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Air contamination by legacy and current-use pesticides in Brazilian mountains: An overview of national regulations by monitoring pollutant presence in pristine areas☆

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ABSTRACT

In the last decades, research regarding the dynamics of pesticides has grown, even in remote regions. Due to long-range atmospheric transport, environmental persistence and toxicological potential of organochlorine pesticides (OCPs), similar characteristics of current-use pesticides (CUPs) and their massive use in Brazil, these contaminants have become a major concern for environmental and human life. Thus, this study aimed to evaluate subgroups or individual chemicals of OCPs and CUPs, which could have travelled over two Conservation Unit sites in the Rio de Janeiro state. The study was carried out for 24 months, (2013–2015), in Itatiaia National Park (INP) and in the Serra dos Órgãos National Park (SONP), at ~2400 and ~2200 meters above sea level, respectively. The study was based on atmospheric passive sampling (polyurethane foam disks). Target pesticides were detected by means of gas chromatography device coupled with mass spectrometry (GC-MS). Significantly higher concentrations were measured in SONP when compared to INP. However, in broad terms, the contamination profile was quite similar for both national parks: The highest concentrations of endosulfan (INP - 1275 pg m^{-3} and SONP - 3202 pg m^{-3}) were followed by cypermethrin (INP - 148 pg m^{-3} and SONP - 881 pg m^{-3}) and chlorpyrifos (INP - 67 pg m^{-3} and SONP - 270 pg m^{-3}). In agreement with previous studies, the atmospheric concentrations of legacy OCPs showed background air levels. The decrease of endosulfan over the years was highlighted with a parallel increase of chlorpyrifos, suggesting a collateral effect of the national bias of permissive and massive use of agrochemicals. CUPs seemed to behave like pseudo-persistent pollutants (pseudo-POPs). This is the first report of atmospheric concentrations of pyrethroids in Brazilian mountain regions, and possibly the first to investigate them in the air in South America or in any mountain region in the world.

1. Introduction

Since the 1960s, several research groups, from all over the world, turned their attention to an environmental concern raised by Rachel Carson in the beginning of the decade. The massive use of organohalogen compounds – in that case, dichloro-diphenyl-trichloroethane (DDT) – was pointed out as a major threat to environmental and wildlife health (Carson, 1962). Therefore, following the 'boom' of scientific work – which described many chemicals as persistent, bioaccumulative, toxic and prone to long-range spreading – in 2001 many countries signed a global treaty at the Stockholm Convention, to protect human and environmental health from Persistent Organic Pollutants (POP) (UNEP, 2001). These restrictive measures went into effect in 2004, initially listing twelve chemicals. Nowadays the Stockholm Convention counts up to 152 signatory countries, includes 33 restricted chemicals with their respective related compounds and keeps working to list any substance proved to behave like POP (UNEP, 2015). Nonetheless, it is a long journey for the scientific community to establish a comprehensive understanding of all chemicals and provide enough data to support restrictive measures – when new chemicals are continually released by industries.

Even though Brazil is among the first signatories of the Stockholm Convention, it is historically affected by the massive use of

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such contaminants and national regulations still fail to prohibit many other potentially harmful substances (Pelaez et al., 2010). Since before the Green Revolution in Brazil, organochlorine pesticides (OCPs) were widely used to fight vectors of tropical endemic diseases (Almeida et al., 2007). Moreover, for agricultural production growth, Brazil has adopted permissive laws in order to expand its agribusiness. These out-of-date legislations, such as the National Program of Agricultural Defensives, implemented in 1975 – that restrained granting credit to the purchase of agrochemicals – enabled quick registration of chemicals and boosted their trade, even when many of them were already banned in other countries (Pelaez et al., 2015). As a result, agrochemicals became extremely important in Brazilian agricultural development.

Therefore, since 2008 Brazil has stood as the leader of the agrochemical consumption. In 2010, Brazil held almost 20% of the agrochemical global market and, according to the Brazilian Association of Collective Health, in 2012, 823,000 tons of agrochemicals were commercialized in the country (Carneiro et al., 2015). Nowadays, in Brazil, 525 active ingredients are allowed to be used in agrochemicals with different purposes. Many of them are already banned or in the process of being banned in the Europe Union (EU); e.g. acephate and atrazine are, respectively, the third and seventh most sold active ingredients in the Brazilian market (ANVISA, 2018). This could be taken as a consequence of more restrictive measures adopted in the EU, since these industries would transfer their “final life” production to less restrictive markets, such as Brazil (Pelaez et al., 2015).

The worldwide application of current-use pesticides (CUPs) is supported by a belief that CUPs are unlikely to persist in the environment to the same extent as OCPs, due to the belief that they are relatively more water soluble, less bioaccumulative and less persistent (Gouin et al., 2008). However, considering CUPs ongoing use, for different purposes, with frequent applications – agricultural (in different production types and steps), domestic (insecticide), veterinary (on cattle and pets), sanitary (health purposes such as lice, scabies and vectors fight…) –, these contaminants can behave not only as emerging pollutants but also as “pseudo-persistent” pollutants (Gouin et al., 2008; Primost et al., 2017). Moreover, several CUPs are prone to regional-, or even long-range, atmospheric transport (Muir et al., 2004; Yao et al., 2006).

Several studies have highlighted the increase of semi-volatile organic contaminants (SVOCs) – including legacy and current-use pesticides – at remote or pristine areas, such as in the polar circles and mountains (Wania and Mackay, 1995; Van Den Brink, 1997; Kelly and Gobas, 2003; Fernández et al., 2005; Livingstone, 2005; Meire et al., 2012). Although, according to Kallenborn (2006), uplands are more impacted by such contaminants than the polar circles, due to their closer proximity to emission sources and the mountain cold-trapping effect. Furthermore, compounds with short atmospheric lifetimes are more likely to travel and deposit nearby their emission sources (Daly et al., 2007a). Mountains ridges have also been recently recognized by the Intergovernmental Panel on Climate Change as one of the most vulnerable ecosystems in the world (IPCC, 2014).

Brazilian subalpine regions have already been pointed out as extremely important sites to monitor, not only the dynamic of semi-volatile organic compounds SVOCs, but also climate changes (Meire et al., 2012; Assis and Mattos, 2016; Scarano et al., 2016). These mountain grasslands, known as *campos de altitude*, form a unique ecosystem in the Brazilian Atlantic rainforest biome. Scattered among the three major mountain chains in Brazil – Serra do Mar, Serra da Mantiqueira and Serra do Caparaó – this ecosystem is restricted in sky-islands (over 2000 meters), which enables a high occurrence of endemic species (Myers et al., 2000; Scarano, 2002; Castro, 2008). Threatened by vertical displacement, due to global warming (Behling and Safford, 2010), the *campos de altitude* were also reported to be under atmospheric levels of selected pesticides as high as in agricultural sites (Meire et al., 2012). That is not at all surprising, considering that in 2009 the Rio de Janeiro state stood out with the largest consumption per capita of agrochemicals – 11 kg ha^{-1}, while the national average was around 3.5 kg ha^{-1} – (IBGE, 2012).

