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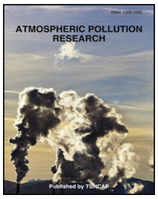

Passive sampler-derived concentrations of PAHs in air and water along Brazilian mountain transects

R.O. Meire[a,*], M. Khairy[b,c], Dave Aldeman[b], P.M.A. Galvão[a], J.P.M. Torres[a], O. Malm[a], R. Lohmann[b]

[a] Biophysics Institute, Rio de Janeiro Federal University, CCS, 21941-902, Rio de Janeiro, RJ, Brazil
[b] University of Rhode Island, Graduate School of Oceanography, South Ferry Rd., Narragansett, RI, 02882, USA
[c] Department of Environmental Sciences, Faculty of Science, Alexandria University, Alexandria, Egypt

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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.

1. Introduction

Maintaining mountain biodiversity is part of the current National Biodiversity Council (CBD) agenda and international agreements such as the “Global Strategy for Plant Conservation” (Martinelli, 2007; UNEP, 2011). Mountains have notorious susceptibility to environmental and climate change. The atmospheric deposition of semi-volatile organic compounds (SVOCs) in mountainous regions is highlighted as 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 (Blais et al., 2006, 1998; Calamari et al., 1991). The input of persistent toxic substances over upland regions is mainly controlled by meteorological and geographical conditions such as orographic winds, relatively low temperatures and high precipitation rates, commonly found in mountainous regions (Daly and Wania, 2005; Sheng et al., 2013). Moreover, the proximity to metropolitan areas, industry and agriculture areas can amplify critical environmental scenarios for mountains rendering highlands as good “sentinels” for local and global air quality (Kallenborn, 2006).

Polycyclic aromatic hydrocarbons (PAHs) are a unique class of SVOC consisting of two or more fused benzene rings in linear, angular or cluster arrangements (Page et al., 1999). PAHs are from natural and anthropogenic sources, mostly from the incomplete burning of organic matter. Petrogenic and pyrogenic sources are common, and among pyrogenic sources, there are natural fires and anthropogenic practices that lead to deforestation and wood burning (Stogiannidis et al., 2013; Yunker et al., 2002). In this context, anthropogenic activities can sharply increase the levels of these contaminants in the environment. Moreover, PAHs are considered priority organic pollutants in view of their carcinogenic potential (i.e., benzo-*a*-pyrene diol epoxide) and their ability to act as mutagenic promoters in biological systems (IARC, 2010). The intensive use of forest resources (intentional and unintentional biomass burning) makes PAHs one of the high priority SVOCs for

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[*] Corresponding author.

E-mail addresses: rodrigo@xerem.ufrj.br, romeire@biof.ufrj.br (R.O. Meire).

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the South America region (Barra et al., 2007). In Brazil, emissions were estimated at 467-6607 tonnes/year for PAHs, with wood combustion accounting for at least 90% of these values (UNEP, 2002). However, petroleum production, refining and transport activities have greatly increased over the last decades which contribute to ambient PAHs in the region (da Silva and Bícego, 2010; Taniguchi et al., 2016).

The use of passive sampling to detect SVOCs in the environment has become common over the last few years (Fauvelle et al., 2017; Harner et al., 2006; Levy et al., 2009; Lohmann and Muir, 2010; Pozo et al., 2009). In the last decade, low density polyethylene passive samplers (LDPE) have extensively been used to detect a range of SVOCs in water and air, and to evaluate the risk to wild-life and humans at regional and global scales (M. A. Khairy and Lohmann, 2013; Liu et al., 2007; Lohmann, 2015; Smedes et al., 2017; Zhao et al., 2018). Most of these pollutants strongly partition into the LDPE matrix (Sacks and Lohmann, 2011). This feature offers methodological advantages in relation to other environmental measurements, such as easier/and less costly laboratory methods and lower detection limits, making LDPE a useful tool for first-order risk assessment.

