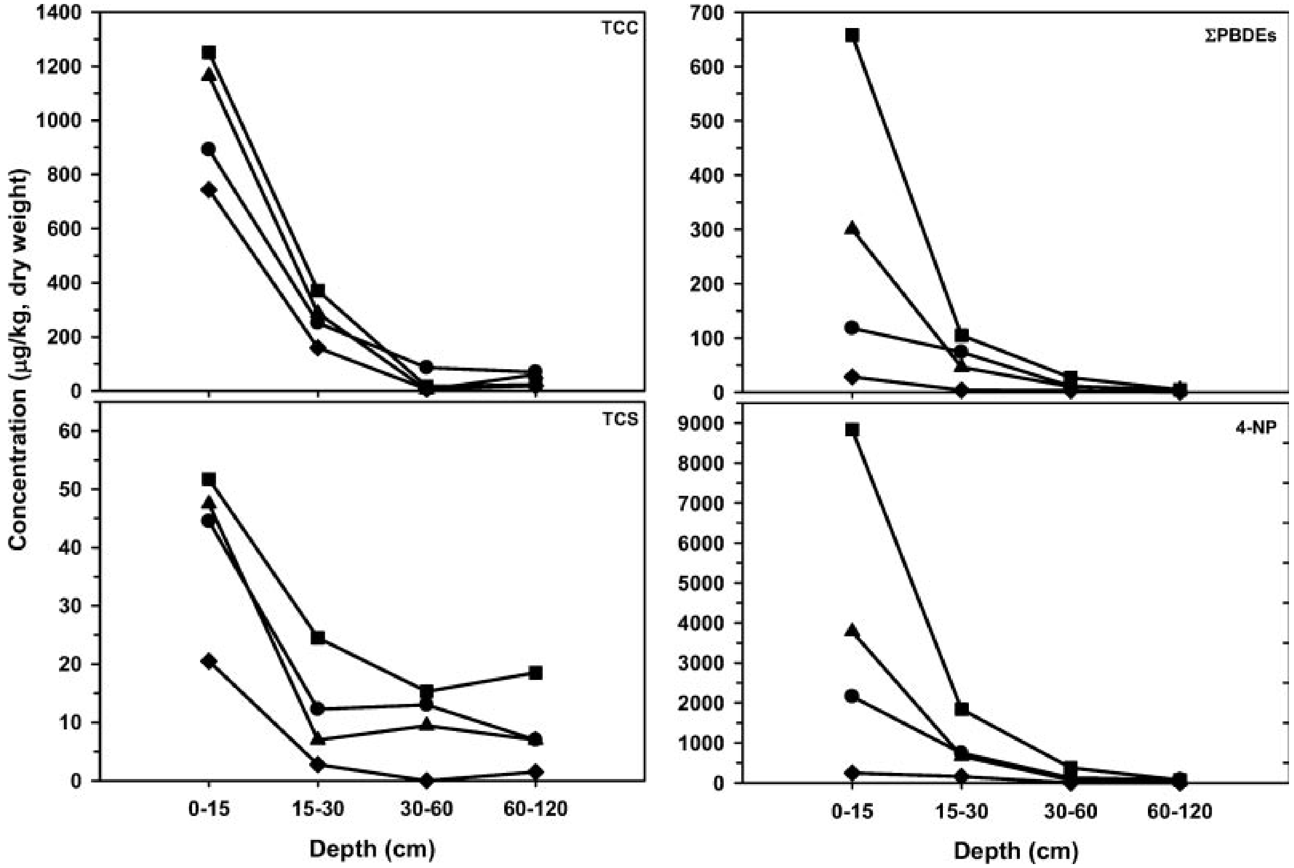

Fig. 4. Average concentrations of triclocarban (TCC), triclosan (TCS), total polybrominated diphenyl ethers (ΣPBDEs), and 4-nonylphenol (4-NP) in a soil profile of the control and biosolids-amended plots. Lozenges represent control treatment; circles, triangles, and squares represent cumulative loadings of 554.5, 1,109, and 2,218 mg biosolids/ha, respectively.

lower-than-estimated concentrations in biosolids applied in some years or a combination of both. The data in Figure 5 suggest that PBDEs are more persistent than 4-NP, TCC, and TCS in biosolids-amended soils.

