

## SEASONAL AND ALTITUDINAL VARIATIONS OF LEGACY AND CURRENT-USE PESTICIDES IN THE BRAZILIAN TROPICAL AND SUBTROPICAL MOUNTAINS

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### Introduction:

According to the last South America PTS regional report, the huge use of pesticides in South America was highlighted mainly for agriculture and sanitary uses<sup>1</sup>. Historically, South America was one of the continents that experienced high use of pesticides in the past which may include DDT, lindane and toxaphene. Both Brazil and Argentina are considered two of the highest production and importing countries of legacy pesticides in South America. Especially in Brazil, it is estimated that 80 tons of DDT production was used and imported by other South American countries till 1980's and also about more than 30 tons were imported in the same period<sup>2</sup>. Although there is a huge knowledge gap of the PTS fate processes for the majority of the South American countries, different studies have investigated the presence and trends of these organic pollutants in many abiotic and biotic environmental matrices<sup>3,4,5</sup>. Nevertheless, just a few of them are focused on remote or pristine areas where it is believed that atmospheric deposition is the main transport of these semi-volatile compounds<sup>6</sup>.

Over the last decade, mountainous areas have been receiving more concern about organic pollution due to atmospheric transport and deposition processes. Similar to the polar regions, mountainous areas are considered one of the most pristine and remote ecosystems worldwide<sup>7</sup>. However, just as with polar regions, mountains and uplands are subject to the atmospheric deposition of PTS and others emerging pollutants which include several pesticides compounds. Generally, PTS are environmentally persistent substances that can be found in remote areas far removed from their sources and still display some level of toxicity. Their transport from emission sources are controlled by climate and geographical parameters like mountain winds, precipitation rates and low temperatures<sup>8</sup>. In tropical and subtropical mountains areas, it is believed that the precipitation rates and also the soil re-emissions could have an important role in the atmospheric deposition of organic pollutants. Nowadays, the application of current-use pesticides (CUPs) is also a cause for concern in many different countries. Even though it is believed that CUPs are relatively more water soluble, less persistent and less bioaccumulative than legacy organochlorine pesticides, these emerging pollutants still represent an increased risk exposure to both humans and sensitive ecosystems<sup>9</sup>. Moreover, some CUPs are susceptible to regional-scale atmospheric transport that is enabling them to be deposited in remote areas such as mountains and uplands. In South America, especially in Brazil, many of these pesticides are still legally permitted for commercial use on different agricultural crops.

Passive air samplers consisting of polyurethane foam (PUF) disks were deployed over winter and summer periods following altitudinal transects in two Brazilian mountains to investigate legacy and current-use pesticides. This work is a subproject of the *Global Atmospheric Passive Sampling* (GAPs) Network that operates at more than 50 global monitoring sites annually for Persistent Toxic Substances (PTS) since 2004. This research is motivated by the lack of understanding of PTS fate processes in the South American remote areas, mainly in the mountainous regions of Brazil. The present work makes a first screening of legacy and current-use pesticides in the atmosphere along vertical gradients in two National Parks situated in the south and southeast part of Brazil during 2007 and 2008 and discusses the possible seasonal trends and levels as well.

### Material and Methods:

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

**Sample Preparation:** Prior to exposure, PUF disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm<sup>2</sup>; mass, 4.40 g; volume, 207 cm<sup>3</sup>; density, 0.0213 g cm<sup>3</sup>; 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 for 24 h and fortified with seven deuration compounds (*d*<sub>6</sub>- $\gamma$ -hexachlorocyclohexane and <sup>13</sup>C-labelled PCB-3, 9, 15, and 32, and PCB-30, 107 and 198) at the Hazardous Air Pollutants 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 lids<sup>10</sup>. **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 following a vertical gradient (500 m of altitudinal distance between them) and mounted at open areas with no obstruction airflow. Four field blanks were deployed once at each seasonal period for the two National Parks involved. The meteorological data as temperature variations were compiled from the Brazilian National Institute of Meteorology (INMET) which has meteorology instruments fixed along the surrounding area of each National Park investigated. The mean temperatures during winter and summer deployment are shown below (Table 1).

Table 1: Deployment description of sampling site locations, seasonal periods and latitude/longitude. Details of exposure time, mean temperature during winter /summer periods and sample rate range for PUF samplers are reported as well.

