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RECENT TREND IN DIOXINS IN BIOSOLIDS AND THE LEVELS OF DIOXINS IN SOIL AND CORN TISSUES FROM PLOTS AFTER THIRTY YEARS OF BIOSOLIDS APPLICATION

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RECENT TREND IN DIOXINS IN BIOSOLIDS AND THE LEVELS OF DIOXINS IN SOIL AND CORN TISSUES FROM PLOTS AFTER THIRTY YEARS OF BIOSLIDS APPLICATION

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SUMMARY AND CONLUSIONS

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzo-p-furans (PCDFs), and polychlorinated biphenyls (PCBs) (collectively referred to as dioxins) are ubiquitous in the environment. Detectable levels of dioxins have been reported in biosolids but the information regarding their fate in biosolids-amended soils is scarce. The United States Environmental Protection Agency (USEPA) had considered imposing a limit of 300 pg TEQs g^{-1} (picogram toxic equivalents per gram) on the levels of dioxins in land-applied biosolids. After reviewing the available data on human health and environmental risks of dioxins, the USEPA decided that it will not regulate dioxins in land-applied biosolids. However, there is very little information available on the effect of long-term application of biosolids on dioxins accumulation in soil and uptake by plants. In this study, we analyzed dioxins in several samples of sludge and biosolids collected in 1994, 2000, and 2004 from the seven water reclamation plants (WRPs) operated by the Metropolitan Water Reclamation District of Greater Chicago (District). Dioxins analyses were also done on soil (0-15 cm depth), corn grain, and corn stover samples collected in 2002 from field plots at the District's Fulton County land reclamation site, consisting of a 0 (Control), 504, and 2016 Mg ha^{-1} cumulative biosolids loading applied through annual applications from 1973 to 2002. The data on sludge and biosolids analyses showed that total dioxins levels ranged from 15.5 to 112.6 pg TEQs g^{-1}, and there were no consistent differences in total dioxins levels among the WRPs or the type of sludge and biosolids. However, the data showed a declining trend in levels of dioxins in biosolids over time and the levels detected were much lower than the 300 pg TEQs g^{-1} limit proposed by the USEPA. We found dioxins levels of only 79.9, 115.5, and 247.5 pg TEQs g^{-1} in the soil from the plots that have received cumulative loadings of 0, 504, and 2,016 Mg biosolids ha^{-1}, respectively. There were no detectable levels of dioxins in the corn grain, but trace levels (6.8 – 7.5 pg TEQs g^{-1}) were found in the corn stover from the control and biosolids-amended plots. Overall, our data show that the levels of dioxins in District biosolids had declined over time and the levels were much lower than the regulatory limit initially considered by the USEPA. Although long-term application of biosolids tended to increase the level of dioxins in soil, there was no uptake in corn grain and only trace levels were found in the vegetative tissue. These findings support the USEPA's decision not to regulate dioxins in land-applied biosolids.

INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzo-p-furans (PCDFs), and polychlorinated biphenyls (PCBs), collectively referred to as dioxins are ubiquitous in the environment at ultra-trace levels. Dioxins are strongly hydrophobic, have high bioaccumulation potential, and are well known for their acute toxicity and persistence in the environment (Tanabe, 1988; Wild and Jones, 1992b; Alcock et al., 1995; Jones and Sewart. 1997). The PCDD/Fs found in the environment are due mostly to trace amounts that are present as impurities in many herbicides, such as 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and pentachlorophenol, and their release from various combustion processes, such as forest fires and incineration of industrial and municipal wastes. Although the production, import, and use of PCBs were banned in the U.S. in 1979, detectable levels of PCBs are still found in some soils, sediments, water, and municipal sludge.

Biosolids – a byproduct of municipal and industrial wastewater treatment process – have high organic matter content and may act as a sink for dioxins due to high affinities of dioxins for the organic matter rich media. The dioxins found in biosolids may originate from municipal and industrial sources, but atmospheric deposition may also be a potential source via runoff from roads (e.g., Jones and Sewart, 1997). Formation of dioxins during sludge treatment processes has also been reported (Oberg et al., 1992).

Large quantities of biosolids are generated in the U.S. and throughout the world. Due to their high nutrient and organic carbon contents, biosolids are valuable as a fertilizer and soil amendment. Application to agricultural land is gaining popularity as an environmentally benign and cost-effective alternative for managing biosolids. However, the presence of detectable levels of dioxins in biosolids led to the concerns that land application of biosolids may result in accumulation of dioxins in soil and their subsequent translocation through the human food chain since several dioxins congeners are extremely bioreactive.