The main goals of the current study were to (i) assess the occurrence of PAHs in air and water at two National Parks in Brazil; (ii) identify emission sources of PAHs and the contribution of different sources in the tropical and subtropical mountain regions of Brazil, and (iii) investigate altitudinal variations of gaseous and dissolved PAHs. 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 present work provides an initial screening of gaseous and freely dissolved PAH concentration levels in tropical and subtropical 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°22′38″S, lon.: 44°41′35″W, Rio de Janeiro and Minas Gerais State) and “Serra Geral” (National Park of São Joaquim - NPSJ, lat.: 28°00′49″S, lon.: 49°35′17″W, Santa Catarina State), located in southeast and south Brazil, respectively (Fig. 1). These two conservation areas comprise high-altitude grasslands and mountainous rainforests which harbour high biodiversity with several endemic species (Myers et al., 2000). The NPIT borders are surrounded by Resende, Itatiaia, Bocaina de Minas, Alagoa and Itamonte municipalities – harbouring more than 180,000 inhabitants. Around the NPIT, mixed land uses characterize the region, such as agriculture, livestock and industrial activities. On the other hand, the National Park of São Joaquim is surrounded by extended agricultural areas with a variety of farming activities such as apple, maize and tobacco. Urubici, Bom Jardim da Serra, Grão Pará and Orleans are the main municipalities that surround the NPSJ, accounting for ∼45,000 inhabitants (Brazil census bureau, 2018). Further details on the National Park are provided in the SM.

2.2. Passive sampling field deployment

Field deployment details and LDPE theory/calculation methodology were performed as described previously (Liu et al., 2016; McDonough et al., 2014; Meire et al., 2016). Briefly, the LDPEs were cut from 50-µm thick commercial sheeting (Carlisle Plastics, Inc., Minneapolis, MN), yielding a 10 × 30-cm strip of 1- to 2-g each. Prior to exposure, the LDPEs were spiked with deuterated PAHs (naphthalene-d_8, pyrene-d_{10} and benzo(a)pyrene-d_{12}) as performance reference compounds (PRCs) via a method adapted from Booij et al. (2002). Four sampling sites were established along altitudinal gradients at each National Park (NPIT: 700–2400 m above sea level – m a.s.l.; NPSJ: 990–1700 m a.s.l.) during late fall and early winter seasons (May and June) in 2012 (Figs. S1 and S2). For each sampling site, passive LDPE sheets (n = 2) were deployed in the surface shallow waters and overlying atmosphere simultaneously for 30–40 days (Figs. S3 and S4). Replicate tests were carried out at the highest altitudinal sites for both National Parks (Rebouças IT4, NPIT; Cindacta 2 SJ4, NPSJ). Five field blanks were collected at both parks to assess possible sample contamination during transport and storage. The water temperature was measured for each site using a Yellow Spring multiparametric probe (model 600 QS). Air temperature data were compiled from surrounding meteorological stations provided by Brazilian National Institute of Meteorology (INMET, 2018) (Table S1).

