

DIOXIN, FURAN AND DIOXIN-LIKE PCBs IN THE ATMOSPHERE OF SÃO PAULO, BRAZIL: LOCAL TRENDS USING PASSIVE SAMPLING

Silva CR*, Melo JP, Souza CAM, Niwa NA, Sato MIZ, Tominaga MY.

CETESB – São Paulo State Environmental Company – Av. Prof. Frederico Hermann Júnior, 345, 05459-900, São Paulo – Brazil.

Introduction

São Paulo is the major South America city with a census-estimated 2014 population of more than 11 million people¹ and about 8 million vehicles². The ubiquitous contamination of the environment by polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) is primarily caused by atmospheric deposition of the emissions from several sources (waste incineration and other industrial thermal processes, production of chemicals, vehicular emissions). In the other side, historically PCBs were used in commercial mixtures such as Aroclors 1242, 1248, 1254 and 1260, these were probably the most used in Brazil, since the majority of them were purchased from “Monsanto”³. The PCB commercially used in transformers, called Ascarel, is an oily product that contains 40-60%(w/w) of PCBs. Brazil signed the prohibition of use and commercialization of PCBs in 1981 with law n° 19 (29/01/81)⁴, but it is still in use in old machines.

These POPs (PCDD/PCDF and PCBs) are included in the list of Stockholm Convention and Brazil as a Part of this Convention has been working to develop strategies and action plans to reduce emission of these pollutants. The national action plan proposed to reduce emissions and highlights the need to evaluate the effectiveness of the strategies implemented by monitoring these pollutants in the environment.

Passive sampling has been adopted for the Global Monitoring Plan (GMP) for POPs⁵ from Stockholm Convention, for the monitoring of levels and trends of POPs in the atmosphere. The use of passive sampling has spread globally because it is versatile, cheap and do not require electrical connections. During the period of 2009 and 2012, the United Nations Environmental Programme (UNEP) funded by Global Environmental Facility (GEF), developed the project “Supporting the implementation of GMP in Latin America and Caribbean Region” and CETESB, received from this project some passive air samplers and since 2010, have been monitoring some group of POPs in the atmosphere of São Paulo.

The present work reports the results of PCDD, PCDF and dl-PCBs monitoring data during the period of 2010 and 2014 in one sampling site of São Paulo city.

Materials and methods

Sampling site: São Paulo city – urban area. Geographic coordinate: latitude -23°33'41.32''S, longitude -46°42'7.51''W. The sampling site chosen receives a significant contribution of vehicular emissions and there is no industrial activity in its immediate neighborhood. The sampling site, located at CETESB, is very close (500 meters far) to Marginal Pinheiros, one of the main avenue of Metropolitan Region of São Paulo, an avenue with intense vehicular traffic where circulate many types of vehicles fueled with gasohol (a mix from gasoline and 20-25% of anhydrous ethanol), only ethanol, natural gas or diesel.

The passive air sampler consisting of polyurethane foam (PUF) disks (diameter: 14 cm, height: 1.35 cm, surface area: 365 cm², density: 0.0213 g/cm³) housed in a protective stainless steel chamber was placed about 2 meter above the ground, except in 2011, the sampler was placed about 32m above the ground, at the top of the building. The PUF disks were deployed during 3 months periods, except during 2012 and 2013 they were deployed during 6 months. Before deployment the PUF disks were cleaned (last cleaning solvent: toluene) and kept in glass bottles with PTFE lined cap. A field blank was checked every sampling period.