There are only a limited number of reports on the fate of dioxins in biosolids-amended soils. Studies have shown that PCDD/Fs congeners of the lower homologue groups such as tetra (T)-, penta (Pe)-, and hexa (Hx)-CDD/Fs tend to volatilize from soil, while the higher homologue groups such as hepta (Hp)- and octa (O)-CDD/Fs, due to their extremely low vapor pressures, are expected to be bound to the soil (Podoll et al., 1986; Freeman and Schroy, 1989). Sewart (1995) found higher concentrations of Hp- and OCDD in a pastureland soil with over a 20-year history of biosolids application compared to an untreated soil. McLachlan et al. (1996) analyzed archived soil samples from a long-term field experiment established in 1968. They selected soil samples collected in 1972 and 1990 from a field that received a one time application of 125 dry ton biosolids ha^{-1}. They reported that the cumulative toxicity equivalents (TEQs) of PCDD/Fs in soil declined with time, and approximately 50% of the total PCDD/Fs concentration in the soil found in 1972 was still present in 1990.

Land application of biosolids in the U.S. is regulated by the Clean Water Act (CWA) under 40 CFR Part 503 Rule, which was promulgated in 1993 by the U.S. Environmental Protection Agency (USEPA). The CWA requires the USEPA to conduct additional rounds of regulations periodically to address other pollutants, which were either unknown or for which

scientific information was scarce at the time the Part 503 Rule was developed. Based on the second round of investigations in 1999, the USEPA proposed a numeric limit of 300 pg TEQs g^{-1}dioxins in biosolids to be land-applied. In June 2002, the USEPA published a Notice of Data Availability (NODA) (USEPA, 2002) and requested comments on new information related to dioxins in land-applied biosolids. The USEPA presented the results of two national surveys that were conducted to determine the levels of dioxins in biosolids and the results of a multimedia risk assessment for dioxins in land-applied biosolids. The USEPA also performed a Screening Ecological Risk Analysis on the risks to wildlife due to exposure to dioxins from land-applied biosolids.

Based on the information obtained from the two surveys on exposure, toxicity, and cancer risks from dioxins, the USEPA concluded that no numeric limits or management practices are required to protect human and environmental health from the adverse effects of dioxins in land-applied biosolids (USPEA, 2003). However, there are still public concerns that continuous annual applications of biosolids could result in accumulation of dioxins in soils in the long-term, and may increase the risk of plant uptake and translocation to human food chain.

The purpose of this investigation was to evaluate recent trend in levels of dioxins in sludge and biosolids produced at the District, and the effect of continuous and long-term application of biosolids on the levels of dioxins in soil and corn tissues collected from a long-term field study that the District conducts at its Fulton County land reclamation site.

MATERIALS AND METHODS

Biosolids Samples

Samples of the sludge or biosolids generated from the District's seven wastewater reclamation plants (WRPs) were collected for dioxins analysis in 1994, 2000, and 2004. The types of sludges or biosolids sampled from each WRP are described in Table 1. The seven WRPs vary with respect to their geographic service area, the contribution of domestic and industrial inputs to the total wastewater flow, and the extent to which the final solids are processed. The service areas for the Stickney, Calumet, North Side, and James C. Kirie WRPs contain extensive combined sewer systems which convey storm water runoff in addition to sanitary sewage to the treatment plants. Average proportion of industrial input to the total daily flow is highest for the Calumet WRP (average daily flow 225 million gallons per day, MGD) followed by the Stickney WRP (average daily flow 641 MGD). The sludges from the Lemont (average daily flow 2.01 MGD) and Northside (average daily flow 234 MGD) WRPs are sent to the Stickney WRP, and sludge from the Kirie WRP (average daily flow 25.38 MGD) is sent to the John E. Egan WRP (average daily flow 23.4 MGD) for final processing. Final biosolids products are produced for land application at the Stickney, Calumet, Egan, and Hanover Park WRPs. Primary and waste-activated sludges produced at these WRPs and received from other plants are treated further to produce Class B biosolids through mesophilic anaerobic digestion process. The biosolids products that are land-applied include Class B centrifuge cake (Calumet, Egan, and Stickney WRPs), lagoon-aged, air-dried Class A biosolids (Calumet and Stickney WRPs), and Class B digester draw biosolids (Hanover Park WRP – design average flow 12 MGD). Additional details about the flow characteristics and amount of solids produced at all the seven WRPs are given in Table 1.

Field Plots

The long-term field plots (4.6- by 12.2-m) were established in 1973 on a calcareous mine spoil (pH 7.8, bulk density 1.6 g cm^{-3}, cation exchange capacity 12.6 cmol kg^{-1}, $CaCO_3$ eq. 3.2%) at the District's land reclamation site located in Fulton County, Illinois. Data on the metal uptake by corn from these plots were used in the risk assessments conducted by the USEPA to develop the Part 503 biosolids regulations. Treatments consisting of a Control (receiving no biosolids) and anaerobically digested biosolids were applied annually to the plots at 16.8, 33.6, and 67.2 Mg biosolids ha^{-1}. Corn was grown on the plots every year. The experimental design was a randomized block of four treatments and four replications.

