Airborne PCB patterns and urban scale in the Southern Río de la Plata Basin, Argentina

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HIGHLIGHTS
• First regional scale assessment of airborne PCBs in the Río de la Plata basin
• Atmospheric PCB concentrations range in a low/very low global level.
• Spatial pattern confirms the role of urbanization scale in airborne PCB pollution.
• Lighter compositional pattern suggests an actual re-emission PCBs in urban sites.
• Aged background signal prevails in distant rural sites.

GRAPHICAL ABSTRACT

Abstract

Atmospheric Polychlorinated Biphenyls (PCBs: ∑ 42 congeners) collected by polyurethane passive samplers (PAS-PUFs) in 29 stations from July 2010 to February 2014 (n = 141) in the most productive and populated Southern Río de la Plata area in Argentina were evaluated to assess concentration gradients, potential sources and compositional profiles related to different land use and urbanization. On a global scale, total airborne PCBs concentrations are low/very low (below detection limit to 937 pg m⁻³) and show a significant potential correlation with urban scale increasing 2.5 times each 10 times increase of population reflecting the primary role of urbanization controlling PCB emissions. Compositional patterns evaluated by principal component analysis (PCA) of individual congeners indicated that highly populated atmospheres are enriched in lighter, more volatile tri, tetra and penta chlorine congeners of lighter Aroclor mixtures (from 1242 to 1254) suggesting actual emission of fresh PCBs signatures from sealants, combustion and/or electrical equipment. Sub urban and rural sites show a gradual transition to heavier Aroclor mixtures (from 1254 to 1260) with predominance of more persistent hexa and hepta PCBs indicating an aged background signal resulting from long range transport and/or re-emission from historic reservoirs such as soils.

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1. Introduction

Polychlorinated biphenyls (PCBs) have been produced on an industrial scale since 1930 and have been exported to virtually every country in the world (Breivik et al., 2002). They were commonly used in closed systems such as electrical transformers and capacitors and open applications as additives in several building materials (lubricating and cutting oils, paints, adhesives, sealants and plastics; UNEP, 1999; ATSDR, 2002; Park et al., 2002). Because of their chemical and physical properties (permeability, moderate volatility, long half-lives, lipophilicity, hydropobicity) they were classified as Persistent Organic Pollutants (POPs) by the Stockholm Convention and carcinogens to humans by the International Research Agency on Cancer (IARC, 2015). In this line, the biological activity of twelve non-ortho and mono-ortho PCBs (dioxin-like PCBs or dl-PCBs) which exerts a similar action as the highly toxic 2,3,7,8-tetrachlorodibenz-p-dioxin resulted in the adoption of an equivalent toxicity scheme to comparatively evaluate possible health risks (TEFs; Van den Berg et al., 2006). Although PCB production has globally ceased in 90s (Breivik et al., 2007), they are still distributed in the environment along dynamic, continuous cycles of volatilization from water and soils, long range transport through the atmosphere and removal to aquatic and terrestrial ecosystems via wet/dry deposition (Dobson and van Esch, 1993). Cities are main sources of PCBs due to the out-gassing of PCBs from buildings and leakage from closed systems such as electrical equipment (Halsall et al., 1995; Harner et al., 2004).

In order to assess airborne PCBs concentrations, as well as human exposure and risk associated to inhalation at local, regional and global scales, in last decades air monitoring studies have been carried out using both active (Colombo et al., 2013; Gregoris et al., 2014), and passive samplers (Xu et al., 2013; Villavert et al., 2014; Cappelletti et al., 2015). Among these latter devices, Polyurethane Foam disk passive samplers (PUFs) have proved to be very efficient because of their high retention capacity of POPs, low costs and simple handling.

