SHORT-CHAIN CHLORINATED PARAFFINS IN AIR FROM SOUTHEASTERN BRAZILIAN MOUNTAINS

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Introduction

During recent years, chlorinated paraffins (CPs) have been drawing increased attention of the scientific community due to their adverse environmental and human health effects, as well as their massive global production volume. CPs are produced by the chlorination of *n*-alkane feedstocks to different degrees of chlorination, typically ranging from 40 to 70% by weight. According to the chain length, CPs are subdivided into short- (C_{10}-C_{13}), medium- (C_{14}-C_{17}), and long-chain (C_{18}-C_{30})[1].

Short-chain chlorinated paraffins (SCCPs) were shown to be persistent, bioaccumulative, and toxic compounds, and they have also been found in remote areas due to long-range transport[2]. SCCPs have been used worldwide for several applications, such as flame retardants, plasticisers, extreme pressure additives and additives in paints. The global SCCP production has been estimated, in a minimum scenario, as at least 165 kt/year[3]. Therefore, SCCPs have become subject to regulation at national and international level. Finally, last year, SCCPs were listed under the Stockholm Convention on Persistent Organic Pollutants (POPs)[4].

Brazil is the only country in Latin America which reported the production of SCCPs so far. According to the submission information for Brazil, specified in Annex E to the Stockholm Convention in February 2007, 150 t/year of SCCPs were produced in the country[5]. However, in the same report, the Brazilian authorities claimed that approximately 300 t of SCCPs are used per year, which are mostly applied as flame retardant in rubber and vehicles accessories (except tires). Further, it was stated that the use of SCCPs would be negligible in leather processing, painting and coating.

Brazilian subalpine regions have already been pointed out as extremely important sites to monitor, not only the dynamic of semi-volatile organic compounds (SVOCs), but also climate changes[6]. These mountain grasslands, known as *campos de altitude*, form a unique ecosystem in the Brazilian Atlantic rainforest biome. This ecosystem is restricted in sky-islands (>2000 meters), which enables a high occurrence of endemic species[7]. Threatened by vertical displacement, due to global warming, the *campos de altitude* were also reported to be under atmospheric levels of pesticides as high as in agricultural sites and relatively high levels of other POPs[8,9]. Passive air samplers (PAS) are feasible tools for environmental monitoring due to the fact that they are easy to handle, cost effective and do not require an electrical supply, even considering their semiquantitative downside when compared to active air samplers[10]. Therefore, PAS such as polyurethane foam (PUF) disks, have been used worldwide to access local to global trends of several SVOCs[11,12].

In this study we aimed to quantify SCCPs in atmospheric air of two sky-islands in Southeast Brazil, namely Itatiaia and Serra dos Órgãos National Parks (INP and SONP, respectively). Furthermore, we tried to confirm the viability of these findings through the analyses of other atmospheric air monitoring study carried out at along spatial and seasonal gradients over environmental transects in Rio de Janeiro state, around the Guanabara Bay.

Materials and methods

Atmospheric passive air sampling was performed with PUF disks. Regarding altitudinal grassland sites, sampling was carried out in two national parks, INP at 2,470 meters high and SONP at 2,200 meters high, over two years (2013-2015) with periodic replacement of PUFs after each season (~3 months). The second sampling study (eleven sampling points), over environmental transects around the Guanabara Bay, was carried out covering background, urban, suburban, industrial and historically contaminated areas. In this case, PUFs were deployed only twice covering winter and summer seasons (2015-2016). Detailed Material and Methods, such as

sample preparation, extraction and measurements steps were published elsewhere[13]. To ensure that the samples were still appropriated for quantification, the relative area of at least two compounds which had been previously determinate were compared to current measurements. Measurements were performed with gas chromatography (7890A) coupled with electron-capture negative ion mass spectrometry (5975C) (GC/ECNI-MS) operated in the SIM mode (Agilent, Waldbronn, Germany). SCCPs were quantified according to Reth *et al*. (2005)[14].