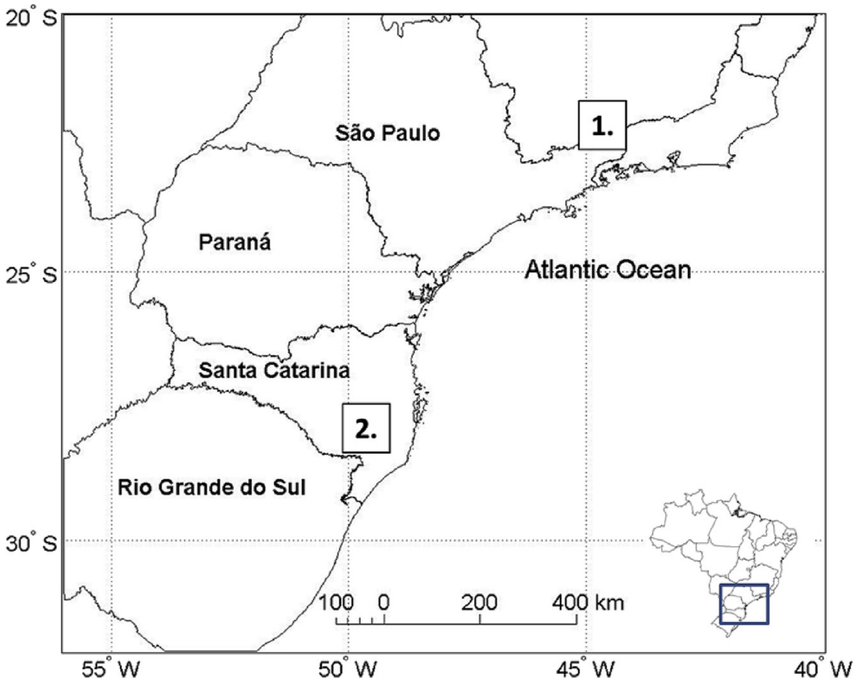

Fig. 1. Map showing the south and southern regions of Brazil. The two National Parks where the sampling was conducted are also indicated: 1. National Park of Itatiaia (NPIT) – Rio de Janeiro State. 2. National Park of São Joaquim (NPSJ) – Santa Catarina State (modified from Meire et al., 2016). See map details in Figs. S1 And S2.

2.3. Analytical methodology

Analytical methodologies of LDPEs were extensively described elsewhere (Lohmann et al., 2011; Ruge et al., 2015). After sampling exposure, LDPEs were wiped clean with Kimwipes and extracted (24 h) twice at room-temperature with ethylacetate and condensed after being spiked with 50 ng of labelled PAH surrogates (acenaphthalene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} from Ultra Scientific, North Kingstown, RI) to evaluate quality assurance performance during sample processing. 42 individual PAHs were analysed on an Agilent 6890 Series gas chromatograph (GC) coupled to an Agilent 5973 MS (mass spectrometer). Out of the target 42 PAHs, only 20 PAHs were regularly detected (at a detection frequency $>$ 30%). These selected PAHs are listed in supplementary material (SM). The limit of detection (LOD) was calculated as the average laboratory blanks plus three times the standard deviation. The LODs ranged from 0.1 to 9.1 ng g^{-1} of LDPE in the passive samplers. Methods for preparation, extraction, theory/calculations of LDPEs as well as the instrumental analyses of the extracts and quality assurance/quality control are given in the SM.

3. Results and discussion

3.1. Quality assurance/quality control

Recoveries of acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} ranged from 65 to 93% for all sample. Concentrations of individual PAHs were recovery-corrected for each LDPE sample. There was no significant difference between concentrations of selected PAHs in the field and laboratory blanks, indicating negligible contamination during transport, storage and analyses. For the most frequently detected PAHs, reproducibility ranged from 1.2% (retene) to 37% (fluoranthene), which is in agreement with previous LDPE studies at the same laboratory (average value around 20%) (Khairy and Lohmann, 2013).

3.2. Sampling rates and PAH equilibrations in field-deployed LDPE samplers

Sampling rates (*Rs*) for the atmospheric and water samplers are given in supplementary material (SM) (Table S3). Atmospheric *Rs* ranged from 6.1 to 77 m^3.day^{-1}, which is consistent with *Rs* values (7.0–75 m^3.day^{-1}) measured previously for atmospheric PAHs in the North American lower Great Lakes (McDonough et al., 2014). *Rs* values as large as 56 and 77 m^3.day^{-1} were observed for highest elevations at both National Parks (1700 and 2400 m a.s.l., NPSJ and NPIT, respectively), probably due to higher wind speeds at these high-altitude sites.

Most detected PAHs were far from reaching equilibrium ($<$ 50%). The only chemicals that approached equilibrium ($>$ 90%) were the 2 and 3-ring PAHs (log K_{LDPE}-air $<$ 7.76), except at two sites (ITA1 and ITA2). Calculated % equilibrium for gaseous PAHs are presented in Tables S5 and S6. Khairy and Lohmann (2012) also observed a similar equilibrium pattern for gaseous PAHs, using LDPE air samplers in Alexandria (Egypt).

