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Original article

Semivolatile Organic Compounds (SVOCs) in the atmosphere of Santiago de Cali, Valle del Cauca, Colombia along north-south transect using polyurethane foam disk as passive air samplers



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ABSTRACT

A preliminary evaluation of Semivolatile Organic Compounds (SVOCs) was performed in the atmosphere of Santiago de Cali, Colombia, using passive air samplers based polyurethane foam (PAS-PUF) disks. PAS-PUF were deployed in four sites, along a north-south transect (~15 km), during one sampling period of ~4 months in 2011, from the industrial area of Yumbo (EF site) to the agricultural area of Valle del Cauca (FCNE). Results showed, for PCBs and PAHs, a clear north-south (IN > AG) decreasing concentration gradient (~3 times) while OCPs exhibited an opposite gradient (UR < AG). Endosulfan I showed the highest concentrations in air (~0.8–60 ng m⁻³). The HCHs (α - and γ -) concentrations ranged from BDL to ~19 ng m⁻³, with α -HCH showing the highest levels (suggesting recent use of technical HCHs) and for DDTs levels fluctuated from BDL to ~29 ng m⁻³ (with *p,p'*-DDE accounting for 50–80% of total DDTs). PAHs levels (~25–66 ng m⁻³) were characterized by the abundance of Phenanthrene (34%), fluoranthene (18%) and pyrene (16%). For PCBs, concentrations in air ranged from ~0.2 to 0.9 ng m⁻³ and were characterized by middle to a higher molecular weight PCB composition pattern. The results of OCPs are much higher than those found in other areas of Latin America. These results are likely influenced by the proximity of agricultural cultivations (i.e., sugarcane crops) in the southern part of the city. These results provide preliminary information about the presence of SVOCs in the atmosphere of Santiago de Cali, and constitute the basis for future monitoring programs.

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1. Introduction

Semivolatile Organic Compounds (SVOC) are compounds that resist photolytic, biological and chemical degradation, they can be accumulated in the human and animal tissue, biomagnify along

food chains, and are associated with chronic and (eco)toxicological effects (Fernández and Grimalt, 2003; UNEP, 2011). In addition, they are semivolatile, which helps them to be in the vapor phase of the atmosphere or ad/ab-sorbed by atmospheric particles, thereby facilitating transport over long distances through the atmosphere (long range atmospheric transport – LRAT).

Owing to the environmental problems caused by these pollutants, they were banned and severely restricted in many countries around the world and consequently to the implementation of international treaties. International efforts to manage a group of SVOCs, include the international treaty of the Stockholm Convention (SC) on Persistent Organics Pollutants (POPs) that was signed

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in 2001 and came into effect in 2004, with the aim of eliminating and reducing their release in the environment (UNEP, 2010). Colombia is a signatory country of the SC, and some national measures have been taken for its implementation (MAVDT, 2007).

Under the SC on POPs air is one of the target environmental media because it responds relatively quickly to changes in primary emissions of atmospheric pollutants and is expected to be useful for the evaluation of the effectiveness of the Convention. Moreover, the Guidance of the UNEP incentive features the use of passive air sampling (PAS-PUF disk) methods in developing countries, due to their low cost, small size, and, they can be easily managed compare with conventional air measurements techniques which rely on active air sampling involving more expensive and complex devices, for example they require electricity and maintenance for their operations. In the last decade the passive air sampler has become a useful air sampling technique to assess level of atmospheric pollutants, including POPs, at local, regional and global scale studies (Jaward et al., 2004a; 2004b; Pozo et al., 2006, 2009; Klánová et al., 2009; Bogdal et al., 2013).

Santiago de Cali is the capital of Valle del Cauca department and the most populous city in southwest Colombia. Cali is the third-largest city and metropolitan area in term of population and the second-largest city by area in the country. As the only major Colombian city, with access to the Pacific Coast, Cali is the main urban and economic center in southwest Colombia, and has one of the fastest-growing economies in the country (Cali en cifras, 2011). In particular, Valle del Cauca main industrial activity is the production of sugar, paper, chemicals, machinery and equipment (Cali en cifras, 2011). Although, many anthropogenic and intensive industrial activities are carried out in this area of Colombia, only a few investigations have measured atmospheric levels of SVOCs.

In 2006, levels of chlorinated pesticides were reported, under the Global atmospheric passive sampling (GAPS) network, at the rural site of Sede Arauca, in the north-east, of Colombia (Pozo et al., 2006, 2009). Recently, Cortés et al. (2016) have reported environmental variations of PCDD/Fs and dioxin-like-PCBs, using PAS-PUF disks, between the Andean cities of Bogota and Manizales (Cortés et al., 2014, 2016). However, there is still a lack of information regarding other cities of Colombia. This information is very important to ascertain and understand the environmental distribution, transport and fate of such chemicals and also to identify potential local or regional sources.

In this investigation PUF disk passive air samplers were deployed at Santiago de Cali, Valle del Cauca in Colombia, along a north-south transect, during one sampling period in 2011. The aims of this study were to i) contribute new data regarding SVOCs in the atmosphere of Santiago de Cali, ii) assess the influence of different anthropogenic activities in Valle del Cauca and iii) compare and discuss the collected data with other studies within the region of Latin America that rely on the same sampling technique.

2. Materials and methods

2.1. Study area

The city of Santiago de Cali is located in the Valle del Cauca (western part). Santiago de Cali has an estimated population of 2 319 655 according to 2005–2020 population projections. The city spans 560 km² (216 sq mi) with 121 km (ATSDR (Agencia para Sustancias Tóxicas y el Registro de Enfermedades), 2012) (~47 sq mi) of urban area. Valle del Cauca area is of approximately ~40 000 m² and is surrounded by the Colombian Andes Mountains (SM, Figure S6 and S7). Santiago de Cali is close to the equator line, therefore there are no major seasonal variations, its average temperature is 25 °C the year-round with a daily range from 18 °C to

31 °C. To the west of the city rises the western Mountain Range in the northern part of the city has an average altitude of 2000 m and in the southern part 4000 m. This difference of altitude cause a difference in the annual precipitations ranging from 900 to 1800 mm (Ortiz et al., 2001).

Valle del Cauca main economic activity is the production of sugar cane (78 000 tonnes per day) and other minor crops (potatoes, coffee and soybean) (FONADE, 2016). The Valle of Cauca is one of the few areas of the world where sugarcane can be cultivated the year-round.

2.2. Sampling site selection and deployment

Four sampling sites were selected in the city of Santiago de Cali, Colombia. The sampling sites covered a north-south transect and consisted of one industrial site (IND), Success Flora (EF), two urban areas (UR), School Republic of Argentina (ERA) (Downtown), Residential Gratamira (CRG), and one agricultural site, and the Faculty of Natural Sciences of the University of Valle (FCNE) (close to sugarcane cultivations). Details are given in the Supplementary Material (SM) Table S1 and Figure S1. The PUF disks were exposed during one period of approximately four months, from May to September in 2011 (tropical climate).