PCDD/Fs and PCBs were analyzed according to the U.S. EPA 8290A⁶ and U.S. EPA 1668C⁷, respectively. PUF samples were spiked with ¹³C₁₂-PCDD/F and ¹³C₁₂-PCB surrogate standards and extracted during 24h in a Soxhlet extractor with toluene: acetone (9:1). The extracts were purified in a multilayer silica column (40% H₂SO₄ and 10% AgNO₃) using n-hexane as eluent, and after in an alumina column using dichloromethane to elute the fraction containing PCDD/F and toluene/n-hexane (2:1) to elute PCB fraction. The final extracts were concentrated to dryness and then added PCDD/F/PCB internal standards. PCDD/F and PCB final extract were analyzed in an Agilent 6890 model gas chromatography coupled in an AutoSpec high resolution mass

spectrometer (HRGC/HRMS), operating with electron impact ionization of 35eV at a mass resolution of 10.000. The GC was fitted with a VF-Xms capillary column (60m x 0.25mm id x 0.25µm film thickness).

Results and discussion

The air concentrations of PCDD/F and dl-PCB were calculated considering the WHO 2005 toxic equivalent factors (TEF)⁸ and the results are summarized in the table 1. For the conversion of the amount accumulated in the PUF disk (pg/PUF) to a concentration basis (fg/m³), it was considered the sampling rate of PUF disk of 4m³/day (Shoeib & Harner⁹; Schuster et al¹⁰). Total TEQ was calculated according to the lower and upper bound concept. For lower bound TEQ calculation; all results below limit of detection (LOD) were considered as zero whereas for upper bound TEQ calculation; all results below LOD were considered equal to ½ of the LOD value or equal to the limit of quantitation limit (LOQ) value.

Table 1 – Air concentrations (pg TEQ WHO₂₀₀₅/PUF and fg TEQ WHO₂₀₀₅/ m³) of PCDD/F and dl-PCB

Period of sampling	Lower bound		Upper bound			
	TEQ Σ PCDD/F+dlPCB (<LOD = 0)		TEQ Σ PCDD/F+dlPCB (<LOD = ½ LOD)		TEQ Σ PCDD/F+dlPCB (<LOD = LOQ)	
	pg/PUF	fg/m ³	pg/PUF	fg/m ³	pg/PUF	fg/m ³
July – September 2010 (3 months)	13.10	36.4	15.45	42.9	25.59	71.1
October – December 2010 (3 months)	8.25	22.9	10.03	27.9	17.76	49.3
July – September 2011 (3 months)*	11.67	32.4	12.58	34.9	17.73	49.3
January – June 2012 (6 months)	19.36	26.9	19.90	27.6	22.95	31.9
July – December 2012 (6 months)	9.39	13.0	14.04	19.5	40.39	56.1
December 2012 – May 2013 (6 months)	8.31	11.5	9.45	13.1	15.94	22.1
June – September 2013 (3 months)	4.53	12.6	5.48	15.2	10.84	30.1
September – December 2013 (3 months)	3.08	8.6	3.46	9.6	5.58	15.5
July – September 2014 (3 months)	4.66	12.9	5.74	15.9	9.72	27.0
September – December 2014 (3 months)	5.10	14.2	5.58	15.5	8.27	23.0

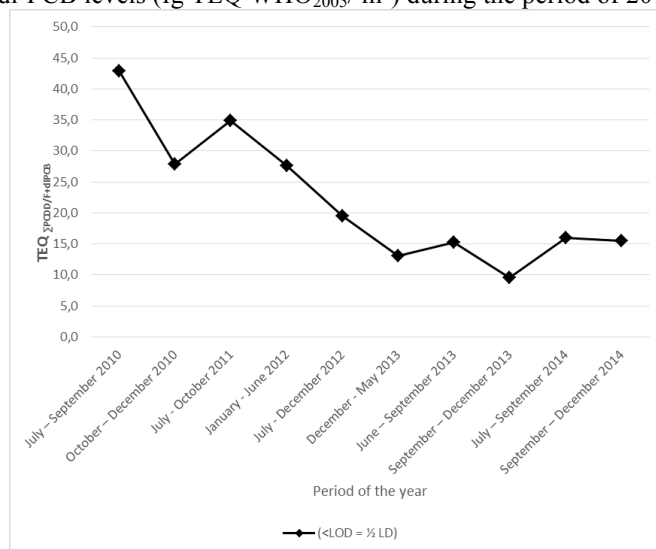
*in 2011, the sampler was placed 32m above the ground, for all other periods the sampler was placed at about 2m above the ground

The current data does not allow identifying a seasonal variation. The highest TEQ found was in the winter of 2010 (13.10 pg TEQ/PUF- lower bound), but in the following years there is no significant differences between the seasons.

