# Spatial Distribution of Polychlorinated Biphenyls in Air Considering Three Areas from the Metropolitan Region of São Paulo, Brazil

Francisco AP<sup>1</sup>, Tominaga MY<sup>2</sup>, Silva CR<sup>2</sup>, Assunção JV<sup>1</sup>

<sup>1</sup>Department of Environmental Health, University of São Paulo, São Paulo/State of São Paulo, Brazil, Av. Doutor Arnaldo, 715

<sup>2</sup>Environmental Company of the State of São Paulo, São Paulo/State of São Paulo, Brazil, Av. Prof. Frederico Hermann Jr, 345

## Introduction

Polychlorinated biphenyls (PCBs) were introduced in Brazil, as a result of the importation of equipment containing these chemicals, and also from the formulation of oils for several commercial uses. PCBs have never been produced in the country, and its production was prohibited in the 1970s<sup>1</sup>. There is a lack of information about the real amount of PCBs still in use in Brazil. On the other hand, some studies have reported PCB levels and trends in the environment as well as biotic matrices<sup>2</sup>. These studies are useful in order to show PCB hotspots. Here we focus on the Metropolitan Region of Sao Paulo (MRSP), which is the fifth most populous metropolitan region in the world<sup>3</sup>, with a total population around 20 million inhabitants<sup>3</sup>. Passive samplers have been used as an alternative for active samplers, because of their convenience, low cost and independence of electrical power<sup>4</sup>. Polyurethane foam (PUF) disks have been widely employed for POP monitoring<sup>5</sup>. Thus, this study aims to measure the atmospheric levels of seven indicator PCBs (PCB-28, -52, -101, -118, -138, -153 and -180) in the MASP using PUF disks.

## Materials and methods

This study was conducted at three sites: Urban/Industrial (Santo André), Urban (São Paulo), and Background (Cotia), see Figure 1. Passive air samplers consisting of the polyurethane foam disks (diameter: 14 cm, height: 1.35 cm, surface area:  $365 \text{ cm}^2$ , density:  $0.0213 \text{ g/cm}^3$ ) housed in protective chambers were employed in this study. The air samples were collected for 4 consecutive months, from September to December 2014 (Period 1) and from May to August 2015 (Period 2). A total of 6 samples were collected, and 2 field blanks. Extraction and clean-up procedures were carried out according to US EPA 1668C<sup>6</sup>, All samples were extracted with toluene:acetone (9:1) in a Soxhlet apparatus for 24 hours and surrogate standards ( $^{13}C_{12}$ -PCB) were spiked on each sample media prior to extraction procedure. Sample extract volumes were reduced using rotary evaporator system. The extracts were purified on an acid silica column (40% H<sub>2</sub>SO<sub>4</sub> and 10% AgNO<sub>3</sub>), using n-hexane as eluent, followed by an alumina column, using n-hexane/toluene (1:2). Purified extracts were concentrated first in a rotatory evaporator and then under a gentle nitrogen stream until dryness and re-suspended with  $10\mu$ L of internal standards <sup>6</sup>. Samples were analyzed using high resolution gas chromatography (HRGC) coupled to high resolution mass spectrometry (HRMS), Agilent 6890 model HRGC; AutoSpec HRMS, equipped with VF-Xms capillary column (60m x 0.25mm id x 0.25 µm film thickness) operating in electron impact ionization with an energy of 35 eV in SIM mode and 10.000 resolution power. The air volume was calculated using the linear gas-phase sampling rate of the PUF disk (4 m³/day).

#### **Results and discussion**

Figure 2 shows PCB profile from the three sites and both periods. In period 2, PCB-28 and -52 congener concentrations from background site were equal or less than those from the blanks, which result of a different profile in period 2 compared to period 1 at urban and urban/industrial sites. PCB air levels were in the following order: urban/industrial > urban > background. Urban and urban/industrial PCB levels are about 5 times higher than those at background site (period 1).

PCB levels ranged from 0.17 to 19 pg/m<sup>3</sup> (average of 5.1 pg/m<sup>3</sup>) in Period 1, and from 0.11 to 12 pg/m<sup>3</sup> (average of 3.3 pg/m<sup>3</sup>) in Period 2. The congener profile were dominated by PCB-28, -52 and -101 in both periods 1 and 2. This profile corroborates the findings of PCB levels in a urban area from the city of Sao Paulo<sup>5</sup>, where PCB congeners show decreasing concentrantions in air with an increasing degree of chlorination. Also, Meire et al.<sup>2</sup>, reported PCB profile with the greatest contributions (40 to 80%) from the tri-CB, including PCB-28, and tetra-CB congeners in mountains of southeast and southern Brazil.

Table 1 shows dioxin-like PCB levels and the seven indicator PCBs in air. PCB indicators are from 4 to 7 times higher than dl-PCBs, except for backgound site in period 2. This study show higher influence of PCB emission sources at urban and urban/industrial sites compared to background area, and passive air samples is a powerful tool for spatial and temporal variations of PCB in tropical areas.



**Figure 1**. Sampling sites in the Metropolitan Region of São Paulo, Brazil. The cities of Cotia, São Paulo and Santo André represent background, urban and urban/industrial areas respectively.







Figure 2. PCB profiles in air at background, urban and urban/industrial sites in the Metropolitan Region of São Paulo, Brazil. Period 1 represents the spring in the South Hemisphere (from September to December/2014) and Period 2 represents the end of autumn and the winter (from May to August/2015).

Period	Local	*dl-PCBs <sup>7</sup>	PCBs (7 indicators) (This study)
	Urban	2.60	50.5
	Urban/Industrial	2.64	46.4
Period 1			
(Spring/2014)	Background	0.511	9.27
Period 2	Urban	3.62	33.4
(Autunm/winter,2015)	Urban/Industrial	3.78	28.7
	Background	1.41	1.25
*diavin like DCDe (DCD	77 01 105 114	100 106 166 167 10	57 160 100)

Table 1. PCB co	ncentrations at thr	ee sites (pg/m <sup>3</sup>	) from	passive samp	oles.
-----------------	---------------------	-----------------------------	--------	--------------	-------

'dioxin-like PCBs (PCB-77, -81, -105, -114, -123, -126, -156, -157, -167, -169, -189)

# Acknowledgements

This study was supported by grant N.2013/20299-0 from the Sao Paulo Research Foundation (FAPESP). We thank Tom Harner for donating passive sampling chambers and polyurethane foams.

#### References

1 MMA (Ministry of the Environment) (2015) National implementation plan Brazil: Convention Stockholm/ Ministry of the Environment.

2 Meire RO, Lee SC, Targino AC, Torres JPM, Harner T. (2012) Atmospheric Pollution Research, 3 417-425.

3 Kumar P, et al. (2017) Atmospheric Environment, 140 364-369, 2016.

4 Tuduri L, Millet M, Briand O, Montury M (2012) TrAC, Trends Anal. Chem. 31 38-49.

UNEP - United Nations Environment Programme (2012) Supporting the Implementation of the Global 5 Monitoring Plan of POPs in Latin America and Caribbean States. Final Brazil Report.

6 (2010). Method 1668C–Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. US EPA, Washington.

7 Francisco AP, Nardocci AC, Tominaga MY, da Silva CR, de Assunção JV (2017). Atmospheric Pollution Research (In Press, Corrected Proof, Available online 4 April 2017).