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Dioxins and furans in the atmosphere of São Paulo City, Brazil

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Abstract

Air samples were collected simultaneously at three urban sites in São Paulo City, Brazil, in winter, spring, summer and fall (in 2000 and 2001). Andersen PUF samplers were used for gas and particles sequential sampling. Samples were analyzed using HRGC/HRMS according to US EPA Method 8290. The greater metropolitan area of São Paulo is the largest industrialized region of Latin America and has a highly polluted atmosphere. Concentrations of dioxins and furans, which are well-known toxic chemicals, ranged from 1.14 $\mathrm{pg\,m^{-3}}$ to 13.8 $\mathrm{pg\,m^{-3}}$ (0.047 $\mathrm{pg\,I\text{-}TEQ\,m^{-3}}$ to 0.751 $\mathrm{pg\,I\text{-}TEQ\,m^{-3}}$). Principal component analysis showed that all the variables are highly correlated with one another except the 2,3,7,8-TCDD one. This is consistent with the similar concentration profiles observed for the tetra, penta, hexa, hepta and octa-homologous groups of the three sampling sites studied. At all sites, the most abundant compounds were the hepta and octa congeners. The 2,3,4,7,8-PeCDF accounted for 37–46% of the total toxicity and the 2,3,7,8-TCDD accounted for 7–16%. Highest mass concentrations of PCDD/Fs were found in the site where there is influence of industrial activities and heavy vehicular traffic fueled by gasohol, diesel, and ethanol.

Keywords: Urban air pollution; PCDD; PCDF; São Paulo City; Principal component analysis

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), commonly known as dioxins and furans are of non-natural origin and extremely persistent in the environment. Among 2,3,7,8 substituted toxic congeners, the 2,3,7,8-TCDD is the congener of highest toxicological significance. They have been detected in sediment, air, water, animals and plants. These pollutants are primarily emitted to the atmosphere from combustion processes. The presence of a chlorine donor in combustion seems to be the major source of their release. High levels are emitted from incineration of municipal, clinical and industrial wastes as well as in chlorine production, metal smelters, paper and pulp industries, petroleum refining processes, vehicle emissions, accidental fires, and combustion of

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biomass and biogenic fuels (De Assunção and Pesquero, 1999; Kouimtzis et al., 2002).

Urban measurements of the atmospheric PCDD/Fs in several cities have been reported recently (Mandalakis et al., 2001; Sin et al., 2002; Chang et al., 2003), but only few measurements have been carried out in São Paulo, Brazil (CETESB, 1996). To evaluate the chemical profile from a megacity with serious air pollution problems, dioxins and furans were analyzed on atmospheric particulate matter and gaseous air collected from a major South American city São Paulo, Brazil, whose population of ~16.3 million is exposed primarily to industrial and motor vehicle emissions. The urban area of São Paulo City has an unconventional mixture of vehicle types, in which a variety of fuel blends, including oxygenated ones, are used (Montero et al., 2001). For example, approximately 62% of the motor vehicles are fueled with gasohol (gasoline + 20–22% anhydrous ethanol), 8% with diesel and 30% with ethanol.

The goal of this article is to report the atmospheric PCDD/Fs pattern in highly polluted urban areas of São Paulo City. Measurements of these toxic pollutants were carried out in winter, fall, spring and summer. Occurrence of PCDD/Fs levels at a residential site located near a municipal incinerator, in downtown and in an area with mixed commercial and industrial activities is presented. PCDD/Fs levels and meteorological conditions, as well as their possible emission sources are discussed.

2. Experimental section

2.1. Sampling

In this work, three urban sites in São Paulo City were chosen on the basis of local differences in the type, distribution, and proximity of emission sources, as well as differences in wind direction frequencies.

The sampling site 1, very close to downtown, located in the park of the School of Public Health of the University of São Paulo, is near the confluence of two main streets with intense vehicular traffic where circulate many buses fueled with diesel and cars fueled with gasohol or ethanol. The area receives a significant contribution of vehicular emissions and there is no industrial activity in its immediate vicinity. Air quality data provided by monitoring station of the State Environmental Protection Agency (CETESB) located in the central area of the city (downtown) are very similar to those of site 1 and, for this reason, site 1 was assumed in this study as a downtown area (CETESB, 2002).

