2015

Use of passive samplers to detect Organochlorine Pesticides in air and water at Wetland Mountain region sites (S-SE Brazil)

R. O. Meire

M. Khairy
University of Rhode Island

A. C. Targino

P. M.A. Galvão

J. P.M. Torres

See next page for additional authors

Citation/Publisher Attribution

Meire, R.O., Khairy, M., Targino, A.C., Galvão, P.M.A., Torres, J.P.M., Malm, O., & Lohmann, R. (2016). Use of passive samplers to detect Organochlorine Pesticides in air and water at Wetland Mountain region sites (S-SE Brazil). *Chemosphere,* 144, 2175-2182.
Available at: http://dx.doi.org/10.1016/j.chemosphere.2015.10.133

Use of passive samplers to detect Organochlorine Pesticides in air and water at Wetland Mountain region sites (S-SE Brazil)

Authors

R. O. Meire, M. Khairy, A. C. Targino, P. M.A. Galvão, J. P.M. Torres, O. Malm, and Rainer Lohmann

This is a pre-publication author manuscript of the final, published article.

Use of passive samplers to detect Organochlorine Pesticides in air and water at Wetland Mountain region sites (S-SE Brazil)

Meire, R.O[1*]; Khairy, M[2,3]; Targino, A. C.[4]; Galvão, P.M.A[1]; Torres, J.P.M[1]; Malm, O[1]; Lohmann, R[2].

[1]Biophysics Institute, Rio de Janeiro Federal University, CCS, 21941-902 Rio de Janeiro, RJ, Brazil

[2]University of Rhode Island, Graduate School of Oceanography, South Ferry Rd., Narragansett, RI 02882, USA

[3]Department of Environmental Sciences, Faculty of Science, Alexandria University, Alexandria, Egypt

[4]Graduate Programme in Environmental Engineering, Federal University of Technology, Av. dos Pioneiros, 3131, 86036-370, Londrina, Brazil

*Corresponding author´s email: rodrigo@xerem.ufrj.br, romeire@biof.ufrj.br

Abstract

Low-density polyethylene (LDPE) passive samplers were deployed in upland surface waters and the overlying atmosphere during May and June 2012, to determine the transport and trends of freely dissolved and gaseous organochlorine pesticides (OCPs) along altitudinal gradients in mountain regions in south and southeast Brazil. Gaseous OCP concentrations were dominated by hexachlorobenzene (3.0 to 29 $pg.m^{-3}$) and endosulfans ($\Sigma = \alpha$-endosulfan + β-endosulfan + endosulfan sulphate, 170 to 260 $pg.m^{-3}$), whereas freely dissolved endosulfans were significantly higher than all other OCPs ($p < 0.001$). The presence of some target pesticides at the highest elevation sites indicated their efficient high-altitude transport from regional sources. Air-water exchange gradients indicated net deposition of most volatile and recently banned OCPs (e.g., HCB, endosulfan) over Brazilian mountains. Moreover, the exposure of these sites to large-scale continental airflows with varying source contributions may partly explain the atmospheric deposition of selected OCPs over upland freshwaters at tropical and subtropical mountains sites in Brazil. These findings, coupled with LDPE passive air and water sampling measurements, point out the potential inputs from distant sources of semi-volatile chemicals to the two high-altitude sites.

Keywords: Low density polyethylene (LDPE) passive samplers, organochlorine pesticides, long-range atmospheric transport, Brazil.

1. Introduction

Mountain cold-trapping of persistent organic pollutants (POPs) has been receiving considerable attention over the last decades (Calamari et al., 1991; Blais et al., 1998; Wania and Westgate, 2008). POPs are recalcitrant chemicals with relatively high potential for bioaccumulation and environmental mobility, and display toxic effects on organisms and humans even at relative low concentration levels (UNEP, 2002). Their re-emissions, long-range atmospheric transport (LRAT), and deposition are controlled by meteorological and geographical parameters such as orographic winds, high precipitation rates and low temperatures, typically found in mountainous regions (Daly and Wania 2005; Kirchner et al., 2009; Sheng et al., 2013).

It is well-established that higher precipitation rates coupled with transport of pollutants from sources in lowland crop soils –either current use or revolatilisation of previously applied compounds– could have an important role in the atmospheric deposition of semi-volatile organic pollutants in tropical and subtropical mountain regions (Daly et al., 2007; Estellano et al. 2008). Although several POPs -including organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs)- are already regulated and even banned in many South American countries, recent studies have highlighted the atmospheric transport of OCPs to tropical and subtropical remote mountain regions, such as the Bolivian and Chilean Andes, and also Brazilian uplands (Estellano et al., 2008; Meire et al., 2012; Pozo et al., 2004).

Numerous studies have shown the feasibility of using passive samplings to detect POPs in several environmental compartments, to monitor the exposure and evaluate the risk of wild-life and humans at regional and global scales (Harner et al., 2006; Levy et al., 2009; Lohmann et al., 2010; Pozo et al., 2009). Low density polyethylene passive samplers (LDPE) have been widely used in recent years to detect a range of trace hydrophobic organic contaminants (HOCs) in aquatic and air media, including legacy and emerging pollutants (Khairy and Lohmann 2012, 2013; Sacks and Lohmann, 2011). HOCs strongly partition into the LDPE matrix at a high-accumulation rate (Sacks and Lohmann, 2011). This feature offers advantages compared to the traditional environmental measurements, such as lower detection limits and easier and less costly laboratory methods, making LPDE a very useful tool for first-order risk assessment.

The aims of this study were to (i) assess the presence of legacy and recently banned OCPs in air and water in two National Parks in Brazil; (ii) investigate the altitudinal variation of target OCPs over shallow freshwaters in tropical and subtropical mountain regions in Brazil, and (iii) determine whether the OCPs had reached equilibrium between lakes and atmosphere. To achieve these aims, we deployed passive air and water samplers consisting of low-density polyethylene strips during fall and winter seasons (May-June 2012), following altitudinal transects in south and southeast Brazil. The current work presents original data of OCPs in the waters over Brazilian uplands.

2. Material and Methods

2.1. Site description

We conducted this study in the mountain ranges of “Serra do Mar” (National Park of Itaiaia - NPIT, lat.: 22^{o}22´38”S, lon.: 44^{o}41´35”W, Rio de Janeiro State) and “Serra Geral” (National Park of São Joaquim - NPSJ, lat.: 28^{o}00’49’’S, lon.: 49^{o}35’17’’W, Santa Catarina State), located in southeast and south Brazil, respectively.

The two national parks comprise rainforests and high-altitude ecosystems and are considered important conservation areas for biodiversity and endemic species (Myers et al., 2000).

2.2. Field Deployment

Four sampling sites were established along altitudinal gradients at each National Park during late fall and early winter seasons (May and June) in 2012. Passive LDPE sheets were deployed in the surface waters and overlying atmosphere concomitantly over four to five weeks (Figure 1). Water LDPE samplers were deployed 1 m below the surface attached to small buoys, whilst air samplers were fixed at 1.5 m above ground, inside inverted stainless steel bowls to form a clam-shell shape. The bowl design also protects the sampling medium (LDPE sheet) from direct radiation and rainfall, and diminishes the wind speed effect (Shoeib and Harner, 2002). Site and deployment details are given in Table S1. Additionally, five field blanks were collected at both parks to assess possible sample contamination during transport and storage. Methods for preparation and extraction of LDPEs as well as the instrumental analyses of the extracts and quality assurance/quality control are given in supplementary material (SM).

