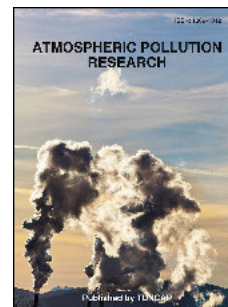# Accepted Manuscript

Passive sampler-derived concentrations of PAHs in air and water along Brazilian mountain transects

R.O. Meire, M. Khairy, Dave Aldeman, P.M.A. Galvão, J.P.M. Torres, O. Malm, R. Lohmann
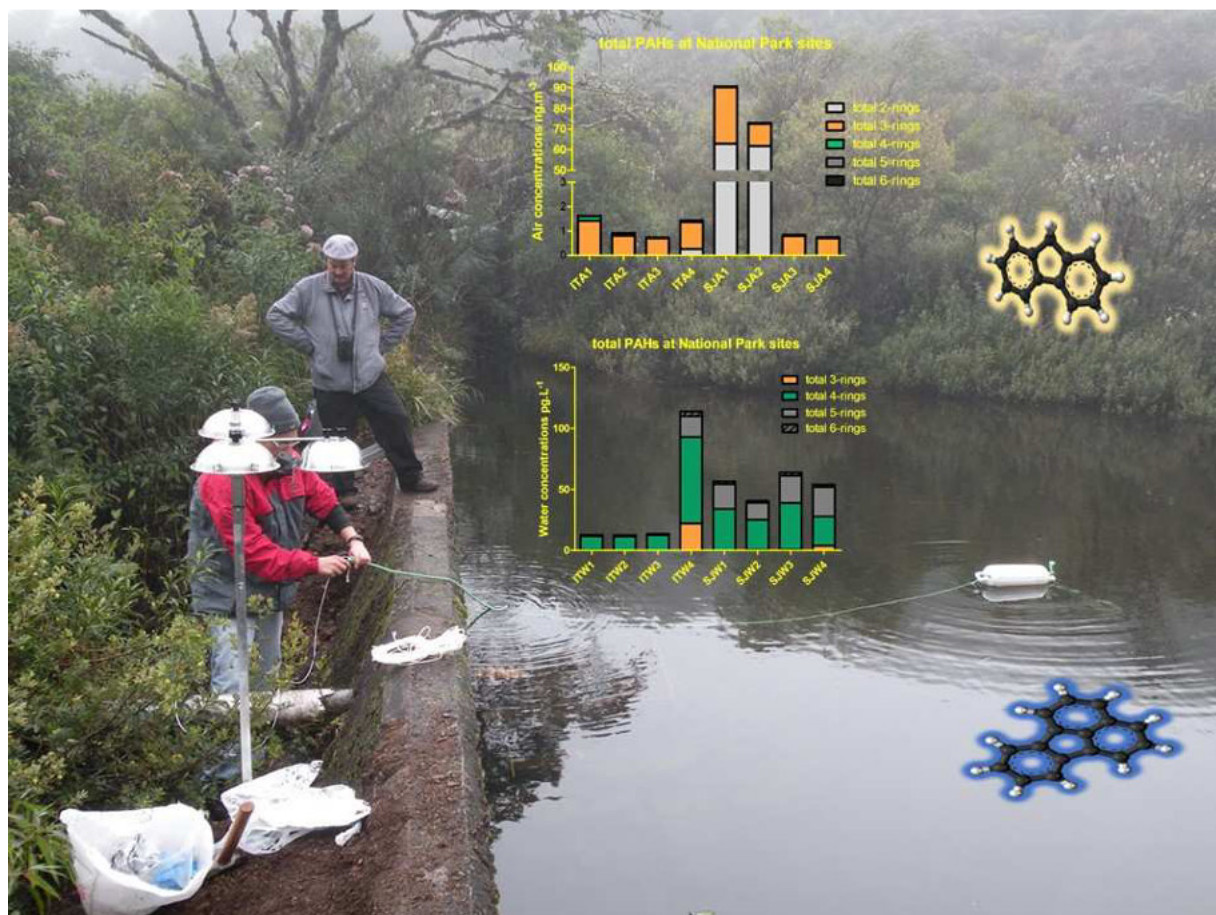
1 **Passive sampler-derived concentrations of PAHs in air and water**

2 **along Brazilian mountain transects**

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Abstract

The atmospheric deposition of semi-volatile organic compounds represents a potential threat to pristine mountains, in particular by persistent toxic substances which have high environmental mobility, potential for bioaccumulation and display toxic effects even at relative low concentrations. Low density polyethylene passive samplers were deployed in upland surface waters and the overlying atmosphere in subtropical and tropical mountain regions in south and southeast Brazil, respectively, to determine the concentrations, transport and sources of freely dissolved and gaseous polycyclic aromatic hydrocarbons (PAHs) along altitudinal gradients. Gaseous PAH concentrations (0.70- 90 ng.m^{-3}) were dominated by phenanthrene and fluorene, though methylnaphthalenes displayed high concentrations at upland sites. Fluoranthene and chrysene were the most frequently detected PAHs in shallow waters (10-110 pg.L^{-1}). Individual PAHs indicated a wood/grass combustion origin at both national parks due to current and historical man-made fires, with a minor petrogenic fingerprint, probably due to the proximity of highway traffic and touristic activities. A slightly increasing trend of 2-3 ring PAHs was observed along tropical elevation transect which may reflect long-range atmospheric transport of more volatile PAHs over tropical elevated altitudes. However, local PAH emission sources probably explain the opposite trend detected at subtropical elevation transect.

45

Introduction

47   Maintaining mountain biodiversity is part of the current National Biodiversity

48 Council (CBD) agenda and international agreements such as the "Global Strategy for

49 Plant Conservation" (Martinelli, 2007; UNEP, 2011). Mountains have notorious

50 susceptibility to environmental and climate change. The atmospheric deposition of

51 semi-volatile organic compounds (SVOCs) in mountainous regions is highlighted as a

52 potential threat to pristine mountains, in particular by persistent toxic substances which

53 have high environmental mobility, potential for bioaccumulation and display toxic

54 effects even at relative low concentrations (Blais et al., 2006, 1998; Calamari et al.,

55 1991). The input of persistent toxic substances over upland regions is mainly controlled

56 by meteorological and geographical conditions such as orographic winds, relatively low

57 temperatures and high precipitation rates, commonly found in mountainous regions

58 (Daly and Wania, 2005; Sheng et al., 2013). Moreover, the proximity to metropolitan

59 areas, industry and agriculture areas can amplify critical environmental scenarios for

60 mountains rendering highlands as good "sentinels" for local and global air quality

61 (Kallenborn, 2006).

62   Polycyclic aromatic hydrocarbons (PAHs) are a unique class of SVOC

63 consisting of two or more fused benzene rings in linear, angular or cluster arrangements

64 (Page et al., 1999). PAHs are from natural and anthropogenic sources, mostly from the

65 incomplete burning of organic matter. Petrogenic and pyrogenic sources are common,

66 and among pyrogenic sources, there are natural fires and anthropogenic practices that

67 lead to deforestation and wood burning (Stogiannidis et al., 2013; Yunker et al., 2002).

68 In this context, anthropogenic activities can sharply increase the levels of these

69 contaminants in the environment. Moreover, PAHs are considered priority organic

70 pollutants in view of their carcinogenic potential (i.e., benzo-*a*-pyrene diol epoxide) and

71 their ability to act as mutagenic promoters in biological systems (IARC, 2010). The

72 intensive use of forest resources (intentional and unintentional biomass burning) makes

73 PAHs one of the high priority SVOCs for the South America region (Barra et al., 2007).

74 In Brazil, emissions were estimated at 467-6,607 tonnes/year for PAHs, with wood

75 combustion accounting for at least 90% of these values (UNEP, 2002). However,

76 petroleum production, refining and transport activities have greatly increased over the

77 last decades which contribute to ambient PAHs in the region (da Silva and Bícego,

78 2010; Taniguchi et al., 2016).

79   The use of passive sampling to detect SVOCs in the environment has become

80 common over the last few years (Fauvelle et al., 2017; Harner et al., 2006; Levy et al.,

81 2009; Lohmann and Muir, 2010; Pozo et al., 2009). In the last decade, low density

82 polyethylene passive samplers (LDPE) have extensively been used to detect a range of

83 SVOCs in water and air, and to evaluate the risk to wild-life and humans at regional and

84 global scales (M. A. Khairy and Lohmann, 2013; Liu et al., 2007; Lohmann, 2015;

85 Smedes et al., 2017; Zhao et al., 2018). Most of these pollutants strongly partition into

86 the LDPE matrix (Sacks and Lohmann, 2011). This feature offers methodological

87 advantages in relation to other environmental measurements, such as easier/ and less

88 costly laboratory methods and lower detection limits, making LDPE a useful tool for

89 first-order risk assessment.