The sampling site 2 is a residential area, which can be considered potentially impacted by many different types of sources. The site is ~1 km NW of a health service waste incinerator used to process approximately 90 metric tons of waste per day without air pollution control system. During this study, unexpectedly, real work capacity of this incinerator was gradually diminished.

The sampling site 3, located in an area with industrial and commercial activities, receives impact from local emissions from a glass industry, non-ferrous foundry and rubber products plant as well as motor vehicular exhaust emissions from diesel heavy-duty vehicles and ethanol- and gasohol-light-duty vehicles. The sampling local is ~50 m from a major highway that has a constant dense vehicular traffic. Site 3 is distant 6.1 km NNW from site 1.

Sampling of dioxins and furans was performed according to US EPA Method TO-9A (US EPA, 1999) using Andersen GPS1 Samplers equipped with quartz micro fiber filters for particle collection and a polyurethane foam plug for gas retention. Simultaneous 24 h-samples were collected at three sampling sites in November 29, 2000, February 21, May 30 and August 28, 2001 (total number of samples taken = 12). Samplers were calibrated before and after sampling.

At site 2, inhalable particulate matter was collected using a wedding PM_{10} critical flow high volume sampler with glass–fiber filter. PM_{10} 24 h-samples were collected at a flow rate from 1.17 to 1.19 $m^3 min^{-1}$ in parallel with dioxins and furans sampling. The sampler was calibrated using an U-tube water manometer before and after sampling. The filters were weighed before and after sampling in a Mettler Toledo AG-204 analytical balance with a precision of 0.1 mg. Before weighting, filters were placed in a desiccator for 24 h for moisture removal. For the correlation study, PM_{10} data used for sites 1 and 3 were provided by CETESB monitoring stations located near sites 1 and 3.

2.2. Extraction and gas chromatography/mass spectrometry analysis

Prior sampling, filters and PUF cartridges were cleaned and spiked with 4 ng of $^{13}C_6$ 1,2,3,7,8,9-HxCDD (field surrogate). After sampling, samples and blanks were placed in an original glass container and wrapped with aluminum foil. The PCDD/Fs analyses were carried out in a laboratory (Analytical Solutions Laboratory) in Rio de Janeiro City, Brazil, according to the US EPA Method 8290 (US EPA, 1994). Samples were transported in a refrigerator with dry ice. Each filter and the corresponding PUF were combined and spiked with twelve $^{13}C_6$PCDD/F internal standards, and then Soxhlet extracted with dichloromethane for 16 h. Each extract was then cleaned-up in a sulfuric acid–silica gel column using hexane as eluent and a Florisil column using dichloromethane as eluent. The extracts were concentrated to almost dryness and $^{13}C_6$-1,2,3,4-TCDD was added in 15 µl of nonane immediately before analysis.

Extracts were analyzed in a Hewlett Packard 6890 model high-resolution gas chromatograph/VG Autospec Ultima mass spectrometer (HRGC/HRMS) equipped with a Hewlett Packard 7673 auto sampler operating with electron impact ionization energy of 30 eV at a mass resolution of 5000. The GC was fitted with a J&W DB-5 capillary column (30 m × 0.25 mm id. fused silica column coated with 0.25 μm film thickness). The GC oven temperature program used was: 70 °C, 4 min, 15 °C min^{-1} to 220 °C, 1.5 °C min^{-1} to 240 °C, 2 min, 4 °C min^{-1} to 310 °C, 10 min. Helium was used as the gas carrier, at a head pressure of 10 psi at constant flow.

The PCDD/Fs quantification was done using twelve $^{13}C_6$-labeled internal standards. The labeled PCDD/F internal standards and their response factors were used for quantification of unlabeled PCDD/Fs of homologous groups. Recoveries of $^{13}C_6$-labeled internal standards, determined against external standards, ranged from 48% to 121%. The recovery of the $^{13}C_6$-1,2,3,7,8,9-HxCDD, spiked onto the filter prior to ambient air sampling in order to determine the collection efficiency, ranged from 77% to 132%. The detection limits of the PCDD/Fs congeners, calculated by signal-to-noise ratio, ranged from 0.006 to 0.009 pg m^{-3}.

