



Airborne PCDD/F profiles in rural and urban areas of Buenos Aires Province, Argentina



N. Cappelletti^{a,b,*}, M. Astoviza^{a,b}, M.C. Migoya^{a,b}, J.C. Colombo^{a,c}

^a Laboratorio de Química Ambiental y Biogeoquímica, Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata, Av. Calchaqui km 23500, 1888 Florencio Varela, Buenos Aires, Argentina

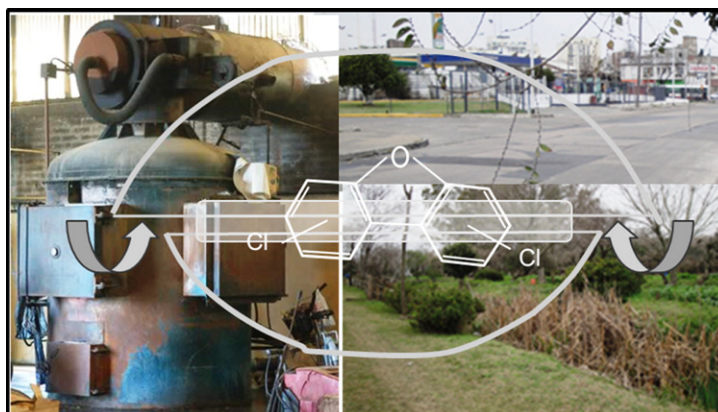
^b Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina

^c Comisión de Investigaciones Científicas, Provincia de Buenos Aires, Argentina

HIGHLIGHTS

- Atmospheric PCDD/Fs concentrations were determined in atmosphere a range of urban agglomerations in Argentina
- PCDD/Fs concentrations in rural and small towns are greater than an order of magnitude less than urbanized area
- PCDD/F profiles are influenced by diesel, industrial, and open burning emissions

GRAPHICAL ABSTRACT



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ABSTRACT

Passive air samplers were deployed in 18 rural and urban locations in the densely populated Buenos Aires district to investigate airborne polychlorinated dibenzo-*p*-dioxin and polychlorinated-dibenzofuran (PCDD/Fs) profiles, sources and spatial patterns. Atmospheric concentrations reported as total toxic equivalents (TEQs), 2378-substituted (\sum_{17} PCDD/F) and 4–8 homologous groups (\sum_{4-8} PCDD/F) were highly variable and significantly correlated to urban scale. The rural average (3.0 ± 2.7 fg TEQ m⁻³) was thirty times less than metropolitan values (90 ± 51 fg TEQ m⁻³), with urban cluster (5.4 ± 4.0 fg TEQ m⁻³) and urbanized area (33 ± 50 fg TEQ m⁻³) in an intermediate position. A rural outlier exhibited the highest TEQ values ($295\text{--}296$ fg TEQ m⁻³) suggesting a local source. Principal component analyses (PCA) performed for \sum_{17} PCDD/F and \sum_{4-8} PCDD/F to identify source contributions showed more significant results for homologue groups compared to 17 congeners (83 and 45% of total variability explained, respectively) pointing to dominant diesel emissions enriched in TeCDF in rural areas, and open burning and industrial sources characterized by TeCDD, PeCDD contributing most in urbanized and metropolitan areas. Homologue group PCA also performed better clustering samples according to sources and TEQ

* Corresponding author at: Universidad Nacional de La Plata. Facultad de Ciencias Naturales y Museo Laboratorio de Química Ambiental y Biogeoquímica, Av. Calchaqui km 23500, 1888 Florencio Varela, Buenos Aires, Argentina.

E-mail address: ncappelletti.laqab@gmail.com (N. Cappelletti).

concentrations. The PCDD/Fs profile of the rural outlier dominated by HxCDF and HpCDD/F showed a typical municipal incineration signature confirming the presence of local source.

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1. Introduction

Polychlorinated dibenzo-p-dioxins and polychlorinated-dibenzofurans (PCDD/Fs) are persistent organic pollutants (POPs) unintentionally formed as by products in many industrial activities and combustion processes globally distributed in the environment (Hites, 2011). The most toxic seventeen 2378 PCDD/F congeners containing 4 to 8 chlorines have received considerable public and scientific attention, and a toxic equivalent scheme (TEQs) has been developed to assess health risks and overall toxicity of complex mixtures (Van den Berg et al., 1998).