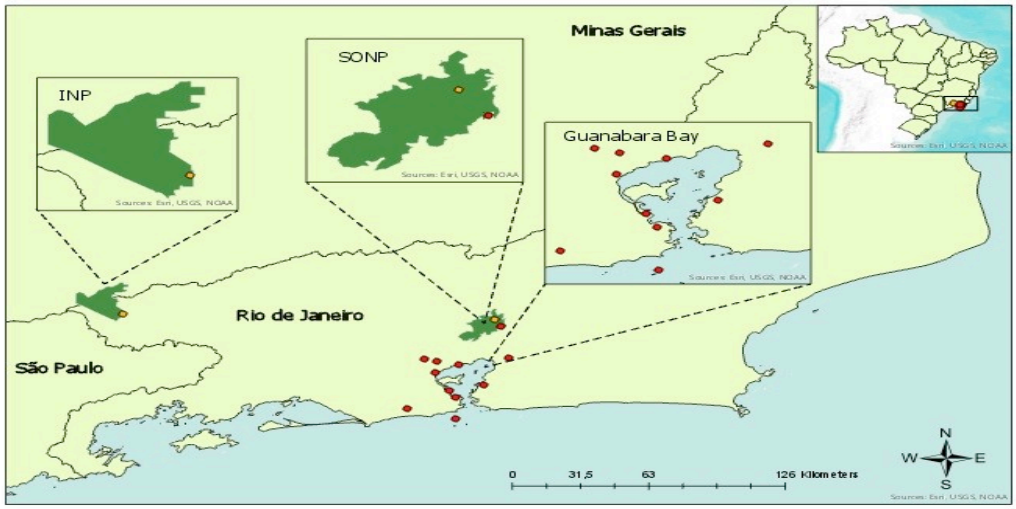

Figure 1: Outline zoom of Itatiaia (INP) and Serra dos Órgãos National Parks (SONP) and Guanabara Bay, in the Brazilian southeast region. Altitudinal grassland sampling points (2013-2015) are shown in yellow dots; Sampling points of the environmental transect study, around the Guanabara Bay (2015-2016), are shown in red dots.

Sampling rate (*R)* was based on the literature[8,9]. An average *R* value equal to 6.3 m^3 per day was assumed for the whole monitoring. Method limit of detection (LOD) was calculated as the average of all analytical and field blanks plus three times the standard deviation. Data normality was checked by Shapiro Wilk test. As only non-parametric distributions were found, Kruskall-Wallis test and posteriori Dunn's multiple test were used to compare more than two groups and Mann Whitney U test was applied to compare two groups. Significance level was 5% for all tests.

Results and discussion

SCCPs were initially detected during the routine analysis of selected samples by GC/ECNI-MS in full scan mode. These screening tests confirmed the presence of SCCPs in some samples, but not in the blanks (or at much lower levels; blanks showed some background levels of SCCPs from 0.01 to 0.68 ng μL^{-1}). Moreover, MCCPs were not detected in the samples. Therefore, the subsequent quantification via GC/ECNI-MS-SIM was restricted to SCCPs. Surprisingly, only a single chain length (C_{10}) of SCCPs was detected in the samples. Several studies have reported the predominance of C_{10} congeners in remote areas and a positive correlation between higher abundance of C_{10}-CPs in higher latitudes, due to their higher vapor pressure[15,16]. However, C_{10}-CPs hitherto never contributed more than ~70% to the total SCCPs[15]. Thus, the single presence of C_{10}-CPs in Brazilian mountains is noteworthy and suggests the production and/or use of a special technical SCCP formulation (only C_{10}-CPs) in Brazil. This hypothesis was reinforced by results from transect air monitoring around the Guanabara Bay, where also only C_{10}-SCCPs were detected.

Atmospheric air concentrations of SCCPs in altitudinal grassland sites were only detected in SONP (<LOD to 3.2 ng m^{-3}; average of 1.1 ng m^{-3}), with the highest SCCP concentrations measured during fall (Figure 2). Regarding the transect study, SCCP air concentrations (<LOD to 2.3 ng m^{-3}; average of 0.8 ng m^{-3}) were

detected in nine of the eleven sampling points, with the highest air concentrations measured during summer in industrial areas. In both cases SCCP air concentrations were dominated by hepta- (42%) hexa- (30%) and octa-C_{10}-CPs (16%) and total chlorination percent was 62%. Previous studies have already reported significantly higher concentrations of POPs in SONP than in INP[8,9,13]. These authors have pointed out agricultural and industrial areas on the outskirts of SONP being the major source of its atmospheric contamination. SCCP air concentrations in both studies, altitudinal grasslands and around the Guanabara Bay, were in between reported mean levels for remote regions, such as Arctic and Antarctica (0.1 ng m^{-3}), and for urban areas in Switzerland (2.9 ng m^{-3}), Japan (2.3 ng m^{-3}) and South Korea (2.1 ng m^{-3})[17]. Studies regarding seasonal trends in air concentrations of SCCPs have reported higher concentrations in summer than in winter and have showed that in winter SCCPs tend to be mostly associated to the particle phase and mostly in the gas phase in summer[16].