Passive air samplers (PAS) are excellent tools for environmental monitoring due to the fact that they are easy to handle, cost effective and do not require an electrical supply, even considering their semiquantitative downside when compared to active air samplers (Gouin et al., 2005). Therefore, PAS such as polyurethane foam (PUF) disks, have been used worldwide to access local to global trends of several SVOCs (Jaward et al., 2004, 2005; Harner et al., 2004, 2006; Pozo et al., 2004, 2006; 2009; Liu et al., 2009; Genualdi et al., 2010). In this context, this study aimed to conduct an atmospheric air monitoring, based on PAS-PUF, of legacy and current-use pesticides at two sky-islands in Southeast Brazil, at Itatiaia and Serra dos Órgãos National Parks (INP and SONP, respectively).

2. Materials and methods

2.1. Studied area

Sampling was carried out in altitudinal grassland sites from two national parks in Southeast Brazil (Fig. 1). INP and SONP are Federal Conservation Units of Full Protection created during the thirties – 1937 and 1939 respectively – to protect their exceptional landscape and their biodiversity. Currently, INP protects an area of ~38,084 hectares and SONP protects an area of ~20,024 hectares. Both of them are part of the Biosphere Reserve of Atlantic Forest (ICMBio, 2018) and in both vegetation varies according to the altitudinal layers, with sub-montane rainforest until 500 meters, montane rainforest between 500 and 1500 meters, nebular forest from 1500 to 2000 meters and altitudinal grasslands over 2000 meters (ICMBio, 2018). These national parks shelter more than a thousand animal species, which comprise hundreds of endangered species and many endemic species as well (Castro, 2008). This biodiversity hotspot can be explained by many factors such as climate, soil, geological and vegetational formation variance and the high altitudinal amplitude of the national parks – from 600 to 2791 meters (IPN) and from 80 to 2263 meters (SONP) – (ICMBio, 2018).

2.2. Sampling

The atmospheric passive air sampling was performed with PUF. It took place over two years, from September 2013 to October 2015, with seasonal replacement of PAS-PUF approximately every 3 months. Two atmospheric passive samplers were deployed in each national park – INP = 2470 meters high (22° 22′ 26″ S/44° 42′ 11″ W); SONP = 2200 meters high (22° 27′ 24″ S/43° 01′ 42” W). Specific sampling information is given on Supporting Material (Table S1). PUF disks (14 cm diameter; 1.35 cm thickness; surface area, 365 cm^2; mass, 4.40 g; volume, 207 cm^3; density, 0.0213 g cm^{-3}) were housed in stainless-steel sampling chambers (external superior and inferior diameters of 30 cm and 20 cm, respectively), both purchased from TISCH Environmental, Cleves, Ohio, U.S.A.

2.3. QA/QC

All glassware was pre-cleaned under water, water and detergent and demineralized water. Those that could not be submitted to high

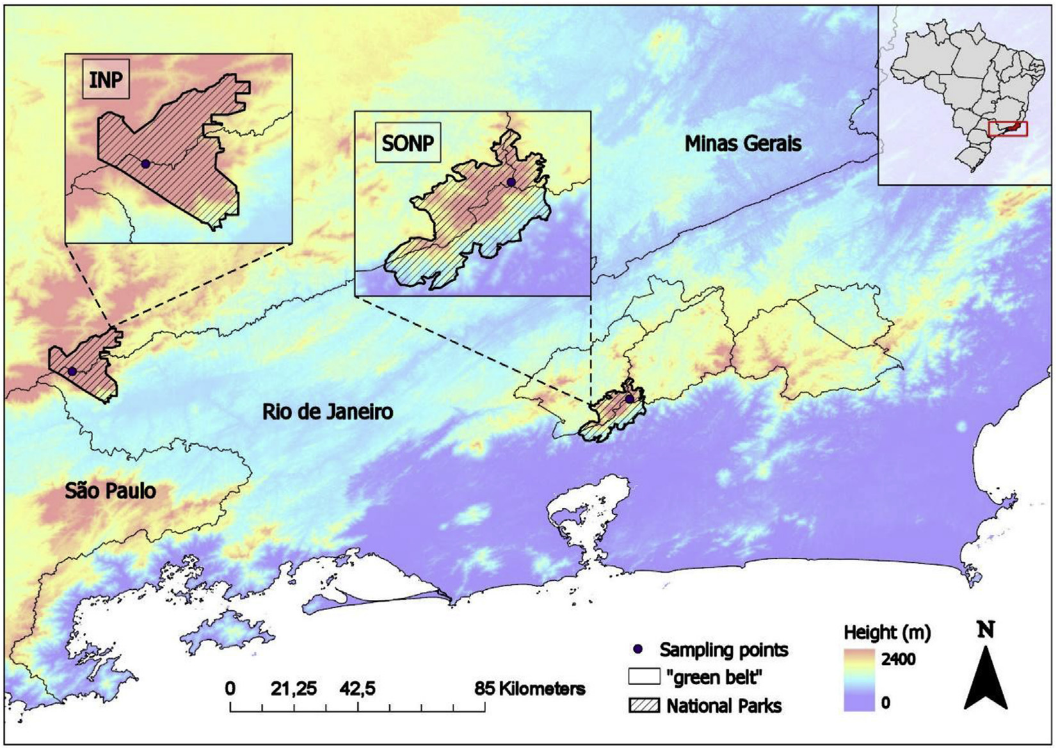

Fig. 1. Sampling points at Itatiaia (INP) and Serra dos Órgãos National Parks (SONP) in the Brazilian southeast region, highlighting their respective outline zoom and the main agricultural producers municipalities, known as the "green-belt", in Rio de Janeiro state.

temperature (400 °C overnight) were washed with acetone, dichloromethane and n-hexane (3 times each) before use. Chemical reagents such as solvents and adsorbents were all pesticide residue analysis grade. Prior to exposure, PUF disks were washed under running water. Then, they were pre-cleaned by the automatic Soxhlet system (*Buchi, Extraction system B-811*), with acetone (120 mL), followed by petroleum ether (120 mL) in the warm extraction program: 40 min extraction plus 20 min of rinsing for each solvent. The whole Soxhlet system was washed between PUF disk extraction following the same setup program as described before. Decontaminated PUF disks were stocked in pre-cleaned amber glasses and sealed with Teflon® tape prior and after field deployment. PUF disks handling was always done using pre-cleaned tongs. Stainless-steel chambers were pre-cleaned in the same way as all glassware prior to field deployment and rinsed with acetone between PUF disk replacements.

