COMPARISON OF DIOXIN, FURAN AND DIOXIN-LIKE POLYCHLORINATED BIPHENYL AIR LEVELS IN INDUSTRIAL, URBAN AND BACKGROUND ENVIRONMENTS OF SÃO PAULO, BRAZIL

Francisco AP[1]*, Silva CR[2], Tominaga MY[2], Pesquero, CR[1], Latorre MRDO[1], De Assunção JV[1]
[1]University of São Paulo, School of Public Health, Av. Dr. Arnaldo, 715, São Paulo, Brazil; [2]Sao Paulo State Environmental Company, Av. Prof. Frederico Hermann Jr, 345, São Paulo, Brazil

Introduction

The atmosphere plays an important role in the transport of persistent organic pollutants (POPs) such as PCDD/Fs and dl-PCBs and air monitoring is a key to the control of environmental pollution and to prevent harm to human. In general, polychlorinated dibenzo-p-dioxin (PCDDs) and polychlorinated dibenzofuran (PCDFs) air concentrations are typically < 10 fg TEQ/ m³ in remote areas, 20 – 50 fg TEQ/ m³ in rural areas and 100 – 400 fg TEQ/ m³ in urban and industrial environments[1], however in suburban/industrial areas a level of 7 – 1,196 fg TEQ/m³ was found. Dioxin-like polychlorinated biphenyls (dl-PCBs) usually present lower toxic air levels than PCDD/Fs, < 10 fg TEQ/ m³. [2] To evaluate the air levels of the most industrialized area of Brazil, the purpose of this study is the comparison of PCDD/Fs and dl-PCBs in three different environments in São Paulo.

Materials and methods

Air samples were collected at three sites, as follows: (1) **Industrial**: Latitude -23°38'22.9"S, Longitude -46°29'29.3" W, (2) **Urban**: Latitude -23° 33' 14.1984" S, Longitude -46° 40' 16.4634" W, and (3) **Background**: Latitude: -23° 39'12.8952" S, Longitude -46° 58' 4.71" W. Site 1 is 1000 m from a petrochemical industrial complex, Site 2 is characterized by intense vehicle emissions and Site 3 is a large green area surrounding a reservoir. Sites 1 and 3 are situated in the Metropolitan Region of São Paulo (MRSP) while Site 2 is in a downtown area of São Paulo city, for which there are previous data about PCDD/F air levels resulting from research carried out by De Assunção et al [4,5] in 2000/2001 and 2006.

Active sampling was performed, according to method US EPA TO-09A[3], between September and December 2014 using high-volume PS-1 apparatus (Andersen Instruments Inc. USA), and sampling volume was from 0.21 to 0.24 m³ in 120 h sampling time, with a quartz fiber filter (QFF) for collecting the particle phase and a PUF (polyurethane foam) plug for trapping gas-phase chemicals. Surrogate standard ($^{37}Cl_4$-2,3,7,8-TCDD) was added prior to field exposure in the majority of PUF samples. The analytical procedure was carried out by Eurofins GfA Lab Service GmbH to determine the 17-PCDD/Fs and 12-dl-PCBs, using HRGC/HRMS (High Resolution Gas Chromatograph/High Resolution Mass Spectrometer). A total of 18 air samples and 5 field blank samples were collected.

Results and discussion:

The air level data of the ∑PCDD/F and ∑dl-PCB and TEQ total, at the three sites, are summarized in Table 1; as expected the background site presents the lowest concentration. Kruskal-Wallis rank sum test (KW) was carried out using average concentrations of the PCDD/F and dl-PCB. The KW test confirmed that there are statistical differences between background and industrial/urban concentrations both for PCDD/Fs and dl-PCBs (p-value=0.05). On the other hand, industrial and urban concentrations of PCDD/Fs are not statistically different. Furthermore, these sites present statistical differences as between dl-PCB concentrations just between urban and background sites. In addition, Figure 1 shows the spread of the data at each site for PCDD/Fs and dl-PCBs.