3. Theory/calculation

3.1. Atmospheric and water concentrations derived from LDPEs

We added performance reference compounds (PRCs) added to the samplers before deployment in order to gauge whether organochlorine pesticides had reached equilibrium and to adjust for disequilibrium in polyethylene samplers. Assuming that uptake and elimination rates are equivalent, the freely dissolved (or gas-phase) concentrations of individual OCPs ($C_{water\ or\ air}$) were then calculated by the following equation:

$$C_{water\,(air)} = C_{LDPE} / K_{LDPE\text{-}water\,(LDPE\text{-}air)}\; x\; [1\text{-} \exp^{-Rs\; x\; t\, /\, K_{LDPE\text{-}water\,(LDPE\text{-}air)}\; x\; m_{LDPE}}] \qquad (1)$$

where C_{LDPE} is the OCP concentration in the LDPE (L.kg^{-1}), R_s is the sampling rate [m^3.day^{-1}], t is the deployment period (days), m_{LDPE} is the mass of the LDPE sheet (kg) and $K_{LDPE\text{-}water}$ (*or* $_{LDPE\text{-}air}$, when applicable) is the sampler-water (air) partitioning coefficients (m^3.kg^{-1}). Sampling rates (Table S3) were calculated using the PRCs as follows:

$$f = \exp\,(-Rs\; x\; t\, /\, K_{LDPE\text{-}water\,(LDPE\text{-}air)}\; x\; m_{LDPE}) \qquad (2)$$

where f is the fraction of PRC retained in the passive sampler after deployment. Details on the PRC method have been described elsewhere (Booij et al., 2002; Khairy et al., 2014). Physico-chemical properties used to calculate the sampler-water partitioning coefficients ($K_{LDPE\text{-}water}$s) are given in supplementary material (SM).

3.2. Air mass back trajectory analysis.

To investigate the influence of atmospheric large-scale circulation on the concentrations of air pollutants at the highest altitudinal sites, 5-day backward air trajectories were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) (Draxler et al., 2012). In this study, we used cluster analysis to identify source regions and to investigate how different atmospheric flow patterns influence the concentrations of OCPs at the monitored sites. The Supporting Material (SM) provides additional details on the model and input dataset.

3.3. Air-Water Exchange Gradients

Air-water exchange gradients were calculated as the ratio of OCP concentrations measured in the LDPE (ng/LDPE) in each reservoir (water and air), corrected for non-equilibrium, minus one:

$$\text{Air – Water exchange} = (C_{LDPE\ (Water)} / C_{LDPE\ (air)}) - 1 \qquad (3)$$

In effect, the LDPE samplers reflect dissolved and freely OCPs in water or air, respectively, and thus they easily enable to derive the gradient across the air-water interface. Positive values indicate net volatilisation of OCPs and negative values indicate net deposition. We did not apply any temperature correction, as suggested by Lohmann et al. (2011), so the gradients indicate conditions in the field.

4. Results and Discussion

4.1. Sampling rates and OCP equilibrations in field-deployed LDPE samplers

Sampling rates (*Rs*) for the atmospheric and water samplers are given in Table S3. Atmospheric *Rs* ranged from 8.0 to 43 $m^3.day^{-1}$, which is consistent with *Rs* values measured for atmospheric OCPs (Khairy and Lohmann, 2013). Greater *Rs* values were observed at the highest altitudes at both National Parks, however the relationship between *Rs* and altitude was statistically insignificant.

Tables S5 and S6 depict calculated % equilibrium for gaseous OCPs. HCB, α- and γ- HCHs (log $K_{LDPE\text{-}air} \leq 7.15$) were the only detected OCPs that approached equilibrium (> 97 %) in all deployed samplers. All the other detected OCPs were still far from reaching equilibrium (< 50 %). Khairy and Lohmann (2014) observed a similar pattern for gaseous OCPs in the USA.

Rs values for the water samplers ranged from 18 to 81 L.day^{-1}. A similar range was observed for pyrene and higher molecular weight polycyclic aromatic hydrocarbons (PAHs) sampled in Narragansett Bay (Lohmann et al., 2011) and in the Great Lakes (McDonough et al., 2014), and for extended OCP studies (15 to 80 L.day^{-1}) in the Lower Great Lakes (Lakes Ontario and Erie) (Khairy et al., 2014). The sampling rates for National Park of Itatiaia were significantly higher (p = 0.006) than those for National Park of São Joaquim, and the calculated % equilibrium values for freely dissolved OCPs showed variations between the two parks. At the National Park of Itatiaia, all the detected OCPs (except *p,p'*-DDT) approached equilibrium by the end of the deployment period, whilst at the National Park of São Joaquim, only HCB, *α*-endosulfan and endosulfan sulphate were at equilibrium (Table S5 and S6). This difference is a consequence of different *Rs* values (higher *Rs* values indicate faster equilibration).

4.2. Air and water concentrations of target pesticides

At both National Parks, the most frequently detected compounds in air were HCB and endosulfans (*α*-endosulfan, *β*-endosulfan and endosulfan sulphate). The highest atmospheric concentrations were detected for HCB (4.0 to 29 pg.m^{-3}) followed by *α*-endosulfan (1.8 to 20 pg.m^{-3}), *β*-endosulfan (<LOD to 7.1 pg.m^{-3}), *α*- HCH (<LOD to 3.2 pg.m^{-3}), endosulfan sulphate (0.5 to 2.5 pg.m^{-3}), endrin (<LOD to 1.9 pg.m^{-3}) and *p,p´*- DDT (<LOD to 0.6 pg.m^{-3}). All the other investigated OCPs were below detection

limits. Figure 2, and Tables S7 and S8 of the SM summarise the air concentrations of target pesticides.

Similar to the atmospheric findings, endosulfans accounted for highest frequency detection in shallow waters amongst target OCPs (100s pg.L^{-1}) (Tables S7 and S8). However, amongst the less frequently detected pesticides (*p,p´*- DDT, *p,p´*-DDD, *p,p´*- DDE and *trans*-nonachlor) dieldrin stands out with intermediate concentration levels at the National Park of São Joaquim (< LOD to 31 pg.L^{-1}) (Figure 2). The greatest concentrations were reported for endosulfan sulphate (162 to 260 pg.L^{-1}), followed by dieldrin (15 to 31 pg.L^{-1}), α-endosulfan (<LOD to 6.5 pg.L^{-1}), HCB (1.2 to 2.3 pg.L^{-1}) and DDTs (0.1 to 0.6 pg.L^{-1}). The results for individual pesticides are discussed below. We chose to present geometric mean (GM) values are presented rather than arithmetic means to prevent extreme values (outliers) from skewing the mean.

4.2.1. Hexachlorobenzene (HCB)

Although HCB has been widely used in the past, its commercial use has been banned worldwide (Barber et al., 2005). However, HCB is currently released as an intermediate and by-product in the manufacture of a large number of chlorinated solvents, aromatics and pesticides and continues to volatilize from contaminated soils to the atmosphere (Bailey, 2001). In Brazil, there are well-known hotspots and stockpiles of HCB (e.g. Cubatão, São Paulo State) (UNEP, 2002) that may still represent a significant local environmental sources. On top of that, Brazil imported ca. 800 t of HCB in the middle of 60s (UNEP 2002).

