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GAPS-megacities: A new global platform for investigating persistent organic pollutants and chemicals of emerging concern in urban air☆

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ABSTRACT

A pilot study was initiated in 2018 under the Global Atmospheric Passive Sampling (GAPS) Network named GAPS-Megacities. This study included 20 megacities/major cities across the globe with the goal of better understanding and comparing ambient air levels of persistent organic pollutants and other chemicals of emerging concern, to which humans residing in large cities are exposed. The first results from the initial period of sampling are reported for 19 cities for several classes of flame retardants (FRs) including organophosphate esters (OPEs), polybrominated diphenyl ethers (PBDEs), and halogenated flame retardants (HFRs) including new flame retardants (NFRs), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD). The two cities, New York (USA) and London (UK) stood out with ~3.5 to 30 times higher total FR concentrations as compared to other major cities, with total concentrations of OPEs of 15,100 and 14,100 pg/m^3, respectively. Atmospheric concentrations of OPEs significantly dominated the FR profile at all sites, with total concentrations in air that were 2−5 orders of magnitude higher compared to other targeted chemical classes. A moderately strong and significant correlation ($r = 0.625$, $p < 0.001$) was observed for Gross Domestic Product index of the cities with total OPEs levels. Although large differences in FR levels were observed between some cities, when averaged across the five United Nations regions, the FR classes were more evenly distributed and varied by less than a factor of five. Results for Toronto, which is a 'reference city' for this study, agreed well with a more in-depth investigation of the level of FRs over different seasons and across eight sites representing different urban

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source sectors (e.g. traffic, industrial, residential and background). Future sampling periods under this project will investigate trace metals and other contaminant classes, linkages to toxicology, non-targeted analysis, and eventually temporal trends. The study provides a unique urban platform for evaluating global exposome.

1. Introduction

Urban and metropolitan areas across the globe are home to 4.2 billion people, constituting 55% of the world's total population (United Nations, 2018). Urbanization results in increasing need for housing, transportation and infrastructure as well as an increase in the challenges related to them such as ambient air pollution which is one of the main global health risks causing increased mortality (Lelieveld et al., 2020). According to the World Health Organization (WHO), in the urban areas where air quality is being monitored consistently, 80% of the residents are exposed to air quality levels that exceed WHO limits (WHO, 2016). Air quality is a complex term representing a range of pollutants but the WHO assessments have mostly used particulate matter (e.g. PM_{10} or less) as a proxy indicator of exposure to air pollution. The health effects associated with PM are not only because of their physical mass concentrations but the chemical compositions are also critical to understand the toxicity of PM (Cao et al., 2012; Chung et al., 2015; Wyzga and Rohr, 2015). We hypothesize that in large megacities, persistent organic pollutants (POPs), particularly the ones associated with particles present in the air, contribute significantly to the chemical burden and hence the toxicity of PM and the air mixture. There is previously established evidence as well as growing literature based on *in vitro* and *in vivo* studies, showing adverse health effects caused by the exposure to old and new POPs and POPs-like chemicals (Loganathan and Masunaga, 2009; Kim et al., 2013; Lyche et al., 2015; Abdel-Shafy and Mansour, 2016; Lam et al., 2017; Guigueno et al., 2019; Blum et al., 2019) and the importance of considering chemical mixtures in air (Escher et al., 2020).

The urban environment is a subject of extensive study due to elevated concentrations and emissions of POPs such as flame retardants (FRs) and other chemicals of emerging concern (CECs) as compared to remote or background areas (Liu et al., 2009; Bogdal et al., 2014; Peverly et al., 2015; De la Torre et al., 2016; Muñoz-Arnanz et al., 2016; Chakraborty et al., 2017; Rodgers et al., 2018). Given the importance of urban emission sources of FRs and CECs, surveillance of urban air can be used to track the dynamic nature of these emissions, provide updated scenarios of emerging/replacement chemicals, and therefore provide better information for assessing the effectiveness of imposed regulations (Stockholm Convention, 2008).

The goal of this study is to provide for the first time a snapshot of levels of different classes of FRs in megacities and/or major cities across the globe. The Global Atmospheric Passive Sampling (GAPS) network has been operational since 2005 in five United Nations regional groups across the globe: Africa, Asia and Pacific, Central and Eastern Europe (CEE), Group of Latin American and the Caribbean (GRULAC), and Western Europe and Other States Group (WEOG) (Harner et al., 2006; Pozo et al., 2006). Overall, GAPS contributes to the initiatives under Canada's Chemical Management Plan (CMP) on the domestic level. Internationally, GAPS reports to the Global Monitoring Plan (GMP) supporting Canada's obligations as a Party to the Stockholm Convention on POPs (Stockholm Convention, 2008). The Stockholm Convention, which came into force in 2004, is one of the largest international treaties and the air monitoring data reported to GMP contributes to the "Effectiveness Evaluation" of the regulatory efforts on POPs implemented under the Convention. The current project, which is a sub-study under the GAPS network, is named 'GAPS-Megacities (GAPS-MC)'. GAPS-MC will provide comparable information on POPs and CEC in ambient air at representative sites of global cities, to complement existing information on background sites that is available under the core GAPS program. Under the GAPS-MC project, a range of FR chemicals was chosen for evaluation including organophosphate esters (OPEs), polybrominated diphenyl ethers (PBDEs), new flame retardants (NFRs), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD) – all of which have important emission sources in urban air. To our knowledge, this is a first report on FRs in the urban environment at a global scale from a single sampling network.

2. Materials and methods

2.1. Sampling locations

Twenty cities were selected for a sampling campaign with a population ranging from 2 million to 22 million (Table S1 and Figure S1). The megacity, by definition, is a large metropolitan area with a population of more than 10 million (Cambridge dictionary, 2019). However, some of the countries selected for this study such as Canada, USA, Poland, Spain and Australia, do not have any city with a population over 10 million. In such cases, the most populous city of the country was chosen. Study collaborators were requested to select a "representative site" with the following criteria:

i.) well away from any potential sources of FRs such as adjacent industries or exhaust/ventilation ducts and large motorways;
ii.) situated centrally in the city, preferably in a less active area such as a park, campus or rooftop.
iii.) located in an area with unobstructed airflow, at least 2m above ground. Rooftop sites were encouraged, where possible.

2.2. Passive air sampling

Passive air sampling was opted for monitoring the target chemicals using the polyurethane foam (PUF) disk samplers with a similar configuration as used in GAPS network previously (Rauert et al., 2018). These samplers are able to gather both gas- and particle-phase chemicals (Markovic et al., 2015; Gaga et al., 2019), hence the samples represent the whole air mixture. The sampling campaign was conducted in 2018 for two consecutive periods of 3 months each, referred to as period 1 and 2. However, samples were deployed but not returned on time for laboratory analysis from the Nairobi, Kenya site, hence the site was excluded from this report of the study. Period 1 samples were analyzed for FRs and reported here, and sampling details are given in Table S1. Details of sample deployment and collection are previously reported by Schuster

et al. (2015) and a brief description is provided in SI, Text S1. Period 2 samples were analyzed for trace metals and results are pending and will be reported separately. Ongoing sampling under GAPS-MC will be used for targeting other chemical classes, including non-targeted analysis, and for evaluating the toxicity of the mixture of chemicals in air. Eventually, the extension of the pilot program may help to reveal longer term temporal trends that reflect changing use patterns of FRs and the impact of chemical management efforts.

