Science of the Total Environment 491–492 (2014) 67–74

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

PCDD/PCDF and dl-PCB in the ambient air of a tropical Andean city: Passive and active sampling measurements near industrial and vehicular pollution sources

J. Cortés [a,*], C.M. González [a], L. Morales [b], M. Abalos [b], E. Abad [b], B.H. Aristizábal [a]

[a] Hydraulic Engineering and Environmental Research Group, Universidad Nacional de Colombia Sede Manizales, Cra 27 64-60 Bloque H Palogrande, Manizales, Colombia
[b] Laboratory of Dioxins, Environmental Chemistry Department, IDAEA-CSIC, Jordi Girona 18-26, Barcelona 08034, Spain

HIGHLIGHTS

• PCDD/F and dl-PCB concentrations were measured at four urban locations of the densely populated Andean city of Manizales.
• Manizales has an Andean forest climate with high vehicular density and relatively low wind velocity.
• Concentrations of passive samples are more associated with industrial source areas.
• Concentrations in particle phase (PM_{10}) are more associated with mainly vehicular source areas.
• Results obtained are the first data from passive monitoring in urban zones of Colombia.

ARTICLE INFO

Article history:
Received 15 November 2013
Received in revised form 29 January 2014
Accepted 29 January 2014
Available online 18 February 2014

Keywords:
Persistent organic pollutants (POPs)
Polychlorinated dibenzo-p-dioxin (PCDD)
Polychlorinated dibenzofuran (PCDF)
Dioxin like-PCB (dl-PCB)
Passive air sampling (PAS)
Particulate matter less than 10 μm (PM_{10})

ABSTRACT

Concentration gradients were observed in gas and particulate phases of PCDD/F originating from industrial and vehicular sources in the densely populated tropical Andean city of Manizales, using passive and active air samplers. Preliminary results suggest greater concentrations of dl-PCB in the mostly gaseous fraction (using quarterly passive samplers) and greater concentrations of PCDD/F in the mostly particle fraction (using daily active samplers). Dioxin-like PCB predominance was associated with the semi-volatility property, which depends on ambient temperature. Slight variations of ambient temperature in Manizales during the sampling period (15 °C–27 °C) may have triggered higher concentrations in all passive samples.

This was the first passive air sampling monitoring of PCDD/F conducted in an urban area of Colombia. Passive sampling revealed that PCDD/F in combination with dioxin-like PCB ranged from 16 WHO-TEQ_{2005}/m^3 near industrial sources to 7 WHO-TEQ_{2005}/m^3 in an intermediate zone—a reduction of 56% over 2.8 km. Active sampling of particulate phase PCDD/F and dl-PCB were analyzed in PM_{10} samples. PCDD/F combined with dl-PCB ranged from 46 WHO-TEQ_{2005}/m^3 near vehicular sources to 8 WHO-TEQ_{2005}/m^3 in the same intermediate zone, a reduction of 83% over 2.6 km. Toxic equivalent quantities in both PCDD/F and dl-PCB decreased toward an intermediate zone of the city.

Variations in congener profiles were consistent with variations expected from nearby sources, such as a secondary metallurgy plant, areas of concentrated vehicular emissions and a municipal solid waste incinerator (MSWI). These variations in congener profile measurements of dioxins and dl-PCBs in passive and active samples can be partly explained by congener variations expected from the various sources.

1. Introduction

Knowledge of persistent organic pollutant (POPs) levels in different environmental matrices has become a global concern due to their environmental characteristics of persistence, bioaccumulation, toxicity and global dispersion (UN, 2003). Polychlorinated dibenzo-p-dioxin (PCDD), polychlorinated dibenzofuran (PCDF) and dioxin-like PCB (dl-PCB) are semi-volatile compounds characteristic of this chemical group. PCDD/F and dl-PCB (PCB with properties similar to dioxins) are formed as unwanted by-products in many industrial activities and combustion processes (UN, 2003).

Studies of POPs in ambient air have used passive (Bogdal et al., 2013) and active samplers (Abad et al., 2007; Martínez et al., 2006; Rivera-Austrui et al., 2011), which employ different materials and methods

* Corresponding author at: Universidad Nacional de Colombia Sede Manizales, Cra. 27 # 64-60, Bloque H Palogrande, Manizales, Colombia. Tel.: +57 6 8879300x50337; fax: +57 6 8879300x50130.
E-mail address: jpcortesa@unal.edu.co (J. Cortés).

0048-9697/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2014.01.113

for analysis of the gaseous and particulate forms. Methodologies include polyurethane foams (PUFs) and collection plate ports with filters for deposition of particles. The use of passive samplers (PAS) has spread globally because of its easy handling, low cost and no electrical connection requirements. Different designs of PAS have been used to monitor other POPs such as PAH (Xiao et al., 2008), OCPs (Pozo et al., 2006), PCB (Chaemfa et al., 2008; Estellano et al., 2008) and PCN (Harner et al., 2006; Mari et al., 2008), but few studies have been reported for PCDD/F and dl-PCB, especially in Colombia, where there are studies in emissions from incinerators (Aristizábal et al., 2007; Hoyos et al., 2008) and analysis of adsorption of PCDD/F in PM_{10} in ambient air (Aristizábal et al., 2011). Passive air sampling has been adopted by the Stockholm Convention on POPs, which include activities related with researching and monitoring levels and trends of POPs in ambient air (UNEP, 2002). Studies have reported data for passive sampling from different countries around the world to support the Global Monitoring Plan (GMP), including some Latin American countries (Bogdal et al., 2013; Klánová and Harner, 2013). In Colombia, passive monitoring has been carried out in remote and background zones within the Global Atmospheric Passive Sampling (GAPS) network; however, there are important deficiencies in studies and knowledge about levels, dynamics and sources of POPs in other regions including urban zones.

