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Current Levels of Dioxins in Surface Soils from Santiago, Chile

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Santiago, the capital of Chile, is geographically located in a closed basin surrounded by mountains. Meteorologically, the city is located under permanent layers of subsidence inversion. Because of the peculiar landform, the atmospheric flow becomes stagnant easily. This characteristic indicates that suspended particulate matter, including hazardous chemicals, descend to the surface. Furthermore, the population density of the city is extremely high (more than 40% of the national population lives there), and it is thought that air pollution and soil pollution are brought from human activities. An emission source of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) in Santiago is not yet identified because no systematic data have been available. Generally speaking, the PCDD/Fs become unintentional by-products of a variety of processes; however, their major source is the combustion of waste (Karasek and Hutzinger 1986; Brzuzy and Hites 1996). On the other hand, the city has adopted a policy of landfill processing of waste treatment; therefore, other factors such as vehicle exhaust particles (Miyabara et al. 1999; Marklund et al. 1990) and chemical synthesis (PCP, i.e., pentachlorophenol, Fries et al. 2002; and CNP, i.e., chloronitrofen, Masunaga et al. 2001) are more capable of contributing PCDD/Fs than is the combustion of waste.

An international agreement aiming to restrict persistent organic pollutants (POPs) was formally adopted in May 2001. Also known as the "dirty dozen", these POPs consist of eight organochlorine pesticides, two industrial chemicals, and PCDD/Fs. POPs are characterized by strong persistency, bioaccumulation through the food web and long-range, even global transport. The impact of POPs has already reached wildlife and human beings living at high latitudes. PCDD/Fs have the most serious toxicity among the POPs; therefore, the monitoring of PCDD/F data in Chile plays an especially important role in developing a reliable fate assessment. In this paper, the PCDD/F concentrations of soils in Santiago were determined by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) to clarify their distribution patterns. The relative compositions of homologues were compared among sampling locations. As far as we know, the present study is the first to examine PCDD/Fs in Chile.

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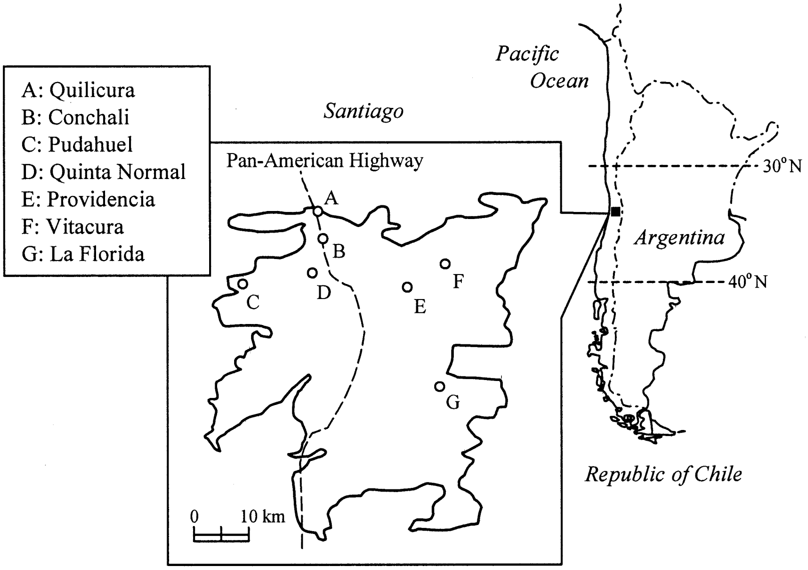

Figure 1. Map of sampling locations in Santiago.

MATERIALS AND METHODS

In January 2002, soils were collected at Santiago, Chile (Figure 1). The ground was carefully dug to the depth of 5 cm from the surface. After the soils were dried for three days at room temperature, they were run through the sieve equipped with 2 mm mesh size. These samples were stored at –20 °C in sealed glass containers until analysis. All the collected soils were sandy loam soils.

