# AIRBORNE PCDD/F PROFILES IN RURAL AND URBAN AREAS OF BUENOS ARES PROVINCE, ARGENTINA.

Cappelletti N.[a,b], Astoviza M.[a,b], Migoya M.C.[a,b], Colombo J.C.[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 laqab@fcnym.unlp.edu.ar [b]Consejo Nacional de Investigaciones Científicas y Técnicas [c]Comisión de Investigaciones Científicas, Provincia de Buenos Aires

**Introduction**

Atmospheric emissions are the main source pathway in the biogeochemical cycle of *Polychlorinated dibenzo-p-dioxins* and *polychlorinated-dibenzo furans* (PCDD/Fs) emphasizing the requirement of air monitoring studies to evaluate the current status and potential risk of these compounds. This information is very scarce in South America and is normally focused on large metropolitan areas, i.e. San Pablo, Brazil. In this context, passive air samplers (PAS) are alternative low-cost and low-maintenance sampling devices for semi-quantitative measurement of POPs in air[1] that have been validated for the Stockholm Convention Global Monitoring Program [2].

Buenos Aires Province in Argentina (~300000 $km^2$) concentrates 39% of 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. The large Metropolitan area includes the autonomous capital city of Buenos Aires and densely populated adjacent Municipalities constituting the second urban agglomeration of South America (~13 million inhabitants; ~4000 $km^2$) yet there are no atmospheric PCDD/F measurements in this area.

In this work we evaluate atmospheric PCDD/F concentrations and compositional patterns in rural, urban and industrial sites of Buenos Aires province to identify hot spots and potential sources through the detailed analysis of homologues profiles.

**Methods**

*Passive air samplers*

PAS were designed and constructed at the Environmental Chemistry and Biogeochemistry Laboratory (LAQAB, La Plata National University) based on prototypes from RECETOX (Research Centre for Toxic Compounds in the Environment, Czech Republic) and Environment Canada (EC). Briefly, they consist of polyurethane foam disks (14 cm diameter; 1.5 cm thick; 385 cm2 surface area; 0.03 g cm–3 density) housed in a chamber of 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[3,4]. Regression analysis performed between the total mass captured by LAQAB device compared with the other samplers (LAQAB vs. RECETOX-LAQAB vs. EC) showed very significant correlations (R2) for several compounds (PCB: 0.97-0.98; PAHs: 0.94-0.92; Organochlorine Pesticides: 0.94-0.66) indicating no significant differences (t Student test, $\alpha$=0.05) between samplers performance. Depuration compounds (PCBs 30, 119 y 207; Absolute Standard Inc.) were added to the PUFs prior to exposure to calculate site-specific sampling rates. After exposure period, PUFs were removed, wrapped in aluminum foil and stored cold until extraction.

Sampling rates (R: $m^3\ d^{-1}$) used to calculate concentrations in air (PCDD/F mass in PUF/volume=R x sampling time) were obtained from the fraction of depuration compounds retained by PUFs after deployment[5].

*Sampling sites*

PAS were deployed at 19 sampling locations for 3-4 months during two periods: March to October 2012 and October to February 2013. Sampling sites were classified as rural (R; <5000 inhabitants), urban cluster (UC; >5000 to 50000 inhabitants), urbanized area (UA; >50000 to 500000 inhabitants) and metropolitan area (M; >500000 inhabitants). Additional site information is presented in Table 1.

*Analytical methods*

The analytical procedure was based on EPA Method 1613. Briefly, each sample was spiked with $^{13}C_{12}$ PCDD/F recovery standard (LCS 1613; Wellington) and Soxhlet-extracted with EP for 24 h. The extract volume was reduced under nitrogen, and fractionated on successive chromatography on silica gel and silica gel-charcoal columns. The PCDD/F fraction was concentrated (20 µl) and spiked with isotopic labeled internal standard (ISS 1613;

Wellington) and analyzed by high resolution gas chromatography (DB 5 MS column: 30 m long, 0.25 mm i.d., 0.25 µm film) coupled to high resolution mass spectrometry (Agilent 7890-Autospect Micromass Ltd. UK). The mass spectrometer was operated under positive electron impact (35 eV) and selected ion monitoring (SIM) at resolving power of 10000 amu. The detection limits (3:1 signal versus noise value) ranged between 2-20 fg $m^{-3}$ for tetra to octa PCDD/F. Recovery efficiency ranged from 20 to 74% for each individual congener. Field and procedure blanks were analyzed for every batch of ten samples.