While PCBs have been never produced in Argentina, nearly 3100 tonnes have been imported into the country (Breivik et al., 2002). In the last 25 years, several studies have reported environmental concentrations of PCBs both in biotic and abiotic compartments (Colombo et al., 1990, 1995, 2005, 2007b, 2011; Ondarza et al., 2014; Cappelletti et al., 2014; Torres et al., 2015), including a peak discharge in the Río de la Plata estuary in 2001–2002 evidenced by a threefold increase of muscle concentrations in a detritivorous fish coinciding with PCB banning in 2002 (Colombo et al., 2007a). Nevertheless, air data from Argentina are scarce and limited to a local area in the southern Buenos Aires Province monitored for two periods showing higher PCB levels at urban sites relative to agricultural areas (Tombesi et al., 2014).

The purpose of this study was to more comprehensively evaluate atmospheric PCB patterns in the most productive and populated area of Argentina. We performed an exhaustive regional scale assessment focused on the evaluation of the sources, spatial variability and compositional patterns of airborne PCBs in areas with contrasted land uses and urbanization.

2. Materials and methods

2.1. Study area

The Southern Río de la Plata basin comprised by Argentinean provinces of Entre Ríos and Buenos Aires and the Autonomous City of Buenos Aires (CABA), is the most populated area of the country concentrating 19.7 million people (48% of total country; INDEC, 2010). It also presents a great economic significance due to important port activity exporting

Table 1

| Sampling site, acronym | Latitude/longitude | Population | Classification | \( \Sigma \) PCB (pg m\(^{-3}\)) |
|------------------------|--------------------|------------|----------------|-------------------------------|
| **Entre Ríos Province** |                    |            |                | Range                         |
| La Paz, LPZ            | 30°43′35.5″S/59°38′5.5″W | 28000      | Urban (small)  | 5–32                          |
| Concordia, CON         | 31°21′59.3″S/57°59′41.6″W | 170033     | Urban (medium) | 4–81                          |
| Paraná, PAR            | 31°42′20.5″S/60°33′37.8″W | 339930     | Urban (medium) | 20–115                        |
| Villaguay, VGY         | 31°54′46.8″S/39°5′55.4″W | <100       | Rural          | b.d.l.                         |
| Victoria, VIC          | 32°37′47.9″S/80°10′6.4″W | 35767      | Rural          | 9–309                         |
| Gualeguaychú, GUA      | 33°4°03.5″S/58°23′24.9″W | <100       | Rural          | 9–17                          |
| **Buenos Aires Province** |                   |            |                | Avg ± sd                      |
| San Nicolás, SN        | 33°22′29.1″S/60°10′10″W | 145857     | Urban (medium) | 73–284                        |
| Bergamino, BER         | 33°54′43.3″S/60°35′33.3″W | 104590     | Urban (medium) | 130–728                       |
| Zárate, ZAR            | 34°5′31.9″S/59°1′2.47″W | 114269     | Urban (medium) | 41–100                        |
| San Antonio de Areco, SAA | 34°14′22.3″S/59°29′55.9″W | 23138     | Urban (small)  | 11–110                        |
| Inés Idart, INI        | 34°24′24.3″S/60°32′17.9″W | 911       | Rural          | 2–23                          |
| Magdalena, MGD         | 35°1′44.6″S/57°30′27.1″W | 19301      | Suburban       | 10–70                         |
| Punta Indio, PT        | 35°16′38.9″S/57°13′24.5″W | 9888      | Suburban       | 3–35                          |
| Saladillo, SAL 1       | 35°38′13.3″S/59°47′28.7″W | 23313     | Suburban       | 15–25                         |
| SAL 2                  | 35°36′30.5″S/59°50′14.0″W | <100       | Rural          | 1–14                          |
| Treinta de Agosto, TR 1 | 36°11′50.6″S/62°33′7.7″W | 4777      | Rural          | 6–19                          |
| TR 2                   | 36°16′38.1″S/62°32′14.4″W | <100       | Rural          | Suburban                      |
| Bolivar, BOL           | 36°23′38.2″S/61°8′30.3″W | <100       | Rural          | 58–99                         |
| Rauch, RAU 1           | 36°46′04.8″S/59°05′33.7″W | 15176      | Rural (small)  | 11–12                         |
| RAU 2                  | 36°49′51.8″S/59°16′43″W | <100       | Rural          | 2                              |
| Quilmes, QUI           | 34°44′18.7″S/58°12′6.5″W | 582943     | Urban (medium) | 49–490                        |
| Ensenada, ENS          | 34°48′54.4″S/57°38′31.2″W | 8410      | Urban (medium) | 406–409                       |
| La Plata, LPT 1        | 34°54′51.9″S/57°56′40.3″W | 654324     | Urban (medium) | 245–821                       |
| LPT 2                  | 34°53′25.6″S/57°56′0.9″W | 654324     | Urban (medium) | 27–130                        |
| LPT 3                  | 35°1′4′58″S/2′10″W | 17872     | Urban (medium) | 37–13                          |
| La Balandra, BLD       | 34°55′45.8″S/57°43′1.9″W | 2729      | Rural          | 53–36                         |
| Florencio Varela, VAR  | 34°50′24.6″S/58°14′31.1″W | 426005     | Urban (medium) | 209–893                       |
| **Buenos Aires City** |                   |            |                | 478 ± 318                     |