HCB was detected at all sampling sites at both National Parks, and exhibited the highest air concentrations among the target compounds (Figure 2). HCB concentrations in air ranged from 21 to 29 pg.m^{-3} (GM 25 pg.m^{-3}) and from 4.3 to 9.9 pg.m^{-3} (GM 8.0

pg.m^{-3}) for NPIT and NPSJ, respectively. These air concentrations are much lower than air concentrations measured in high-mountain areas worldwide, such as: Central Pyrenees, High Tatras (36 to 120 pg.m^{-3}) (Van Drooge et al., 2004) and Swiss Alps (102 pg.m^{-3}) (Shunthirasingham et al., 2013), Canadian Rocky mountains (21 to 149 pg.m^{-3}) (Daily et al., 2007), Tibetan plateau, (>50 pg.m^{-3}) (Kang et al., 2009; Liu et al., 2010) and above the Arctic circle (48 to 71 pg.m^{-3}) (Wong et al., 2011). Only few studies have reported the presence of HCB in South American mountain regions (Barra et al., 2004; Shunthirasingham et al., 2011). Generally, air concentrations are in the same range as those reported in the atmosphere of coastal/open Southern Atlantic (Bidleman et al., 1993; Montone et al., 2005), Pacific Oceans, and Antarctic Peninsula region (Zhang et al., 2010). These results suggest that lower air concentration levels of HCB are fairly uniformly distributed across the Southern Hemisphere (Table S10), which indicates that its historical use in this hemisphere was lower than in the Northern Hemisphere.

HCB exhibited fairly uniform vertical distributions at all monitoring sites for both monitored National Parks. The HCB distribution pattern is consistent with previous mountain studies along altitudinal transects (10 to 4400 m.a.s.l.) in the Southern and Northern Hemispheres (Shunthirasingham et al., 2011; Wong et al., 2011). Generally, these findings demonstrate well-mixed conditions of HCB in the atmosphere and the lack of strong source-receptor relationships.

HCB concentrations in the water were in a narrow range, from 2.1 to 2.3 pg.L^{-1} and from 1.2 to 2.3 pg.L^{-1} for NPIT and NPSJ, respectively. These values are comparable to concentrations found at other remote mountain lakes worldwide (<10 pg.L^{-1}) (Barber et al., 2005; Catalan et al., 2004; Vilanova et al., 2001). Low HCB concentrations in water have been recently reported along the South Atlantic (1.9 to 3.3 pg.L^{-1}), and South Pacific (0.4 to 0.8 pg.L^{-1}) open water transects (Booij et al., 2007;

Zhang et al., 2010) (Table S11). However, these HCB levels are much lower than concentrations reported in South American contaminated freshwaters (1,000-10,000 ng.L^{-1}) (UNEP, 2002).

4.2.2. Endosulfans

Only recently listed on the Stockholm Convention, endosulfan was one of the most widely used organochlorine insecticides globally. Since its introduction in the 1950s, the cumulative global use of endosulfan on crops is estimated to be 308 kt (1950 - 2000) and its isomers have been intensely used in South American countries (Li and McDonald et al., 2005). In this study, endosulfans ($\Sigma = \alpha + \beta$ + sulphate) were detected at all sampling sites at the two National Parks. Gaseous endosulfan concentrations ranged from 5.8 to 29 pg.m^{-3} (GM 15 pg.m^{-3}) and from 2.9 to 8.7 pg.m^{-3} (GM 5.0 pg.m^{-3}) for NPIT and NPSJ, respectively. These concentrations are considerably lower than reported in other studies in Chilean (63 to 100 pg.m^{-3}), Bolivian (28 to 1800 pg.m^{-3}) and even Brazilian (40 to 5600 pg.m^{-3}) uplands (Estellano et al., 2008; Meire et al., 2012; Pozo et al., 2004) (Table S10). However, previous studies in South American mountainous regions have generally associated the highest air concentration levels of recently banned pesticides with intense seasonal applications on lowland crops, mainly during summer periods (Estellano et al., 2008; Meire et al., 2012). These findings suggest that fall-winter seasons monitored in this study reflect the expected lower air concentrations levels of endosulfans at all upland sites.

For NPIT, the air concentrations of endosulfans at the highest monitored sites (ITA3 and ITA4) were about 2- to 5-fold higher than those measured at lowest altitudinal sites (figure 3). This is consistent with previous findings for other tropical Brazilian mountains in the vicinity of the sites investigated here (e.g., Rio de Janeiro state), especially during similar seasons. However, no clear trends of endosulfan and its isomers were observed along altitudinal gradients at NPSJ sites. These results conflict with previous studies conducted at the same National Park, which reported a strong correlation between air concentrations of endosulfans and altitude (Meire et al., 2012). Recent studies in the South American mountain regions have in general shown strong upslope enrichment for endosulfans, which were attributed to atmospheric transport from regional and continental agricultural sources (Meire et al., 2012; Shunthirasingham et al., 2011).

Technical grade endosulfan contains *α*-endosulfan and *β*-endosulfan as the main isomers (>95%). Depending on the technical mixture, the ratio of Endo-*α*/*β* in technical formulations ranges from 2.0 to 2.3 (Weber et al., 2010). *β*-endosulfan is less stable in the atmosphere and, thus, an elevated *α/β* ratio represents an aged signature scenario (Yao et al., 2006). In this study, the ratios of *α*/*β* ranged from 1.2 to 3.7 (average 2.0) which suggests fresh applications of endosulfans (lower ratios <2.3) (figure 3). Other studies have shown a seasonal variation of *α*/*β* values at Brazilian and Bolivian mountain sites with higher atmospheric ratio levels (>2.3), especially during the summer period (Estellano et al., 2008; Meire et al., 2012).According to Meire et al. (2012), this seasonal trend may be attributed to more rapid or enhanced weathering of endosulfan during the summer. The winter period contains mainly fresh endosulfan, however at lower emission levels. As shown in Figure 3, the predominance of *α*-endosulfan over the total endosulfan profile (60%, average value) was observed at almost all sites with higher air concentrations (>10 pg.m^{-3}) followed by *β*-endosulfan (25%) and endosulfan sulphate (13%). The lower air concentration levels for endosulfan sulphate (< 3 pg.m^{-3}) were similar to previous studies (Estellano et al., 2008; Meire et al., 2012; Pozo et al., 2009).

Endosulfans were detected at high concentrations in water, ranging from 190 to 264 pg.L^{-1} (GM 219 pg.L^{-1}) and from 166 to 236 pg.L^{-1} (GM 185 pg.L^{-1}) at NPIT and NPSJ, respectively. These findings are consistent with concentrations found in mountain waters as well as snowpack samples across Western US National Parks (44 to 1500 pg.L^{-1}), Canadian Rocky Mountains (> 100 pg.L^{-1}), Alps (40 to 288 pg.L^{-1}), Pyrenees (520 to 1770 pg.L^{-1}), and Caledonian Mountains (100 to 140 pg.L^{-1}) (Blais et al., 1998, 2001; Brandford et al., 2010; Hageman et al., 2006; Vilanova et al., 2001). Even lower concentrations of endosulfans (12 to 24 pg.L^{-1}) were recently reported in waters of the Tatra Mountains, Slovakia (Arellano et al., 2011) (Table S11).

