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1 **Use of passive samplers to detect Organochlorine Pesticides in air and**

2 **water at Wetland Mountain region sites (S-SE Brazil)**

3

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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 (Σ= α-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.

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.: 22º22´38''S, lon.: 44º41´35''W, Rio de Janeiro State) and "Serra Geral" (National Park of São Joaquim - NPSJ, lat.: 28º00'49''S, lon.: 49º35'17''W, Santa Catarina State), located in southeast and south Brazil, respectively.

94 The two national parks comprise rainforests and high-altitude ecosystems and are

95 considered important conservation areas for biodiversity and endemic species (Myers et

96 al., 2000).

97

98 *2.2. Field Deployment*

99 Four sampling sites were established along altitudinal gradients at each National

100 Park during late fall and early winter seasons (May and June) in 2012. Passive LDPE

101 sheets were deployed in the surface waters and overlying atmosphere concomitantly

102 over four to five weeks (Figure 1). Water LDPE samplers were deployed 1 m below the

103 surface attached to small buoys, whilst air samplers were fixed at 1.5 m above ground,

104 inside inverted stainless steel bowls to form a clam-shell shape. The bowl design also

105 protects the sampling medium (LDPE sheet) from direct radiation and rainfall, and

106 diminishes the wind speed effect (Shoeib and Harner, 2002). Site and deployment

107 details are given in Table S1. Additionally, five field blanks were collected at both

108 parks to assess possible sample contamination during transport and storage. Methods for

109 preparation and extraction of LDPEs as well as the instrumental analyses of the extracts

110 and quality assurance/quality control are given in supplementary material (SM).

111

112 **3. Theory/calculation**

113 *3.1. Atmospheric and water concentrations derived from LDPEs*

114 We added performance reference compounds (PRCs) added to the samplers

115 before deployment in order to gauge whether organochlorine pesticides had reached

116 equilibrium and to adjust for disequilibrium in polyethylene samplers. Assuming that

117 uptake and elimination rates are equivalent, the freely dissolved (or gas-phase)

118 concentrations of individual OCPs ($C_{water\ or\ air}$) were then calculated by the following

119 equation:

120

121 $$C_{water\ (air)} = C_{LDPE} / K_{LDPE\text{-}water\ (LDPE\text{-}air)} \ x \ [1 - \exp\ ^{-Rs\ x\ t\ /\ K_{LDPE\text{-}water\ (LDPE\text{-}air)}\ x\ m_{LDPE}}] \quad (1)$$

122

123 where C_{LDPE} is the OCP concentration in the LDPE (L.kg^{-1}), R_s is the sampling rate

124 [m^3.day^{-1}], t is the deployment period (days), m_{LDPE} is the mass of the LDPE sheet (kg)

125 and $K_{LDPE\text{-}water}$ (*or LDPE-air*, when applicable) is the sampler-water (air) partitioning

126 coefficients (m^3.kg^{-1}). Sampling rates (Table S3) were calculated using the PRCs as

127 follows:

128 $$f = \exp\ (-Rs\ x\ t\ /\ K_{LDPE\text{-}water\ (LDPE\text{-}air)}\ x\ m_{LDPE}) \quad (2)$$

129 where f is the fraction of PRC retained in the passive sampler after deployment. Details

130 on the PRC method have been described elsewhere (Booij et al., 2002; Khairy et al.,

131 2014). Physico-chemical properties used to calculate the sampler-water partitioning

132 coefficients ($K_{LDPE\text{-}water}$s) are given in supplementary material (SM).

133

134 *3.2. Air mass back trajectory analysis.*

135 To investigate the influence of atmospheric large-scale circulation on the

136 concentrations of air pollutants at the highest altitudinal sites, 5-day backward air

137 trajectories were calculated using the Hybrid Single Particle Lagrangian Integrated

138 Trajectory Model (HYSPLIT) (Draxler et al., 2012). In this study, we used cluster

139 analysis to identify source regions and to investigate how different atmospheric flow

140 patterns influence the concentrations of OCPs at the monitored sites. The Supporting

141 Material (SM) provides additional details on the model and input dataset.

142

143 *3.3. Air-Water Exchange Gradients*

144   Air-water exchange gradients were calculated as the ratio of OCP concentrations

145 measured in the LDPE (ng/LDPE) in each reservoir (water and air), corrected for non-

146 equilibrium, minus one:

147

148 $$\text{Air} - \text{Water exchange} = (C_{LDPE\,(Water)} \, / \, C_{LDPE\,(air)}) \text{ -1} \qquad (3)$$

149

150 In effect, the LDPE samplers reflect dissolved and freely OCPs in water or air,

151 respectively, and thus they easily enable to derive the gradient across the air-water

152 interface. Positive values indicate net volatilisation of OCPs and negative values

153 indicate net deposition. We did not apply any temperature correction, as suggested by

154 Lohmann et al. (2011), so the gradients indicate conditions in the field.

155

156 **4. Results and Discussion**

157 *4.1. Sampling rates and OCP equilibrations in field-deployed LDPE samplers*

158   Sampling rates (Rs) for the atmospheric and water samplers are given in Table

159 S3. Atmospheric Rs ranged from 8.0 to 43 $m^3.day^{-1}$, which is consistent with Rs values

160 measured for atmospheric OCPs (Khairy and Lohmann, 2013). Greater Rs values were

161 observed at the highest altitudes at both National Parks, however the relationship

162 between Rs and altitude was statistically insignificant.