The biosolids were applied in liquid form (~3 – 7 % solids content) during 1973 to 1984 and as dewatered holding basin cake (~20% solids content) or lagoon-aged, air-dried biosolids during 1985 to 2002. At the end of 2002, the cumulative loadings were 504, 1008, and 2016 Mg biosolids ha^{-1} in the plots receiving annual applications of biosolids at the rate of 16.8, 33.6, and 67.2 Mg ha^{-1}, respectively. Inorganic fertilizers were applied annually as N-P-K (336-224-112 kg ha^{-1}) to the Control plots and 112 kg K ha^{-1} to the biosolids plots. Additional details about the field plots are given elsewhere (Pietz et al., 1982).

TABLE 1. SERVICE AREA, DESIGN MAXIMUM AND AVERAGE DAILY FLOWS, APPROXIMATE DOMESTIC INPUT, YEARLY TOTAL SOLIDS PRODUCTION, AND THE TYPE OF SLUDGE/BIOSOLIDS SAMPLED FOR DIOXINS ANALYSIS FROM THE DISTRICT'S WATER RECLAMATION PLANTS

WRP[1]	Service Area	Design Max Flow	Average Daily Flow[2]	Domestic Input[3]	Solids Production	Product Sampled
	Sq. mile	--------10^6 x gallon--------		%	DT yr^{-1}	
Stickney	260	1,440	641	60	140,000	Centrifuge cake, aged, air-dried
Calumet	320	430	225	55	30,000	Centrifuge cake, aged, air-dried
John E. Egan	44	50	23.4	65	7,000	Centrifuge cake
Hanover Park	11	22	7.7	80	850	Digester draw
North Side	142	450	234	65	45,000	Thickened WAS[4]
James C. Kirie	65	110	25.4	65	7,000	Thickened PS[5]
Lemont	21	4	2	85	300	Thickened WAS

[1]WRP = Water reclamation plant.
[2]Based on daily flow recorded in 2005.
[3]Percent of average daily flow. The remainder of the flow is assumed to be from industrial/commercial inputs.
[4]WAS = Waste activated sludge.
[5]PS = Primary sludge.

Soil and corn tissue (grain, leaf, and stover) samples were collected each year. Soil (0-15 cm depth), stover, and grain samples collected in 2002 from the Control, and cumulative loadings of 504 Mg and 2016 Mg biosolids ha^{-1} plots were selected for this investigation. The soil samples were air-dried, ground, and sieved to <2 mm and stored in glass jars. The stover and grain samples were air-dried, ground and stored in glass jars.

Dioxins Analysis

Only 17 congeners in the PCDD and PCDFs groups and 12 congeners of co-planar PCBs are believed to posses toxic characteristics similar to 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD), the most toxic dioxins congener. These 29 congeners were selected by the USEPA for exposure risk assessment evaluation (USEPA, 1989). The set of 29 congeners in the PCDD/Fs and PCBs groups will be referred to as dioxins herein. Extraction and analyses of dioxins in soil and corn tissue samples were performed by a certified commercial laboratory using the USEPA approved methods. PCDD/Fs were extracted and analyzed by using the USEPA 1613B HRGC/HRMS method. The method uses isotope dilution, high-resolution gas chromatography (HRGC), and high-resolution mass spectrometry. Extraction and analysis of 12 congeners of co-planar PCBs were performed by using the USEPA 1668A method. The PCDD/Fs and PCBs analyses are labor intensive and time-consuming, making these analyses prohibitively expensive. Because of the high cost of these analyses, only a limited number of sludge or biosolids were analyzed in a given year from each of the WRPs. The soil and plant tissue samples collected from the field experiment in 2002 were analyzed in duplicate only. One soil sample collected from the control plot in 1973 was also analyzed in 2002. Strict QA/QC protocols were followed to ensure the highest quality of data.

Data Analysis

Dioxins are complex mixtures of many congeners with different toxicity, variable ratios, and are rarely encountered individually in the environment. Because of the wide range in the toxicities of dioxins congeners, toxic equivalency factors (TEFs) have been established for standardizing concentrations of dioxin-like compounds to toxicologically equivalent amounts of 2,3,7,8-TCDD. The toxic equivalents (TEQs) for 29 congeners of dioxins (17 PCDD/Fs congeners and 12 PCBs congeners) were calculated using the following equation:

$$\text{Total TEQs} = \sum_{i=1}^{29} (C_i \ x \ TEF_i) \qquad \text{Eq. 1}$$

where *TEQ* is the concentration, pg g^{-1}, of a 29 congener mixture of dioxin-like compounds expressed as toxic equivalent of 2,3,7,8-TCDD; C_i is concentration of congener *i*, pg g^{-1}; and TEF_i is toxic equivalency factor for the congener *i* (unitless).