2.3. Extraction, instrumental analysis, QA/QC and data analysis

Samples were extracted and analyzed for FRs using previously described methods (Rauert et al., 2016, 2018). Briefly, petroleum ether and acetone solvents (83/17, v/v) were used for extraction using an accelerated solvent extractor (ASE) instrument (ASE 350, Dionex Corporation, Sunnyvale, CA, USA) followed by reducing the sample to 0.5 mL using rotary evaporation and nitrogen blowdown. The sample was then split after the addition of 100 ng of mirex. The one half of the sample was reconstituted to 0.5 mL using isooctane for analyses of PBDEs and NFRs. The other half of sample underwent silica column cleanup followed by addition of internal standards (details provided in SI, Table S2) and constituting the final volume in methanol for analyses of OPEs, HBCDD and TBBPA. PBDEs and NFRs were analyzed on an Agilent (Mississauga, ON, Canada) 7890B Gas Chromatograph (GC) using a 15 m Restek RTX-1614 column (15 m, 0.25 mm i.d., 0.1 μm film thickness) for separation, coupled with an Agilent 7010 triple quadrupole Mass Spectrometer (MS/MS). OPEs, HBCDD and TBBPA were analyzed using Waters Acquity I-class Ultra Performance Liquid Chromatograph (UPLC) coupled with a Xevo TQ-S MS/MS (Waters, Boston, MS, USA). Separation of target analytes was obtained by using a Waters Acquity (Waters, Boston, MS) BEH C18 reversed-phase analytical column (50 mm, 2.1 mm i.d., 1.6 μm particle size) for OPEs and a Waters Acquity HSS T3 reversed-phase analytical column (50 mm, 2.1 mm i.d., 1.6 μm particle size) for HBCDD and TBBPA. A detailed list of target analytes including 18 OPEs, 14 PBDE congeners, spanning from tri-to deca-BDE and other halogenated flame retardants (HFRs) including 17 NFRs, TBBPA and 3 isomers of HBCDD is given in Table S2. Blanks and recoveries were monitored throughout the extraction and processing to rule out any potential contamination and losses throughout the process. Further details on QA/QC and data analysis is provided in the SI, Text S2.

3. Results and discussion

3.1. Spatial profile and correlation analysis with socio-economic indices of the cities

New York, USA and London, UK exhibited the highest concentrations of total FRs, which were 3–30 times higher compared to the other major cities (Fig. 1 and Table 1). FRs levels for all cities were dominated by the OPEs. City rankings of FR levels differed for the OPEs versus other FR classes and are discussed later. The total concentrations of FRs in New York and London ranged between 14,000 and 16000 pg/m^3 followed by Tokyo (Japan), Beijing (China), Lagos (Nigeria), Toronto (Canada) and São Paulo (Brazil) with the total concentrations ranging between ~2000–4000 pg/m^3. The remaining cities had total concentrations ranging from 500 to 1700 pg/m^3.

Correlation analysis of measured levels of FRs was conducted with population density, total population and two socio-economic development indices i.e Gross Domestic Product (GDP) and Human development index (HDI) of the cities in the current study (Table S4). GDP and HDI are explained in SI, Text S3. HBCDD was excluded from correlation analysis as it was detected at <30% of sites. A moderately strong and significant correlation was observed for GDP with total OPEs only ($r = 0.625$, $p < 0.001$; Figure S2). Since GDP is related to the production of commercial products (which contain the FRs targeted here), the strong correlation of OPEs and GDP might explain the high levels in New York, USA and London, UK which have among the highest of the GDPs, with the exception of Tokyo, Japan (Table S1). The stronger correlation (with GDP) for the OPEs, rather than for the PBDEs and NFRs, may also reflect increasing production volumes and use of OPEs due to the phase-out of PBDEs. The industry has shifted towards more usage of OPEs across the globe, for a wide range of applications from FRs to plasticizers and additives in commercial products (Reemtsma et al., 2008; Van der Veen and de Boer, 2012; Schreder et al., 2016; Blum et al., 2019; Yang et al., 2019; He et al., 2020).

PBDEs and NFRs had a statistically significant but weak positive correlation with population density and total population ($r = 0.22$ to 0.48, $p < 0.01$). It might be reflective of the association of inventory of products containing these FRs with the population and its density. TBBPA had a negative to weak positive insignificant correlations with the target indices ($r = -0.021$ to 0.47). The additional data obtained from ongoing sampling will be used for further in-depth correlation analysis of FR concentrations with socio-economic indices.

3.2. Assessment of intra-city variability of FR levels

Toronto, Canada was assigned as a 'reference city' for the GAPS-MC pilot study. A sampling campaign was conducted in 2016–2017 in Toronto across 8 sites under the study named: Assessing Toxicity of Organics in Urban Source Sectors for Air (ATOUSSA) (Saini et al., 2019). Based on the results of ATOUSSA study, we observed relatively small (i.e. less than an order of magnitude) variability for OPEs, PBDEs (Fig. 2) and NFRs (Figure S3) in the air across different site types (spanning sources from urban, traffic, semi-urban, industrial to residential and background sites) and also relatively small seasonal variability in FR levels in air over time (6 periods of sampling of 2 months each) at the same site. Some of the observed variability in derived concentrations is inherent in the sampling and analysis methodology. Gouin et al. (2005) deployed duplicate PUF disk samplers across several sites in the Great Lakes Basin over multiple sampling periods and showed that the coefficient of variation was <50% in 91% of samples.

Based on the detailed Toronto study, we were confident that one representative sampling site for each major city in this study, with care being taken to avoid sampling near potential sources, would provide a reasonable representation of average ambient concentrations within each city to evaluate average levels to which the populations are exposed. However, we acknowledge that each city is subject to unique source sectors and therefore uncertainties and variabilities in air concentrations of targeted compounds over space and time (e.g. seasonality), which we are not able to evaluate based on one sampling site/period. Furthermore, because passive air samplers are deployed for an extended 3-month period, they are able to integrate ambient concentrations effectively and dampen the high and low concentration episodes that sometimes arise from short term (e.g. 24hr), intermittent (e.g. weekly) high volume sampling data (Pozo et al., 2009).