163   Tables S5 and S6 depict calculated % equilibrium for gaseous OCPs. HCB, α-

164 and γ- HCHs (log $K_{LDPE-air} \leq 7.15$) were the only detected OCPs that approached

165   equilibrium (> 97 %) in all deployed samplers. All the other detected OCPs were still

166   far from reaching equilibrium (< 50 %). Khairy and Lohmann (2014) observed a similar

167   pattern for gaseous OCPs in the USA.

168   Rs values for the water samplers ranged from 18 to 81 L.day^{-1}. A similar range

169   was observed for pyrene and higher molecular weight polycyclic aromatic hydrocarbons

170   (PAHs) sampled in Narragansett Bay (Lohmann et al., 2011) and in the Great Lakes

171   (McDonough et al., 2014), and for extended OCP studies (15 to 80 L.day^{-1}) in the

172   Lower Great Lakes (Lakes Ontario and Erie) (Khairy et al., 2014). The sampling rates

173   for National Park of Itatiaia were significantly higher (p = 0.006) than those for

174   National Park of São Joaquim, and the calculated % equilibrium values for freely

175   dissolved OCPs showed variations between the two parks. At the National Park of

176   Itatiaia, all the detected OCPs (except p,p'-DDT) approached equilibrium by the end of

177   the deployment period, whilst at the National Park of São Joaquim, only HCB, α-

178   endosulfan and endosulfan sulphate were at equilibrium (Table S5 and S6). This

179   difference is a consequence of different Rs values (higher Rs values indicate faster

180   equilibration).

181

182   *4.2. Air and water concentrations of target pesticides*

183   At both National Parks, the most frequently detected compounds in air were

184   HCB and endosulfans (α-endosulfan, β-endosulfan and endosulfan sulphate). The

185   highest atmospheric concentrations were detected for HCB (4.0 to 29 pg.m^{-3}) followed

186   by α-endosulfan (1.8 to 20 pg.m^{-3}), β-endosulfan (<LOD to 7.1 pg.m^{-3}), α- HCH (<LOD

187   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

188   p,p'- DDT (<LOD to 0.6 pg.m^{-3}). All the other investigated OCPs were below detection

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

190 target pesticides.

191   Similar to the atmospheric findings, endosulfans accounted for highest

192 frequency detection in shallow waters amongst target OCPs (100s pg.L^{-1}) (Tables S7

193 and S8). However, amongst the less frequently detected pesticides (*p,p´*- DDT, *p,p´*-

194 DDD, *p,p´*- DDE and *trans*-nonachlor) dieldrin stands out with intermediate

195 concentration levels at the National Park of São Joaquim (< LOD to 31 pg.L^{-1}) (Figure

196 2). The greatest concentrations were reported for endosulfan sulphate (162 to 260 pg.L^{-}

197 ^{1}), followed by dieldrin (15 to 31 pg.L^{-1}), α-endosulfan (<LOD to 6.5 pg.L^{-1}), HCB (1.2

198 to 2.3 pg.L^{-1}) and DDTs (0.1 to 0.6 pg.L^{-1}). The results for individual pesticides are

199 discussed below. We chose to present geometric mean (GM) values are presented rather

200 than arithmetic means to prevent extreme values (outliers) from skewing the mean.

201

202 *4.2.1. Hexachlorobenzene (HCB)*

203   Although HCB has been widely used in the past, its commercial use has been

204 banned worldwide (Barber et al., 2005). However, HCB is currently released as an

205 intermediate and by-product in the manufacture of a large number of chlorinated

206 solvents, aromatics and pesticides and continues to volatilize from contaminated soils to

207 the atmosphere (Bailey, 2001). In Brazil, there are well-known hotspots and stockpiles

208 of HCB (e.g. Cubatão, São Paulo State) (UNEP, 2002) that may still represent a

209 significant local environmental sources. On top of that, Brazil imported ca. 800 t of

210 HCB in the middle of 60s (UNEP 2002).

211   HCB was detected at all sampling sites at both National Parks, and exhibited the

212 highest air concentrations among the target compounds (Figure 2). HCB concentrations

213 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

214   pg.m^{-3}) for NPIT and NPSJ, respectively. These air concentrations are much lower than

215   air concentrations measured in high-mountain areas worldwide, such as: Central

216   Pyrenees, High Tatras (36 to 120 pg.m^{-3}) (Van Drooge et al., 2004) and Swiss Alps (102

217   pg.m^{-3}) (Shunthirasingham et al., 2013), Canadian Rocky mountains (21 to 149 pg.m^{-3})