TEQs were calculated using the international TEFs as recommended by the World Health Organization (WHO) and endorsed by the USEPA (Van den Berg et al., 1998; WHO, 1998). The non-detects were treated as one-half the reporting limit as recommended by the USEPA (USEPA, 1989). The TEFs and reporting limits for all the 29 congeners of dioxins analyzed in this study are given in Table 2.

TABLE 2: TOXICITY EQUIVALENCY FACTORS AND REPORTING LIMITS FOR PCDD/Fs AND PCBs CONGENERS

Congener	Toxicity Equivalency Factor[1]	Reporting Limit ($pg\ g^{-1}$)
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	5
1,2,3,4,7,8-HxCDD	0.1	5
1,2,3,6,7,8-HxCDD	0.1	5
1,2,3,7,8,9-HXCDD	0.1	5
1,2,3,4,6,7,8-HpCDD	0.01	5
OCDD	0.0001	10
2,3,7,8-TCDF	0.1	5
1,2,3,7,8-PeCDF	0.05	5
2,3,4,7,8-PeCDF	0.5	5
1,2,3,4,7,8-HxCDF	0.1	5
1,2,3,6,7,8-HxCDF	0.1	5
2,3,4,6,7,8-HxCDF	0.1	5
1,2,3,7,8,9-HXCDF	0.1	5
1,2,3,4,6,7,8-HpCDF	0.01	5
1,2,3,4,7,8,9-HpCDF	0.01	5
OCDF	0.0001	10
PCB-77, 81, 105, 118, 123, 189	0.0001	24.2
PCB-114, 156/157	0.0005	24.2
PCB-126	0.1	24.2
PCB-167	0.00001	24.2
PCB-169	0.01	24.2

[1]The values of toxicity equivalency factors were assigned by WHO (Van den Berg et al., 1998).

RESULTS AND DISCUSSION

Dioxins in Biosolids

The concentrations of dioxins (expressed as TEQs) observed in the District's biosolids in 1994, 2000, and 2004 are presented in Table 3. Air-dried biosolids were not analyzed in 1994 and thickened sludges from the Kirie, North Side, and Lemont WRPs were not analyzed in 2004. The trend in concentrations of dioxins for the three years sampled varied among the types of sludge and biosolids, and among the WRPs.

In the air-dried biosolids, the concentrations of dioxins were lower in 2004 than in 2000 samples, except for Calumet WRP samples in which PCBs concentration was slightly higher in 2004. In the centrifuge cake biosolids, the concentrations of dioxins in the Stickney WRP samples and the PCDDs and PCDFs in the Egan WRP samples declined from 1994 to 2004, but the levels of dioxins in the Calumet WRP centrifuge cake biosolids were higher in 2004. The levels of total dioxins in the thickened sludge from the Kirie, Lemont, and North Side WRPs were lower in 2000 than in 1994. There were no consistent trends in the levels of dioxins among the types of sludge and biosolids, or between the WRPs (Table 3). The results did not indicate any relationship between the concentrations of dioxins and the relative contribution of domestic and industrial/commercial wastewater flow to the WRPs.

The total dioxins TEQ values for all the sludges and biosolids tended to decline over time, except that the highest levels occurred in 2004 for the Calumet WRP centrifuge cake, and in 2000 for the Hanover Park digester draw biosolids (Table 3). There were no consistent trends in the contribution of PCDDs, PCDFs, and PCBs to total dioxins TEQs, except that the contribution of PCBs to the total dioxins TEQs in the Calumet WRP centrifuge cake and air-dried biosolids was much higher in 2004 than in 1994 and 2000. The levels of dioxins in biosolids did not indicate any noteworthy differences among the WRPs (Table 3). Overall, the data show that total dioxins TEQs in biosolids declined over time and were much lower than the USEPA's proposed limit of 300 pg TEQs g^{-1}. These findings strongly support the USEPA's decision not to set regulatory limits for dioxins in land-applied biosolids.