Sampling Sites	Altitude m a.s.l.	Seasonal Period	Latitude/Longitude	Exposure Time (days)	Mean Temp. (Celsius)	Sample Rate (R) (m <sup>3</sup> /day)
Serra dos Órgãos National Park – Rio de Janeiro State						
Guapimirim	400	Winter/summer	22°29'39"S/43°00'03"W	90 / 112	20.8 / 22.6	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	13.6 / 15.4	1.4- 2.0
Pedra do Sino	2200	Winter/summer	22°27'24"S/43°01'42"W	90 / 112	11.6 / 12.4	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	11.3 / 15.0	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	5.9 / 9.6	1.9- 3.7
Pedra Furada	1800	Winter/summer	28°07'32"S/49°29'24"W	89 / 97	4.1 / 7.8	4.3- 7.1

**Extraction and Analysis:** The PUF disk extractions were analyzed for a suite of target compounds that included organochlorines (OCPs) and organophosphates (OPPs). Samples were screening for 20 OCPs:  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  -HCHs, aldrin, dieldrin, heptachlor, heptachlor epoxide, *cis*-chlordane, *trans*-chlordane, *trans*-nonachlor, endosulfan I, endosulfan II, endosulfan sulfate, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT; and for three OPPs: chlorpyrifos, malathion and dimethoate. Details of sample extraction and clean-up are presented elsewhere<sup>10,11</sup>. Briefly, the PUF disk samples were Soxhlet extracted over 20 hours with 250 mL of petroleum ether. Afterward, the 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 sulfate, and then eluted with 15 mL of dichloromethane/methanol mixture (9:1). The cleaned extracts were reduced by rotary evaporation and nitrogen blow-down to a volume of 500  $\mu$ L and solvent exchanged to isoctane. 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 negative chemical ionization (NCI). The both conditions of the NCI analysis and selection of target/qualifier ions are described elsewhere<sup>9,10</sup>. Limits of detection (LOD) in air

samples were defined as average of field blanks (n= 4) plus three time 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 LOD<sup>11</sup>. The IDL calculation is also defined elsewhere<sup>11,12</sup>.

### Results and Discussions:

In this study, both laboratory blanks (n= 8) and field blanks (n= 4) were below the IDL values for OCPs and OPPs. Generally, all target compounds were detected for the majority of the sample extracts, except for:  $\beta$ ,  $\delta$  -HCHs, heptachlor, *cis-and, trans* -chlordanes, *o,p'*-DDE *o,p'*-DDD *p,p'*-DDD *p,p'*-DDT (OCPs); malathion and dimethoate (OPPs) which were detected below 30% of the total analyzed samples and therefore, the results are not shown in this paper. The method recoveries for OCPs and OPPs were previously been assessed in the same laboratory and also are presented elsewhere<sup>9,10</sup>.

Table 2: Comparison of range and mean concentrations (pg.m<sup>-3</sup>) in air for pesticides in the two National Parks investigated following altitudinal transects

Code	Altitude	Period	$\Sigma$ HCH <sup>1</sup>	$\Sigma$ Endo <sup>2</sup>	Chlorp.	$\Sigma$ DDT <sup>3</sup>	Dield.	Heptx.
Serra dos Órgãos National Park - Rio de Janeiro State								
PNSO(9,10)	400 <sup>a</sup>	Winter	22 <sup>b</sup> ±1.3 <sup>c</sup>	50 ±9	8 ±0.1	7 ±0.6	7 ±1.7	4 ±0.7
PNSO(11,12)	1000	Winter	34 ±2.4	148 ±13	4 ±0.2	44 ±18	6 ±9	8 ±1.7
PNSO(15,16)	1700	Winter	21 ±5	195 ±14	4.5 ±0.5	3 ±4	ND	ND
PNSO(13,14)	2200	Winter	21 ±1	241 ±19	12 ±1	2 ±2	9 ±5	3 ±0.3
min- max			17.4 - 36	50.3 - 241	3.7 - 13	ND- 57	ND- 13	ND- 10
PNSO(27,28)	400	Summer	20 ±2	432 ±68	11 ±0.3	21 ±17	9 ±1	5 ±1
PNSO(25,26)	1000	Summer	16 ±2	914 ±135	6 ±1	6 ±0.6	8 ±0.1	4 ±0.2
PNSO(31,32)	1700	Summer	19 ±15	2167 ±1555	6 ±2	5 ±7	5 ±7	4 ±6
PNSO(29,30)	2200	Summer	22 ±12	3810 ±2520	30 ±7	4 ±2	13 ±9	10 ±6
min- max			8.3 - 30	384 - 5592	4.4 - 35	ND- 33	ND- 19	ND- 14
São Joaquim National Park - Santa Catarina State								
PNSJ(19,20)	600	Winter	10 ±0.2	45 ±3	53 ±4	7 ±7	ND	ND
PNSJ(17,18)	1000	Winter	20 ±10	87 ±21	35 ±7	3 ±3	ND	ND
PNSJ(22,24)	1500	Winter	23 ±3	205 ±29	19 ±1	11 ±6	5 ±7	ND
PNSJ(21,23)	1800	Winter	15 ±1	106 ±7	68 ±13	3 ±0.2	4 ±3	ND
min- max			9.9 - 26	42.6 - 226	18 - 77	ND- 16	ND- 10	ND
PNSJ(3,4)	600	Summer	8 ±4	339 ±134	19 ±1	3 ±4	ND	ND
PNSJ(1,2)	1000	Summer	7 ±1	685 ±235	123 ±14	6 ±9	ND	ND
PNSJ(5,6)	1500	Summer	4 ±1	929 ±61	16 ±0.4	1.4 ±1.9	ND	ND
PNSJ(7,8)	1800	Summer	6 ±3	1331 ±33	42 ±2	4 ±6	3 ±0.3	0.9 ±1.3
min- max			3.5 - 11	244 - 1354	15 - 133	ND- 12	ND- 3	ND- 1.9