218   (Daily et al., 2007), Tibetan plateau, (>50 pg.m^{-3}) (Kang et al., 2009; Liu et al., 2010)

219   and above the Arctic circle (48 to 71 pg.m^{-3}) (Wong et al., 2011). Only few studies have

220   reported the presence of HCB in South American mountain regions (Barra et al., 2004;

221   Shunthirasingham et al., 2011). Generally, air concentrations are in the same range as

222   those reported in the atmosphere of coastal/open Southern Atlantic (Bidleman et al.,

223   1993; Montone et al., 2005), Pacific Oceans, and Antarctic Peninsula region (Zhang et

224   al., 2010). These results suggest that lower air concentration levels of HCB are fairly

225   uniformly distributed across the Southern Hemisphere (Table S10), which indicates that

226   its historical use in this hemisphere was lower than in the Northern Hemisphere.

227   HCB exhibited fairly uniform vertical distributions at all monitoring sites for

228   both monitored National Parks. The HCB distribution pattern is consistent with

229   previous mountain studies along altitudinal transects (10 to 4400 m.a.s.l.) in the

230   Southern and Northern Hemispheres (Shunthirasingham et al., 2011; Wong et al., 2011).

231   Generally, these findings demonstrate well-mixed conditions of HCB in the atmosphere

232   and the lack of strong source-receptor relationships.

233   HCB concentrations in the water were in a narrow range, from 2.1 to 2.3 pg.L^{-1}

234   and from 1.2 to 2.3 pg.L^{-1} for NPIT and NPSJ, respectively. These values are

235   comparable to concentrations found at other remote mountain lakes worldwide (<10

236   pg.L^{-1}) (Barber et al., 2005; Catalan et al., 2004; Vilanova et al., 2001). Low HCB

237   concentrations in water have been recently reported along the South Atlantic (1.9 to 3.3

238   pg.L^{-1}), and South Pacific (0.4 to 0.8 pg.L^{-1}) open water transects (Booij et al., 2007;

239   Zhang et al., 2010) (Table S11). However, these HCB levels are much lower than

240   concentrations reported in South American contaminated freshwaters (1,000-10,000

241   ng.L^{-1}) (UNEP, 2002).

242

243   *4.2.2. Endosulfans*

244   Only recently listed on the Stockholm Convention, endosulfan was one of the

245   most widely used organochlorine insecticides globally. Since its introduction in the

246   1950s, the cumulative global use of endosulfan on crops is estimated to be 308 kt (1950

247   - 2000) and its isomers have been intensely used in South American countries (Li and

248   McDonald et al., 2005). In this study, endosulfans ($\Sigma = \alpha + \beta$ + sulphate) were detected

249   at all sampling sites at the two National Parks. Gaseous endosulfan concentrations

250   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}

251   ^{3}) for NPIT and NPSJ, respectively. These concentrations are considerably lower than

252   reported in other studies in Chilean (63 to 100 pg.m^{-3}), Bolivian (28 to 1800 pg.m^{-3}) and

253   even Brazilian (40 to 5600 pg.m^{-3}) uplands (Estellano et al., 2008; Meire et al., 2012;

254   Pozo et al., 2004) (Table S10). However, previous studies in South American

255   mountainous regions have generally associated the highest air concentration levels of

256   recently banned pesticides with intense seasonal applications on lowland crops, mainly

257   during summer periods (Estellano et al., 2008; Meire et al., 2012). These findings

258   suggest that fall-winter seasons monitored in this study reflect the expected lower air

259   concentrations levels of endosulfans at all upland sites.

260   For NPIT, the air concentrations of endosulfans at the highest monitored sites

261   (ITA3 and ITA4) were about 2- to 5-fold higher than those measured at lowest

262   altitudinal sites (figure 3). This is consistent with previous findings for other tropical

263   Brazilian mountains in the vicinity of the sites investigated here (e.g., Rio de Janeiro

264   state), especially during similar seasons. However, no clear trends of endosulfan and its

265   isomers were observed along altitudinal gradients at NPSJ sites. These results conflict

266   with previous studies conducted at the same National Park, which reported a strong

267   correlation between air concentrations of endosulfans and altitude (Meire et al., 2012).

268   Recent studies in the South American mountain regions have in general shown strong

269   upslope enrichment for endosulfans, which were attributed to atmospheric transport

270   from regional and continental agricultural sources (Meire et al., 2012;

271   Shunthirasingham et al., 2011).

272   Technical grade endosulfan contains α-endosulfan and β-endosulfan as the main

273   isomers (>95%). Depending on the technical mixture, the ratio of Endo-α/β in technical

274   formulations ranges from 2.0 to 2.3 (Weber et al., 2010). β-endosulfan is less stable in

275   the atmosphere and, thus, an elevated α/β ratio represents an aged signature scenario

276   (Yao et al., 2006). In this study, the ratios of α/β ranged from 1.2 to 3.7 (average 2.0)

277   which suggests fresh applications of endosulfans (lower ratios <2.3) (figure 3). Other

278   studies have shown a seasonal variation of α/β values at Brazilian and Bolivian

279   mountain sites with higher atmospheric ratio levels (>2.3), especially during the

280   summer period (Estellano et al., 2008; Meire et al., 2012).According to Meire et al.