The global biogeochemical cycle of PCDD/F is principally controlled by atmospheric emissions, depletion reactions (e.g. OH radical destruction) and transport to terrestrial and aquatic ecosystems through dry and wet deposition (Lohmann et al., 2006). Thus, atmospheric assessment of PCDD/F is a first very relevant step for monitoring surveys, especially in South America where this information is very scarce. In this context, passive air samplers (PAS) are alternative low-cost and low-maintenance sampling devices for semi-quantitative measurement of POPs in air that have been adopted by Stockholm Convention (UNEP, 2011). In a worldwide PAS air monitoring study, Bogdal et al. (2013) reported a wide range of concentrations for Latin America (9–678 fg TEQ m⁻³), with the highest concentration found in Peru. A more conservative range (0.9–30 fg TEQ m⁻³) has been recently reported for Latin America and Caribbean by the Global Monitoring Network (Schuster et al., 2015). Comparable concentrations have been reported for an urban area of Manizales, Colombia (18–39 fg TEQ m⁻³), where the industrial use of coal has been identified as the main PCDD/F source (Cortés et al., 2014). There is little information available for South American megacities, i.e. for San Pablo, Brazil with 17 million inhabitants, active sampling combining gas and particulate phases revealed high concentrations (47–753 fg TEQ m⁻³; De Assunção et al., 2005), whereas more recent PAS study yielded lower concentrations (20–30 fg TEQ m⁻³; Schuster et al., 2015).

In Argentina, the province of Buenos Aires (~300,000 km²) includes ~40% of the population and 36% of gross production of the country with an important industrial sector (petrochemical, iron and steel, automotive) and a vast development of agriculture and livestock (12,000 km²; Ministerio de Economía, 2012). Buenos Aires Metropolitan area (~13 million inhabitants; ~4000 km²) includes the autonomous capital city of Buenos Aires and densely populated adjacent municipalities, constituting the second largest urban agglomeration in South America and the largest populated area in Argentina, yet there are no comprehensive air PCDD/F measurements in this region.

In this study we report atmospheric PCDD/F concentrations and compositional patterns in rural, urban and industrial sites of Buenos Aires province to assess the overall status of air quality and evaluate the relationship between population size and atmospheric PCDD/F concentrations. A comparative assessment of 17 congeners and homologue groups by principal component analysis (PCA) is performed to explore the overall variability of the data and elucidate principal sources.

2. Methods

2.1. Passive air samplers

Passive air samplers (PAS) were designed and constructed at the Environmental Chemistry and Biogeochemistry Laboratory (LAQAB, La Plata National University) based upon those used at RECETOX (Research Centre for Toxic Compounds in the Environment, Masaryk University,

Czech Republic) and Environment Canada (EC). Briefly, they consist of polyurethane foam disks (PUF; 14 cm diameter; 1.5 cm thick; 385 cm² surface area; 0.03 g cm⁻³ density) housed in two stainless steel domes (external diameters of 24.5 and 22.5 cm) separated by a 2 cm gap. The performance of this design was compared with the devices employed by RECETOX and EC (Klanova et al., 2006; Harner et al., 2006). Regression analysis performed between the total mass captured by LAQAB device compared with the other samplers (LAQAB vs. RECETOX-LAQAB vs. EC) showed strong correlation (R²) for PCBs (0.97–0.98), PAHs (0.94–0.92) and Organochlorine Pesticides (0.94–0.66), indicating no significant differences between samplers (t Student test, $\alpha = 0.05$; Astoviza et al., 2016).

PUFs were rinsed with tap and deionized water, air dried, Soxhlet extracted for 24 h with acetone: petroleum ether (1:1), dried and finally wrapped with solvent cleaned aluminum foil until deployment. To assess site-specific sampling rates, depuration compounds were added prior deployment (10 ng each of PCBs 30, 119 y 207; Absolute Standard Inc.) in washed and solvent rinsed sampling chambers.

In general, samplers were placed 3–4 m above the ground on street lights or trees in public or private lands (yacht clubs, fishing/sport clubs, private houses/farms). At rural sites PAS were placed at variable distances (200–1000 m) from farmlands. After the sampling period PUF disks were removed using solvent-rinsed tongs, wrapped in aluminum foil and stored at -10 °C until extraction.

Sampling rates (R; m³ d⁻¹) were calculated according to passive air sampling theory (Pozo et al., 2004), based on the amount of depuration compounds retained by PUFs after sampling. Concentrations were calculated as mass of PCDD/F in each PUF over volume (volume = R × sampling time). Meteorological conditions and R values are detailed in Supplementary material, Table S2.

