Occurrence and Distribution of Persistent Organic Pollutants (POPs) in the Atmosphere of the Andean City of Medellin, Colombia.

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Research Article

Abstract

Passive air sampling (PAS) was used to evaluate organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), hexabromocyclododecanes (HBCDDs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and per- and polyfluoroalkyl substances (PFASs) in the atmosphere of Medellin, Colombia. This was in accordance with a special initiative of the Global Monitoring Plan (GMP), which was implemented to provide information on new and emerging persistent organic pollutants (POPs).

PAS was carried out for three months (four quartiles per year) over two consecutive years (2017 and 2018), and two punctual peaks of contamination in the monitored time were observed. The first peak was related to chlorinated compounds in the quartile 2017-Q3, in which the highest concentration of pentachlorobenzene (PeCB, 755.5 $pg\cdot m^{-3}$) was observed, and air concentration of PeCB in quartile 2018-Q4 (125.0 $pg\cdot m^{-3}$) was 3.7 times more than the initial concentration (33.7 $pg\cdot m^{-3}$). These results may be associated with waste incineration in or near the city. The second peak of contamination was associated with brominated compounds in the quartile 2018-Q1, which could be linked to recycling, incineration, and landfill deposit of these compounds. In this peak, the highest levels of PBDEs and HBCDD-isomers were observed (Σ_{10}PBDEs, 107.2 $pg\cdot m^{-3}$ and Σ_3HBCDDs-isomers, 289.0 $pg\cdot m^{-3}$). With regard to the concentrations of PBDEs, HBCDDs, PCDDs, and PCDFs, these showed a slight tendency to increase between 2017 and 2018. Finally, constants concentrations of pollutants such as DDT isomers and dieldrin were observed, although these compounds were banned in Colombia many years ago. In contrast, a slight decrease in some pollutants, such as aldrin, and α-endosulfan, was observed.

Our study allowed the assessment of air levels of chlorinated, brominated, and fluorinated pollutants in Medellin, Colombia. These results provide an overall view of POPs levels and represent an initial attempt to identify local sources in order to monitor and surveillance the releases of these pollutants in the city and country.

1 Introduction

Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), organochlorine pesticides (OCPs), polybrominated biphenyls (PBBs), hexabromocyclododecanes (HBCDDs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and per- and polyfluoroalkyl substances (PFASs) are a group of organic chemicals recognized as persistent organic pollutants (POPs) that, due to their physicochemical properties, are toxic, persistent, exhibit potential to be biomagnified throughout the food chain, and have inherent toxicity to wildlife and humans (Fitzgerald and Wikoff, 2014; Lohmann et al., 2007). Moreover, these compounds can travel through air, water and migratory species, and have been shown to travel across international boundaries, allowing a global distribution (Lohmann et al., 2007; Wöhrnschimmel et al., 2016).

Although POPs are restricted under the Stockholm Convention, they are released as by-products of chlorinated hydrocarbons, internal combustion engines, and thermal processing of waste (Cortés et al., 2016; Lee et al., 2004; Villa et al., 2016). The quantity of POPs originating from these sources is such that they are even found in quantitative levels in abiotic and biotic matrices around large Latin American and Caribbean urban areas (Bogdal et al., 2013; Rauert et al., 2018a; Saini et al., 2020).

The Stockholm Convention on POPs, created in 2001 under the auspices of the United Nations Environmental Program, is a multilateral environmental treaty aimed at reducing and ultimately eliminating the release of these compounds into the environment and subsequent human exposure (Rauert et al., 2018b; Villa et al., 2016). One of the major pillars for the evaluation of compliance with the Convention is the monitoring of data in core media through the Global Monitoring Plan for POPs (GMP) (Magulova and Priceputu, 2016). The air is a selected matrix under the GMP, given that atmospheric transport has been identified as the key global dispersal mechanism for most legacy POPs (Lohmann et al., 2007; Schuster et al., 2015). Moreover, air monitoring data are important in order to identify changes in the concentrations of atmospheric contaminants over time and to provide information on their regional and global environmental transport. However, the generally low concentrations of POPs in air mean that elaborate sampling techniques, and comprehensive analytical methods and resources, are required. Although several monitoring studies on POPs in the air at a global scale have been conducted, atmosphere monitoring of POPs remains a challenging task (Bogdal et al., 2013).

Studies of POP in atmosphere have used passive or active samplers (Abad et al., 2007; Bogdal et al., 2013; Rivera-Austrui et al., 2011). Active air samplers require an electric pump to pass the air through the adsorbent, while passive air sampling (PAS) requires the diffusive uptake of chemical vapor in an adsorbent across time. In the case of PAS, the amount of vapor adsorbed during sampling can be related in terms of volumetric air concentrations based on a quantitative interpretation of them (Wania and Shunthirasingham, 2020). The use of PAS is widespread globally because of their ease of handling; low price; simple operation, as there is no need for calibration; and the fact that no electrical connection is required (Romo-Melo et al., 2018; Wania and Shunthirasingham, 2020). Passive samplers employ several different materials and methods for analysis of gases, such as polyurethane foam (PUF) disks, which have proved to be an adequate adsorbent for deposition of particles (Shoeib and Harner, 2002).