Dioxins in Biosolids-amended Soil

The concentrations of dioxins in the soil samples collected from the plots in 2002 are presented in Table 4. Most of the 29 congeners of dioxins analyzed in this study were detected in the soil samples collected from the Control and biosolids plots in 2002, except 1, 2, 3, 7, 8, 9-HxCDF which was detected only in the 504 Mg biosolids ha^{-1} plot. However, OCDD was the only congener detected in the soil sample collected from the Control plot in 1973 (data not shown). Since no biosolids were applied to the Control plot, the increase in the number of dioxins congeners detected in 2002 could be due to atmospheric deposition. Jones and Sewart (1997) found similar trends in concentrations of dioxins between unamended and biosolids-amended soils in the United Kingdom (U.K.), and postulated that atmospheric deposition and biosolids

TABLE 3: TOXICITY EQUIVALENTS (TEQs) OF DIOXINS IN THE SLUDGE AND BIOSOLIDS SAMPLES COLLECTED FROM THE DISTRICT'S WATER RECLAMATION PLANTS IN 1994, 2000, AND 2004

	PCDDs			PCDFs			PCBs			Total Dioxins		
Sample Type	1994	2000	2004	1994	2000	2004	1994	2000	2004	1994	2000	2004
	---------- pg TEQ g^{-1} ----------											
Calumet - Aged, Air-Dry[1]	na	54.5	26.6	na	15.9	9.3	na	36.5	44.0	na	106.9	79.9
Calumet - Centrifuge Cake[1]	14.0	16.7	26.3	5.7	4.6	9.8	17.7	11.5	47.9	37.4	32.8	84.0
Stickney - Aged, Air-Dry[1]	na	48.7	30.9	na	18.8	12.0	na	35.2	17.6	na	102.7	60.5
Stickney - Centrifuge Cake[2]	47.5	19.6	22.0	22.4	8.2	11.2	42.7	14.8	15.9	112.6	42.6	49.1
Egan - Centrifuge Cake[1]	82.7	8.2	10.2	13.1	3.4	4.6	9.7	3.3	16.6	105.5	14.9	31.4
Hanover Park Digester Draw[1]	7.8	12.0	8.7	3.2	3.3	3.1	4.5	4.8	4.7	15.5	20.1	16.5
Kirie Thickened[3]	20.4	7.8	na	7.4	4.2	na	6.6	5.3	na	34.4	17.3	na
Northside Thickened[3]	30.8	10.8	na	18.7	3.7	na	17.7	5.6	na	67.2	20.1	na
Lemont Thickened[3]	20.2	11.3	na	7.7	4.1	na	9.4	3.6	na	37.3	19.0	na

[1]Values are mean of 3 samples, except the 2000 values which are from a single analysis.
[2]Values are mean of 4 samples, except the 2000 values which are from a single analysis.
[3]Values are mean of 2 samples, except the 2000 values which are from a single analysis.
na = Not analyzed.

TABLE 4: MEAN CONCENTRATIONS OF 29 CONGENERS OF DIOXINS IN SOIL SAMPLES COLLECTED IN 2002 FROM THE CONTROL AND BIOSOLIDS-AMENDED PLOTS

Congener	Cumulative Biosolids Loading (Mg ha^{-1})[1]		
	0	504	2016
	pg g^{-1}		
2,3,7,8-TCDD	7 (0.3)[2]	11 (1.0)	26 (1.9)
1,2,3,7,8-PeCDD	16 (1.7)	21 (0.3)	49 (2.2)
1,2,3,4,7,8-HxCDD	14 (2.1)	19 (1.4)	46 (4.7)
1,2,3,6,7,8-HxCDD	82 (2.8)	112 (11)	230 (15)
1,2,3,7,8,9-HXCDD	52 (2.9)	65 (5.2)	138 (3.5)
1,2,3,4,6,7,8-HpCDD	1,690 (155)	2,380 (170)	5,730 (805)
OCDD	21,750 (350)	29,400 (566)	57,800 (7350)
2,3,7,8-TCDF	16 (0.9)	21 (0.1)	45 (3.2)
1,2,3,7,8-PeCDF	11 (0.1)	18 (0.8)	34 (4.1)
2,3,4,7,8-PeCDF	12 (3.1)	18 (1.8)	38 (8.3)
1,2,3,4,7,8-HxCDF	30 (5)	57 (25)	114 (38)
1,2,3,6,7,8-HxCDF	11 (0.1)	20 (4.2)	47 (10.3)
2,3,4,6,7,8-HxCDF	11 (4.9)	17 (4.2)	41 (4.6)
1,2,3,7,8,9-HXCDF	2 (0.8)	3 (4.2)	4 (2.5)
1,2,3,4,6,7,8-HpCDF	255 (6)	466 (36)	955 (106)
1,2,3,4,7,8,9-HpCDF	18 (2.5)	30 (11.7)	78 (19.2)
OCDF	803 (3.5)	1,300 (0.7)	2,720 (113)
PCB-77	1,735 (615)	2,605 (1110)	4,745 (1930)
PCB-81	nd	nd	nd
PCB-105	5,435 (1220)	8,700 (1710)	13,700 (2120)
PCB-114	73 (85)	114 (140)	342 (85)
PCB-118	9,980 (2150)	13,950 (3040)	26,100 (4950)
PCB-123	488 (18)	488 (146)	1,069 (140)
PCB-126	30 (25)	40 (40)	85 (100)
PCB-156/157	3,000 (340)	4,455 (430)	9,195 (80)
PCB-167	1,260 (170)	1,885 (300)	3,955 (540)
PCB-169	90 (110)	205 (195)	355 (480)
PCB-189	277 (25)	488 (60)	1,135 (80)