3.3. Concentrations and profiles of each FR class

OPEs clearly dominated the profile at all sites with 2–5 orders of magnitude higher total concentrations as compared to other targeted FRs (ANOVA and student's t-test assuming unequal variance, $p < 0.002$) (Table 1). There was no significant difference between ΣPBDEs and ΣNFRs levels across sites ($p > 0.05$). Out of the total 54

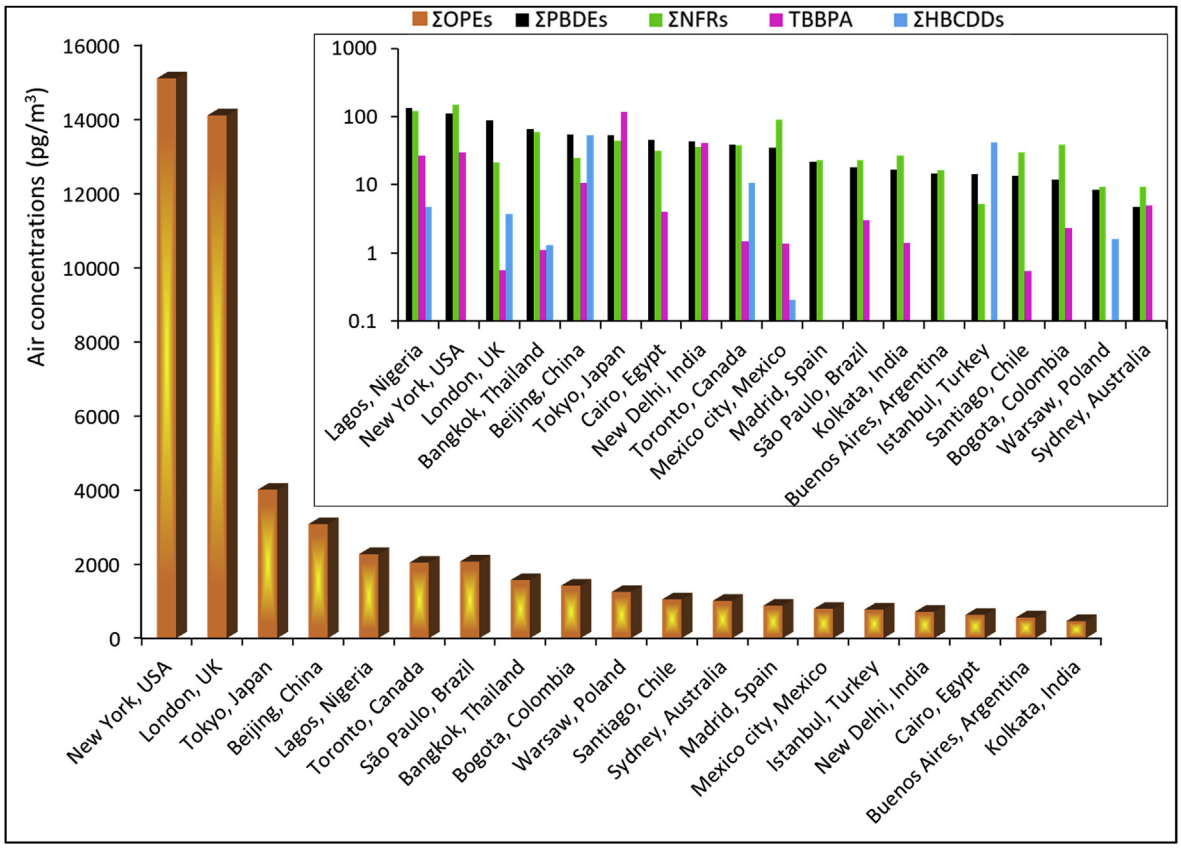

Fig. 1. Ranking of the 19 major cities based on the total concentration of Σ_{10}OPEs (outer graph) and Σ_9PBDEs, Σ_{11}NFRs, ΣHBCDDs and TBBPA (inset graph) as derived from passive air samples. Y-axis of both graphs represents air concentrations in pg/m^3. Note that the y-axis of the inset graph is on a log scale. The sequences of the sampling site are based on the decreasing order of concentrations of OPEs and PBDEs in the outer and inset graph, respectively.

Table 1
Total concentrations (pg/m^3) of OPEs, PBDEs, NFRs, HBCDD and TBBPA as measured in passive air samples collected from 19 major cities. Note: ND stands for non-detect and the concentrations are rounded off to 3 significant figures.

United Nations' region	Site code	Sites	Σ_{10}OPEs	Σ_9PBDEs	Σ_{11}NFRs	HBCDD	TBBPA
WEOG	WE01	Toronto, Canada	2040	38.6	38.2	10.8	1.49
	WE02	New York, USA	15,100	111	149	ND	29.7
	WE03	Sydney, Australia	1010	4.75	9.41	ND	4.95
	WE04	Istanbul, Turkey	774	14.1	5.24	41.8	ND
	WE05	London, UK	14,100	88.0	21.1	3.75	0.56
	WE06	Madrid, Spain	880	22.0	23.0	ND	ND
		Average	**5650**	**46.4**	**41.0**	**18.8**	**9.16**
		Median	**1520**	**30.3**	**22.1**	**10.8**	**3.20**
GRULAC	GR01	São Paulo, Brazil	2070	18.3	23.0	ND	3.02
	GR02	Bogota, Colombia	1420	11.7	39.2	ND	2.33
	GR03	Mexico city, Mexico	795	34.9	88.9	0.21	1.37
	GR04	Santiago, Chile	1050	13.6	30.0	ND	0.54
	GR05	Buenos Aires, Argentina	563	14.5	16.1	ND	ND
		Average	**1180**	**18.6**	**39.5**	**0.21**	**1.81**
		Median	**1050**	**14.5**	**30.0**	**0.21**	**1.85**
CEE	CEE01	Warsaw, Poland	1250	8.48	9.32	1.60	ND
Asia-Pacific	AS01	Kolkata, India	464	16.9	26.8	ND	1.39
	AS02	Beijing, China	3080	54.8	24.9	53.3	10.6
	AS03	Bangkok, Thailand	1570	65.5	59.3	1.30	1.10
	AS04	Tokyo, Japan	4010	53.1	43.9	ND	118
	AS05	New Delhi, India	714	43.3	35.6	ND	41.0
		Average	**1970**	**46.7**	**38.1**	**27.3**	**34.4**
		Median	**1570**	**53.1**	**35.6**	**27.3**	**10.6**
Africa	AF01	Lagos, Nigeria	2270	134	121	4.69	27.0
	AF02	Cairo, Egypt	633	45.7	31.7	ND	4.08
		Average (& median)	1450	89.9	76.4	4.69	15.5
		Total Average	***2830***	***41.7***	***41.9***	***14.7***	***16.5***
		Total Median	***1250***	***34.9***	***30.0***	***4.22***	***3.02***