In this study, the mixture of endosulfan in freshwater samples were dominated by endosulfan sulphate (162 to 260 pg.L^{-1}), which accounted for up to 80% of this dissolved insecticide group in upland waters (Figure S1). α-endosulfan exhibited the lowest concentrations (<10 pg.L^{-1}) while β-endosulfan was not detected in water samples. These results correlate well with endosulfan sulphate as the predominant metabolite in aquatic systems worldwide (Booij et al., 2007). The microbiologic oxidation of the technical-grade endosulfan in soils, and its further re-emission to air is regarded as the main source to the atmosphere. In natural aquatic ecosystems, endosulfan sulphate degrades at a slower rate and hence is more persistent than the parent isomers; with a half-life in water of several weeks (Weber et al., 2010). Much greater concentrations of endosulfan sulphate (>100 ng.L^{-1}) than its parental isomers (α- and β-endosulfan) have been detected in contaminated waters close to intensive crop production areas in Argentina and Brazil (Bonansea et al., 2013; Laabs et al., 2002), (Table S11) reinforcing the historical use of this insecticide in South America.

Brazil is considered the biggest user of endosulfan in South America and one of the top endosulfan users worldwide (Li and Mcdonald 2005). According to the Brazilian

Ministry of Development, Industry and Foreign Trade's database (http://aliceweb.mdic.gov.br), Brazil imported approximately 23 kt of endosulfan from 2001 to 2011 with an estimated annual consumption of 2.3 kt.yr^{-1}. As several other South American countries, Brazil started to phase out the commercial use of endosulfan in 2010. However, the agriculture use of endosulfans to control insect populations in sugar-cane, cocoa, coffee, soybean and cotton plantations was totally banned only in 2013 (Brazilian Health Surveillance Agency - ANVISA).

4.2.3. DDTs

For DDTs, the parent compound *p,p´*-DDT and its metabolite *p,p´*-DDE were the main detected compounds for both monitored National Parks. Atmospheric DDT concentrations ranged from 0.1 to 0.6 pg.m^{-3} (GM 0.2 pg.m^{-3}) and from 0.1 to 0.3 pg.m^{-3} (GM 0.2 pg.m^{-3}) for NPIT and NPSJ, respectively. These concentrations were much lower than concentrations observed at high-mountain sites in Europe (0.2 to 12 pg.m^{-3}) (Van Drooge et al., 2004), North America (1.6 to 55 pg.m^{-3}) (Daly et al., 2007), Asia (0.3 to 75 pg.m^{-3}) (Liu et al., 2010; Wang et al., 2008) and even in South America (1.0 to 119 pg.m^{-3}) (Estellano et al., 2008; Meire et al., 2012) (Table S10).

Similar to atmospheric levels, freely dissolved concentrations of DDTs indicated background levels (NPIT: 0.1 to 0.4 pg.L^{-1}, GM 0.2 pg.L^{-1}; NPSJ: 0.2 to 0.3 pg.L^{-1}, GM 0.3 pg.L^{-1}). Only few studies have pointed out the presence of DDTs in South American highland waters (Barra et al., 2005; Schreiber et al., 2013). Schreiber et al. (2013) reported higher dissolved DDT (*p,p´*-DDE) concentrations in upland surface waters of River Xanaes in Central Argentina (70 to 340 pg.L^{-1}). On the other hand, Barra et al. (2005) did not detect the presence of dissolved DDTs along altitudinal gradients in Laja River Basin waters of Central Southern Chile. The concentrations detected in our measurements were also generally much lower than dissolved DDT concentrations reported at other mountains and remote sites worldwide (Table S11).

Over the past few decades (1950-1990), Brazil has experienced a historical use of DDT, primarily for sanitary purposes to control insect pests that are vectors for tropical diseases, such as malaria and typhus (D’Amato et al., 2002). It is estimated that Brazil used and exported to other South American countries a total of 80 t of DDT until the 1980s, whilst more than 30 t were imported in the same period (Almeida et al., 2007).

4.3. Air mass back trajectory analysis

The cluster analysis performed on the 5-day back trajectories unveiled that about 40% of the trajectories arriving at both sites come from the northern sector of Brazil with purely continental influences. At the NPIT, two other clusters accounted for the remainder of the trajectories. A southerly cluster of trajectory (30%) was identified moving from the South Atlantic Ocean with no contact with the continent. The third cluster (29%) was dominated by continental trajectories that stemmed from western South America.

At NPSJ, 35% of the trajectories were maritime, with southerly origin. These trajectories had anticyclonic curvature, which suggests that the airflow associated with these pathways is part of the semi-permanent anticyclonic over the southern Atlantic. The third cluster (24%) consisted of fast-travelling trajectories that originated over the southern Pacific and spent most of the time over Patagonia and southern Brazil before reaching the monitoring site.

The exposures of these sites to large-scale continental airflows with varying source contributions (e.g., from extensive crop areas in central Brazil and Argentina) may partly explain the atmospheric deposition of selected OCPs over upland freshwaters at tropical and subtropical mountains sites in Brazil. These findings, coupled with LDPE passive air and water sampling measurements, point out the potential inputs from distant sources of semi-volatile chemicals to the two high-altitude sites (1700 m a.s.l. NPSJ; 2400 m a.s.l. NPIT). Northerly and westerly (continental) back trajectories represented 70% of the airflow reaching NPIT high-altitude site, which may account for higher air concentrations of endosulfans (>10 pg.m^{-3}) at this site compared to NPSJ site (4.0 pg.m^{-3}), which received only 41% of continental flows (figures S2 and S3). A similar pattern was also observed on surface upland waters, where concentration of endosulfans at NPIT site (>200 pg.L^{-1}) was slightly higher than in NPSJ water samples (166 pg.L^{-1}). These results highlight the role of atmospheric long-range dynamics on transporting organochlorine pesticides from distant source regions and probably enhancing concentrations at high altitude mountain sites in Brazil.

4.4. Air-water Exchange Gradients

In this study, HCB, α-endosulfan and endosulfan sulphate displayed air-water exchange values < 0 (Eq. 3) at almost all sites, indicating net deposition along the two altitudinal transects (figure 4). An exception was only observed at the lowest altitudinal site (990 m. a.s.l.) of NPSJ, when HCB showed net volatilisation > 0. These results reinforce the major atmospheric input of volatile organochlorine pesticides at tropical and subtropical Brazilian mountains. Similar to our results, Galbán-Malagón et al. (2013) reported net deposition for HCB from the Weddell, Bransfield and Bellingshausen Seas (Antarctica Peninsula Region) in two sampling cruises in 2008 and 2009. Net deposition or equilibrium of HCB and endosulfans (α-endosulfan) has been also reported in studies in the Arctic (Lohmann et al., 2009; Wong et al., 2011).

In contrast, net volatilisation gradients were observed for *p,p´*-DDE at NPIT monitored sites. This indicates that NPIT sites still received sufficient *p,p´*-DDE in water, probably from runoff and headwater stream input, to cause net volatilisation of legacy organochlorine pesticides. Air–water exchange gradients suggested net volatilisation for organochlorine pesticides, including *p,p′*-DDE, along Chinese coastline ocean (Lin et al., 2012). These results pointed out the surface waters net volatilisation after a long period of OCP prohibition.