Water *Rs* values ranged from 5.0 to 55 L.day^{-1}. A similar range was previously observed for pyrene and higher molecular weight PAHs sampled in Narragansett Bay (Lohmann et al., 2011) and in the Lower Great Lakes (McDonough 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 PAHs showed variations between the two parks. At both National Parks, 2-3-ring PAHs approached equilibrium by the end of the deployment period (92–100%) whilst higher molecular weight PAHs (HWM) were far from reaching equilibrium ($<$ 20%).

3.3. Air and water concentrations of PAHs

Gaseous PAH were dominated by phenanthrene and fluorene (50% and 17% respectively of Σ_{20}PAHs). LDPE-derived gaseous concentrations ranged from 0.40 to 0.93 ng m^{-3} and from 0.070 to 0.42 ng m^{-3} for phenanthrene and fluorene, respectively. However, extremely elevated gaseous concentrations (70–90 ng m^{-3}) were detected for other PAHs at NPSJ sites, in particular methylnaphthalenes (BDL-30 ng m^{-3}), acenaphthene (BDL-16 ng m^{-3}) and biphenyl (BDL-9 ng.m^{-3}). 4-5-ring PAHs displayed no more than 10% of Σ_{20}PAHs (i.e., benzo(*b*)fluoranthene, benzo(*e*)pyrene and 7,12-dimethylbenz(*a*)anthracene), with higher molecular weight PAHs (HWM), accounting for less than 1% of sum of PAHs (i.e. benzo(*g,h,i*)perylene) (Figs. S5 and S6).

As opposed to gas-phase concentrations, fluoranthene (40%) and chrysene (20%) were the most abundant and frequently detected dissolved PAHs in the water with concentrations ranging from 7.0 to 40 pg L^{-1} and 2.0–18 pg L^{-1} respectively. Moreover, perylene (BDL-14 pg L^{-1}) and dimethylbenzo(*a*)anthracene (0.5–12 pg L^{-1}) were frequently detected in this study (8% and 10% respectively of Σ_{20}PAHs) especially at NPSJ sites. Other 4-5-ring PAHs showed only a minor contribution $<$ 10% of the total PAHs (i.e. benzo(*e*)pyrene, benzo(*a*)pyrene and perylene) as well as HMW PAHs ($<$ 2%, i.e. indeno(1,2,3-*c,d*)pyrene) (Figs. S7 and S8). Since the used method had no protection from UV radiation, it is important to note that PAHs in passive samplers can be degraded by exposure to sunlight, ultimately changing the concentration of target analytes. The results for individual PAHs are discussed below. Geometric means (GM) are presented rather than arithmetic means to prevent extreme values (outliers) from skewing the mean.

3.4. Levels and spatial trends in air

For gaseous concentrations of PAHs, no statistically significant differences in median values for PAHs were found between the two national parks (Mann Whitney test – $p < 0.05$). The NPSJ displayed higher concentrations of PAHs in air compared to NPIT. Gaseous concentrations (ng.m^{-3}) of Σ_{20} PAH ranged from 0.70 to 1.6 ng m^{-3} (geometric mean, GM = 1.2) and from 0.70 to 91 ng m^{-3} (GM = 37) for NPIT and NPSJ, respectively (Fig. 2). The gaseous concentrations of PAHs at NPSJ sites were considerably higher than reported in most other studies in mountainous regions, although these data should be viewed with caution, since the much higher concentrations (10 s ng.m^{-3}) were only detected at the low-altitudinal sites (SJA1 and SJA2). In fact, high air concentrations of PAHs reported here are more consistent with results for impacted sites by urban centres and surroundings such as reported in other studies worldwide (Álvarez et al.,