Seventeen 2,3,7,8 substituted PCDD/F congeners were quantitated and reported individually and as total ($\sum_{17}$PCDD/F) and as Toxic equivalent (TEQs) using WHO equivalent factors[6] (TEFs). Additionally, homologous groups ($\sum_{4\text{-}8}$PCDD/F) were quantified by summing the concentrations of all isomers identified in each level of chlorination (TCDD, PCDD, HxCDD, HpCDD, OCDD, TCDF, PCDF, HxCDF, HpCDF, OCDF). For calculations, non-detected chemicals were assumed to have a concentration equal to one half of the respective detection limit.

**Results and Discussion**

PCDD/F airborne concentrations are highly variable (0.7 to 296 fg TEQ $m^{-3}$; Table 1), basically reflecting the contrasting population/industrial size of the different locations in Buenos Aires Province. The plot of airborne TEQ and $\sum_{17}$PCDD/F concentrations versus the population of each site (Figure 1) revealed a significant increase from rural areas (3.0 ± 2.7 fg TEQ $m^{-3}$), which include an outlier peak (TA2: 295-296 fg TEQ $m^{-3}$) to urban-industrial clusters. Our rural concentrations are almost an order of magnitude lower than those of metropolitan area (57±37 fg TEQ $m^{-3}$) with urban cluster (12 ± 22 fg TEQ $m^{-3}$) and urbanized area (28 ± 42 fg TEQ $m^{-3}$) in an intermediate position. The particular case of the outlier TA2 located in rural Buenos Aires but with highest TEQ values (295-296 fg TEQ $m^{-3}$) point to a local contribution[7].

$\sum_{4\text{-}8}$ Dioxins and $\sum_{4\text{-}8}$ Furans ratios averaged 0.40±0.27, pointing to a general predominance of combustion as the principal PCDD/F [8]

PCDD/F congener patterns showed a general predominance of OCDD (15 ± 3%) and 1,2,3,4,6,7,8 HpCDF (13±7), which are characteristic of several emission sources such as waste incinerators, metallurgical industries and traffic[9,10]. Both outliers from TA2 exhibited a distinctive profile with predominance of 1,2,3,4,6,7,8 HpCDF (23-30%), 2,3,4,6,7,8 HxCDF (20-19%) and OCDF (11-18%), similar to solid waste and hospital waste incineration profiles[11].The general homologue composition (except site TA2) show the dominance of TCDF and TCDD (58±22% and 14±8% of total PCDD/Fs), with decreasing proportions of higher chlorinated homologues. TCDFs have been reported as dominant homologues in most burning emissions, such as biomass, wood and coal and waste combustion [12,13,14]. The homologue profile of outlier TA2 stand out by the clear predominance of HxCDF and HpCDF (29-33%), similar to the pattern reported for some municipal solid waste incinerators [15,16], and exhaust gases from PVC and PET combustion[17] .

In summary, the results indicate that the concentrations of PCDD/F in Buenos Aires province are influenced by largely distributed unregulated sources such as traffic or biomass burning with some point source contributions and follow an increasing trend with population size. Our results suggested that large urban and industrialized centers could act as source of PCDD/F to less populated areas. The outlier rural site TA2 presented highest TEQ concentration with a particular profile indicating local emissions from MSWI.