90   The main goals of the current study were to (i) assess the occurrence of PAHs in

91 air and water at two National Parks in Brazil; (ii) identify emission sources of PAHs and

92 the contribution of different sources in the tropical and subtropical mountain regions of

93 Brazil, and (iii) investigate altitudinal variations of gaseous and dissolved PAHs. To

94 achieve these aims, we deployed passive air and water samplers consisting of low-

95 density polyethylene strips during fall and winter seasons (May-June 2012), following

96 altitudinal transects in south and southeast Brazil. The present work provides an initial

97 screening of gaseous and freely dissolved PAH concentration levels in tropical and

98 subtropical Brazilian uplands.

99 **Material and Methods**

100 *Site description*

101 We conducted this study in the mountain ranges of "Serra do Mar" (National

102 Park of Itaiaia - NPIT, lat.: 22°22´38"S, lon.: 44°41´35"W, Rio de Janeiro and Minas

103 Gerais State) and "Serra Geral" (National Park of São Joaquim - NPSJ, lat.:

104 28°00'49''S, lon.: 49°35'17''W, Santa Catarina State), located in southeast and south

105 Brazil, respectively (Figure 1). These two conservation areas comprise high-altitude

106 grasslands and mountainous rainforests which harbour high biodiversity with several

107 endemic species (Myers et al., 2000). The NPIT borders are surrounded by Resende,

108 Itatiaia, Bocaina de Minas, Alagoa and Itamonte municipalities – harbouring more than

109 180,000 inhabitants. Around the NPIT, mixed land uses characterize the region, such as

110 agriculture, livestock and industrial activities. On the other hand, the National Park of

111 São Joaquim is surrounded by extended agricultural areas with a variety of farming

112 activities such as apple, maize and tobacco. Urubici, Bom Jardim da Serra, Grão Pará

113 and Orleans are the main municipalities that surround the NPSJ, accounting for ~

114 45,000 inhabitants (Brazil census bureau, 2018). Further details on the National Park are

115 provided in the SM.

116 *Passive Sampling Field Deployment*

117 Field deployment details and LDPE theory/calculation methodology were

118 performed as described previously (Liu et al., 2016; McDonough et al., 2014; Meire et

119 al., 2016). Briefly, the LDPEs were cut from 50-µm thick commercial sheeting (Carlisle

120 Plastics, Inc., Minneapolis, MN), yielding a 10x30-cm strip of 1- to 2-g each. Prior to

121 exposure, the LDPEs were spiked with deuterated PAHs (naphthalene-d_8, pyrene-d_{10}

122 and benzo(a)pyrene-d_{12}) as performance reference compounds (PRCs) via a method

123 adapted from Booij et al. (2002). Four sampling sites were established along altitudinal

124 gradients at each National Park (NPIT: 700- 2400 meters above sea level – m a.s.l.;

125 NPSJ: 990- 1700 m a.s.l.) during late fall and early winter seasons (May and June) in

126 2012 (Figures S1 and S2). For each sampling site, passive LDPE sheets (n=2) were

127 deployed in the surface shallow waters and overlying atmosphere simultaneously for 30

128 to 40 days (Figure S3 and S4). Replicate tests were carried out at the highest altitudinal

129 sites for both National Parks (Rebouças IT4, NPIT; Cindacta 2 SJ4, NPSJ). Five field

130 blanks were collected at both parks to assess possible sample contamination during

131 transport and storage. The water temperature was measured for each site using a Yellow

132 Spring multiparametric probe (model 600 QS). Air temperature data were compiled

133 from surrounding meteorological stations provided by Brazilian National Institute of

134 Meteorology (INMET, 2018) (table S1).

135 *Analytical Methodology*

136   Analytical methodologies of LDPEs were extensively described elsewhere

137 (Lohmann et al., 2011; Ruge et al., 2015). After sampling exposure, LDPEs were wiped

138 clean with Kimwipes and extracted (24 h) twice at room-temperature with ethylacetate

139 and condensed after being spiked with 50 ng of labelled PAH surrogates

140 (acenaphthalene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} from Ultra

141 Scientific, North Kingstown, RI) to evaluate quality assurance performance during

142 sample processing. 42 individual PAHs were analysed on an Agilent 6890 Series gas

143 chromatograph (GC) coupled to an Agilent 5973 MS (mass spectrometer). Out of the

144 target 42 PAHs, only 20 PAHs were regularly detected (at a detection frequency >30%).

145 These selected PAHs are listed in supplementary material (SM). The limit of detection

146 (LOD) was calculated as the average laboratory blanks plus three times the standard

147 deviation. The LODs ranged from 0.1 to 9.1 $ng.g^{-1}$ of LDPE in the passive samplers.

148 Methods for preparation, extraction, theory/calculations of LDPEs as well as the

149 instrumental analyses of the extracts and quality assurance/quality control are given in

150 the SM.

151

152 **Results and Discussion**

153 *Quality Assurance/Quality control.*

154 Recoveries of acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-

155 d_{12} ranged from 65 to 93% for all sample. Concentrations of individual PAHs were

156 recovery-corrected for each LDPE sample. There was no significant difference between

157 concentrations of selected PAHs in the field and laboratory blanks, indicating negligible

158 contamination during transport, storage and analyses. For the most frequently detected

159 PAHs, reproducibility ranged from 1.2 % (retene) to 37% (fluoranthene), which is in

160 agreement with previous LDPE studies at the same laboratory (average value around

161 20%) (Khairy and Lohmann, 2013).

162 *Sampling rates and PAH equilibrations in field-deployed LDPE samplers*

163 Sampling rates (*Rs*) for the atmospheric and water samplers are given in

164 supplementary material (SM) (Table S3). Atmospheric *Rs* ranged from 6.1 to 77 $m^3.day^{-1}$

165 ^{1}, which is consistent with *Rs* values (7.0-75 $m^3.day^{-1}$) measured previously for

166 atmospheric PAHs in the North American lower Great Lakes (McDonough et al., 2014).

167 *Rs* values as large as 56 and 77 $m^3.day^{-1}$ were observed for highest elevations at both

168 National Parks (1700 and 2400 m a.s.l., NPSJ and NPIT, respectively), probably due to

169 higher wind speeds at these high-altitude sites.

170   Most detected PAHs were far from reaching equilibrium (< 50 %). The only

171   chemicals that approached equilibrium (> 90%) were the 2 and 3-ring PAHs (log $K_{LDPE\text{-}air}$ < 7.76), except at two sites (ITA1 and ITA2). Calculated % equilibrium for gaseous

173   PAHs are presented in Tables S5 and S6. Khairy and Lohmann (2012) also observed a

174   similar equilibrium pattern for gaseous PAHs, using LDPE air samplers in Alexandria

175   (Egypt).

176   Water Rs values ranged from 5.0 to 55 L.day^{-1}. A similar range was previously

177   observed for pyrene and higher molecular weight PAHs sampled in Narragansett Bay

178   (Lohmann et al., 2011) and in the Lower Great Lakes (McDonough et al., 2014). The

179   sampling rates for National Park of Itatiaia were significantly higher (p = 0.006) than

180   those for National Park of São Joaquim and the calculated equilibrium values for freely

181   dissolved PAHs showed variations between the two parks. At both National Parks, 2-3-

182   ring PAHs approached equilibrium by the end of the deployment period (92-100%)

183   whilst higher molecular weight PAHs (HWM) were far from reaching equilibrium

184   (<20%).

185   *Air and water concentrations of PAHs*

186   Gaseous PAH were dominated by phenanthrene and fluorene (50 % and 17 %

187   respectively of $\sum_{20}$PAHs). LDPE-derived gaseous concentrations ranged from 0.40 -

188   0.93 ng.m^{-3} and from 0.070 - 0.42 ng.m^{-3} for phenanthrene and fluorene, respectively.

189   However, extremely elevated gaseous concentrations (70-90 ng.m^{-3}) were detected for

190   other PAHs at NPSJ sites, in particular methylnaphthalenes (BDL-30 ng.m^{-3}),

191   acenaphthene (BDL-16 ng.m^{-3}) and biphenyl (BDL-9 ng.m^{-3}). 4-5-ring PAHs displayed

192   no more than 10% of $\sum_{20}$PAHs (i.e., benzo(*b*)fluoranthene, benzo(*e*)pyrene and 7,12-

193   dimethylbenz(*a*)anthracene), with higher molecular weight PAHs (HWM), accounting

194   for less than 1% of sum of PAHs (i.e. benzo(*g,h,i*)perylene) (Figures S5 and S6).

