

PASSIVE AIR SAMPLING OF POLYCHLORINATED BIPHENYLS (PCBs) AND POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN BRAZILIAN TROPICAL AND SUBTROPICAL MOUNTAINS

R.O. Meire¹, S.C. Lee², J.P.M. Torres¹; T. Harner²

¹Instituto de Biofísica Carlos Chagas Filho / Universidade Federal do Rio de Janeiro, Brazil.

²Atmospheric Science & Technology Directorate, Environment Canada, Toronto, Canada.

Introduction:

Over the last decade, mountain areas have been receiving more concern about organic pollution due to atmospheric transport and deposition processes. Similar to the polar regions these areas are considered some of the most pristine and remote ecosystems worldwide¹. However, mountains and associated highlands are subject to the atmospheric deposition of Persistent Toxic Substances (PTS) that include polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and several organochlorine pesticides. Generally, PTS can be found in remote areas far removed from their sources but still display some level of toxicity. Their long-range transport from emission sources is controlled by climate and geographical parameters like orographic winds, high precipitation rates and low temperatures². In tropical and subtropical mountain regions, it is believed that the precipitation rates and re-emissions from soils could have an important role in the atmospheric deposition of organic pollutants.

According to the South America United Nations Environment Programme (UNEP) Persistent Toxic Substances regional report, the massive use of PCBs in South America is derived mainly from industrial and domestic electric transformer oil usage (Askarel)³. Historically, Brazil is one of the highest PCB consumers in South America accounting for around 6.7% of the total amount of Aroclor used globally⁴. Although there is still a huge knowledge gap regarding the fate of PCBs in the majority of the South American countries, some studies have investigated the presence of PCBs and trends in abiotic and biotic environmental matrices^{5,6}. However, only a few studies have focused on PCBs in remote and pristine areas where it is believed that atmospheric deposition is the main transport process of these semi-volatile compounds⁷.

PBDEs are considered emerging pollutants and were recently included in the Stockholm Convention on Persistent Organic Pollutants (POPs) for production and emissions regulation (www.pops.int). PBDEs have been extensively used as flame retardants worldwide in a variety of commercial products such as plastics, electronic devices and furnishing foams, to name a few⁸. Similar to other POPs, PBDEs are environmentally persistent with a high bioaccumulation potential, indicating an increased exposure risk to both humans and sensitive ecosystems. PBDEs are susceptible to regional-scale atmospheric transport and can be deposited in remote areas such as mountains and highlands. Although some recent studies have highlighted the presence of PBDEs along the Brazilian environmental coast⁸, there is limited information on the atmospheric transport of PBDEs for South American countries. This is the first study in Brazil to investigate PCBs and PBDEs in air along vertical (altitudinal) gradients and seasonal trends.

Material and Methods:

Study of Area: This work included two National Parks situated in the southeastern (National Park of *Serra dos Orgãos* – 22°26'56''S; 42°59'05''W – Rio de Janeiro State) and the southern (National Park of *São Joaquim* – 28°00'49''S; 49°35'17''W – Santa Catarina State) parts of Brazil with sampling conducted during 2007 and 2008.

Sample Preparation: Prior to exposure, PUF disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm²; mass, 4.40g; volume, 207 cm³; density, 0.0213 g cm³; Tisch Environmental, Village of Cleaves, Ohio) were pre-cleaned by washing with water and then Soxhlet extraction in acetone for 24 h, followed by petroleum ether (PE) for 24 h and fortified with seven deuration compounds (*d*₆- γ -hexachlorocyclohexane and ¹³C-labelled PCB congeners 3, 9, 15, and 32, and native PCB congeners 30, 107 and 198). Work was carried out at the Hazardous Air Pollutants (HAPs) Laboratory, Thomson Laboratories, Environment Canada, in

Toronto. Prior to and after sample collection and during shipping, PUF disks were stored in solvent-cleaned, 1-L amber glass jars having Teflon-lined lids⁹.

Deployment: For each National Park, eight PUF samplers were deployed (two samplers per site) at four background sites over the winter and summer periods for approximately 90 days each (Table 1). The samples were deployed along a vertical gradient (with ~500 m of altitudinal distance between them) and mounted in open areas to ensure no obstruction airflow. Field blanks were deployed once during each season for the two National Parks involved (n=4 in total). Meteorological data was compiled from the Brazilian National Institute of Meteorology (INMET) which has meteorology instruments fixed along the surrounding area of each National Park. The mean temperatures during winter and summer deployment are shown below (Table 1).

Table 1: Site and sampling information.