Twice a year, field blanks were deployed, for 5 min, between PUF disk samples exchange – spring/summer and autumn/winter – in each sampling site ($n = 8$). Procedural reagent blanks were performed within each analytical batch ($n = 13$) and method limit of detection (LOD) was defined as the blank's average plus three standard deviation (SD). All blanks values (Table S2; S3) and LOD (Table S4) are reported on Supporting Material. Measured concentrations were subtracted by the respective reagent blank value of its analytical batch. Recovery of sample extraction and clean-up procedure was tested for each target analyte prior to analysis (86–102%). Moreover, labelled surrogate standards (*d*6 -*α*-HCH and *d*8 - *p,p*'-DDT at 200 ng mL^{-1}) were added to each sample prior to analysis. Recovery mean values of 97% and 99% were measured for *d*6-*α*-HCH and *d*8-*p,p*'-DDT, respectively, with a maximum variation coefficient at 20%. Target pesticides concentrations were not extrapolated by recovery standard concentrations.

2.4. Extraction

After the exposure period in the field, each PUF disk was treated as a sample and extractions of chemicals were carried out exactly as in the pre-cleaning step. Extracts were then concentrated, still in the Soxhlet system, under a continuous nitrogen flow, in a reduced temperature (half of the previous program setting), for 15 min. Concentrated extracts were then submitted to a clean-up step through an open chromatographic column filled with 1 g of activated silica gel (~5 cm) and a thin layer of sodium sulphate at the ends. Silica columns were pre-washed/activated with 10 mL of n-hexane and the extracts were eluted with 15 mL of n-hexane:dichloromethane (60:40 v/v). Cleaned extracts were dried under nitrogen smooth flow and resuspended in 100 μL of tetrachloro-m-xylene (TCMX - 100 ng mL^{-1}), used as an internal standard for volume correction to all sample extracts prior to instrumental analysis.

2.5. Instrumental analysis

Gas chromatography (7890A) coupled with electron-capture negative ion mass spectrometry (5975C) (GC/ECNI-MS), both Agilent Technologies (Palo Alto, CA, U.S.A.), was used to trace legacy and current-use target pesticides. GC/NCI-MS operated on selected ion monitoring (SIM) mode with a HP-5MS capillary column (60m × 250 μm x 0.25 μm film thickness) containing methyl 5% phenyl polysiloxane from Quadrex Corporation (Woodbridge, U.S.A.). Injections (2 μL) were made at 265 °C, under splitless mode. Helium and methane were used as carrier (1.3 mL per min. constant flow) and as reaction gases, respectively. Transfer line, source and quadrupole were set at 250 °C, 150 °C and 150 °C, respectively. The column temperature program was the only distinguished parameter between legacy and current-use pesticides measurement. For legacy OCPs, standard solution Pesticide Mix 1 from AccuStandard (New Haven, U.S.A.): hexachlorobenzene (HCB); hexachlorocyclohexane (α, β, γ and δ-HCH); *cis* and *trans*-chlordane; oxychlordane; *o,p'*-1,1-dichloro-2,2-bis(p-chlorophenyl)-ethylene (DDE) and *p,p'*-DDE; *o,p'*- dichloro diphenyl dichloroethane (DDD) and *p,p'*-DDD; *o,p'*- dichloro diphenyl trichloroethane (DDT) and *p,p'*-DDT; aldrin; dieldrin; endrin; isodrin; α and β-endosulfan; heptachlor; *cis* and *trans*-heptachlor epoxide; methoxychlor and mirex, the column was heated from 90 °C (1 min hold time) at 10 °C per min to 150 °C with subsequent heating at 3 °C per min to 240 °C (5 min hold time) and again 10 °C per min to 300 °C and further hold time of 8 min. The same parameters were used to quantify the labelled standards (*d*6 -α-HCH and *d*8 - *p,p'*-DDT) purchased from Cambridge Isotope Laboratories (Massachusetts, U.S.A.). For the CUPs, a mixture of single standards was used (Absolute Standards, Inc. U.S.A.): chlorpyrifos; chlorpyrifos methyl; endosulfan sulphate (SO_4); *cis* and *trans*-permethrin; *cis*1, *cis*2 and *trans*1, *trans*2-cypermethrin. In this case, the column was heated from 90 °C (1 min hold time) at 20 °C per min to 180 °C with subsequent heating at 5 °C per min to 280 °C (5 min hold time) then, 10 °C per min to 300 °C and further hold time of 6 min. Target chemicals were identified based on the standards retention times with monoisotopic and base peaks (m/z) confirmation. Quantification was based on a linear calibration curve (area x concentration) of 6 different concentrations (from 0.5 to 100 ng mL^{-1}).

2.6. Sampling rate

To estimate PUF sampling rates (*R*), previous studies have used a range of depuration compounds (DC) to access chemical specific air concentrations (Shoeib and Harner, 2002; Bartkow et al., 2005). This is, so far, the most accurate tool for *R* estimation in PAS. However, over global scales, *R* values are typically reported as 3–5 $m^3\,d^{-1}$ (Pozo et al., 2006, 2009). Thus, when site-specific *R* is not available, it is reasonable – considering uncertainty – to use mean values that are consistent with previous calibrations (Pozo et al., 2017). Due to the absence of such DCs, our *R* was based on a previous study carried out at the same sampling point in SONP (Lag: 22° 27′ 24″ S. Long: 43° 01’ 42” W. Alt: 2200 m a.s.l.) (Meire et al., 2012), which in turn corroborates other studies conducted at sites with high elevation and/or high wind speed (Pozo et al., 2004, 2006; Tuduri et al., 2006). Therefore, an average *R* value, from winter (7–7.8 $m^3\,d^{-1}$) and summer (4.8–5.7 $m^3\,d^{-1}$) periods, equal to 6.3 $m^3\,d^{-1}$ was assumed for the whole monitoring. The effective air volume ranged from 422 to 750 m^3 at INP and 542 to 655 m^3 at SONP.

2.7. Data analysis

To summarize data, pesticides were grouped as the sum of their respective isomers and/or metabolites as follows: $\sum$-chlordane (cis- and trans-chlordane + oxychlordane); $\sum$-heptachlor (heptachlor + cis- and trans-heptachlor epoxide); $\sum$-drin (aldrin + isodrin + dieldrin + endrin); $\sum$-HCH (α-, β-, δ- and γ-HCH); $\sum$-DDT (*o,p'* and *p,p'*-DDD + *o,p'* and *p,p'*-DDE + *o,p'* and *p,p'*-DDT); $\sum$-endosulfan (α- and β-endosulfan + endosulfan SO_4); $\sum$-chlorpyrifos (chlorpyrifos + chlorpyrifos methyl) $\sum$-cypermethrin (*cis*1-, *cis*2-and *trans*1-, *trans*2-cypermethrin); $\sum$-permethrin (*cis* and *trans*-permethrin). Methoxychlor, mirex and HCB are always presented as their single form concentrations.

For statistical purposes, concentrations below LOD were replaced by 1% of the respective analyte LOD value. Data normality was verified by Shapiro-Wilk test. Mann Whitney *U* test was applied for non-parametric distributions and Student's T-test was applied for parametric distributions, in order to verify the differences of pesticide concentrations in atmospheric air between the two national parks and among seasonal periods. For all statistical tests, the significance adopted level was 5% ($p < 0.05$). Microsoft Office Excel (2016) ® and Graphpad Prism 5.0 ® statistical programs were used to perform graphs and tests.