According to the literature, several studies have used passive sampling to support monitoring plans in different parts of the world. For example, the PUFs-PASs used in the present research are similar to the devices used in the regional and local monitoring of POPs in previous studies in Latin America and Colombia (Cortés et al., 2016, 2014; Rauert et al., 2018a, 2018b; Saini et al., 2020; Schuster et al., 2015).

In Colombia, passive monitoring data of PCDDs, PCDFs and dioxin-like PCBs (dl-PCBs) has been carried out in two tropical Andean cities, specifically Manizales and Bogotá, to identify potential sources of POPs contamination. High concentrations of PCDD/Fs were observed in Bogotá, ranging from 373 $fg \cdot m^{-3}$ and 26.5 $fgWHO_{2005}\text{-}TEQ \cdot m^{-3}$ and high dioxin concentrations were found throughout the range of congeners (Cortés et al., 2016).

Meanwhile, in Manizales higher PCDD/Fs concentrations were found in high vehicular density areas (151 $fg \cdot m^{-3}$ and 7.0 $fgWHO_{2005}$-TEQ$\cdot m^{-3}$), than in residential areas (64 $fg \cdot m^{-3}$ and 3.6 $fgWHO_{2005}$-TEQ$\cdot m^{-3}$) (Cortés et al., 2016).

Likewise, the network Global Atmospheric Passive Sampling (GAPS) has been established the monitoring in the Group of Latin American and Caribbean Countries (GRULAC) region in Colombia (Bogotá, Manizales and Arauca), Brazil (São Luis, São Paulo and São Jose dos Ausentes), Mexico (Sonora, Yucatan), Costa Rica (Tapanti), Ecuador (Quito) and Argentina (Mendoza, Salta, Malargue, Rio Gallegos) (Schuster et al., 2015). The GAPS study reported values for mean Σ_{4-8}PCDD/Fs of 373 $fg \cdot m^{-3}$ in Bogota, 51 $fg \cdot m^{-3}$ in the zone of high vehicular influence in Manizales and 167 $fg \cdot m^{-3}$ in Arauca, which were much lower than the levels reported in the urban zones of Sao Paulo and São Luis (1580 $fg \cdot m^{-3}$ 2560 $fg \cdot m^{-3}$, respectively) and the agricultural region of Sonora (1310 $fg \cdot m^{-3}$), but higher than that of Tapanti (10.8 $fg \cdot m^{-3}$).

In addition, a pilot study under the GAPS network monitoring the level of PBDEs, HBCDDs and other emerging contaminants in Bogota, Colombia has been reported, the results of which showed levels of Σ_9PBDEs of 11.7 $pg \cdot m^{-3}$ (Saini et al., 2020).

Given the importance of urban emission sources of POPs, urban sites are a subject of extensive study due to the elevated concentration and emission of these compounds. Thus, the aim of this project was to assess the levels of OCPs, PCBs, PBDEs, PBB, PCDDs, PCDFs, HBCDDs, and PFASs in the atmosphere of Medellin, Colombia, between 2017 and 2018, using passive air sampling. This represents an important contribution to research on this topic, because PFASs levels in the atmosphere of Medellin, Colombia have not been reported, and to the best of our knowledge, this is the first study.

Moreover, this research offers comparable information on POPs with other regions and countries to complement existing information on the distribution patterns in air of these pollutants. These results can be used to develop regulatory treaties and assess risks to human health in the city and country.

2 Material And Methods

2.1 Sampling site

Passive air samplers were deployed between January 2017 and January 2019 in Medellin, Colombia. The sampling site was located at 6°15'38"N 75°34'04"W, and the average temperature at the site during the deployment period was 21.6°C. Medellin is categorized as urban, is the second-largest city in terms of population in Colombia (2,508,452 inhabitants) and is an industrialized city.

Polyurethane foam passive air samplers (PUF-PASs) were deployed in an urban site with high traffic flow. Each sampling campaign was conducted for three months, giving four sampling quarters, referred to as quartile 1 (Q1), quartile 2 (Q2), quartile 3 (Q3), and quartile 4 (Q4), throughout each sampling year

(between 2017 and 2018). The exception to this was the evaluation of PCDD/Fs and dl-PCBs, for which the four PUF samples per year were combined due to low concentrations of these contaminants in the air. PUF-PAS deployment details are listed in Table S1 in the Supporting Information (SI).

The pre-conditioned PUFs were shipped from the Laboratory of Dioxins of the Institute of Environmental Assessment and Water Research (IDAEA-CSIC) (Barcelona, Spain) to the sampling site. After collection, the samples were shipped back to the different reference laboratories for the analysis of POPs.

OCPs, PCBs, PBDEs, PBB, PCDD/Fs were analyzed at the Laboratory of Dioxins of the IDAEA-CSIC, while HBCDDs were analyzed at Vrije Universiteit Amsterdam (Amsterdam, Netherlands). Moreover, PFASs were analyzed at Man-Technology-Environment research center (MTM), Örebro University (Örebro, Sweden).

