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Polychlorinated dibenzo-*p*-dioxins, Dibenzofurans and Polychlorinated biphenyls in Street Dusts and Soil Samples from Savannah, Georgia

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Abstract

Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and polychlorinated biphenyl congeners (PCBs) were analyzed in street dust and soil samples collected near industrial and residential areas in and around Savannah, Georgia, U.S.A. Among the various analytes measured, PCB congeners were found in almost all samples analyzed. In general, PCB-101 (2,2',4,5,5'-pentachlorobiphenyl), PCB-153 (2,2',4,4',5,5'-hexachlorobiphenyl), PCB-180 (2,2',3,4,4',5,5'-heptachlorobiphenyl) and PCB-187 (2,2',3,4',5,5',6-heptachlorobiphenyl) were the most prominent congeners found in the samples from Savannah area and contributed more than 50% of the total PCB load. Among the various sampling sites, street dust collected at Brunswick near EPA superfund site recorded the highest total (sum of PCB congeners measured) PCB concentration of 88.1 ng/g $^{-1}$ dry wt.. Interestingly, the samples from crude oil fire accident site contained very low levels of PCBs, however, these samples contained detectable concentrations of chlorinated dioxins and furans. Among the 2,3,7,8-substituted dioxins and furans measured, 1,2,3,7,8- pentachlorodibenzo-*p*-dioxin was found in detectable concentrations in about 70% of the samples with maximum concentration of 698 pg/g $^{-1}$ dry wt. in a street dust collected near a paper mill. Comparatively, less percent (<50%) of detects and very low concentrations (< 50 pg/ g $^{-1}$ dry wt.) of dibenzofurans were found in the street dust and soil samples. To our knowledge, this is the first report on PCB congeners, chlorinated dioxins and dibenzofurans in the street dust and soil from Savannah, Georgia.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and non-*ortho*-PCB congeners are among the most toxic man-made chemical substances to a variety of animal species including humans[1-5]. PCDDs and PCDFs are found as byproducts in the production of PCBs, polychlorinated naphthalenes and chlorinated phenols. PCDFs are also routinely detected during the combustion of chlorinated chemicals, incineration of industrial and municipal waste[6,7]. These pollutants are widely dispersed in the environment[8,9] and their presence was reported

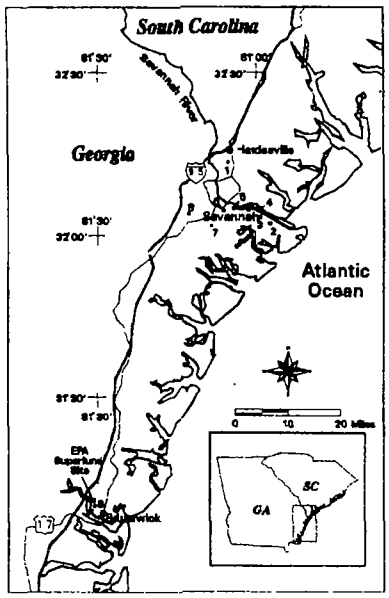

Fig. 1. Map showing sampling locations in the southeastern United States:
1. Wildlife Refuge, Hardeeville, SC.
2. Near Crude Oil Fire Accident Site (Powell Duffryn Terminals Inc.)
3. Island Expressway
4. Near Kemira, Inc.
5. River Street near Savnnah Electric
6. Near Union Camp Paper Mill
7. I-16 near Garden City
8. Near Gulf Stream Aerospace
9. Near EPA Superfund site at Brunswick

in air, water, soil, sediment, aquatic and terrestrial organisms including human tissues[7-10]. Due to persistent and bioaccumulative properties of these compounds, higher trophic level animals, receive the largest amount of these contaminants and are implicated in a variety of health effects such as body weight loss, thymic atrophy, dermal disorder, hepatic damage, teretogenicity, reproductive toxicity and immunotoxicity in some animals[11-14]. Recent report by Patterson *et al.*[10] on the levels of non-*ortho*-substituted (coplanar), mono- and di-*ortho*-substituted polychlorinated biphenyls, dibenzo-*p*-dioxins and dibenzofurans in human serum and adipose tissues from peoples from Atlanta, Georgia have raised concern about the environmental contamination of PCBs, PCDDs and PCDFs in this region. Although food is considered to be the major source of these chemicals for humans[15], soil and street dust are ranked with respect to impact, as one of the important direct pathway (skin contact, inhalation of ambient air with dusts and food web biomagnification) that account for the accumulation of these toxic contaminants in human tissues[16]. Present study was initiated to measure the levels of selected PCB congeners, chlorinated dioxins and furans in the street dust and soil samples from industrial and general locations in the city of Savannah, and to understand any local sources for these contaminants in this region.