195   As opposed to gas-phase concentrations, fluoranthene (40%) and chrysene

196   (20%) were the most abundant and frequently detected dissolved PAHs in the water

197   with concentrations ranging from 7.0 - 40 pg.L^{-1} and 2.0 - 18 pg.L^{-1} respectively.

198   Moreover, perylene (BDL-14 pg.L^{-1}) and dimethylbenzo(*a*)anthracene (0.5-12 pg.L^{-1})

199   were frequently detected in this study (8 % and 10 % respectively of $\sum_{20}$PAHs)

200   especially at NPSJ sites. Other 4-5-ring PAHs showed only a minor contribution <10%

201   of the total PAHs (i.e. benzo(*e*)pyrene, benzo(*a*)pyrene and perylene) as well as HMW

202   PAHs (<2%, i.e. indeno(1,2,3-*c,d*)pyrene) (Figures S7 and S8). Since the used method

203   had no protection from UV radiation, it is important to note that PAHs in passive

204   samplers can be degraded by exposure to sunlight, ultimately changing the

205   concentration of target analytes. The results for individual PAHs are discussed below.

206   Geometric means (GM) are presented rather than arithmetic means to prevent extreme

207   values (outliers) from skewing the mean.

208   *Levels and spatial trends in air*

209   For gaseous concentrations of PAHs, no statistically significant differences in

210   median values for PAHs were found between the two national parks (Mann Whitney

211   test – p< 0.05). The NPSJ displayed higher concentrations of PAHs in air compared to

212   NPIT. Gaseous concentrations (ng.m^{-3}) of $\sum_{20}$ PAH ranged from 0.70 - 1.6 ng.m^{-3}

213   (geometric mean, GM = 1.2) and from 0.70 - 91 ng.m^{-3} (GM = 37) for NPIT and NPSJ,

214   respectively (Figure 2). The gaseous concentrations of PAHs at NPSJ sites were

215   considerably higher than reported in most other studies in mountainous regions,

216   although these data should be viewed with caution, since the much higher

217   concentrations (10s ng.m^{-3}) were only detected at the low-altitudinal sites (SJA1 and

218   SJA2). In fact, high air concentrations of PAHs reported here are more consistent with

219   results for impacted sites by urban centres and surroundings such as reported in other

220 studies worldwide (Álvarez et al., 2016; Liu et al., 2015; McDonough et al., 2014; Pozo

221 et al., 2015, 2012; Schuster et al., 2015).

222   For LDPEs, recent studies have reported variable ranges of gaseous PAH

223 worldwide, especially close to urban regions in North America. McDonough et al.

224 (2014) observed elevated gaseous PAH concentrations throughout the lower Great

225 Lakes ($\sum_{15}$PAH, 2.0 – 97 ng.m^{-3}, GM = 9.0) which were strongly correlated with

226 surrounding populations, suggesting urban centers as primary source of PAHs into the

227 atmosphere.

228   Additionally, Ruge et al. (2015) reported a wider an even range of PAH air

229 concentrations ($\sum_{21}$PAH, 0.05 – 140 ng.m^{-3}) at Lake Superior sites, with similar

230 environmental trends. These PAH levels are also in agreement with Lohmann et al.

231 (2011), who reported similar concentrations ($\sum_{17}$PAH, 2.0- 110 ng.m^{-3}, GM = 11) in the

232 gas-phase within the atmosphere around Narragansett Bay (RI, USA).

233   Outside of North America, Khairy and Lohmann, (2012) reported much higher

234 PAH levels in urban center of Alexandria (Egypt). These gaseous PAH concentrations

235 derived from LDPE samplers ranged from hundreds to thousands of ng.m^{-3} (GM = 580),

236 indicating both industrial and vehicle emissions as the major source of PAHs in

237 Alexandria City.

238   Few studies have reported the presence of gaseous PAH in South American

239 mountain regions. Generally, air concentrations were dominated by four-ring PAHs,

240 detected using XAD-2 as a passive air sampler (Wania et al., 2003). In the current

241 study, gaseous concentration of four-ring PAHs (ng.m^{-3}) ranged from 0.040 - 0.19 and

242 from 0.040 - 0.31 for NPIT and NPSJ, respectively. These results are within the range

243 observed at mountain sites in Costa Rica (0.04-0.65 ng.m^{-3}), Chile (BDL-1.3 ng.m^{-3})

244 and even at Western Canada (0.02-0.45 ng.m^{-3}) (Choi et al., 2009; Daly et al., 2007;

245 Shunthirasingham et al., 2011), with higher gaseous PAH levels in samplers deployed

246 close to roads and settlements. In agreement with those previous studies, truly remote

247 sites, i.e. sites far from houses and major roads (such as at high-elevation sites > 1500 m

248 a.s.l., in this study), are likely more reflective of PAH background air concentrations

249 $(0.04 – 0.06$ ng.m^{-3}) in South-Southeast Brazil.

250 Despite some outliers, phenanthrene was detected at all sites in both National

251 Parks and exhibited the highest air concentration among the target PAHs. Phenanthrene

252 concentrations in air measured in this study at NPIT $(0.48- 0.99$ ng.m^{-3}, GM = 0.72) and

253 NPSJ $(0.41-1.30$ ng.m^{-3}, GM = 0.79) are comparable to concentrations found at other

254 remote mountainous regions, such as: Tibetan Plateau uplands, China $(0.25- 7.2$ ng.m^{-3},

255 GM = 0.81); Øvre Neådalsvatn, Central Norway (average value, 0.84 ng.m^{-3}), Estany

256 Redon, Central Pyrenees, Spain (average value, 0.87 ng.m^{-3}), Gossenköllesee, Tyrolean

257 Alps, Austria (average value, 0.98 ng.m^{-3}) and Skalnaté Pleso, High Tatras, Slovakian

258 Republic (average value, 3.1 ng.m^{-3}) (Ren et al., 2017; van Drooge et al., 2010).

259 Generally, gaseous phenanthrene concentrations found at National Park sites are higher

260 than reported in the atmosphere of coastal/open seas, especially along Atlantic Ocean

261 transects (North to South: $0.02 – 2.2$ ng.m^{-3}, GM = 0.15; West to East: BDL-1.3 ng.m^{-3},

262 GM = 0.21), North Pacific $(0.03- 0.3$ ng.m^{-3}, GM = 0.12), Baltic coast $(0.1- 0.2$ ng.m^{-3},

263 GM = 0.18) and Arctic Sea (Broman et al., 1991; Lohmann et al., 2013; Ma et al., 2013;

264 Nizzetto et al., 2008). However, studies along urban-industrial-rural transects in South

265 America have reported higher gaseous phenanthrene concentrations than observed in

266 this study, such as: Santiago de Cali, Colombia $(10- 20$ ng.m^{-3}), Concepción, Chile (10-

267 100 ng.m^{-3}, GM = 29) and Temuco, Chile $(1.2-17$ ng.m^{-3}, GM = 6.7 ng.m^{-3}) (Álvarez et

268 al., 2016; Pozo et al., 2015, 2012).

269 *Levels and spatial trends in water*

270   In contrast to gaseous concentrations, freely dissolved concentrations of PAH in

271   the water were consistently low. Freely dissolved PAH concentrations ranged from 10 -

272   110 pg.L^{-1} (GM = 22) at NPIT and in a narrower range of 40 - 60 pg.L^{-1} (GM = 53) at

273   NPSJ, respectively (Figure 3). Similar to gas-phase concentrations, no significant

274   differences were observed between dissolved PAH concentrations in the two national

275   parks, using Mann Whitney test (p < 0.05). Few data are available for freely dissolved

276   PAH concentrations in mountain regions worldwide. Low PAH concentrations in

277   surface waters have been reported across European and Asian (100-1000s pg.L^{-1})

278   mountain regions (Fernández et al., 2005; Guzzella et al., 2011; Vilanova et al., 2001).

279   Additionally, Ren et al., 2017 recently reported rather elevated PAH levels in Tibet

280   Plateau, Nam Co Lake (>80 ng.L^{-1}), suggesting that local combustion emissions were

281   likely the main source of PAHs there. Local human activities, rather than long-range

282   transport, probably also explain the elevated freely dissolved PAH concentrations

283   ($\sum_{17}$PAHs, 14-360 ng.L^{-1}) in remote areas such as the Antarctic inland lakes (Yao et al.,

284   2016). Despite that, those PAH levels were much higher than freely dissolved

285   concentrations measured in the current study. In this context, our results are more

286   consistent with freely dissolved PAH concentrations reported in open sea transects from

287   Atlantic, Pacific, Arctic and Antarctic oceans (tens to thousands of pg.L^{-1}) (Cincinelli et

288   al., 2008; Lohmann et al., 2013; Ma et al., 2013).

