Airborne PAHs and PCBs along a coastal, urban-industrial gradient in Rio de la Plata Estuary, Argentina

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Introduction

Atmospheric transport is the principal route of transference of Semivolatile Organic Compounds (SVOCs) from local to global distances. Airborne SVOCs such as Polycyclic aromatic hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) are included in the POP protocol under the Convention on Long-Range Transboundary Air Pollution (LRTAP) and the Stockholm Convention due to their toxicity and environmental persistence [1, 2].
Owing to their practicality (autonomous, easy handled and affordable), in the last decades, polyurethane foam passive air samplers (PUF-PAS) have been widely used to evaluate spatial and temporal patterns of SVOCs allowing a higher temporal resolution than active air samplers [1, 2, 3]. La Plata city, capital of Buenos Aires state, is located 15 km away from the Rio de la Plata Estuary coast, in a highly industrialized (major oil refinery of the country and associated industries [4], an important shipyard and container port) and densely populated region of the country (about 1,000,000 inhabitants). In this study, we report the patterns of airborne PAHs and PCBs along a transitional gradient from the coast to urban-suburban area of La Plata City in order to evaluate their sources, composition and spatial variability.

Materials and Methods

PUF-PAS (14 cm-diameter; 1.5 cm-thick; 0.03 g cm^{-3} disks housed in stainless steel dome chambers) were deployed along a 25 km transect from Rio de la Plata coast (0 km) to urban-suburban area in La Plata City for 30 days (Fig. 1). Pre-cleaned PUF disks were fortified with 10 ng of Depuration Compounds (PCB 30. 119 and 207; AbsoluteStandard Inc.) to assess site-specific sampling rates (R: m^3 d^{-1}) and individually stored at −10 °C until deployment [3]. After exposure, samples were spiked with internal standards (PCB 103 and 198 and deuterated PAHs: d-12 Chrysene and d-10 Phenanthrene), Soxhlet extracted with petroleum ether 24 h and cleaned-up on silica gel columns (SamplingQ. Agilent). Forty-two PCB congeners (Σ_{42}PCBs), 16 non-alkylated PAHs (16 EPA PAHs) and 41 alkylated PAHs (mono-, di-, tri- tetra- methyl Naphthalene, Fluorene, Phenanthrene/Anthracene, Fluoranthene, Pyrene and Chrysene) were quantified by HRGC-ECD (Agilent 6890, Agilent) and HRGC-MS (Perkin Elmer Clarus 5000, in electron impact ionization and selected ion monitoring), respectively [3].

Results and discussion

Airborne ΣPAH (alkylated + non-alkylated) and Σ_{42}PCBs concentrations and compositional patterns are presented in Fig. 1 and 2, respectively.

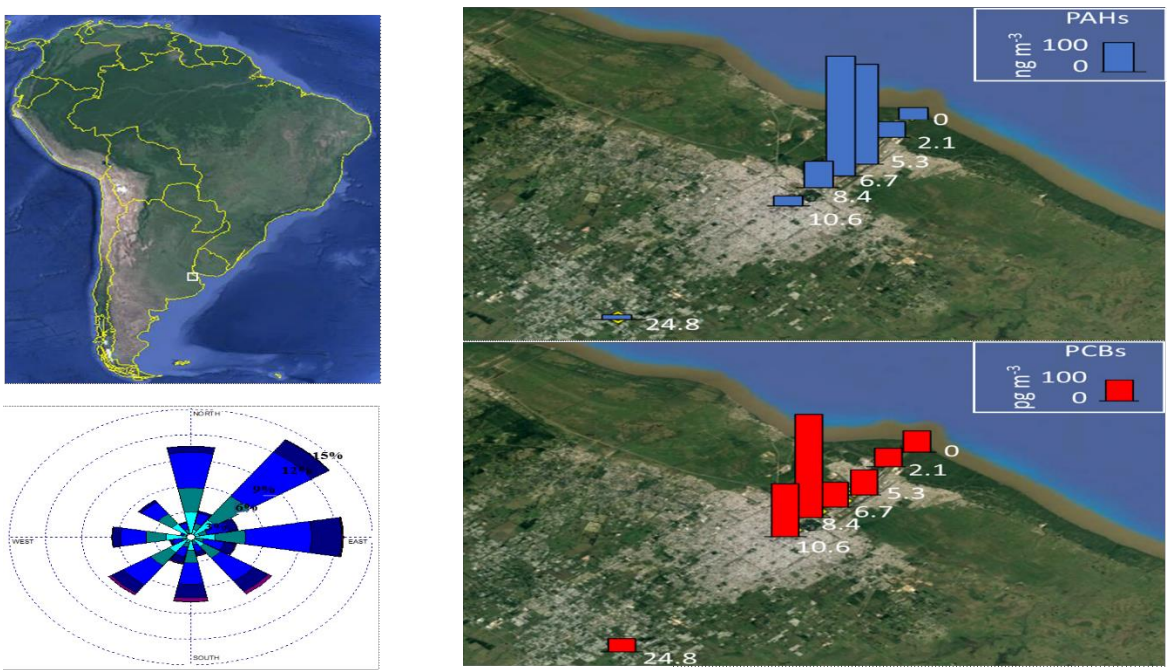

Fig 1. Spatial patterns of airborne ΣPAH (ng m^{-3}) and Σ_{42}PCBs (pg m^{-3}) along the coastal gradient (Suburban sites: 0, 2.1 and 24.8; Industrial sites: 5.3 and 6.7; urban sites: 8.4 y 10.6). Prevailing wind rose in the bottom left.