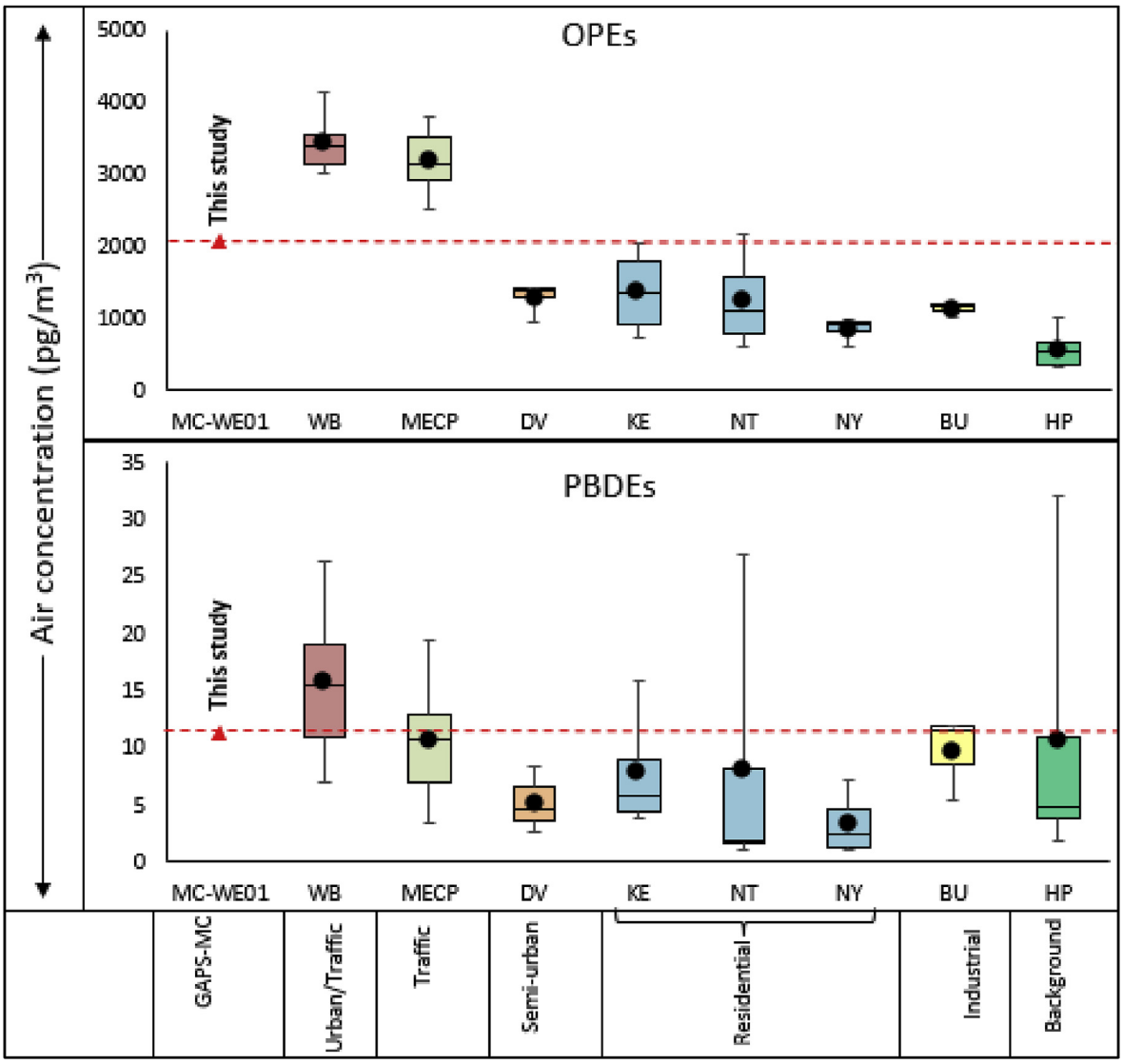

Fig. 2. A plot showing the comparison of air concentrations of ΣOPEs and ΣPBDEs measured at Toronto, Canada (Red triangle and dashed line, this study) at 8 sites representing different source sectors in a sampling campaign conducted in 2016–2017 under ATOUSSA study (box and whisker plots) (Saini et al., 2019). Black markers indicate the average; top, middle and bottom lines of the boxes show 75th percentiles, medians and 25th percentiles, respectively, and whiskers represent the minimum and maximum total concentration measured in ATOUSSA study samples. MC-WE01 and WB samplers were located at the same site. Note: For comparison, BDE-209 was excluded from MC-WE01 total concentrations since it was not reported in the ATOUSSA study. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

target analytes, 29 analytes were detected with detection frequencies of ≥80%, 4 analytes were detected in the range 21%–58% of samples and the remaining were non-detects across all sites (Table S2).

OPEs: Total concentration of OPEs in air across the 19 cities spanned over two orders of magnitude, from 464 to 15,100 pg/m^3. Ten out of 18 target OPEs were detected in >84% of samples (Table S2). The highest concentration of Σ_{10}OPEs was measured at New York, USA (15,100 pg/m^3) followed by London, UK (14,100 pg/m^3) (Fig. 1 and S4 and Table 1). The Σ_{10}OPEs at other sites ranged from 464 to 4010 pg/m^3. Table S6 presents the comparison of levels of OPEs reported in previous studies conducted in urban areas across the world. The range of total OPEs measured in the current study is in agreement with the atmospheric levels reported previously in the urban areas such as Chicago and Cleveland, USA (1500 and 2100 pg/m^3, respectively; Salamova et al., 2014); Toronto, Canada (3430 pg/m^3; Saini et al., 2019); Stockholm, Sweden (3900 pg/m^3; Wong et al., 2018); Paris, France (7770 pg/m^3, Rauert et al., 2018); Bursa, Turkey (8400 pg/m^3; Kurt-Karakus et al., 2018), São Luis, Brazil (919 pg/m^3; Rauert et al., 2018) and Concepcion, Chile (1190 pg/m^3; Rauert et al., 2018). However, in comparison to background concentration of total OPEs (median = 230 pg/m^3; range = 40–1300 pg/m^3) reported for 31 background sites under GAPS network (Rauert et al., 2018), the median value for the megacities in the current study is 7 times higher. The elevated levels of OPEs in megacities versus background locations, as well as instances of extremely high concentrations of OPEs in some cities, highlight the chemical burden in urban air due to the multitude of source sectors and hence, associated impacts of human health and environment.