289   Despite the scarcity of data regarding the levels of PAHs in the South American

290   waters, freely dissolved PAHs are relatively high along some major rivers in the

291   continent, such as the Uruguay and Rio de la Plata rivers (1800-12,000 ng.L^{-1}) (Barra et

292   al., 2007). In Brazil, hotspots of PAH contaminations have also been reported in waters

293   from Brazilian tropical main rivers and estuaries, especially close to urban centers

294   (>100 ng.L^{-1}). Among them, Paraiba do Sul River should be highlighted (> 260 ng.L^{-1})

295   as a main freshwater system that supplies energy and drinking water for millions of

296   inhabitants in Rio de Janeiro state (Azevedo et al., 2004; Lemos et al., 2014; Ribeiro et

297   al., 2012).

298   Generally, water bodies in urban areas show higher PAH concentrations

299   worldwide (Honkonen and Rantalainen, 2016; Lohmann et al., 2011). Using LDPE as

300   passive water samplers, Ruge et al. (2015) and McDonough et al. (2014) have recently

301   observed elevated freely dissolved PAH concentrations at Lake Superior ($\sum_{20}$PAH, 0.2-

302   70 ng.L^{-1}) and the lower Great Lakes ($\sum_{18}$PAH, 2.5- 80 ng.L^{-1}) in North America,

303   respectively, compared to our findings. Nevertheless, even higher PAH water levels

304   have been measured in Meiliang Bay, Taihu Lake, the third largest lake in China (40 –

305   180 ng.L^{-1}) and along Seine River, France ($\sum_{16}$PAH >200 ng.L^{-1}) (Gasperi et al., 2009;

306   Qiao et al., 2008).

307   *Source indicator by PAH ratios and other individual PAHs*

308   Molecular ratios for selected PAHs isomers were used in the current study to

309   better understand the sources of the PAHs (Tobiszewski and Namieśnik, 2012; Yunker

310   et al., 2002) (see SI for details). In general, pyrogenic sources were deduced for both

311   National Parks, in particular wood and grass combustion (Flra/Flra+Pyr >0.5;

312   Phe/$\sum$MePhn>0.5). In shallow water, a minor contribution of petroleum combustion

313   was evident (ITW1- *Lagoa azul* – 700 m a.s.l.) at NPIT and (SJW2, *St. Barbara* – 1400

314   m a.s.l.) NPSJ sites.

315   There is good evidence of large-scale forest and grass fires in the region. In the

316   Itatiaia massif (>2200 m a.s.l.), some of the largest fires in high altitude grasslands have

317   been observed in recent years (2001 = 741.6 ha; 2007 = 763.8 ha; 2010 = 1023.3 ha)

318   (Aximoff, 2011; Medina et al., 2016; Tomzhinski et al., 2011). This is further

319   supported by a recent fire zoning risk assessment for the NPSJ; it was concluded that

320 39% of the area is under high risk, and 7% under extreme risk of fire (Omena et al.,

321 2016). Furthermore, meteorological parameters such as fall/winter dry seasons, upland

322 windy conditions and frost events, resulting in extensively dry biomass areas enhance

323 the risks of fire ignition and could spread inside National Park borders (Aximoff et al.,

324 2016).

325 Moreover, high gaseous concentrations of 3-ring alkyl PAHs (1-

326 methylphenathrene) and retene were mainly detected at low altitudinal NPSJ sites.

327 These two individual PAHs are mainly produced from abietic and pimaric acids, both

328 present in pine wood resin (Stogiannidis et al., 2013). Extensive Pinus sp. farms (*Pinus*

329 *taeda* and *Pinus elliottii*) are an important agricultural activity that surrounded NPSJ

330 borders, reinforcing the influence of softwood combustion sources (McDonough et al.,

331 2014; Omena et al., 2016).

332 Natural origins also could be tracked by individual PAHs. Among them,

333 perylene could be linked to diagenetic (slow transformation of organic materials) and/or

334 biogenic production (synthesized by plants, algae and microorganisms), especially

335 found under anoxic conditions in soil and subtidal, marine and freshwater sediments.

336 However, perylene or other biogenic-diagenetic PAHs also potentially have

337 anthropogenic sources, especially after pyrolytic processes such as coal pyrolysis and

338 automotive emissions. (Stogiannidis et al., 2013; Tobiszewski and Namieśnik, 2012).

339 Several studies have highlighted microbial activity as the major process for natural PAH

340 origins (da Silva and Bícego, 2010; Readman et al., 2002; Wilcke et al., 2003). Indeed,

341 perylenequinone structures exist in many fungal bodies and have been previously

342 described as natural precursors for perylene in aquatic systems (Cavalcante et al., 2009;

343 da Silva and Bícego, 2010). In the tropics the biologic origin of perylene and other

344 individual PAHs have well known links with vast biogenic precursors, especially over

345   pristine areas such as tropical Atlantic rainforest, Amazon basin and natural savanna

346   fields (Barra et al., 2007; Meire et al., 2008; Wilcke et al., 2003, 2000). In this study,

347   perylene was mainly detected in all water sampling sites for NPSJ which could indicate

348   biological PAH sources in subtropical rainforests.

349   *Elevation Transects*

350   PAHs as well as other SVOCs have been measured at high altitudinal sites in

351   South American and worldwide regions (Barra et al., 2006; Choi et al., 2009; Estellano

352   et al., 2008; Meire et al., 2012; Shunthirasingham et al., 2011; Wang et al., 2013, 2011).

353   For selected SVOCs, positive correlations between altitudinal transects and

354   environmental concentrations were mainly observed for more volatile constituents,

355   relative to the less volatile constituents of contaminant mixtures. A marked seasonality

356   in the precipitation rates combined with other parameters (i.e. diurnal winds and low

357   temperatures) seemed to enhance SVOCs atmospheric deposition over mountainous

358   regions, especially at tropical upland locations(Daly and Wania, 2005).

359   For total PAHs, no clear trends (water and air) were observed for altitudinal

360   gradients over either National Park, except at the NPSJ site which showed an inversion

361   trend between total gaseous PAH concentrations and altitudinal transects. Additionally,

362   the highest total PAH levels in air were also measured at high altitude sites in NPIT

363   (ITW4, >2000 m a.s.l.). Light (2-3 rings) and heavy (5-6 rings) PAH ratio has been used

364   as an index to estimate the origin of pollution as well as to evaluate altitudinal

365   fractionation of PAHs along transects over mountainous regions (Choi et al., 2009). In

366   this context, we investigated air L/H ratio over altitudinal transects for both National

367   Parks.

368   In this study, National Park transects showed opposite altitudinal trends for

369   PAHs in air (Figures S9 and S10). A slightly increasing trend of low over high MW

370 PAH ratios was observed along vertical NPIT transects. This trend may reflect a long-

371 range atmospheric transport of more volatile PAHs (2 and 3 rings) over tropical

372 elevated altitudes. This is consistent with previous findings for other semivolatile

373 chemicals such as endosulfans (an organochlorine pesticide recently banned in Brazil)

374 which at the same highest monitored sites (ITA3 and ITA4) were about 2–5-fold higher

375 than those measured at lowest altitudinal sites (ITA1 and ITA2) (Meire et al., 2016).

376   On the other hand, an inverse profile between low over high MW ratios and

377 altitude was found at NPSJ sites. Similar results have demonstrated the decrease of

378 atmospheric PAH levels with increasing distance from main roads and suggested that

379 mobile sources are the main PAHs sources in Latin American cities as well as other

380 National Parks worldwide (Bradford et al., 2013; Fernandes et al., 2002;

381 Shunthirasingham et al., 2011). Nevertheless, inside National Park borders there are

382 pyrolytic emissions, especially during wood and grass fire events, which may represent

383 the dominant PAH contribution at the monitored sites in this current work.

384

385 **Conclusion / implications**

386   By and large, concentrations of selected PAHs found in air and shallow waters

387 were comparable to concentrations at other remote mountainous regions worldwide.

388 PAH ratios strongly indicate wood and grass combustions as main pyrolytic sources

389 over upland transects, in-line with recent major wildfires and agricultural practices

390 prevalent in the region. On the other hand, minor petrogenic inputs at National Park

391 sites could be related to the proximity of highway traffic and steady tourism access. As

392 observed in other South American biomes, biogenic precursors are probably linked to

393 natural origin of perylene over subtropical pristine shallow waters. National Park

394 transects showed opposite altitudinal trends for PAHs in air. These contrasting trends

395   may reflect a mix input of long-range atmospheric transport for more volatile PAHs (2

396   and 3 rings) combined with local PAH emission sources along altitudinal transects.

397

398   **Acknowledgments**

406   **References**

407   Álvarez, Á.L., Pozo, K., Paéz, M.I., Estellano, V.H., Llanos, Y., Focardi, S., 2016.