5. Conclusions

As atmospheric transport is faster than dilution in the water column, the volatile OCPs –especially the recently banned pesticides– are experiencing net deposition over pristine National Park areas. We observed this behaviour especially for endosulfan. Surprisingly, even HCB was still mostly undergoing net deposition, with only DDTs displaying net volatilisation. This implies that net deposition of endosulfans at these and other sites will continue for the foreseeable future. Moreover, the exposure of these sites to large-scale continental airflows with varying source contributions may partly explain the atmospheric deposition of selected OCPs over upland freshwaters at tropical and subtropical mountains sites in Brazil. These findings, coupled with LDPE passive air and water sampling measurements, point out the potential inputs from distant sources of semi-volatile chemicals to the two high-altitude sites.

Brazil is a signatory to the Stockholm and since 2001 the country has had to comply with reductions in the use of POPs, including several organochlorine pesticides. According to a federal law (CONAMA 430/11) the shallow waters investigated in this study are classified as “special waters” and should be protected to preserve their natural conditions. This study is a first effort to quantify OCPs in mountain spring waters and to understand air-water exchange over pristine uplands in Brazil. Further studies are necessary to address these issues, especially monitoring of recently banned and current-use pesticides in waters of highland tropical sites.

Acknowledgments

This work was partially funded by the Coordination for the improvement of Higher Education Personnel (CAPES) (grant BEX 8972/11-7) and the National Council of Technological and Scientific Development (CNPq) (grant number 150136/2013-7). The authors are especially grateful to the Chico Mendes Biodiversity Institute for having granted access to the national parks investigated here.

References

Almeida, F.V., Bisinoti, M.C., Jardim, W.F. 2007. Persistent Toxic Substances (PTS) in Brazil. Quim. Nova. 30 (8), 1976-1985.

Arellano, L., Fernández, P., Tatosova, J., Stuchlik, E., Grimalt, J.O., 2011. Long-range transported atmospheric pollutants in snowpacks accumulated at different altitudes in the Tatra Mountains (Slovakia). Environ. Sci. Technol. 45, 9268–9275.

Bailey, R.E., 2001. Global hexachlorobenzene emissions. Chem. 43, 167–182.

Barber, J.L., Sweetmana, A.J., Wijk, D.V., Jones, K.C., 2005. Hexachlorobenzene in the global environment: Emissions, levels, distribution, trends and processes. Sci. Total Environ. 349, 1– 44.

Barra, R., Popp, P., Quiroz, R., Bauer, C., Cid, H., Tuempling, W., 2005. Persistent toxic substances in soils and waters along an altitudinal gradient in the Laja river basin, central southern Chile. Chem. 58, 905–915.

Bidleman, T.F., Walla, M.D., Roura, R., Carr, E., Schmidt, S., 1993. Organochlorine pesticides in the atmosphere of the southern ocean and Antarctica, January-March, 1990. Mar. Pollut. Bull. 26 (5), 258–262.

Blais, J.M., Charpentie, S., Picka, F., Kimpea, L.E., Amanda, A., Regnault-Rogerb, C., 2006. Mercury, polybrominated diphenyl ether, organochlorine pesticide, and polychlorinated biphenyl concentrations in fish from lakes along an elevation transect in the French Pyrenees. Ecotoxicol. Environ. Safe. 63, 91–99.

Blais, J.M., Schindler, D.W., Muir, D.C.G., Kimpe, L.E., Donald, D.B., Rosenberg, B., 1998. Accumulation of persistent organochlorine compounds in mountains of western Canada. Nature. 395, 585–588.

Blais, J.M., Schindler, D.W., Muir, D.C.G., Sharp, M., Donald, D., Lafrenière, M., Braekevelt, E., Strachan, W.M.J., 2001. Melting glaciers: a major source of persistent organochlorines to subalpine bow lake in Banff National Park, Canada. Ambio. 30 (7), 410-415.

Bonansea, R.I., Améa, M.V., Wunderlin, D.A., 2013. Determination of priority pesticides in water samples combining SPE and SPME coupled to GC–MS. A case study: Suquía River basin (Argentina). Chem. 90, 1860–1869.

Booij, K., van Bommel, R., Jones, K.C., Barber, J.L., 2007. Air-water distribution of hexachlorobenzene and 4,4′-DDE along a North-South Atlantic transect. Mar. Pollut. Bull. 54, 814–819.

Booij, K., Smedes, F., Weerlee, E.M., 2002. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. Chem. 46, 1157–1161.

Brandford, D.F., Stanley, K., McConnell, L.L., Tallent-Halsell, N.G., Nash, M.S., Simonich, S.M., 2010. Spatial patterns of atmospherically deposited organic contaminants at high elevation in the southern Sierra Nevada mountains, California, USA. Environ. Toxicol. Chem. 29 (5), 1056–1066.

Brazilian Ministry of Development, Industry and Foreign Trade's database [WWW document]. <http://aliceweb.mdic.gov.br>.

Brazilian Institute for the Environment and Renewable Natural Resources (IBAMA), *Pesticides and Related Products Commercialized in Brazil in 2009: An Environmental Approach*. 2010. Brasília, Brazil [WWW document]. <http://www.ibama.gov.br/phocadownload/qualidade_ambiental/pesticides_commercialized_in_brazil_2009.pdf>.

Calamari, D., Bacci, E., Focardi, S., Gaggi, C., Morosini, M., Vighi, M., 1991. Role of plant biomass in the global environmental partitioning of chlorinated hydrocarbons. Environ. Sci. Technol. 25, 1489–1495.

Catalan, J., Ventura, M., 2004. The roles of food and water in the bioaccumulation of organochlorine compounds in high mountain lake fish. Environ. Sci. Technol. 38,4269–4275.

Daly, G., Lei, D.Y., Teixeira, C., Muir, D.G., Castillo, L.E., Jantunen, L.M.M., Wania, F., 2007. Organochlorine pesticides in the soils and atmosphere of Costa Rica. Environ. Sci. Technol. 41, 1124–1130.

Daly, G., Lei, D.Y., Teixeira, C., Muir, D.G., Wania, F., 2007. Pesticides in western Canadian mountain air and soil. Environ. Sci. Technol. 41, 6020–6025.

Daly, G.L., Wania, F., 2005. Organic contaminants in mountains. Environ. Sci. Technol. 39, 385–398.

D'Amato, C., Torres, J.P.M., Malm, O., 2002. DDT (dichlorodiphenyltrichloroethane): Toxicity and environmental contamination - A review. *Quim. Nova*. 25, 995–1002.

Davidson, D.A., Wilkinson, A.C., Blais, J.M., Kimpe, L.E., McDonald, K.M., Schindler, D.W., 2003. Orographic cold-trapping of persistent organic pollutants by vegetation in mountains of western Canada. Environ. Sci. Technol. 37, 209–215.

Draxler, R.R., Rolph, G.D., 2012. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model. NOAA Air Resources Laboratory, Silver Spring, MD [WWW document]. <http://ready.arl.noaa.gov/HYSPLIT.php>.