2.2. Sampling sites

PAS were deployed at 18 different sampling locations during 3–4 months. Two sampling campaigns were conducted in cold (May 2012 to October 2012) and warm season (October 2012 to April 2013) with a duplicated deployment in the most populated site, totaling 38 samples. Sampling sites were classified as rural (R; <5000 inhabitants), urban cluster (UC; 5000 to 50,000 inhabitants), urbanized area (UA; 50,000 to 500,000 inhabitants) and metropolitan area (M; >500,000 inhabitants) according to United States Census Bureau scheme (United States Census Bureau, 2010). Additional site information is presented in Table 1 and Fig. 1. To make a more precise comparison between urban scale and atmospheric PCDD/F concentration, population was calculated within a 25-km-diameter circle centered on the sampling location using the Gridded Population of the World, Version 3 (Center for International Earth Science Information Network; GPWv3). All population estimates were reviewed and double-checked using online census data.

2.3. Analytical methods

PCDD/Fs were extracted following the 1613 EPA method (US EPA, 1994). Briefly, samples, laboratory blanks and field blanks were spiked with 13C₁₂ PCDD/F recovery standard (LCS 1613; Wellington Laboratories Inc.) and Soxhlet-extracted with petroleum ether for 24 h. The extracts were reduced to 3 mL under nitrogen and fractionated on successive chromatography on silica gel and silica gel-charcoal columns (Molina et al., 2000). The PCDD/F fraction was evaporated to a volume

Table 1
Sampling site information and airborne PCDD/F concentrations in each sampling period (cold/warm).

Station	Code	Coordinates	Inhabitants	Main activity	Class	Σ_{4-8} PCDD/F	Σ_{17} PCDD/F fg m ⁻³	TEQ
Patagones	Pa	S 39°59'43" W 63°22'55"	2000	A	Rural	137/1549	37/12	5.0/1.44
Saladillo	Sa	S 35°36'30" W 59°50'14"	2084	A	Rural	473/260	19/6.0	1.3/0.71
Ines Indart	I	S 34°24'24" W 60°32'18"	1000	A	Rural	NA/139	NA/11	NA/1.29
Bolivar	Bo	S 36°23'38" W 61°08'30"	4540	A	Rural	NA/778	NA/12	NA/1.44
30 de Agosto 1	TA1	S 36°11'57" W 62°33'08"	4777	A	Rural	2214/561	476/70	3.9/4.1
30 de Agosto 2	TA2	S 36°16'38" W 62°32'14"	4777	A	Rural	4522/11,527	2749/5824	295/296
Copetonas	Co	S 38°43'32" W 60°29'33"	1017	A	Rural	217/2941	74/13	9.3/1.5
Rauch 1	Ra1	S 36°49'52" W 59°16'43"	15,176	A	Urban cluster	549/1625	16/19	1.1/2.2
Rauch 2	Ra2	S 36°49'52" W 59°16'43"	15,176	A	Urban cluster	549/NA	140/NA	10/NA
San Antonio de Areco	SAA	S 34°14'25" W 59°29'45"	23,138	A	Urban cluster	752/373	114/14	8.7/1.47
Bolivar city	BoC	S 36°13'35" W 61°06'28"	26,242	A	Urban cluster	NA/525	NA/48	NA/5.00
Saladillo city	SaC	S 35°38'58" W 59°47'07"	26,763	A	Urban cluster	671/3301	54/41	5.7/2.7
Olmos 1	OI1	S 35°01'04" W 58°02'10"	19,000	H	Urban cluster	1417/1390	109/24	11/2.3
Olmos 2	OI2	S 35°01'04" W 58°02'10"	19,000	H	Urban cluster	713/1792	69/160	7.3/12
Pergamino	Pe	S 33°54'04" W 60°35'33"	104,590	A/I	Urbanized area	8319/NA	760/NA	90/NA
San Nicolas	SN	S 34°06'22" W 59°00'03"	143,557	A/I	Urbanized area	529/1311	63/12	6.3/1.2
Great Buenos Aires	GBA	S 34°46'12" W 58°15'36"	1,300,000	I	Metropolitan	13,050 ± 4583	2405 ± 1269	108 ± 47
Florencio Varela	Va	S 34°50'25" W 58°14'31"	1,300,000	I/H	Metropolitan	7640/12,673	624/285	88/19

A: agricultural.
I: industrial.
H: horticultural.
NA: not analyzed.

of about 1 mL and 20 uL of n-nonane (keeper) were introduced, and it was concentrated by gentle stream of dry nitrogen to about 20 uL, spiked with isotopic labeled internal standard (ISS 1613; Wellington