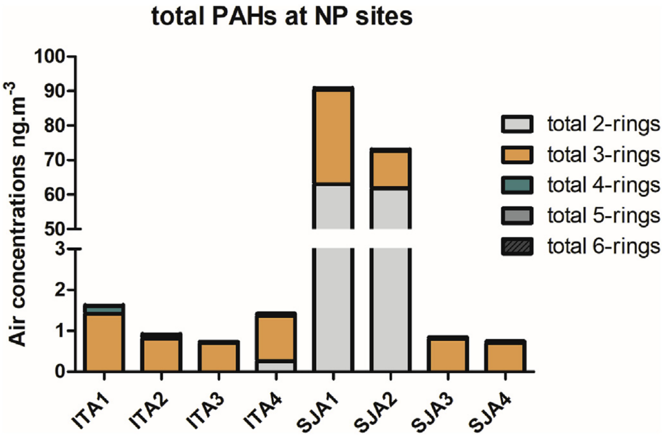

Fig. 2. Profile and total PAHs (ng.m^{-3}) along altitudinal transects at National Park sites (IT – National Park of Itatiaia; SJ – National Park of São Joaquim).

2016; Liu et al., 2015; McDonough et al., 2014; Pozo et al., 2015, 2012; Schuster et al., 2015).

For LDPEs, recent studies have reported variable ranges of gaseous PAH worldwide, especially close to urban regions in North America. McDonough et al. (2014) observed elevated gaseous PAH concentrations throughout the lower Great Lakes (Σ_{15}PAH, 2.0–97 ng m^{-3}, GM = 9.0) which were strongly correlated with surrounding populations, suggesting urban centers as primary source of PAHs into the atmosphere.

Additionally, Ruge et al. (2015) reported a wider an even range of PAH air concentrations (Σ_{21}PAH, 0.05–140 ng m^{-3}) at Lake Superior sites, with similar environmental trends. These PAH levels are also in agreement with Lohmann et al. (2011), who reported similar concentrations (Σ_{17}PAH, 2.0–110 ng m^{-3}, GM = 11) in the gas-phase within the atmosphere around Narragansett Bay (RI, USA).

Outside of North America, Khairy and Lohmann (2012) reported much higher PAH levels in urban center of Alexandria (Egypt). These gaseous PAH concentrations derived from LDPE samplers ranged from hundreds to thousands of ng.m^{-3} (GM = 580), indicating both industrial and vehicle emissions as the major source of PAHs in Alexandria City.

Few studies have reported the presence of gaseous PAH in South American mountain regions. Generally, air concentrations were dominated by four-ring PAHs, detected using XAD-2 as a passive air sampler (Wania et al., 2003). In the current study, gaseous concentration of four-ring PAHs (ng.m^{-3}) ranged from 0.040 to 0.19 and from 0.040 to 0.31 for NPIT and NPSJ, respectively. These results are within the range observed at mountain sites in Costa Rica (0.04–0.65 ng m^{-3}), Chile (BDL-1.3 ng m^{-3}) and even at Western Canada (0.02–0.45 ng m^{-3}) (Choi et al., 2009; Daly et al., 2007; Shunthirasingham et al., 2011), with higher gaseous PAH levels in samplers deployed close to roads and settlements. In agreement with those previous studies, truly remote sites, i.e. sites far from houses and major roads (such as at high-elevation sites $>$ 1500 m a.s.l., in this study), are likely more reflective of PAH background air concentrations (0.04–0.06 ng m^{-3}) in South-Southeast Brazil.

