DIOXINS, FURANS AND DIOXIN-LIKE POLYCHLORINATED BIPHENYLS IN THE ATMOSPHERE OF SÃO PAULO, BRAZIL: SPATIAL TRENDS USING PASSIVE AIR SAMPLER

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Introduction

Metropolitan Region of São Paulo (MRSP) is the biggest agglomeration of Brazil with a total population roughly 20 million inhabitants, where the main contributions to air pollution are the vehicle emissions along with industries. Persistent Organic Pollutants (POPs) are an environmental concern, especially after Stockholm Convention, which requires its parties to eliminate or reduce the release of POPs into the environment[1]. Since 2010, POPs have been monitored by the Sao Paulo State Environmental Company at an urban area from São Paulo city using passive sampler. ΣPCDD/Fs ranged from 6.5 to 23.0 pg TEQ/filter while Σdl-PCBs ranged from 3.1 to 4.9 pg TEQ/filter under around 90 days of exposure time [2]. These levels are of similar magnitude to that observed for PCDD/Fs and/or dl-PCBs along urban areas around the world [2]. In order to improve the knowledge about air levels of POPs in the MRSP, as part a collaboration project between researchers from University of São Paulo and the São Paulo State Environmental Company, it was designed a study encompassing three monitoring areas in the MRSP – urban, industrial and rural background environments. Therefore, the purpose of this study is to identify spatial trends in the atmosphere of the São Paulo using passive air sampler.

Materials and methods

Sampling sites

The study was conducted at three sites: (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) **Rural 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 MRSP while Site 2 is in a downtown area of São Paulo city.

Air Sampling

Passive air samplers consisting of the polyurethane foam disks (diameter: 14 cm, height: 1.35 cm, surface area: 365 cm^2, density: 0.0213 g/cm^3) housed in protective chambers were employed in this study. Duplicate samples were deployed at Industrial and Urban sites. PUF disks were exposure for 4 consecutive months, between September and December 2014. Duplicate samples represented two configurations: 1 PUF was deployed for 4 months and 2 PUFs were deployed, each one, for 2 months. These 2 PUFs were extracted together. A total of 5 samples were collected besides of 1 field and 1 laboratory blank samples.

Extraction and clean-up procedures

According to US EPA 8290A[3] and US EPA 1668C[4], respectively, PCDD/Fs and dl-PCBs concentrations were determinated. All samples were extracted with toluene:acetone (9:1) in a Soxhlet apparatus for 24 hours and surrogate standards (^{13}C12-PCDD/F and ^{13}C12-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_2SO_4 and 10% $AgNO_3$), using n-hexane as eluent, followed by an alumina column, using dichloromethane to elute the fraction containing PCDD/Fs and n-hexane/toluene (1:2) to elute dl-PCBs fraction. Purified extracts were concentrated first in a rotatory evaporator and then under a gentle nitrogen stream until dryness and re-suspended with 10μL of internal standards.

Instrumental Analysis

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.

Results and discussion:
Air concentrations for ΣPCDD/Fs ranged from 2.5 to 14.7 TEQ[1] pg/filter and for Σdl-PCBs between 0.70 and 3.4 TEQ pg/filter under approximately 120 days of exposure time. High concentrations were observed at industrial site, these results are not similar to those measurements reported previously[2] for an urban area, which presented concentrations higher than this study. Probably because this study was carried out just under good meteorological conditions (during spring and summer) while UNEP[2] represents all seasons,

Figure 1 depicts homologous group's profile; PCB-118 congener is the highest followed by PCB-105 and PCB-156, this profile is similar to those of previous findings in urban and industrial areas[5]. PCDD/F profiles are dominated by OCDD, 1234678-HpCDD, 1234678-HpCDF and OCDF. Although there is a typical increase of PCDD/F concentrations according to chlorinated atoms (Cl_4<Cl_5<Cl_6<Cl_7<Cl_8) , the results show that hepta-CDF homologue groups are slightly higher than those of OCDFs.

