

Results of a National Survey for Polychlorinated Dibenzo-*p*-dioxins, Dibenzofurans, and Coplanar Polychlorinated Biphenyls in Municipal Biosolids

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The application of municipal biosolids to agricultural land in the United States is widely practiced by municipal sewerage treatment facilities as a part of municipal sludge management practices. The potential impact of this practice with regard to reintroducing environmental estrogens, such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (non-ortho PCBs), into the environment is unknown but has been estimated by other researchers ^{1,2}. Concentrations of these

contaminants in municipal sludges ³ have been determined in the United Kingdom ³, Sweden ⁴, the Federal Republic of Germany ⁵, and in the United States ⁶.

The objective of this study was to estimate the impact of current sludge management practices on environmental dioxin exposure. The results reported included over one hundred samples from a random survey of municipal sewerage treatment facilities in the continental United States. Summary results for PCDDs, PCDFs, and eight non-ortho PCBs are presented, as well as calculations for TCDD Toxic Equivalents using the International Toxic Equivalent Factor system for PCDD/PCDF ⁷ and the system proposed by S. Safe for PCBs ⁸. These results have been submitted to the USEPA for use in the reassessment of exposure to dioxin-like compounds.

Analytical Methods

Sample Preparation

Samples were collected in amber glass jars by survey participants and shipped at 4°C overnight to the analytical laboratory. The samples were homogenized, and the percent solids were determined in an aliquot by drying in an oven overnight (110°C). For samples that were physically liquid and contained greater than 1% solids, a wet weight of the sample was taken equivalent to 10 g on a dry weight basis. The sample was fortified with ¹³C-labeled PCDD/PCDF/PCB analogs (2 to 4 ng, Cambridge Isotope Laboratories) and allowed to equilibrate for one hour. After equilibration, the sample was filtered or centrifuged to separate the solids; the water portion of the sample was discarded; the solids were mixed

with approximately 50 g of quartz sand; and the mixture was placed in a Soxhlet extractor equipped with a Dean Stark adapter. The sample was then extracted for 21 hours with toluene (pesticide grade, Burdick & Jackson). Samples that were physically solid were mixed with quartz sand, fortified with ^{13}C -labeled PCDD/PCDF/PCB analogs, and extracted with toluene using a Soxhlet extractor equipped with a Dean Stark adapter.

After extraction, the toluene extracts were solvent exchanged to hexane (pesticide grade, Burdick & Jackson); fortified with ^{37}Cl -2,3,7,8-TCDD (200 pg); and washed with 5% aqueous NaCl, 20% aqueous KOH, 5% aqueous NaCl, concentrated sulfuric acid, and 5% aqueous NaCl. The extracts were dried through sodium sulfate and eluted through a 6-g 40% H_2SO_4 silica gel (top):1-g silica gel (bottom) (70-230 mesh, EM Science) with 90 mL of hexane. The extract was evaporated to approximately 2 mL and applied to a layered column of sodium sulfate, neutral alumina (4 g, ICN Biomedicals), and sodium sulfate. The interferences were removed by eluting the column with 10 mL of 8% (v/v) dichloromethane/hexane. The PCDD/PCDF/coplanar PCBs were removed by eluting with 20 mL of 60% (v/v) dichloromethane/hexane. The extract was reduced in volume to approximately 2 mL and applied to a 0.5-g column of 8% AX-21/Celite 545® (Anderson Development Co. and J.T. Baker). The carbon column was sequentially eluted with 2 x 3 mL hexane, 4 mL cyclohexane/dichloromethane (50:50), and 1 mL dichloromethane/methanol/benzene (75:20:5). After these eluents were collected, the column was inverted, and the analytes of interest were eluted with 20 mL of toluene. The toluene was reduced in volume under nitrogen to about 100 μL , fortified with two ^{13}C -labeled recovery standards in tridecane, and further reduced to a volume of 20 μL .