3. Results and discussion

3.1. Atmospheric concentrations of OCPs and CUPs at both national parks

Individual chemical concentrations, for each sampling period and site, are given on Supporting Material (Table S5; S6). On the whole, pesticide concentrations in atmospheric air were mostly composed of $\sum$-endosulfan (INP -75% and SONP-59%), $\sum$-cypermethrin (INP -5% and SONP-20%) and $\sum$-chlorpyrifos (INP -5% and SONP-6%) (Table 1). The atmospheric contamination pattern is illustrated in Fig. 2. During the whole monitoring period, half of the contaminant groups were always measured above LOD at SONP, while only HCB was always measured above LOD at INP. All pesticide concentrations were significantly higher in SONP than in INP, with the exception of methoxychlor ($P = 0.317$). However, it is noteworthy that methoxychlor was only measured in two sampling periods at each site (INP - autumn and winter 2014 and SONP-autumn 2014 and summer 2015). Therefore, as its concentrations have not been measured in half of the sampling period, a methoxychlor discussion shall be skipped.

Such a difference between measured concentrations in INP and

Table 1
Comparison between pesticide concentrations in atmospheric air (pg m^{-3}) from uplands at Itatiaia and Serra dos Órgãos National Parks. For each contaminant from each sampling site is given: concentration range, average, standard deviation, significant difference when $P < 0{,}05$ and the statistical test used to verify the difference of pesticide mean concentrations in atmospheric air between the two national parks.

Pesticide	Min - Max	Average ± SD	Min - Max	Average ± SD	P value	Test
	INP		SONP			
$\sum$-Chlordane	ND - 111	17 ± 39	ND - 331	73 ± 111	0.0281	Mann Whitney U
$\sum$-Heptachlor	ND	ND	ND - 32	9 ± 10	0.0002	Mann Whitney U
$\sum$-Drin	ND - 23	5 ± 8	25–79	49 ± 17	0.0002	Mann Whitney U
Methoxychlor	ND - 44	9 ± 17	ND - 115	19 ± 40	0.317	Mann Whitney U
Mirex	ND - 3	2–1	5–18	12 ± 5	0.0001	Student's T-test
HCB	19–67	35 ± 18	43–87	60 ± 18	0.0207	Mann Whitney U
$\sum$-HCH	ND - 14	2–5	18–118	48 ± 38	0.0009	Mann Whitney U
$\sum$-DDT	ND	ND	ND - 169	83 ± 47	0.0009	Mann Whitney U
$\sum$-Endosulfan	ND - 1275	377 ± 421	390–3202	1485 ± 1045	0.0147	Student's T-test
$\sum$-Chlorpyrifos	ND - 67	24 ± 28	55–270	157 ± 71	0.0003	Mann Whitney U
$\sum$-Cypermethrin	ND - 148	25–51	ND - 881	504 ± 291	0.0011	Mann Whitney U
$\sum$-Permethrin	ND	ND	ND - 40	21 ± 12	0.0019	Mann Whitney U

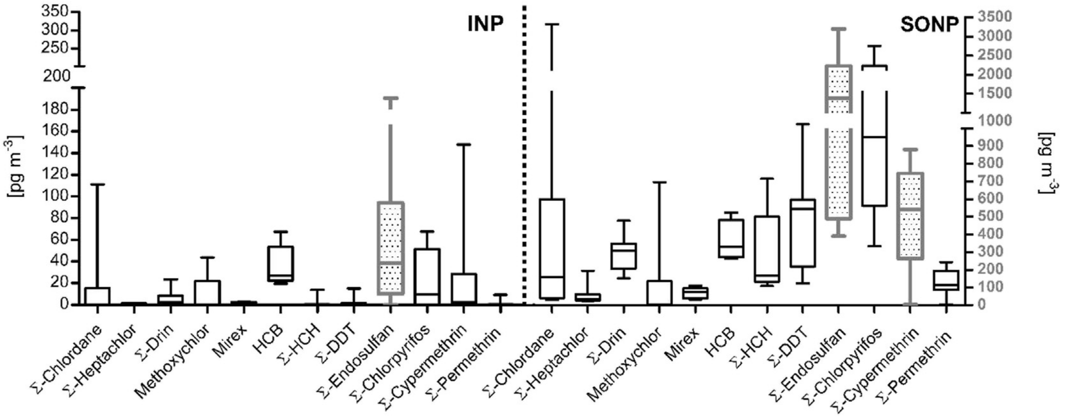

Fig. 2. Box plot representing (–) median; ([]) 25%–75%; (I) minimum and maximum of total pesticide concentrations in air, monitored at Itatiaia (INP - left side) and Serra dos Órgãos National Parks (SONP - right side) over two years. Dotted pattern filled boxes (∑-endosulfan in both sections and ∑-cypermethrin in SONP section) are related to right-sided Y axis scale (grey and bold). All others are related to left-sided Y axis scale (black).

SONP might be explained by emission sources around SONP. Aside from being closer to urban and industrial areas in Rio de Janeiro capital and Guanabara Bay – Guanabara Bay is known to be the most anthropogenically disturbed area along the Brazilian shoreline (Kjerfve et al., 1997), SONP is surrounded by intense agricultural activities. This region, known as the “green belt”, is responsible for ~70% of the state agricultural production (Fernandes et al., 2006), and it is also the second largest producer of ornamental flowers in Brazil (Costa et al., 2006). Moreover, a wide use of agrochemicals for both food and flower productions has been reported in this region (Queiroz, 2007; Hoshi, 2009).

Most legacy OCPs were measured in background levels, corroborating previous studies carried out at mountains and pristine areas around the world (Van Drooge and Grimalt, 2004; Pozo et al., 2006, 2009; Estellano et al., 2008; Gong et al., 2010; Wang et al., 2010). Nevertheless, to better understand each measured concentration of both OCPs and CUPs at such pristine mountains in Brazil, it is extremely important to discuss the current national legislations without losing the historical overview.

3.2. ∑-chlordane

Technical chlordane is a mix of many chemicals which contains mainly trans- and cis-chlordade, heptachlor and nonachlor (Dearth and Hites, 1991a). Its main metabolite in the environment is oxychlordane, which is more toxic and persistent than the technical mix (Dearth and Hites, 1991b; Bondy et al., 2003). In Brazil, chlordane use was limited to agricultural practices and has been forbidden since 1980 (MMA, 2015). However, as a persistent pollutant, it is still present in the environment. ∑-chlordane was mainly composed of cis-chlordane (87%), followed by oxychlordane (7%) and trans-chlordane (6%), which is also expected since the isomer trans is more reactive (Pozo et al., 2011). Even being higher at SONP than in INP, ∑-chlordane mean concentrations measured at both sites (INP - 17 pg m^{-3} and SONP - 73 pg m^{-3}) are into the range of background concentrations around the world (Pozo et al., 2004, 2006; 2011; Shunthirasingham et al., 2011; Gevao et al., 2018). However, the maximum concentrations measured at both national parks during the summer of 2015 (INP - 111 pg m^{-3} and SONP - 331 pg m^{-3}) are noteworthy. These maximum concentrations were 31 (INP) and 9 (SONP) times higher than the average of the other periods. Moreover, chlordane was not detected in a previous study carried out at the same sampling point in SONP (Meire et al., 2012), which could suggest an analytical interference, rather than a one-off event.