2.3. Extraction and analysis

The PUF disk (4 cm diameter; 1.35 cm thick; surface area, 365 cm²; mass, 4.40 g; volume, 207 cm³; density, 0.0213 g cm⁻³; Tisch Environmental, Village of Cleaves, Ohio) extraction was performed by Soxhlet, with 200 ml of petroleum ether (Sigma–Aldrich, Italy, reactive grade ACS and ISO) for 24 h (Pozo et al., 2012; Estellano et al., 2012) at a temperature between 35 and 40 °C. The extracts were concentrated by rotary evaporation (Buchi) to 10 ml and blown down under a gentle stream of nitrogen to 0.5 ml and solvent exchanged to isooctane (Figure S3).

The samples were analyzed at the Department of Physical, Earth and Environmental Science of the University of Siena, Italy. An analysis of PUF disk extracts of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated pesticides (OCPs) was carried out by GC–MS on a GC-Trace TM GC 2000 (equipped with auto sampler AS3000), and MS PolarisQ ionic trap (ThermoFinnigan, Italy). PAHs and PCBs analyses were done by positive electron impact selected ion monitoring (EI-SIM) and OCPs were analyzed by negative chemical ionization (NCI). PUF disk samples were analyzed for PCBs (n = 18): PCB-28, -52, -95, -99, -101, -110, -118, -123, -138, -146, -149, -151, -153, -157, -167, -177, -180, -187; PAHs (n = 14): acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(123cd)pyrene, dibenz(a,h)anthracene, benzo(ghi)pyrene and OCPs (n = 9): α -, γ -HCH, endosulfan I and II, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDT (Supelco Analytica, USA).

2.4. Derived air sample volumes

Details regarding information on sampler performance and calculations of SVOC concentrations have been presented elsewhere (Shoeib and Harner, 2002; Estellano et al., 2012; 2014). The uptake of the SVOCs by the PUF-PAS shows that it is controlled mostly by the side mass transfer coefficient (K_A), which is a weak function of temperature (Shoeib and Harner, 2002). The concentrations in air for the target SVOCs were calculated from the amount of chemicals accumulated in the PUF disk (ng sampler⁻¹) during the deployment period of the PUF-PAS (expressed in days), and divided by the effective air volume (EAV) (V_{air} , m³).

For the estimation of the EAV, we used the eq. 2 from [Shoeib and Harner \(2002\)](#). This equation considers the full uptake profile as well as the linear and the plateau phases. A typical sampling rate (R) of 4 m³ of air per day (m³/day) was used in the present study. R value was estimated based on previous investigations ([Shoeib and Harner, 2002](#); [Pozo et al., 2004, 2009](#)). The calculation resulted in sampling volumes of approximately 50 m (Alegria et al., 2006) to 600 m³, depending on the deployment length (days), the average temperature of each sampling site (°C), and the specific physical–chemical properties of the molecules analyzed. More details are presented elsewhere ([Shoeib and Harner, 2002](#); [Pozo et al., 2004, 2009](#); [Estellano et al., 2012, 2014](#)).

2.5. Quality assurance and quality control (QA/QC)

For QA/QC purposes, all the analytical procedures were monitored by field blanks (n = 4), laboratory blanks (n = 6) and recovery standards. Laboratory blanks consisted of two types: first, pre-extracted PUF disks (clean PUFs) and second, solvent blanks. Both blank types were analyzed in the same way as real samples. Recovery standards were used to assess the efficiency of the extraction procedures using a mix of OCPs and recovery standards (¹³C PCB-105 and d₁₀ phenanthrene). Recovery results were satisfactory and showed values of 70 ± 5%, and 90–120%, respectively. Field blanks showed very low concentrations from 0.3 to 1 pg m⁻³.

A signal-to-noise value ≥ 3 of the lower concentration of the standard curve of each SVOCs was used to calculate the instrumental detection limits (IDL). The average SVOCs concentration of the laboratory blanks (n = 6) plus three standard deviations was used to calculate the method detection limits (MDL). When the SVOCs were not detected in blanks, ½ of the IDL value was used as MDL. The IDL and MDL values for each target compound are reported in [Tables 1–3](#).

3. Results and discussion

3.1. Organochlorine pesticides (OCPs)

3.1.1. Hexachlorocyclohexanes (HCHs)

HCHs are environmental contaminants and have been widely used for the control of agricultural pests. The technical HCHs is a mixture of mainly five congeners which differ only in the orientation of the chlorine atoms around the cyclohexane ring. The major isomers present in the mixture are: α-HCH (53–70%), β-HCH (3–14%), γ-HCH (11–18%) and δ-HCH (6–10%). The γ-HCH is the isomer that has the insecticide properties ([ATSDR, 2012](#)). Lindane is constituted by 99% of the γ-HCH isomer ([UNEP, 2006](#)). Both the technical HCH mixture and lindane have been banned in Colombia since 1997 by the Ministry of Health ([ICA, 2012](#)).

In this study both main isomers, α-HCH and γ-HCH, were detected at all sampling sites ([Fig. 1](#)). The α-HCH, showed the

highest concentrations in air (~0.8–19 ng m⁻³) with the highest levels detected at FCNE which is located in the border areas of sugarcane cultivations ([Table 1](#)). Since sugarcane production is one of the main agricultural activities in this region we suspect that, the high levels of α-HCHs could be attributed either to off-gassing from previously treated agricultural soils or to continued usage in agriculture.

These results are far higher, by a factor of 2–3 order of magnitude, than those detected in other studies around Latin American countries using PAS-PUF. For instance, low α-HCH levels (~BDL–0.001 ng m⁻³) were detected in a rural area, of sede Arauca, in Colombia under GAPS network ([Pozo et al., 2009](#)); in remote/background sites in Chile (0.006–0.04 ng m⁻³) by [Pozo et al. \(2004\)](#), in the Bolivian Andes (~BDL to 0.05 ng m⁻³) by [Estellano et al. \(2008\)](#), and in urban sites in Bahía Blanca, Argentina (~0.003–0.02 ng m⁻³) [Tombesi et al. \(2014\)](#) (see SM, [Table S2](#)).

γ-HCH ranged from BDL (0.08) to ~1 ng m⁻³ (0.88 ± 0.61) ([Table 1](#)). These results are higher than other studies in Latin America; in Chile, at remote/background sites (0.003–0.06 ng m⁻³) ([Pozo et al. \(2004\)](#)) and at rural, urban and industrial sites (0.006–0.12 ng m⁻³) ([Pozo et al., 2012](#)), in Bolivia Andes (BDL – 0.02 ng m⁻³) ([Estellano et al., 2008](#)) and in urban sites (~0.001–0.03 ng m⁻³) in Argentina ([Tombesi et al., 2014](#)) and in a rural area (0.03 ng m⁻³) of Sede Arauca in Colombia ([Pozo et al., 2009](#)).