Table 1: Summary of average concentrations and standard deviation (sd) of the ∑PCDD/Fs and ∑dl-PCBs (pg/m³) and TEQ total (fg/m³)

Site	**Number of samples**	**∑ PCDD/Fs** (pg/m³)	**∑ dl-PCBs** (pg/m³)	**∑WHO-2005-TEQ** (fg TEQ/m³)
		Average (sd)	**Average (sd)**	**Average (sd)**
Industrial	6	1.86 (0.68)	4.34 (0.66)	106.0 (35.62)
Urban	7	1.75 (1.67)	4.50 (0.82)	86.88 (77.23)
Background	5	0.50 (0.20)	0.93 (0.12)	21.33 (11.35)

In terms of 2005-WHO-TEQ, the background site presented the lowest average PCDD/F and dl-PCB concentrations, 21.33 ± 11.35 fg TEQ/m³, and both industrial and urban environments showed similar TEQ concentrations, 106.0 ± 35.62 and 86.88 ± 77.23 2005-WHO-TEQ pg/m³, respectively. PCDD/F compounds were responsible for the majority of the TEQ total, the maximum contribution of dl-PCBs for total TEQ was 12%, ranging from 0.003 to 13.31 TEQ fg/m³. PCB-126 congener contributes with more than 90% of TEQ total among the 12-dl-PCBs. The PCDFs contributed with 69 to 76% of the TEQ total as compared to PCDD/Fs, of which 2,3,4,7,8-PeCDF is responsible for 24 to 26% of the TEQ total, while 2,3,7,8-TCDD contributes with 3 to 5% of the TEQ total.

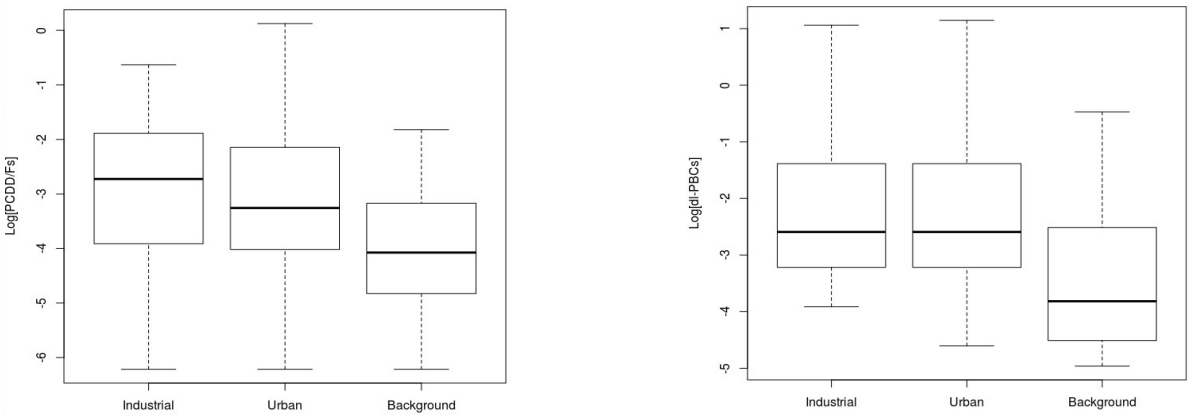

Figure 1. Logarithm of Median, maximum and minimum from PCDD/F and dl-PCB concentrations (pg/m³) at three different sites in São Paulo, Brazil, considering total measurements at each site (industrial=166, urban=190 and background=114).

Although there are differences in PCDD/F concentrations from background site and industrial/urban sites, the PCDD/F profile of the homologue groups is similar (Figure 2). The relative contribution of OCDD is 22% at the background site showing a difference of 5% and 8% compared, respectively, to the industrial and urban sites. The most abundant homologue group is 1,2,3,4,6,7,8-HpCDF that contributes between 20 and 23% of the total ∑PCDD/Fs at the three sites. As expected, OCDD and Hepta-CDD/F congeners are predominant in air ambient seeing that higher chlorinated congeners are more stable than lower ones[1]. There is an increase of PCDD/F concentrations according to chlorinated atoms (Cl_4<Cl_5<Cl_6<Cl_7<Cl_8)[4], nevertheless in this study concentrations of the hepta-CDF homologue groups are higher than those of OCDFs.

