LEVELS OF DIOXIN LIKE POPs IN THE PARTICLE BOUND FRACTION OF AMBIENT AIR IN AN INTERMEDIATE SIZE ANDEAN CITY

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Introduction

There is increased interest in identifying and quantifying levels of organic contaminants in tropical mountain regions due to their unique meteorology and modes of atmospheric transport[1]. Among organic contaminants most important are by-products of combustion that include dioxin-like polychlorinated biphenyls (dl-PCBs). One of the largest industrial source of dl-PCBs is ferrous and non-ferrous metal production in the iron and steel industry[2,3]. Another important source of dl-PCBs is the thermal processing of waste – or incineration. Incineration can produce dl-PCBs emissions from the combustion of waste streams that include chlorine like polyethylene. Internal combustion engines are also important as sources of dl-PCBs and other persistent organic pollutants (POPs). Dioxin-like polychlorinated biphenyls are one of many types of POPs. Combustion sources of POPs are potentially greater at higher elevations due to lower atmospheric O_2 pressures and less complete combustion. Finally, additional sources include evaporation from the use, storage and disposal of commercial PCB products[4]. Levels of POPs and dl-PCBs from these various sources and their associated human exposure must not only be identified for making local public policy decisions, but the fate and transport these persistent pollutants must also be understood. Documenting concentration trends of these pollutants in Manizales could contribute to environmental studies conducted throughout the world[5], as Manizales represents an intermediate-size city in a tropical mountain forest ecosystem.

Manizales (population 380,000) is an intermediate size city located on the western slopes of the central range of the Andes (2150 m.a.s.l). Manizales has unique climate, with large diurnal variation in temperature (12 °C - 24 °C), pressure (589 mm Hg - 593 mm Hg), humidity (50% - 100%); and a relatively high annual rainfall (1870 mm yr^{-1}). Manizales is located on a northern spur of the active volcano Nevado del Ruiz (elevation 5,455 m.a.s.l), and steep slopes surrounding the city have limited the area available for development. This has resulted in relatively high urban population density (approximately 760 people/sq km) in a city with the highest vehicular ownership in Colombia (130 vehicles per 1,000 inhabitants). Typical air movement in Manizales follows a diurnal pattern of upslope movement of heated air during the day, reversing to a downslope direction of cooled air at night. Nighttime parcels of air could include volcanic emissions from Nevado del Ruiz (located 27 km) from the city, contributing oxidized and reduced forms of sulfur, nitrogen and carbon. However, low average wind velocities for Manizales suggest limited diurnal delivery of volcanic pollutants to Manizales. At the same time, low wind velocities also limit dispersion of urban contaminants from sources like non-point vehicular combustion emissions to point-sources like the thermal processing of waste, and scrap metal recycling emissions. In our previous study we found concentrations of PDCC/PCFs in the particle bound fraction of ambient air in Manizales[6], and in this study, we complement by extending analysis to include dl-PCBs.

Materials and Methods

During September of 2009 and July of 2010, PM_{10} samples were collected on glass fiber filters using Hi-Vol samplers according to EPA-40 method[7] and US EPA Method TO-9A[7]. Sohxlet extraction, clean-up and instrumental analysis were carried out and analyzed by HRGC/MS or HRGC/MS/MS to determine dl-PCBs according to the isotope-dilution method.

Three monitoring stations were established and labeled as Nubia (N), Palogrande (P) and Liceo (L). Liceo is characterized by high public transportation density, which uses diesel as principal fuel. Palogrande, located in a central zone of the city, is influenced by one of the most important avenues that connects south east with downtown. Nubia is located outside of the city without direct influence of transport or industries in its immediate vicinity. However, of the three monitoring stations, Nubia is closest to the industrial area.

Results and discussion

Table 1 shows dl-PCBs results. WHO-TEQ values were calculated according to van den Berg et al. (2006)[8]. Behavior of dl-PCB was characterized by higher values at Liceo ranged from 0.47 fg WHO-TEQ m^{-3} to 9.63 fg WHO-TEQ m^{-3} (170 fg m^{-3} to 480 fg m^{-3}). Palogrande exhibited values in a range of 0.41 fg WHO-TEQ m^{-3} to 1.14 fg WHO-TEQ m^{-3} (330 to 425 fg m^{-3}) and Nubia presented the lowest values of dl-PCB with 0.22 fg WHO-TEQ m^{-3} (100 fg m^{-3}).