[1]From 1973 to 2002, annual biosolids application rates were 0, 16.8, and 67.2 Mg ha^{-1}, which resulted in the cumulative loadings of 0, 504, and 2016 Mg biosolids ha^{-1}, respectively.
[2]Value in parentheses is standard deviation.
nd = Concentration below the reporting limit.

application supply approximately equal amounts of total TEQs from PCDD/Fs to the U.K. soils each year. As expected, the concentrations of the heavier congeners (Hp- and O-CDD/CDFs) in soil were higher than the lighter congeners (Table 4). These results are consistent with the findings of previous reports (Jones and Sewart, 1997).

The congener, PCB 81, was below detection limits in all plots (Table 4). Detectable concentrations of all congeners of PCBs in soil were observed in the Control plot, but the levels of most congeners increased with increasing the cumulative loadings of biosolids. These observations suggest that land application of biosolids may not be the only source of PCBs in soil. Alcock et al. (1995) reported that the PCB content in soil was dominated by atmospheric inputs, even in the plots amended with high rates of biosolids.

The concentrations of all congeners of dioxins, except PCB 123, were higher in the biosolids plots than in the Control and the highest levels were observed in the 2016 Mg biosolids ha^{-1} plot (Table 4). The levels of most congeners appeared to increase linearly with the cumulative loadings of biosolids when the concentrations observed in the Control plot were subtracted from those observed in the biosolids plots. Similarly, McLachlan and Reissinger (1990) reported a positive relationship between the PCDD/Fs concentrations in soil and the duration of fertilization with biosolids. They also noted that after 30 years of biosolids application, the concentrations of PCDD/Fs in soil were 11 times higher than in the unamended soil.

The concentrations of dioxins in soil expressed as TEQs are presented in Table 5. To further evaluate the contribution of nondetected congeners on the magnitude of TEQ values, we also calculated TEQs by using zero for the nondetected congeners (data not shown). The TEQ values calculated by using zero for nondetected congeners were 5-15 percent lower than the values calculated by one-half the detection limit for the nondetects. This observation emphasizes that treatment of nondetects in the calculation may have significant impact on the magnitude of reported dioxins TEQs.

The contribution of the various homologue groups of CDDs and CDFs to the total dioxins TEQs in soil from the Control and biosolids-amended plots is presented in Figure 1. In both the Control and biosolids-amended plots, the PeCDD and HpCDD in the CDDs and PeCDF and HpCDF homologue groups in the CDFs, respectively, were the predominant contributors to the total dioxins TEQs in soil. Although, the actual concentrations of Pe-CDD/F homologue groups in soil were quite low, their contributions to the total dioxins TEQs were relatively high because the TEF values for Pe-CDD/F congeners are very high (Table 2).