Figure 1 shows the map of coastal regions of Georgia (GA) and South Carolina (SC) and the sampling locations in and around Savannah. The city of Savannah, is one of the polluted cities in the state of Georgia[17,18], has variety of industries such as chemical (chlorine, methanol, sulfur dioxide, titanium tetrachloride, methyl ethyl ketone), paper mills, fertilizers, oils etc., Nine street dust and three soil samples were collected at roadside near (about 1 km) the industrial lots and relatively undisturbed residential locations respectively (Fig. 1 and Table 1a). Site #1 is at Hardeeville, South Carolina, at the vicinity of National Wildlife Refuge was chosen, since this is located downwind from industries of Savannah. Site #2: On April 10 to12, 1995, a major fire accident in a crude oil storage facility (Powell Duffryn Terminals Inc.) burned several hundreds of thousand litres of sodium hydrosulfide (when breathed, can irritate mucous membranes and

cause respiratory and heart problems), used to make pulp for paper, crude sulfate turpentine (contact with skin or eyes can cause irritation), a useless chemical byproduct, antiblaze-80 (could cause birth defects), a fire retardant, and briquest-80 PA 60 (exposure to this chemical can aggravate anemia and known to possibly cause birth defects), a water treatment chemical. Continuous and uncontrollable fire evacuated people from this area and produced heat up to 1500 to 3000°C[19]. Site # 3. An Island Expressway. Site # 4. Near titanium dioxide manufacturing company (Kemira, Inc.). Site # 5. On the River Street near Savannah Electric Co. Site # 6. Near Union Camp Paper mill. Site # 7. On I-16 near Garden City, which has a cluster of chemical, fertilizers manufacturing companies. Site # 8. Near Gulf Stream Aerospace- Air Craft building Co. Site# 9. Near EPA Superfund site at Brunswick, known to contain very high levels of PCBs and mercury. The street dusts and soils were analyzed for polychlorinated biphenyl congeners, polychlorinated dibenzo-*p*-dioxins and dibenzofurans.

Experimental Methods

About 50-100 g of street dust and soil samples were collected using pre-cleaned (cleaned with detergents and high purity solvents) stainless steel scoop and transferred to pre-cleaned I-Chem jars and sieved (with 500 micrometer diameter sieve) to remove non-representative larger pebbles. About 20 grams of the sample was Soxhlet extracted using 3:1 mixture of methylene chloride and acetone for 16 hrs. The extract was K-D concentrated, cleaned up with silica gel column chromatography,. PCBs and dioxins and furans were separated using Alumina column chromatography. PCB fraction was further cleaned up with activated copper, concentrated sulfuric acid prior to injection into gas chromatograph. Dioxin and furan fraction was concentrated using rotary evaporator and passed through silica gel impregnated with activated carbon. Dioxins and furans were eluted with toluene and the extract was exchanged to hexane. PCB congeners were analyzed using Shimadzu model GC-17A gas chromatograph (GC) with Shimadzu model AOC-17 autoinjector. The GC was equipped with DB-5 (30m; 0.25mm i.d.; 0.25μ film thickness) capillary column and a ^{63}Ni electron capture detector. Column oven temperature program was: 90°C (1.0 min^{-1}.) ..@ 5°C/min^{-1} .. 150°C (0 min.).. @ 2°C/min^{-1} 260°C (15 min.). Injector and detector temperatures were set at 270°C and 330 °C respectively. Helium (2ml/min^{-1}) and nitrogen (28ml/min^{-1}) were used as carrier and makeup gases respectively. PCB calibration standard -SRM-2262 obtained from National Institute of Standards and Technology was used for quantitation PCB congeners 1, 8, 18, 29, 50, 28, 52, 104, 44, 66+95, 101+90, 87, 77, 154, 118, 188, 153, 105+132, 138+163+164, 126, 187+182+159, 128, 200, 180, 170+190, 195, 206 and 209 in the samples. Surrogate standard 4,4'-dibromooctafluorobiphenyl spike recovery was 100±30%. Method detection limits for PCB congeners were 0.2 ng/g^{-1}.