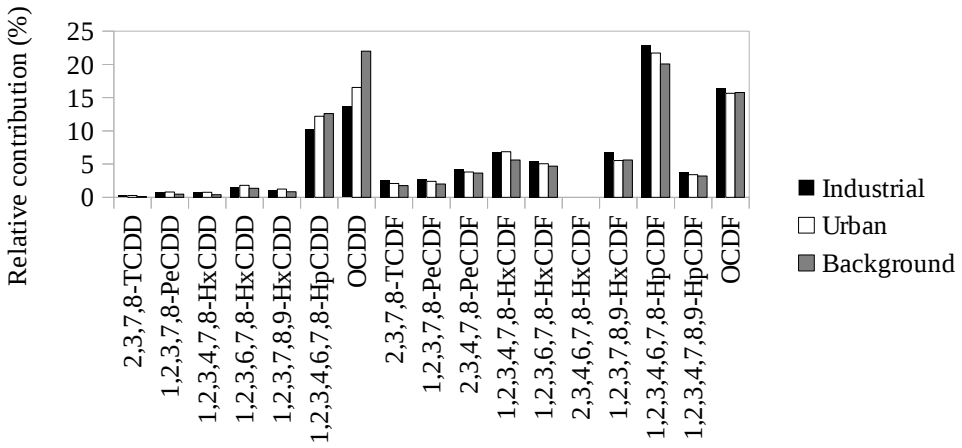

Figure 2. Relative contribution (%) of PCDD/Fs at three different sites.

The dl-PCB homologue groups present a difference of <1% compared with those of the three sites. Concentrations of dl-PCBs are twice as high as than PCDD/F concentrations. PCB-118 congener is the highest

followed by PCB-105 (Figure 3), this profile is similar to those of previous findings in urban and industrial areas[2]. PCBs were produced on an industrial scale until the 1980s. It is recognized that PCB-118 and PCB-77 are the main congeners in the Arochlor® with low chlorination.

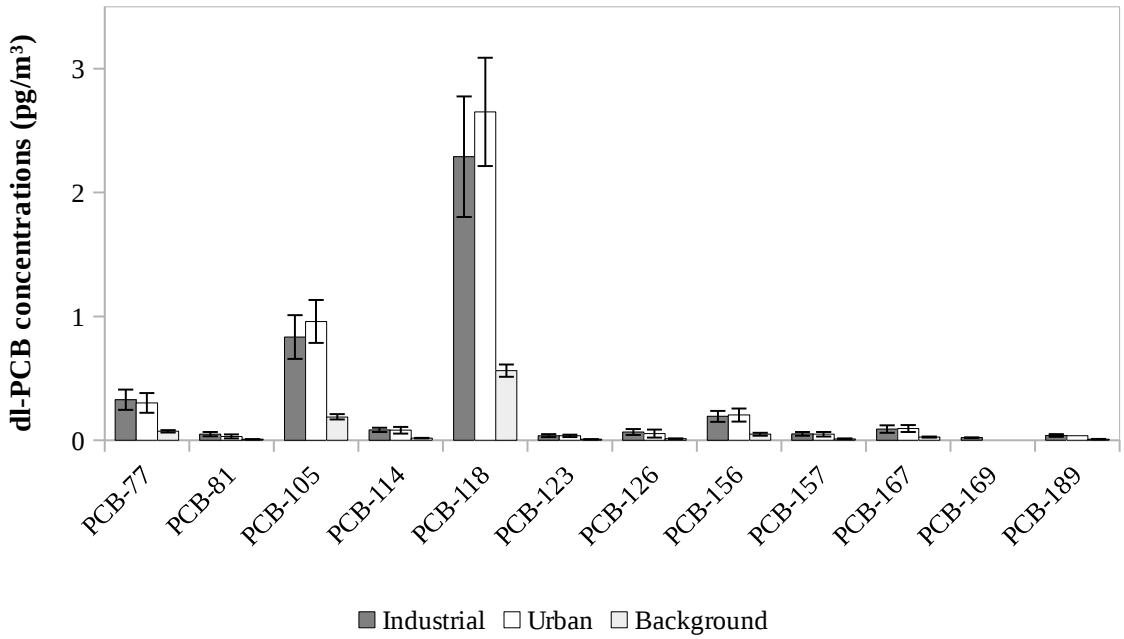

Figure 3. Concentrations of dl-PCBs (pg/m³) at industrial, urban and background sites.