2.3. Statistical data treatment

The statistical calculations were carried out using the Statistica commercial microcomputer package (Statosoft, Inc., Statistica for Windows 6.0, 2300 East 14th St. Tulsa, OK, USA).

2.4. Meteorological conditions

Meteorological parameters (Table 1) revealed air dispersion and stagnation conditions in some sampling days. On May 30, 2001 (fall), there was no precipitation and, during 50% of the day, no winds. Although local air circulation in the region occurs frequently due to winds from both south-southeast (SSE) and north-northeast (NNE) directions, mainly associated with Atlantic Ocean breeze circulation, SSE wind direction was predominant for 50% of August 28, 2001 (winter) and NNE wind direction was predominant for 37.5% of November 29, 2000 (summer). On August 28, 2001(winter), there was rain during the sampling period.

3. Results and discussion

3.1. Dioxins and furans levels

By examining mass concentrations of the seventeen PCDD/Fs congeners in Table 1 it is possible to observe that the highest total concentrations of these air pollutants were found at site 3 ranged from 1.58 to 13.8 pg m^{-3}. The concentration ranges of PCDD/Fs were 1.41–4.08 pg m^{-3} at site 2 and 1.14–4.01 pg m^{-3} at site 1. The average concentrations at site 1 were about three times lower than those at site 3 and 10% lower at site 2. Among PCDD/Fs, the most abundant compounds were the hepta and octa congeners. Some results of dioxin congeners concentrations were found at very low concentrations whose values were below the detection limits but they are included in Table 1 using 1/2 value of detection limit. It is important to mention here that few measurements of dioxins and furans were done in this work because of the high cost of the PCDD/F analyses.

For all sites, PCDD/Fs levels in fall (May) sampling were two to ten times higher than those of other season. The meteorological parameters presented in Table 1 show that episodes of pollutant stagnation occurred in this sampling period. The second (WNW) wind direction with 20.8% predominance probably influenced PCDD/Fs levels at site 3, since air masses come from highway (see Section 2.1.) and arrive to sampling site 3. Local industrial activities and heavy vehicular traffic from a nearby highway are the main emission sources at site 3.

In winter (August) sampling, differently to our usual winter time, pollutant dispersion conditions and a local weak rainfall over the whole sampling period were recorded (Table 1). Lower levels of PCDD/Fs were found when compared to those in fall sampling. As wet deposition is the major removal mechanism for most suspended organic compounds, rainfall lead to lower environmental levels of PCDD/Fs (Chang et al., 2003). As shown in Table 1, relatively low PM_{10} concentrations were also observed in this sampling period.

The PCDD/Fs contribution of the incinerator emissions at residential area, site 2, was not observed because mostly of the wind directions were not favorable in the sampling periods and the work capacity of the incinerator was reduced during the study.

Considering homologous groups, it is possible to observe similar profiles (Fig. 1) for all three sites studied. Generally, an increase in the PCDDs concentrations was observed as chlorination level increased ($Cl_4 < Cl_5 < Cl_6 < Cl_7 < Cl_8$). The same was found for PCDFs compounds, except the octa one whose concentrations were lower ($Cl_4 < Cl_5 < Cl_6 < Cl_7 > Cl_8$). It is interesting to note that the homologous groups profile found in this study is quite similar to that of urban air particulate from Standard Reference Material (SRM-1649) of National Institute Standards and Technology (NIST) (Bacher et al., 1992).