Laboratories Inc.) and analyzed by high resolution gas chromatography (Agilent 7890) coupled to high resolution mass spectrometry (Autospect Micromass). The mass spectrometer was operated using

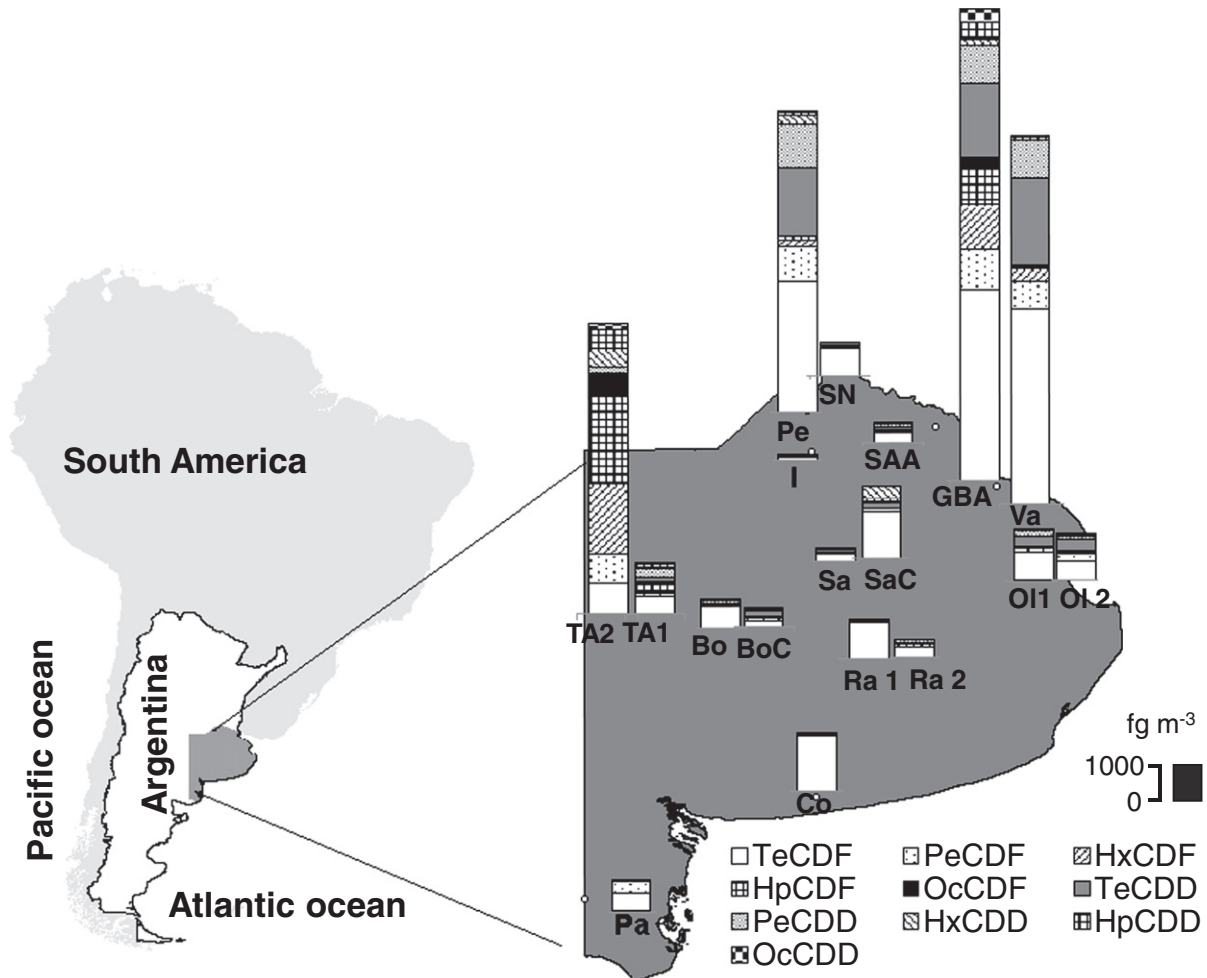


Fig. 1. Average airborne Σ_{4-8} PCDD/F concentrations in Buenos Aires Province, Argentina.

positive electron ionization at mass resolution of 10,000 and the two most abundant ions in the cluster were monitored. Detailed analytical information is included in the Supplementary data (Table S1 and S2).