One hundred grams (on a dry weight basis; d.w.) of soil was extracted for 18 hours with 150 ml of toluene. After $^{13}C_{12}$-labeled PCDD/Fs (100 pg) were spiked to the extract, the extract was evaporated to 2 ml. The concentrate was purified using the column (300 mm length, 15 mm i.d.) containing from top to bottom: 6 g of anhydrous sodium sulfate, 3 g of 10% (w/w) silver nitrate-silica gel, 0.9 g of silica gel, 6 g of 22% (w/w) sulfuric acid-silica gel, 4.5 g of 44% (w/w) sulfuric acid-silica gel, 0.9 g of silica gel, 3 g of 2% (w/w) potassium hydroxide-silica gel, 0.9 g of silica gel and a quartz wool plug. After the column was pre-rinsed with hexane, the sample was loaded; PCDD/Fs were eluted with 120 ml of hexane. The eluate was then evaporated to 2 ml and further applied to the column (300 mm length, 10 mm i.d.) containing from top to bottom: 0.5 g of anhydrous sodium sulfate, 1 g of active charcoal-silica gel, 0.5 g of anhydrous sodium sulfate and a quartz wool plug. The column was washed first with 80 ml of 25% dichloromethane-hexane. PCDD/Fs were recovered with 200 ml of toluene. After the PCDD/F fraction was evaporated to 2 ml, the sample was transferred to a centrifuge tube. A hundred picograms of $^{13}C_{12}$-labeled 1,2,3,4-tetrachlorinated dibenzo-p-dioxin as an internal standard was added into the tube; the final concentrate (100 μl) was obtained by reducing the volume with a gentle stream of dry nitrogen.

An Agilent 6890 series unit (Agilent, Palo Alto, CA, USA) equipped with a JMS-700 (JEOL, Tokyo, Japan) mass spectrometer was used. A CP-Sil8CB MS capillary column (30 m, 0.25 mm i.d. with 0.25 μm film thickness, Varian, Walnut Creek, CA, USA) and an SP-2331 capillary column (60 m, 0.25 mm i.d. with 0.20 μm film thickness, Sigma-Aldrich, Tokyo, Japan) were employed for separation of congeners. One microliter was injected into the columns using splitless mode. The column temperature of the CP-Sil8CB MS was maintained at 120 °C for 1.5 min, ramped to 200 °C at a rate of 30 °C min^{-1}, to 240 °C at a rate of 5 °C min^{-1}, to 290 °C at a rate of 30 °C min^{-1}, and maintained at 290 °C for 6.5 min. The column temperature of the SP-2331 was maintained at 120 °C for 1.5 min, ramped to 200 °C at a rate of 25 °C min^{-1}, to 240 °C at a rate of 2 °C min^{-1}, to 270 °C at a rate of 20 °C min^{-1}, and maintained at 270 °C for 14.5 min. The temperature of the injection port was 270 °C, the temperature of the interface line was 270 °C, the temperature of the ion source was maintained at 270 °C and the flow rate of helium was 1.0 ml min^{-1}. The ionizing current, the ionizing energy and the accelerating voltage were 700 μA, 42 eV, 10 kV, respectively. The resolution (R) was maintained at $R > 10{,}000$, and the measurement was carried out according to selected ion monitoring (SIM). Recoveries of PCDD/Fs ranged from 60–120%.