3.2. Concentrations of PCDD/Fs in toxicity equivalency

The $\sum$TEQ values of the seventeen congeners of PCDD/Fs calculated using I-TEF (International Toxicity Equivalency Factor) are given in Table 1. The results

Table 1
Summary of PCDD/Fs sampling results of the three sites

PCDD/Fs (pg m^{-3})	November 29, 2000			February 21, 2001			May 30, 2001			August 28, 2001		
	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3
2,3,7,8-TCDD	0.003[a]	0.004[a]	0.004[a]	0.069	0.012	0.026	0.017	0.019	0.037	0.039	0.003[a]	0.049
1,2,3,7,8-PeCDD	0.003[a]	0.004[a]	0.004[a]	0.003[a]	0.004[a]	0.004[a]	0.021	0.023	0.069	0.003[a]	0.004[a]	0.004[a]
1,2,3,6,7,8-HxCDD	0.004[a]	0.004[a]	0.005[a]	0.017	0.027	0.005[a]	0.052	0.045	0.161	0.039	0.028	0.043
1,2,3,4,7,8-HxCDD	0.004[a]	0.004[a]	0.005[a]	0.020	0.029	0.005[a]	0.027	0.024	0.072	0.004[a]	0.004[a]	0.019
1,2,3,7,8,9-HxCDD	0.004[a]	0.004[a]	0.005[a]	0.022	0.025	0.034	0.045	0.039	0.115	0.042	0.030	0.019
1,2,3,4,6,7,8-HpCDD	0.197	0.266	0.234	0.194	0.241	0.396	0.619	0.473	1.58	0.246	0.185	0.260
OCDD	0.590	0.567	0.506	0.004[a]	0.501	0.762	1.49	1.11	3.39	0.496	0.392	0.640
2,3,7,8-TCDF	0.027	0.053	0.019	0.049	0.068	0.110	0.089	0.116	0.258	0.029	0.041	0.029
1,2,3,7,8-PeCDF	0.040	0.070	0.052	0.032	0.047	0.055	0.042	0.063	0.143	0.029	0.039	0.040
2,3,4,7,8-PeCDF	0.085	0.106	0.049	0.049	0.074	0.110	0.176	0.213	0.774	0.054	0.044	0.063
1,2,3,4,7,8-HxCDF	0.062	0.069	0.076	0.052	0.074	0.113	0.104	0.152	0.459	0.047	0.064	0.069
1,2,3,6,7,8-HxCDF	0.056	0.077	0.062	0.037	0.062	0.091	0.069	0.092	0.315	0.039	0.052	0.066
2,3,4,6,7,8-HxCDF	0.071	0.119	0.091	0.052	0.077	0.122	0.131	0.145	0.602	0.056	0.072	0.101
1,2,3,7,8,9-HxCDF	0.004	0.004	0.005	0.021	0.027	0.043	0.042	0.055	0.192	0.017	0.023	0.029
1,2,3,4,6,7,8-HpCDF	0.225	0.371	0.242	0.221	0.324	0.518	0.566	0.706	2.86	0.147	0.243	0.314
1,2,3,4,7,8,9-HpCDF	0.004	0.053	0.030	0.032	0.047	0.005	0.077	0.121	0.315	0.024	0.033	0.043
OCDF	0.184	0.306	0.195	0.270	0.004	0.335	0.446	0.683	2.50	0.088	0.149	0.182
$\sum$PCDD/Fs (pg m^{-3})	1.56	2.08	1.58	1.14	1.64	2.73	4.01	4.08	13.8	1.40	1.41	1.97
$\sum$TEQ (pg I-TEQ m^{-3})	0.047	0.063	0.047	0.066	0.097	0.148	0.187	0.223	0.751	0.101	0.066	0.129
PM 10 (μg m^{-3})	39.8[b]	25.1	61.9[b]	60.2[b]	29.3	51.3[b]	35.5[b]	39.5	82.1[b]	–	19.1	28.8[b]
Meteorological parameters												
Precipitation (mm)	13			0			0			5		
Average temperature (°C)	24.4			23.5			19.1			15.1		
Winds	NNE; 37.5%; 5.4 km h^{-1}[c] WNW; 29.2%; 12.4 km h^{-1}[d]			ESE; 37.5%; 5.1 km h^{-1}[c] E; 29.5%; 3.7 km h^{-1}[d]			Calm; 37.5%; 0.0 km h^{-1}[c] WNW; 20.8%; 7.4 km h^{-1}[d]			SSE; 50%; 5.3 km h^{-1}[c] ESE; 25%; 4.5 km h^{-1}[d]		

[a] Values below the detection limits (DL) are included using 1/2 DL.
[b] Data from CETESB.
[c] First wind direction.
[d] Second wind direction.