b.d.l.: Below detection limit.
manufacture products (i.e. vehicles, textiles, chemicals, petrochemicals, and steel) and agricultural commodities. Furthermore, it is the prime agricultural land in Argentina (Merini et al., 2007) producing 40–70% of the cereal and legume crops (~100 million tonnes; NMACH, 2014).

2.2. Air sampling

Passive Air Samplers (PUF-PAS) consisting of a polyurethane disk (14 cm diameter; 1.5 cm thick; 385 cm² surface area; 0.03 g cm⁻³ density) housed in two stainless steel dome chambers (internal diameters: 24.5 and 22.5 cm) were deployed at twenty-nine sites covering an area of ~400,000 km² (30°43′–36°46′S and 57°13′–62°33′W) from July 2010 to December 2014. PUF-PAS were placed 3–4 m above the ground on street lights or trees on public or private lands (yacht clubs, fishing/sport clubs, private houses/farms). Individual deployments (2 to 12 depending on the stations) lasted for ~4 months each (mean period span: 133 days, total sample N = 141).

Sampling locations were classified according to population into rural (<1000 inhabitants), suburban (1000–10,000 inhabitants) and urban sites with a further sub-division into small (10,000–100,000); medium (100,000–1 million) and large cities (>1 million inhabitants; Table 1).

Prior to each campaign, sampling chambers were prewashed, solvent-rinsed (acetone and petroleum ether), and stored in polyethylene acetone:petroleum ether Soxhlet extraction for 24 h) were fortified with a further sub-division into small (10,000 inhabitants) and urban (10,000–10,000 inhabitants) and urban sites with a further sub-division into small (10,000–100,000); medium (100,000–1 million) and large cities (>1 million inhabitants; Table 1).

To prior each campaign, sampling chambers were prewashed, solvent-rinsed (acetone and petroleum ether), and stored in polyethylene bags. Pre-cleaned PUF disks (distilled water wash and 1:1 v/v acetone:petroleum ether Soxhlet extraction for 24 h) were fortified with 10 ng of Depuration Compounds (PCB 30, 119 and 207; Absolute Standard Inc.) to assess site-specific sampling rates (R; m⁻³ d⁻¹) according to Astoviza et al. (2016) and individually stored at ~10 °C until deployment.

2.3. Chemical analysis

After exposition PUF disks were wrapped in aluminium foil, labelled, placed into ziplock polyethylene bags and transported in a cooler to the laboratory where they were stored frozen until analysis. Field blanks (n = 15) were obtained by transporting, installing and immediately removing PUF disks during each deployment.