3.3. ∑-heptachlor

Heptachlor was first isolated from chlordane in 1946 and was largely used as an insecticide from 1950 to 1970 (Felix et al., 2007). Its main metabolites are the isomers cis- and trans-heptachlor epoxide. Some studies showed that in a few hours ~20% of the heptachlor applied is switched to heptachlor epoxide (Bidleman et al., 1998; ATSDR, 2007). In a previous study, Meire et al. (2012), reported the lack of information about the total amount of heptachlor used in Brazil. However, it is known that ~7 kt were imported from 1961 to 2003 (MMA, 2015). ∑-Heptachlor was mainly composed of cis-heptachlor epoxide (86%), followed by trans-heptachlor epoxide (10%) and heptachlor (4%). Which confirm the higher persistence and the longer-range transport of heptachlor epoxide (Daly and Wania, 2005). It is important to highlight that ∑-heptachlor was only measured in SONP. ∑-heptachlor mean concentrations (SONP - 9 pg m^{-3}) were quite similar to those reported in USA mountains (0.18–12 pg m^{-3}). Slightly higher than in Chilean mountains (~0.4 pg m^{-3}) (Pozo et al., 2009) and in the previous study carried out at the same site (SONP - <0.01–14 pg m^{-3}) (Meire et al., 2012). However, even higher heptachlor concentrations have been reported in Bolivian mountains (250 pg m^{-3}) (Estellano et al., 2008) and other remote regions such as the poles (Pozo et al., 2006, 2009).

3.4. ∑-drin

This whole group of cyclodienes (aldrin, dieldrin, endrin and isodrin) were manufactured as insecticides and mostly used as an alternative to DDT (Koshlukova and Reed, 2014). Even with individual productions, they are strictly related as isomers and metabolites. Brazil has recorded a consumption of ~30 kt of aldrin/dieldrin/endrin from 1961 to 2005 (Almeida et al., 2007). However, according to the National Implementation Plan for the Stockholm Convention, dieldrin and isodrin were never registered for any purpose in Brazil. Aldrin and endrin had their agricultural use forbidden in 1985, although aldrin could still be used to control ants and termites until 1992 and as a wood preservative until 2000 (MMA, 2015). The ∑-Drin, reported in the present study, in INP (<LOD - 23 pg m^{-3}) is exclusively composed of dieldrin and in SONP (25–79 pg m^{-3}) it is mostly composed of dieldrin (70–97%) with lower contributions of endrin. The same predominance of dieldrin

was previously reported in Brazilians mountains (Meire et al., 2012) and other atmospheric monitoring studies (Yao et al., 2006). These authors suggested that the predominant occurrence of dieldrin in the atmosphere is mainly due to secondary emission sources and the quick metabolization of aldrin in dieldrin. While aldrin's half-life in soil is estimated to range from 20-100 days, dieldrin's and endrin's half-life in soil can reach 3–4 years and 12 years, respectively (Almeida et al., 2007). Measured concentrations of $\sum$-Drin were higher than those reported for mountain regions in Chile and Canada (4–10 pg m^{-3}) (Pozo et al., 2004, 2009; Harner et al., 2006; Estellano et al., 2008). Moreover, similar to chlordane and heptachlor, actual concentrations of $\sum$-Drin were also higher than those reported in a previous study conducted at SONP (<LOD - 19 pg m^{-3}) (Meire et al., 2012).

3.5. *Mirex*

Initially used to fight ants and termites, mirex was also used as a flame retardant later on. It is highly stable in the environment – being a saturated molecule – with high bioaccumulative and biomagnificative potentials (Kaiser, 1978; Braune and Malone, 2006). Legally, in Brazil, mirex was mostly used against ants until 1992, but also in livestock productions until 1985. However, the last national implementation plan for the Stockholm Convention reports that ~314 t of mirex were imported from 1989 to 1998 (MMA, 2015). Furthermore, mirex – together with DDT – showed the highest concentrations in dolphins and human milk in Brazil (Alonso et al., 2010; FIOCRUZ, 2014). In the atmosphere, mirex is strictly associated with solid particulates (ATSDR, 1995). Thus, many atmospheric studies based on passive air sampling use mirex as an internal standard, which precludes further comparison (Pozo et al., 2004, 2006; 2009, 2011; Estellano et al., 2008, 2015; Meire et al., 2012). Mirex concentrations – INP (<LOD - 3 pg m^{-3}) and SONP (5–18 pg m^{-3}) – were similar to those in the only study that so far reported mirex atmospheric concentrations (0.1–22 pg m^{-3}) in Canada. Although the authors consider it a contaminated area, mirex was only measured in 5 of the 143 samples.

3.6. *HCB*

HCB is an industrial product which can also be found in technical formulations of pesticides. It can be released into the atmosphere from chlorine pesticide breakdown, chlorine solvent incineration and incomplete combustion of waste, biomass, coal and fuel (Bailey, 2001). Some authors have reported HCB potential to long-range transport and deposition in mountain regions, with significant positive correlation between HCB concentrations and altitude increase (Jaward et al., 2005; Shen et al., 2005). During the 1960s, Brazil imported ~800 t of HCB and there is a history of storage and contamination in São Paulo, which is still a potential secondary source of HCB to the atmosphere (UNEP, 2002). HCB was the only contaminant consistently measured at the two sites during the whole monitoring – INP (19–67 pg m^{-3}) and SONP (43–87 pg m^{-3}) –, although, both of them have background concentrations, similar to those reported in Antarctica throughout several years, 1995 (22–25 pg m^{-3}) (Montone et al., 2005); 2007–2010 (10–80 pg m^{-3}) (Kallenborn et al., 2013a,b) and 2010 (08–50 pg m^{-3}) (Pozo et al., 2017). Moreover, HCB had already been shown to be homogeneously distributed over the southern hemisphere (Bidleman et al., 1993; Montone et al., 2005). The larger production and use of HCB in the northern hemisphere is reflected in higher atmospheric concentrations measured at the Pyrenees (36–120 pg m^{-3}) (Van Drooge and Grimalt, 2004), at the Swiss Alps (102 pg m^{-3}) (Shunthirasingham et al., 2013) and at Canadian mountains (21–149 pg m^{-3}) (Daly et al., 2007a,b,c). The consistency of measured concentrations in both INP and SONP during this monitoring and in Antarctica might be explained by HCB physicochemical properties. Its low reaction with hydroxyl radicals and its high Henry's law constant, leads to a long atmospheric residence – HCB half-life can exceed 4 years in atmosphere – (Pozo et al., 2017). In a study carried out during the winter of 2012, based on low density polyethylene (LDPE) passive samplers, slightly lower concentrations were reported in the same sampling point at INP (21–29 pg m^{-3}) (Meire et al., 2016). Thus, the consistent air concentration level of HCB in the same range as global background levels (20–60 pg m^{-3}) endorses PAS-PUF feasibility.