281   (2012), this seasonal trend may be attributed to more rapid or enhanced weathering of

282   endosulfan during the summer. The winter period contains mainly fresh endosulfan,

283   however at lower emission levels. As shown in Figure 3, the predominance of α-

284   endosulfan over the total endosulfan profile (60%, average value) was observed at

285   almost all sites with higher air concentrations (>10 pg.m^{-3}) followed by β-endosulfan

286   (25%) and endosulfan sulphate (13%). The lower air concentration levels for endosulfan

287   sulphate (< 3 pg.m^{-3}) were similar to previous studies (Estellano et al., 2008; Meire et

288   al., 2012; Pozo et al., 2009).

289   Endosulfans were detected at high concentrations in water, ranging from 190 to

290   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

291   NPSJ, respectively. These findings are consistent with concentrations found in

292   mountain waters as well as snowpack samples across Western US National Parks (44 to

293   1500 pg.L^{-1}), Canadian Rocky Mountains (> 100 pg.L^{-1}), Alps (40 to 288 pg.L^{-1}),

294   Pyrenees (520 to 1770 pg.L^{-1}), and Caledonian Mountains (100 to 140 pg.L^{-1}) (Blais et

295   al., 1998, 2001; Brandford et al., 2010; Hageman et al., 2006; Vilanova et al., 2001).

296   Even lower concentrations of endosulfans (12 to 24 pg.L^{-1}) were recently reported in

297   waters of the Tatra Mountains, Slovakia (Arellano et al., 2011) (Table S11).

298   In this study, the mixture of endosulfan in freshwater samples were dominated

299   by endosulfan sulphate (162 to 260 pg.L^{-1}), which accounted for up to 80% of this

300   dissolved insecticide group in upland waters (Figure S1). α-endosulfan exhibited the

301   lowest concentrations (<10 pg.L^{-1}) while β-endosulfan was not detected in water

302   samples. These results correlate well with endosulfan sulphate as the predominant

303   metabolite in aquatic systems worldwide (Booij et al., 2007). The microbiologic

304   oxidation of the technical-grade endosulfan in soils, and its further re-emission to air is

305   regarded as the main source to the atmosphere. In natural aquatic ecosystems,

306   endosulfan sulphate degrades at a slower rate and hence is more persistent than the

307   parent isomers; with a half-life in water of several weeks (Weber et al., 2010). Much

308   greater concentrations of endosulfan sulphate (>100 ng.L^{-1}) than its parental isomers (α-

309   and β-endosulfan) have been detected in contaminated waters close to intensive crop

310   production areas in Argentina and Brazil (Bonansea et al., 2013; Laabs et al., 2002),

311   (Table S11) reinforcing the historical use of this insecticide in South America.

312   Brazil is considered the biggest user of endosulfan in South America and one of

313   the top endosulfan users worldwide (Li and Mcdonald 2005). According to the Brazilian

314 Ministry of Development, Industry and Foreign Trade's database

315 (http://aliceweb.mdic.gov.br), Brazil imported approximately 23 kt of endosulfan from

316 2001 to 2011 with an estimated annual consumption of 2.3 kt.yr^{-1}. As several other

317 South American countries, Brazil started to phase out the commercial use of endosulfan

318 in 2010. However, the agriculture use of endosulfans to control insect populations in

319 sugar-cane, cocoa, coffee, soybean and cotton plantations was totally banned only in

320 2013 (Brazilian Health Surveillance Agency - ANVISA).

321

322 *4.2.3. DDTs*

323 For DDTs, the parent compound *p,p´*-DDT and its metabolite *p,p´*-DDE were

324 the main detected compounds for both monitored National Parks. Atmospheric DDT

325 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}

326 ^{3} (GM 0.2 pg.m^{-3}) for NPIT and NPSJ, respectively. These concentrations were much

327 lower than concentrations observed at high-mountain sites in Europe (0.2 to 12 pg.m^{-3})

328 (Van Drooge et al., 2004), North America (1.6 to 55 pg.m^{-3}) (Daly et al., 2007), Asia

329 (0.3 to 75 pg.m^{-3}) (Liu et al., 2010; Wang et al., 2008) and even in South America (1.0

330 to 119 pg.m^{-3}) (Estellano et al., 2008; Meire et al., 2012) (Table S10).

331 Similar to atmospheric levels, freely dissolved concentrations of DDTs indicated

332 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

333 0.3 pg.L^{-1}). Only few studies have pointed out the presence of DDTs in South American

334 highland waters (Barra et al., 2005; Schreiber et al., 2013). Schreiber et al. (2013)

335 reported higher dissolved DDT (*p,p´*-DDE) concentrations in upland surface waters of

336 River Xanaes in Central Argentina (70 to 340 pg.L^{-1}). On the other hand, Barra et al.

337 (2005) did not detect the presence of dissolved DDTs along altitudinal gradients in Laja

338 River Basin waters of Central Southern Chile. The concentrations detected in our

339   measurements were also generally much lower than dissolved DDT concentrations

340   reported at other mountains and remote sites worldwide (Table S11).