Sample Analysis

Sample analysis was conducted using a Hewlett Packard 5890 gas chromatograph interfaced with a VG70-250S mass spectrometer. Instrument resolution was 10,000 or greater. Due to potential contribution from hexa-substituted PCBs, two additional mass ions were monitored for the native and ^{13}C -labeled penta-substituted dioxins. Specifically, the molecular ion (*m*) responses for native penta-substituted dioxin (*m/z* 353.8576) and ^{13}C -labeled penta-substituted dioxin (*m/z* 365.8979) were monitored, in addition to the *m*+2 and *m*+4 ions. Quantitation was based on the *m* and *m*+2 ions for the penta-substituted dioxin compounds. Calculations were performed using isotope dilution where possible. This entailed calculations as indicated in EPA Method 1613 for the PCDD/PCDFs and for 3,3',5,5'-tetrachlorobiphenyl (BZ #80), 3,3',4,4'-tetrachlorobiphenyl (BZ #77), 3,3',4,4',5-pentachlorobiphenyl (BZ #126), and 3,3',4,4',5,5'-hexachlorobiphenyl (BZ #169), where ^{13}C -labeled analogs were used. Concentrations of the other coplanar PCBs were calculated using response factors determined from ^{13}C -labeled analogs with similar structures and elution times.

The analytes were chromatographically separated using a 60-m DB-5MS fused silica column (J&W Scientific). The temperature program was: initial temperature 200°C for 2 min, 200° to 220°C at 5°C/min (hold for 16 min), 220° to 235°C at 5°C/min (hold for 7 min), and then 235° to 330°C at 5°C/min (hold for 3 min), which allowed at least 25% valley separation between 2,3,7,8-TCDD and all other TCDD isomers.

Results and Discussion

The geographical extent of this survey is given in Table 1. Typically, a facility submitted one sample from each treatment plant or process for analysis. Each participant also answered a questionnaire. The questionnaire addressed information regarding average daily sewage flow, average daily sludge production, percent industrial flow, and treatment processes.

Table 1. Survey Response

Census Division	Number of Samples	Number of States	Number of Municipalities
Pacific	17	3	11
Mountain	2	1	1
West North Central	12	2	2
West South Central	4	2	3
East North Central	21	3	9
East South Central	5	2	3
New England	0	0	0
Middle Atlantic	20	3	5
South Atlantic	26	4	8
Total	107	20	42

A summary of the analytical results is given in Table 2. Average Toxic Equivalent (TEQ)^{7,8)} concentrations, standard deviation, standard error, and mean TEQ concentrations are given. Results from all samples collected from the same facility were averaged before calculating statistics describing the data set. This ensured that the results were not biased towards the concentrations found at facilities collecting more than one sample. The TEQ for each sample was calculated using zero or the detection level for undetected analytes. The major contributors to the TEQ are the 3,3',4,4'-tetrachlorobiphenyl (BZ#77) and 3,3',4,4',5-pentachlorobiphenyl (BZ #126) isomers. Significant contributions also were made by 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD, 1,2,3,4,6,7,8-HpCDD, and OCDD isomers. Approximately 2 % of the average TEQ is attributable to the average 2,3,7,8-TCDD concentration. The average TEQ ranged between 95.2 and 112.7 pg/g on a dry weight basis. The median TEQ ranged between 56.9 and 77.9 pg/g on a dry weight basis. Maximum toxic equivalents in single samples ranged as high as 653 pg/g on a dry weight basis.

Isomers with the highest concentrations included 1,2,3,4,6,7,8-HpCDD, OCDF, OCDD, 3,3',5,5'-tetrachlorobiphenyl (BZ #80), and 3,3',4,4'-tetrachlorobiphenyl (BZ #77). PCB isomer BZ #80 exhibited the highest concentration of all analytes at approximately 85 ppb. OCDD ranked next with a maximum of 65 ppb, followed by PCB BZ #77 with an estimated concentration of 23 ppb on a dry weight basis.

Table 2. Summary of TEQ Concentrations in Biosolids

Treatment of Non-detects	Data Subset	Average (pg TEQ/g)	Standard Deviation (pg TEQ/g)	Standard Error of the Mean (pg TEQ/g)	Median (pg TEQ/g)
Detection limits used for nondetects	Total	112.7	114.3	13.3	77.9
	PCDD/PCDF	64.6	50.6	5.89	49.1
	PCBs 77, 126, and 169	48.1	89.2	10.4	23.9
Zero used for nondetects	Total	95.2	110.2	12.8	56.9
	PCDD/PCDF	47.7	45.0	5.23	30.0
	PCBs 77, 126, and 169	47.5	89.4	10.4	22.6

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