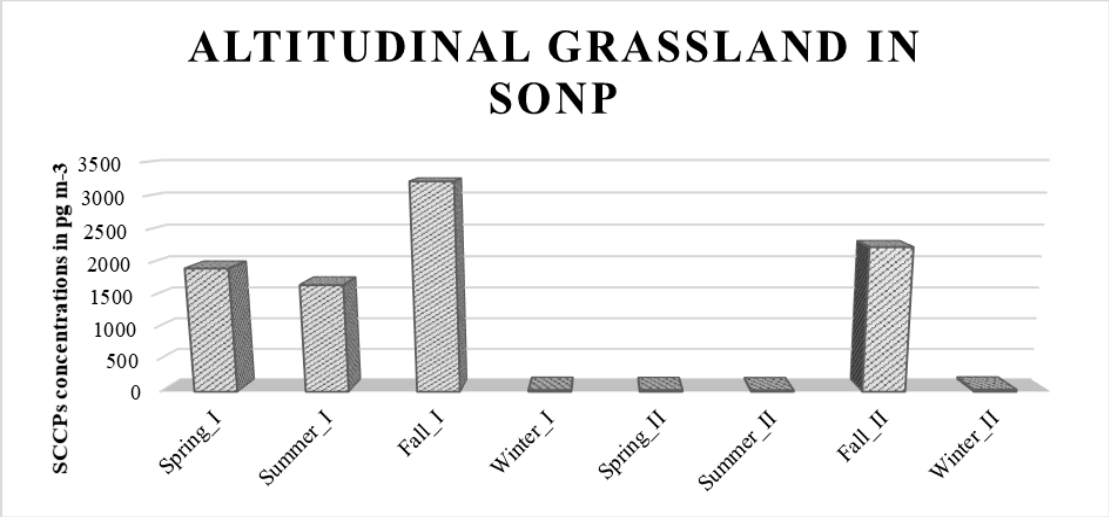

Figure 2: Atmospheric air concentrations of short-chain chlorinated paraffins (SCCPs) measured in different seasonal periods, in Serra dos Órgãos National Park (SONP) from 2013 to 2015.

Due to recurring failures on meteorological stations, it was not possible to compile meteorological data continuously. Thus, this lack of data precluded any precise approach of correlation between SCCP concentrations in atmospheric air and temperature or precipitation. However, in a previous study on pesticide atmospheric air concentrations in the same samples, HCB concentrations – and less pronounced HCH and DDT – were also higher in fall. Some authors reported higher scavenge of from the atmosphere during rainy seasons[18]. However, at the present sites, summer is the rainy season. As in subtropical regions temperature changes are not so abrupt, it seemed reasonable to accept higher atmospheric concentrations of some SVOCs during drier but not much colder seasons. Moreover, backward air trajectories (5-day; every 48 h for each seasonal period, calculated using HYSPLIT trajectory model[19]) showed that air masses in fall predominantly originated from upward streams from urban/industrial areas at the sea level in Rio de Janeiro, while in other seasonal periods air masses predominantly originated from downward streams (Figure 3).

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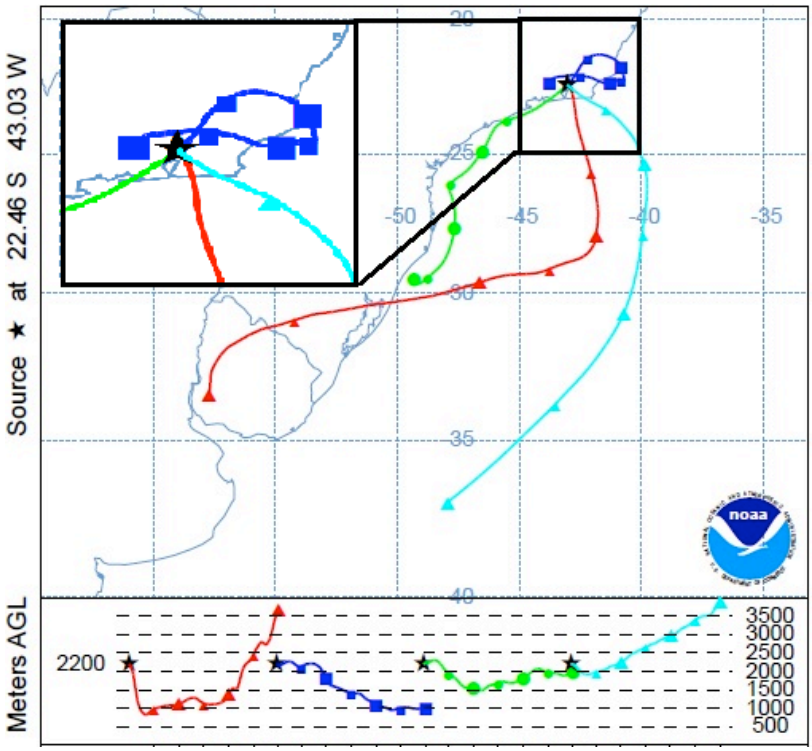

Figure 3: Backward air trajectory for 5-days; every 48 hours during fall period at the sampling point on altitudinal grassland on Serra dos Órgãos National Park. Zoom in Guanabara Bay region, in Rio de Janeiro state.

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