341   Over the past few decades (1950-1990), Brazil has experienced a historical use

342   of DDT, primarily for sanitary purposes to control insect pests that are vectors for

343   tropical diseases, such as malaria and typhus (D'Amato et al., 2002). It is estimated that

344   Brazil used and exported to other South American countries a total of 80 t of DDT until

345   the 1980s, whilst more than 30 t were imported in the same period (Almeida et al.,

346   2007).

347

348   *4.3. Air mass back trajectory analysis*

349   The cluster analysis performed on the 5-day back trajectories unveiled that about

350   40% of the trajectories arriving at both sites come from the northern sector of Brazil

351   with purely continental influences. At the NPIT, two other clusters accounted for the

352   remainder of the trajectories. A southerly cluster of trajectory (30%) was identified

353   moving from the South Atlantic Ocean with no contact with the continent. The third

354   cluster (29%) was dominated by continental trajectories that stemmed from western

355   South America.

356   At NPSJ, 35% of the trajectories were maritime, with southerly origin. These

357   trajectories had anticyclonic curvature, which suggests that the airflow associated with

358   these pathways is part of the semi-permanent anticyclonic over the southern Atlantic.

359   The third cluster (24%) consisted of fast-travelling trajectories that originated over the

360   southern Pacific and spent most of the time over Patagonia and southern Brazil before

361   reaching the monitoring site.

362   The exposures of these sites to large-scale continental airflows with varying

363   source contributions (e.g., from extensive crop areas in central Brazil and Argentina)

364 may partly explain the atmospheric deposition of selected OCPs over upland

365 freshwaters at tropical and subtropical mountains sites in Brazil. These findings,

366 coupled with LDPE passive air and water sampling measurements, point out the

367 potential inputs from distant sources of semi-volatile chemicals to the two high-altitude

368 sites (1700 m a.s.l. NPSJ; 2400 m a.s.l. NPIT). Northerly and westerly (continental)

369 back trajectories represented 70% of the airflow reaching NPIT high-altitude site, which

370 may account for higher air concentrations of endosulfans (>10 $pg.m^{-3}$) at this site

371 compared to NPSJ site (4.0 $pg.m^{-3}$), which received only 41% of continental flows

372 (figures S2 and S3). A similar pattern was also observed on surface upland waters,

373 where concentration of endosulfans at NPIT site (>200 $pg.L^{-1}$) was slightly higher than

374 in NPSJ water samples (166 $pg.L^{-1}$). These results highlight the role of atmospheric

375 long-range dynamics on transporting organochlorine pesticides from distant source

376 regions and probably enhancing concentrations at high altitude mountain sites in Brazil.

377

378 *4.4. Air-water Exchange Gradients*

379 In this study, HCB, α-endosulfan and endosulfan sulphate displayed air-water

380 exchange values < 0 (Eq. 3) at almost all sites, indicating net deposition along the two

381 altitudinal transects (figure 4). An exception was only observed at the lowest altitudinal

382 site (990 m. a.s.l.) of NPSJ, when HCB showed net volatilisation > 0. These results

383 reinforce the major atmospheric input of volatile organochlorine pesticides at tropical

384 and subtropical Brazilian mountains. Similar to our results, Galbán-Malagón et al.

385 (2013) reported net deposition for HCB from the Weddell, Bransfield and

386 Bellingshausen Seas (Antarctica Peninsula Region) in two sampling cruises in 2008 and

387 2009. Net deposition or equilibrium of HCB and endosulfans (α-endosulfan) has been

388 also reported in studies in the Arctic (Lohmann et al., 2009; Wong et al., 2011).

389   In contrast, net volatilisation gradients were observed for $p,p´$-DDE at NPIT

390 monitored sites. This indicates that NPIT sites still received sufficient $p,p´$-DDE in

391 water, probably from runoff and headwater stream input, to cause net volatilisation of

392 legacy organochlorine pesticides. Air–water exchange gradients suggested net

393 volatilisation for organochlorine pesticides, including p,p'-DDE, along Chinese

394 coastline ocean (Lin et al., 2012). These results pointed out the surface waters net

395 volatilisation after a long period of OCP prohibition.

396

397 **5. Conclusions**

398   As atmospheric transport is faster than dilution in the water column, the volatile

399 OCPs –especially the recently banned pesticides– are experiencing net deposition over

400 pristine National Park areas. We observed this behaviour especially for endosulfan.