Toxic effects on reproduction, development and immunological functions (Magulova et al., 2011) and cancer (WHO, 2010) have been reported in epidemiologic studies based on the exposure levels of PCDD/F. The occurrence of PCDD/F in ambient air (Pozo et al., 2004; Aristizábal et al., 2011), point sources (Aristizábal et al., 2007, 2008), soil (Schuhmacher et al., 2003), human blood (Nguyen et al., 2011), breast milk (Someya et al., 2010), food fats (Weber and Watson, 2011), ashes (Hung et al., 2011) and sediments have been analyzed in many countries. The fate and associated risk of POPs is influenced by factors that include emission source, physicochemical degradation, adsorption and desorption processes and scavenging by rainfall.

The weather and morphological characteristics of Manizales make the knowledge of these variables of crucial importance when assessing the impact of POPs in ambient air. The at-risk population of Manizales is located on the Central Cordillera of the Andes, 2150 meters above sea level (m.a.s.l). The city has a tropical climate with low annual variations in temperature (15 °C–27 °C). Local morphology is characterized by an upper valley, descending into a ridge and mesa topography, all of which are influenced by a diurnal rising and falling of near-surface air masses.

The urban area of the city is limited by the presence of steep surrounding slopes; as a result, the area available for development is limited. This limitation has encouraged the development of relatively high urban density, ~6800 inhabitants/km^2. Manizales is also affected by the active Nevado del Ruiz volcano 28 km to the southwest, and its emissions influence the atmospheric chemistry of the city and neighboring towns. Manizales has an industrial zone with processes like coal-fired metal foundry recycling plants, food processing plants, plastic processing industries and MSWIs. Other important sources of pollution are areas of high vehicular density, located mainly in the downtown area of the city.

Our goals in this study are to provide data on the concentrations of PCDD/F and dl-PCB in the urban zone of Manizales, Colombia, using passive samplers analyzed in PUF and active samplers analyzed in PM_{10} and to identify potential sources of pollution and the influence of meteorological variables such as temperature on the dynamics of these pollutants. Passive sampling devices add a new dimension to previous studies developed for particulate phase measurements in Manizales.

2. Materials and methods

2.1. Sampling sites

PCDD/PCDF and dl-PCB were monitored in four locations. Table 1 lists the stations and their specific characteristics. Stations were chosen for their proximity to different pollution sources, which influence patterns of PCDD/F and dl-PCB. The locations are characterized as having more industrial influence (Nubia and Sena) or more vehicular influence (Liceo), and with a more intermediate zone having less proximity to the principal vehicular and industrial sources. Fig. 1 shows location of the stations in Manizales and some anthropogenic sources of atmospheric pollutants. The Liceo station is located downtown and has a strong influence from vehicular traffic and public transport. Toward the North, there is a municipal solid waste incinerator (MSWI). Palogrande station is located in the geographic center of the city—this is a residential area and is characterized by the influence of emissions by a nearby avenue that connects downtown with Southeast. Nubia station is located at the Southeast of the city, near the industrial zone of Manizales. Topographically, the upper valley morphology above Nubia and Sena could facilitate the concentration of industrial emissions during diurnal periods of cooling and descending air masses. The surrounding area of Sena is influenced by industrial activities such as food processing companies, secondary metallurgy industry and plastic processing industries. The active Nevado del Ruiz volcano is located 28 km Southeast of Manizales, and it is a constant potential source of gas and particle contamination for Manizales and neighboring towns.

2.2. Sample collection

In Liceo, Palogrande and Nubia, passive and active samplers were employed, while only passive sampling (PAS) was used at Sena. For PAS, 12 samples were collected (three samples per station) during 1 year of monitoring, including three monitoring periods (June 2012–October 2012, October 2012–February 2013 and February 2013–June 2013). In the case of active sampling campaign, Hi-Vol samplers were employed for PM_{10} collection. Four samples of PM_{10} were obtained in Liceo station, six in Palogrande station and three in Nubia station. A list of sampling dates for active samplers is shown in Table 2 and Table A1 (Supplementary material). Sampling dates were enumerated and resulted from the combination of aerosol measurements from an associated study. Active sampling protocols followed the Colombian standard guidelines for PM_{10} data location. Passive

Table 1
Summary of sampling station characteristics.

Station	Main economic activity around the station	Station details—sources of pollutants	Altitude (m.a.s.l.)	Geographical coordinates
Liceo (Northwest)	Urban/commercial	High vehicular traffic and low industrial influence	2156	5°03′58.9″N 75°28′30″W
Palogrande (Center zone)	Urban/residential	Mid–low vehicular traffic and null industrial influence	2166	5°03′24″N 75°29′30″W
Sena (Southeast)	Urban/industrial	Industrial, and mid–low vehicular traffic influence	2220	5°01′48″N 75°26′59″W
Nubia (Southeast)	Urban/industrial	Industrial, and low vehicular traffic influence	2104	5°01′57.3″N 75°30′49″W