DIOXINS AND FURANS IN SÃO PAULO CITY – BRAZIL: 2006 LEVELS, COMPARISON WITH 2000-2001 LEVELS, AND DISCUSSION OF POTENTIAL EMISSION SOURCES

João V de Assunção[1], Célia R Pesquero[1], Lilian R.F. Carvalho[2], Raimundo P Nóbrega[1], Rui de Abrantes[3] and Rejiane de A Sant'ana[1]

[1]Department of Environmental Health, School of Public Health, University of São Paulo, Av. Dr. Arnaldo, 715, São Paulo – 01246.904, Brazil
[2] Chemistry Institute, University of São Paulo, Brazil
[3]Vehicular Emission Laboratory, Cetesb, São Paulo, Brazil

Introduction

Vehicles are the main contributors to air pollution in the City of São Paulo, Brazil according to CETESB air quality report[1], typical for big urban centers around the world. Contributions from other sources, like industries and the diffuse burning of coal and wood in typical restaurants - barbecue houses, pizzerias and bakeries etc. - also exist. High levels of PCDD/Fs detected in one of the regions of São Paulo in 2000/2001, by Assunção et al[2], the large number of vehicles in the area (6 million vehicles and 1.8 persons per car), as well as the few measurements of PCDD/Fs levels in São Paulo, show the importance of this study, part of bigger one that has the objective of evaluating air levels and possible emission sources of toxic pollutants in urban areas of the State of São Paulo.

Material and Methods

The air samples were collected in the city of São Paulo, in three regions, simultaneously, a central region exposed mainly to vehicular emissions named as **Central**, a commercial/residential region exposed to vehicular emissions, city airport emissions, and commercial/industrial named as **Congonhas** and a region exposed to vehicular and commercial/industrial emissions named as **Lapa**. For the sample collection, we adopted TO-9A method of US.EPA[3], with the use of PS 1 PUF samplers from Andersen Instruments Inc. (USA), assembled with 10.16 cm diameter quartz micro fiber filter, followed by a 6 cm diameter and 7.62 cm length polyurethane foam (PUF), also from Andersen Instruments. In each selected site 24-hour sampling had been carried out for PCDD/Fs analysis. Four samples were collected in each place, one day per month, from May 2006 to August 2006 that, together with a Blank per month totaled 16 samples. Tuesday was the prevalent sampling day except in the August samplings which occurred on Friday due to operational problems; no sampling was performed on holidays or weekends. The chemical analysis for PCDD/Fs had been carried out by a certified laboratory in the city of Rio de Janeiro, based on US.EPA method 8290[4] by HRGC/HRMS.

Results and Discussion

Table 1 presents the results of the concentration of the 17 PCDD/Fs analyzed. In absolute values the general average (Σ17 PCDD/F) of 2,581fg.m^{-3} with standard deviation of 1,926 fg.m^{-3}. Lapa was the site that presented the highest average - 3,124 fg.m^{-3} - with concentration values varying from 661 fg.m^{-3} to 6,633 fg.m^{-3} , the lower value in May and the higher value in June. The second highest average (2,490 fg.m^{-3}) was detected in the Central site, with concentrations varying from 575 fg.m^{-3} to 5,417 fg.m^{-3}. Congonhas was the site that presented the lowest average (2,129 fg.m^{-3}), with values varying from 695 fg.m^{-3} to 3,900 fg.m^{-3}. Statistical analysis was done by using one way Anova method with unique factor, and it showed p-value higher than 0.05 showing that there are no differences in the averages of the sum of 17 PCDD/Fs absolute concentrations for the three sites; average concentration by sampling date differ one from another ($p<0.05$).

In relation to PCDD/Fs congeners, the hepta and octa congeners were the most abundant ones. In all samples collected in May some congeners were not detected - 2,3,7,8-TCDD; 1,2,3,7,8-PeCDD; 1,2,3,6,7,8-HxCDD; 1,2,3,4,7,8-HxCDD and 1,2,3,7,8,9-HxCDD. Identical fact had happened on one of the sampling dates in a previous study done by Assunção et al.[2] in 2000. Similar homologous group profiles were observed in the three sampling sites, as shown in Figure 1; an increase of concentration of PCDDs was observed with the increase of

chlorine atoms (Cl4< Cl5< Cl6< Cl7< Cl8). The same happened for PCDFs. The profiles of the homologue groups found in this study are similar to the one observed by Assunção et al.[2] in the 2000/2001 study.