408   Semivolatile Organic Compounds (SVOCs) in the atmosphere of Santiago de Cali,

409   Valle del Cauca, Colombia along north-south transect using polyurethane foam

410   disk as passive air samplers. Atmos. Pollut. Res. 7, 945–953.

411   https://doi.org/10.1016/j.apr.2016.05.006

412   Aximoff, I., 2011. O que Perdemos com a Passagem do Fogo pelos Campos de Altitude

413   do Estado do Rio de Janeiro? Biodiversidade Bras. 1, 180–200.

414   Aximoff, I., Felippe, A., De Freitas[2], N., Marcelo, J., Braga[3], A., 2016. Regeneração

415   Natural Dos Campos De Altitude Pós-Fogo No Parque Nacional Do Itatiaia,

416   Sudeste Do Brasil 20, 62–80. https://doi.org/10.4257/oeco.2016.2002.05

417   Azevedo, D.D.A., Gerchon, E., Dos Reis, E.O., 2004. Monitoring of pesticides and

418   polycyclic aromatic hydrocarbons in water from Paraíba do Sul River, Brazil. J.

419   Braz. Chem. Soc. 15, 292–299. https://doi.org/10.1590/S0103-

420   50532004000200021

421   Barra, R., Castillo, C., Torres, J.P., 2007. Polycyclic aromatic hydrocarbons in the

422   South American environment. Rev Env. Contam Toxicol 191, 1–22.

423   Barra, R., Popp, P., Quiroz, R., Treutler, H.C., Araneda, A., Bauer, C., Urrutia, R.,

424   2006. Polycyclic aromatic hydrocarbons fluxes during the past 50 years observed

425   in dated sediment cores from Andean mountain lakes in central south Chile.

426   Ecotoxicol. Environ. Saf. 63, 52–60. https://doi.org/10.1016/j.ecoenv.2005.07.025

427   Blais, J.M., Charpentié, S., Pick, F., Kimpe, L.E., Amand, A.S., Regnault-Roger, C.,

428   2006. Mercury, polybrominated diphenyl ether, organochlorine pesticide, and

429   polychlorinated biphenyl concentrations in fish from lakes along an elevation

430   transect in the French Pyrénées. Ecotoxicol. Environ. Saf. 63, 91–99.

431   https://doi.org/10.1016/j.ecoenv.2005.08.008

432   Blais, J.M., Schindler, D.W., Muir, D.C.G., Kimpe, L.E., Donald, D.B., Rosenberg, B.,

433   1998. Accumulation of persistent organochlorine compounds in mountains of

434   western Canada. Nature 395, 585–588. https://doi.org/Doi 10.1038/26944

435   Booij, K., Smedes, F., Van Weerlee, E.M., 2002. Spiking of performance reference

436   compounds in low density polyethylene and silicone passive water samplers.

437   Chemosphere 46, 1157–1161. https://doi.org/10.1016/S0045-6535(01)00200-4

438   Bradford, D.F., Stanley, K.A., Tallent, N.G., Sparling, D.W., Nash, M.S., Knapp, R.A.,

439   Mcconnell, L.L., Massey Simonich, S.L., 2013. Temporal and spatial variation of

440   atmospherically deposited organic contaminants at high elevation in yosemite

441   national park, California, USA. Environ. Toxicol. Chem. 32, 517–525.

442   https://doi.org/10.1002/etc.2094

443   Brazil census bureau, 2018. IBGE [WWW Document].

444   Broman, D., Näf, C., Zebühr, Y., Näf, C., Zebühr, Y., 1991. Long-Term High- and

445   Low-Volume Air Sampling of Polychlorinated Dibenzo-p-dioxins and

446   Dibenzofurans and Polycyclic Aromatic Hydrocarbons along a Transect from

447   Urban to Remote Areas on the Swedish Baltic Coast. Environ. Sci. Technol. 25,

448   1841–1850. https://doi.org/10.1021/es00023a001

449 Calamari, D., Bacci, E., Focardi, S., Gaggi, C., Morosini, M., Vighi, M., 1991. Role of

450   Plant Biomass in the Global Environmental Partitioning of Chlorinated

451   Hydrocarbons. Environ. Sci. Technol. 25, 1489–1495.

452   https://doi.org/10.1021/es00020a020

453 Cavalcante, R.M., Sousa, F.W., Nascimento, R.F., Silveira, E.R., Freire, G.S.S., 2009.

454   The impact of urbanization on tropical mangroves (Fortaleza, Brazil): Evidence

455   from PAH distribution in sediments. J. Environ. Manage. 91, 328–335.

456   https://doi.org/10.1016/j.jenvman.2009.08.020

457 Choi, S.D., Shunthirasingham, C., Daly, G.L., Xiao, H., Lei, Y.D., Wania, F., 2009.

458   Levels of polycyclic aromatic hydrocarbons in Canadian mountain air and soil are

459   controlled by proximity to roads. Environ. Pollut. 157, 3199–3206.

460   https://doi.org/10.1016/j.envpol.2009.05.032

461 Cincinelli, A., Martellini, T., Bittoni, L., Russo, A., Gambaro, A., Lepri, L., 2008.

462   Natural and anthropogenic hydrocarbons in the water column of the Ross Sea

463   (Antarctica). J. Mar. Syst. 73, 208–220.

464   https://doi.org/10.1016/j.jmarsys.2007.10.010

465 da Silva, D.A.M., Bícego, M.C., 2010. Polycyclic aromatic hydrocarbons and petroleum

466   biomarkers in São Sebastião Channel, Brazil: Assessment of petroleum

467   contamination. Mar. Environ. Res. 69, 277–286.

468   https://doi.org/10.1016/j.marenvres.2009.11.007

469 Daly, G.L., Lei, Y.D., Castillo, L.E., Muir, D.C.G.G., Wania, F., 2007. Polycyclic

470   aromatic hydrocarbons in Costa Rican air and soil: A tropical/temperate

471   comparison. Atmos. Environ. 41, 7339–7350.

472   https://doi.org/10.1016/j.atmosenv.2007.05.014

473 Daly, G.L., Wania, F., 2005. Critical Review Organic Contaminants in Mountains.

474   Environ. Sci. Technol. 39, 385–398. https://doi.org/10.1021/es048859u

475 Estellano, V.H., Pozo, K., Harner, T., Franken, M., Zaballa, M., 2008. Altitudinal and

476   seasonal variations of persistent organic pollutants in the Bolivian Andes

477   mountains. Environ. Sci. Technol. 42, 2528–2534.

478   https://doi.org/10.1021/es702754m

479 Fauvelle, V., Montero, N., Mueller, J.F., Banks, A., Mazzella, N., Kaserzon, S.L., 2017.

480   Glyphosate and AMPA passive sampling in freshwater using a microporous

481   polyethylene diffusion sampler. Chemosphere 188, 241–248.

482   https://doi.org/10.1016/j.chemosphere.2017.08.013

483 Fernandes, M.B., Brickus, L.S.R., Moreira, J.C., Cardoso, J.N., 2002. Atmospheric

484   BTX and polyaromatic hydrocarbons in Rio de Janeiro, Brazil. Chemosphere 47,

485   417–425. https://doi.org/10.1016/S0045-6535(01)00319-8

486 Fernández, P., Carrera, G., Grimalt, J.O., 2005. Persistent organic pollutants in remote

487   freshwater ecosystems. Aquat. Sci. 67, 263–273. https://doi.org/10.1007/s00027-

488   005-0747-8

489 Gasperi, J., Garnaud, S., Rocher, V., Moilleron, R., 2009. Priority pollutants in surface

490   waters and settleable particles within a densely urbanised area: Case study of Paris

491   (France). Sci. Total Environ. 407, 2900–2908.

492   https://doi.org/10.1016/j.scitotenv.2009.01.024

493 Guzzella, L., Poma, G., De Paolis, A., Roscioli, C., Viviano, G., 2011. Organic

494   persistent toxic substances in soils, waters and sediments along an altitudinal

495   gradient at Mt. Sagarmatha, Himalayas, Nepal. Environ. Pollut. 159, 2552–2564.