Samples were spiked with internal standards (PCB 103 and 198) and Soxhlet extracted with petroleum ether 24 h. Extract clean-up was performed on silica gel columns (SamplingQ, Agilent) eluted with petroleum ether and concentrated to 500 μl under a gentle stream of dry nitrogen. In this study, 42 congeners (di-Cl: BS/85; tri-Cl: BS/62; 17, 18, 31, 28, 33/20; tetra-CBs: 41, 44, 49, 52, 70, 74; penta-CBs: 82, 87/115, 95/66, 99, 101, 110/77, 118; hexa-CBs: 128/167, 132/105, 138, 141, 149/123, 151, 153, 158, 171/156, 187; hepta-CBs: 170, 174, 177, 180, 183, 191; octa-CBs: 194, 195/208, 199, 203/196, 205; nona-CBs: 206; deca-CBs: 209) were analyzed by HRGC-ECD (Agilent 6890, Agilent Tech., USA) equipped with a DB5 capillary column (30 m × 320 μm i. d. × 0.25 μm film thickness). The working conditions were: injector temperature 250 °C, detector temperature 330 °C; oven temperature program 65 °C (2 min), 10 °C min⁻¹ to 130 °C (1 min), 5 °C min⁻¹ to 300 °C (10 min) and carrier gas Nitrogen (purity >99.9%) at 1.5 ml min⁻¹. Quantification was performed by a four-point calibration curve using external standard solutions (2, 10, 50, 250 pg/ul; Quebec Ministry, AccuStandard Inc.).

2.4. Quality assurance/quality control (QA/QC)

Method detection limits (MDL: 131–1621 pg PUF⁻¹, Table S1) were defined as the average of field (n = 15) and laboratory blanks (n = 8) plus three standard deviations. For non-detected compounds, one half of the instrumental detection limit (IDL: equivalent amount of the signal-to-noise ratio ≥ 3) was used as MDL. Recovery efficacy averaged 74 ± 29% for PCB 103 and 70 ± 32% for PCB 198; correction was applied when sample recovery was below 85%.

2.5. Deriving air concentrations from depuration compounds

Site specific sampling rates (R) and air concentrations of each PCB congener were calculated based on the loss of DCs, the average ambient temperature for each sampling period and site, and congener specific effective air volumes (Ve) according to previously described methods (Astoviza et al., 2016). The average R value for the entire study (6.3 ± 3.6 m³ day⁻¹) is comparable to other PAS-PUF reports around the globe, i.e. 4.8 ± 2.3 m³ day⁻¹ (Pozo et al., 2004), 5.9 ± 0.9 m³ day⁻¹ (Gouin et al., 2008) and 6.1 ± 1.8 m³ day⁻¹ (Persoon and Hornbuckle, 2009).

2.6. Statistical analyses

Statistical analyses were performed with XLSTAT 2014 software package (Addinsoft, 2014); ANOVA tests were used to compare differences between sampling areas (significance level set at p < 0.05) and regression analysis was used to evaluate covariation of population and total PCB air concentrations. Spatial and compositional patterns compared to different source profiles (e.g. Aroclor mixtures, combustion sources and potential emission sources such as electrical equipment and building supplies, Frame et al., 1996; Conolly, 2001; Ishikawa et al., 2007) were further evaluated by principal component analysis (PCA) based on 36 standardized PCB congener concentrations which were present in >40% of samples. PCA facilitates the interpretation of complex, multivariate data by transforming the original set of variables into a smaller set of linear combinations preserving the greatest amount of information or variance (Wannaz et al., 2013). Original variables
which are positively correlated plot together whereas negatively associated variables oppose in the PCA; their similarity is described by the Euclidean distance (Blanchard et al., 2006).

3. Results and discussion

Airborne concentrations of $\sum_{42}$PCBs at each sampling site are summarized in Table 1, and compared to other passive air monitoring programs in Table 2. Detailed information for each sampling period is included in Supplementary material (Table S1).