Figure 1 shows the trends of PCDD/F and dl-PCB over the time. It is difficult in that limited time to highlight all the trends. However, some observations can be made: the levels of the PCDD/F and dl-PCB showed a slightly decrease over these years. Between 2013 and 2014 no remarkable difference was observed.

As can be seen the figure 2 the dl-PCB contribution for the total TEQ is lower than for PCDD/F, in all cases the dl-PCB contribution is around 30%, the worst case was September to December of 2013 where the contribution was 33.5%. However in terms of concentration levels it is possible to observe a decrease between 2010 and 2014 (Figure 3). It can be better observed in the levels of PCB-118, as expected this congener presented the highest concentration in all samples, the PCB-118 is known as marker-PCB because it is found in high concentration in all kind of environmental samples. The most toxic PCB congener (PCB-126) was found in all samples, the lowest result was 10.8 pg/PUF in 2013 and the highest was 39.8 pg/PUF in 2010, during the first sampling period.

Figure 1 – PCDD/F and dl-PCB levels (fg TEQ WHO₂₀₀₅/ m³) during the period of 2010 - 2014



Regarding to PCDD/F concentration, the same trend can be observed as dl-PCB: a slightly decrease between 2010 and 2014. The congener that presented the highest concentration was OCDD, but the PCDF concentration found was higher than PCDD, a typical profile finding in places that presents high PCB concentration levels. Only the heptas and octa-dioxins were found in all samples, while almost all furans congeners were found in all samples. The most toxic PCDD congener (2,3,7,8-TCDD) was not found in any sample.

Figure 2 - PCDD/F and dl-PCB contribution (%) for the total TEQ (3 months sampling)

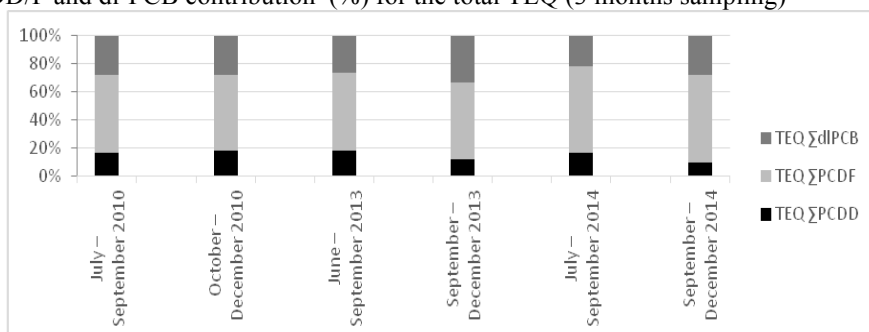


Figure 3 - dl-PCB levels (pg/PUF) during the period of 2010 – 2014 (3 months sampling)