The concentrations of individual OPEs in each city are listed in Table S5. The three chlorinated OPEs (Cl-OPEs): tris (2-chloroethyl) phosphate (TCEP), tris (chloroisopropyl) phosphate (TCIPP), and tris (1,3 dichloro-2-propyl) phosphate (TDCIPP), constituted 40–87% of the total and were detected in 95–100% of samples. The Σ_3Cl-OPEs ranged from a low of 254 pg/m^3 in Kolkata, India to a high of

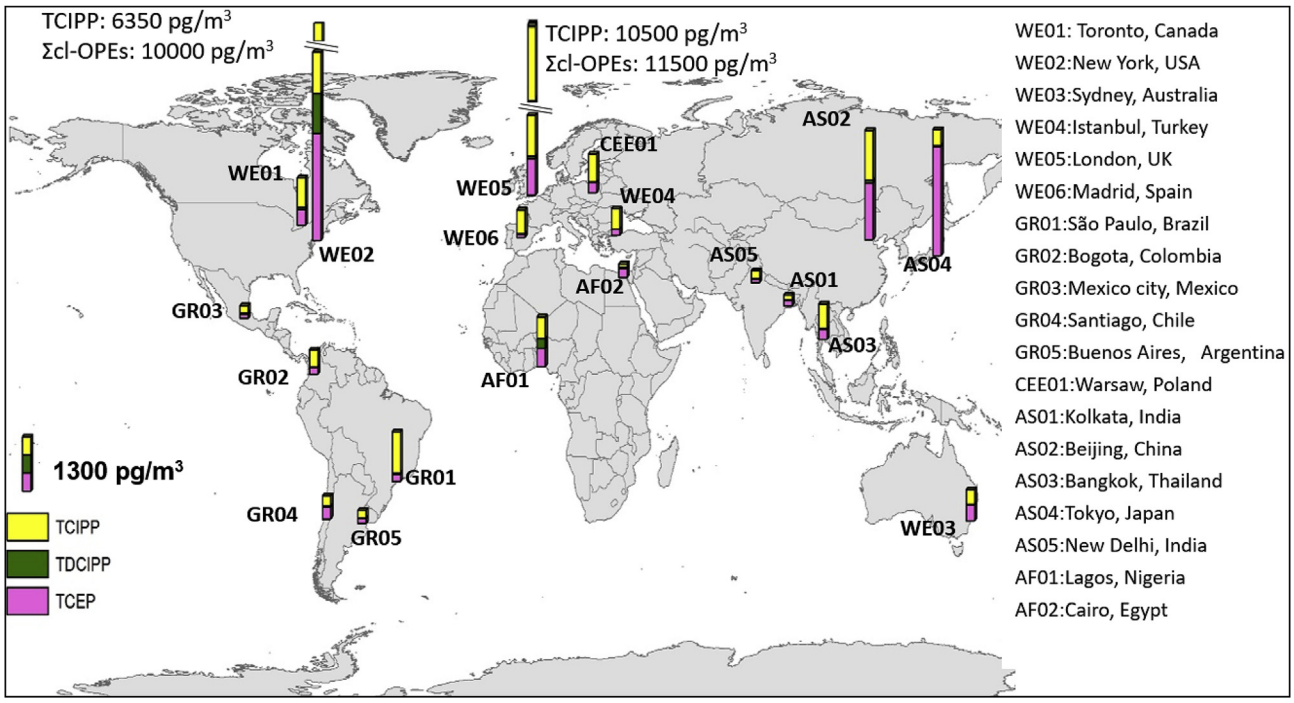

Fig. 3. Concentrations (pg/m^3) of three chlorinated OPEs (TCIPP, TDCIPP and TCEP) as measured at 19 major cities across the globe.

11,500 pg/m^3 in London, UK (Fig. 3). The second-highest levels of Σ_3Cl-OPEs were measured at New York, USA (9930 pg/m^3). For the other WEOG cities (i.e. Toronto, Madrid, Istanbul and Sydney), Σ_3Cl-OPEs were about an order of magnitude lower. In the GRULAC region, Σ3Cl-OPEs ranged from 304 to 1420 pg/m^3. Tri-phenyl phosphate (TPHP) and tri-*p*-tolyl phosphate (m-TMPP) were the two aryl OPEs detected in the current study constituting 4–35% of total OPEs (Figure S5). TPHP was the predominant one at the majority of the sites with the levels ranging from 24 pg/m^3 (Istanbul, Turkey) to 2100 pg/m^3 (London, UK). The further discussion on the levels of other individual OPEs has been given in SI Text S4 and shown in Figures S5 and S6.

PBDEs: The detection frequencies of PBDE congeners ranged between 58% (BDE-154) to 100% (BDE-28, -47, −99, −100 and −209) (Table S2). The total concentrations of Σ_9PBDEs ranged from 4.75 pg/m^3 (Sydney, Australia) to 134 pg/m^3 (Lagos, Nigeria) (Fig. 1 and S7 and Table 1). Lagos has seen unprecedented urbanization and industrialization in the past decades with an annual urban growth rate of 5.8%, resulting in an increase in atmospheric emissions (Aliyu and Amadu, 2017). Furthermore, it is also home to vast amounts of electronic waste, exported from developed countries, thus adding to the environmental challenges (Sullivan, 2014). Landfill fires is also a burning issue in Nigeria due to poor waste disposal practices (Aderemi and Otitoloju, 2012). For instance, in the Olusosun landfill in Lagos (~8 km from our sampling site in Lagos), which is the largest open dumpsite in Africa, there was a fire outbreak in March 2018 that persisted for months and overlapped with Period 1 of this study (Kalu, 2018). The Olusosun landfill is known to receive all types of unsorted waste including a substantial amount of plastic and electronic waste. Open burning of waste is reported as one of the main sources of emission of POPs including PBDEs to the environment (Gullett et al., 2010). All these factors speak to the elevated concentrations of PBDEs in Lagos's atmosphere.

New York, USA had a second-highest ΣPBDE concentration (111 pg/m^3) followed by London, UK (88.0 pg/m^3) and Bangkok, Thailand (65.5 pg/m^3). Table S8 presents the levels of PBDEs in urban areas across the world as reported in previous studies. The total PBDE concentrations reported previously in urban areas of North America ranged between 15.7 and 52 pg/m^3 (Liu et al., 2016b; Saini et al., 2019), which is in agreement with levels reported in the current study in the same region. In the GRULAC region, Σ_9PBDEs ranged from 11.7 (Bogota, Colombia) to 34.9 pg/m^3 (Mexico City, Mexico). PBDEs in the GRULAC urban environment have been reported previously by Rauert et al. (2018) in Cordoba and Mar del Plata, Argentina (118 and 1.16 pg/m^3) which bracket the values measured in Buenos Aires, Argentina (14.5 pg/m^3) in the current study and demonstrate that the intercity variability of FR burdens in air, within the same country, can be substantial. However, total PBDEs levels reported in Concepcion, Chile (10 pg/m^3) and São Luis, Brazil (11.3 pg/m^3) (Rauert et al., 2018) are close to 13.6 and 18.3 pg/m^3 of total PBDE levels reported in Santiago, Chile and São Paulo, Brazil, respectively, in the current study. In the Asia-Pacific region, Σ_9PBDEs ranged from 16.9 pg/m^3 in Kolkata, India to 65.5 pg/m^3 in Bangkok, Thailand. These levels are in line with those reported by Qi et al. (2014) in Harbin, China (69.0 pg/m^3) but lower than those reported by Chakraborty et al. (2017) in four metropolitan cities of India including New Delhi and Kolkata (135–264 pg/m^3). Two previous studies reported averages of 16 and 45.8 pg/m^3 of ΣPBDEs (ranges: 0.08–211 and 0.073–942 pg/m^3, respectively) from 4 to 5 urban locations for the years 2008–2013 under the Spanish air monitoring program (De la Torre et al., 2016; Muñoz-Arnanz et al., 2016). The levels of Σ_9PBDEs in Madrid, Spain in the current study was 22 pg/m^3, which is towards the lower end of the range reported in the Spanish studies. In comparison to the GAPS measurements at background sites, the median concentration of 34.9 pg/m^3 representing all megacities in the current study, is approximately 12 times higher than the median of 3 pg/m^3 (range = 0.08–44 pg/m^3) reported under GAPS network for 31 background sites (Rauert et al., 2018).