496   https://doi.org/10.1016/j.envpol.2011.06.015

497 Harner, T., Bartkow, M., Holoubek, I., Klanova, J., Wania, F., Gioia, R., Moeckel, C.,

498   Sweetman, A.J., Jones, K.C., 2006. Passive air sampling for persistent organic

499   pollutants: Introductory remarks to the special issue. Environ. Pollut. 144, 361–

500   364. https://doi.org/10.1016/j.envpol.2005.12.044

501 Honkonen, O., Rantalainen, A.L., 2016. Transport of urban-derived organic

502   contaminants into a boreal lake: A case study with passive samplers. Boreal

503   Environ. Res. 21, 87–100.

504 IARC, 2010. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans:

505   Some Non-heterocyclic Polycyclic Aromatic Hydrocarbons and Some Related

506   Exposures. Iarc Monogr. Eval. Carcinog. Risks To Humans 92, 1–868.

507   https://doi.org/10.1002/14356007.a04

508 INMET, 2018. Brazilian National Meteorology Institute [WWW Document].

509 Kallenborn, R., 2006. Persistent organic pollutants (POPs) as environmental risk factors

510   in remote high-altitude ecosystems. Ecotoxicol. Environ. Saf. 63, 100–107.

511   https://doi.org/10.1016/j.ecoenv.2005.02.016

512 Khairy, M. a, Lohmann, R., 2013. Field Calibration of Low Density Polyethylene

513   Passive Samplers for Gaseous POPs Total number of pages : 34 ; total number of

514   Figures : 1 total number of Tables : 25 Table of contents S3 S29 S30 S31-S32 S33

515   S34 S2.

516 Khairy, M.A., Lohmann, R., 2013. Source apportionment and risk assessment of

517   polycyclic aromatic hydrocarbons in the atmospheric environment of Alexandria,

518   Egypt. Chemosphere 91, 895–903.

519   https://doi.org/10.1016/j.chemosphere.2013.02.018

520 Khairy, M.A., Lohmann, R., 2012. Field Validation of Polyethylene Passive Air

521   Samplers for Parent and Alkylated PAHs in Alexandria, Egypt. Environ. Sci.

522   Technol. 46, 3990–3998. https://doi.org/10.1021/es300012u

523 Lemos, R.T. de O., Carvalho, P.S.M. de, Zanardi-Lamardo, E., 2014. Petroleum

524   hydrocarbons in water from a Brazilian tropical estuary facing industrial and port

525   development. Mar. Pollut. Bull. 82, 183–188.

526   https://doi.org/10.1016/j.marpolbul.2014.03.010

527 Levy, W., Henkelmann, B., Pfister, G., Bernhöft, S., Kirchner, M., Jakobi, G., Bassan,

528   R., Kräuchi, N., Schramm, K.W., 2009. Long-term air monitoring of

529   organochlorine pesticides using Semi Permeable Membrane Devices (SPMDs) in

530   the Alps. Environ. Pollut. 157, 3272–3279.

531   https://doi.org/10.1016/j.envpol.2009.05.043

532 Liu, S., Tao, S., Liu, W., Liu, Y., Dou, H., Zhao, J., Wang, L., Wang, J., Tian, Z., Gao,

533   Y., 2007. Atmospheric polycyclic aromatic hydrocarbons in north China: A winter-

534   time study. Environ. Sci. Technol. 41, 8256–8261.

535   https://doi.org/10.1021/es0716249

536 Liu, Y., Wang, S., Lohmann, R., Yu, N., Zhang, C., Gao, Y., Zhao, J., Ma, L., 2015.

537   Source apportionment of gaseous and particulate PAHs from traffic emission using

538   tunnel measurements in Shanghai, China. Atmos. Environ. 107, 129–136.

539   https://doi.org/10.1016/j.atmosenv.2015.02.041

540 Liu, Y., Wang, S., McDonough, C.A., Khairy, M., Muir, D.C.G., Helm, P.A., Lohmann,

541   R., 2016. Gaseous and Freely-Dissolved PCBs in the Lower Great Lakes Based on

542   Passive Sampling: Spatial Trends and Air-Water Exchange. Environ. Sci. Technol.

543   50, 4932–4939. https://doi.org/10.1021/acs.est.5b04586

544 Lohmann, R., 2015. Correction to Critical Review of Low-Density Polyethylene's

545   Partitioning and Diffusion Coefficients for Trace Organic Contaminants and

546   Implications for Its Use As a Passive Sampler. Environ. Sci. Technol. 49, 3985–

547   3985. https://doi.org/10.1021/acs.est.5b01017

548   Lohmann, R., Dapsis, M., Morgan, E.J., Dekany, V., Luey, P.J., 2011. Determining air-

549   water exchange, spatial and temporal trends of freely dissolved PAHs in an urban

550   estuary using passive polyethylene samplers. Environ. Sci. Technol. 45, 2655–

551   2662. https://doi.org/10.1021/es1025883

552   Lohmann, R., Klanova, J., Pribylova, P., Liskova, H., Yonis, S., Bollinger, K., 2013.

553   PAHs on a west-to-east transect across the tropical Atlantic Ocean. Environ. Sci.

554   Technol. 47, 2570–2578. https://doi.org/10.1021/es304764e

555   Lohmann, R., Muir, D., 2010. Global aquatic passive sampling (AQUA-GAPS): Using

556   passive samplers to monitor POPs in the waters of the world. Environ. Sci.

557   Technol. 44, 860–864. https://doi.org/10.1021/es902379g

558   Ma, Y., Xie, Z., Yang, H., Möller, A., Halsall, C., Cai, M., Sturm, R., Ebinghaus, R.,

559   2013. Deposition of polycyclic aromatic hydrocarbons in the North Pacific and the

560   Arctic. J. Geophys. Res. Atmos. 118, 5822–5829.

561   https://doi.org/10.1002/jgrd.50473

562   Martinelli, G., 2007. Mountain biodiversity in Brazil. Rev. Bras. Botânica 30, 587–597.

563   https://doi.org/10.1590/S0100-84042007000400005

564   McDonough, C.A., Khairy, M.A., Muir, D.C.G., Lohmann, R., 2014. Significance of

565   population centers as sources of gaseous and dissolved PAHs in the lower Great

566   Lakes. Environ. Sci. Technol. 48, 7789–7797. https://doi.org/10.1021/es501074r

567   Medina, B.M.O., Ribeiro, K.T., Aximoff, I.A., Scarano, F.R., 2016. Effects of fire on

568   population dynamics of an endemic high altitude rupicolous geophyte. Oecologia

569   Aust. 20, 147–159. https://doi.org/10.4257/oeco.2016.2002.11

570   Meire, R.O., Azeredo, A., Pereira, M. d. S., Torres, J.P.M., Malm, O., 2008. Polycyclic

571   aromatic hydrocarbons assessment in sediment of national parks in southeast

572   Brazil. Chemosphere 73. https://doi.org/10.1016/j.chemosphere.2007.01.089

573   Meire, R.O., Khairy, M., Targino, A.C., Galvão, P.M.A., Torres, J.P.M., Malm, O.,

574   Lohmann, R., 2016. Use of passive samplers to detect organochlorine pesticides in

575   air and water at wetland mountain region sites (S-SE Brazil). Chemosphere 144.

576   https://doi.org/10.1016/j.chemosphere.2015.10.133

577   Meire, R.O.R.O., Lee, S.C.S.C., Yao, Y., Targino, A.C.A.C., Torres, J.P.M.J.P.M.,

578   Harner, T., 2012. Seasonal and altitudinal variations of legacy and current-use

579   pesticides in the Brazilian tropical and subtropical mountains. Atmos. Environ. 59,

580   108–116. https://doi.org/10.1016/j.atmosenv.2012.05.018

581   Myers, N., Mittermeier, R.A., Mittermeier, C.G., da Fonseca, G.A.B., Kent, J., 2000.

582   Biodiversity hotspots for conservation priorities. Nature 403, 853–858.

583   https://doi.org/10.1038/35002501

584   Nizzetto, L., Lohmann, R., Gioia, R., Jahnke, A., Dachs, J., Herckes, P., Guardo, A.D.I.,

585   Jones, K.C., Guardo, A.D.I., 2008. PAHs in Air and Seawater along a North –

586   South Atlantic Transect : Trends , Processes and Possible Sources PAHs in Air and

587   Seawater along a North – South Atlantic Transect : Trends , Processes and Possible

588   Sources. Oceans 42, 1–14. https://doi.org/10.1021/es0717414

589   Omena, M.T.R.N. De, Araki, E.K., Schimalski, M.B., Taniwaki, M.H., Santos, P.S.,

590   2016. Zoneamento do Risco de Incêndio Florestal para o Parque Nacional de São

591   Joaquim – SC. Biodiversidade Brasileira 6, 173–186.

592   Page, D.S., Boehm, P.D., Douglas, G.S., Bence, A.E., Burns, W.A., Mankiewicz, P.J.,

593   1999. Pyrogenic Polycyclic Aromatic Hydrocarbons in Sediments Record Past

594   Human Activity: A Case Study in Prince William Sound, Alaska. Mar. Pollut.

595   Bull. 38, 247–260. https://doi.org/10.1016/S0025-326X(98)00142-8

596   Pozo, K., Estellano, V.H., Harner, T., Diaz-Robles, L., Cereceda-Balic, F., Etcharren,

597   P., Pozo, K., Vidal, V., Guerrero, F., Vergara-Fernández, A., 2015. Assessing

598   Polycyclic Aromatic Hydrocarbons (PAHs) using passive air sampling in the

599   atmosphere of one of the most wood-smoke-polluted cities in Chile: The case

600   study of Temuco. Chemosphere 134, 475–481.

