LEVELS OF PCDD/PCDFs AND DL-PCBs IN AMBIENT AIR OF MANIZALES USING PASSIVE AND ACTIVE SAMPLERS

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Introduction

People in cities are exposed to POPs (POPs = PCDD/Fs + dl-PCBs) in the form of gases and aerosols, with the gaseous fraction more important in industrial emissions (Ren et al, 2011[1]), and particulate fraction in vehicular emissions (Martínez et al, 2006[2]). It follows that concentration gradients observed of gaseous dioxins increase with proximity to their industrial sources, while particulate dioxins increase towards traffic zones - as observed by passive and active air samplers, respectively. Although determining the mass balance of gas to particulate fraction is complicated due to large differences in sample duration (100 day for passive samplers versus 1 day for active), it is possible to combine the data to identify critical areas and their relative levels of exposure. This study analyzes passive and active air-sampling data of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) taken from air monitoring stations throughout a mid-size densely populated tropical Andean City. Dispersive dynamics of POPs in the ambient air of Andean cities has not fully developed relationships and differences between the factions of gaseous and particulate POPs. The objectives of this study are to identify dominant patterns of dispersion of the two fractions, review relative concentrations of congeners and identify important areas of future research development.

Materials and methods

PCDD/PCDFs and dl-PCBs in the gaseous and particulate fraction of air were measured in the city of Manizales, Colombia, and compared to potential industrial and vehicular source. Manizales is located on the Central Cordillera of the Andes at 2150 m.a.s.l. (see Fig 1). The urban area of the city is bordered by pronounced slopes, as a result, the area available for development is limited and there is a relatively high urban density. Four stations were chosen, two stations at southeast (Nubia and Sena), one station in the central zone (Palogrande) and one station located in downtown Manizales (Liceo station). Passive sampling (PAS) was carried out at the four stations, from June 2012 to October 2012; using polyurethane foam (PUF) as adsorbent medium. In Liceo, Palogrande and Nubia, active sampling was carried out collecting a total of 22 samples during September 2009 to June 2012, and using HiVol samplers with quartz fiber filters. Active sampling was limited to collecting particulate material.

Collection and analysis procedures followed the methodologies described in U.S. EPA 40[3] and US EPA 1613[4] protocols. Samples were subject to soxhlet extraction, clean-up and instrumental analysis by HRGC/MS to determine the concentrations of PCDD/PCDF and dl-PCBs, according to the isotope dilution method. WHO-TEQ_{2005} values for passive and active sampling were calculated according to van den Berg[5] and showed in Table 1.

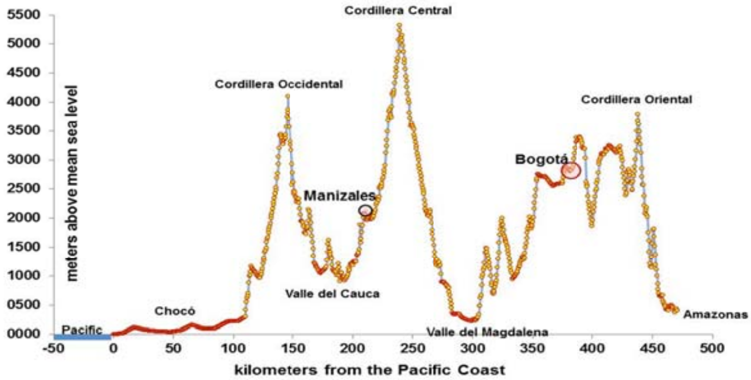
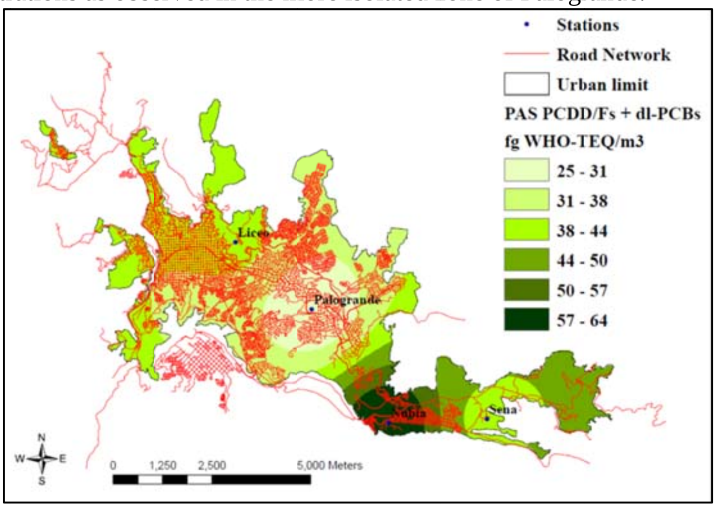