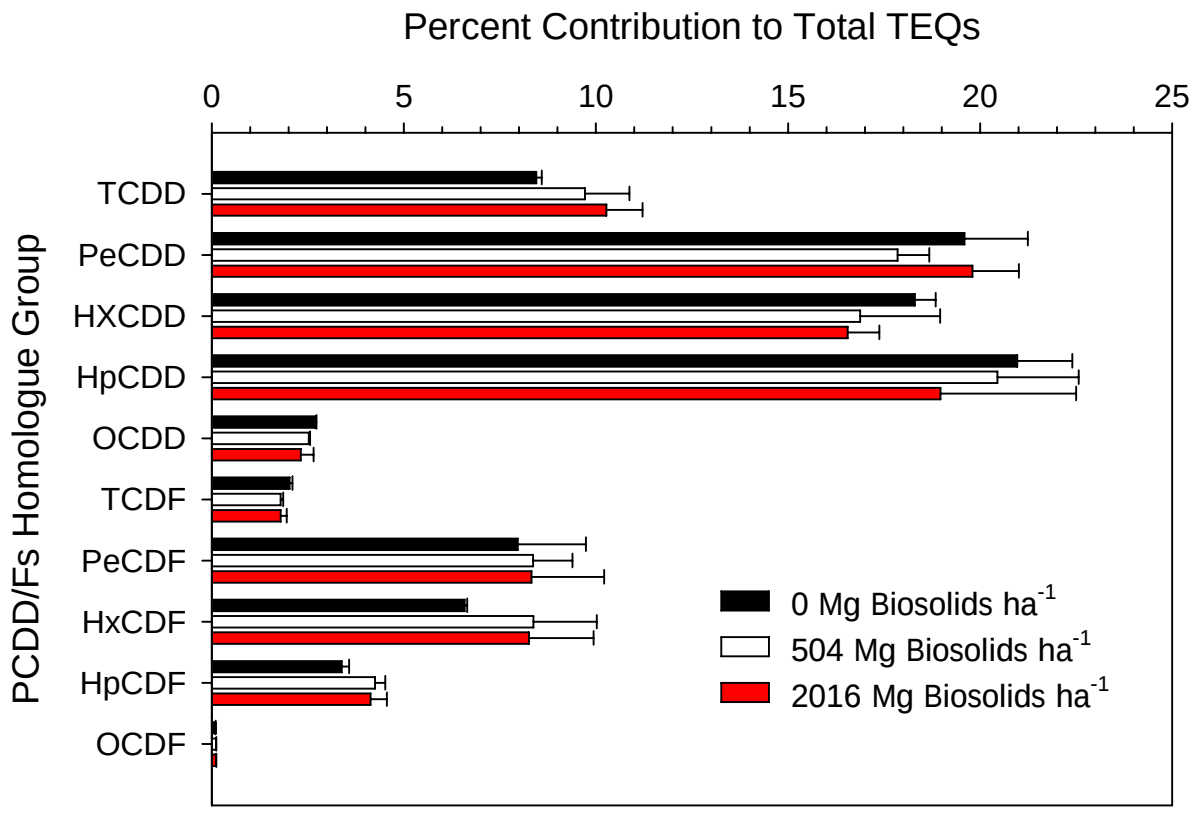
The highest TEQ value (247.5 pg g^{-1}) in soil was observed in the 2016 Mg biosolids ha^{-1} plot. Although the highest TEQ value observed in soil samples from the 2016 Mg biosolids ha^{-1} plot was higher than the maximum TEQ value (112.6 pg g^{-1}; Table 3) found in the sludges and biosolids analyzed in 1994, 2000, and 2004, it was lower than the 300 pg TEQs g^{-1} limit proposed by the USEPA. It would take over 100 years of repeated annual application of biosolids to reach the cumulative loading of 2016 Mg biosolids ha^{-1} at the USEPA's recommended agronomic rate of biosolids application which for the District biosolids is approximately 20 Mg dry biosolids ha^{-1}.

TABLE 5: TOXICITY EQUIVALENTS (TEQs) OF DIOXINS IN SOIL SAMPLES COLLECTED IN 2002 FROM THE CONTROL AND BIOSOLIDS-AMENDED PLOTS

Parameter	Cumulative Biosolids Loading (Mg ha^{-1})[1]		
	0	504	2016
	---------- pg TEQ g^{-1} ----------		
PCDDs	56.4 (4.3)[2]	78.5 (4.7)	169.5 (14.3)
PCDFs	16.2 (1.7)	26.7 (1.8)	56.5 (1.1)
PCBs	7.2 (3.1)	10.4 (5.2)	21.5 (14.1)
Total dioxins[3]	79.9 (2.9)	115.5 (2.3)	247.5 (0.9)

[1]From 1973 to 2002, annual biosolids application rates were 0, 16.8, and 67.2 Mg ha^{-1}, which resulted in the cumulative loadings of 0, 504, and 2016 Mg biosolids ha^{-1}, respectively.
[2]Value in parentheses is standard deviation.
[3]Total dioxins = Sum of PCDDs, PCDFs, and PCBs.

FIGURE 1: CONTRIBUTION OF PCDD/Fs HOMOLOGUE GROUPS TO THE TOTAL DIOXINS TEQs IN SOIL SAMPLES COLLECTED IN 2002 FROM THE CONTROL AND BIOSOLIDS-AMENDED PLOTS



Since the concentration of dioxins in biosolids is less than 300 pg TEQs g^{-1} and incorporation of biosolids in soil after application generally results in 100-fold dilution, the dioxins level of 300 pg TEQ g^{-1} would never be attained in agricultural soil through biosolids application at the recommended agronomic rates. In addition, given the declining trend in dioxins concentration in biosolids over time, as shown in this study, this level of dioxins in soil would be even further unattainable through land application of biosolids.

The PCDD/Fs accounted for approximately 82, 85, and 91 percent of the total TEQs for control, 504, and 2016 Mg biosolids ha^{-1} plots, respectively. The contribution of PCBs to the total TEQs was similar (18 and 15 percent) in the Control and 504 Mg biosolids ha^{-1} plots, but it was quite low (9 percent) in the 2016 Mg biosolids ha^{-1} plot. The relative contribution of PCBs to the total TEQs was highest in the Control and lowest in the 2016 Mg biosolids ha^{-1} plot (Table 5). These results suggest that the concentrations of PCBs detected in soil were not the result of biosolids application alone. These observations are consistent with other previous reports (Alcock et al., 1995).