RESULTS AND DISCUSSION

The sampling locations included three residential areas (Quinta Normal, La Florida, and Vitacura), two rural areas (Conchali and Quilicura), a commercial area (Providencia), and an airport area (Pudahuel). The toxic 2,3,7,8-chlorinated congeners (except for 2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,7,8,9-HxCDF, and 1,2,3,4,7,8,9-HpCDF) were detected in all of the analyzed samples (Table 1). No clear tendency in the detection frequencies of the 2,3,7,8-chlorinated congeners was observed, whereas their total concentrations in each homologue increased in proportion to the degree of chlorination. OCDD, which showed the highest average concentration, ranged from 6.8–350 pg g^{-1}. In contrast, the lowest average concentration was that of the most toxic POP, 2,3,7,8-TeCDD (n.d.–0.08 pg g^{-1}). Total TEQs were determined to be in the range of 0.22–2.2 pg I-TEQ g^{-1}, which is similar to background levels of the PCDD/Fs in soils from Spain (0.27–2.24 pg I-TEQ g^{-1}, Eljarrat et al. 2001), Sweden (1 pg I-TEQ g^{-1}, Fiedler et al. 1999), England (< 1.4 pg I-TEQ g^{-1}, Green et al. 2001), the United States (< 1 pg I-TEQ g^{-1}, Wood et al. 1999), South Korea (7.31 pg I-TEQ g^{-1}, Ok et al. 1999), China (0.086–3.7 pg WHO-TEQ g^{-1}, Chen et al. 2003), and Japan (< 10 pg I-TEQ g^{-1}, Nakao et al. 1999). The order of total TEQs at the seven locations was as follows: Pudahuel > La Florida > Quinta Normal > Providencia > Vitacura > Quilicura > Conchali. The relative contribution ratio of PCDDs-TEQs and PCDFs-TEQs to the total TEQs differed among the locations. Except for Quinta Norma (38%) and Conchali (37%), all locations exhibited the dominance of the PCDDs-TEQs in the range of 56–66%.

Table 1. Concentrations of 2,3,7,8-chlorinated congeners and total PCDD/Fs.

	Concentration/pg g^{-1} d.w.						
Compound	Conchali	Quinta N.	Pudahuel	Providen.	Florida	Quilicura	Vitacura
2,3,7,8-TeCDD	n.d.	n.d.	0.08	n.d.	0.05	0.07	n.d.
1,2,3,7,8-PeCDD	n.d.	0.09	0.31	0.05	0.19	0.07	n.d.
1,2,3,4,7,8-HxCDD	0.11	0.18	0.68	0.17	0.40	0.06	0.14
1,2,3,6,7,8-HxCDD	0.16	0.36	1.6	0.42	1.2	0.13	0.27
1,2,3,7,8,9-HxCDD	0.16	0.29	1.1	0.24	0.75	0.15	0.23
1,2,3,4,6,7,8-HpCDD	2.5	4.3	41	6.0	21	0.87	6.5
OCDD	12	26	350	43	150	6.8	60
2,3,7,8-TeCDF	0.11	0.37	0.57	0.12	0.71	0.09	0.25
1,2,3,7,8-PeCDF	0.14	0.41	0.62	0.17	0.65	0.11	0.14
2,3,4,7,8-PeCDF	0.10	0.31	0.49	0.16	0.48	0.06	0.07
1,2,3,4,7,8-HxCDF	0.18	0.36	0.83	0.17	0.67	0.10	0.17
1,2,3,6,7,8-HxCDF	0.22	0.32	1.2	0.21	0.67	0.09	0.21
1,2,3,7,8,9-HxCDF	n.d.	n.d.	1.5	n.d.	n.d.	0.06	n.d.
2,3,4,6,7,8-HxCDF	0.13	0.26	0.62	0.16	0.47	0.07	0.16
1,2,3,4,6,7,8-HpCDF	1.4	1.2	8.8	1.0	2.7	0.43	2.6
1,2,3,4,7,8,9-HpCDF	0.08	0.08	1.1	0.09	0.19	n.d.	n.d.
OCDF	1.5	0.79	21	1.1	4.4	0.22	2.4
PCDDs-TEQ	0.080	0.20	1.3	0.21	0.74	0.15	0.19
PCDFs-TEQ	0.14	0.32	0.87	0.17	0.56	0.081	0.15
Total TEQs	0.22	0.52	2.2	0.38	1.3	0.24	0.34
Total PCDDs	20	47	450	65	210	13	80
Total PCDFs	14	22	82	12	39	5.2	19
D/F ratio	1.4	2.1	5.5	5.4	5.4	2.5	4.2

TEQs of PCDD/Fs were calculated on the basis of the I-TEF (1988) values. n.d.: not detected.