2.2 Extraction and analysis

The PUFs were extracted and analyzed for different contaminant groups by Laboratory of Dioxins of the IDAEA-CSIC, Vrije Universiteit Amsterdam, and Man-Technology-Environment research center, which included the following twenty-eight organochlorine pesticides: pentachlorobenzene (PeCB); hexachlorobenzene (HCB); hexachlorocyclohexanes (α, β, γ and δ-HCHs); drins (aldrin, dieldrin, endrin); chlordanes (cis, and trans-nonachlors, cis, and, trans-chlordanes, oxychlordane, and chlordecone); DDTs (o,p'-DDD, o,p'-DDE, o,p'DDT, p,p'-DDD, p,p'-DDE and p,p'DDT); endosulfans (α, and β-isomers and endosulfan sulfate); heptachlor, cis, and trans-heptachlor epoxide; and mirex; six indicator PCB congeners: (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, and PCB 180); twelve dl-PCBs congeners (PCB 77, PCB 81, PCB 126, PCB 169, PCB 105, PCB 114, PCB 118, PCB 123, PCB 156, PCB 157, PCB 167, PCB 189); seventeen PCDFs and PCDDs (2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, OCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, and OCDD); ten PBDEs (BDE 17, BDE 28, BDE 47, BDE 66, BDE 100, BDE 99, BDE 85, BDE 154, BDE 153, BDE 183); nine PFASs (l-PFOS, br-PFOS, PFOA, PFHxS, FOSA, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE); one polybrominated biphenyl (PBB 153); and HBCDD-isomers (α, β, and γ-HBCDDs).

2.3 Volumetric air concentrations

Air concentrations ($pg \cdot m^{-3}$ or $fg \cdot m^{-3}$) were derived using the mass quantified in the sample divided by an effective air sampling volume (V_{air}). The V_{air} was calculated using the GAPS template, version 2021_v10 (Harner, 2021). The estimated sampling rates and equivalent volumes are a function of the octanol−air partition coefficients, the temperature, the sampling days, and the PUF-PAS geometry (Rauert et al., 2018a). The sampling rates were assumed as $4\ m^3 \cdot day^{-1}$. The sampling periods between 85 and 96 days had approximately V_{air} of 130, 132, 122, 132, 132, 73, 132 m^{-3} to PCBs, PBDEs, OCPs, HBCDDs, PBB 153, PFASs, and PCDD/Fs, respectively (Table S2). The toxic equivalents (TEQs) were calculated in WHO_{2005}-TEQ (Van den Berg et al., 2006).

2.4 Quality assurance and quality control

Air concentrations ($pg \cdot m^{-3}$ or $fg \cdot m^{-3}$) were derived from the mass of target analyte quantified, these values were obtained from IDAEA-CSIC (OCPs, PBDEs, PCBS, PBB, PCDDs, and PCDFs), Vrije Universiteit Amsterdam (HBCDDs), and Man-Technology-Environment research center (PFASs) divided by an V_{air} (Table S2), these effective air sampling volume were determined using GAPS template, version 2021_v10 (Harner, 2021). The PFOA and FOSA were assumed to stay in the linear sampling phase during deployment, and air sampling volumes were calculated as the number of days the sample was deployed multiplied by a sampling rate of 4 $m^3 \cdot day^{-1}$ (Pozo et al., 2004a). In the cases of the analyte were not detected to convert method limits of quantification to $pg \cdot m^{-3}$ or $fg \cdot m^{-3}$, the average air sampling volume was applied.

3 Results And Discussion

In general, the results showed two punctual peaks of contamination in the monitored time. The first peak was associated with chlorinated compounds in the quartile 2017-Q3, in which the higher concentrations of PeCB and indicator PCBs were observed. Meanwhile, the second peak of contamination was associated with brominated compounds in the quartile 2018-Q1, in which the higher levels of PBDEs and HBCDD-isomers were observed, as was a slight tendency for the air concentrations of PBDEs, HBCDDs, PCDDs, and PCDFs to increase in the year 2018 with respect to 2017. Also, constant concentrations in air were observed of pollutants banned in Colombia many years ago, such as DDT isomers and dieldrin, in contrast to a slight decrease in some pollutants such as aldrin, and α-endosulfan. Finally, the results provided a general vision of the air concentrations of chlorinated, brominated, and fluorinated pollutants in Medellin, Colombia, and can be a starting point for the identification of local sources and monitoring of the release of these pollutants in the city.

3.1 Organochlorine pesticides (OCPs) and indicators polychlorinated biphenyls (indicators PCBs)

Twenty-eight organochlorine pesticides and six indicator PCBs were monitored in the air in Medellin, Colombia during the period 2017 to 2018. The PeCB showed the highest levels of this chlorinated compounds group, generally called basic POPs, with values between 33.7 and 755.5 $pg \cdot m^{-3}$ (Fig. 1a). These high levels of PeCB with respect to the other basic POPs was due to the contamination peak observed in the quartile 2017-Q3 (Fig. 1b).