Effect of Biosolids on Dioxins in Corn Stover and Grain

The concentrations of dioxins in stover are given in Table 6. Two congeners of PCDDs were detected in the stover from all plots. Two congeners of PCDFs were also detected in the stover, but only in the 504 Mg biosolids ha^{-1} plot. The concentrations of dioxins in stover expressed as TEQs are given in Table 7. There was very little difference in TEQ values among the plots. Because a majority of the dioxins congeners in stover were below detection limits, we also calculated the TEQs using zero for nondetects (data not shown). As expected, the TEQs determined using zero for nondetects were much lower than the TEQs calculated using one-half the detection limits for nondetects. None of the 29 congeners of dioxins analyzed in this study were detected in the corn grain.

Although the levels of dioxins in soil tended to increase with increasing the loadings of biosolids, the total TEQs in corn stover were identical in the Control and 2016 Mg biosolids ha^{-1} plots, but slightly higher in the 504 Mg biosolids ha^{-1} plot, indicating that the uptake of dioxins by corn stover was not affected by the levels of dioxins in soil. The PCBs accounted for approximately 19 percent of the total TEQs in corn stover in all plots. The levels of dioxins detected in the corn stover from the Control and the biosolids-amended plots were more likely due to atmospheric deposition. The fact that corn grain did not have detectable concentrations of dioxins is also consistent with atmospheric deposition as a source of dioxins since the grains are shielded by the husks from direct atmospheric deposition. It was further observed that the total amount of dioxins removed by corn stover (calculated by multiplying dioxins concentration in stover by the stover yield) was greater in the Control plot (22.5 µg ha^{-1}) than in the biosolids plots (16.5 – 20.0 µg ha^{-1}), which indicates that dioxins uptake by corn stover did not increase with biosolids application. It has been postulated that under normal conditions, the atmospheric deposition is responsible for most of the PCDD/Fs and PCBs detected in plant leaves (McLachlan, 1991; Hülster and Marschner, 1993). It has also been documented that PCDD/Fs and PCBs in soil are strongly bound and thus are relatively unavailable for plant uptake (Wild and Jones, 1992; Schroll et al., 1994; Wang and Jones, 1994; Duarte-Davidson et al., 1994).

TABLE 6: MEAN CONCENTRATIONS OF PCDD/Fs AND PCBs CONGENERS IN CORN STOVER SAMPLES COLLECTED IN 2002 FROM THE CONTROL AND BIOSOLIDS-AMENDED PLOTS

	Cumulative Biosolids Loading (Mg ha^{-1})[2]		
Congener[1]	0	504	2016
	---------- pg g^{-1} ----------		
1,2,3,4,6,7,8-HpCDD	9 (0.7)[3]	33 (12)	12 (3.2)
OCDD	92 (5)	389 (115)	125 (21)
1,2,3,4,6,7,8-HpCDF	nd	7 (0.6)	nd
OCDF	nd	16 (0.6)	nd
PCB-77	nd	50 (32)	23 (8)
PCB-105	94 (22)	183 (75)	90 (24)
PCB-118	189 (46)	358 (126)	175 (41)
PCB-156	75 (23)	159 (42)	81 (28)
PCB-167	nd	47 (14)	25 (4)

[1]The congeners not detected in any of the samples are not listed.
[2]From 1973 to 2002, annual biosolids application rates were 0, 16.8, and 67.2 Mg ha^{-1}, which resulted in the cumulative loadings of 0, 504, and 2016 Mg biosolids ha^{-1}, respectively.
[3]Value in parentheses is standard deviation.
nd = Concentration below the reporting limit.

TABLE 7: TOXICITY EQUIVALENTS (TEQs) OF DIOXINS IN CORN STOVER SAMPLES COLLECTED IN 2002 FROM THE CONTROL AND BIOSOLIDS-AMENDED PLOTS

Parameter	Cumulative Biosolids Rate (Mg ha^{-1})[1]		
	0	504	2016
	---------- pg TEQ g^{-1} ----------		
PCDDs	3.6 (0.3)[2]	2.7 (2.1)	3.6 (0.5)
PCDFs	1.7 (1.1)	1.9 (0.8)	1.8 (1.0)
PCBs	2.1 (0.9)	2.2 (0.9)	2.1 (1.0)
Total dioxins[3]	7.5 (0.5)	6.8 (2.0)	7.5 (0.50

[1]From 1973 to 2002, annual biosolids application rates were 0, 16.8, and 67.2 Mg ha^{-1}, which resulted in the cumulative loadings of 0, 504, and 2016 Mg biosolids ha^{-1}, respectively.
[2]Value in parentheses is standard deviation.
[3]Total dioxins = Sum of PCDD, PCDFs, and PCBs.

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