3.7. $\sum$-*HCH*

Hexachlorocyclohexanes were mainly commercialized under two different formulations. The technical HCH – mostly composed of α-HCH (~70%) and lower quantity of other isomers (β, δ and γ-HCH) – and lindane – almost exclusively γ-HCH (~99%) – (Almeida et al., 2007). Global production of technical HCH reached tens of millions of tons just in the 1990s and most of it was used in the northern hemisphere (Li, 1999; Li and Macdonald, 2005). After the prohibition of technical HCH, lindane remained used for agricultural and sanitation purposes until the first decade of this century (UNEP, 2009). In Brazil, technical HCH was mainly used to fight vectors of endemic diseases such as leishmaniasis, typhus and malaria (Braga et al., 2002). Its production and importation exceeded 100 kt for the period of 1955–2003 (UNEP, 2002; Almeida et al., 2007; MMA, 2015). Lindane started to be used in Brazil during the 1960s and its consumption was estimated at more than 1.6 kt. Lindane was last legally used as a wood preservative until 2006 (ANVISA, 2006). It is extremely important to highlight that one of the worst cases of environmental contamination in Brazil happened in Rio de Janeiro, concerning a HCH and DDT factory from the Brazilian Ministry of Health. The factory was deactivated leaving ~300 t of chemical residue behind and until present time the impacts on human health are unclear (Oliveira and Brilhante, 1996; Braga et al., 2002).

$\sum$-HCH concentrations in INP were measured only during autumn 2014 (<LOD - 14 pg m^{-3}) with exclusivity of γ-HCH isomer. In SONP (18–118 pg m^{-3}) the $\sum$-HCH presented a mixed composition (α-HCH - 46.4%; β-HCH - 4.8%; δ-HCH - 7.1%; γ-HCH - 41%). The ratio α/γ-HCH has been widely used to differ between technical HCH ($\alpha/\gamma\text{-HCH} \geq 5$) and lindane use ($\alpha/\gamma\text{-HCH} \leq 5$) (Shen et al., 2005; Estellano et al., 2008; Liu et al., 2010). Thus, as the ratio α/γ-HCH ranged from 0.01 to 2.4 in SONP and in INP only γ-HCH was measured, these results endorse the more recent use of lindane and its presence in the atmosphere, corroborating the results reported by Meire et al. (2012), in the same sampling point (PNSO- 0.4 to 1.5) and several other studies – Chilean mountains from 0.6 to 0.9 (Pozo et al., 2004); Bolivian mountains from 0.06 to 1.19; along the coastline of Brazil, Uruguai and Argentine from 0.3 to 3.3 (Estellano et al., 2008); Antarctic from 0.4 to 0.8 (Montone et al., 2005) and in European and Asian mountains $\alpha/\gamma\text{-HCH} < 4$ (Van Drooge and Grimalt, 2004; Gong et al., 2010; Wang et al., 2010). Meanwhile, even with similar α/γ-HCH ratios, $\sum$-HCH concentrations tend to be higher in the northern (France ~710 pg m^{-3}; China ~460 pg m^{-3}; India ~4.700 pg m^{-3}) than in the southern hemisphere (from 11 to 112 pg m^{-3}) (Harner et al., 2006; Pozo et al., 2009; Meire et al., 2012). Although the mean concentrations of $\sum$-HCH (INP - 5 pg m^{-3} and SONP - 49 pg m^{-3}) were similar to those reported for Chilean (12 pg m^{-3}) (Pozo et al., 2004) and Bolivian mountains (~60 pg m^{-3}) (Estellano et al., 2008), once again, currently HCHs air concentrations were also slightly higher than those previously measured at the same sampling point (SONP – 8 to 36 pg m^{-3}) (Meire et al., 2012).

3.8. $\sum$-DDT

DDT was synthesized on wide scales (~5 millions of tons) and used with several different purposes around the world (Li and Macdonald, 2005). Technical DDT is mostly composed of *p,p'*-DDT (~77%) with lower proportions of *o,p'*-DDT (~15%), *p,p'* and *o,p'*-DDD and impurities (D'Amato et al., 2002). In Brazil, DDT was largely used in agriculture, livestock and sanitation campaigns since the 1940s (Torres et al., 2009). Its use began to be restricted in the 1980s, for agricultural purposes and in the 1990s for sanitary purposes. However, its definitive prohibition only happened in 2009 (Ferreira et al., 2011). $\sum$-DDT concentrations were always below the LOD in INP, while in SONP they ranged from <LOD to 169 pg m^{-3}. $\sum$-DDT contamination in SONP showed similar proportions of metabolites and technical DDT (*p,p'*-DDE (~30%); *p,p'*-DDD (~30%); *p,p'*-DDT (~25%); *o,p'*-DDT (<15%). $\sum$-DDT concentrations were higher than all concentrations reported for mountain regions in other countries (Pozo et al., 2004, 2009; Estellano et al., 2008; Van Drooge and Grimalt., 2004; Harner et al., 2006; Daly et al., 2007a,b,c; Gong et al., 2010; Wang et al., 2010) and also higher than in the previous study from Meire et al. (2012), conducted in the same sampling point (PNSO - 57 pg m^{-3}). However, they were quite similar to the concentrations reported by Montone et al. (2005) to the coastline of Rio de Janeiro and São Paulo (25–102 pg m^{-3}). The ratio DDE/DDT equal to 1.5 could also dismisses fresh inputs of DDT in the region.

3.9. $\sum$-endosulfan

Endosulfan was one of the most used OCPs – ~310 kt only from 1950 to 2000 – (Li and Macdonald, 2005) and it is the most recently forbidden one listed in the Stockholm Convention in 2011 (UNEP, 2015). Its technical formulation is almost absolutely composed (~95%) of the two stereoisomers (α and β) in the proportion of 2:1 to 7:3, depending on its commercial formulation (Weber et al., 2010). Endosulfan is reported to be one of the most abundant OCPs in the air (Shen et al., 2005) and is the only one detected in all sampling points of the Global Atmospheric Passive Sampling program (GAPS) (Pozo et al., 2009). Brazil produced around 50 kt of endosulfan and imported ~40 kt until 2011, when its phase-out period started. Following the Stockholm Convention guidelines, the Brazilian government established the complete prohibition of endosulfan into four steps: Forbid endosulfan importation in 2011, its production in 2012, its commercialization in 2013 and, finally, its use in 2014 (MMA, 2015). Among all pesticides, $\sum$-Endosulfan showed the highest concentrations in both INP (<LOD - 1725 pg m^{-3}) and SONP (390–3202 pg m^{-3}). If compared to other legacy OCPs or even endosulfan air concentrations in different mountain regions, these results highlight the massive use of endosulfan in Brazil, until recently – endosulfan could still be used when this monitoring started. The present concentrations were at least one order of magnitude higher than those reported in North American (11–321 pg m^{-3}), European (0.4–42 pg m^{-3}) and Asian mountains (4–28 pg m^{-3}) (Van Drooge and Grimalt., 2004; Gong et al., 2010; Daly et al., 2007b; Harner et al., 2006; Bradford et al., 2010; Choi et al., 2008; Weber et al., 2010). They were more similar to the concentrations reported, while endosulfan use was still allowed, in Costa Rican (~1000 pg m^{-3}) (Daly et al., 2007a) and Bolivian mountains (28–1751 pg m^{-3}) (Estellano et al., 2008), or even closer to those reported in agricultural regions of São Paulo, Brazil (~2.800 pg m^{-3}) (Pozo et al., 2009). However, the decrease of atmospheric concentrations of $\sum$-Endosulfan over time must be highlighted.