Eastern and Western South America – Regional Report; United Nations Environmental Programme (UNEP) Chemicals. Viña del Mar, Chile, 2002 [WWW document]. <http://www.chem.unep.ch/pts/regreports/eastern%20and%20western%20south%20america%20full%20report.pdf.x>.

Endosulfan monograph database. Brazilian Health Surveillance Agency (ANVISA), Brasília, DF, 2014. [WWW document]. <http://portal.anvisa.gov.br/wps/wcm/connect/af90f080474580548c47dc3fbc4c6735/E02++endossulfam_final.pdf?mod=ajpere>.

Estellano, V.R.H., Pozo, K., Harner, T., Franken, M., Zaballa, M., 2008. Altitudinal and seasonal variations of persistent organic pollutants in the Bolivian Andes mountains. Environ. Sci. Technol. 42, 2528–2534.

Galbán-Malagón, C., Cabrerizo, A., Caballero, G., Dachs, J., 2013. Atmospheric occurrence and deposition of hexachlorobenzene and hexachlorocyclohexanes in the Southern Ocean and Antarctic Peninsula. Atmos. Environ. 80, 41–49.

Hageman, K., Simonich, S.L., Campbell, D.H., Wilson, G.R., Landers, D.H., 2006. Atmospheric deposition of current-use and historic-use pesticides in snow at National Park in the western United States. Environ. Sci. Technol. 40, 3174–3180.

Harner, T., Bartkow, M., Holoubek, I., Klanova, J., Wania, F., Gioia, R., Moeckle, C., Sweetman, A.J., Jones, K.C., 2006. Passive air sampling of persistent organic pollutants: introductory remarks to the special issue. Environ. Pollut. 144, 361–364.

Kang, J.H., Choi, S.D., Park, H., Baek, S.Y., Sungmin Hong, S., Chang, Y.S., 2009. Atmospheric deposition of persistent organic pollutants to the East Rongbuk Glacier in the Himalayas. Sci. Total Environ. 408, 57–63.

Khairy, A.M., Lohmann, R., 2012. Field Validation of polyethylene passive air samplers for parent and alkylated PAHs in Alexandria, Egypt. Environ Sci. Technol. 46, 3990−3998.

Khairy, A.M., Lohmann, R., 2013. Feasibility of using low density polyethylene sheets to detect atmospheric organochlorine pesticides in Alexandria, Egypt. Environ. Poll. 181, 151–158.

Khairy, M.A., Lohmann R., 2014. Field calibration of low density polyethylene passive samplers for gaseous POPs. Environ. Sci.: Processes Impacts. 16, 414–421.

Khairy, M., Muir, D., Teixeira, C., Lohmann, R., 2014. Spatial trends, sources and air-water exchange of organochlorine pesticides in the Great Lakes Basin using low density polyethylene passive samplers. Environ. Sci. Technol. 48 (16), 9315–9324.

Kirchner, M.; Faus-Kessler, T.; Jakobi, G.; Levy, W.; Henkelmann, B.; Bernhoft, S.; Kotalik, J.; Zsolnay, A.; Bassan, R.; Belis, C.; Krauchi, N.; Moche, W.; Simoncic, P.; Uhl, M.; Weiss, P.; Schramm, K. W., 2009. Vertical distribution of organochlorine pesticides in humus along Alpine altitudinal profiles in relation to ambiental parameters. Environ. Pollut. 157, (12), 3238-47.

Laabs, V., Amelung, W., Pinto, A.A., Wantzen, M., Silva, C.J., Zech, W., 2002. Pesticides in surface water, sediment, and rainfall of northeastern Pantanal Basin, Brazil. J. Environ. Qual. 31, 1636–1648.

Levy, W.; Henkelmann, B.; Pfister, G.; Bernhoft, S.; Kirchner, M.; Jakobi, G.; Bassan, R.; Krauchi, N.; Schramm, K. W., 2009. Long-term air monitoring of organochlorine pesticides using Semi Permeable Membrane Devices (SPMDs) in the Alps. Environ. Pollut. 157, (12), 3272-9.

Li, Y.F., Macdonald, R.W., 2005. Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: a review. Sci. Total Environ. 342, 87–106.

Lin, T., Li, J., Xu, Y., Liu, X., Luo, C., Cheng, H., Chen, Y., Zang, G., 2012. Organochlorine pesticides in seawater and the surrounding atmosphere of the marginal seas of China: Spatial distribution, sources and air–water exchange. Sci. Total Environ. 435–436, 244–252.

Liu, W., Chen, D., Liu, X., Zheng, X., Yang, W., Westgate, J., Wania, F., 2010. Transport of semivolatile organic compounds to the Tibetan Plateau: Spatial and temporal variation in air concentrations in mountainous western Sichuan, China. Environ. Sci. Technol. 44, 1559–1565.

Lohmann, R., 2012. Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. Environ. Sci. Technol. 46, 606–618.

Lohmann, R., Dapsis, M., Morgan, E.J., Dekany, V., Luey, P.J., 2011. Determinig air-water exchange, spatial and temporal trends of freely dissolved PAHs in an urban estuary using passive polyethylene samplers. Environ. Sci. Technol. 45, 2655–2662.

Lohmann, R., Gioia, R., Jones, K.C., Nizzetto, L., Temme, C., Xie, Z., Schulz-Bull, D., Hand, I., Morgan, E., Jantunen, L., 2009. Organochlorine pesticides and PAHs in the surface water and atmosphere of the North Atlantic and Arctic Ocean. Environ. Sci. Technol. 43, 5633–5639.

Lohmann, R., Muir, D.C.G., 2010. Global aquatic passive sampling (AQUAGAPS): Using passive samplers to monitor POPs in the waters of the world. Environ. Sci. Technol. 44, 860–864.

McDonough, C.A., Khairy, M.A., Muir, D.C.G., Lohmann, R., 2014. Significance of population centers as sources of gaseous and dissolved PAHs in the lower Great Lakes. Environ. Sci. Technol. 48 (14), 7789–7797.

Meire, R.O., Lee S.C., Yao, Y., Targino, A.C., Torres, J.P.M., Harner, T., 2012. Seasonal and altitudinal variations of legacy and current-use pesticides in the Brazilian tropical and subtropical mountains. Atmos. Environ. 59, 108–116.

Montone, R.C., Taniguchi, S., Boian, C., Weber, R.R., 2005. PCBs and chlorinated pesticides (DDTs, HCHs and HCB) in the atmosphere of southwest Atlantic and Antarctic oceans. Mar. Pollut. Bull. 50, 778–786.

Myers, N., Mittermeier, R.A., Mittermeier, C.G., da Fonseca, G.A.B., Kent, J., 2000. Biodiversity hotspots for conservation priorities. Nature. 403, 853–858.

Pozo, K., Harner, T., Lee, S.C., Wania, F., Muir, D.C.G., Jones, K.C., 2009. Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS study. Environ. Sci. Technol. 43, 796–803.

Pozo, K., Harner, T., Shoeib, M., Urrutia, R., Barra, R., Parra, O., Focardi, S., 2004. Passive-sampler derived air concentrations of persistent organic pollutants on a north-south transect in Chile. Environ. Sci. Technol. 38, 6529–6537.

Sacks, V.P., Lohmann, R., 2011. Development and use of polyethylene passive samplers to detect tricosans and alkylphenols in an urban estuary. Environ. Sci. Technol. 45, 2270–2277.