The concentrations of total PCDDs and total PCDFs ranged from 13–450 pg g^{-1} and 5.2–82 pg g^{-1}, respectively. The concentrations of total PCDD/Fs ranged between 18.2 (Quilicura) and 532 pg g^{-1} (Pudahuel). These results agreed well with those reported by Green et al. (2001) for surface soil dating to 1856–1913, which were 40–110 pg g^{-1}. Homologue patterns of the PCDD/Fs among the seven locations are shown in Figure 2. In all samples, the PCDDs as a whole accounted for 59–85% the total PCDD/F concentrations and were larger than the total concentration of PCDFs. In particular, OCDD was the most dominant component, representing 35–66% of the PCDD/F total. The patterns in Figure 2 are divided into two groups by the ratio of OCDD to the total PCDD/Fs: Group 1 (Pudahuel, Providencia, La Florida, and Vitacura) and Group 2 (Conchali, Quinta Normal, and Quilicura). OCDD made up the majority of total PCDD/Fs in Group 1; for the remainder in that group, the relative ratios of the PCDFs and of low-chlorination PCDDs were very minor, mostly below 5%. On the other hand, the low-chlorination PCDD/Fs were more dominant in Group 2. The three indicators (PCP derivation, CNP derivation, and aerial deposition) that had seemed to be an origin of PCDD/Fs were demonstrated as such by these results. The congeners selected in these indicators were as follows (Sakurai et al. 1998): OCDD/F, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,8,9-HpCDF, 1,2,3,4,7,8,9-HpCDF, and 1,2,4,6,8,9-