Airborne ΣPAH concentrations ranged from 16 to 413 ng m^{-3} (mean: 143 ± 164 ng m^{-3}) with 16 EPA PAHs comprising 24-91% (15-116 ng m^{-3}; 50 ± 40 ng m^{-3}), comparable to rural-urban sites from Chile (30-230 ng m^{-3} [2]) and Philippines (41 – 170 ng m^{-3} [5]). There is a clear spatial pattern peaking in the center of the transect at sites 5.3 – 6.7 km from the coast, in the oil refinery sector, with a characteristic petrogenic signature [4] enriched in low molecular weight and alkylated PAHs (66- 76%). Rapidly decreasing concentrations are observed at both ends of the transect, with the lowest levels, basically from combustion sources (16.5 ng m^{-3}; 9% Alkylated PAHs) at the farthest suburban site (24.8 km). Intermediate stations show transitional PAH levels and compositions, with increasing petrogenic signatures towards the center (33-51% at 0-2.1 km and 33-52% at 8.4-10.6 km). Interestingly, the increase of petrogenic alkylated PAHs from the coast to the center follows a linear trend (R^2: 0.95) whereas their inland attenuation is exponential (R^2: 0.97). Prevailing winds from the first quarter (N, NE, SE; Fig. 1) favor the transport of petrogenic PAHs inland; their rapid attenuation denotes the absence of major local petrogenic sources with prevailing combustion patterns (i.e. traffic). Diffuse petrogenic inputs from large tankers, sailboats and port could contribute alkylated PAHs in the coastal and port area. However, the Fluoranthene/Pyrene ratio (Fla/Fla+Pyr) reflect the petrogenic-pyrogenic transition from de center (5.3-6.7 km; ratios= 0.3) to both extremes of the transect with higher values more typical from biomass combustion [4].

Airborne Σ_{42}PCB concentrations (63- 491 pg m^{-3}; 177 ± 151 pg m^{-3}) correspond to a global low range value compared to the First Year of the Global Atmospheric Passive Sampling Programme (GAP: 332 pg m^{-3}, [5]), and are similar to urban sites from Chile (40-350 pg m^{-3} [2]) and Spain (59-422 pg m-3; [6]). The spatial pattern differs from that of PAHs, with the highest PCB concentrations in urban sites, 8.4 and 10.6 km (border of industrial area > downtown) followed by fairly homogeneous levels towards the coast and minimum values in the most distant suburban site (24.8 km). PCB composition shows a progressive enrichment of lighter 2-3 CBs and the labile/recalcitrant ratio, (tetra101/hexaCB 153 ratio) from the coast to the urban peak concentration area (Fig. 2) suggesting fresher inputs.

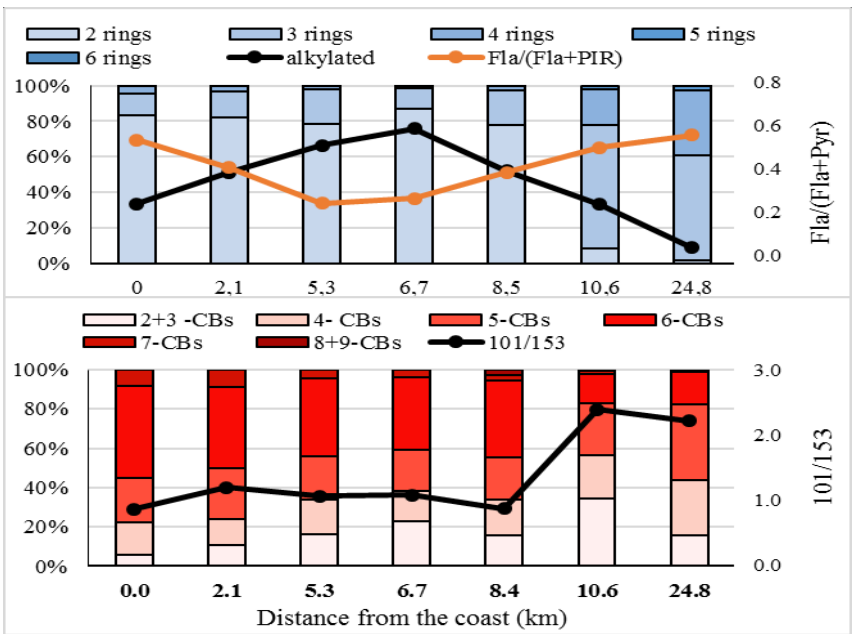

Fig 2. Airborne PAHs (top) and PCBs (bottom) composition. PAH discriminated by ring number, % of alkylated species and Fluoranthene/Pyrene ratios whereas PCBs are grouped by chlorine number and 101/153 ratio.

Conclusions

PUF-PAS deployed along a coastal-industrial-urban gradient in La Plata city revealed clear spatial patterns of airborne PAHs and PCBs. PAHs maximized in the central petrochemical area of the transect whereas PCBs peaked in urban-suburban sites. A clear compositional shift is observed from petrogenic (alkykated PAHs, low Fla/Fla+Pyr ratios) to pyrogenic signatures (unsubstituted PAHs, high Fla/Fla+Pyr ratios) from the industrial to suburban areas of La Plata City. PCBs show a rather homogeneous signal across the gradient with higher concentrations enriched in lighter congeners in urban sites.

References

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