**Table 1.** Sampling sites details .NA: non analyzed

| | | | | $\sum_{17}$PCDD/F | | TEQ | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Station** | **Code** | **Geographical coordinates** | **Inhabitants** | 1st | 2nd | 1st | 2nd | **Main Activity** | **Class** |
| Patagones | Pa | S 39º59´42,9´´ W 63º22´54,7´´ | 2000 | 37 | NA | 5 | NA | Agricultural | Rural |
| Saladillo | Sa | S 35°36´30,5´´ W 59°50´14´´ | 2084 | 19 | 6 | 1 | 1 | Agricultural | Rural |
| Ines Indart | I | S 34°24´24,3´´ W 60°32´17,99´ | 1000 | 12 | 11 | 1 | 1 | Agricultural | Rural |
| Bolivar | Bo | S 36°23´38,2´´ W 61°08´30,3´´ | 4540 | 387 | 12 | 56 | 1 | Agricultural | Rural |
| 30 de Agosto 1 | TA1 | S 36°11´56,9´´ W 62°33´07,7´´ | 4777 | 476 | 70 | 4 | 4 | Agricultural | Rural |
| 30 de Agosto 2 | TA2 | S36°16'38.1" W62°32'14.4" | 4777 | 2749 | 5824 | 295 | 296 | Agricultural | Rural |
| Copetonas | Co | S 38º43´31,7´´ W60º29´33,2´´ | 1017 | 74 | 13 | 9 | 2 | Agricultural | Rural |
| Rauch 1 | Ra1 | S 36º49´51,8´´ W 59º16´43,0´´ | 15176 | 16 | 18 | 1 | 2 | Agricultural | Urban Cluster |
| Rauch 2 | Ra2 | S 36º49´51,8´´ W 59º16´43,0´´ | 15176 | 140 | NA | 10 | NA | Agricultural | Urban Cluster |
| San Antonio de Arec | SAA | S 34º14´25,42´´ W59º29´45,35´ | 23138 | 114 | 14 | 9 | 1 | Agricultural | Urban Cluster |
| Bolivar city | BoC | S 36°23´38,2´´ W 61°08´30,3´´ | 26242 | 148 | 48 | 27 | 5 | Agricultural | Urban Cluster |
| Saladillo city | SaC | S 35°36´30,5´´ W 59°50´14´´ | 26763 | 54 | 41 | 6 | 3 | Agricultural | Urban Cluster |
| Pergamino | Pe | S 33º54´04,31´´ W60º35´33,26´ | 104590 | 760 | NA | 90 | NA | Agricultural/Industrial | Urbanized area |
| Zarate | Za | S 33º22´29,13´´ W60º10´19,00´ | 114268 | 147 | 35 | 8 | 2 | Agricultural/Industrial | Urbanized area |
| San Nicolas | SN | S 34º06´22,22´´ W59º00´02,68´ | 143557 | 63 | 12 | 6 | 1 | Industrial/Agricultural | Urbanized area |
| Great Buenos Aires | GBA | S34º50'24.6" W58º14'31.1" | 1300000 | 3339 | 611 | 94 | 57 | Industrial | Metropolitan area |
| Olmos 1 | Ol1 | S 35°01´04,0´´ W 58°02´10,1´´ | 19000 | 109 | 24 | 11 | 2 | Horticultural | Urban Cluster |
| Olmos 2 | Ol2 | S 35°01´04,0´´ W 58°02´10,1´´ | 19000 | 69 | 160 | 7 | 12 | Horticultural | Urban Cluster |
| Florencio Varela | Va | S 34°50´24,6´´ W 58°14´31,1´´ | 10000 | 53 | 624 | 2 | 88 | Horticultural | Urban Cluster |