Table 1. Summary of dioxin like PCBs sampling results

Congener	Palogrande			Nubia	Liceo			WHO-TEF
	Conc.(fg m^{-3})							
	P1	P2	P3	N1	L1	L2	L3	
PCB-81	1	2	7	1	2	8	8	0.0001
PCB-77	19	10	16	14	32	64	57	0.0001
PCB-126	3	4	10	2	4	12	11	0.1
PCB-169	2	1	8	3	2	9	9	0.01
PCB-123	6	8	14	1	1	16	16	0.0001
PCB-118	174	182	190	51	58	221	214	0.0001
PCB-114	4	3	5	1	6	7	7	0.0005
PCB-105	70	46	46	23	34	91	91	0.0001
PCB-167	33	21	12	2	7	16	14	0.00001
PCB-156	70	45	26	2	18	38	37	0.0005
PCB-157	11	5	5	1	4	7	6	0.0005
PCB-189	33	7	6	ND	2	7	7	0.0001
Total dl-PCBs	**425**	**334**	**346**	**101**	**170**	**496**	**477**	
dl-PCBs fg WHO-TEQ m^{-3}	**0.41**	**0.44**	**1.14**	**0.22**	**0.47**	**1.34**	**9.63**	
Meteorological parameters*								
Total Precipitation (mm)	0	0	5	34	18	7	2	
Average Precipitation (mm)	0	0	3	3	2	7	2	
Wind velocity (m s-1)	1.1	1.2	0.7	1.1	1.1	1.1	0.9	
Prevailing wind direction (%) (day / night)	SW(12)/ E(33)	SE(11)/ SE(42)	ESE(12)/ ESE(27)	SW(12)/ E(33)	SW(12)/ E(33)	SE(12)/ SE(47)	NW(14)/ SE(50)	

ND: Non detectable, * Mean values

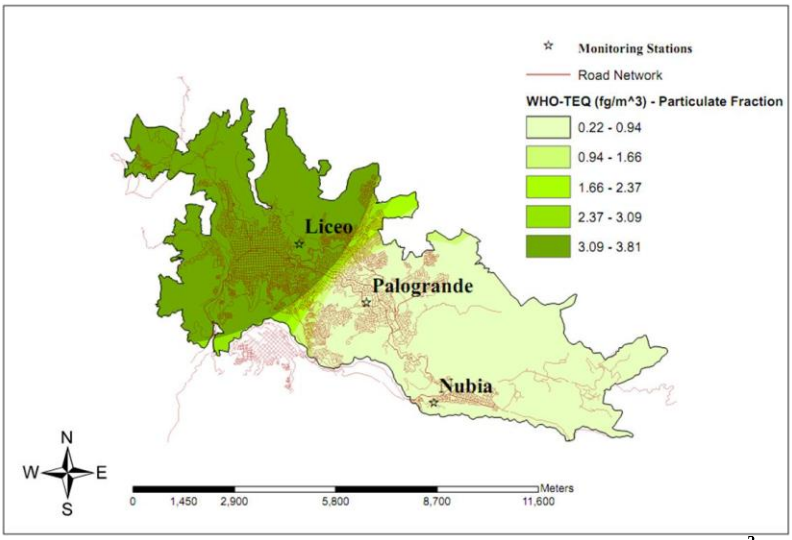
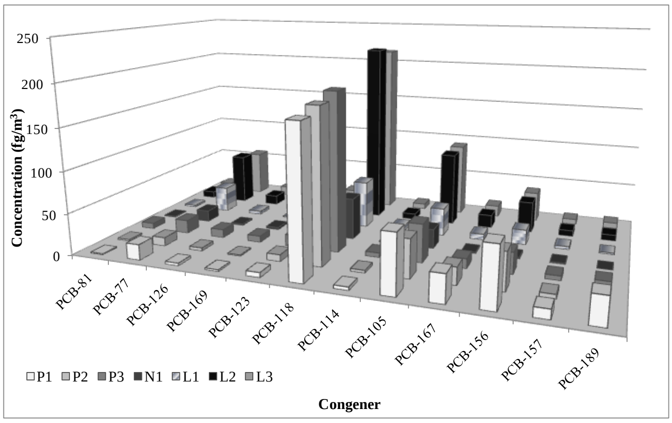


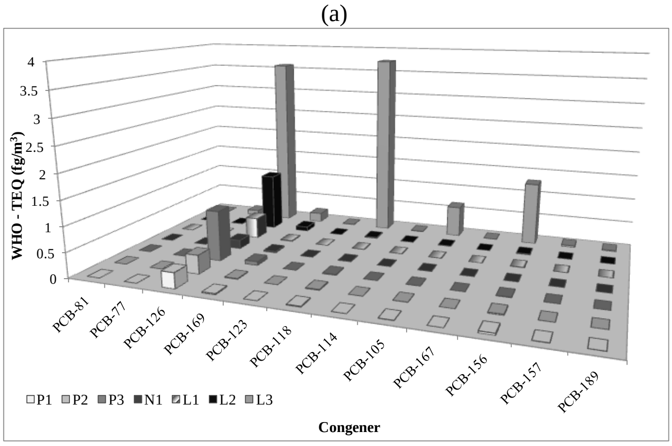
Figure 1. Monitoring stations and spatial distribution of total PCDD/Fs (fg WHO-TEQ m^{-3}) over urban area of Manizales