In this period elevated emissions of this pollutant occurred, which could be associated with discharges of PCBs or waste incineration, given that the same was observed in this quartile (2017-Q3) for indicator PCBs (Fig. 1b). This association is due to the use of PeCB in dielectric fluids with PCBs, and its unintentional formation in the combustion process; additionally, it is a precursor of PCBs formation under these conditions (Liu et al., 2001). The increase in air concentrations was more evident for the low chlorinated PCBs (tri and tetra-chlorinated congeners) respect to the high chlorinated PCBs, and the highest concentrations were 56.7 and 54.4 $pg \cdot m^{-3}$, for PCB 28, and PCB 52 respectively, in the quartile

2017-Q3 (Table S3). The air concentrations of PeCB and indicator PCBs decreased in the quartiles subsequent to 2017-Q3, which confirms the punctual contamination in 2017-Q3 of these pollutants. However, the air concentrations of PeCB in the 2018 period were higher than in 2017 and tended to stabilize at ~ 125 pg·m^{-3}, which is 3.7 times higher than the initial concentration observed in 2017-Q1 (33.7 pg·m^{-3}). These results indicate that air concentrations of PeCB in the city of Medellin increased by approximately four times in two years of monitoring.

On the other hand, concentrations in the air of DDT, DDE, and DDD isomers were constant during the monitoring time (Fig. 1a,1b). The air concentration range of Σ_4DDTs was 213.5−269.1 pg·m^{-3}; with p,p'-DDE being the isomer with the highest levels in this family (109.6−145.0 pg·m^{-3}, Table S3). In this respect, it is important to mention that DDT was banned in Colombia many years ago. Similarly, other basic POPs, such as dieldrin (38.3−57.8 pg·m^{-3}), trans-chlordane (28.3−42.9 pg·m^{-3}), cis-chlordane (14.2−20.2 pg·m^{-3}), trans-nonachlor (18.1−20.8 pg·m^{-3}), heptachlor (10.6−17.6 pg·m^{-3}), penta, hexa, and hepta-chlorinated indicator PCBs (PCB 101, 10.2−20.9 pg·m^{-3}, PCB 153, 8.0−12.2 pg·m^{-3}, PCB 138, 7.1−11.4 pg·m^{-3}, and PCB 180, 3.3−9.3 pg·m^{-3}), tended to have constant air concentrations despite having been banned years ago. These results confirm the great persistence of these compounds and might be associated with the global transport and background levels of these pollutants in the environment.

In contrast with the above results, slight decreases were observed of HCB (32.3−55.1 pg·m^{-3}), α, γ-HCH-isomers (< 1.8−4.2 pg·m^{-3}, and 67.5−132.5 pg·m^{-3}, respectively), aldrin (2.4−4.8 pg·m^{-3}), and α-endosulfan (< 8.0−13.5 pg·m^{-3}). Trends for the other basic POPs were not identified due to their low concentrations in air, and in several cases were not detected at all (cis,trans-heptachlore epoxide, β-endosulfan, endosulfan sulfate, β, δ-HCH-isomers, oxychlordane, cis-nonachlor, chlordecone, endrin, and mirex). All OCPs and indicators PCBs results are summarized in Table S3.

These results are in the same order of magnitude as those of other studies in Colombia and Latin America, which also suggests the persistent and global transport of basic POPs as DDTs, endosulfan, and heptachlor (Rauert et al., 2018a).

3.2 Dioxin like- polychlorinated biphenyls (dl-PCBs), Polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs)

dl-PCBs concentrations in air observed during the two years of monitoring are presented in Fig. 2a and Table S4. The dl-PCBs congeners with the highest concentrations in air were PCB 118 (9404.9 fg·m^{-3}), PCB 105 (4137.8 fg·m^{-3}), and PCB 77 (1568.8 fg·m^{-3}), respectively. The air concentrations of PCB 77, PCB 81, PCB 105, PCB 114, PCB 118, PCB 123 were slightly higher in the year 2017 than in 2018. In contrast, the air concentrations of PCB 126, PCB 169, PCB 156, PCB 157, PCB 167, and PCB 189 were higher in the year 2018 (Table S4).

The air concentrations of Σdl-PCBs were 17539.9 fg·m^{-3} in 2017, and 16970.9 fg·m$^{-3,}$ in 2018; and the TEQ concentrations were 16.1 fgWHO$_{2005}$-TEQ·m^{-3} in 2017 and 19.1 fgWHO$_{2005}$-TEQ·m^{-3} in 2018 (Fig. 2c). The sampling site of this study in Medellin had vehicular influence and was near to the city center, hence, comparable values to other urban sites in Colombia are expected.

Similar results from Colombia were reported by (Cortés et al., 2016), in which higher dl-PCBs concentrations, in the range 4599 to 8744 fg·m^{-3} and 3.5 to 3.7 fgWHO$_{2005}$-TEQ·m^{-3}, were observed in industrial areas of the city of Manizales, while values around 4388 fg·m^{-3} and 9.2 fgWHO$_{2005}$-TEQ·m^{-3} were observed in vehicular influence areas of Bogotá. Furthermore, the results of this study are in the same scale as other concentrations in air reported in the GRULAC region (Bogdal et al., 2013; Estellano et al., 2008; Meire et al., 2012; Pozo et al., 2009, 2004b; Rauert et al., 2018a; Tombesi et al., 2014). The above suggests that dl-PCBs concentrations in the Medellin air are mainly associated with local sources.