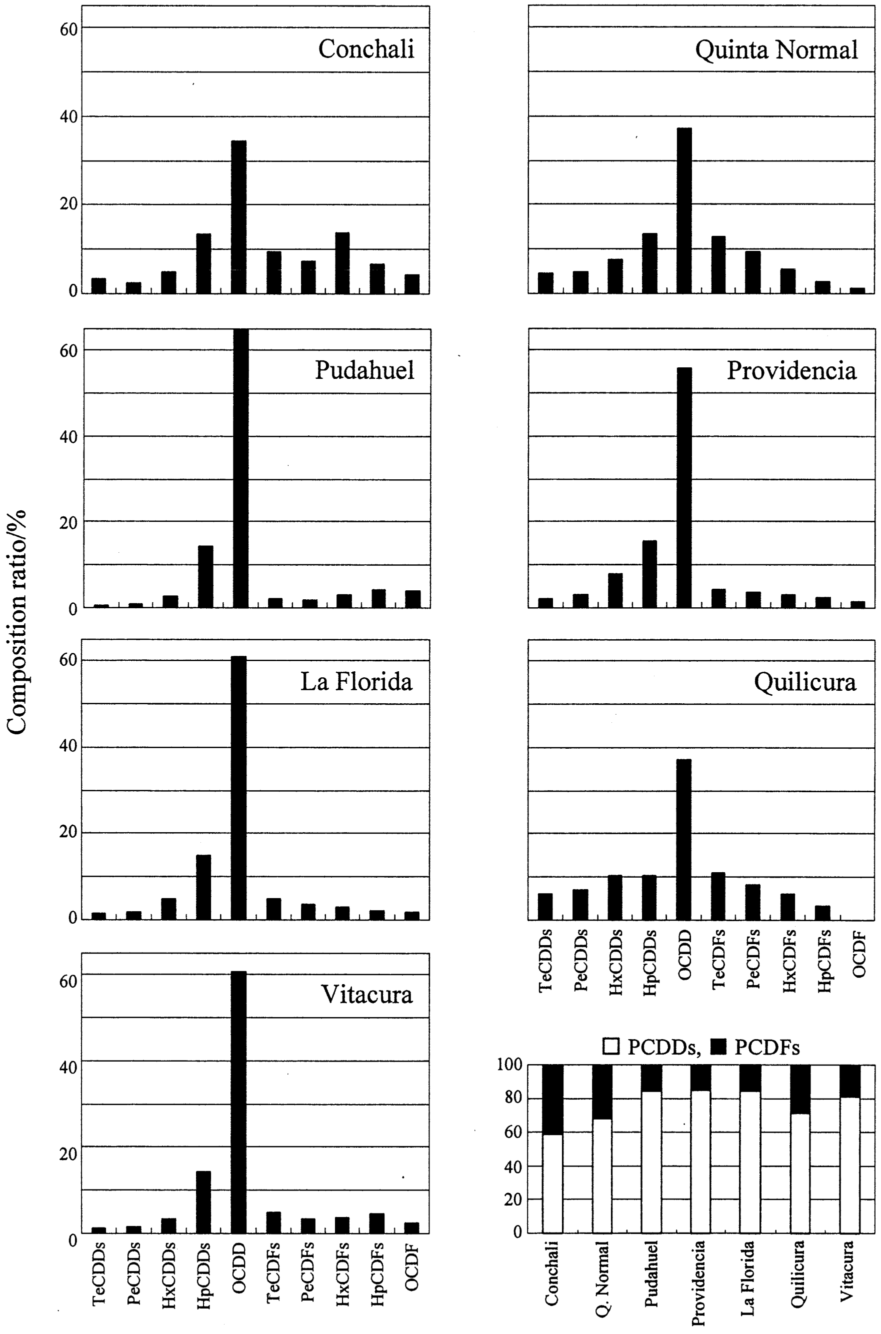

Figure 2. Relative composition ratio of homologues to the total PCDD/Fs.