The concentration of individual BDE congeners at each sampling site is given in Table S7. Penta-BDE congeners (BDE-47, 66, 99, 100,

153 and 154) and BDE-209 constituted >90% of the total concentrations at all sampling locations. Penta- and deca-BDE formulations were listed in the Stockholm Convention in 2009 and 2017, respectively. These regulations do not address the existing stocks of in-use PBDE and other POPs-containing products or the products that have entered the waste phase. Environmentally sound management and transboundary movement of hazardous waste and recyclable materials and hazardous chemicals are being regulated under UNEP's Basel Convention and Rotterdam Convention, respectively (Basel Convention, 2019; Rotterdam Convention, 2019). Regardless, the in-use products stock, e-waste and recycled polymer are expected to continue to be the sources of POPs e.g. PBDEs to the environment (Ionas et al., 2014; Abbasi et al., 2015; Breivik et al., 2016). In the current study, except in Sydney and Bangkok, BDE-209 dominated the profile which reflects the shift in usage pattern with the earlier phase-out of penta-BDE formulation in comparison to BDE-209 (Figure S8). Further discussion on individual BDEs is given in Text S5.

BDE-209 constituted ≥70% of the total concentrations at 14 out of 19 sites. The highest concentration of 84.8 pg/m^3 of BDE-209 was measured at London, UK followed by 63.8 and 49.9 pg/m^3 at Lagos, Nigeria and Tokyo, Japan, respectively (Figure S8 and Table S7). The comparison of BDE-209 levels reported in the current study and previous studies is given in Text S5 and Table S8.

HFRs: *NFRs*: The NFRs were measured with a higher range of detection frequencies (Table S2) and at similar or higher levels in comparison to PBDEs at all locations (Table 1 and Fig. 1 and S7). This configuration also indicates the shift towards using alternative FRs with the phase-out of PBDEs in the past decade. New York, USA had the highest concentrations of Σ_{11}NFRs (149 pg/m^3) followed by Lagos, Nigeria (121 pg/m^3). The concentrations at other sites ranged from 5.24 pg/m^3 (Istanbul, Turkey) to 89.0 pg/m^3 (Mexico City, Mexico). The NFR levels reported in the current study are in the range of those previously reported by Drage et al. (2016); Liu et al. (2016a, b); Rauert et al. (2018); Wong et al. (2018) and Saini et al. (2019) at urban sites of UK, USA, France, Sweden and Toronto, respectively (Table S10). However, the total levels of NFRs reported in Istanbul, Turkey and in Guangzhou and Tianjin, China by Kurt-Karakus et al. (2017) and Li et al. (2017), respectively, were a factor of ≥3 higher than the maximum levels reported in the current study. The median level of 30 pg/m^3 in the current study is ~23 times higher than the background median level of 1.3 pg/m^3, (range = 0–16 pg/m^3) reported by Rauert et al. (2018). Moreover, the detection frequencies of NFRs at background sites were ≤40% whereas, the detection frequencies of NFRs in the current study were ≥90%. It highlights another advantage of monitoring these compounds in an urban environment where the levels are more likely well above the detection limits and would provide better updated scenarios of changing use and emission patterns of FRs.

Table S9 and Fig. 4, S9 and S10 summarize the concentration of 11 out of 17 NFRs that were detected in the samples with the detection frequency of 89–100%. Bis(2-ethyl-1-hexyl)tetrabromophthalate (BEHTEBP) had the highest levels among the detected NFRs at 89% of the sites with the concentrations ranging between 1.19 pg/m^3 (Beijing, China) and 68.3 pg/m^3 (New York, USA). Pentabromobenzene, pentabromotoluene, pentabromoethylbenzene, 2,3-dibromopropyl-2,4,6-tribromophenyl ether and hexabromobenzene (PBBZ, PBT, PBEB, TBP-DBPE and HBB, respectively) were among other brominated NFRs that were detected in the samples in the range of 0.14–7.85, 0.30–8.66, 0.03–6.84, 0.13–7.72 and 0.02–14.7 pg/m^3, respectively (Figure S10). Their levels were comparatively lower in the GRULAC region than in other regions. A summary of the comparison of their levels measured in the current study and to those reported by other urban studies is given in SI, Text S6 and Table S10.

Among chlorinated FRs, the highest concentration of Σsyn- and anti-dechlorane plus (ΣDP; 27.9 pg/m^3) and Σdechlorane-602 and -604 (ΣDec; 5.81 pg/m^3) were observed at Lagos, Nigeria (Table S9 and Fig. 4). DP and Dec compounds were introduced as replacements for Mirex following the ban on latter's usage back in the late 1970s. In the technical mixture of DP, different ratios of syn- and anti-DP (i.e. *f*syn = syn-DP/ΣDP) ranging between 0.20 and