PCDD/Fs concentrations in air monitored during the two-year period are presented in Fig. 2b and Table S4. The highest concentrations of PCDDs and PCDFs were 123.1 fg·m^{-3} (OCDD) and 43.7 fg·m^{-3} (2,3,7,8-TCDF) in 2017, and 139.0 fg·m^{-3} (OCDD), and 39.4 fg·m^{-3} (1,2,3,4,6,7,8-HpCDF) in 2018, respectively; while the lowest concentrations were 2.5 fg·m^{-3} (2,3,7,8-TCDD) and < 2.3 fg·m^{-3} (1,2,3,7,8,9-HxCDF) in 2017, and 3.6 fg·m^{-3} (2,3,7,8-TCDD) and 4.0 fg·m^{-3} (1,2,3,7,8,9-HxCDF) in 2018. Other studies have reported seasonal variations for PCDD and PCDF concentrations in air (Bogdal et al., 2014; Li et al., 2011; Lohmann and Jones, 1998). Nevertheless, one year sampling periods in this study include all months of the year, so no seasonal variations are expected.

The PCDD/Fs TEQ values were 26.5 fgWHO$_{2005}$-TEQ·m^{-3} in 2017 and 34.3 fgWHO$_{2005}$-TEQ·m^{-3} in 2018, and the total TEQ values were 41.8 fgWHO$_{2005}$-TEQ·m^{-3} in 2017 and 53.5 fgWHO$_{2005}$-TEQ·m^{-3} in 2018 (Fig. 2c). These results are similar to those previously reported in urban areas of Manizales and Bogota (Aristizábal et al., 2011; Cortés et al., 2016). On the other hand, in this study air concentrations of ΣPCDD/Fs were 375.4 and 420.5 fg·m^{-3} in 2017 and 2018, respectively. These values are between 100 and 1000 fg·m^{-3} that are typical concentrations of ΣPCDD/Fs for urban and industrial areas reported in other studies (Bogdal et al., 2014; Colombo et al., 2013; Cortés et al., 2014; Li et al., 2011; Lohmann and Jones, 1998; Meire et al., 2012; Pozo et al., 2004a, 2004b; Schuster et al., 2015; Tombesi et al., 2014).

Finally, the PCDD/Fs ratios were calculated and are shown in Table S4. The PCDD/Fs ratios obtained were lower than 1.00 in the two years of monitoring, being 0.89 and 0.97 in 2017 and 2018, respectively. These results indicate a high contribution of PCDF congener. According to (Buekens et al., 2000), this pattern is possibly due to steel and iron furnaces. On the other hand, similar ratio values were found in areas of Manizales influenced by industries such metallurgy, food, and plastic by (Cortés et al., 2014). The ratio values found in this study suggest that PCDD/Fs concentrations in air are more associated with local sources in Medellin and could be associated with the metallurgy industries and steel and iron furnaces in the city.

3.3 Polybrominated diphenyl ethers (PBDEs), Hexabromocyclododecanes (HBCDDs), and Polybrominated biphenyl (PBB 153)

The atmospheric concentrations of PBDEs and HBCDDs-isomers were significatively higher in the year 2018 with respect to 2017 (Fig. 3a), mainly due to the high contamination peak observed in the quartile 2018-Q1 (Fig. 3b).

This peak indicates punctual releases of these pollutants in this monitoring time, given that in the subsequent quartiles the air concentrations decrease significantly. The principal PBDE congeners released in the quartile 2018-Q1 were BDE 183 ($81.8\ pg \cdot m^{-3}$) and BDE 153 ($12.5\ pg \cdot m^{-3}$), respectively. Meanwhile, γ-HBCDD was the isomer with the highest concentration in quartile 2018-Q1 ($153.8\ pg \cdot m^{-3}$), followed by α-HBCDD ($89.0\ pg \cdot m^{-3}$), and β-HBCDD ($46.1\ pg \cdot m^{-3}$) respectively, the results are summarized in Table S5.

PBDEs are commonly added to electronic products (shells, cables, and printed circuit boards), building materials, furniture, foam, textiles, and automobile parts, due to their flame retardant effects (M. L. Chen et al., 2012). In addition, PBDEs do not react with polymer components and can be easily leached from a polymer throughout their life cycle (Y. Chen et al., 2012; Naert et al., 2007; Yu et al., 2017). HBCDDs are widely applied in polystyrene, foams for thermal insulation of buildings in upholstery textiles, and back-coating of fabrics for furniture, among other applications (Covaci et al., 2006; Remberger et al., 2004).

Based on the above, there are three potential releases stages in the life cycle of PBDEs and HBCDDs, specifically, their manufacture, use, and disposal (Chen et al., 2015; Remberger et al., 2004). The high releases in quartile 2018-Q1 could be associated with any of the above-mentioned stages, given that several industrial activities are carried out in Medellin.

When comparing the results obtained in this study with other researchers in Colombia and the GRULAC region (Rauert et al., 2018a, 2018b; Saini et al., 2020; Tombesi et al., 2014), the results found for PBDEs are in the same order in magnitude; for example, $11.7\ pg \cdot m^{-3}$ of Σ_9PBDEs in Bogota was reported by (Saini et al., 2020). On the other hand, HBCDDs air concentrations in this study are higher than previous value reported by (Saini et al., 2020) in the which HBCDD isomers were not detected in Bogota. This suggests that the air concentrations of these compounds in Medellin are due to local sources.

Finally, PBB 153 was monitored in 2017 and 2018 but was not detected, the levels in the air being $< 0.2\ pg \cdot m^{-3}$ in all cases.