Moreover, the α/γ HCH ratio (~10–20) suggested recent technical HCH mixture utilization. Interestingly, these results were significantly different from other studies in Latin American countries ([Pozo et al., 2004, 2012](#); [Estellano et al., 2008](#); [Meire et al., 2012](#)) and around the world ([Pozo et al., 2009](#); [Bogdal et al., 2013](#); [Halse et al., 2011](#)) which showed a prevalence of lindane in air samples and a transition from the technical HCH mixture to lindane ([Table S2](#)).

3.1.2. Endosulfans (I, and II)

Endosulfan, vapor pressure of 1.05 × 10⁻³ Pa, is a persistent and very volatile compound, that is easily disseminated in the environment after its application. This process allows endosulfan to reach the troposphere and travel great distances in the air, either in the gas and/or particle phases ([Bejarano et al., 2008](#)). Endosulfan distributes with a ratio of 2:1 to 7:3, between the endosulfan I and endosulfan II isomers. Because of its persistence and toxicity, in Colombia, Endosulfan was banned in 2001 by the Council of State ([Nivia, 2001](#)). Because of its threats to human health and the environment, a global ban on the manufacture and use of endosulfan was negotiated under the Stockholm Convention in April 2011. The ban took effect in mid-2012, with certain uses exempted for five additional years ([UNEP, 2011](#)).

In this study, Endosulfan I was the most abundant compound detected with concentrations (ng m⁻³) in air between ~2 and 60 (26 ± 24) ([Table 1](#)). Endosulfan I is oxidized more rapidly in the environment by photolysis, hydrolysis and bio-transformation,

Table 1
Concentrations (ng m⁻³) in air of OCPs in Santiago de Cali, Valle del Cauca in Colombia May–September 2011.

Location	α-HCH	γ-HCH	End I	End II	p,p'-DDE	p,p'-DDT
EF	14 ± 0.04	1 ± 0.02	21 ± 0.06	2 ± 0.03	9 ± 0.03	8 ± 0.05
ERA	0.8 ± 0.01	BDL	2 ± 0.03	0.2 ± 0.03	0.7 ± 0.02	0.3 ± 0.04
CRG	10 ± 0.03	1 ± 0.02	23 ± 0.06	0.1 ± 0.03	9 ± 0.03	10 ± 0.05
FCNE	20 ± 0.05	1 ± 0.02	60 ± 0.2	0.8 ± 0.03	23 ± 0.06	4 ± 0.04
IDL(ng m ⁻³)	0.01	0.015	0.026	0.026	0.019	0.041
MDL (ng m ⁻³)	0.005	0.008	0.013	0.013	0.01	0.02
Vair (m ³)	190	250	410	410	510	520

aOCP: (α,γ-HCH) hexachlorocyclohexanes, (End I, II) endosulfan I, endosulfan II, (o,p'-DDE, p,p'-DDE) dichlorodiphenyldichloroethylene, (o,p'-DDD) dichlorodiphenyldichloroethane, (p,p'-DDT) dichlorodiphenyltrichloroethane. IDL: instrumental detection limit; BDL: Below Detection Limit.

Table 2
Concentrations (pg m^{-3}) in air of PCBs in Santiago de Cali Valle del Cauca in Colombia May–September 2011.

Location	–28	–52	–95	–99	–101	–110	–118	–123	–138	–146	–149	–151	–153	–157	–167	–177	–180	–187	$\Sigma_{18}\text{PCB}$
EF	34 ± 2	16 ± 2	460 ± 8	14 ± 2	34 ± 1	30 ± 2	100 ± 8	140 ± 8	<6 ± 6	BDL	BDL	BDL	<8 ± 8	BDL	8 ± 2	3 ± 2	BDL	BDL	850
ERA	46 ± 2	10 ± 2	140 ± 8	9 ± 2	20 ± 1	8 ± 2	BDL	110 ± 8	7 ± 6	BDL	<8 ± 8	BDL	10 ± 8	BDL	7 ± 2	BDL	BDL	<2 ± 2	370
CRG	20 ± 2	BDL	100 ± 8	BDL	16 ± 1	BDL	BDL	70 ± 8	BDL	BDL	BDL	BDL	BDL	2 ± 2	5 ± 2	BDL	BDL	BDL	220
FCNE	140 ± 2	30 ± 7	BDL	BDL	60 ± 1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	<8 ± 8	BDL	23 ± 2	<2 ± 2	4 ± 2	BDL	270
IDL (pg m^{-3})	3	14	16	3	2	3	15	15	13	15	15	15	15	4	4	4	4	4	
MDL (pg m^{-3})	1.5	7	8	1.5	1	1.5	8	8	6	8	8	8	8	2	2	2	2	2	
Vair (m^3)	290	360	450	480	470	500	520	520	530	520	510	510	520	540	530	540	540	530	

IDL: instrumental detection limit; BDL: Below Detection Limit.

Table 3
Concentrations (ng m^{-3}) in air of PAHs in Santiago de Cali Valle del Cauca in Colombia May–September 2011.

Location	Acy	Ace	Flu	Phe	Flt	Pyr	BaA	Chry	BbF	BaP	I123cdP	DahA	BghiP	$\Sigma_{13}\text{PAH}$
EF	0.5 ± 0.002	0.8 ± 0.002	2 ± 0.005	14 ± 0.03	8 ± 0.02	8 ± 0.02	4 ± 0.01	3 ± 0.01	1 ± 0.003	2 ± 0.005	0.3 ± 0.01	3 ± 0.01	3 ± 0.01	49
ERA	0.8 ± 0.003	0.6 ± 0.002	3 ± 0.01	21 ± 0.05	13 ± 0.03	12 ± 0.03	5 ± 0.01	6 ± 0.01	1 ± 0.003	0.8 ± 0.003	BDL	0.5 ± 0.002	0.6 ± 0.003	66
CRG	0.3 ± 0.002	0.6 ± 0.002	2 ± 0.005	10 ± 0.03	5 ± 0.01	4 ± 0.01	4 ± 0.01	1 ± 0.003	0.1 ± 0.001	BDL	BDL	0.3 ± 0.002	0.4 ± 0.003	26
FCNE	BDL	0.6 ± 0.002	2 ± 0.005	11 ± 0.03	4 ± 0.01	3 ± 0.01	2 ± 0.01	1 ± 0.003	BDL	BDL	BDL	BDL	0.8 ± 0.003	25
IDL (ng m^{-3})	0.0017	0.001	0.0017	0.0017	0.0035	0.0019	0.0004	0.0004	0.0014	0.0018	0.0075	0.0017	0.0028	
MDL (ng m^{-3})	0.0009	0.0005	0.0009	0.009	0.0017	0.001	0.0002	0.0002	0.0007	0.0009	0.0038	0.0009	0.0014	
Vair (m^3)	30	40	90	200	450	450	530	530	550	550	550	550	550	

PAH: (Acy) Acenaphthylene, (Ace) Acenaphthene, (Flu) Fluorene, (Phe) Phenanthrene, (Flt) Fluoranthene, (Pyr) Pyrene, (BaA) Benzo(a)anthracene, (Chry) Chrysene, (BbF) Benzo(b)fluoranthene, (BaP) Benzo(a)pyrene, (I123cdP) Indeno(123cd)pyrene, (DahA) Dibenz(a,h)anthracene, (BghiP) Benzo(ghi)pyrene, (Anthracene was not reported because analytical interference). IDL: instrumental detection limit; BDL: Below Detection Limit.