The detection limits (3:1 signal:noise) ranged between 0.8 and 6.0 fg m^{-3} for tetra to octa PCDD/F (Table S1). Field and procedural blanks analyzed for every batch of ten samples indicated in all cases below-detection limit concentrations. Recovery efficiency ranged from 50 to 82% for the different congeners (average: $56 \pm 9\%$). Five samples with lower recovery efficiency (<50%) were discarded (NA; Table 1). Seventeen 2378 substituted PCDD/F congeners were quantitated and reported individually and as total ($\sum_{17}\text{PCDD/F}$) and as toxic equivalent concentrations (TEQs) using WHO equivalent factors (TEFs; Van den Berg et al., 2006). Additionally, homologous groups were quantified by summing all isomers identified at each level of chlorination (TeCDD, PeCDD, HxCDD, HpCDD, OCDD, TeCDF, PeCDF, HxCDF, HpCDF, OCDF) and reported including both 2378-substituted and non-substituted isomers ($\sum_{4-8}\text{PCDD/F}$).

Statistical analyses were performed with XLSTAT 2014 software package; ANOVA and the Tukey test were used for sample comparison at a significance level of $P < 0.05$. For calculations, non-detected chemicals were considered to be one half of the respective detection limits.

3. Results and discussion

3.1. Total air concentrations

PCDD/F airborne concentrations ($\sum_{17}\text{PCDD/F}$: 6–5824, mean: $632 \pm 1317 \text{ fg m}^{-3}$; TEQ: 0.71–296, $39 \pm 76 \text{ fg TEQ m}^{-3}$; $\sum_{4-8}\text{PCDD/F}$: 15–19690, mean: $3578 \pm 4902 \text{ fg m}^{-3}$; Table 1) are highly variable and generally lower than previous reports for Latin American ($9\text{--}678 \text{ fg TEQ m}^{-3}$; mean: $137 \text{ fg TEQ m}^{-3}$) and African countries ($18\text{--}532$; mean $147 \text{ fg TEQ m}^{-3}$; Bogdal et al., 2013), and for Caribbean and Latin American cities ($0.7\text{--}43 \text{ fg TEQ m}^{-3}$; Schuster et al., 2015). Our data are comparable to urban air PCDD/F measurements obtained by active sampling in Mexico ($0.6\text{--}410 \text{ fg}$; $67 \pm 137 \text{ fg TEQ m}^{-3}$; Cardenas et al., 2011) and South Korea (ND-617; 28 fg TEQ m^{-3} ; Shin et al., 2011).

This general comparison is biased by the dependence of PCDD/F emissions/concentrations on the type and scale of urban agglomerations. A positive relationship between atmospheric pollutants and population has been demonstrated for polycyclic aromatic hydrocarbons (Hafner et al., 2005; McDonough et al., 2014), polychlorinated biphenyls (Sun et al., 2007), polybrominated biphenyl ethers (Venier and Hites, 2008) and PCDD/F (Venier et al., 2009). The exponents of the power law functions fitted to these regressions range from 0.30 to 0.60 (PAH: 0.40–0.60; PCB: ~ 0.35 ; PBDE: 0.35; PCDD/F: 0.30), indicating a 23 to 52% increase in air concentrations when population doubles. In a study of PCDD/F in coastal sites of Laurentian Great Lakes, Venier et al. (2009) report a positive Log-Log relationship between population and $\sum_{17}\text{PCDD/F}$ concentration ($p < 0.0001$; slope: 0.30 ± 0.04 ; author's personal communication). Our data also show a direct relationship between Log population and Log $\sum_{17}\text{PCDD/F}$ air concentrations with a significant two order of magnitude increase from rural areas (excluding an outlier peak TA2) to urban-industrial clusters ($p < 0.0001$; Fig. 2). The slope is in the high range of reported values (0.57 ± 0.10 ; $p < 0.0001$) reflecting the significant role of large urban and industrialized centers as PCDD/F sources. Additional factors such as environmental conditions (i.e. temperature), economic activity, pollution regulation measures, and energy consumption patterns are also important drivers of PCDD/F pollution and may explain slope differences (Hafner et al., 2005).