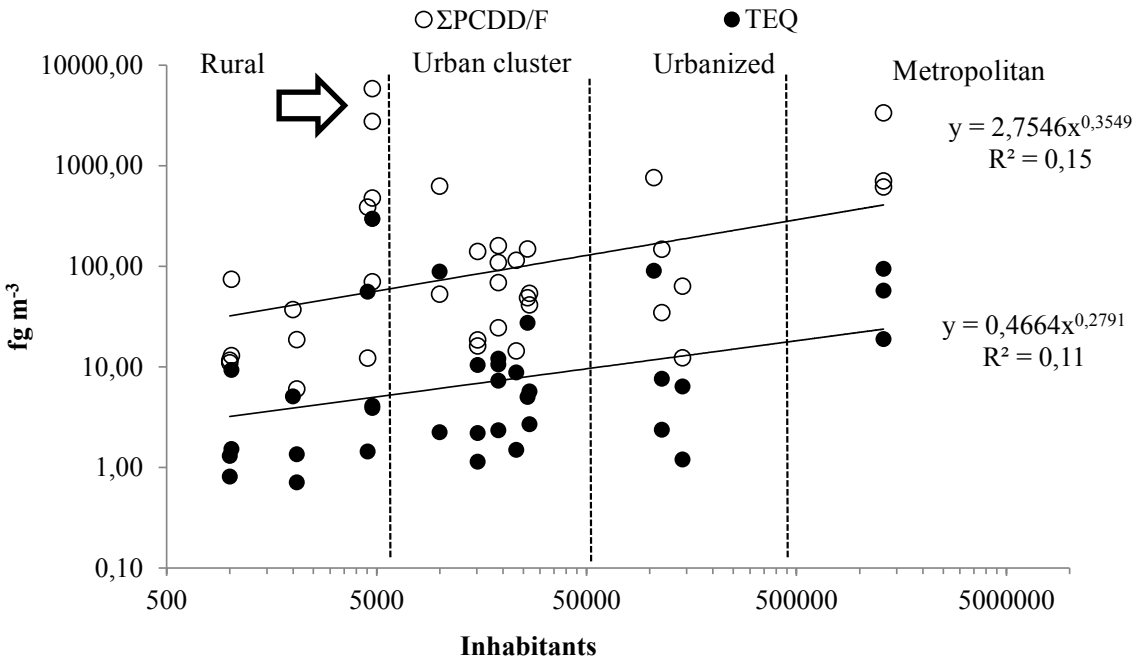


**Figure 1.** $\sum_{17}$PCDD/F and TEQ concentration in air versus number of inhabitants in each sampling localities. Outlier rural site is indicated with the arrow.

**Reference**


1. Mari M, Schuhmacher M, Feliubadaló J, Domingo JL. (2008); *Chemosphere* 70:1637-1643
2. UNEP POPs GMP (2014) Second regional monitoring report GRULAC region.
3. Klanova J, Kohoutek J, Hamplova L., Urbanova P., Holoubek I. (2006); *Environmental Pollution* 144, 393-405.
4. Harner T., Shoeib M., Diamond M., Stern G., Rosenberg, B. (2004); *Environ. Sci. Technol*. 38, 4474-4483.
5. Pozo K., Harner T., Shoeib M., Urrutia R., Barra, R., Parra, O., Focardi, S. (2004); *Environ. Sci. Technol*., 38, 6529-6537.
6. Van den Berg M., Birnbaum L. S., Denison M., De Vito M., Farland W., Feeley M., Peterson, R. E. (2006);*Toxicological Sciences : An Official Journal of the Society of Toxicology*, *93*(2), 223–41.
7. WHO Air Quality Guidelines Regional Publications, European Series, No. 91
8. Li X., Li Y., Zhang Q., Wang P., Yang H., Jiang G., & Wei F. (2011); *Chemosphere*, *84*(7), 957–963.
9. Lee W.-S.; Chang-Chien G.-P.; Wang L.-C.; Lee W.-J.; Tsai P.-J.; Wu 351 K.-Y; Lin, C. (2004); *Environmental Science & Technology* 353 2004, 38, (19), 4937-4944.
10. Shin S. K., Jin, G. Z., Kim, W. Il, Kim, B. H., Hwang, S. M., Hong, J. P., & Park, J. S. (2011); *Chemosphere*, *83*(10), 1339–1344.
11. Moussaoui Y., Tuduri L., Kerchich, Y., Meklati B. Y., & Eppe, G. (2012); *Chemosphere*, *88*(3), 270–277.
12. Zhang, H. J., Ni, Y. W., Chen, J. P. & Zhang, Q. (2008); *Chemosphere*, *70*(4), 721–730.
13. Lee R. G. M., Coleman, P., Jones J. L., Jones K. C., & Lohmann, R. (2005); *Environmental Science and Technology*, *39*(6), 1436–1447.
14. Gullett B., Touati a., & Oudejans, L. (2008); *Atmospheric Environment*, *42*(34), 7997–8006.
15. Lundin L, Gullett B, Carroll F, Touati A, Marklund S, & Fiedler H. (2013); *Atmospheric Environment*, *79*, 433–441.
16. Ogura, I., Masunaga S., & Nakanishi J. (2001); *Science And Technology*, *45*, 173–183.
17. Oh J.-E., Chang Y.-S., & Ikonomou M. G. (2002); *Journal of the Air & Waste Management Association (1995)*, *52*(1), 69–75.
18. Yasuhara, A., Katami, T., Okuda, T., & Shibamoto, T. (2002); *Environmental Science and Technology*, *36*(18), 3924–3927.