Table 2 shows PCDD/Fs detected in two studies carried out in the same location in 2000/01 and 2006 and in this one carried out in 2014. In this case, the main source of air pollution is vehicular emission. The ranges of total ΣPCDD/Fs and total TEQ are similar in the three studies. However, the minimum value of the Tetra to Hexa-CDDs homologue groups were detected below the limit of quantification or were not detected by De Assunção et al [4,5]. In this study, the sampling was carried out per 120h as against 24h by De Assunção et al [4,5], in the same range of flow (0.240 a 0.275 m^3/min) and, probably, because of this, the resolution of low chloride compounds is better than in the previous studies. Although the sampling exposure was 5 times longer than in the studies in 2000/01 and 2006, it seems that the results are in good agreement with quality assurance/quality control, as recoveries based on sampling standards, added prior to field exposure, were 92% to 118%.

Conclusions

PCDD/F air levels are not statistically different as between industrial and urban sites, while dl-PCB air levels are just statistically different as between urban and background sites. The background site shows the lowest PCDD/F and dl-PCB concentrations (average of 21 fg TEQ/m³), a typical rural concentration, and also the industrial and urban sites present typical concentrations for these areas, with averages of 86 and 106 fg TEQ/m³, respectively.
At the three sites, the dl-PCB profiles are relatively similar and PCB-118 congener is the highest followed by PCB-105. Also, the PCDD/F profiles are similar in urban, industrial and background sites, except for OCDD congener that shows a difference between background and industrial/urban sites, of about 5 – 8%. Although dl-PCB concentrations are about twice as high as those of PCDD/F, the maximum contribution for TEQ total of dl-PCBs was 12%. The dl-PCBs air levels, from 0.003 to 13.31 fg TEQ/m³, are in agreement with those of a previous study[2].
The findings of this study of PCDD/F air levels are very similar to those of previous studies carried out by De Assunção et al [4,5], at the same urban sampling site in 2000/01 and 2006. However, the minimum values for tetra,penta hexa-CDD congeners present better resolution in this study than in previous studies [4,5], as the average of volume sampled was 1555 m³, about 5 times greater than the volume sampled before.

Table 2: PCDD/F concentrations (pg/m³) in urban area in São Paulo.

Compounds	This study	De Assunção et al (2005)[4]	De Assunção et al (2008)[5]
2,3,7,8-TCDD	0.002 – 0.009	0.003* – 0.069	nd** – 0.019
1,2,3,7,8 PeCDD	0.004 – 0.037	0.003* – 0.021	nd – 0.035
1,2,3,4,7,8-HxCDD	0.003 – 0.038	0.004* – 0.027	nd – 0.029
1,2,3,6,7,8-HxCDD	0.08 – 0.089	0.004* – 0.052	nd – 0.077
1,2,3,7,8,9-HxCDD	0.005 – 0.058	0.004* – 0.045	nd – 0.072
1,2,3,4,6,7,8-HpCDD	0.056 – 0.58	0.19 – 0.62	0.092 – 0.64
OCDD	0.092 – 0.74	0.004 – 1.49	0.22 – 1.23
2,3,7,8-TCDF	0.019 – 0.073	0.027 – 0.089	0.019 – 0.061
1,2,3,7,8 -PeCDF	0.018 – 0.098	0.029 – 0.042	0.012 – 0.085
2,3,4,7,8 PeCDF	0.025 – 0.168	0.049 – 0.176	0.010 – 0.157
1,2,3,4,7,8-HxCDF	0.034 – 0.342	0.047 – 0.104	0.022 – 0.219
1,2,3,6,7,8-HxCDF	0.029 – 0.240	0.037 – 0.069	0.019 – 0.160
1,2,3,7,8,9-HxCDF	<0.0050	0.004 – 0.042	0.009 – 0.077
2,3,4,6,7,8-HxCDF	0.028 – 0.257	0.052 – 0.131	0.028 – 0.245
1,2,3,4,6,7,8-HpCDD	0.098 – 1.132	0.147 – 0.566	0.079 – 1.013
1,2,3,4,7,8,9-HpCDF	0.017 – 0.166	0.004 – 0.77	nd – 0.155
OCDF	0.061 – 0.788	0.088 – 0.446	0.064 – 1.146
Total PCDD/Fs (pg/m³)	**0.50 – 4.82**	**1.56 – 13.80**	**0.58 – 5.42**
Total 2005-WHO-TEQ (pg TEQ/m³)	**0.029 – 0.229**	**0.047 – 0.751**	**0.019– 0.225**

*Values below the detection limits (DL) are included using 1/2 DL [5]
**nd = not detected [4]

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