401 Surprisingly, even HCB was still mostly undergoing net deposition, with only DDTs

402 displaying net volatilisation. This implies that net deposition of endosulfans at these and

403 other sites will continue for the foreseeable future. Moreover, the exposure of these sites

404 to large-scale continental airflows with varying source contributions may partly explain

405 the atmospheric deposition of selected OCPs over upland freshwaters at tropical and

406 subtropical mountains sites in Brazil. These findings, coupled with LDPE passive air

407 and water sampling measurements, point out the potential inputs from distant sources of

408 semi-volatile chemicals to the two high-altitude sites.

409   Brazil is a signatory to the Stockholm and since 2001 the country has had to

410 comply with reductions in the use of POPs, including several organochlorine pesticides.

411 According to a federal law (CONAMA 430/11) the shallow waters investigated in this

412 study are classified as "special waters" and should be protected to preserve their natural

413 conditions. This study is a first effort to quantify OCPs in mountain spring waters and to

414 understand air-water exchange over pristine uplands in Brazil. Further studies are

415 necessary to address these issues, especially monitoring of recently banned and current-

416 use pesticides in waters of highland tropical sites.

417

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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.
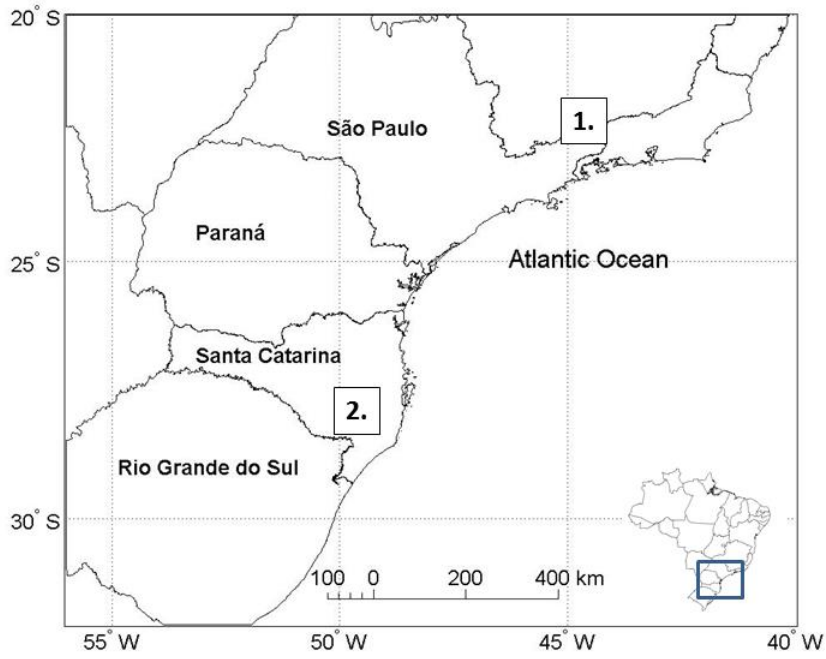

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694 **Figure 2.** "Box and whisker" plots showing summaries of the estimated atmospheric
695 (pg.m^{-3}) and dissolved (pg.L^{-1}) concentrations of selected organochlorine pesticides at
696 the two National Parks (NPIT – National Park of Itatiaia; NPSJ – National Park of São
697 Joaquim.). The results represent measurements during fall-winter periods in 2012 and
698 over altitudes ranging from 800 to 2200 m a.s.l. The following abbreviations are used:
699 HCB = hexachlorobenzene; α-endo = alpha-endosulfan; β-endo = beta-endosulfan;
700 eSO$_4$ = endosulfan sulphate (plotted in the right axis for water samples); Dield =
701 dieldrin.