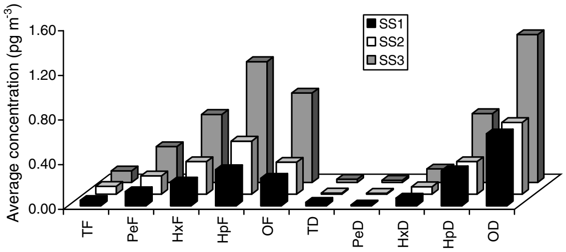

Fig. 1. Comparison of the PCCD/Fs homologues groups in the three sites studied.

show a relatively large variability in the PCDD/Fs concentrations at each sampling site. At site 1, concentrations ranged from 0.047 to 0.187 pg I-TEQ m^{-3}, at site 2 from 0.063 to 0.223 pg I-TEQ m^{-3} and at site 3 from 0.047 to 0.751 pg I-TEQ m^{-3}. The highest concentrations in I-TEQ were observed in May (fall) sampling while the lowest concentrations were observed in November (spring) sampling. A comparison between PCDD/Fs concentrations in mass and in I-TEQ is shown in Fig. 2 and similar profiles are observed.

Compared to other cities over the world (Table 2), PCDD/Fs concentrations observed at both sites 1 and 2 (0.047–0.223 pg I-TEQ m^{-3}) were higher than those observed in some urban cities of Europe, such as, Hessen (0.078–0.146 pg I-TEQ m^{-3}), Rome (0.048–0.277 pg I-TEQ m^{-3}), Rotterdam (0.005–0.140 pg I-TEQ m^{-3}), Stockholm (0.0026–0.024 pg I-TEQ m^{-3}), Athens (0.042–0.073 pg I-TEQ m^{-3}) and London (0.067–0.204 pg I-TEQ m^{-3}). On the other hand, higher PCDD/Fs concentrations were found at site 3 (0.047–0.751 pg I-TEQ m^{-3}) compared with other urban cities, such as Taipei (0.056–0.348 pg I-TEQ m^{-3}), Hong-Kong (0.018–0.429 pg I-TEQ m^{-3}), Manchester (0.086–0.476 and 0.026–0.220 pg I-TEQ m^{-3}), Phoenix (0.092–0.448 pg I-TEQ m^{-3}), Porto (0.0244–0.547 pg I-TEQ m^{-3}) and Catalonia (0.013–0.618 pg I-TEQ m^{-3}). PCDD/Fs concentrations at four distinct urban sites in United Kingdom (nd–1.80 pg I-TEQ m^{-3}), San Bernardino, USA (0.092–2.228 pg I-TEQ m^{-3}) and Krakow (0.950–11.95 pg I-TEQ m^{-3}) surpassed those of site 3.

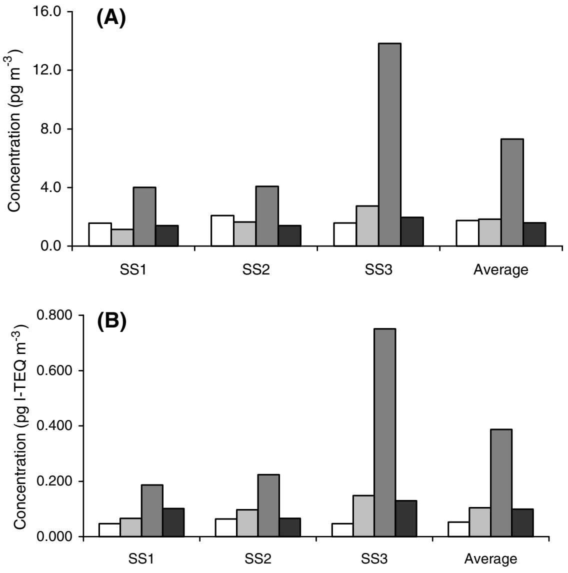

Fig. 2. Total of 17 PCDD/Fs in the three sites: concentrations in mass (A) and in I-TEQ (B).