601   https://doi.org/10.1016/j.chemosphere.2015.04.077

602   Pozo, K., Harner, T., Lee, S.C., Wania, F., Muir, D.C.G., Jones, K.C., 2009. Seasonally

603   resolved concentrations of persistent organic pollutants in the global atmosphere

604   from the first year of the GAPS Study. Environ. Sci. Technol. 43, 796–803.

605   https://doi.org/10.1021/es802106a

606   Pozo, K., Harner, T., Rudolph, A., Oyola, G., Estellano, V.H., Ahumada-Rudolph, R.,

607   Garrido, M., Pozo, K., Mabilia, R., Focardi, S., 2012. Survey of persistent organic

608   pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) in the atmosphere

609   of rural, urban and industrial areas of Concepción, Chile, using passive air

610   samplers. Atmos. Pollut. Res. 3, 426–434. https://doi.org/10.5094/APR.2012.049

611   Qiao, M., Huang, S., Wang, Z., 2008. Partitioning characteristics of PAHs between

612   sediment and water in a shallow lake. J. Soils Sediments 8, 69–73.

613   https://doi.org/10.1065/jss2008.03.279

614   Readman, J.W., Fillmann, G., Tolosa, I., Bartocci, J., Villeneuve, J.P., Catinni, C., Mee,

615   L.D., 2002. Petroleum and PAH contamination of the Black Sea. Mar. Pollut. Bull.

616   44, 48–62. https://doi.org/10.1016/S0025-326X(01)00189-8

617   Ren, J., Wang, X., Wang, C., Gong, P., Yao, T., Attribution, C.C., Ren, J., Wang, X.,

618   2017. Supplement of Atmospheric processes of organic pollutants over a remote

619   lake on the central Tibetan Plateau : implications for regional cycling. Atmos.

620   Chem. Phys. 17, 1401–1415. https://doi.org/10.5194/acp-17-1401-2017

621 Ribeiro, A.M., da Rocha, C.C.M., Franco, C.F.J., Fontana, L.F., Pereira Netto, A.D.,

622   2012. Seasonal variation of polycyclic aromatic hydrocarbons concentrations in

623   urban streams at Niterói City, RJ, Brazil. Mar. Pollut. Bull. 64, 2834–2838.

624   https://doi.org/10.1016/j.marpolbul.2012.09.014

625 Ruge, Z., Muir, D., Helm, P., Lohmann, R., 2015. Concentrations, Trends, and Air-

626   Water Exchange of PAHs and PBDEs Derived from Passive Samplers in Lake

627   Superior in 2011. Environ. Sci. Technol. 49, 13777–13786.

628   https://doi.org/10.1021/acs.est.5b02611

629 Sacks, V.P., Lohmann, R., 2011. Development and use of polyethylene passive

630   samplers to detect triclosans and alkylphenols in an Urban estuary. Environ. Sci.

631   Technol. 45, 2270–2277. https://doi.org/10.1021/es1040865

632 Schuster, J.K., Harner, T., Su, K., Mihele, C., Eng, A., 2015. First Results from the Oil

633   Sands Passive Air Monitoring Network for Polycyclic Aromatic Compounds.

634   Environ. Sci. Technol. 49, 2991–2998. https://doi.org/10.1021/es505684e

635 Sheng, J., Wang, X., Gong, P., Joswiak, D.R., Tian, L., Yao, T., Jones, K.C., 2013.

636   Monsoon-driven transport of organochlorine pesticides and polychlorinated

637   biphenyls to the tibetan plateau: Three year atmospheric monitoring study.

638   Environ. Sci. Technol. 47, 3199–3208. https://doi.org/10.1021/es305201s

639 Shunthirasingham, C., Barra, R., Mendoza, G., Montory, M., Oyiliagu, C.E., Lei, Y.D.,

640   Wania, F., 2011. Spatial variability of atmospheric semivolatile organic

641   compounds in Chile. Atmos. Environ. 45, 303–309.

642   https://doi.org/10.1016/j.atmosenv.2010.10.027

643 Smedes, F., Rusina, T.P., Beeltje, H., Mayer, P., 2017. Partitioning of hydrophobic

644   organic contaminants between polymer and lipids for two silicones and low density

645   polyethylene. Chemosphere 186, 948–957.

646   https://doi.org/10.1016/j.chemosphere.2017.08.044

647   Stogiannidis, E., Laane, R., Stogiannidis, E; Lanne, R., 2013. Source characterization of

648   polycyclic aromatic hydrocarbons by using their molecular indices: an overview of

649   possibilities. Rev. Environ. Contam. Toxicol. 234, 38. https://doi.org/10.1007/978-

650   3-319-10638-0_2

651   Taniguchi, S., Colabuono, F.I., Dias, P.S., Oliveira, R., Fisner, M., Turra, A., Izar,

652   G.M., Abessa, D.M.S., Saha, M., Hosoda, J., Yamashita, R., Takada, H., Lourenço,

653   R.A., Magalhães, C.A., Bícego, M.C., Montone, R.C., 2016. Spatial variability in

654   persistent organic pollutants and polycyclic aromatic hydrocarbons found in beach-

655   stranded pellets along the coast of the state of São Paulo, southeastern Brazil. Mar.

656   Pollut. Bull. 106, 87–94. https://doi.org/10.1016/j.marpolbul.2016.03.024

657   Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of

658   pollution emission sources. Environ. Pollut. 162, 110–119.

659   https://doi.org/10.1016/j.envpol.2011.10.025

660   Tomzhinski, G.W., Coura, P.H.F., Fernandes, M. do C., 2011. Avaliação da detecção de

661   focos de calor por Sensoriamento Remoto para o Parque Nacional do Itatiaia.

662   Biodiversidade Bras. 1, 201–211.

663   UNEP, 2011. Living in harmony with nature Convention on Biological Diversity 70.

664   UNEP, 2002. Reagionally Based Assessment of Persistent Toxic Substances - Eastern

665   and Western South America Regional Report.

666   van Drooge, B.L., Fernández, P., Grimalt, J.O., Stuchlík, E., García, C.J.T., Cuevas, E.,

667   2010. Atmospheric polycyclic aromatic hydrocarbons in remote European and

668   Atlantic sites located above the boundary mixing layer. Environ. Sci. Pollut. Res.

669   17, 1207–1216. https://doi.org/10.1007/s11356-010-0296-0

670   Vilanova, R.M., Fernández, P., Martínez, C., Grimalt, J.O., 2001. Polycyclic aromatic

671   hydrocarbons in remote mountain lake waters. Water Res. 35, 3916–3926.

672   https://doi.org/10.1016/S0043-1354(01)00113-0

673   Wang, S., Ni, H.-G., Sun, J.-L., Jing, X., He, J.-S., Zeng, H., 2013. Polycyclic aromatic

674   hydrocarbons in soils from the Tibetan Plateau, China: distribution and influence

675   of environmental factors. Environ. Sci. Process. Impacts 15, 661.

676   https://doi.org/10.1039/c2em30856h

677   Wang, W., Simonich, S., Giri, B., Chang, Y., Zhang, Y., Jia, Y., Tao, S., Wang, R.,

678   Wang, B., Li, W., Cao, J., Lu, X., 2011. Atmospheric concentrations and air-soil

679   gas exchange of polycyclic aromatic hydrocarbons (PAHs) in remote, rural village

680   and urban areas of Beijing-Tianjin region, North China. Sci. Total Environ. 409,

681   2942–2950. https://doi.org/10.1016/j.scitotenv.2011.04.021

682   Wania, F., Shen, L., Lei, Y.D., Teixeira, C., Muir, D.C.G., 2003. Development and

683   calibration of a resin-based passive sampling system for monitoring persistent

684   organic pollutants in the atmosphere. Environ. Sci. Technol. 37, 1352–1359.

685   https://doi.org/10.1021/es026166c

686   Wilcke, W., Amelung, W., Krauss, M., Martius, C., Bandeira, A., Garcia, M., 2003.

687   Polycyclic aromatic hydrocarbon (PAH) patterns in climatically different

688   ecological zones of Brazil. Org. Geochem. 34, 1405–1417.