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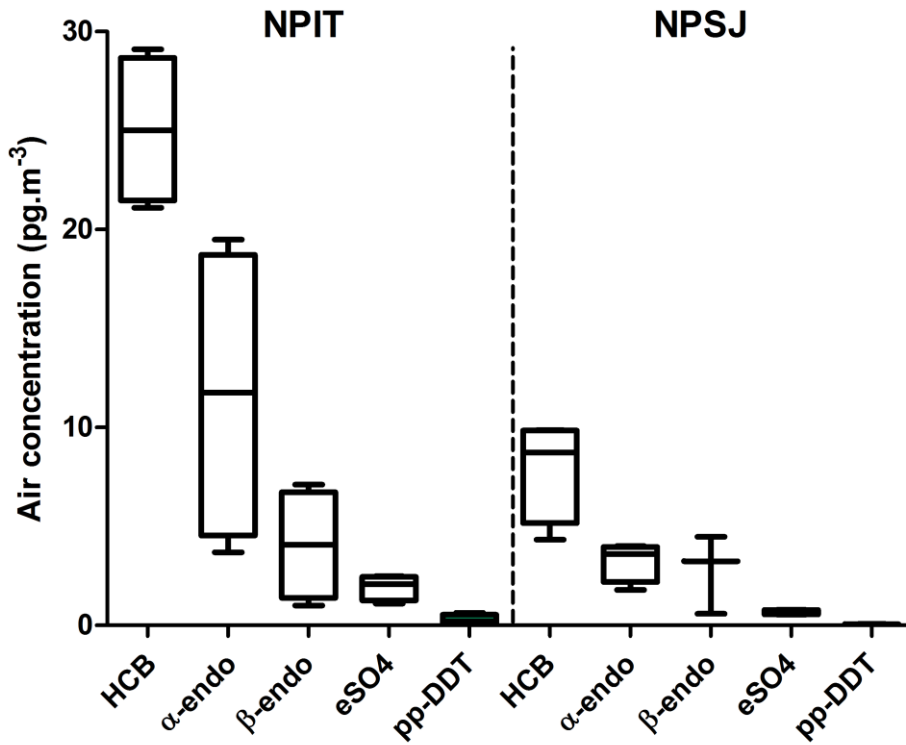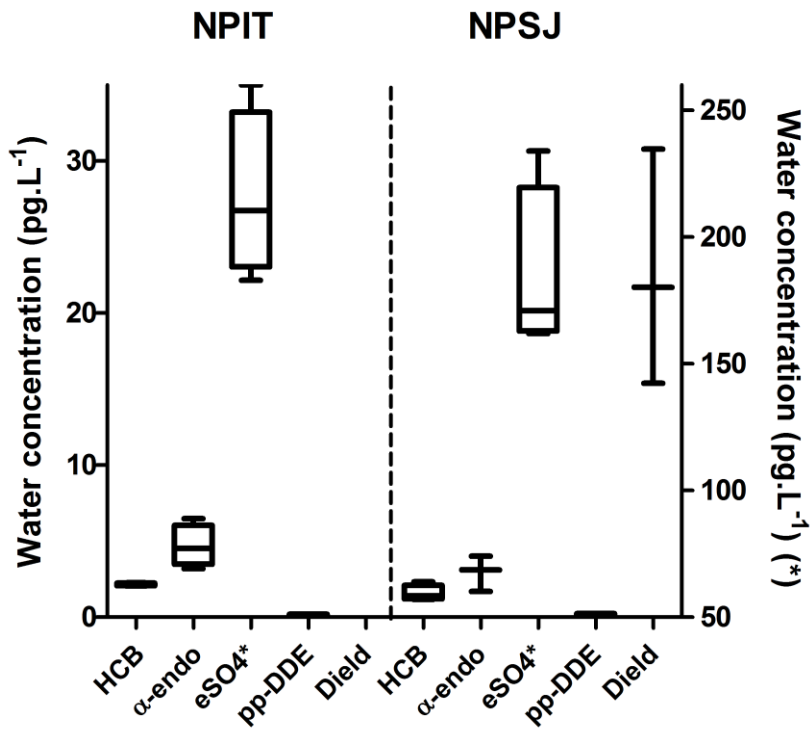
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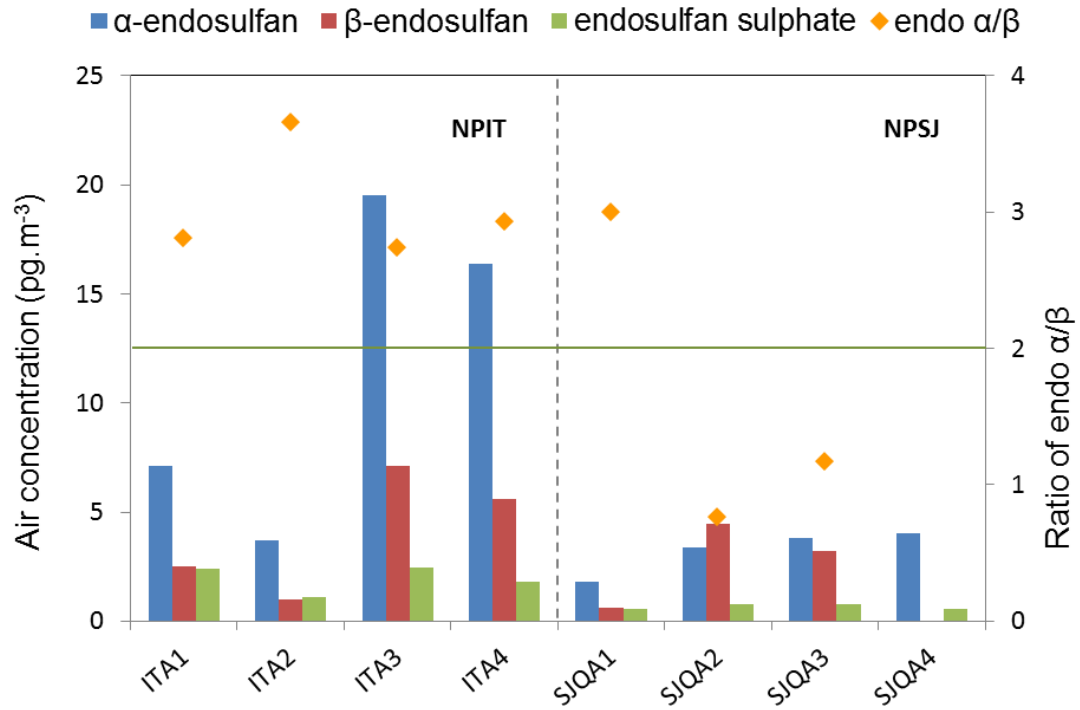
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Figure 3. Atmospheric endosulfan composition at the sampling sites. Green line
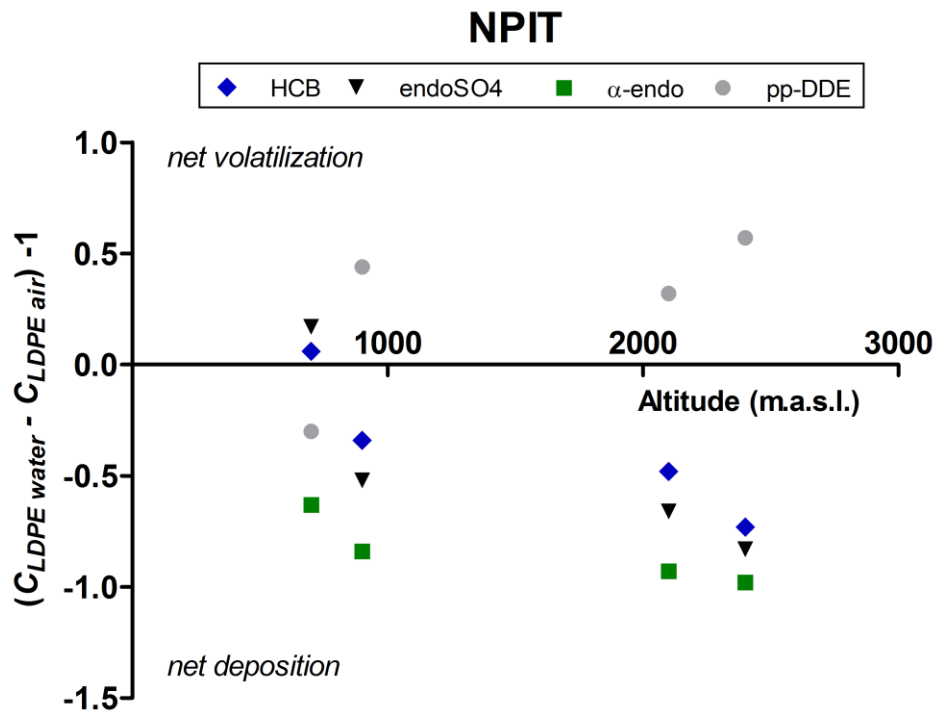represents the average endo-α/β ratio value.