The contribution, in percentage, of the individual 2,3,7,8-congeners in relation to the total I-TEQ concentrations of three sampling sites is shown in Fig. 3. The 2,3,4,7,8-PeCDF accounted for 37–46% of the total toxicity and the 2,3,7,8-TCDD accounted for 7–16%. Therefore, more than 50% of the total toxicity was accounted for these two congeners. The OCDD and OCDFF congeners contribute with <1% to the $\sum$TEQ. Results of 26 worldwide urban measurements performed by several authors (Lohmann and Jones, 1998) show that PCDFs contributed typically with more than 50% to the $\sum$TEQ.

3.3. PM_{10} versus PCDD/Fs levels

Inhalable particulate matter data, shown in Table 1, indicate that air quality in the sampling time periods at three sites ranged from regular to good. All samples presented PM_{10} concentrations below the Brazilian 24 h guideline value (150 μg m^{-3}), and only 36% of the values are above the Brazilian annual air quality standard (50 μg m^{-3}). The highest value was found at site 3 (82.1 μg m^{-3}) and the lowest value was observed at site 2 (19.1 μg m^{-3}). The PM_{10} and $\sum$PCDD/Fs concentrations are strongly correlated at site 2 ($r^2 = 0.81$), which may indicate that they arise from similar sources and/or sinks (Chang et al., 2003). On the other hand, relatively weak correlations were observed at sites 1 and 3 ($r^2 = 0.53$ and 0.41, respectively), which suggest that PM_{10} and $\sum$PCDD/Fs are from different emission sources.

3.4. Multivariate statistical evaluation

Although it was possible to study only three sampling sites on four different days the large number of compound concentrations measured makes this data especially suitable for multivariate statistical analysis, specifically principal component and hierarchical cluster analyses.

A principal component score graph and hierarchical cluster dendrogram, not shown in this report, involving data for all sampling sites and dates shows a clear discrimination between the May results of site 3 and those

Table 2
Comparison of PCDD/F levels with other urban studies

Site	Year	Range (pg I-TEQ m^{-3})	Reference
São Paulo^{1} (Brazil)	2000–2001	0.047^{a}–0.223^{c}	This study
São Paulo^{2} (Brazil)	2000–2001	0.047^{a,b}–0.751^{a,b}	This study
São Paulo (Brazil)	1995	0.086–0.169^{c}	CETESB, 1996
Cubatão (Brazil)	1995	0.038–0.048	CETESB, 1996
Araraquara (Brazil)	1995	0.046–0.267^{d}	CETESB, 1996
Athens (Greece)	2000	0.042–0.073	Mandalakis et al., 2001
Hong-Kong (China)	2000	0.018–0.429	Sin et al., 2002
Taipei (Taiwan)	1999–2000	0.056^{c}–0.348^{c}	Chang et al., 2003
Catalonia (Spain)	1994–2000	0.013^{b}–0.954^{c}	Abad et al., 2002
Thessaloniki (Greece)	1999	***0.004–***0.119	Kouimtzis et al., 2002
Oporto (Portugal)	1998–1999	**0.0244–**0.547	Coutinho et al., 2001
Manchester (United Kingdom)	1998	**0.026^{a,b}–**0.220^{a,b}	Lohmann et al., 2000
Lancaster (United Kingdom)	1997	0.0071–0.0176	Lohmann et al., 1999
London (United Kingdom)	1991–1995	0.067–0.204	Coleman et al., 1997
Manchester (United Kingdom)	1991–1995	0.086–0.467	Coleman et al., 1997
4 urban sites (United Kingdom)	1991–1993	Nd–1.80	Duarte-Davidson et al., 1994
Krakow (Poland)	1995	*0.950–*11.95^{a}	Grochowalski et al., 1995
Phoenix (USA)	1994	0.092^{a}–0.448^{a}	Hunt et al., 1997
Flanders (Belgium)	1992	0.0175–0.379	Wevers et al., 1993
Urban (Japan)	1992	0.300–0.940	Kurokawa et al., 1996
Rome (Italy)	1990–1991	0.048–0.277	Turrio-Baldassarri et al., 1994
Rotterdam (Netherlands)	1991	0.005^{c}–0.140^{c}	Bolt and de Jong, 1993
Hessen (Germany)	1990	0.078^{a}–0.146^{b}	König et al., 1993
Berlin (Germany)	1986–1987	0.020–0.400	Christman et al., 1989
Stockholm (Sweden)	1989	0.0026–0.024	Broman et al., 1991
San Bernardino (USA)	1987–1989	0.192–2.228	Hunt and Maisel, 1992