Schreiber, R., Harguinteguy, C.A., Manetti, M.D., 2013. Dynamics of organochlorine contaminants in surface water and in *Myriophyllum aquaticum* plants of the River Xanaes in Central Argentina during the annual dry season. Arch. Environ. Contam. Toxicol. 65, 466–473.

Sheng, J., Wang, X., Gong, P., Joswiak, D.R., Tian, L., Yao, T., Jones, K.C., 2013. Monsoon-driven transport of organochlorine pesticides and polychlorinated biphenyls to the Tibetan plateau: three year atmospheric monitoring study. Environ. Sci. Technol. 47, 3199−3208.

Shoeib, M., Harner, T., 2002. Characterisation and comparison of three passive air samplers for persistent organic pollutants. Environ. Sci. Technol. 36, 4142−4151.

Shunthirasingham, C., Barra, R., Gonzalo Mendoza, G., Montory, M., Oyiliagu, C.E., Lei, Y.D., Wania, F., 2011. Spatial variability of atmospheric semivolatile organic compounds in Chile. Atmos. Environ. 45, 303−309.

Shunthirasingham, C., Wania, F., MacLeod, M., Lei, Y.D., Quinn, C.L., Zhang, X., Scheringer, M., Wegmann, F., Hungerbu̇hler, K., Ivemeyer, S., Heil, F., Klocke, P., Pacepavicius, G., Mehran Alaee, M., 2013. Mountain cold-trapping increases transfer of persistent organic pollutants from atmosphere to cows’ milk. Environ. Sci. Technol. 47, 9175−9181.

Van Drooge, B.L., Grimalt, J.O., 2004. Atmospheric semivolatile organichlorine compounds in European high-mountain areas (Central Pyrenees and High Tatras). Environ. Sci. Technol. 38, 3525−532.

Vilanova, R., Fernandez, P., Martinez, C., Grimalt J.O., 2001. Organochlorine pollutants in remove mountain lake waters. J. Environ. Qual. 30, 1286–1295.

Wang, X., Yao, T., Wang, P., Wei-Yang, L., T., 2008. The recent deposition of persistent organic pollutants and mercury to the Dasuopu glacier, Mt. Xixiabangma, central Himalayas. Sci. Total Environ. 394, 134–143.

Wania, F., Westgate, J.N., 2008. On the mechanism of mountain cold-trapping of organic chemicals Environ. Sci. Technol. 42, 9092–9098.

Ward, J.H., 1963. Hierarchical grouping to optimize an objective function. J. Am. Stat. Assoc. 58, 236–244.

Weber, J., Halsall, C.J., Muir, D., Teixeira, C., Small, J., Solomon, K., Hermanson, M., Hung, H., Bidleman, T., 2010. Endosulfan, a global pesticide: a review of its fate in the environment and occurrence in the Arctic. Environ. Sci. Technol. 408 (15), 2966–2984.

Wong, F., Jantunen, L., Pućko, M., Papakyriakou, T., Staebler, R.M., Stern, G., Bidleman, T.,2011. Air-water exchange of anthropogenic and natural organohalogens on international polar year (IPY) expeditions in the Canadian arctic. Environ. Sci. Technol. 45, 876–881.

Yao, Y., Tuduri, L., Harner, T., Blanchard, P., Waite, D., Poissant, L., Murphy, C., Belzer, W., Aulagnier, F., Li, Y., Sverko, E., 2006. Spatial and temporal distribution of pesticides air concentrations in Canadian agricultural regions. Atmos. Environ. 40, 4339−4351.

Zhang, L., Lohmann, R., 2010. Cycling of PCBs and HCB in the surface ocean-lower atmosphere of the open Pacific. Environ. Sci. Technol. 44, 3832–3838.

Figure 1. Map showing the south and southern regions of Brazil. The two National Parks where the samplings were conducted are also indicated: 1. National Park of Itatiaia – Rio de Janeiro State, 2. National Park of São Joaquim – Santa Catarina State. The photographs illustrate the deployment of the passive samplers.

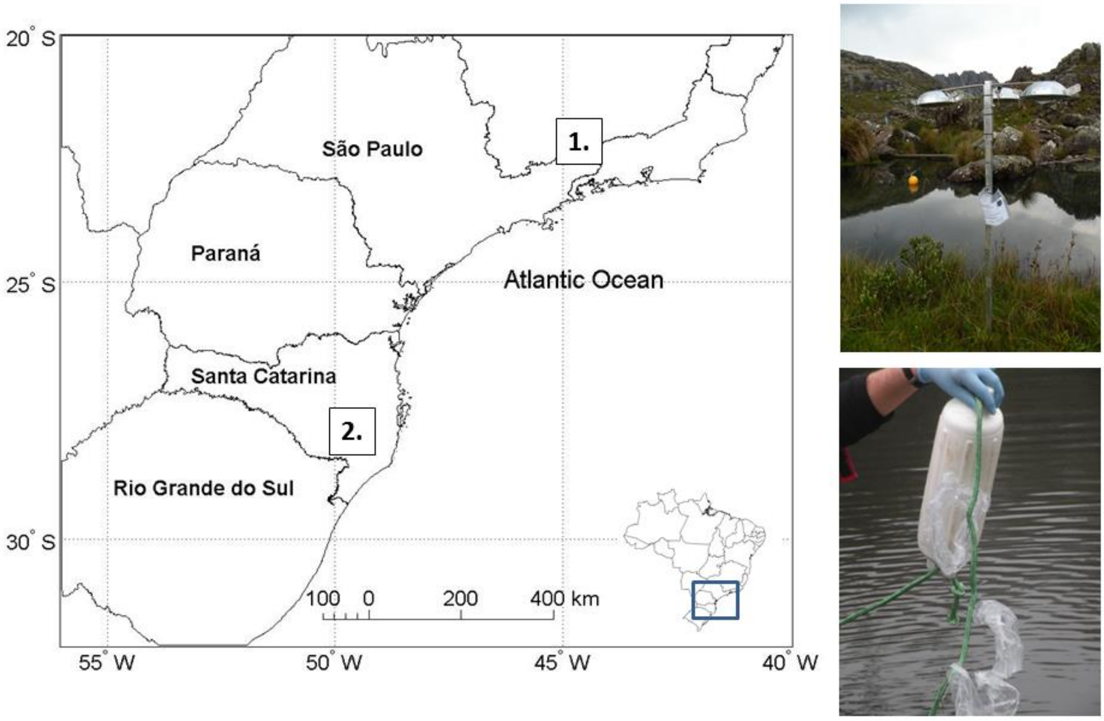
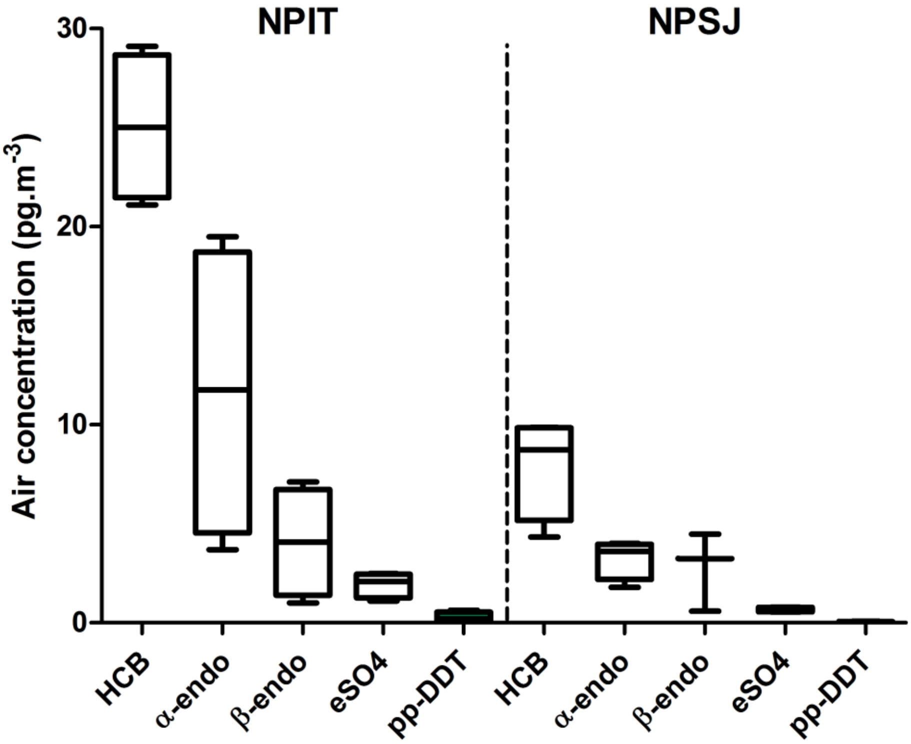