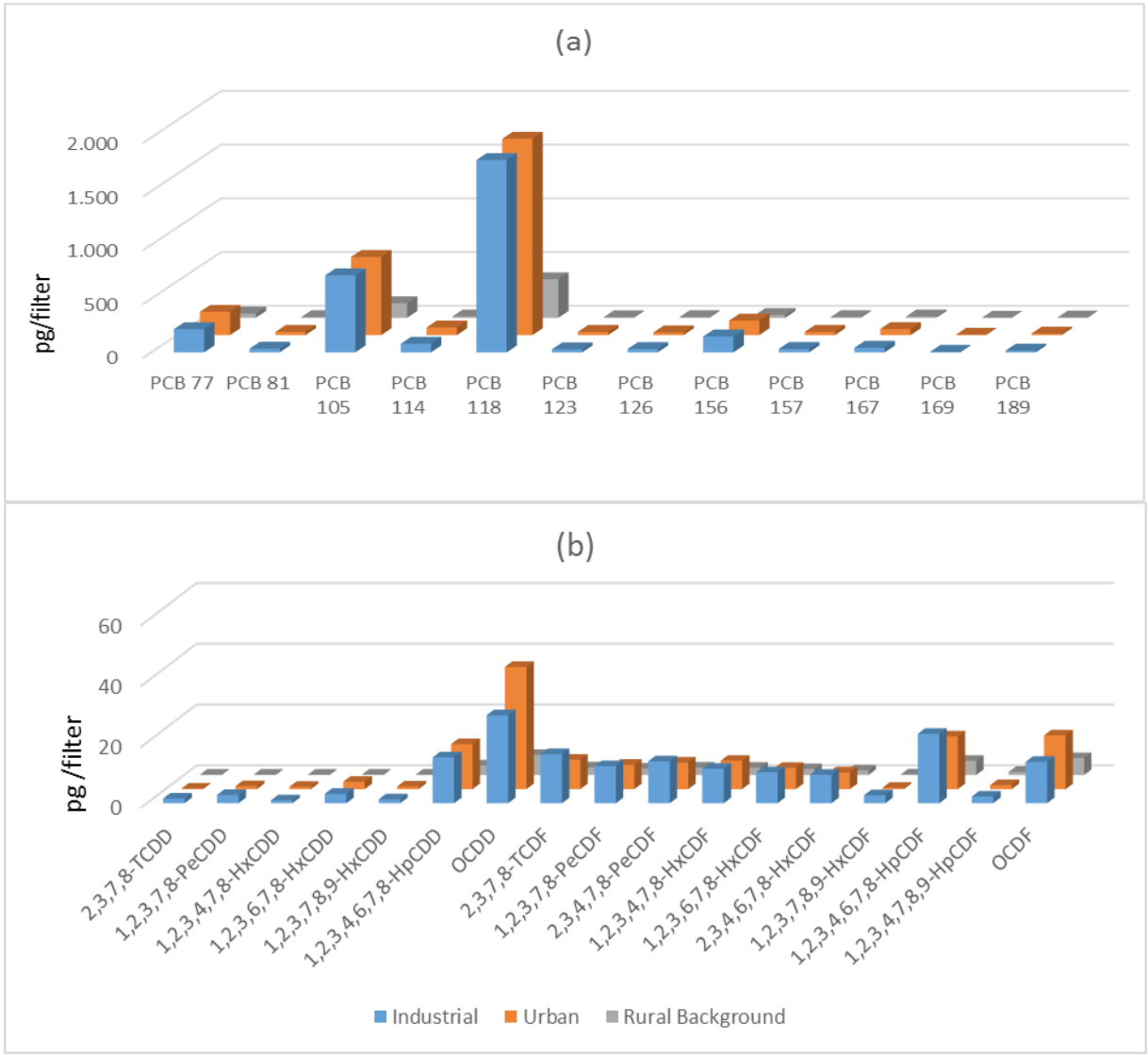

Figure 1: dl-PCB (a) and PCDD/F (b) concentrations at three sites.

Figure 2 shows the spatial trends at sites 1, 2 and 3. PCDD/F and dl-PCB air concentrations for industrial and urban sites were around 5 times higher than that for rural background site. PCDF concentrations are the highest followed by dl-PCB and PCDD concentrations. It seems that this behavior is similar at three sites. In order to

[1]TEQ was calculated using 2005 WHO TEF (Factor of Toxit Equivalent)

evaluate the differences of concentrations between the sites, Kruskal-Wallis rank sum test (KW) was carried out using average concentrations (pg/filter) of the PCDD/Fs and dl-PCBs. The KW test confirmed that there are statistical differences between rural background and industrial/urban concentrations (p-value=0.05).