Chlorinated dioxins and furans were analyzed using Hewlett Packard 5890 Series II Plus Gas Chromatograph interfaced with Hewlett Packard 5972 Mass Selective Detector. Hewlett Packard 7673 Autoinjector was used for sample injection. Split/Splitless injection system and a fused silica capillary column having dimensions of 30m long, 0.25mm i.d. and 0.25 micron of 5% phenyl substituted methylpolysiloxane phase (DB-5MS) was used. The column oven temperature program: 90°C (3min.) .. @ 15°C to 220°C (0 min.) ..@ 2°C to 260°C (15 min.) Injector temperature and transfer line were maintained at 250°C and 300°C respectively. Chlorinated dioxins and dibenzofuran congeners were determined by selected ion monitoring at *m/z* :TCDF/DD: 304, 306, 308, 320, 322, 324; PCDF/DD: 338, 340, 342, 354, 356, 358;

HXCDF/DD: 372, 374, 376, 388, 390, 392; HPCDF/DD: 406, 408, 410, 422,424; OCDF/DD: 442, 444, 458, 460.

Table 1a. Details of sampling locations, sample type and total (sum of 35 congeners) PCB concentrations. All street dust and soil were sampled on October 12, 1996, except a soil sample near the Powell Duffryn crude oil fire accident site was sampled on December 2, 1996.

Site Number	Site Description	Sample Type	Total PCBs (ng/g^{-1} dry wt.)
S-1	National Wildlife Refuge Hardeeville, SC	Soil	4.49
S-2	Crude Oil Accident site (Powell Duffryn)	Soil Street dust	1.70* 1.64
S-3	Island Expressway	Street dust	1.53
S-4	Near Kemira, Inc.	Soil	9.73
S-5	River street near Savannah Electric	Street dust	18.57*
S-6	Near Union Camp Paper Mill	Street dust	<1.0
S-7	I-16- Garden city	Street dust	16.30
S-8	Air Port -near Gulf Stream Aerospace	Soil	2.34
S-9	Brunswick, EPA Superfund Site	Street dust	88.10

Table 1b. PCDD and PCDF concentrations in street dust and soil samples from Savannah, GA.

Analyte	S-1	S-2 **	S-3	S-4	S-5 *	S-6	S-7	S-8	S-9
2,3,7,8-T4CDD	<10	<10	19	14.5	<10	11.4	19.3	30.1	<10
1,2,3,7,8-P5CDD	<10	220	74.8	42.4	37.5	698	<10	150	48
1,2,3,4,7,8-H6CDD	<15	<15	<15	<15	131	<15	<15	<15	<15
1,2,3,4,6,7,8-H7CDD	<25	<25	<25	<25	78.5	<25	<25	<25	<25
1,2,3,4,6,7,8,9-O8CDD	<25	<25	<25	<25	<25	<25	<25	<25	<25
2,3,7,8-T4CDF	<10	<10	<10	18.7	<10	12.8	<10	10	<10
1,2,3,7,8-P5CDF	<10	15	<10	<10	<10	<10	<10	<10	<10
1,2,3,4,7,8-P6CDF	<15	25.2	<15	<15	15	<15	<15	14.3	23.2
1,2,3,4,6,7,8-H7CDF	19	139	<15	<15	<15	<15	19	<15	<15
1,2,3,4,6,7,8,9-O8CDF	<25	<25	<25	<25	<25	29.8	<25	<25	<25