The partition between solid and gaseous phases was not carried out in this study. Existing data in the literature has shown that this partition may vary from 13% to 76% for the most toxic dioxin (2,3,7,8-TCDD); for homologue groups with higher number of chlorine atoms, both for dioxins an furans, the solid phase accounts for most part of the mass, being that, for dioxins and furans with seven and eight chlorine atoms, the solid phase accounts for more than 90% of the mass, according to Lohmann and Jones[5].

In terms of equivalent toxicity (TEQ) the general average was 104.9 fg TEQ.m^{-3} with a standard deviation of 68.2 fg TEQ.m^{-3}. The results showed different ranges in concentration among sampling dates, as shown in Figure 2. PCDD/Fs concentrations in Congonhas had varied from 25.9 fg TEQ.m^{-3} to 176.3 fg TEQ.m^{-3}; at the Lapa sampling site the variation ranged from 21.4 fg TEQ.m^{-3} to 164.9 fg TEQ.m^{-3}; at the Central site the highest variation occurred, that is from 18.7 fg TEQ.m^{-3} to 224.6 fg TEQ.m^{-3}. The lowest concentration occurred in May (autumn) and the highest one occurred in July (winter). The general average in this study was 34.4% lower than the general average of the 2000-2001 study[2].

Statistical analysis done by using one way Anova method with unique factor, for the data in equivalent toxicity, showed that the averages do not differ in relation to sampling sites, as p-value was higher than 0.05. However, the same evaluation among sampling dates, showed again that their averages are different. The contribution of individual congeners to total TEQ, in the three sampling sites is shown in Figure 3. It can be observed that PCDFs were responsible for 63% to 81% of the total TEQ, being 2,3,4,7,8-PeCDF responsible for 26% to 38% of the total TEQ. Although OCDD/Fs were the most abundant congeners, they were responsible only for approximately 1% of the total TEQ.

The comparison of the results of this study with data from a study done in 1995-1996 by CETESB[6] in three cities in the State of São Paulo (São Paulo city, Cubatão and Araraquara) - including sampling days with and without pre-harvesting sugarcane burning in Araraquara - and with the data from Assunção et al. in the study done in the city of São Paulo in 2000-2001[2], excluding its highest value (751 fg TEQ.m^{-3}), showed that these results are in the same range of those ones.

Regarding air quality and meteorological conditions, according to data from the São Paulo Environmental Agency, air quality was classified as good and favorable meteorological conditions on May 9, regular and not favorable on June 20 and July 18, and in the boundary of good to regular air quality and favorable meteorological conditions on August 17. Comparison of PM_{10} data and PCDD/Fs results in each sampling site showed good correlation with the total concentration of PCDD/Fs in Lapa (r^2 = 0.77), regular correlation with the total concentration in the Central site (r^2=0.55) and no correlation in Congonhas (r^2=0.07), whichsuggests that PM_{10} and PCDD/Fs came from different emission sources in Congonhas and from similar emission sources both in Lapa and Central sites. Meteorological conditions seem to have played an important role on the results.

Conclusions

The average PCDD/Fs concentration in this study (104.9 fg TEQ.m^{-3}) was lower than the average of the 2000/2001 study (160 fg TEQ.m^{-3}), a decrease of 34.4%. Also, the highest concentration found in this study was much smaller than in the previous study (225 fg TEQ.m^{-3} against 751 fg TEQ.m^{-3}). The decrease can be attributed partially to the decrease in PM10 levels in the city of Sao Paulo in the same period, which was about 24%[7,1] due to enforcement and also to replacement of old vehicles, not equipped with catalyst converter, by vehicles with improved technology and or equipped with emission control devices, specially the Otto vehicles. Even so, the present concentrations still represents a condition that deserves attention and continuation of preventive and corrective actions. To locate and estimate contribution of important emission sources is still a challenge.