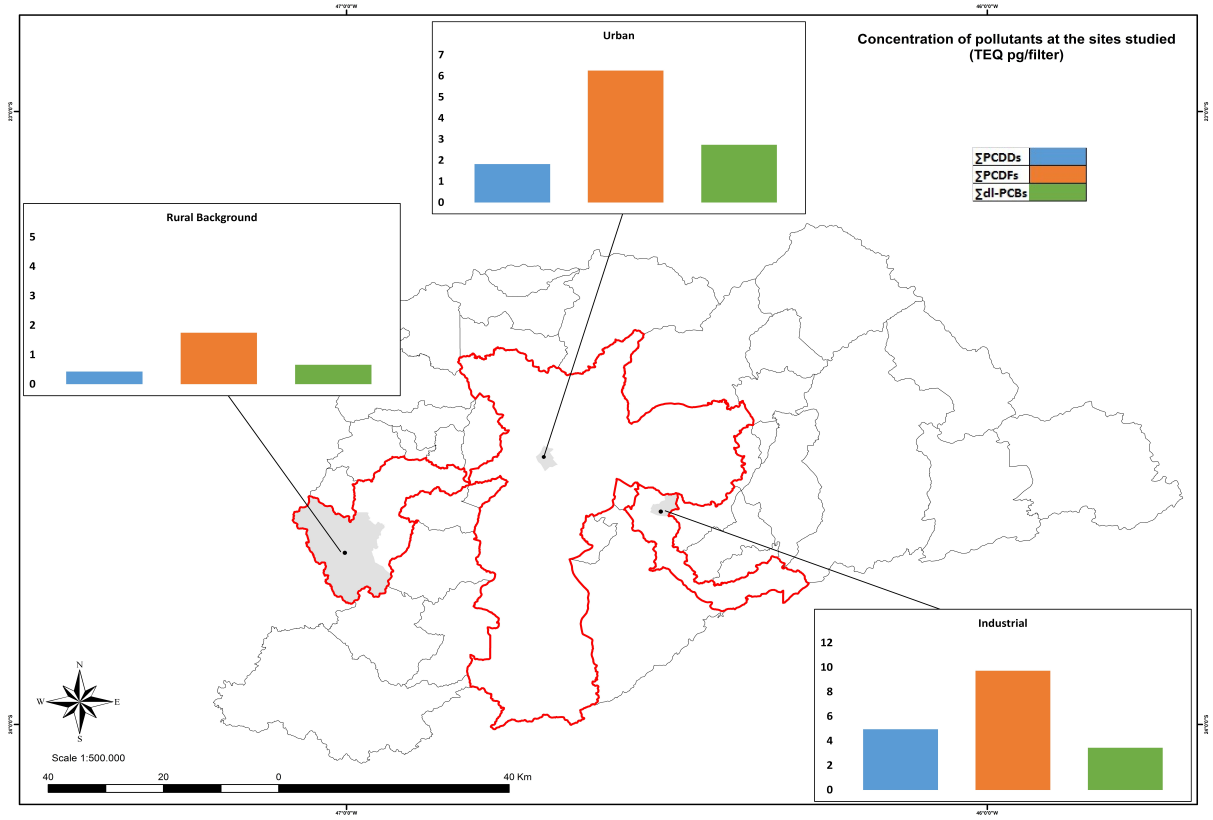

Figure 2: PCDD/F and dl-PCB concentrations in the MRSP at three sites.

Figures 3 and 4 depict the performance of PUF disks for 4 or 2 months of exposure time at industrial and urban sites. Values lower than LQ (Limit of Quantification), were replaced by ½ LD (Limit of Detection). The main congeneres with results <LQ are: 1,2,3,7,8,9- HxCDF, 2,3,7,8-TCDD; 1,2,37,8-PeCDD and all HxCDDs. It seems that PUF disks are not enough efficient for most of the compounds of PCDD/Fs under 3 months of exposure time [6].We will evaluate the relation between PUF disks and active samplers in other other study. In fact, performance of PUF disks for 4 or 2 months of exposure time are in good agreement (see Figures 3 and 4).

Conclusions

PUF disks are a powerful tool to show spatial trends especially when the objective is to screen the air levels to establish a monitoring program. In this study, dl-PCB air levels are higher than that of PCDD/F, consisting a typical congener profiles except for hepta-CDF homologue group that presents concentration slightly higher than those of OCDFs. There are differences between urban/industrial and rural background air levels, representing roughly 5 times higher for those ones. It seems that performance of the PUF duplicates, 4 or 2 months of exposure time, are in good agreement.