Sampling Sites	Altitude m a.s.l.	Seasonal Period	Latitude/Longitude	Exposure Time (days)	Mean Temp. (Celsius)	Sample Rate (R) (m ³ /day)
Serra dos Órgãos National Park – Rio de Janeiro State						
Guapimirim	400	Winter/summer	22°29'39"S/43°00'03"W	90 / 112	19.2 / 21.0	2.0- 3.5
Teresópolis	1000	Winter/summer	22°27'05"S/43°00'05"W	90 / 112	17.2 / 19.0	1.4- 1.9
Abrigo 3	1700	Winter/summer	22°27'07"S/43°01'11"W	90 / 112	14.9 / 16.7	1.4- 2.0
P. Sino	2200	Winter/summer	22°27'24"S/43°01'42"W	90 / 112	11.2 / 13.0	4.8- 7.8
São Joaquim National Park - Santa Catarina State						
Chapadão	600	Winter/summer	28°11'27"S/49°23'32"W	89 / 97	9.9 / 13.6	4.4- 6.4
Urubici	1000	Winter/summer	28°00'49"S/49°35'17"W	89 / 98	8.9 / 12.6	1.7- 3.3
Rio Pelotas	1500	Winter/summer	28°07'51"S/49°29'20"W	89 / 97	7.2 / 10.9	1.9- 3.7
P. Furada	1800	Winter/summer	28°07'32"S/49°29'24"W	89 / 97	6.2 / 9.9	4.3- 7.1

Extraction and Analysis: PUF disk samples were extracted by Soxhlet in PE for 20-24 hrs. Laboratory blanks (n=8 in total) were also collected periodically and involved Soxhlet extraction of 350 mL of PE. All extracts were concentrated to 1.0 mL by rotary evaporation and exchanged to isooctane with a final volume of 0.5 mL. Extracts were analyzed for a suite of target compounds that included polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). Samples were screened for 48 PCBs: di PCBs -8; tri PCBs -17 -18, -16/32, -28, -31, -33, -37; tetra PCBs -42, -44, -49, -52, -56/60, -66, -70, -74; penta PCBs -87, -95, -99, -101, -110, -114, -118, -123; hexa PCBs -128, -137, -138, -149, -151, -153, -156, -157; hepta PCBs -171, 174, -177, -180, -183, -185, -187; octa PCBs -195, -194, -199, -200, -203; nona PCBs -207, -206; deca PCBs -209; and 14 PBDEs congeners: tri BDEs -17, -28; tetra BDEs -47, -66, -71; penta BDEs -85, -99, -100; hexa BDEs -138, -153, -154; hepta BDEs -183, -190; Deca BDEs-209.

Prior to analysis, extracts were cleaned-up on an open column filled with 0.75 g of deactivated acid silica (10%) and topped with 0.20 g of sodium sulphate, and then eluted with 15 mL of dichloromethane/methanol mixture (9:1). The cleaned extracts were reduced by nitrogen blow-down to a volume of 500 µL and solvent-exchanged to isooctane. Mirex (100 ng) was added as an internal standard for volume correction to all sample extracts prior to analysis. The instrumental analysis of the extracts was carried out by gas chromatography mass spectrometry (Agilent 6890, 5973 CG-MS) using electron impact (EI) and negative chemical ionization (NCI) for PCBs and PBDEs, respectively. Operating conditions for both EI and NCI and the selection of target/qualifier ions are described previously^{9,10}. Limits of detection (LOD) in air samples were defined as the average of field blanks (n= 4) plus three times the standard deviations. When the target compounds were not detected in blanks, one-half of the instrumental detection limits (IDL) value was substituted for the LOD⁹. The IDL is based on the response of the lowest calibration standard and extrapolating this concentration to one that would generate a signal:noise of 3:1.^{9,10}

Results and Discussions

Previous studies have calibrated the PUF disk sampler and described the estimation of the air sample volumes (m^3) based on the loss of depuration compounds (*d6- γ* -hexachlorocyclohexane; ^{13}C -labelled PCB congeners 3, 9, 15, 32; and native PCB congeners 30, 107, and 198) which were spiked onto each PUF disk before deployment^{10, 11}. Dividing the air sampling volumes by the deployment period yields the uptake sampling rates (R). Based on earlier calibration studies, the R value of PUF disk samplers ranges from 2.5 to 5 $m^3 \cdot day^{-1}$ with a mean value of about 3.5 to 4 $m^3 \cdot day^{-1}$ ^{9, 11}. The average value of R value for all samples collected in this study was 3.6 $m^3 \cdot day^{-1}$ which is in good agreement with previous estimations^{9, 11, 12}. A few high R values, such as 7.1 and 7.8 $m^3 \cdot day^{-1}$, were reported for the highest elevation sites at Pedra Furada (1800 m a.s.l.) and Pedra do Sino (2200 m a.s.l.), respectively, and may be attributed to high wind speed conditions at these two sites¹² (Table 1).