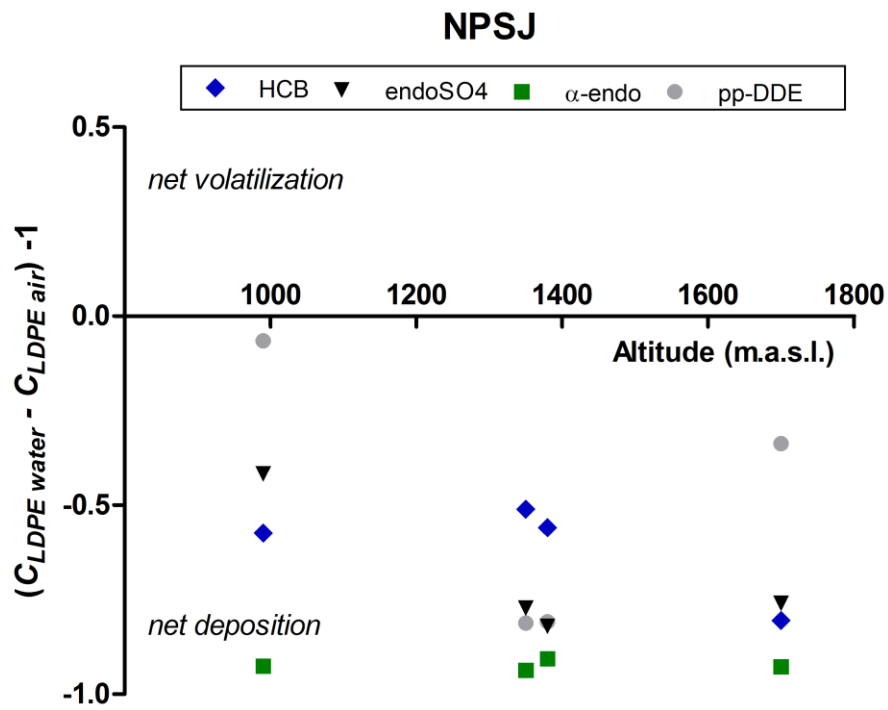**Figure 4.** Air-water exchange gradients along altitudinal transects at NPIT and NPSJ
sites for HCB, α- endosulfan, endosulfan sulphate (endoSO$_4$), and pp-DDE. Positive
values indicate net volatilisation of OCPs; negative values indicate net deposition.