3.4 Per- and polyfluoroalkyl substances (PFASs)

The PUF 2018-Q1 corresponding to PFASs was not able to quantify because the PUF was so deteriorated, thus, the data relating to the first quarter of 2018 is not reported for these contaminants. On the other

hand, ΣPFOS (perfluorooctanesulfonic acid (PFOS) - linear and branched) was 9.8 pg·m^{-3} in 2017 and 11.2 pg·m^{-3} in 2018; perfluorooctanoic acid (PFOA) was 0.7 pg·m^{-3} in 2017 and 0.9 pg·m^{-3} in 2018; perfluorohexanesulfonic acid (PFHxS) was 0.04 pg·m^{-3} in 2017 and 0.05 pg·m^{-3}and perfluorooctanesulfonamide (FOSA) was 0.2 pg·m^{-3} in 2017 and 0.1 pg·m^{-3} in 2018; the rest of the PFASs were not detected at all (N-methylperfluorooctanesulfonamide (NMeFOSA), N-ethylperfluorooctanesulfonamide (NEtFOSA), N-methylperfluorooctanesulfonamidoethanol (NMeFOSE), N-ethylperfluorooctanesulfonamidoethanol (NEtFOSE)). The air concentrations of PFOS and PFOA were slightly higher in 2018 with respect to 2017 (Table 1). A similar trend was reported previously by the GAPS network between 2009 and 2015 (Rauert et al., 2018c).

Table 1

Concentrations (pg·m^{-3}) of PFASs in PUF-PAS collected in 2017 and 2018. Where an analyte was not quantified < LOQ is provided.

Compounds	2017 (pg·m^{-3})	2018 (pg·m^{-3})
l-PFOS	5.6	7.0
br-PFOS	4.2	4.2
Sum-PFOS	9.8	11.2
PFOA	0.7	0.9
PFHxS	0.04	0.05
FOSA	0.2	0.1
NMeFOSA	< 3.9	< 3.9
NEtFOSA	< 4.9	< 4.9
NMeFOSE	< 6.4	< 6.4
NEtFOSE	< 2.8	< 2.8

On the other hand, the air concentrations of PFHxS and FOSA compounds did not change significantly in the two years of monitoring.

PFOS were in the same order of magnitude previously reported in the GRULAC region and country (Rauert et al., 2018b). The FOSA and FOSE air concentrations in this study were lower than those reported previously in the GRULAC region and the country (Rauert et al., 2018b). There are many sources of PFASs, for this reason, and due to the nature of this study, it is complex to associate the levels found to sources of release.

4 Conclusions

Air concentrations of a variety of POPs (chlorinated, brominated, and fluorinated) were monitored in the atmosphere of Medellin, Colombia for two consecutive years. The results showed two punctual contamination peaks. The first of these was associated with chlorinated compounds due to high releases of PeCB in the quartile 2017-Q3; emissions of PeCB are probably associated with unintentional formation in combustion processes in Medellin. The second contamination peak was associated with brominated compounds (PBDEs and HBCDD-isomers) and was observed in the quartile 2018-Q1. This contamination peak may be associated with recycling, incineration, and deposit at landfill of these compounds. On the other hand, the results suggest that PCDD/Fs concentrations in air are more associated with local sources in Medellin, such as the metallurgy industries and steel and iron furnaces in the city. Additionally, a slight tendency was observed for the air concentrations of PBDEs, HBCDDs, PCDDs, and PCDFs to increase in the year 2018 with respect to 2017. Furthermore, constant concentrations in air of pollutants banned in Colombia many years ago, such as DDT isomers and dieldrin, were observed, in contrast to a slight decrease in some pollutants such as aldrin, and α-endosulfan. Finally, the results provided a general vision of the air concentrations of chlorinated, brominated, and fluorinated pollutants in Medellin, Colombia, and can be a starting point to find the local sources of these pollutants and monitor their release in the city.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

All data generated and analyzed during this study are included in this published article and in the supplementary information files.

Competing interests

The authors declare that they have no competing interests

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Authors' contributions

BA was responsible for the analysis of results and, writing original draft paper; AR participated in all stages of research and, review and editing of paper, DP participated in review and editing paper, and GP participated in all stages of research and, review and editing of paper. All authors read and approved the final manuscript.