The restrictive measures adopted by the Brazilian Government, according to the Stockholm Convention, were reflected in falling levels of $\sum$-Endosulfan in both national parks. The first time endosulfan was not measured in an atmospheric monitoring, was during the period of winter-2015, in INP, as reported here. Furthermore, the decrease of endosulfan in the atmosphere is also noteworthy in SONP, mainly if compared with the results (43–5600 pg m^{-3}) reported by Meire et al. (2012), in a study carried out during 2007–2008, at the same sampling point (Fig. 3). Although, in the most recent study of pesticides in air, carried out in INP and based on PAS-LDPE, gaseous endosulfan concentrations were extremely lower (5.8–29 pg m^{-3}) (Meire et al., 2016). These surprisingly lower concentrations were associated to the seasonal period (autumn-winter) of sampling. However, the present results were considerably higher (INP - winter-2014 - 115 pg m^{-3}) when measured at the same sampling point.

The main product of both α- and β-endosulfan in the environment, endosulfan sulphate (SO$_4$), was also observed during this study. The atmospheric emission of endosulfan SO$_4$ is mainly related to the volatilization from biological activities in surface soils (Lenoir et al., 1999; Laabs et al., 2002; Hageman et al., 2006). Endosulfan SO$_4$ contribution did not reach 5% of the total concentration ($\sum$-Endosulfan) and were within the proportions (2–16%) reported by Meire et al. (2012). Low levels of endosulfan SO$_4$ in the atmosphere can be explained by its lower vapor pressure (0.0013 Pa) if compared to its parental compounds (α- and β-endosulfan = 0,0040 and 0,0044 Pa, respectively) (Weber et al., 2010). In accordance to that, higher contributions of endosulfan SO$_4$ were observed in lowlands – just the opposite of α- and β-endosulfan –, which endorse its restricted capacity of long-range transportation and, consequently, its relation with closer emission sources, as historically treated soils (Weber et al., 2010; Meire et al., 2012).

3.10. Organophosphorus pesticides

Organophosphorus pesticides (OPPs) came to replace OCPs due to the resistance acquired by some pests and nowadays they are widely used for agricultural, livestock, domestic and sanitation purposes (ATSDR, 1997). Chlorpyrifos and chlorpyrifos methyl are examples of OPPs which also have chlorine in their composition. This combination makes them even more efficient, because it combines the shock effect caused by the acetylcholinesterase inhibition with the residual action caused by chlorinated compounds (ATSDR, 1997; Larini, 1999). The presence of chlorpyrifos in the atmosphere is mainly related to its volatilization after application. Due to its physical-chemical properties, as vapor pressure close to

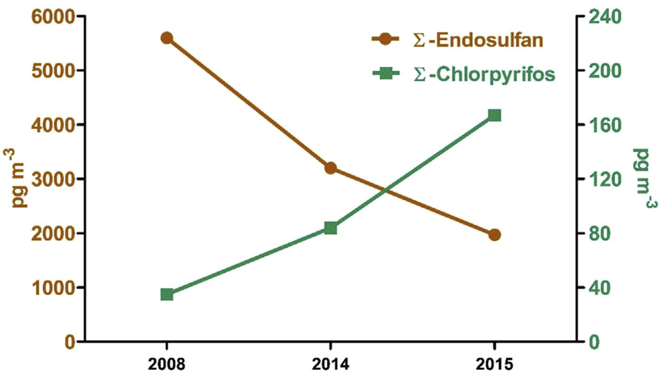

Fig. 3. Trends of maximum air concentrations of endosulfan and chlorpyrifos measured during summer periods at Serra dos Órgãos National Park. Data from 2008 was reported by Meire et al. (2012) at the same sampling point. Both studies were performed with polyurethane foam disks as atmospheric air passive samplers.

~0.4 Pa, chlorpyrifos in the atmosphere is mostly found in gaseous phase (Mackay et al., 2006; Li et al., 2014). Thus, even with short atmospheric residence (~1 day) (Muir et al., 2004), chlorpyrifos can be transported through long distances around the globe (Chernyak et al., 1996; Sadiki and Poissant, 2008; Li et al., 2014). In Brazil, chlorpyrifos is allowed to be used to control agricultural pests, ants and mites, with agricultural and domissanitary purposes and as a wood preservative (ANVISA, 2018). Therefore, there are records of ~78 kt of chlorpyrifos imported from 1989 to 2017 (MDIC, 2018). In 2014, chlorpyrifos was included as one of top five active ingredients most sold in Brazil (Bombardi, 2017). Chlorpyrifos methyl was always below the LOD, thus, the $\sum$-chlorpyrifos was only composed of chlorpyrifos concentrations. Its atmospheric concentrations ranged from <LOD to 67 pg m^{-3} (IPN) and from 55 to 270 pg m^{-3} (SONP). These concentrations are similar to those reported in Czech (360 pg m^{-3}) and Irish (150 pg m^{-3}) remote regions (Koblizkova et al., 2012), although, they are higher than the concentrations reported in Canadian mountains (4.6 pg m^{-3}) (Daly et al., 2007a,b,c). Compared to the previous study carried out at the same sampling point (SONP - 4 to 35 pg m^{-3}) (Meire et al., 2012), the present study showed higher concentrations than those measured around 5 years ago, in all sampling periods, reaching up to 6 times more in the last sampling period (winter-2015). The increase of chlorpyrifos concentrations were also noteworthy during this monitoring, which suggests higher applications of such CUPs over the years. Moreover, their continuous use is proven to give them the environmental persistence that physical-chemical properties would not. Thus, the decrease of endosulfan has been offset by the increase of chlorpyrifos at SONP (Fig. 3).