According to size-population classification (excluding TA2 outlier), our rural and urban cluster mean values are one order of magnitude lower than urbanized and metropolitan sites ($3.0 \pm 2.7/5.4 \pm 4.0$ Vs. $33 \pm 50/90 \pm 51 \text{ fg TEQ m}^{-3}$, respectively). Buenos Aires rural concentrations are lower than those reported for other rural areas in the

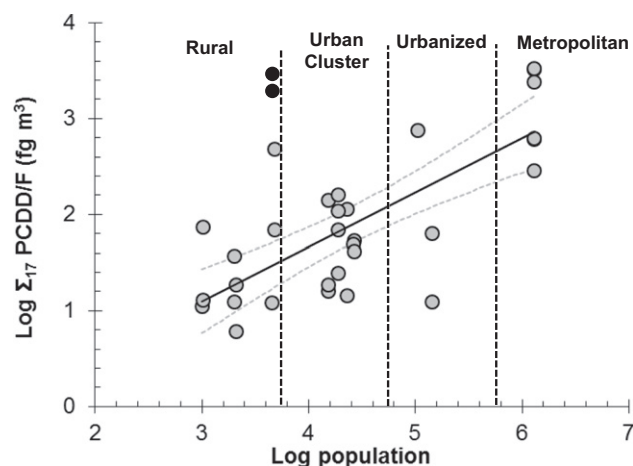


Fig. 2. Airborne $\sum_{17}\text{PCDD/F}$ concentrations versus population at each site ($\text{Log } \sum_{17}\text{PCDD/F} = 0.57 \cdot \text{Log Population} - 0.60$; $R^2 = 0.56$). The grey dotted lines represent the 95% confidence limits. The rural Outlier indicated by filled circles was excluded from the calculations.

Northern Hemisphere reflecting the lower anthropogenic impact of the less industrialized Southern Hemisphere (Lohmann et al., 2001; Morales et al., 2014), i.e. rural sites from United States ($10\text{--}11 \text{ fg TEQ m}^{-3}$; Cleverly et al., 2007) and background sites of Spain (11 fg TEQ m^{-3} ; Mari et al., 2008). On the other side, our metropolitan concentrations are comparable to PAS data from urban areas affected by incineration ($51\text{--}54 \text{ fg TEQ m}^{-3}$; Gao et al., 2014) or industrial sources in China (74 fg TEQ m^{-3} ; Li et al., 2011). The active sampling study of rural, urban and industrial sites in Catalonia Spain also yielded an order of magnitude difference between both extremes but with 3–10 times higher values than our data (33 to $357 \text{ fg TEQ m}^{-3}$; Abad et al., 2004), reflecting the lower anthropogenic impact at Buenos Aires.

The highest TEQ values ($295\text{--}296 \text{ fg TEQ m}^{-3}$) of the outlier TA2, located in rural area of Buenos Aires suggests a particular source. These concentrations are comparable to the values proposed by the World Health Organization as indication of a local emission source ($300 \text{ fg TEQ m}^{-3}$; WHO, 2000). The compositional profile of these samples effectively points to the specific contribution of waste incineration (see Section 3.2).

3.2. PCDD/F composition

3.2.1. PCDD/PCDF ratios

\sum_{4-8} Dioxins and \sum_{4-8} Furans ratios can be used to approximate PCDD/F sources (Li et al., 2011). Generally, agrochemicals present relatively high and variable ratios, i.e. pentachlorophenols ($2\text{--}82$; Masunaga et al., 2001) or phenoxy herbicides ($0.2\text{--}23$; Holt et al., 2010) whereas thermal related sources normally show lower ratios (<1). Consistently low ratios have been reported for ambient air near solid waste incinerators (0.32 ± 0.03 ; Oh et al., 2001), exhaust gases from plastic combustion (0.26 ± 0.10 ; Katami et al., 2002), open burning of waste ($0.27\text{--}0.44$; Lundin et al., 2013), domestic wood and coal burning ($0.36\text{--}0.50$; Lee et al., 2005) and heavy duty diesel engine emissions ($0.39\text{--}0.64$; Ryan and Gullett, 2000). Higher, more variable ratios has been reported for metallurgical processes ($0.16\text{--}1.5$; Buekens et al., 2000) and industrial waste incineration ($0.3\text{--}10$; Ogura et al., 2001). In our study, dioxin/furan ratios are low and relatively homogeneous with no significant differences ($P > 0.05$) among rural (0.30 ± 0.20), urban cluster (0.60 ± 0.45), urbanized area (0.40 ± 0.33) and metropolitan area (0.50 ± 0.14), pointing a general predominance of combustion sources.

3.2.2. PCDD/F congener and homologue profiles

In spite of the recurrent non-detection of some 2378 PCDD/F congeners and some variability, PUFs show an overall congener pattern with a characteristic predominance of 1,234,678 HpCDF ($13 \pm 12\%$) and OCDD ($12 \pm 11\%$). Both samples from outlier TA2 exhibit a distinctive PCDD/F composition with predominance of 1,234,678 HpCDF (23–30%), 234,678 HxCDF (20–19%) and OCDF (11–18%), similar to solid waste and hospital waste incineration profiles (Zhang et al., 2014).