Despite some outliers, phenanthrene was detected at all sites in both National Parks and exhibited the highest air concentration among the target PAHs. Phenanthrene concentrations in air measured in this study at NPIT (0.48–0.99 ng m^{-3}, GM = 0.72) and NPSJ (0.41–1.30 ng m^{-3}, GM = 0.79) are comparable to concentrations found at other remote mountainous regions, such as: Tibetan Plateau uplands, China (0.25–7.2 ng m^{-3}, GM = 0.81); Øvre Neådalsvatn, Central Norway (average value, 0.84 ng m^{-3}), Estany Redon, Central Pyrenees, Spain (average value, 0.87 ng m^{-3}), Gossenköllesee, Tyrolean Alps, Austria (average value, 0.98 ng m^{-3}) and Skalnaté Pleso, High Tatras, Slovakian Republic (average value, 3.1 ng m^{-3}) (Ren et al., 2017; van Drooge et al., 2010). Generally, gaseous phenanthrene concentrations found at National Park sites are higher than reported in the atmosphere of coastal/open seas, especially along Atlantic Ocean transects (North to South: 0.02–2.2 ng m^{-3}, GM = 0.15; West to East: BDL-1.3 ng m^{-3}, GM = 0.21), North Pacific (0.03–0.3 ng m^{-3}, GM = 0.12), Baltic coast (0.1–0.2 ng m^{-3}, GM = 0.18) and Arctic Sea (Broman et al., 1991; Lohmann et al., 2013; Ma et al., 2013; Nizzetto et al., 2008). However, studies along urban-industrial-rural transects in South America have reported higher gaseous phenanthrene concentrations than observed in this study, such as: Santiago de Cali, Colombia (10–20 ng m^{-3}), Concepción, Chile (10–100 ng m^{-3}, GM = 29) and Temuco, Chile (1.2–17 ng m^{-3}, GM = 6.7 ng m^{-3}) (Álvarez et al., 2016; Pozo et al., 2015, 2012).

3.5. Levels and spatial trends in water

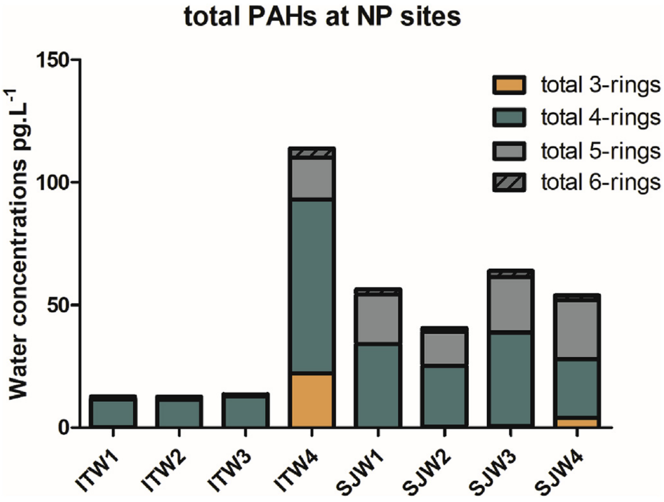

Fig. 3. Profile and freely total PAHs (pg L^{-1}) along altitudinal transects at National Park sites (IT – National Park of Itatiaia; SJ – National Park of São Joaquim).

In contrast to gaseous concentrations, freely dissolved concentrations of PAH in the water were consistently low. Freely dissolved PAH concentrations ranged from 10 to 110 pg L^{-1} (GM = 22) at NPIT and in a narrower range of 40–60 pg L^{-1} (GM = 53) at NPSJ, respectively (Fig. 3). Similar to gas-phase concentrations, no significant differences were observed between dissolved PAH concentrations in the two national parks, using Mann Whitney test ($p < 0.05$). Few data are available for freely dissolved PAH concentrations in mountain regions worldwide. Low PAH concentrations in surface waters have been reported across European and Asian (100–1000 s pg L^{-1}) mountain regions (Fernández et al., 2005; Guzzella et al., 2011; Vilanova et al., 2001). Additionally, Ren et al. (2017) recently reported rather elevated PAH levels in Tibet Plateau, Nam Co Lake ($>$ 80 ng L^{-1}), suggesting that local combustion emissions were likely the main source of PAHs there. Local human activities, rather than long-range transport, probably also explain the elevated freely dissolved PAH concentrations (Σ_{17}PAHs, 14–360 ng L^{-1}) in remote areas such as the Antarctic inland lakes (Yao et al., 2016). Despite that, those PAH levels were much higher than freely dissolved concentrations measured in the current study. In this context, our results are more consistent with freely dissolved PAH concentrations reported in open sea transects from Atlantic, Pacific, Arctic and Antarctic oceans (tens to thousands of pg L^{-1}) (Cincinelli et al., 2008; Lohmann et al., 2013; Ma et al., 2013).