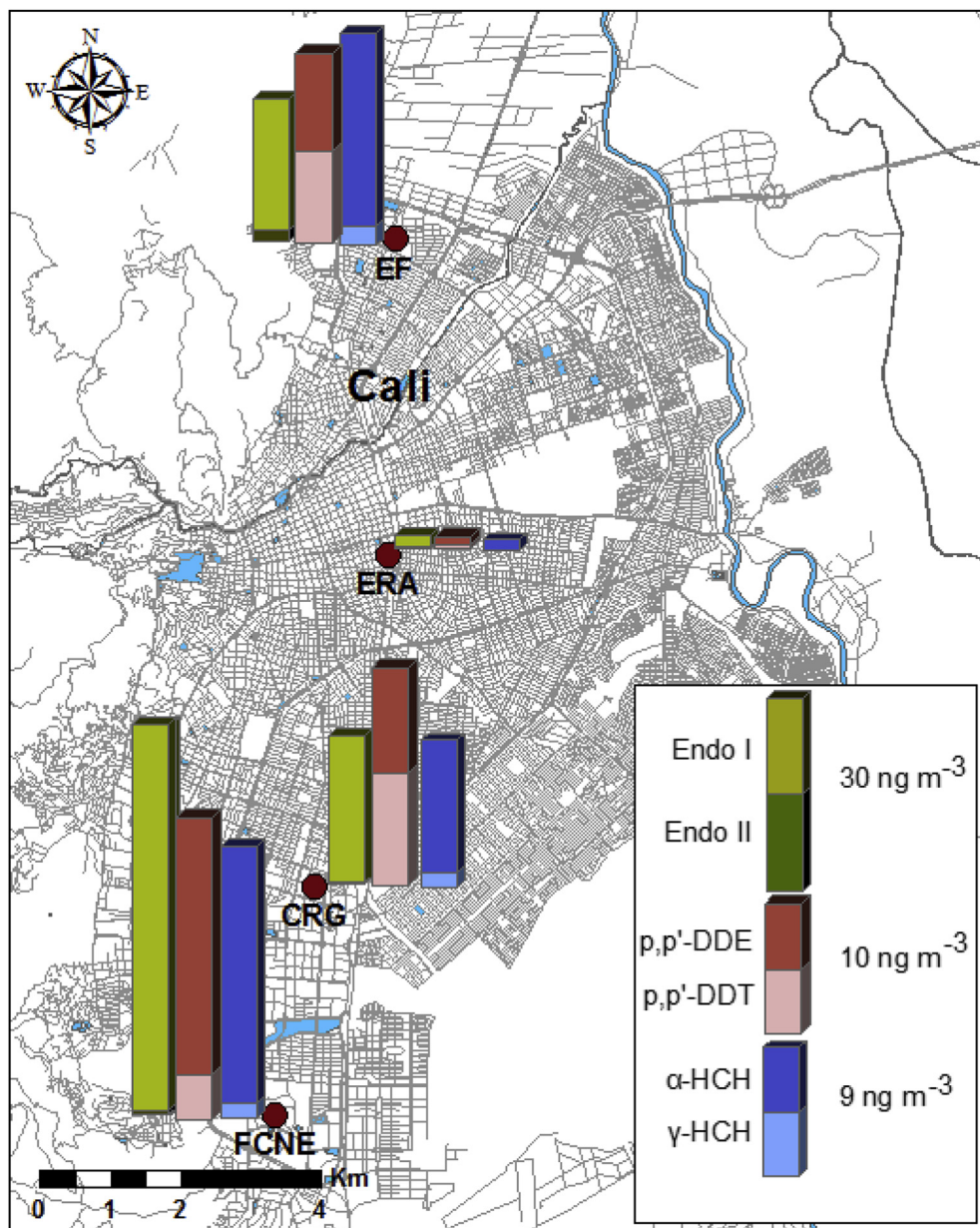


Fig. 1. Concentration in air of OCPs in a north-south transect in the city of Santiago de Cali, Valle del Cauca in Colombia. Map source: OpenStreetMap (OSM).

forming predominantly Endosulfan II and endosulfan sulfate (SO₄) (POPRC, 2009). Endosulfan II was also found and ranged from ~0.8 to 2 ng m⁻³, however Endo SO₄ was not reported in part due to analytical problems (low GC–MS sensitivity) for this degradation product.

These findings are in keeping with other studies using PAS-PUF, in particular at agricultural areas, around the world i.e., in Mudhol-India (0.4–21 ng m⁻³) (Pozo et al., 2011), in Buenos Aires, Argentina (0.15–15 ng m⁻³) (Pozo et al., 2009; Tombesi et al., 2014), and in Mazatlan, Mexico (27 ng m⁻³) (Wong et al., 2009). Nevertheless, these results were much higher (by a factor of 2–3 times) than other studies in Latin America (Table S2). The predominance of Endosulfan I is also consistent with data reported under the Global Atmospheric Passive Sampling (GAPS) network showing concentrations from tens to thousands of pg m⁻³ (Pozo et al., 2009). Bejarano et al., 2008, also reported the predominance of Endosulfan I, accounting for over 90% of total endosulfan concentrations detected in the environment.

3.1.3. Dichlorodiphenyltrichloroethane (DDTs)

DDT is a mixture of two closely related compounds: *p,p'*-DDT (85%), *o,p'*-DDT (15%) and small amounts of *o,p'*-DDT, and may also contain *p,p'*-DDE and *p,p'*-DDD as impurity (ATSDR, 2012). In Colombia about 9220 tons of DDT were imported to control malaria-transmitting vectors, and was banned in 1993 by the Ministry of Health (ICA, 2012). Both, *p,p'*-DDE and *p,p'*-DDD are more stable breakdown products of DDT, and have a longer life, being also quite toxic (Ortiz et al., 2001). The *p,p'*-DDE is up to eight times more volatile than *p,p'*-DDT, while *p,p'*-DDD is five times less volatile than DDT (Ortiz et al., 2001).