The general homologue composition shows the dominance of TeCDF and TeCDD groups ($52 \pm 23\%$ and $13 \pm 9\%$ of total PCDD/Fs), with decreasing proportions of higher chlorinated homologues. TeCDFs which present slight differences between rural ($60 \pm 19\%$) and urban sites ($43 \pm 12\%$), have been reported as dominant homologues in most combustion emissions, such as biomass, wood, coal waste and diesel engine (Lee et al., 2005; Gullett et al., 2008; Laroo et al., 2011; Lundin et al., 2013). The homologue profile of outlier TA2 exhibits a contrasting

pattern with a clear predominance of HpCDF (29–33%) and HxCDF (16–27%).

In order to more clearly identify potential contributing sources, independent principal component analysis (PCA) were performed with the contribution of the seventeen 2378 substituted congeners and PCDD/F homologues in each sample ($n = 33$). To identify source contributions, a total of 11 literature emission profiles were included in the PCA, i.e. three emissions of municipal solid waste incineration (MSWI; Oh et al., 2001; Ogura et al., 2001; Zhang et al., 2014), one profile of open burning of waste (OB; Lundin et al., 2013), two emissions of biomass burning (BB; Gullett and Touati, 2003), two profiles of chemical and refinery industry (Industrial; Oh et al., 2001), and three diesel emissions (Diesel; Oehme et al., 2001; Laroo et al., 2011).

In the case of 2378 congeners, the first two components (PC1 and PC2) explain 45% of the total variability (Fig. 3, upper). PC1 (30%) is basically determined by 123,678-HxCDD, 123,789-HxCDD and 123,478-