Vehicles are the most frequent air emission sources of urban areas, and in the case of Brazil, with a mix of fuels with significant differences in composition in relation to the developed world; ethanol from sugar-cane is used

intensively both as an additive to gasoline as well as a fuel itself , and no leaded-fuel is used anymore since the mid 1980's; eventually garbage and health-service waste burning could be considered emission sources in the city; moreover use of charcoal and wood as a fuel in restaurants, pizza houses and bakeries and, in the winter, wood burning domestic fireplaces, could be considered as potential sources of PCDD/Fs. A more important contribution could come from Otto vehicles not equipped with catalyst converter, still a common situation in Sao Paulo as it is known that these cars has a higher emission factor than those equipped with catalyst converter, according to UNEP's Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases[8]. Brazilian diesel-powered vehicles seem not to be an important source of PCDD/Fs emission according to measurements done by Nóbrega[9], although contribution of these emissions to the formation of PCDD/Fs in the atmosphere was not studied; emission from industry also should not be dismissed.

Acknowledgments
We want to express our gratitude to the Company of Environmental Sanitation Technology - CETESB, for the support given and to the Sao Paulo Foundation for Support to Research – FAPESP for providing the necessary financial support for this project (Grant 2004/02623-6).

References
1. Companhia de Tecnologia de Saneamento Ambiental (*CETESB*). 2007
2. De Assunção, J.V., Pesquero, C.R., Bruns, R.E., Carvalho, L,R,F. *Chemosphere* 2005; 58(10) p.1391-1398.
3. United States Environmental Protection Agency (*US.EPA*). Cincinnati: 1999.
4. United States Environmental Protection Agency (*US.EPA*). Cincinnati: 1994
5. Lohmann, R.; Jones, K.C. *The Science of the Total Environment*. 1998; 219 53-81
6. Companhia de Tecnologia de Saneamento Ambiental (*CETESB*). 2002.
7. Companhia de Tecnologia de Saneamento Ambiental (*CETESB*). 2004
8. United Nations Environment Programme (*UNEP*). 2005
9. Nóbrega RP. *University of Sao Paulo*, School of Public Health, Brazil - Master Dissertation, USP, 2002.

Table 1. Results of PCDD/Fs individual concentration (fg.m^{-3}) in the 3 sampling sites, in 2006.

PCDD/Fs	May 9 - Tuesday			June 20 - Tuesday			July 18 – Tuesday			August 17 - Thursday		
	A	B	C	A	B	C	A	B	C	A	B	C
2,3,7,8-TCDD	nd	nd	nd	7	11	19	24	22	nd	nd	14	nd
1,2,3,7,8-PeCDD	nd	nd	nd	15	39	35	22	25	nd	nd	24	nd
1,2,3,4,7,8-HxCDD	nd	nd	nd	17	39	29	39	39	nd	nd	30	nd
1,2,3,6,7,8-HxCDD	nd	nd	nd	32	80	77	63	57	59	33	69	21
1,2,3,7,8,9-HxCDD	nd	nd	nd	27	77	72	68	52	59	nd	58	nd
1,2,3,4,6,7,8-HpCDD	102	108	92	295	909	640	549	467	439	241	633	160
OCDD	311	300	221	562	1,873	1,226	1,256	856	981	422	909	320
2,3,7,8-TCDF	18	29	19	35	72	61	68	26	59	57	74	48
1,2,3,7,8-PeCDF	nd	nd	12	43	88	85	65	78	77	54	41	35
2,3,4,7,8 PeCDF	30	26	10	75	36	157	102	93	116	57	74	35
1,2,3,4,7,8-HXCDF	18	24	22	91	201	219	139	104	98	81	55	45
1,2,3,6,7,8-HxCDF	19	nd	19	72	140	160	113	91	85	75	47	45
1,2,3,7,8,9-HxCDF	11	nd	9	35	69	77	58	41	41	42	26	22
2,3,4,6,7,8,-HxCDF	21	nd	28	104	201	245	162	127	124	105	58	56
1,2,3,4,6,7,8-HpCDF	75	97	79	402	936	1013	576	363	361	280	179	157
1,2,3,4,7,8,9 -HpCDF	nd	nd	nd	64	154	155	73	44	57	42	24	32
OCDF	90	76	64	348	1,708	1,146	523	285	335	205	118	99
Σ (fg m^{-3})	695	661	575	2,224	6,633	5,417	3,900	2,769	2,893	1,696	2,435	1,075
Σ (pg TEQ m^{-3})	25.9	21.4	18.7	103.8	164.9	224.6	176.3	157.3	127.2	77.3	115.2	46.2