Despite the scarcity of data regarding the levels of PAHs in the South American waters, freely dissolved PAHs are relatively high along some major rivers in the continent, such as the Uruguay and Rio de la Plata rivers (1800–12,000 ng L^{-1}) (Barra et al., 2007). In Brazil, hotspots of PAH contaminations have also been reported in waters from Brazilian tropical main rivers and estuaries, especially close to urban centers ($>$ 100 ng L^{-1}). Among them, Paraiba do Sul River should be highlighted ($>$ 260 ng L^{-1}) as a main freshwater system that supplies energy and drinking water for millions of inhabitants in Rio de Janeiro state (Azevedo et al., 2004; Lemos et al., 2014; Ribeiro et al., 2012).

Generally, water bodies in urban areas show higher PAH concentrations worldwide (Honkonen and Rantalainen, 2016; Lohmann et al., 2011). Using LDPE as passive water samplers, Ruge et al. (2015) and McDonough et al. (2014) have recently observed elevated freely dissolved PAH concentrations at Lake Superior (Σ_{20}PAH, 0.2–70 ng L^{-1}) and the lower Great Lakes (Σ_{18}PAH, 2.5–80 ng L^{-1}) in North America, respectively, compared to our findings. Nevertheless, even higher PAH water levels have been measured in Meiliang Bay, Taihu Lake, the third largest lake in China (40–180 ng L^{-1}) and along Seine River, France (Σ_{16}PAH $>$ 200 ng L^{-1}) (Gasperi et al., 2009; Qiao et al., 2008).

3.6. Source indicator by PAH ratios and other individual PAHs

Molecular ratios for selected PAHs isomers were used in the current study to better understand the sources of the PAHs (Tobiszewski and Namieśnik, 2012; Yunker et al., 2002) (see SI for details). In general, pyrogenic sources were deduced for both National Parks, in particular wood and grass combustion (Flra/Flra + Pyr > 0.5; Phe/ΣMePhn > 0.5). In shallow water, a minor contribution of petroleum combustion was evident (ITW1- *Lagoa azul* – 700 m a.s.l.) at NPIT and (SJW2, *St. Barbara* – 1400 m a.s.l.) NPSJ sites.

There is good evidence of large-scale forest and grass fires in the region. In the Itatiaia massif (> 2200 m a.s.l.), some of the largest fires in high altitude grasslands have been observed in recent years (2001 = 741.6 ha; 2007 = 763.8 ha; 2010 = 1023.3 ha) (Aximoff, 2011; Medina et al., 2016; Tomzhinski et al., 2011). This is further supported by a recent fire zoning risk assessment for the NPSJ; it was concluded that 39% of the area is under high risk, and 7% under extreme risk of fire (Omena et al., 2016). Furthermore, meteorological parameters such as fall/winter dry seasons, upland windy conditions and frost events, resulting in extensively dry biomass areas enhance the risks of fire ignition and could spread inside National Park borders (Aximoff et al., 2016).

Moreover, high gaseous concentrations of 3-ring alkyl PAHs (1-methylphenathrene) and retene were mainly detected at low altitudinal NPSJ sites. These two individual PAHs are mainly produced from abietic and pimaric acids, both present in pine wood resin (Stogiannidis et al., 2013). Extensive Pinus sp. farms (*Pinus taeda* and *Pinus elliottii*) are an important agricultural activity that surrounded NPSJ borders, reinforcing the influence of softwood combustion sources (McDonough et al., 2014; Omena et al., 2016).