Figure 1 indicates the location of monitoring stations in the city and the spatial distribution of total dl-PCBs. These results were calculated using ArcGis software and IDW (Inverse Distance Weighting) method to interpolate mean values of each station. As shown in figure 1, higher values of dl-PCBs are related to higher density of road network; as a consequence, there is a significance influence of vehicle emissions in the city. Public transportation, which uses dieses as fuel, exerts higher influence over Liceo station due to its vicinity with downtown and Santander Avenue, with the higest traffic counts in the city.

Congener profiles were compared at each station. Figure 2 shows congener behavior of dl-PCBs in particulate matter at all stations. The highest congener concentrations observed (figure 2a) were PCB-118 at all stations followed by PCB-105. This was consistent with other studies[2,3] where combustion sources influence PCB levels and patterns in the study area. Martinez et al. (2010)[3] reported data from Catalonian town obtained in three sampling campaigns; dl-PCB concentrations ranged from 20.54 fg WHO-TEQ m^{-3} to 26.78 fg WHO-TEQ m^{-3} (industrial influence) and from 9.66 fg WHO-TEQ m^{-3} to 14.84 fg WHO-TEQ m^{-3} (town with influence of traffic). In contrast, Li et al. (2010)[9] reported data from Northeast China with air concentrations between 415 fg m^{-3} - 24622 fg m^{-3} and WHO-TEQs between 1 fg m^{-3} – 18 fg m^{-3}. In terms of WHO-TEQ congener concentration (figure 2b), PCB-126 was the higher congener. This pattern was agree with the one reported by Martinez et al. (2010)[3].



(a)



(b)

Figure 2. Congener Concentration of dioxin-like PCBs in particulate matter (a) Total (fg m^{-3}), (b) WHO-TEQ (fg m^{-3})

Frequency distribution was analyzed (figure 3) to establish representative patterns of dl-PCBs concentrations obtained in the city. Forty-three percent of samples showed values in a range of 400 fg m^{-3} to 500 fg m^{-3}. Concentrations between 100 fg m^{-3} to 200 fg m^{-3} and 300 fg m^{-3} to 400 fg m^{-3} were roughly equivalent at 29 % each. Results reported by Castro-Jiménez et al. (2008)[10] in a study performed at Lake Maggiore, Italy; shown dl-PCBs patterns in both, particulate and gaseous fraction of air samples. Particle bound concentrations reached 1556 fg m^{-3}, three times higher than results obtained in this study. Particle concentration obtained in Italy seems to be typical for a semi-rural area[10]. In this sense, Manizales could have dl-PCBs patterns equivalent to rural or remote regions. As well as, congener patterns reported by Castro-Jiménez et al. (2008) agree with the one found in Manizales, where concentration profiles were dominated by PeCB-118 and PeCB-105 with higher values than the other congeners evaluated.

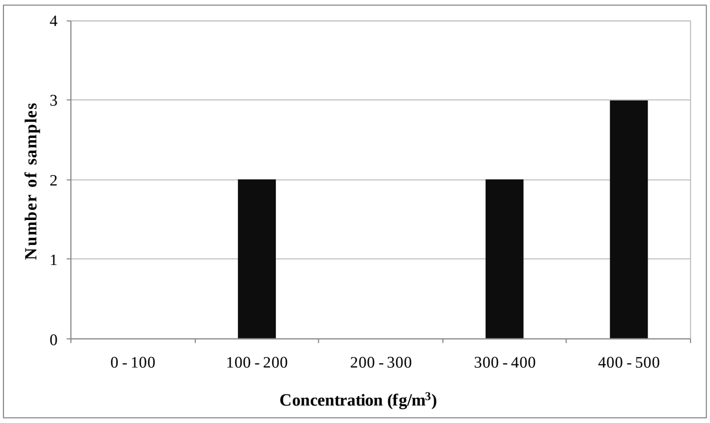


Figure 3. Frequency distribution of dioxin-like PCBs in particulate matter

In conclusion the highest levels of dl-PCB were observed in the downtown area of Manizales. However, more samples are necessary from the Northwest and Southeast areas of the city to have better characterize dl-PCBs patterns throughout the urban zone of Manizales. In addition, only the particle bound fraction of dl-PCBs was analyzed in this study, and gas phase concentrations are typically higher than particle phase concentrations[10]. A more comprehensive study of Manizales could differentiate the values of particulate and gaseous concentrations of dl-PCBs in ambient air and elucidate dl-PCB levels, production, fate and transport.

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