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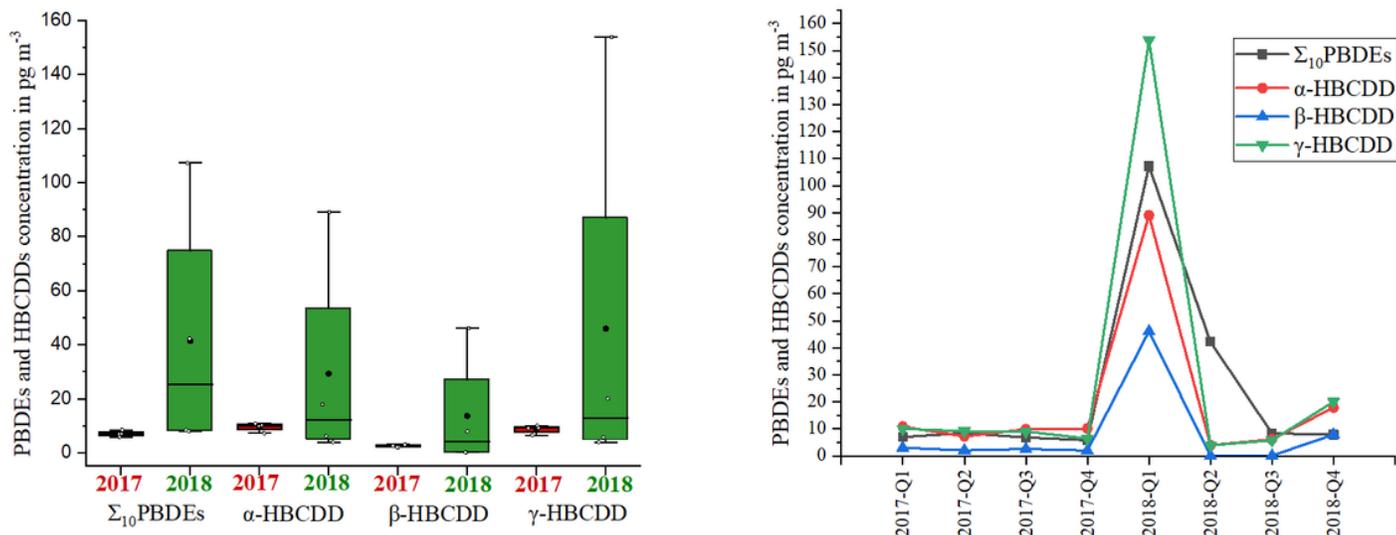
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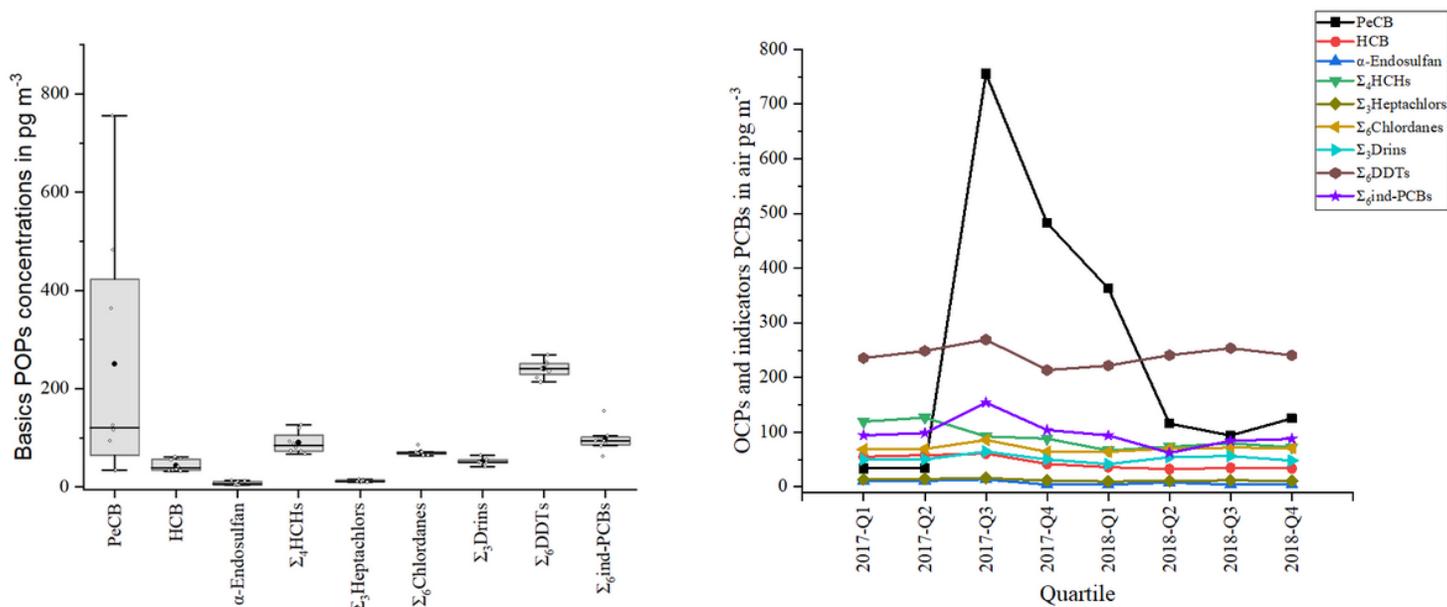
Figure 1