For PCBs, the mean blanks values ranged from 16 pg (PCB-156) to 0.53 ng (PCB-95) for laboratory blanks ($n=8$) and 0.13 pg (PCB-177) to 0.66 pg (PCB-101) for field blanks ($n=4$). For PBDEs, the laboratory blanks values ranged from 4 pg (BDE-85) and 5 pg (BDE-17) to higher levels of 0.5 ng (BDE-99) and 2.4 ng (BDE-47). Similarly, field blanks ranged from below 10 pg (BDE-153 and -154) to high values above 0.5 ng (BDE-47 and -99). Among the 48 monitoring PCBs, only 30 congeners were consistently quantified in all sample extracts that included: PCB-8, -16, -17, -18, -28, -31, -32, -33, -37, -42, -44, -49, -52, -56, -60, -66, -70, -74, -87, -95, -99, -101, -110, -118, -123, -137, -138, -149, -151, -153. Generally, all monitored PBDEs congeners were below the LOD. LOD values for PBDEs were: 0.01 $pg \cdot m^{-3}$ (BDE-71, -85, -138, -183 and -190); 0.1 $pg \cdot m^{-3}$ (BDE-153); 0.2 $pg \cdot m^{-3}$ (BDE-154); 0.3 $pg \cdot m^{-3}$ (BDE-17 and BDE-66); 0.5 $pg \cdot m^{-3}$ (BDE-28); 1.2 (BDE-100); 3.6 $pg \cdot m^{-3}$ (BDE-99); and 13 $pg \cdot m^{-3}$ (BDE-47). Results for PBDEs are not discussed further in this manuscript.

Table 2 – Air concentrations of PCBs ($pg \cdot m^{-3}$) at the two National Parks in winter versus summer and at different altitudes.

Code	Altitude	Seasonal Period	Sampling Site	Site Type	$\Sigma_{(30)}PCBs^I$
National Park of Serra dos Órgãos - Rio de Janeiro St.					
PNSO#(9,10)	400 ^a	Winter	Guapimirim	Suburban	450(280-620) ^b
PNSO#(11,12)	1100	Winter	Teresópolis	Urban	395(330-460)
PNSO#(15,16)	1700	Winter	Antigo abrigo	Remote	209 (208-210)
PNSO#(13,14)	2200	Winter	Pedra do Sino	Remote	84(68-100)
PNSO#(27,28)	400	Summer	Guapimirim	Suburban	338(336-340)
PNSO#(25,26)	1100	Summer	Teresópolis	Urban	215(190-240)
PNSO#(31,32)	1700	Summer	Antigo abrigo	Remote	305(180-430)
PNSO#(29,30)	2200	Summer	Pedra do Sino	Remote	170(120-220)
National Park of São Joaquim - Santa Catarina St.					
PNSJ#(3,4)	600	Winter	Chapadão	Rural	104(100-109)
PNSJ#(1,2)	1000	Winter	Urubici	Rural	184(144-225)
PNSJ#(5,6)	1500	Winter	Rio Pelotas	Remote	177(125-230)
PNSJ#(7,8)	1800	Winter	Pedra furada	Remote	172(125-220)
PNSJ#(19,20)	600	Summer	Chapadão	Rural	43(33-54)
PNSJ#(17,18)	1000	Summer	Urubici	Rural	92(52-130)
PNSJ#(22,24)	1500	Summer	Rio Pelotas	Remote	38(38-39)
PNSJ#(21,23)	1800	Summer	Pedra furada	Remote	25(25-25)

a- Meters above sea level; *b*- mean and range values ($pg \cdot m^{-3}$); *I*- $\Sigma_{(30)}PCBs$: -8, -16, -17, -18, -28, -31, -32, -33, -37, -42, -44, -49, -52, -56, -60, -66, -70, -74, -87, -95, -99, -101, -110, -118, -123, -137, -138, -149, -151, -153.

The air concentrations of PCBs at the two national parks ranged from a few tens to a few hundreds of picograms per cubic meters (Table 2) with highest contributions from the tri-PCBs (-17, -18, -28, -31, -33, -16/32 and -37) and tetra-PCBs congeners (-42, -44, -49, -52, -66, -70 and -74). These PCB air concentrations are relatively high compared with other studies in other mountain regions^{11,13}. The highest PCB concentrations were at the lower altitude sites and likely associated with local sources of emissions. A Spearman's test showed a strong negative correlation between concentration of PCBs in air and altitude ($r^2 = -0.8783$, $p < 0.05$). Previous studies of Jaward et al., (2005) and Estellano et al., (2008) have also reported similar altitudinal trends of PCBs at high mountains sites in Italian Alps (700- 1790 masl) and Bolivian Andes (1820- 5192 masl), respectively^{13,14}.

No clear differences were observed between summer/winter air concentrations of PCBs at the study sites. Although most sites exhibited lower concentrations during the summer period, additional seasonal deployments are required to make definitive conclusions. The use of air parcel back trajectories to interpret transport to sites is complicated due to the relatively small scale of the study and the complex meteorology (vertical air flows) in mountainous regions that are not accounted for by the trajectory models.

The results of this study are important in showing that even remote, high elevation mountain sites in Brazil are impacted by local/regional PCB emissions associated with continued emissions from old PCB stocks and environmental cycling of legacy PCBs.

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