A = Congonhas; B = Lapa; C = Central; nd = not detected

Figura 1. Profiles of PCDD/Fs homologous groups for the three sampling sites (fg.m^{-3}).

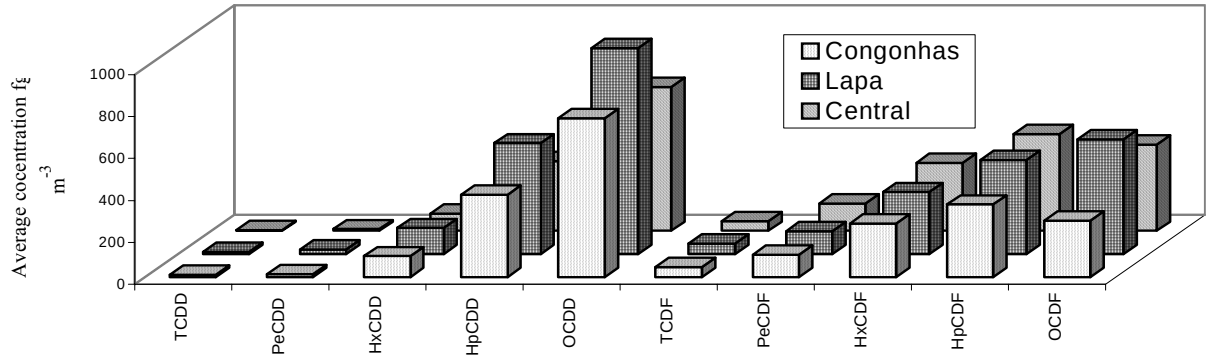

Figure 2. Total concentrations of the 17 PCDD/Fs, in fgTEQ.m^{-3}, for the 4 sampling days, in the 3 sites.

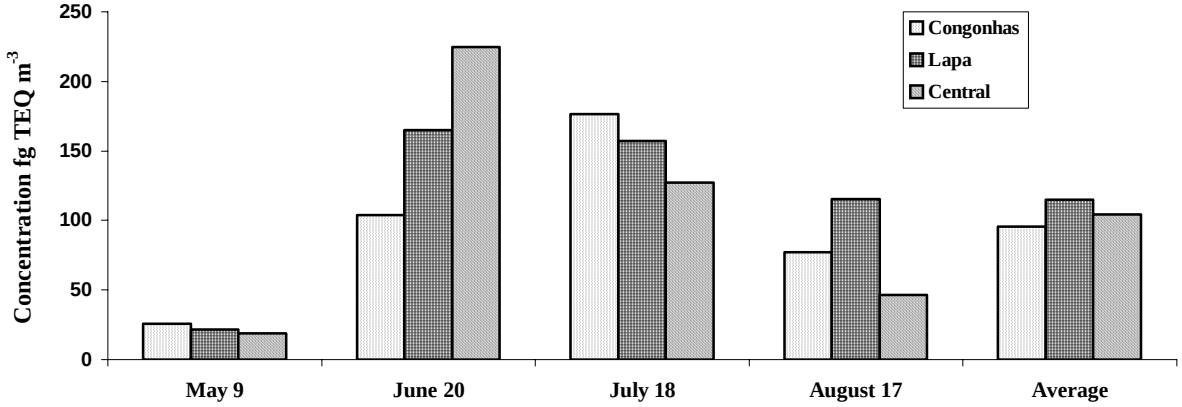

Figure 3. Relative toxicity contribution (%) of each 2,3,7,8-substituted congener for the 3 sites.