In this study two DDT isomers were routinely detected including *p,p'*-DDT, and *p,p'*-DDE (Fig. 1). *p,p'*-DDE showed the highest concentrations (ng m⁻³) in air from ~0.7–23 (10 ± 9), and accounted for 50–80% of total DDT concentrations while *p,p'*-DDT ranged from ~0.3–10 (6 ± 4) (Table 1). These results are higher than those reported in other studies in Latin America using PAS-PUF. Wong et al. (2009), across Mexico, detected concentration for ΣDDTs in the

range of $\sim 0.02\text{--}2\text{ ng m}^{-3}$. Much lower values (ng m^{-3}) were found in the Bolivian Andes by Estellano et al. (2008) (from BDL to 0.1), and across South America (from \sim BDL to 0.01) (Poza et al., 2009; Bogdal et al., 2013). However, similar DDT values were found in agricultural areas of India ($0.06\text{--}9\text{ ng m}^{-3}$) (Poza et al., 2011) and at Kenia in Africa (90 ng m^{-3}) (Klánová et al., 2009) (see SM, Table S2).

Fig. 1 shows high levels of p,p' -DDE and p,p' -DDT along the transect with the highest concentrations at the agricultural site of FCNE (23 ng m^{-3}). Concentrations at urban and industrial areas were approximately ~ 3 times lower, with the exception of the ERA site, downtown of the city, showing the lowest levels (0.7 ng m^{-3}). In general, p,p' -DDT/ p,p' -DDE ratio less than one (>1) is indicative of aged DDT whereas a ratio greater than one (>1) suggests fresh inputs. At Santiago de Cali p,p' -DDT/ p,p' -DDE ($0.1\text{--}1$) ratio were indicative of aged DDT sources probably related to previously treated agricultural soil.

3.2. Polychlorinated biphenyls (PCBs)

PCBs are stable and resistant to thermal, chemical and biological degradation and are highly toxic. They are a non-flammable insulating liquid mainly used in electrical transformers and capacitors. Since 1997, in Colombia, actions have been taken to eliminate these substances (MAVDT et al., 2007). In 2005, a preliminary national inventory was elaborated and reported ~ 926 tons of PCBs produced by electrical equipment, manufacturing processes and in the hydrocarbon industrial sector; for example the department of Valle del Cauca contributes about $\sim 15\%$ of total PCBs in the country (MAVDT et al., 2007).

Results for $\Sigma_{18}\text{PCB}$ are summarized in Fig. 2 and Table 2. Concentrations of PCBs in air (pg m^{-3}) were detected at all sampling sites ranging from 220 (at CRG site, UR) to 850 (at EF, IND) and showed a clear decreasing concentration gradient from North (IND

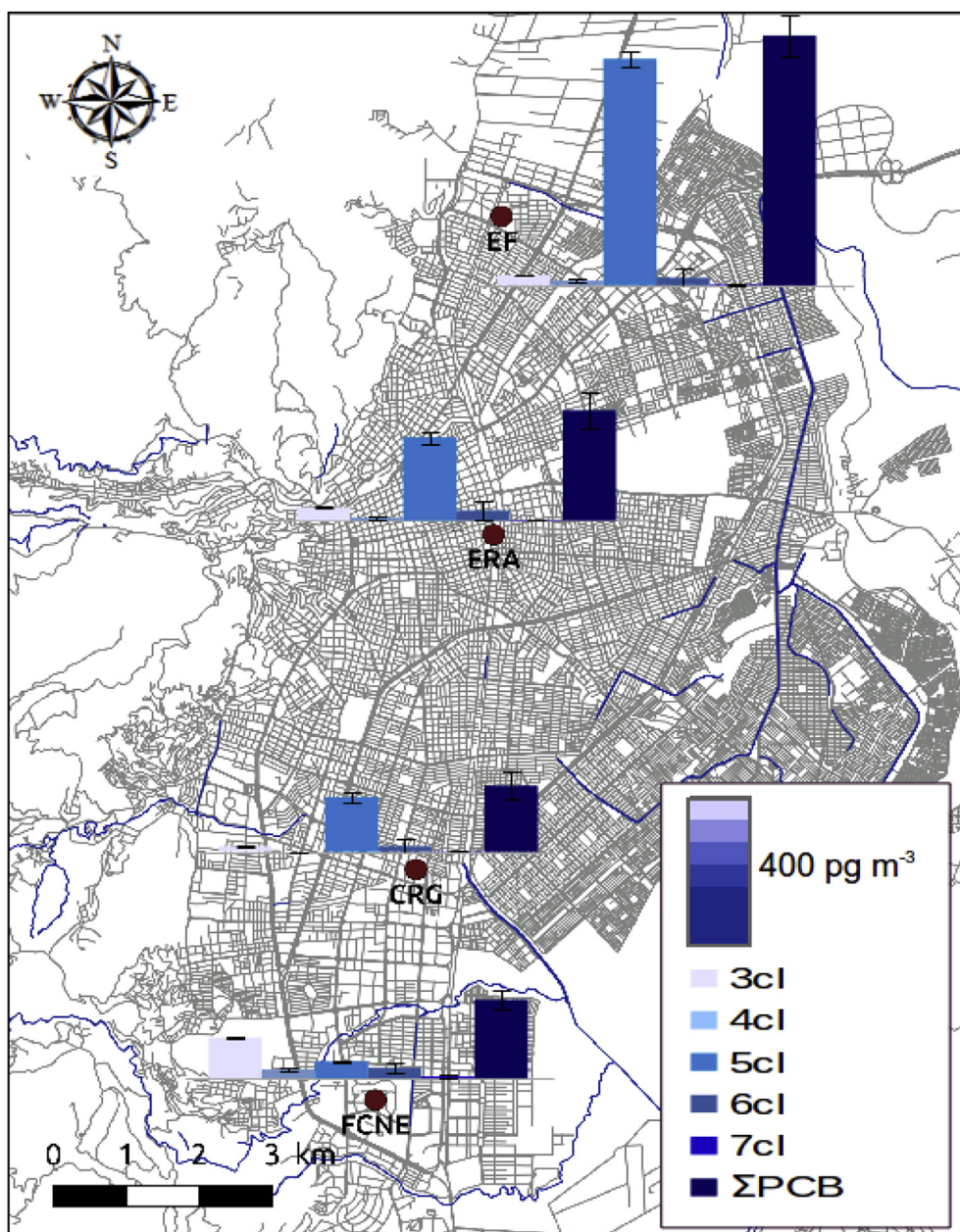


Fig. 2. Concentration in air (\pm expanded uncertainty) of total PCBs and homolog composition in a north-south transect in the city of Santiago de Cali, Valle del Cauca in Colombia. Map source: OpenStreetMap (OSM).

site) to South (AG site) transect (by a factor of ~3 times) (Fig. 2). These results are likely influenced by the industrial area of the city of Yumbo, that host ~2000 industries (Table S2), and borders the north-east site of Santiago de Cali. Yumbo could act as a source of PCBs because, it has been reported, that there are still older electrical equipments/transformers, still in use in that area, that contains PCB fluids (ATSDR, 2012). Therefore, PCBs could enter the environment through accidental fires creating spills, discarded transformers or through leakage from closed systems such as older electrical equipment (ATSDR, 2012).