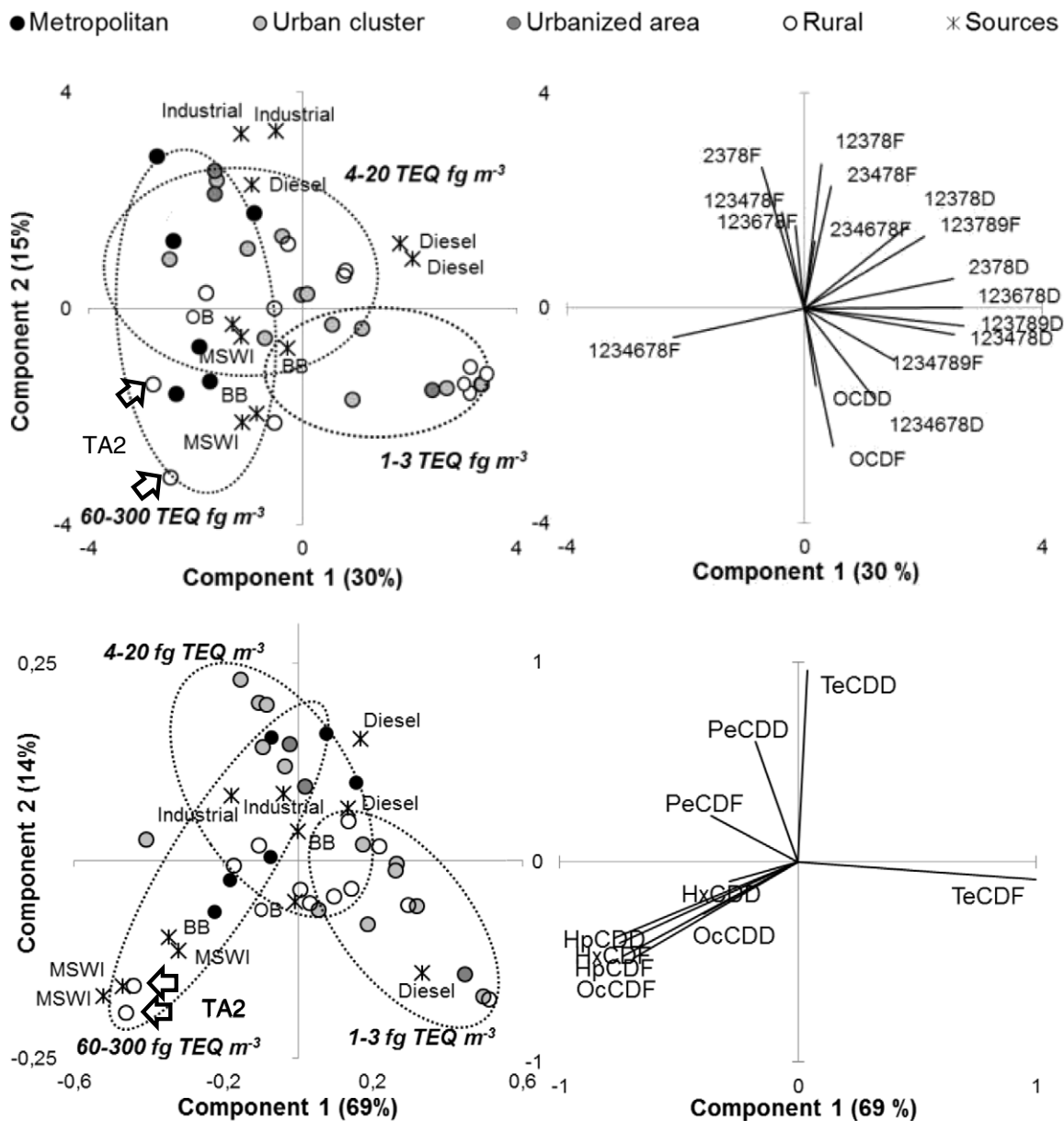


Fig. 3. Principal component analysis performed with the individual contribution of 2378 substituted PCDD/Fs (upper) and PCDD/F homologue groups (bottom). Emission sources are grouped as municipal solid waste incineration (MSWI), open burning of waste (OB) and biomass (BB), steel and refinery industry (Industrial), and diesel emissions (Diesel). Arrows indicate the rural outlier (TA2).

HxCDD (+PC1), and 1,234,678 HpCDF (−PC1), whereas PC2 (15%) has a prevailing contribution of 2378-TeCDF and 12,378-PeCDF (+PC2), and OCDF and 1,234,678-HpCDD (−PC2). Source profiles form three distinctive clusters: to the lower-left side MSWI, OB and BB; to the upper-left side industrial emissions; and to the upper-right side, two profiles of diesel engine emissions. Our rural samples are distributed between diesel and MSWI/OB/BB clusters, whereas metropolitan samples spread close to industrial and MSWI/OB/BB clusters. The highest TEQ outlier (TA2) plots close to MSWI/OB/BB sources. The distribution of TEQ concentrations along the overall separation scheme of the score plot does not show a clear pattern, but the highest TEQ concentrations seem to be linked with open waste burning, biomass burning and MSWI.

In the homologue group PCA (Fig. 3, lower), PC1 and PC2 account for a higher 69 and 14% of the total variability, respectively. PC1 is basically defined by the opposing contribution of TeCDF, (+PC1), and HxCDF, HpCDF, and OCDF (−PC1), whereas PC2 has a dominant contribution of TeCDD and PeCDF (+PC2). Specific sources are distributed in four main groups: MSWI plot in the lower-left; diesel engine emissions spread on the right side; industrial sources in the upper-left, and OB and BB in an intermediate-left position. Rural samples spread mostly in the lower right side, closer to diesel exhaust profiles. Metropolitan samples are distributed between diesel, BB and OB and industrial emissions. Two rural samples from a site located 5 km away of the highest TEQ outlier (TA2) plot in the left side, whereas TA2 samples plot in the lower-left side close to MSWI. Further investigation of this site revealed that 20 km way from site TA2, obsolete incinerators at Trenque Lauquen city produced recurrent complains from nearby populations. The homologue PCA shows a better separation pattern of samples according to composition and TEQ concentrations. Air samples with < 3 fg TEQ m^{−3} plot in the lower-right (close to the diesel pattern), the 5–20 fg TEQ m^{−3} range concentration samples plot in the upper-left (related to industrial, biomass burning and open waste burning) whereas concentrations higher than 60 fg TEQ m^{−3} plot in the upper left to the lower-left side (industrial, biomass burning and MSWI).

The comparative evaluation of PCA results from different levels of PCDD/F monitoring information shows that homologue analysis performs better to explain the overall compositional variability of the data compared to the 17 congeners (83 Vs. 45% variability, respectively). In addition, clustering of samples in the homologue PCA more precisely linked air patterns with specific source signatures and also showed a clearer relationship between sources and TEQ concentrations.

In summary, Buenos Aires airborne PCDD/F profiles are influenced by different emission sources, with a general contribution of unregulated sources such as traffic, biomass or waste burning. In rural sites, PCA clearly identify diesel emissions as the principal contributor whereas in urban areas prevail the influence of industrial and open burning emissions. The homologue patterns associated to industry and MSWI emissions show the highest TEQ concentrations, especially in the rural outlier TA2 which present a clear MSWI signature.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.07.126>.

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