Degradation rates of as fast as 80% after 21 d and 84% after nine months of biosolids application have been reported for 4-NP in biosolids-amended soils [45,46]. Although field information on degradation rates for both TCC and TCS in biosolids-amended soils is lacking, laboratory incubation study and modeling by Ying et al. [33] suggested half-lives of 108 d and 18 d for TCC and TCS, respectively. Field observations for the present study suggest faster degradation rates for TCC than predicted by the laboratory incubation and modeling studies of Ying et al. [33].

Overall, the data presented in Figure 5 show that large portions (72–92%) of total PBDEs, 4-NP, and TCC found in the soil profile (0–120 cm depth) were retained in the top 30 cm layer of the biosolids-amended plots. This observation suggests limited mobility for PBDEs, 4-NP, and TCC in the biosolids-amended soil, and the trace amounts detected below the 30 cm depth most likely were due to soil redistribution via plowing and planting operations and by earthworms and plant root activity. Unlike the case with PBDEs, 4-NP, and TCC, a much higher percentage (49–64%) of the TCS found in the soil profile (0–120 cm depth) appeared in the 30 to 120 cm layer of the biosolids-amended plots (Fig. 5), suggesting higher leaching potential for TCS than the other three target analytes. Figure 5 shows that a large percentage of all four target compounds accumulated in the top 0- to 30-cm depth (77–100% of those detected in the 0–120 cm depth) of the control plots, further supporting the speculation that the detection of those compounds in the Control plots was due mostly to cross-contamination from the biosolids plots over the 33-year time span during biosolids application, plowing, and planting operations as well as possible atmospheric deposition.

In summary, the present study shows that TCC, TCS, 4-NP, and PBDEs are frequently detected in biosolids. The levels of TCC, TCS, 4-NP, and PBDEs observed in the soil from the long-term plots that have received annual applications of biosolids for 33 years suggest that 4-NP, TCS, and TCC are degraded in the biosolids-amended soils under natural field conditions. However, long-term and heavy applications of biosolids may result in accumulation of PBDEs in the surface layer of biosolids-amended soils. The levels and distribution of the investigated compounds in the soil profiles (0–120 cm depth) of long-term plots indicate a limited leaching of 4-NP, TCC, and PBDEs and potential leaching of TCS in the biosolids-amended soils. All four target analytes were below the detection limits in corn tissue samples collected from our experimental plots. Previous investigations on dioxin did not show significant dioxin uptake by corn grown in the same plots [38]. Although other researchers have detected 4-NP in tissues of wheatgrass and beans grown in biosolids-amended soils, it was suggested that removal of NP from biosolids-amended soils