The PCB profile at most of the sampling sites was dominated by 5-Cl accounting 20–80% (Fig. 2). However, two PCB homolog composition patterns were observed, first at the IND and UR sites (60–80% of 5-Cl) and second at AG site (FCNE) with 4-Cl (20%), 5-Cl (40%) and 6-Cl (20%). This profile is consistent with other studies at urban and industrial areas in Concepcion, Chile (Pozo et al., 2012)

and at Izmir, Turkey (Kaya et al., 2012). Table 2 show a list of targeted individual PCBs. The major PCB contribution was from PCB congeners –95, –118 and –123 accounting for ~70% of total PCB concentrations.

The concentrations found in the present study are similar to those found in other studies using PUF PAS in Latin America (pg m^{-3}), such as in Mexico City (90–800) (Bohlin et al., 2008), and in Brasil (60–620) (Meire et al., 2012). Nevertheless, the concentrations (pg m^{-3}) were higher than the results obtained in Concepción, Chile (40–350) (Pozo et al., 2012), in urban areas in the Province of Buenos Aires (40–360) (Tombesi et al., 2014), and in Latin American countries (200) (Bogdal et al., 2013) and much higher, with a factor of ~5–20, than those values reported at back ground areas i.e., Chile Mountains from 2 to 50 (Pozo et al., 2004), in the Bolivian Andes (0.1–12) (Estellano et al., 2008), across South America in the GAPS Study (BDL to 146) (Pozo et al., 2009).

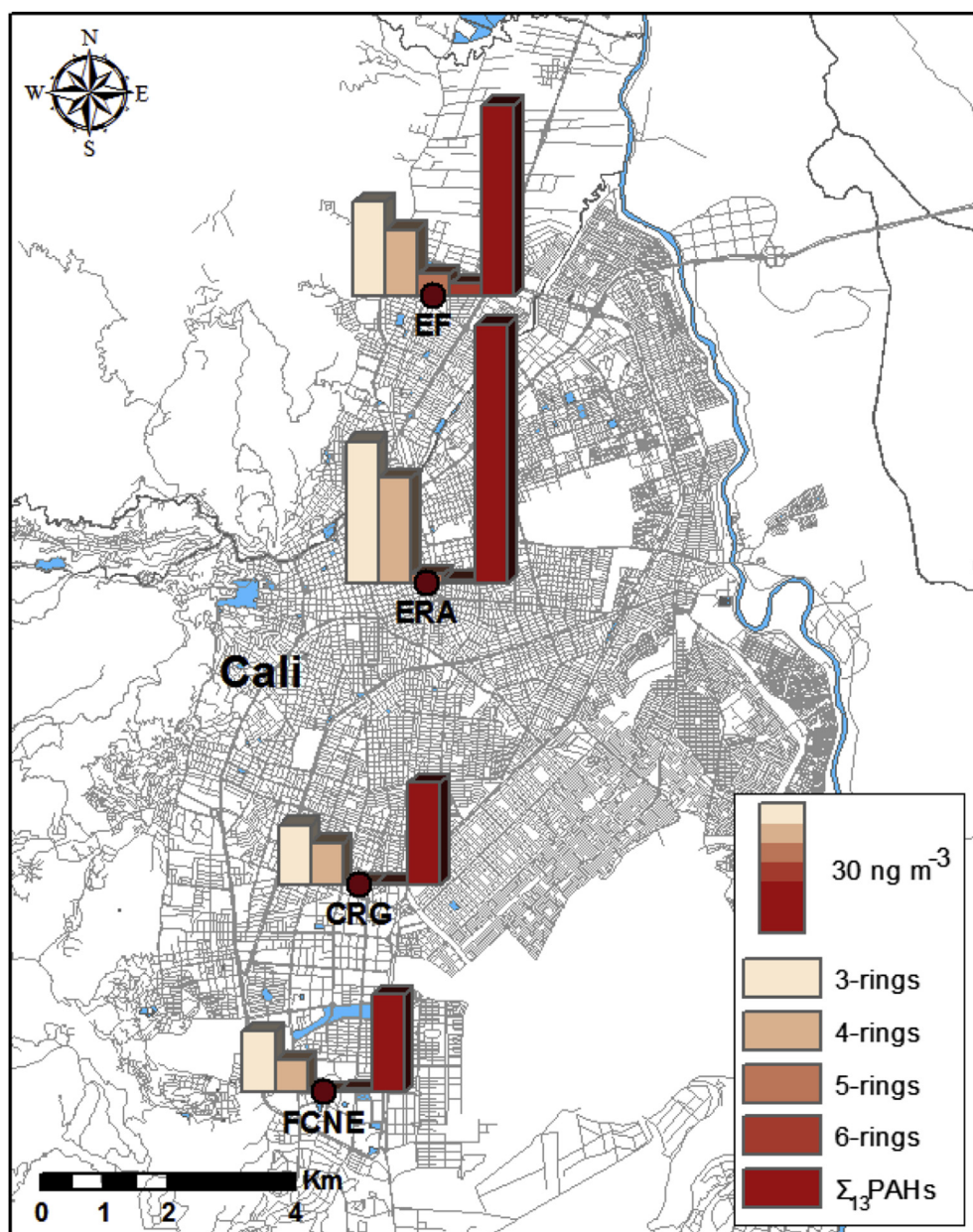


Fig. 3. Concentration in air of total PAHs composition in a north-south transect in the city of Santiago de Cali, Valle del Cauca in Colombia. Map source: OpenStreetMap (OSM).

3.3. Polycyclic aromatic hydrocarbons (PAHs)

The PAHs are a class of organic compounds produced by incomplete combustion or high-pressure processes. PAHs consist of three or more fused benzene rings containing only carbon and hydrogen (Jaward et al., 2004b). PAHs are neutral, nonpolar molecules; they are found in fossil fuels (oil and coal) and in tar deposits, and are produced, generally, when insufficient oxygen or other factors result in incomplete combustion of organic matter (e.g., in engines and incinerators, when biomass burns in forest fires, etc.) In general, they are volatile and relatively persistent as well as susceptible to long range atmospheric transport (LRAT) (MAVDI, 2007).

Table 3 summarizes the concentration of total and individual PAHs compounds at the four sites in Santiago de Cali. The concentrations (ng m^{-3}) of total PAHs in air ranged from 25 to 66 and showed a clear decreasing concentration gradient from the northern (ERA site downtown, UR) to southern (FCNE site, AG) transect (by a factor of ~ 3 times) (Fig. 3). The highest levels are probably associated to different factors like firstly the intensive vehicular traffic because there are a high number of routes crossing the city center (Figure S1). According to DAGMA, the mobile emissions contribute with 60% to environmental pollution in the city (Möller, 2003). Secondly, the potential influence of Forest fires in the area of “Farallones” (~ 10 Km). This is supported by the wind prevalence which come from the west part of the city (see SM, Figure S4), where forest fires are frequently recorded, facilitating the transport from the Pacific area through the “Farrallones” to Santiago de Cali downtown (ERA site).