Broadly, PCB levels in air of the Southern Río de la Plata Basin are largely variable (below detection limit to 937 pg m$^{-3}$; mean 106 ± 160 pg m$^{-3}$) and correspond to a low/very low range compared to values reported for the First Year of the Global Atmospheric Passive Sampling Programme (GAP: 332 pg m$^{-3}$; Pozo et al., 2009) and for Latin America and Caribbean countries (296 pg m$^{-3}$; Bogdal et al., 2013). Significant differences ($p < 0.001$) are found between sampling sites according to population with a decreasing pattern from urban (4–937 pg m$^{-3}$; mean: 146 ± 185 pg m$^{-3}$) to suburban (3–146 pg m$^{-3}$; mean: 48 ± 41 pg m$^{-3}$) and rural sites (below detection limit-35 pg m$^{-3}$; 10 ± 10 pg m$^{-3}$). In general, our data are comparable to previous reports from Southern Buenos Aires Province (40–360 pg m$^{-3}$; Tombesi et al., 2014) and from neighbouring countries such as Chile (40–350 pg m$^{-3}$; Pozo et al., 2012), and Brazil (70–620 pg m$^{-3}$; Ornellas-Meire et al., 2012) but are consistently lower than data reported for Europe, Asia and North America and an order of magnitude lower than global urban sites (Li et al., 2010). The lower airborne PCB profile of South American countries reflects their lower utilization compared to the Northern Hemisphere which concentrates almost 97% of the global historical use of PCBs (Breivik et al., 2002).

3.1. Spatial variability

Airborne PCB concentrations are mapped in Fig. 1. Briefly, higher concentrations correspond to urban sites of Great Buenos Aires metropolitan area (CABA, LPT, QUI and VAR; mean: 478; 287; 253; 509; 217 and 190 pg m$^{-3}$, respectively) and the North of Buenos Aires Province (PER and SN: 364 and 146 pg m$^{-3}$, respectively). All of these locations are urban with populations >100,000 inhabitants and/or industrial sites such as San Nicolas which host the largest steelmaking plant of the country with its own thermal power plant.

In contrast, rural sites from central Entre Ríos and central-south of Buenos Aires (VGY, SAL, BOL and RAU) show the lowest concentrations (mean: 3; 7; 3 and 2 pg m$^{-3}$, respectively), reflecting a baseline level for...
the whole area, whereas suburban concentrations (PI, BLD and ENS; mean: 19; 53 and 86 pg m$^{-3}$, respectively) are intermediate.

Rural-urban increasing patterns for atmospheric PCB have been described for other world areas (e.g. Great Lakes, Canada; Motelay-Massei et al., 2005; Sun et al., 2007). The significant positive potential correlation (p < 0.001; R$^2$: 0.72) between log concentration and log population size (Fig. 2) confirms the role of urbanization scale as the primary driving force of atmospheric pollution in the Southern Río de la Plata Basin. Similar potential slopes have been reported for different organic compounds (PAHs: 0.5–0.6, Hafner et al., 2005; PBDEs: 0.3, Venier et al., 2009; PCDD/Fs: 0.28–0.35, Cappelletti et al., 2015) and inorganic pollutants (nitrogen dioxide: 0.5; Lamsal et al., 2013). According to Bettencourt et al. (2007), scaling exponents for urban indicators vs. city size lower than 1 correspond to infrastructure (e.g. length of electrical networks, road surfaces). In addition to the higher PCB contribution from larger electric networks and buildings with aged paints, the increased heat and reduced air circulation in big cities could have a synergistic effect amplifying atmospheric concentrations, i.e. enhanced volatilization due to heat island effect (Camilloni and Barros, 1997) and/or lower dispersion due to the ‘street canyon effect’ (Radojević and Bashkin, 1999).

### 3.2. Compositional patterns

The general atmospheric profile in Southern Río de la Plata basin is dominated by intermediate volatility PCBs (log Koa: 7.5–10.7), namely penta-CBs (38 ± 14%) followed by hexa-CBs (23 ± 10%) and tri and tetra-CBs (18 ± 13% and 16 ± 7%, respectively) with minimum proportions of di, hepta to deca-CBs. However, there are some compositional differences between sampling sites: urban locations have a relatively
uniform profile of penta-CBs (33 ± 9%) followed by tri- (24 ± 12%), tetra- (20 ± 4%) and hexa-CBs (19 ± 7%); and reduced hepta-, octa- to deca-CBs whereas rural and suburban sites show a heavier pattern enriched in penta- plus hexa-CBs (82 ± 16% and 69 ± 8%, respectively) and lower tetra- (8 ± 6%; 14 ± 7%), tri- (6 ± 9%; 7 ± 6%) and hepta-CBs (3 ± 6%; 7 ± 3%). A similar shift on PCB composition has been reported for urban and rural locations in Europe (Jaward et al., 2004; Fig. S1).