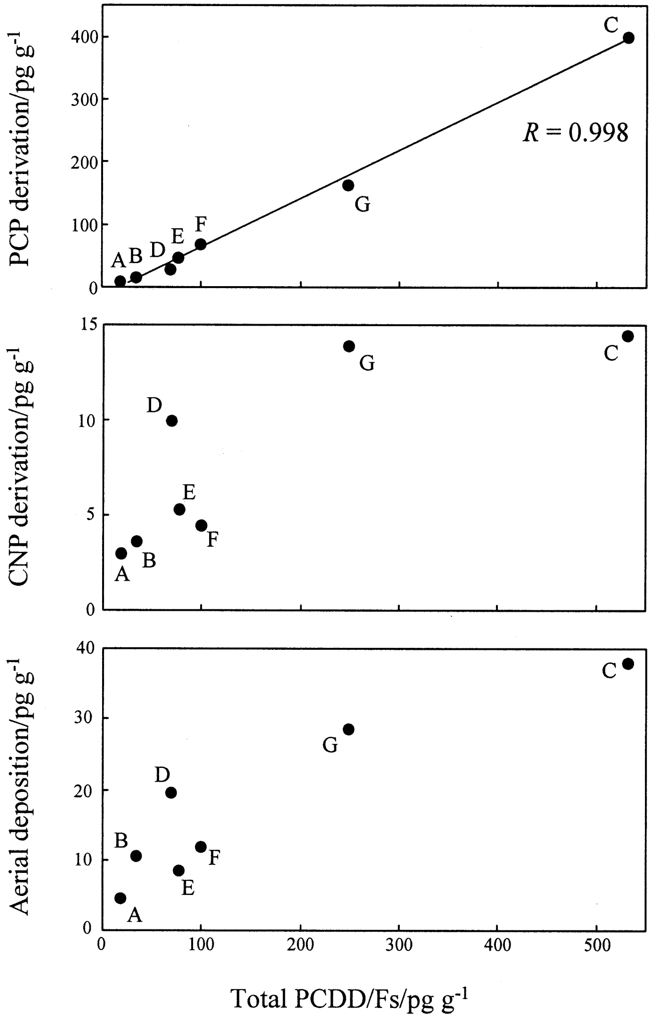

Figure 3. Correlation diagram between three indicators and the total PCDD/Fs. A, Quilicura; B, Conchali; C, Pudahuel; D, Quinta Normal; E, Providencia; F, Vitacura; G, La Florida.

HxCDF were contributors of PCP-derivation; CNP-derived congeners consisted of several tetra- and penta-chlorinated congeners containing 2,4,6,8-TeCDF, 1,3,6,8-TeCDD, and 1,3,7,9-TeCDD; the sum of TeCDFs, PeCDFs, and HxCDFs corresponded to the aerial deposition of low-chlorination PCDD/Fs having higher vapor pressures.

Figure 3 indicates that the PCP-derived PCDD/Fs had the highest correlation coefficient (*R* = 0.998) to the total PCDD/Fs among the three indicators. Group 1 consisted of relatively high contribution ratios (59–75%) of the PCP-derived PCDD/Fs. The relative contribution ratios of PCP derivation in Group 2 (41–46%) were smaller than those of PCP derivation in Group 1. The CNP-derived PCDD/Fs contributed 3–16% to the total PCDD/Fs; therefore, the impact from CNP was independent of at least one major factor. The relative contribution ratios of aerial deposition ranged from 7–31%, with a median contribution of 12%; however, the three areas located along the waysides of the Pan-American Highway had high contribution ratios: Quilicura (25%), Conchali (31%), and Quinta Normal (28%). PCP profiles are generally characterized by relatively high concentrations of PCDFs. The ratio of total PCDDs to total PCDFs (D/F ratio) ranged from 1–10 according to the study by Hagenmaier and Brunner (1987); moreover, 1,2,3,6,7,8-HxCDD is usually present as the dominant congener among the 2,3,7,8-chlorinated HxCDDs in PCP (Hagenmaier and Brunner 1987; Gifford et al. 1996). This agrees with the results of the present study; the ratio ranged from 1.4-5.5 with a median value of 4.2 (Table 1). 1,2,3,6,7,8-HxCDD exhibited dominance at all locations except Conchali and Quilicura; the concentration (0.36 pg g^{-1}) of 1,2,3,6,7,8-HxCDD at Quinta Normal was slightly higher than that of 1,2,3,7,8,9-HxCDD (0.29 pg g^{-1}).

It is reported that a typical worldwide deposition pattern of homologues at background levels provides the highest dominance of OCDD (Green et al. 2001; Brzuzy and Hites 1996). The soils in Santiago maintained the characteristics of global deposition in the background region; however, the soils were allowed to absorb the impact of PCP. The impact in Group 1 was more notable than that in Group 2. Forestry has long been prosperous just outside of the city; in the past, both wood preservatives and a herbicide distributed large amounts of PCP. These facts led us to conclude that the accumulation of PCP impurities in the surface soils has been continued until now. Since Pudahuel is close to the airport, it may have been exposed frequently to PCP used as a herbicide. The contribution of the aerial deposition was especially high in Group 2. The homologue patterns of Group 2 differed from those of typical incineration emissions; (Brzuzy and Hites 1996) however, the patterns seemed to be due at least to combustion. Group 2 (Quilicura, Conchali, and Quinta Normal) faces the Pan-American Highway; therefore, we considered that the flux of particles from vehicle exhaust influenced the soils in the three locations. In fact, the homologue pattern from gasoline cars, as reported by Miyabara et al. (1999), was similar to our data except for OCDD, whose relative contribution was diminished by the higher concentrations of PCDFs and low-chlorination PCDDs.

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