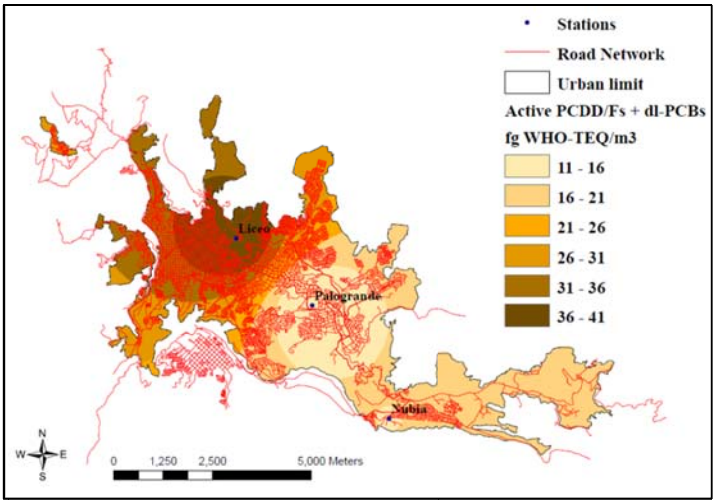
Figure 1. West/East section of the Andean Chains – Pacific to the Amazon

Results and discussion

The influence of both industrial and vehicular emissions and concentration gradients of PCDD/Fs and dl-PCBs from their sources were evident in data collected from both passive (gaseous fraction) and active samplers (particulate fractions). There were distinct concentration gradients for both the gaseous and particulate fractions of POPs, with more industrial sources (of gaseous POPs) greatest near the industrial park at La Nubia (64 fg WHO-TEQ/m^3) and more vehicular sources (of particulate POPs) greatest towards central downtown at Liceo (41 fg WHO-TEQ/m^3) – the downtown zone of Liceo is characterized by a dense road network and is an important area for diesel combustion by public transportation (Figures 2a & 2b). The central zone is furthest from emissions from concentrated industrial and vehicular sources, and exhibited reduced levels of both the gaseous and particulate fractions. These patterns suggest the importance of industrial emissions on the gaseous fractions of POPs and vehicular emissions on the particulate fractions of POPs, and provide important diminution of concentrations as observed in the more isolated zone of Palogrande.



(a)



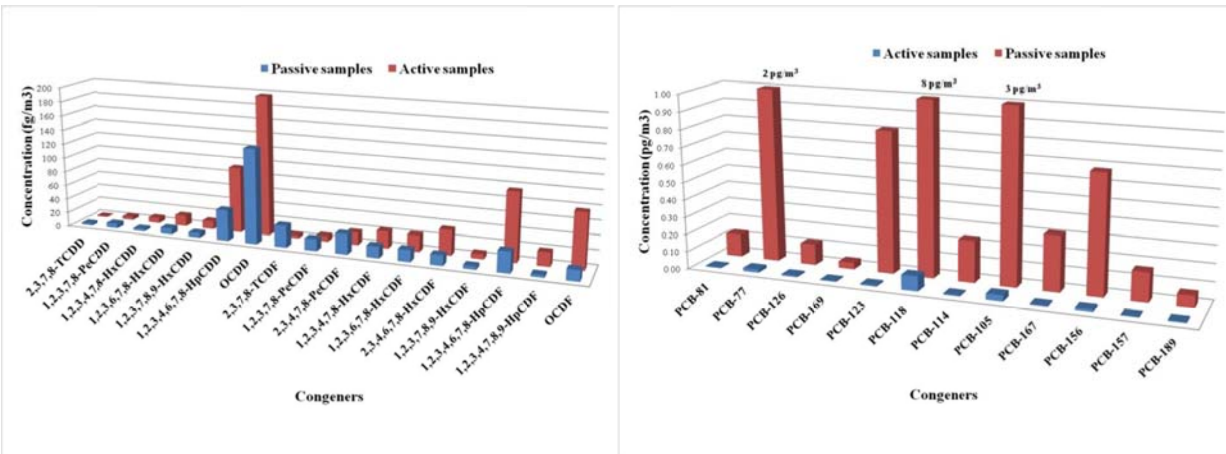
(b)

Figure 2. Spatial distribution of total PCDD/PCDFs + dl-PCB in Manizales city for a) Passive sampling and b) Active sampling

Congener concentration profiles (Table 1, expressed in WHO-TEQ) obtained for passive samples showed greater contributions of OCDD and 1,2,3,4,6,7,8 HpCDD in dioxins. Furan congeners were characterized by higher levels of 2,3,7,8-TCDF and 1,2,3,4,6,7,8 HpCDF (Figure 3a). According to Antunes[6] study, this profile is associated with secondary metallurgy industry with non ferrorus foundry. In active sampling, congener concentration profiles obtained were OCDD, 1,2,3,4,6,7,8 HpCDF, 1,2,3,4,6,7,8 HpCDD and OCDF like greater contributors (Figure 3a). This profile is associated with MSWI, vehicular emissions due to burning unleaded gasoline and diesel fuel combustion in trucks. Different studies developed in Spain[7,8], UK[9], USA[10] and Colombia (Manizales)[11] have reported similar profiles.