1-  $\Sigma(\alpha$ -HCH+  $\gamma$ -HCH); 2-  $\Sigma$ (EndoI+II+SO<sub>4</sub>); 3-  $\Sigma(o,p'$ -DDT+ *p,p'*-DDE); a- Meters above sea level; b- Mean (pg.m<sup>-3</sup>); c- Standard Deviation; ND - Not detectable.

In order to convert the amount of a target compound quantified in a PUF disk extract (in pg) into a volumetric air concentration, we need to divide it by the air sampling volumes (m<sup>3</sup>). The air sampling volumes are estimated based on the loss of depuration compounds (*d*<sub>6</sub>- $\gamma$ -hexachlorocyclohexane and <sup>13</sup>C-labelled PCB-3, 9, 15, 32, and PCB-32,

107, and 198) which were spiked on each PUF disk before deployment<sup>10,11</sup>. Dividing the air sampling volumes by the deployment period yields the uptake sampling rates ( $R$ ). The average of  $R$  value for all samples was  $3.6 \text{ m}^3 \cdot \text{day}^{-1}$  which is considered in good agreement with previous studies<sup>9,11</sup>. However, some high  $R$  values as 7.1 and  $7.8 \text{ m}^3 \cdot \text{day}^{-1}$  were reported for highest elevations at Pedra Furada (1800 m a.s.l.) and Pedra do Sino (2200 m a.s.l.), respectively, suggesting probably high wind speed conditions at these two sites (Table 1). Concentration in air were dominated basically by current-use insecticides as endosulfans (and its metabolites) and chlorpyrifos. The highest concentrations measured for total endosulfans (endosulfan I + endosulfan II + endosulfan sulfate) and chlorpyrifos were 5592 and  $133 \text{ pg} \cdot \text{m}^{-3}$ , respectively (table 2). For others target pesticides, the highest concentration values reported for the total DDTs (*o,p'*-DDT and *p,p'*-DDE), total HCHs ( $\alpha$  and  $\gamma$  -HCHs), dieldrin and heptachlor epoxide were 57, 36, 19 and  $14 \text{ pg} \cdot \text{m}^{-3}$ , respectively.

Generally, the seasonal variations did not show a clearly trends for the pesticides air concentrations, except for endosulfans that reach approximately one order of magnitude higher of the atmospheric concentrations during the summer period compared with the winter season for all investigated sites. Chlorpyrifos also showed in some cases highest concentrations during the summer period that probably indicate a seasonal application of this current-use pesticide. Compared with results reported for sites within the GAPS Network, the concentrations of endosulfans in air reported in this work are considered very high atmospheric levels similar to those of the global agriculture sites ( $>1000 \text{ pg} \cdot \text{m}^{-3}$ )<sup>11,12</sup>. The high air concentrations were found mainly at remote elevated sites that indicate a long range atmospheric transport of endosulfans probably from lowland sources such as agriculture activities and soil re-emissions. Furthermore, a Pearson's test reported a strong positive correlation between concentrations of total endosulfans in air and altitude ( $r^2 = 0.962$ ). In a previous study, Estellano et al., (2008) have also reported a similar altitudinal trends in the mountainous region of Bolivia<sup>13</sup>. These results reinforce the potential of mountainous regions as conversion zones for some semi-volatile current-use pesticides and the concern about the high levels of endosulfans that continue to have wide agriculture use globally, especially in the South American countries.

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