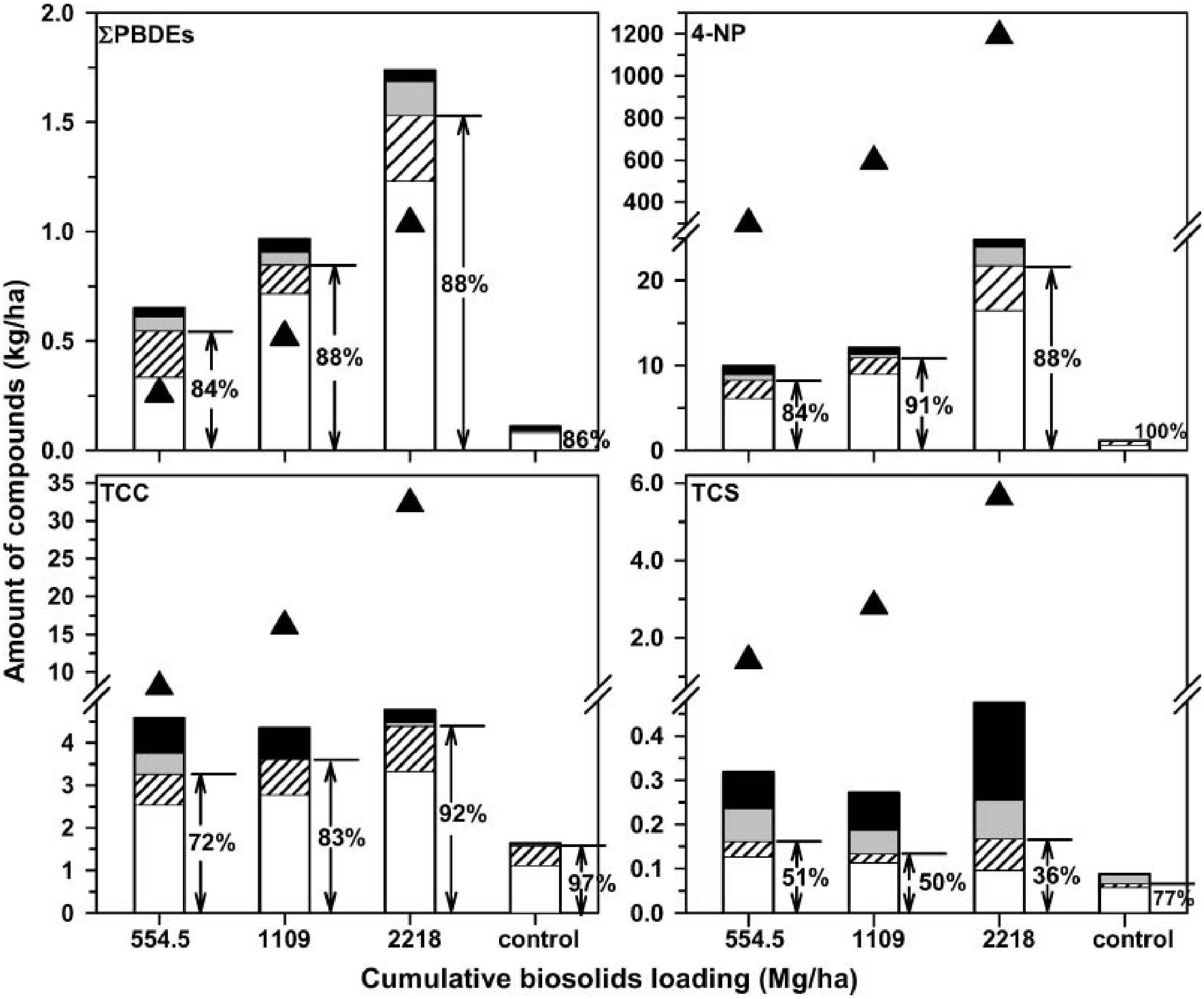

Fig. 5. Estimated 20-year (1985–2005) cumulative input of triclocarban (TCC), triclosan (TCS), total polybrominated diphenyl ethers (ΣPBDEs), and 4-nonylphenol (4-NP) to biosolids-amended soil (triangle; equation 1: Mass of a compound applied [kg/ha] = $[20 \times R_{biosolids} \times C_{biosolids}]/10^6$) and amount of those compounds detected in the 0 to 120 cm depth of biosolids-amended plots and control plots after 33-year biosolids application (bars; equation 2: Mass of a compound remaining in soil [kg/ha] = $[D_{soil} \times A_{soil} \times BD_{soil} \times C_{soil}]/10^9$. Bar symbols represent the amount of target compounds in soils. Open bar = 0 to 15 cm; diagonally hatched bar = 15 to 30 cm; gray bar = 30 to 60 cm; black bar = 60 to 120 cm. The percentage numbers next to each bar indicate the percentage of target compounds detected in the top 30-cm soil depth relative to the amount detected in the 0- to 120-cm depth.

by plant uptake was negligible [47,48]. In those studies, no significant enhancement effect of plants on 4-NP degradation was observed. To date, no detailed studies can be found on plant degradation and uptake of PBDEs, TCC, and TCS.

SUPPLEMENTAL DATA

Supplemental Tables S1–S4. (130KB DOC)

Supplemental Figure S1. Location of experimental plots.

Supplemental Figure S2. PBDE congener composition for aerobically and anaerobically digested biosolids and composted biosolids.

Supplemental Figure S3. Reported concentration ranges of 4-NP in North American biosolids between 1984 and 2005. (82.2 KB PDF)

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