These values are slightly lower than those reported in other urban and industrial areas. For instance, Pozo et al. (2012) found concentrations in the range of 40–230 ng m^{-3} at urban and industrial sites in Concepción city, Chile (Pozo et al., 2012), and Bohlin et al. (2008) detected levels of 6–92 ng m^{-3} at Mexico City and at Gothenburg, Sweden (7.7–180 ng m^{-3}). In other selected studies, Kaya et al. (2012) reported levels from 2 to 800 ng m^{-3} in industrial areas of Izmir, Turkey; and Santiago and Cayetano, 2007 reported levels of 40–170 in Manila, Philippines.

From the 14 PAHs detected, three individual PAHs showed the highest concentrations at all sites i.e., phenanthrene (~ 10 –20 ng m^{-3}), followed by fluoranthene (4–13 ng m^{-3}) and pyrene (3–12 ng m^{-3}) which are primarily in the gas-phase (Odabasi et al., 2006). The percentage (%) of PAHs composition accounted 55% for 3-rings, 38% for 4-rings, 5% for 5-rings and 3% for 6-rings. These results are similar to those found in Mexico City (96% by 3- and 4- rings) (Bohlin et al., 2008), and in Concepcion, Chile (90% for 3- and 4-ring) (Pozo et al., 2012). The prevalence of the 3- and 4- rings PAHs are also in keeping with other PAHs patterns reported around the world, for example, in the Tuscany region (Italy) (Estellano et al., 2012) and Puglia region (Italy) (Estellano et al., 2014), in the Philippines (Santiago and Cayetano, 2007), in Fairbanks (Alaska) (Gouin et al., 2008), and across Europe (Jaward et al., 2004b; Halse et al., 2011).

4. Conclusion

The results of this north-south transect in Santiago de Cali study demonstrate the useful and practical application of passive air samplers to assess spatial distribution of SVOCs. This study identified some chemical for which the city of Santiago de Cali (e.g., PCBs, PAHs) and Valle del Cauca agricultural activities (e.g., OCPs) act as likely sources exhibiting a strong decreasing concentration gradient.

For OCPs, Endosulfan, α -HCHs, and DDTs recorded the highest concentrations in air and were higher by a factor of 2–3 order of magnitude, than those reported in other studies in Latin American

countries. This is probably the result of likely current and/or past usage of these chemicals in rural/agricultural areas, located in the close proximity of the study area, and consistent with the high production of sugarcane in the department of Valle del Cauca. The α/γ HCH ratio (~ 10 –20) suggested a current or past use of the technical HCH mixture in the agricultural fields of Valle del Cauca while the p,p' -DDT/ p,p' -DDE ratio indicated aged DDT utilization. However, more research is needed to assess the contribution primary and secondary sources.

High levels of PCBs in the northern sites are likely influenced by the industrial city of Yumbo (~ 2000 industries) acting as a source. For PAHs, the high concentrations are mainly attributed to direct combustion sources such as high vehicular density and industrial activities taking place within and outside the city. The passive sample data presented here for PAHs and PCBs were relatively similar compared to, other industrial and urban, areas of Latin America.

These results contribute new and useful data of SVOCs in the atmosphere of Santiago de Cali and Valle del Cauca. This investigation contributes significantly to improving the knowledge of some chemicals, listed as POPs, under the Stockholm Convention in Colombia. Further research is still needed in order to assess the potential of human exposure to this type of atmospheric pollutants in other urban and agricultural areas of Colombia.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apr.2016.05.006>.

References

- ATSDR (Agencia para Sustancias Tóxicas y el Registro de Enfermedades), 2012. <http://www.atsdr.cdc.gov/> (accessed in July 2012).
- Alegria, H., Bidleman, T., Salvador, M., 2006. Organochlorine pesticides in the ambient air of Chiapas, Mexico. *Environ. Pollut.* 140, 483–491.
- Bejarano, F., Souza, J., Weber, J.M., Guadarrama, C., Escamilla, E., Beristáin, B., Acosta, M., Cárcamo, M.I., Ramírez, F., 2008. El endosulfán y sus alternativas en América Latina. http://www.rap-al.org/articulos_files/Alternativas_12_Julio.pdf (accessed in August 2012).
- Bogdal, C., Abad, E., Abalos, M., van Bavel, B., Hagberg, J., Scheringer, M., Fiedler, H., 2013. Worldwide distribution of persistent organic pollutants in air, including results of air monitoring by passive air sampling in five continents. *Trends Anal. Chem.* 46, 150–161.
- Bohlin, P., Jones, K., Tovalin, H., Strandberg, B., 2008. Observations on persistent organic pollutants in indoor and outdoor air using passive polyurethane foam samplers. *Atmos. Environ.* 45, 7234–7241.
- Cali en cifras, 2011. Alcaldía de Santiago de Cali. Departamento administrativo de Planeación.
- Cortés, J., Gonzáles, C.M., Morales, L., Abalos, M., Abad, E., Aristizabal, B.H., 2014. 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. *Sci. Total Environ.* 491, 67–74.
- Cortés, J., Cobo, M., Gonzáles, C.M., Gómez, C.D., Abalos, M., Aristizabal, B.H., 2016. Environmental variation of PCDD/Fs and dl-PCBs in two tropical Andean