689   https://doi.org/10.1016/S0146-6380(03)00137-2

690   Wilcke, W., Amelung, W., Martius, C., Garcia, M.V.B., Zech, W., 2000. Biological

691   sources of polycyclic aromatic hydrocarbons (PAHs) in the Amazonian rain

692   forest. J. Plant. Nutr. Soil Sci. 163, 27–30. https://doi.org/10.1002/(SICI)1522-

693   2624(200002)163:1<27::AID-JPLN27>3.0.CO;2-E

694   Yao, Y., Meng, X.Z., Wu, C.C., Bao, L.J., Wang, F., Wu, F.C., Zeng, E.Y., 2016.

695   Tracking human footprints in Antarctica through passive sampling of polycyclic

696   aromatic hydrocarbons in inland lakes. Environ. Pollut. 213, 412–419.

697   https://doi.org/10.1016/j.envpol.2016.02.035

698 Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre,

699   S., 2002. PAHs in the Fraser River basin: A critical appraisal of PAH ratios as

700   indicators of PAH source and composition. Org. Geochem. 33, 489–515.

701   https://doi.org/10.1016/S0146-6380(02)00002-5

702 Zhao, W., Cai, M., Adelman, D., Khairy, M., August, P., Lohmann, R., 2018. Land-use-

703   based sources and trends of dissolved PBDEs and PAHs in an urbanized watershed

704   using passive polyethylene samplers. Environ. Pollut. 238, 573–580.

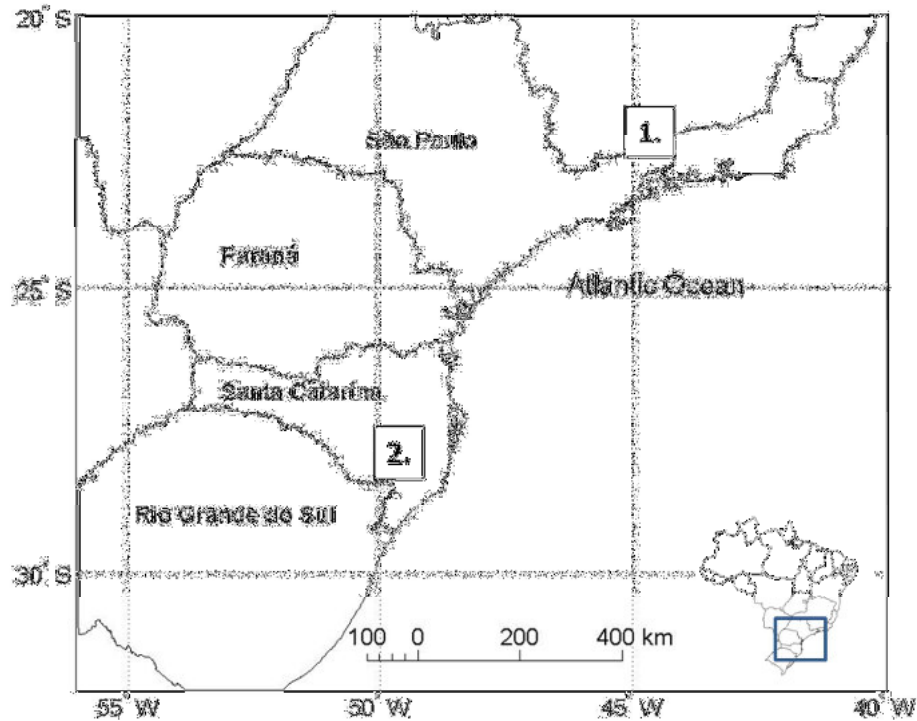705   https://doi.org/10.1016/j.envpol.2018.02.057

706

Figures

Figure 1. Map showing the south and southern regions of Brazil. The two National Parks where the sampling was conducted are also indicated: 1. National Park of Itatiaia (NPIT) – Rio de Janeiro State. 2. National Park of São Joaquim (NPSJ) – Santa Catarina State (modified from Meire et al., 2016). See map details in figures S1 and S2.
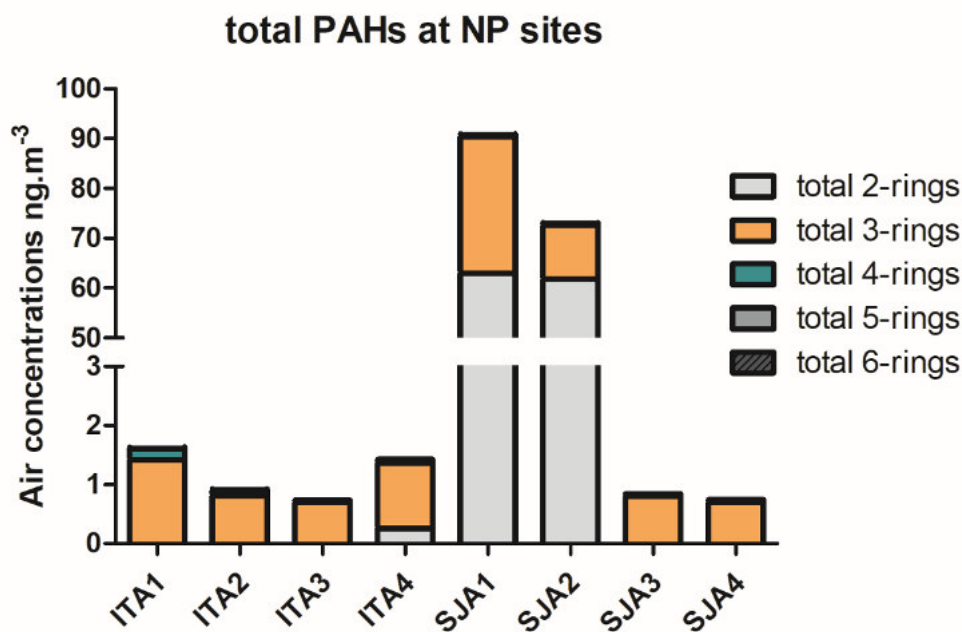
Figure 2. Profile and total PAHs (ng.m^{-3}) along altitudinal transects at National Park sites (IT – National Park of Itatiaia; SJ – National Park of São Joaquim)
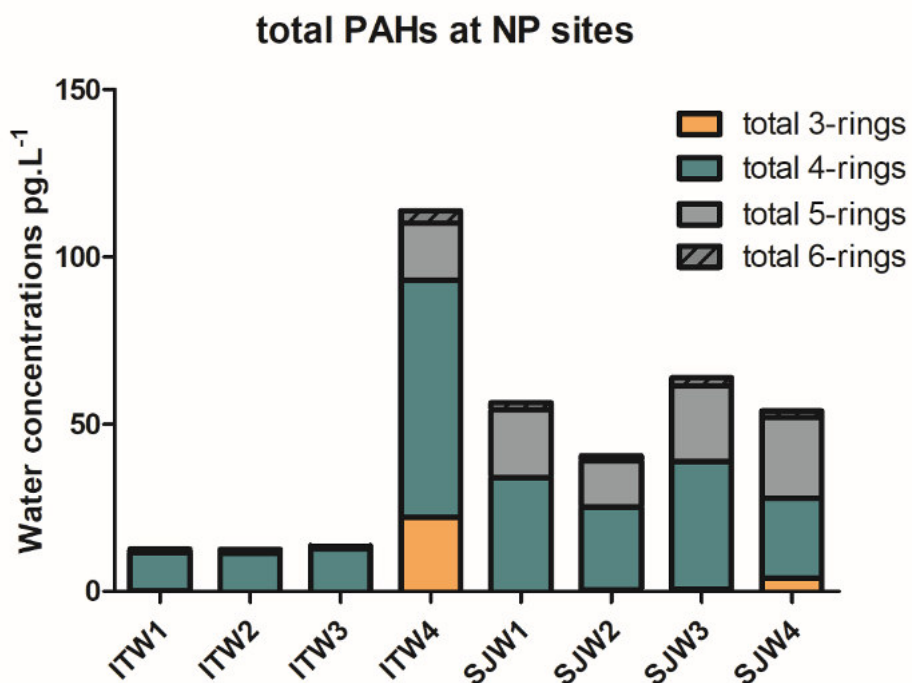

Figure 3. Profile and freely total PAHs (pg.L^{-1}) along altitudinal transects at National Park sites (IT – National Park of Itatiaia; SJ – National Park of São Joaquim).

Highlights

1) LDPE passive samplers were deployed in waters and air to determine PAHs in mountain regions in Brazil.

2) Air (0.70- 90 ng.m^{-3}) and water (10- 110 pg.L^{-1}) concentrations of selected PAHs were comparable to other remote mountainous regions worldwide.

3) PAH ratios indicate wood/grass combustion origins at both national parks due to historical fire events.

4) A mix input of long-range atmospheric transport combined with local PAH emission sources were observed along altitudinal transects.