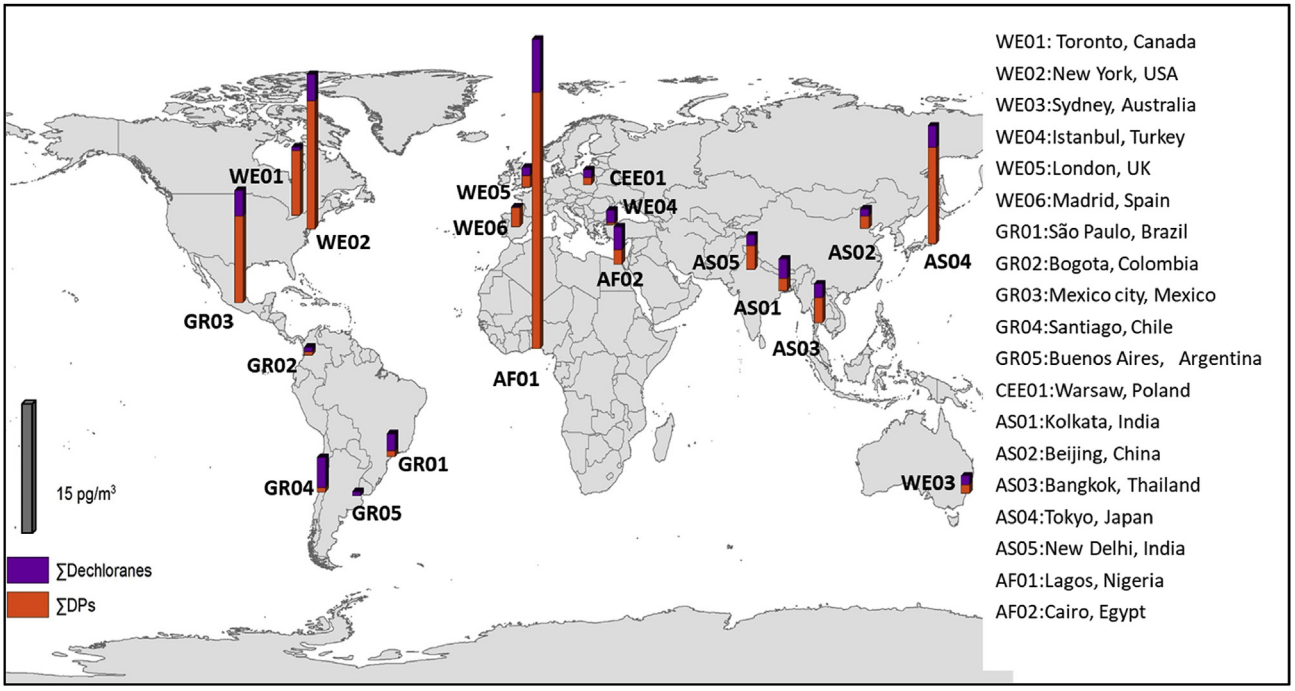

Fig. 4. A map of total concentrations (pg/m^3) and profile of dechloranes (602 and 604) and dechlorane plus (syn- and anti-isomers) at 19 major cities across the globe.

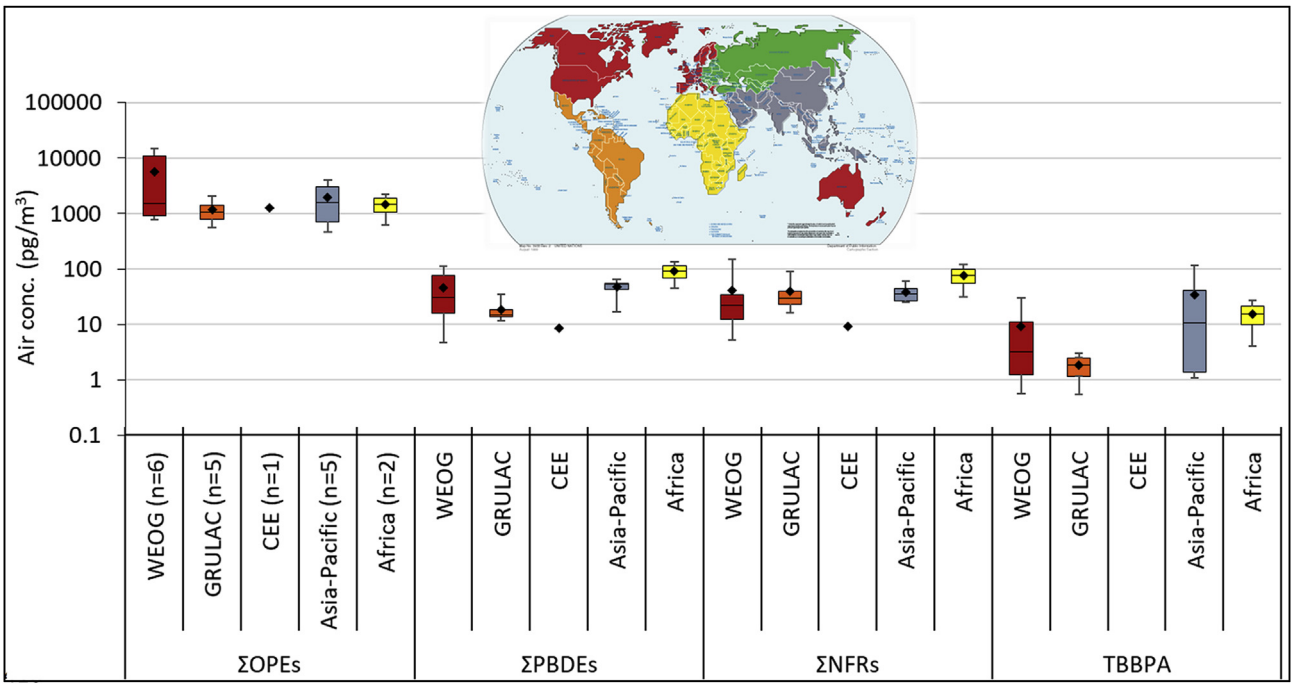

Fig. 5. Comparison of atmospheric concentrations (pg/m^3) of Σ_{10}OPEs, Σ_9PBDEs, Σ_{11}NFRs and TBBPA as shown in box and whisker plots across the five United Nations regional groups. Black markers indicate the average; top, middle and bottom lines of the boxes show 75th percentiles, medians and 25th percentiles, respectively, and whiskers represent the minimum and maximum total concentration. N represents the number of major cities sampled in the given region. Note that HBCDD is not included here because of fewer detections. WEOG = Western Europe and Other States Group; GRULAC = Group of Latin American and the Caribbean; CEE = Central and Eastern Europe (green on map). Source of world map: https://www.informea.org/en/map-5-un-regions.(For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

0.41 have been reported previously, depending upon the manufacturer (e.g. Oxychem, USA and Anpon, China) (Zhu et al., 2007; Wang et al., 2010). The discussion on *f*syn observed in the current study is given in SI, Text S6. DP is currently being considered for listing under the Stockholm Convention (Stockholm Convention, 2019).

TBBPA: TBBPA was detected in 79% of samples with concentrations ranging from 0.54 to 118 pg/m^3 (Table S2). Tokyo, Japan had the highest concentration of TBBPA (118 pg/m^3) followed by New Delhi, India (41.0 pg/m^3) (Fig. 1 and S7 and Table 1). The concentrations at other sites were <30 pg/m^3. There is limited literature on TBBPA levels in outdoor air, especially in urban environments (Liu et al., 2016a). Abdallah et al. (2008) reported 0.8 pg/m^3 of TBBPA in outdoor air in Birmingham, UK whereas in Hokkaido, Japan, 8.3 pg/m^3 of TBBPA was reported by Takigami et al. (2009). Further discussion on TBBPA is given in Text S6.