- Colombian cities using passive samplers. *Sci. Total Environ.* <http://dx.doi.org/10.1016/j.scitotenv.2016.02.094> (In press).
- Estellano, V.H., Pozo, K., Harner, T., Zaballa, M., Franken, M., 2008. Altitudinal and seasonal variation of persistent organic pollutants in the Bolivian Andes mountains. *Environ. Sci. Technol.* 42, 2528–2534.
- Estellano, V.H., Pozo, K., Harner, T., Corsolini, S., Focardi, S., 2012. Using PUF disk passive samplers to simultaneously measure air concentration of persistent organic pollutants (POPs) across the Tuscany Region, Italy. *Atmos. Pollut. Res.* 3, 88–94.
- Estellano, V.H., Pozo, K., Silibello, C., Mulder, M.D., Efstathiou, C., Tomasino, M., Funaro, F., Donadio, 2014. Characterization of urban pollution in two cities of the Puglia region in Southern Italy using field measurements and air quality (AQ) model approach. *Atmos. Pollut. Res.* 5, 34–41.
- Fernández, P., Grimalt, J., 2003. On the global distribution of persistent organic pollutants. *Environ. Anal.* 57, 514–521.
- FONADE, 2016. Fondo Financiero de Proyectos de Desarrollo. Valle del Cauca. https://www.fonade.gov.co/GeoTec/inventario1/zonas/Valle_del_Cauca.php (accessed in April 2016).
- Gouin, T., Shoeib, M., Harner, T., 2008. Atmospheric concentrations of current-use pesticides across south-central Ontario using monthly-resolved passive air samplers. *Atmos. Environ.* 42, 8096–8104.
- Halse, A.K., Schlabach, M., Eckhardt, S., Sweetman, A., Jones, K.C., Breivik, K., 2011. Spatial variability of POPs in European background air. *Atmos. Chem. Phys.* 11, 1549–1564.
- ICA (Instituto Colombiano Agropecuario), 2012. Restricciones, prohibiciones y suspensión de registros de plaguicidas de uso agrícola en Colombia. <http://www.ica.gov.co> (accessed in July 2012).
- Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J., Jones, K.C., 2004a. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environ. Sci. Technol.* 38, 34–41.
- Jaward, F.M., Farrar, J.J., Harner, T., Sweetman, A.J., Jones, K.C., 2004b. Passive air sampling of polycyclic aromatic hydrocarbons and polychlorinated naphthalenes across Europe. *Environ. Toxicol. Chem.* 23, 1355–1364.
- Kaya, E., Dumanoglu, Yetkin, Kara, Melik, Altiok, H., Bayram, A., Elbir, T., Obadasi, M., 2012. Spatial and temporal variations and air-soil exchange of atmospheric PAHs and PCBs in an industrial region. *Atmos. Pollut. Res.* 3, 435–449.
- Klánová, J., Cupr, P., Holoubek, I., Boruvková, J., Příbylová, P., Kares, R., Tomšej, T., Ocelka, T., 2009. Monitoring of persistent organic pollutants in Africa. Part 1: Passive air sampling across the continent in 2008. *J. Environ. Monit.* 11, 1952–1963.
- MAVDT, 2007. Ministerio de Ambiente, Vivienda y Desarrollo Territorial, Global Environment Facility, Banco Mundial, 2007. Inventario preliminar de compuestos bifenilopoliclorados-PCB existentes en Colombia. Proyecto de actividades habilitadoras en el marco del Convenio de Estocolmo sobre contaminantes orgánicos persistentes (COP) (Bogotá D.C. Colombia).
- MAVDT, 2007. Ministerio de Ambiente, Vivienda y Desarrollo Territorial, 2010. Plan Nacional de Aplicación del Convenio de Estocolmo sobre Contaminantes Orgánicos Persistentes (COP), en la República de Colombia—PNA (Bogotá D.C. Colombia).
- Meire, R.O., Lee, S.C., Targino, A.C., Torres, J.P.M., Harner, T., 2012. Air concentrations and transport of persistent organic pollutants (POPs) in mountains of southeast and southern Brazil. *Atmos. Pollut. Res.* 3, 417–425.
- Möller, M., 2003. Movilidad de personas, transporte urbano y desarrollo sostenible en Santiago de Cali, Colombia. Universidad del Valle, Colombia.
- Nivia, E., 2001. Prohibición del endosulfan en Colombia. Breve Historia. http://www.rap-al.org/db_files/PlaguicidAL_PpioAc_Endosulfan_ProhibicionColombia_2001.pdf (accessed in September 2015).
- Odabasi, M., Cetin, E., Sofuoglu, A., 2006. Determination of octanol-air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: application to gas-particle partitioning in an urban atmosphere. *Atmos. Environ.* 40, 6615–6625.
- Ortiz, M., Yáñez, L., Díaz, F., 2001. Comportamiento Ambiental del DDT y de la Deltametrina. Universidad Autónoma de San Luis Potosí, México.
- POPRC (Persistent Organic Pollutants Review Committee), 2009. Endosulfan: Supporting Document for the Draft Risk Profile. UNEP. <http://www.cseindia.org/userfiles/background%20document.pdf> (accessed in August 2012).
- Pozo, K., Harner, T., Shoeib, M., Urrutia, R., Barra, R., Parra, O., Focardi, S., 2004. Passive sampler derived air concentrations of persistent organic pollutants on a north-south transect in Chile. *Environ. Sci. Technol.* 38, 6529–6537.
- Pozo, K., Harner, T., Wania, F., Muir, D., Jones, K., Barrie, L., 2006. Toward a Global network for persistent organic pollutants in air: results from the GAPS Study. *Environ. Sci. Technol.* 40, 4867–4873.
- Pozo, K., Harner, T., Lee, S., Sinha, R., Sengupta, B., Loewen, M., Geethalakshmi, V., Kannan, K., Volpi, V., 2011. Assessing seasonal and spatial trends of persistent organic pollutants (POPs) in Indian agricultural regions using PUF disk passive air samplers. *Environ. Pollut.* 159, 646–653.
- Pozo, K., Harner, T., Lee, S.C., Wania, F., Muir, D.C.G., Jones, K.C., 2009. Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS study. *Environ. Sci. Technol.* 43, 796–803.
- Pozo, K., Harner, T., Rudolph, A., Oyola, G., Estellano, V.H., Ahumada Rudolph, R., Garrido, M., Pozo, K., Mabilia, R., Focardi, S., 2012. Survey of persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) in the atmosphere of rural, urban and industrial areas of Concepcion, Chile, using passive air samplers. *Atmos. Pollut. Res.* 3, 426–434.
- Santiago, E.C., Cayetano, M.G., 2007. Polycyclic aromatic hydrocarbons in ambient air in the Philippines derived from passive sampler with polyurethane foam disk. *Atmos. Environ.* 41, 4138–4147.
- Shoeib, M., Harner, T., 2002. Characterization and comparison of three passive air sampler for persistent organic pollutants. *Environ. Sci. Technol.* 36, 4142–4151.
- Tombesi, N., Pozo, K., Harner, T., 2014. Air concentrations of Persistent Organic Pollutants (POPs) in agricultural and urban areas in the Province of Buenos Aires in Argentina using PUF disk passive air samplers. *Atmos. Pollut. Res.* 5, 170–178.
- UNEP (Programa de las Naciones Unidas para el Medio Ambiente), 2006. Perfil de Riesgos del Lindano. <http://chm.pops.int/Portals/0/Repository/poprc2/UNEP-POPS-POPRC.2-17-Add.4.Spanish.PDF> (accessed in August 2012).
- UNEP (United Nations Environment Programme), 2010. Stockholm Convention on Persistent Organic Pollutants (POPs). <http://chm.pops.int/TheConvention/Overview/History/Overview/tabid/2232/Default.aspx> (accessed in September 2015).
- UNEP (United Nations Environment Programme), 2011. The New POPs under the Stockholm Convention. <http://chm.pops.int/Implementation/NewPOPs/TheNewPOPs/tabid/672/Default.aspx> (accessed in December 2012).
- Wong, F., Alegria, H., Bidleman, T., et al., 2009. Passive air sampling of Organochlorine Pesticides in Mexico. *Environ. Sci. Technol.* 43, 704–710.