Figure 2. "Box and whisker" plots showing summaries of the estimated atmospheric (pg.m^{-3}) and dissolved (pg.L^{-1}) concentrations of selected organochlorine pesticides at the two National Parks (NPIT – National Park of Itatiaia; NPSJ – National Park of São Joaquim.). The results represent measurements during fall-winter periods in 2012 and over altitudes ranging from 800 to 2200 m a.s.l. The following abbreviations are used: HCB = hexachlorobenzene; α-endo = alpha-endosulfan; β-endo = beta-endosulfan; eSO_4 = endosulfan sulphate (plotted in the right axis for water samples); Dield = dieldrin.



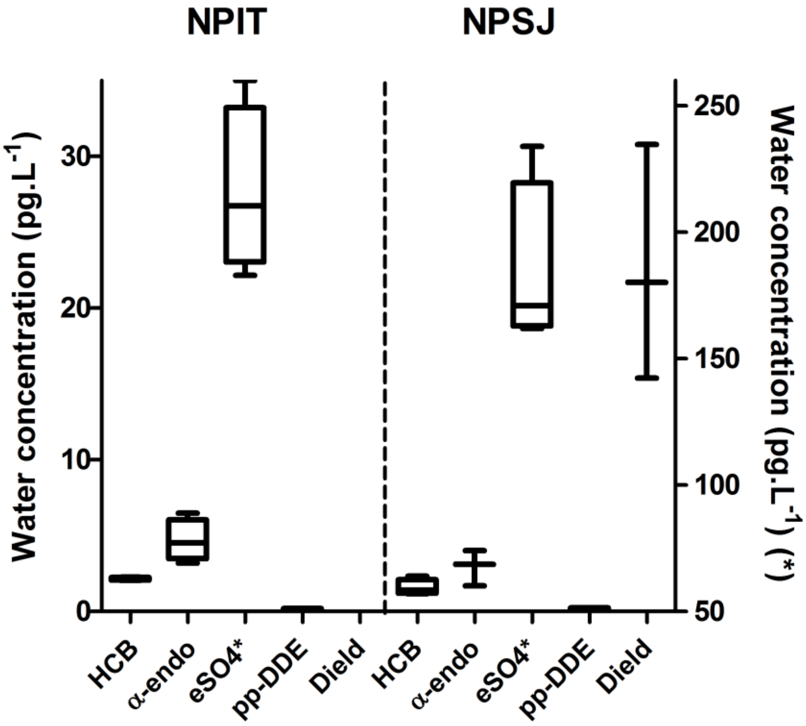

NPIT
NPSJ
Water concentration (pg.L-1)
Water concentration (pg.L-1) (*)
0
10
20
30
50
100
150
200
250
HCB
α-endo
eSO4*
pp-DDE
Dield
HCB
α-endo
eSO4*
pp-DDE
Dield

Figure 3. Atmospheric endosulfan composition at the sampling sites. Green line represents the average endo-α/β ratio value.

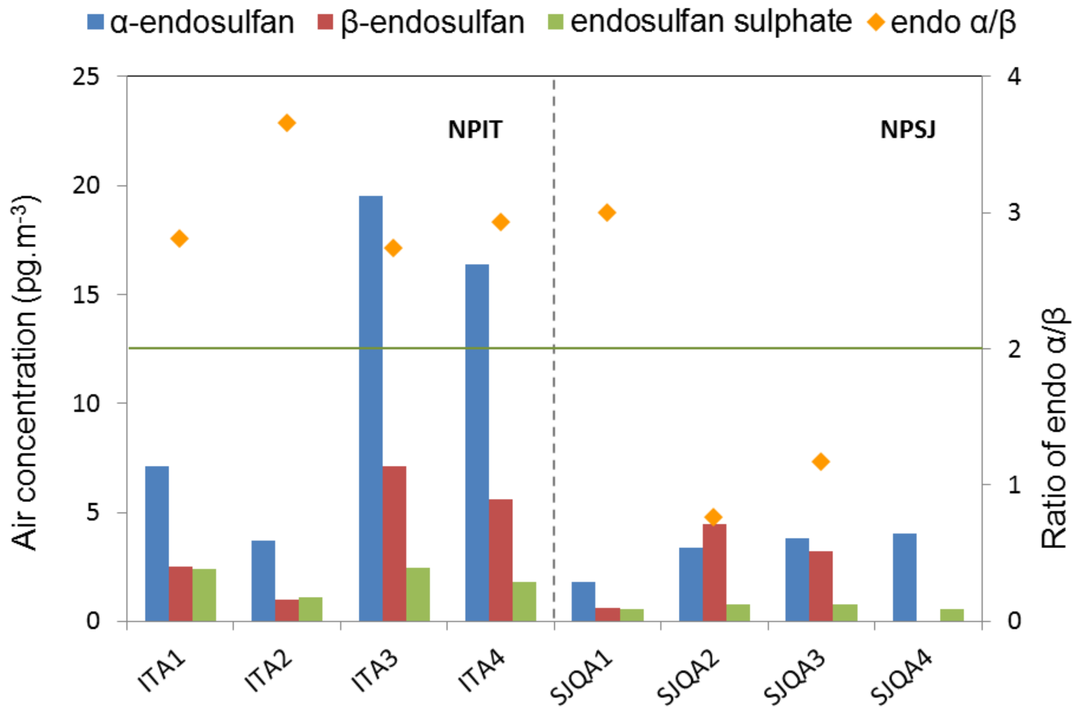


Figure 4. Air-water exchange gradients along altitudinal transects at NPIT and NPSJ sites for HCB, *α*- endosulfan, endosulfan sulphate (endoSO_4), and pp-DDE. Positive values indicate net volatilisation of OCPs; negative values indicate net deposition.