1 = Sites 1 and 2, 2 = Site 3. a = Urban/motor vehicular traffic, b = Urban/industrial, c = Urban/near incinerator, d = Urban/cane burning episodes.
*Gas phase collect on active carbon, **Results in pg WHO-TE m^{-3}, ***Only particulate phase, Nd—non detected.

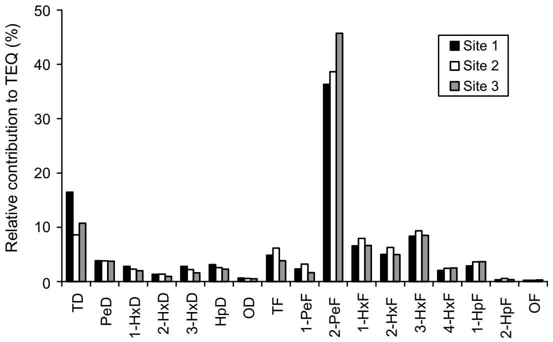

Fig. 3. Contribution (%) of the individual 2,3,7,8-congeners in relation to the total I-TEQ concentrations of three sites. Axis *x* legend: TD = 2,3,7,8-TCDD; PeD = 1,2,3,7,8-PeCDD; 1-HxD = 1,2,3,6,7,8-HxCDD; 2-HxD = 1,2,3,4,7,8-HxCDD; 3-HxD = 1,2,3,7,8,9-HxCDD; HpD = 1,2,3,4,6,7,8-HpCDD; OD = OCDD; TF = 2,3,7,8-TCDF; 1-PeF = 1,2,3,7,8-PeCDF; 2-PeF = 2,3,4,7,8-PeCDF; 1-HxF = 1,2,3,4,7,8-HxCDF; 2-HxF = 1,2,3,6,7,8-HxCDF; 3-HxF = 2,3,4,6,7,8-HxCDF; 4-HxF = 1,2,3,7,8,9-HxCDF; 1-HpF = 1,2,3,4,6,7,8-HpCDF; 2-HpF = 1,2,3,4,7,8,9-HpCDF; OF = OCDF.

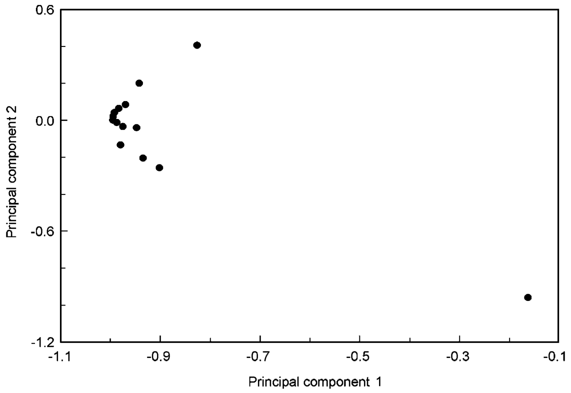

Fig. 4. Loading graph of the first two principal components of the complete data set.

of the other sites and dates. This is expected since the largest concentration found for each compound was at this site and on this date. Fig. 4 contains a graph of the loadings of the first two principal components for the complete data set. A large cluster of points can be observed for all the variables but 2,3,7,8-TCDD that is represented by a point in the lower right hand corner of the graph. This indicates that all these variables, except 2,3,7,8-TCDD, are highly correlated. The largest correlation coefficient involving 2,3,7,8-TCDD with the other variables is 0.32 and is not significant at the 95% confidence level. On the other hand, all possible correlations involving the other variables are significant at this level with values ranging from 0.59 to 1.00.