*mean value of two and ** three samples; S= Site

Results and Discussion

Concentrations of total PCBs, chlorinated dioxins and dibenzofurans in the street dust and soil samples are presented in Table 1a and 1b. Total PCB concentrations in soil and street dusts from the various sampling locations ranged from 1 ng/g^{-1} to 88.1 ng/ g^{-1} dry wt. Interestingly, crude oil fire accident site (#2) street dust and soil samples recorded very low concentrations of PCBs. Similarly, street dusts from Island Expressway (#3), near Union Camp paper mill (#6) and a soil sample collected near Gulf Stream Aerospace (#8) were also low and the values were between 1 to 2.34 ng/ g^{-1} dry wt. Comparatively, higher concentrations of total PCBs were found in soil samples collected near National Wildlife Refuge at Hardeeville, SC (#1) and near titanium dioxide manufacturing company (#4), street dusts from River Street (#5) near Savannah Electric, I-16 at Garden city (#7) and near EPA superfund site at Brunswick (#9) (Table 1a). Except for superfund site at Brunswick, in all of the above samples, PCB-101 (2,2',4,5,5'-pentachlorobiphenyl), PCB-153 (2,2',4,4',5,5'-hexachlorobiphenyl), PCB-180 (2,2',3,4,4',5,5'-heptachlorobiphenyl) and PCB-187 (2,2',3,4',5,5',6-heptachlorobiphenyl) congeners contributed more than 50% of the total PCB load. Among the highly toxic coplanar PCBs (non-*ortho*-chlorine substituted) such as PCB-77 (3,3',4,4'-tetrachloro) and PCB-126 (3,3',4,4',5-pentachloro), PCB-77 was not found in any of the samples analyzed, however, PCB-126 was detected in the samples from Savannah Electric (0.32 ng/g^{-1}) and Garden city (0.26 ng/ g^{-1}) sites. Presence of PCB-101, PCB-153 and PCB-138 in the street dust sample indicate that the sites were contaminated with Aroclor 1254 and 1260. Relatively, higher concentrations of total PCBs in street dusts collected near Savannah Electric may be due to emissions or leak from old electrical transformers/capacitors in this area. Precise reasons for higher concentrations of PCBs in samples from I-16 near Garden city (industrial emissions contaminate air and cause undesirable odor), near Kemira Inc. and National Wildlife Refuge site at Hardeeville, is not known clearly. Further studies are needed for these sites, particularly monitoring air to determine, if these PCBs are airborne. Savannah street dust and soil were an order to two order magnitude less contaminated with PCBs when compared to street dusts from Buffalo, New York[20,21]. However, EPA Superfund site at Brunswick street dust sample recorded the highest total PCBs concentration among all the samples from Savannah and revealed an unique congener composition having heptachloro, octachloro-, nonochloro-, and decachloro biphenyls contributed more than 95% of the total PCB load. This superfund site was extensively contaminated with Aroclor 1268, which was used by a former chlor-alkali plant[22]. High concentration of PCBs in street dust near this site reveals presence of a point source for this roadside and adjacent residential area. Further, the congener composition of the street dust sample resembled the congener composition of Aroclor 1268 in sediments from the superfund site[22]. Presence of Aroclor 1268 congeners in the street dust reveals the escape of contaminated soil beyond the protected area of the superfund site.

Table 1b presents 2,3,7,8 substituted PCDD and PCDF concentrations in the street dust and soil samples. Among the PCDD isomers, 1,2,3,7,8-pentachloro dibenzo-*p*-dioxin was most commonly detected. Unlike total PCBs, highest concentration of chlorinated dioxin congener was found in soil sample collected near paper mill (698 pg/g^{-1}) (#6), followed by street dust obtained near Powell Duffryn crude oil fire accident site (220pg/g^{-1}) (#2). Relatively, low concentration (48 pg/g^{-1}) of PCDDs were found in street dust sample near EPA superfund site. Comparatively low concentrations of furans were detected in street dust and soil samples.

Highest concentration furans (total) of 179 pg/ g^{-1} was found in crude oil fire accident site. Similar range of dioxins and furans were reported in street dusts and soil samples from Stockholm, Sweden[23]. At all other sites, furan concentrations were low or below the detection limit. The results indicate that there exists no direct correlation with total PCB concentrations and PCDDs and PCDFs in the street dusts and soil from the sampling locations.

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