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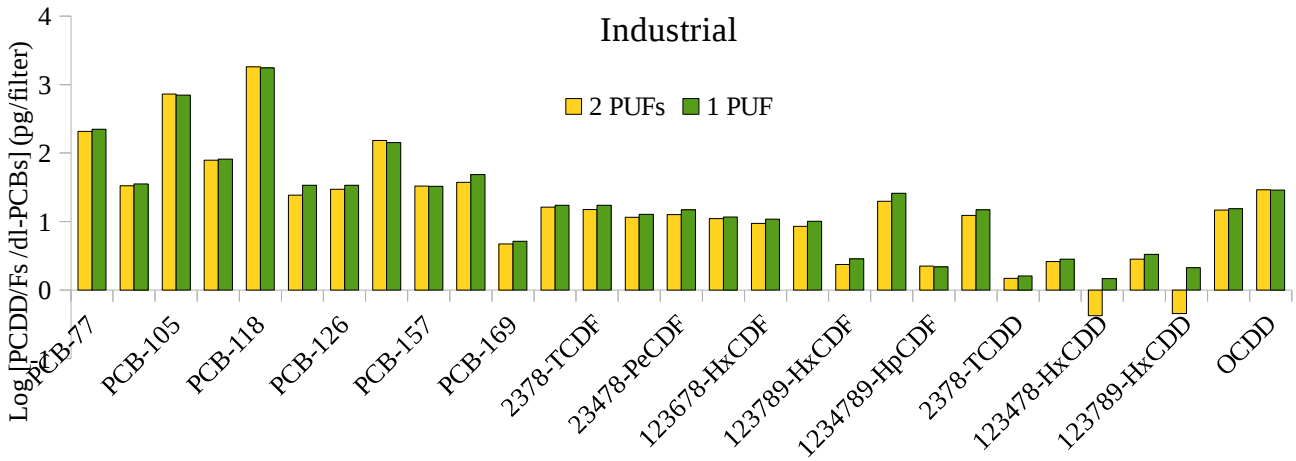

Figure 3: Comparison between two samples, one PUF exposure for 4 months and another for 2 months each PUF at Industrial site.

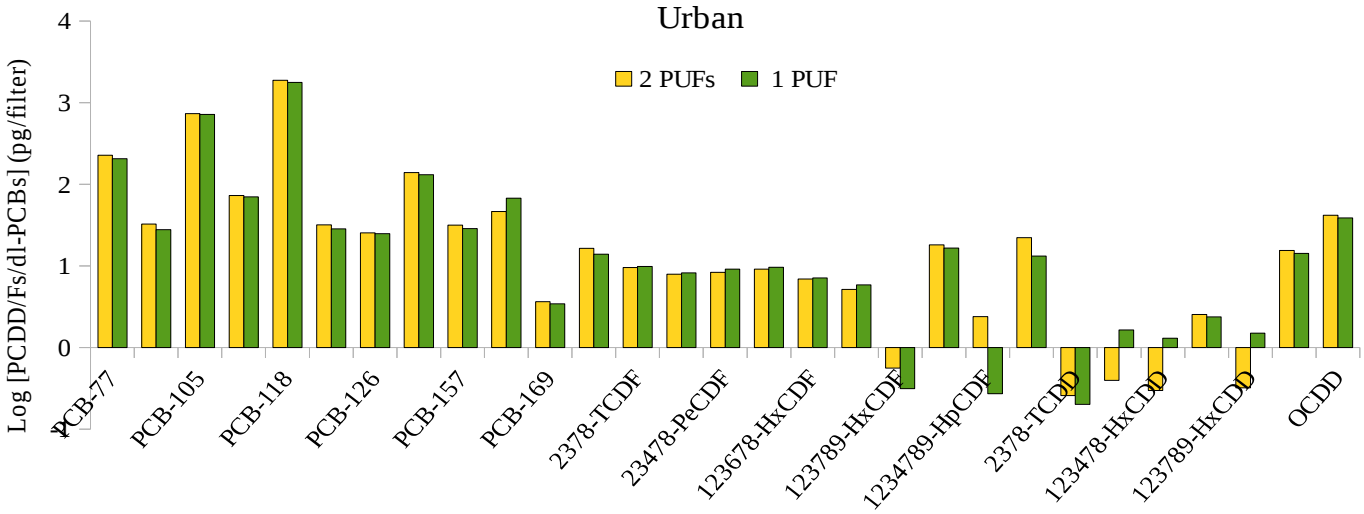

Figure 4: Comparison between two samples, one PUF deployed for 4 months and another for 2 months each PUF at Urban site.x