a OCPs and indicators PCBs concentrations in air (pg·m-3). (a) Box and whisker plots of OCPs and indicator PCBs in Medellin, Colombia, in 2017 and 2018. The circle indicates the mean concentration, and the black line indicates the median. The Σ4HCHs indicates the sum of all HCH isomers (α, β, γ, δ); Σ3Heptachlors indicates the sum of heptachlor, cis-heptachlor epoxide, and trans-heptachlor epoxide; Σ6Chlordanes indicates the sum of oxychlordane, trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor, and chlordecone; Σ3Drins indicates the sum of aldrin, dieldrin, and endrin; Σ6DDTs indicates the sum of all DDT, DDE, and DDD isomers; and Σ6ind-PCBs indicates the sum of PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, and PCB 180. Where an analyte was not detected, ½ LOQ was added. (b) OCPs and indicator PCBs concentrations in air (pg·m-3) by quartiles during the period 2017 to 2018.
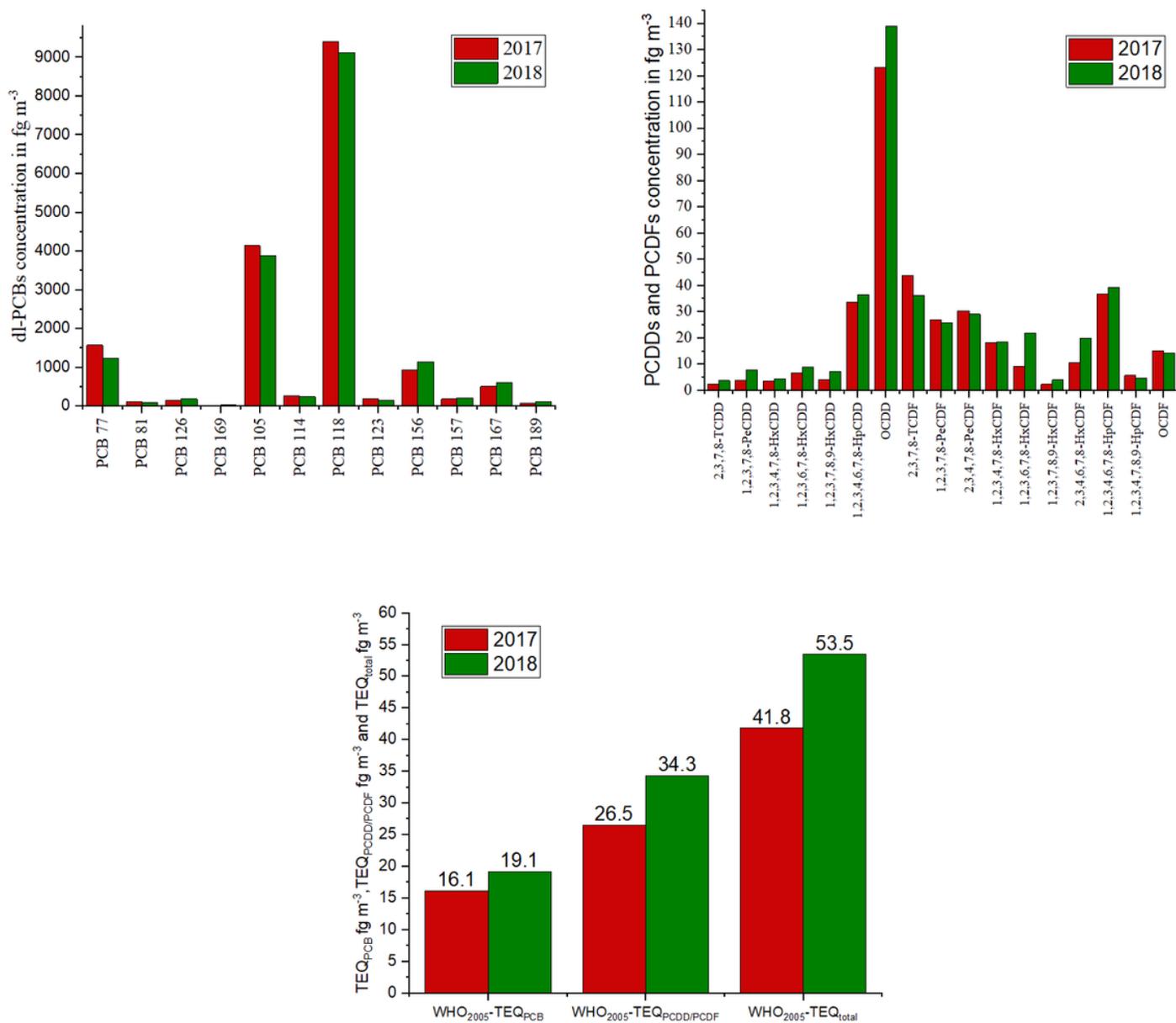
Figure 2

a Air concentrations of dl-PCBs in fg·m-3 in the period 2017 to 2018 in Medellin, Colombia. (a) dl-PCBs congeners concentration in fg·m-3 in the 2017 (red) and 2018 (green) periods. b Air concentrations of PCDDs, and PCDFs in fg·m-3 in the period 2017 to 2018 in Medellin, Colombia. (b) PCDD/Fs congeners concentration in fg·m-3 in the 2017 (red) and 2018 (green) periods. (c) TEQ values with basis in WHO 2005 of dl-PCBs, PCDD/Fs, and total in fgWHO2005-TEQ·m-3 during 2017 (red), and 2018 (green).

Figure 3

a PBDEs and HBCDDs concentrations in air (pg·m-3). (a) Box and whisker plots of PBDEs and HBCDDs in Medellin, Colombia, in 2017 and 2018. The circle indicates the mean concentration, and the black line indicates the median. The $\Sigma 10$PBDEs indicates the sum of BDE-17, BDE-28, BDE-47, BDE-66, BDE-100, BDE-99, BDE-85, BDE-154, BDE-153, and BDE-183. Where an analyte was not detected, ½ LOQ was added. b PBDEs and HBCDDs concentrations in air (pg·m-3). (b) PBDEs and HBCDDs concentrations in air (pg·m-3) by quartile during the period 2017 to 2018.

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