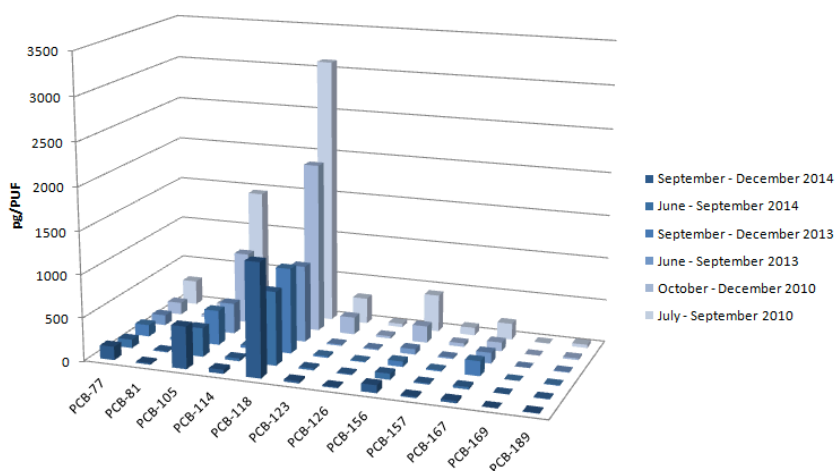
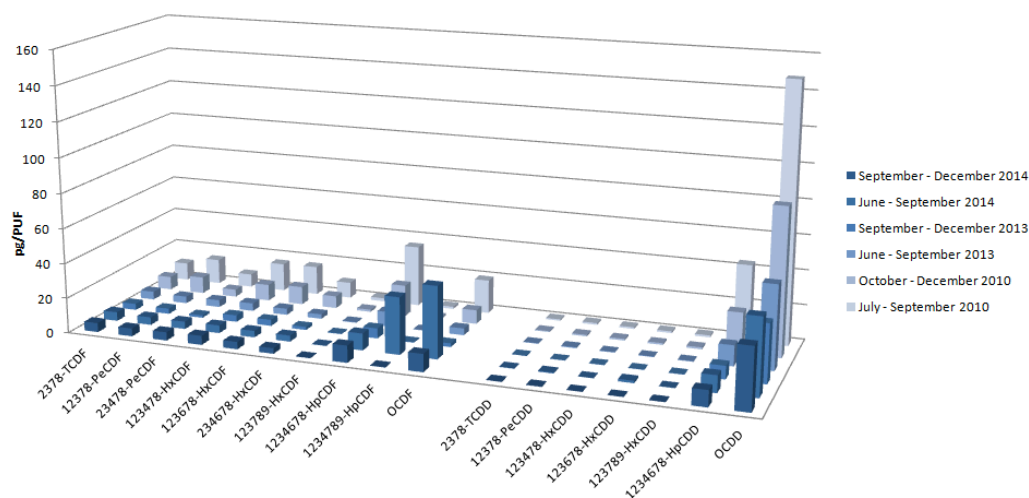


Figure 4 – PCDD/F levels (pg/PUF) during the period of 2010 - 2014 (3 months sampling)



The first results from this project showed the applicability of passive air sampling, it is low cost and the simple handling and allow the air monitoring for long time over the years. The levels of PCDD/F and dl-PCBs seems that are decreasing but is necessary to add more sampling sites and further studies to better understanding of the trends. The future projects will include more sampling sites (background, rural and industrial), and all seasons monitoring besides active sampling comparison and sampling rates studies.

Acknowledgements

We thank UNEP/GEF project and CSIC/Spain for providing the training and the polyurethane foams/passive sampling chambers.

References

1. IBGE, Censo 2014. Available on-line: < <http://cod.ibge.gov.br/232IH>>
2. DETRAN, Frota de veículos, Março 2015. Available on line: < <http://www.detran.sp.gov.br/wps/portal/portaldetran/detran/estatisticastransito/sa-frotaveiculos> >
3. Almeida F V, Centeno A J, Bisinoti M C, Jardim W F. (2007); *Quim. Nova.* 30(8): 1976-85
4. Brasil. Ministério do Interior. Portaria Nº 19 de 29.01.81. D.O.U., 03.09.85 – pag. 12941, 1985.
5. UNEP. Guidance on the Global Monitoring Plan for Persistent Organics Pollutants, 2013.
6. [US EPA] United States Environmental Protection Agency, (2007). Method 8290A. Washington, DC., USA
7. [US EPA] United States Environmental Protection Agency, (2010). Method 1668C. Washington, DC., USA
8. Van den Berg M *et al.* (2006) *Toxicological Sciences.* 93(2), 223-241.
9. Shoeib M, Harner, T. (2002) *Environ. Sci. Technol.* 36(19), 4142-4151.
10. Schuster J K *et al.* (2015) *Environ. Sci. Technol.* 49(6), 3680-3686.