In dl-PCBs, for both passive and active sampling (Figure 3b), PCB 118 and PCB 105 were the greater contributors. Studies realized by Antunes[6] and Mari[7], attribute to these PCBs like typical congeners of MSWI, coal power, siderugies and secondary metallurgy industries sources with non ferrorus foundry emissions.

The results reported for passive sampling corresponded to the first campaign performed in Manizales, with only one value per station, and making no possible a rigorous statistical analysis. However, the measurements are ongoing in order to build a baseline of PCDD/PCDFs and dl-PCBs environment concentrations in the Andean city of Manizales.#



(a) (b)

Figure 3. Concentration profiles by congener both passive and active stations of a) PCDD/PCDFs and b) dl-PCBs.

Table 1. PCDD/PCDFs (fg/m^3-day) and dl-PCBs (pg/m^3-day) concentrations by congener both passive and active stations.

Congeners	Passive stations				Active stations		
	Palogrande station	Liceo station	Sena station	Nubia Station	Min. Values	Mean Values	Max. Values
Number of samples	1	1	1	1	9	8	5
PPCDD/PCDFs							
2,3,7,8-TCDD	2	4	2	3	ND	1	2
1,2,3,7,8-PeCDD	6	7	5	7	ND	4	11
1,2,3,4,7,8-HxCDD	1	1	5	7	ND	7	24
1,2,3,6,7,8-HxCDD	6	8	9	12	ND	15	46
1,2,3,7,8,9-HxCDD	2	8	5	11	ND	11	41
1,2,3,4,6,7,8-HpCDD	24	54	43	54	11	93	343
OCDD	88	217	106	123	ND	197	597
2,3,7,8-TCDF	14	27	37	44	ND	5	17
1,2,3,7,8-PeCDF	21	6	29	10	ND	8	27
2,3,4,7,8-PeCDF	14	21	38	41	ND	18	57
1,2,3,4,7,8-HxCDF	7	12	23	21	ND	24	75
1,2,3,6,7,8-HxCDF	7	13	21	25	3	23	77
2,3,4,6,7,8-HxCDF	6	12	18	21	ND	35	123
1,2,3,7,8,9-HxCDF	1	2	8	8	ND	7	24
1,2,3,4,6,7,8-HpCDF	11	24	42	41	11	96	347
1,2,3,4,7,8,9-HpCDF	1	3	6	4	ND	19	66
OCDF	4	13	23	20	ND	77	323
Total PCDD/Fs (fg WHO-TEQ$_{2005}$/m^3-day)	**18**	**27**	**32**	**39**	**1**	**23**	**72**
dl-PCBs							
PCB-81	0.06	0.09	0.19	0.19	0.00	0.01	0.01
PCB-77	0.51	1.14	2.88	2.36	0.01	0.02	0.06
PCB-126	0.06	0.11	0.09	0.22	0.00	0.01	0.02
PCB-169	0.03	0.03	0.04	0.06	0.00	0.00	0.01
PCB-123	0.22	0.46	1.47	1.10	0.00	0.01	0.02
PCB-118	2.09	4.16	14.77	10.80	0.04	0.09	0.22
PCB-114	0.07	0.13	0.42	0.33	0.00	0.01	0.01
PCB-105	0.80	1.58	6.50	4.88	0.02	0.03	0.09
PCB-167	0.10	0.20	0.54	0.43	0.00	0.01	0.03
PCB-156	0.16	0.35	1.17	1.04	0.00	0.01	0.07
PCB-157	0.05	0.08	0.27	0.26	0.00	0.00	0.01
PCB-189	0.04	0.05	0.08	0.09	ND	0.01	0.03
Total dl-PCBs (fg WHO-TEQ$_{2005}$/m^3-day)	**7**	**12**	**11**	**25**	**0.26**	**0.99**	**1.73**
Sampled period	105 days June-October 2012	106 days June-October 2012	104 days June-October 2012	101 days June-October 2012	2009 - 2012	2009 - 2012	2009 – 2012

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