Principal component and hierarchical cluster analyses were also carried out on two reduced data sets, one without the May site 3 sample and one set with only data from sites 1 and 2. These results also indicate the existence of strong correlations between the variables in the principal component cluster.

The correlation coefficients (not shown) for the complete data set range from 0.94 to 1.00. They are somewhat lower for the data set without the May site 3 result, ranging from 0.80 to 0.96. Somewhat higher correlation coefficients, between 0.82 and 0.97, exist for the data from sites1 and 2. In summary, the high correlation coefficients are quite stable even though there is only a small number sampling days and sites.

An example of the correlation between these variables is given by the graphs in Fig. 5. Both plot the 1,2,3,6,7,8-HxCDF concentration against the 2,3,4,6,7,8-HxCDF one. The small inserted graph in the figure shows the total concentration ranges measured for these compounds. The point on the regression line in the upper right hand corner of the small graph corresponds to the May site 3 sample having concentrations that are much larger than those of the other samples collected. The large graph in Fig. 5 corresponds to the region within the dotted lines of the smaller graph and has concentration ranges of 0.04–0.16 pg m^{-1} and 0.03–0.10 pg m^{-1} for 2,3,4,6,7,8-HxCDF and 1,2,3,6, 7,8-HxCDF, respectively. Even though the May site 3 concentrations have considerable leverage on the correlation coefficient, the regression equations for the data with and without this point are almost the same with slopes of 0.50 and 0.53. This helps us understand why the correlation coefficients do not show large variations for the three data sets treated.

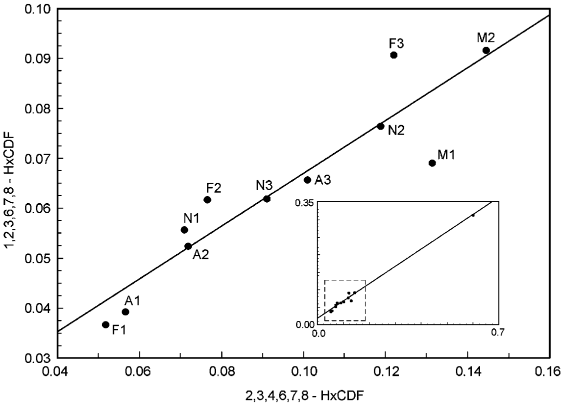

Fig. 5. Graphs of the 1,2,3,6,7,8-HxCDF concentration against the 2,3,4,6,7,8-HxCDF concentration: the small graph contains points for the complete data set and the large graph does not contain the point corresponding to the May site 3 measurements.

4. Conclusions

Measurements of PCDD/Fs showed similarities in the distribution of individual congeners in the three urban sites located in São Paulo City, Brazil. Principal component analysis showed that all the variables are highly correlated with one another except the 2,3,7,8-TCDD one. This is consistent with the similar concentration profiles observed for the tetra, penta, hexa, hepta and octa-homologous groups of the three sampling sites studied.

Highest mass concentrations of PCDD/Fs were found in the site where there is influence of industrial activities and heavy vehicular traffic fueled by gasohol, diesel, and ethanol. At this site, contribution of different emission sources may be evidenced by multivariate statistical analysis. At other two sites, residential area and downtown, vehicular traffic seems to be the main source. The PCDD/Fs contribution of the incinerator emissions at residential area was not observed because unfavorable meteorological conditions and reduced work capacity of the incinerator. Similar PM_{10} and PCDD/Fs sources and/or sinks were proposed in the residential area.

Although a small number of measurements were done in this work, results show that toxic dioxins and furans are present in air at significant concentrations. Occurrence of these toxic pollutants in the urban atmosphere of São Paulo City needs attention. Certainly, further investigation is still necessary for a better understanding of the emission sources of these pollutants in air. A long-term monitoring is fundamental to elucidate the relationship between emissions of dioxins and furans into the atmosphere from primary anthropogenic sources, such as diesel, gasoline and alcohol engines.

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