3.11. Pyrethroids

Pyrethroids are a group of pesticides synthesized from pyrethrin, an environmentally unstable pesticide isolated from the pyrethrum flower. They are the main class of pesticide used worldwide with a huge range of applications (Soderlund et al., 2002; Ray and Fry, 2006). They are also SVOCs, although, some studies highlight a shorter range atmospheric transport, due to their affinity to bind in solid particles (Feo et al., 2010; Li et al., 2014). Although claimed to be safe, due to their metabolization into non-toxic compounds, low mobility and persistence in the environment (Chambers, 1980; Demoute, 1989; Godin et al., 2007), several studies have brought opposing information about their environmental mobility and toxic potential (Shafer et al., 2008; Scollon et al., 2011; Jin et al., 2012). Some studies have highlighted the maternal transference of pyrethroids in marine mammals and their high levels in human milk (Bouwman and Kylin, 2009; Alonso et al., 2012; Feo et al., 2012). Nowadays, there is a large number of pyrethroid compounds being used, however, in this study, only permethrin and cypermethrin were observed due to their larger use in Brazil. Both permethrin and cypermethrin are in the most persistent and toxic group of pyrethroids (type II) (Vijverberg and Van der Bercken, 1990). According to the existing information, cypermethrin is the most used pyrethroid in Brazil, with import amounts of ~21 kt from 1989 to 2017 (MDIC, 2018). The import of permethrin is estimated around 3 kt from 1997 to 2017 (MDIC, 2018).

Permethrin has been reported as the highest concentration of pyrethroids in marine mammals from the Brazilian southeast coastline (Alonso et al., 2012). However, in the present study it was only measured in SONP (<LOD - 40 pg m^{-3}) and showed significantly lower concentrations than cypermethrin in both INP (<LOD - 148 pg m^{-3}) and SONP (<LOD - 881 pg m^{-3}). These results are in accordance with a previous report of pyrethroids in chicken eggs from the highland region of Rio de Janeiro, in the area surrounding SONP (Parente et al., 2017). It is important to highlight that this is the first study to investigate atmospheric concentrations of pyrethroids in Brazilian mountain regions, and perhaps the first to investigate it in the air on the South American continent or at any mountain region in the world. Therefore, it was only possible to compare it with Asian regions where the authors affirm to have pyrethroid use. Nevertheless, they were only slightly lower than the concentrations reported in an urban area with large gardens in China (15–1388 pg m^{-3}) (Li et al., 2014), but considerably lower than those reported in a floriculture region of Malaysia (142–3740 pg m^{-3}) (Sulaiman et al., 2007). The absence of any pattern in atmospheric concentrations of pyrethroids along the whole monitoring is also noteworthy.

3.12. Seasonal variation of OCPs and CUPs concentrations in air

Due to recurring failures on meteorological stations, it was not possible to compile meteorological data continuously (Table S1). Therefore, this lack of data precluded any precise approach of correlation between pesticide concentrations in atmospheric air and temperature or precipitation. Although, considering different seasonal periods, a clear pattern is depicted for OCPs. Concentrations of OCPs – composed mainly by $\sum$-Endosulfan – increased in spring, reached their peak in summer and dropped over autumn and winter (Fig. 4). However, CUPs did not seem to follow any pattern or to be influenced by warmer temperatures and higher precipitation levels, known to happen during summer in this region.

Despite the fact that generally SVOCs are expected to show

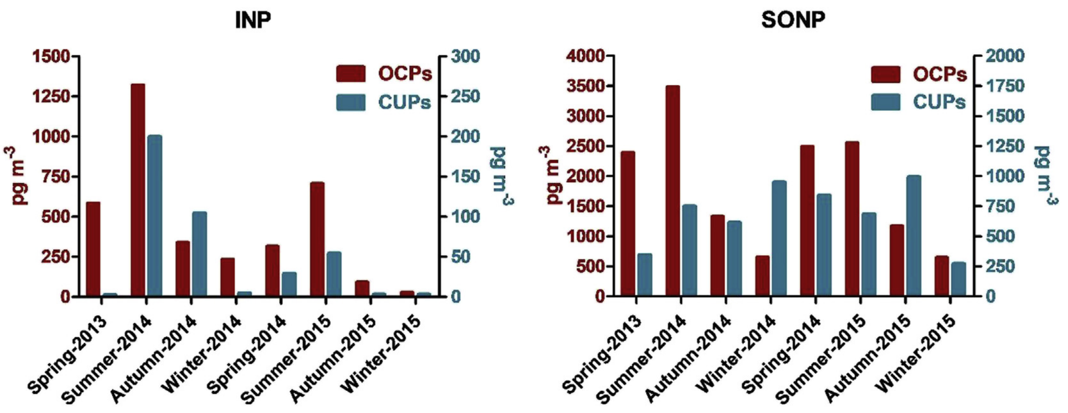

Fig. 4. Seasonal variation of organochlorine pesticides (OCPs) and current-use pesticides (CUPs) air concentrations at Itatiaia (INP) and Serra dos Órgãos National Parks (SONP).

higher volatilization rates at warmer temperatures, it has been reported that atmospheric concentrations of pesticides might be strictly correlated to application seasons while their use is still allowed (Li et al., 2014; Gevao et al., 2018). Thus, as agricultural production continues throughout the year at the highland region of Rio de Janeiro state and some CUPs are very often applied, it may explain random atmospheric concentrations of CUPs among seasons (ANVISA, 2018). It is also interesting to highlight that HCB – and less pronounced $\sum$-HCH and $\sum$-DDT – presented the highest concentrations in autumn seasons. Some authors have reported higher scavenge of SVOCs from the atmosphere during rainy seasons (Weber et al., 2010; Li et al., 2014). However, at the present sites, summer is the rainy season. Thus, as in subtropical regions temperature changes are not so abrupt, it seems reasonable to accept higher atmospheric concentrations of some legacy SVOCs during drier but not extremely colder seasons. Mainly in the case of HCB that has long atmospheric residence and is well distributed in the atmosphere.

4. Conclusion

The massive use of agrochemicals in Brazil is reflected by high atmospheric concentrations of different kinds of pesticides (OCPs, OPPs and pyrethroids). Regarding legacy OCPs, which have been forbidden for a long time, their atmospheric concentrations in Brazilian mountains were reported in background levels. This endorses the importance of restrictive measures for environmental safety. OCPs concentrations in SONP, slightly higher than in the first report of Meire et al. (2012), seem more reasonably explained by adverse weather conditions, such as temperature and rainfall regime, than by fresh inputs of all legacy OCPs. The decrease of endosulfan over the years was highlighted, however, the parallel increase of chlorpyrifos suggests a collateral effect of the national bias of permissive and massive use of agrochemicals. Furthermore, the constant measurements of CUPs during this atmospheric monitoring brings the understanding that their large and wide ongoing use surpasses their “safer” characteristics, making them pseudo-persistent pollutants (pseudo-POPs). The intense agricultural production in the “green-belt” region of Rio de Janeiro, in the outskirts of SONP, is also reflected in significantly higher concentrations of almost all investigated pesticides when compared to those measured at INP. Finally, high atmospheric concentrations of pesticides should definitely be taken into account when thinking about endangered ecosystems, such as the *campos de altitude* and its endemic species.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.06.061.

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