Natural origins also could be tracked by individual PAHs. Among them, perylene could be linked to diagenetic (slow transformation of organic materials) and/or biogenic production (synthesized by plants, algae and microorganisms), especially found under anoxic conditions in soil and subtidal, marine and freshwater sediments. However, perylene or other biogenic-diagenetic PAHs also potentially have anthropogenic sources, especially after pyrolytic processes such as coal pyrolysis and automotive emissions. (Stogiannidis et al., 2013; Tobiszewski and Namieśnik, 2012). Several studies have highlighted microbial activity as the major process for natural PAH origins (da Silva and Bícego, 2010; Readman et al., 2002; Wilcke et al., 2003). Indeed, perylenequinone structures exist in many fungal bodies and have been previously described as natural precursors for perylene in aquatic systems (Cavalcante et al., 2009; da Silva and Bícego, 2010). In the tropics the biologic origin of perylene and other individual PAHs have well known links with vast biogenic precursors, especially over pristine areas such as tropical Atlantic rainforest, Amazon basin and natural savanna fields (Barra et al., 2007; Meire et al., 2008; Wilcke et al., 2003, 2000). In this study, perylene was mainly detected in all water sampling sites for NPSJ which could indicate biological PAH sources in subtropical rainforests.

3.7. Elevation transects

PAHs as well as other SVOCs have been measured at high altitudinal sites in South American and worldwide regions (Barra et al., 2006; Choi et al., 2009; Estellano et al., 2008; Meire et al., 2012; Shunthirasingham et al., 2011; Wang et al., 2013, 2011). For selected SVOCs, positive correlations between altitudinal transects and environmental concentrations were mainly observed for more volatile constituents, relative to the less volatile constituents of contaminant mixtures. A marked seasonality in the precipitation rates combined with other parameters (i.e. diurnal winds and low temperatures) seemed to enhance SVOCs atmospheric deposition over mountainous regions, especially at tropical upland locations(Daly and Wania, 2005).

For total PAHs, no clear trends (water and air) were observed for altitudinal gradients over either National Park, except at the NPSJ site which showed an inversion trend between total gaseous PAH concentrations and altitudinal transects. Additionally, the highest total PAH levels in air were also measured at high altitude sites in NPIT (ITW4, > 2000 m a.s.l.). Light (2–3 rings) and heavy (5–6 rings) PAH ratio has been used as an index to estimate the origin of pollution as well as to evaluate altitudinal fractionation of PAHs along transects over mountainous regions (Choi et al., 2009). In this context, we investigated air L/H ratio over altitudinal transects for both National Parks.

In this study, National Park transects showed opposite altitudinal trends for PAHs in air (Figs. S9 and S10). A slightly increasing trend of low over high MW PAH ratios was observed along vertical NPIT transects. This trend may reflect a long-range atmospheric transport of more volatile PAHs (2 and 3 rings) over tropical elevated altitudes. This is consistent with previous findings for other semivolatile chemicals such as endosulfans (an organochlorine pesticide recently banned in Brazil) which at the same highest monitored sites (ITA3 and ITA4) were about 2–5-fold higher than those measured at lowest altitudinal sites (ITA1 and ITA2) (Meire et al., 2016).

On the other hand, an inverse profile between low over high MW ratios and altitude was found at NPSJ sites. Similar results have demonstrated the decrease of atmospheric PAH levels with increasing distance from main roads and suggested that mobile sources are the main PAHs sources in Latin American cities as well as other National Parks worldwide (Bradford et al., 2013; Fernandes et al., 2002; Shunthirasingham et al., 2011). Nevertheless, inside National Park borders there are pyrolytic emissions, especially during wood and grass fire events, which may represent the dominant PAH contribution at the monitored sites in this current work.

4. Conclusion/implications

By and large, concentrations of selected PAHs found in air and shallow waters were comparable to concentrations at other remote mountainous regions worldwide. PAH ratios strongly indicate wood and grass combustions as main pyrolytic sources over upland transects, in-line with recent major wildfires and agricultural practices prevalent in the region. On the other hand, minor petrogenic inputs at National Park sites could be related to the proximity of highway traffic and steady tourism access. As observed in other South American biomes, biogenic precursors are probably linked to natural origin of perylene over subtropical pristine shallow waters. National Park transects showed opposite altitudinal trends for PAHs in air. These contrasting trends may reflect a mix input of long-range atmospheric transport for more volatile PAHs (2 and 3 rings) combined with local PAH emission sources along altitudinal transects.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apr.2018.10.012.

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