Since there are detailed variations among sites, a principal component analysis (PCA) was performed to further investigate the spatial differences and compare these profiles to different known sources such as Aroclor mixtures (1242, 1254 and 1260; Frame et al., 1996), combustion and potential emission sources (hardwood, sealants, transformers and capacitors; Conolly, 2001). In this study, 70% of variability of 36 PCB congeners detected in at least 40% of the samples is explained by 4 components. The first (PC1) and second principal components (PC2) accounted for 39% and 15% of the variance, respectively. The relationships among the variables are shown in the loading plot (Fig. 3a), whereas the grouping of the sites colored according to population size (directly related to PCB levels) and potential source are displayed in the score plot (Fig. 3b).

PC1 is basically defined by the opposing contribution of lower more volatile PCBs (−PC1) and higher chlorinated PCBs (+PC1) whereas PC2 has a positive loading of five PCB congeners (52, 87, 101, 110 and 118). Emission sources and sampling sites spread in a triangular shape limited by Aroclors mixtures, light 1242 together with emission sources at the bottom left (−PC1, −PC2), intermediate 1254 at the top (+PC2) and heavier chlorinated 1260 at the bottom right (+PC1, −PC2). Most populated large cities with higher PCB concentrations enriched in less chlorinated congeners plot to the left (−PC1) near to lighter Aroclor mixtures and emission sources; suburban and small urban sites related to intermediate-chlorinated Aroclor 1254 occupy the central-upper part (+PC2) and rural sites with background PCB levels dominated by heavier homologues progressively shift to the bottom-right (+PC1, −PC2; Fig. 3b) closer to Aroclor 1260. In fact, our airborne PCB profiles seem to result basically from the combination of Aroclors 1242–1254 in most polluted, large urban sites, and from the gradual shift from 1254 to 1260 in small urban to rural sites.

This pattern of heavier Aroclor predominance in rural sites does not match the expected profile of lighter PCBs prevailing in remote areas due to their increased transport capacity (Wania and Mackay, 1996) or the prevalence of intermediate-chlorinated congeners with longer half-lives and lower Koa than heavier homologues which are more efficiently removed by particle-bond deposition (Shen et al., 2006). Actually, intermediate chlorinated congeners remain in the atmosphere long enough to undergo long-range transport as has been reported from air from Chile (Pozzo et al., 2004; Shunthirasingham et al., 2011), and China (Jaward et al., 2004; Hogarth et al., 2012).

The predominance of heavier compounds in rural samples of the southern Río de la Plata Basin is also reflected by the tri + tetra/hexa CB ratio (31–28 + 49/153 + 138) that seems a good descriptor of the observed compositional variability and is significantly correlated both with total PCB atmospheric concentrations (R²: 0.39) and urban scale (R²: 0.35). This compositional pattern of rural sites probably reflects the long range transport of more persistent congeners and their diffusive input from historical reservoirs (e.g. soils) corresponding to an aged signal. The lighter profiles in large urban centers are probably related to the continuous release of PCBs from electrical equipment (transformers and capacitors), combustion and building supplies (e.g. sealants) with a fresher signature.

4. Conclusions

This first comprehensive regional scale assessment of airborne PCBs in the Southern Río de la Plata basin revealed that concentrations range in a low/very low global level, with a strong spatial variability related to a significant rural-urban increasing trend confirming the driving role of urbanization scale in atmospheric pollution. The increasing rural-urban concentration pattern is accompanied by a compositional shift from heavier to lighter PCB predominance reflecting the transition from an aged, background signal at rural sites to a fresher urban trace, indicated by the predominance of combustion and emission sources (electrical and building supplies) and lighter Aroclor mixtures (1242). The tri + tetra/hexa CB ratio adequately describes this compositional shift.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.07.101.

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