HBCDD: The three isomers of HBCDD (α, β and γ) were the least detected compounds with a detection frequency ranging between 21 and 32% only (Table S2). Beijing, China had the highest ΣHBCDD concentrations in air of 53.3 pg/m^3 followed by Istanbul, Turkey (41.8 pg/m^3) (Tables S4 and S12; Fig. 1 and S7). The remaining sites had <11 pg/m^3 of ΣHBCDD measured in the samples. The discussion on isomer profile observed in samples is given in SI, Text S6 and shown in Figure S11. The comparison of HBCDD reported in previous studies is given in Table S10. Qi et al. (2014) and Kurt-Karakus et al. (2017) reported 150 and 1200 pg/m^3 for ΣHBCDD in Harbin, China and Istanbul, Turkey, respectively, which is ~3 and 30 times higher than the levels in the present study (Table S10). Rauert et al. (2018) also reported 16–58.8 pg/m^3 of ΣHBCDD in Paris, which is within the range of ΣHBCDD reported in the current study. They also reported 110–175 pg/m^3 of γ-HBCDD in 2015 in Concepción, Chile (a city close to an industrial port, Talcahuano, Chile) whereas HBCDD was not detected in Santiago, Chile in the current study. Drage et al. (2016) reported 130 pg/m^3 of ΣHBCDD in Birmingham, UK which is > 30 times higher than the value for London, UK in the present study.

3.4. Comparison of five United Nations' regional groups

The concentrations measured in megacities from different countries were compared according to their United Nations' regional classification (Table 1 and Fig. 5). Despite observing a wide range of concentrations of the given chemical classes between cities, the median values for each region were within a factor of five, excluding the CEE region, which was represented by only one city (Warsaw, Poland). This relative consistency in levels was somewhat surprising given different production and usage patterns among regions. This widespread occurrence of FRs at elevated concentrations in major cities across the globe highlights concerns associated with highly exposed human populations and chemical mixtures in the air that result in uncertain but potentially concerning health impacts.

4. Conclusion

This is the first pilot study to assess levels of FRs in ambient air across major global cities, using a single monitoring platform. The total atmospheric concentrations of FRs ranged from 500 pg/m^3 to 16,000 pg/m^3, with OPEs dominating the profile at each city. Regardless of the wide range of total FRs, a relatively small difference was observed when concentrations were averaged across the United Nations' regions. A significant positive correlation of OPEs and GDP of the cities reflected the increased production and applications of OPEs in commercial products after the phase-out of PBDEs. This study highlights the importance of ambient air surveillance in urban areas to depict the changes in emission patterns

and eventually temporal trends, in order to assess the effectiveness of imposed regulations under international treaties such as the Stockholm Convention. Samples collected under the GAPS-MC pilot study from period 2 are also being analyzed for trace metals using the method recently developed by Gaga et al. (2019). Future work under the GAPS-MC will relate contaminant profiles of FRs and trace metals to a wide range of toxicity indicators based on the air sample extracts and *in vitro* methods. For instance, we have developed a method for generating and identifying FR transformation products in the air that contribute to the mixture toxicity (Liu et al., 2019) and plan to screen for these in our samples. The ultimate goal of this approach is to link chemical mixtures in ambient air to potential health effects, especially considering that the majority of the world's population resides in urban areas and experiences exposure to high levels of pollutants. In the environmental monitoring community, the paradigm is also shifting from selective chemical-by-chemical assessment approach towards identification of the 'unknowns and unforeseen' chemicals in air mixtures using non-targeted screening approaches (Escher et al., 2020), which is also part of the next phase and broader scope of the GAPS-MC study.

CRediT authorship contribution statement

Amandeep Saini: Conceptualization, Project administration, Investigation, Validation, Formal analysis, Writing - original draft, Writing - review & editing. **Tom Harner:** Conceptualization, Resources, Supervision, Writing - review & editing. **Sita Chinnadhurai:** Investigation, Validation, Writing - review & editing. **Jasmin K. Schuster:** Visualization, Writing - review & editing. **Alan Yates:** Investigation, Writing - review & editing. **Andrew Sweetman:** Investigation, Writing - review & editing. **Beatriz H. Aristizabal-Zuluaga:** Investigation, Writing - review & editing. **Begoña Jiménez:** Investigation, Writing - review & editing. **Carlos A. Manzano:** Investigation, Writing - review & editing. **Eftade O. Gaga:** Investigation, Writing - review & editing. **Gavin Stevenson:** Investigation, Writing - review & editing. **Jerzy Falandysz:** Investigation, Writing - review & editing. **Jianmin Ma:** Investigation, Writing - review & editing. **Karina S.B. Miglioranza:** Investigation, Writing - review & editing. **Kurunthachalam Kannan:** Investigation, Writing - review & editing. **Maria Tominaga:** Investigation, Writing - review & editing. **Narumol Jariyasopit:** Investigation, Writing - review & editing. **Nestor Y. Rojas:** Investigation, Writing - review & editing. **Omar Amador-Muñoz:** Investigation, Writing - review & editing. **Ravindra Sinha:** Investigation, Writing - review & editing. **Rose Alani:** Investigation, Writing - review & editing. **R. Suresh:** Investigation, Writing - review & editing. **Takahiro Nishino:** Investigation, Writing - review & editing. **Tamer Shoeib:** Investigation, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.115416.

References

Abbasi, G., Buser, A.M., Soehl, A., Murray, M.W., Diamond, M.L., 2015. Stocks and flows of PBDEs in products from use to waste in the U.S. and Canada from 1970 to 2020. Environ. Sci. Technol. 49 (3), 1521–1528.

Abdallah, M.A.-E., Harrad, S., Covaci, A., 2008. Hexabromocyclododecanes and tetrabromobisphenol-A in indoor air and dust in Birmingham, UK: Implications for human exposure. Environ. Sci. Technol. 42 (18), 6855–6861.

Abdel-Shafy, H.I., Mansour, M.S.M., 2016. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt. J. Petrol. 25 (1), 107–123.

Aderemi, A.O., Otitoloju, A.A., 2012. An assessment of landfill fires and their potential health effects: a case study of a municipal solid waste landfill in Lagos, Nigeria. Int. J. Environ. Protect. 2 (2), 22–26.

Aliyu, A.A., Amadu, L., 2017. Urbanization, cities, and health: the challenges to Nigeria - a review. Ann. Afr. Med. 16 (4), 149–158.

Basel Convention, 2019. http://www.basel.int/TheConvention/Overview/tabid/1271/Default.aspx. (Accessed 12 August 2019).

Blum, A., Behl, M., Birnbaum, L.S., Diamond, M.L., Phillips, A., Singla, V., Sipes, N.S., Stapleton, H.M., Venier, M., 2019. Organophosphate ester flame retardants: are they a regrettable substitution for polybrominated diphenyl ethers? Environ. Sci. Technol. Lett. 6, 638–649.

Bogdal, C., Wang, Z., Buser, A.M., Scheringer, M., Gerecke, A.C., Schmid, P., Muller, C.E., MacLeod, M., Hungerbühler, K., 2014. Emissions of polybrominated diphenyl ethers (PBDEs) in Zurich, Switzerland, determined by a combination of measurements and modeling. Chemosphere 116, 15–23.

Breivik, K., Armitage, J.M., Wania, F., Sweetman, A.J., Jones, K.C., 2016. Tracking the global distribution of persistent organic pollutants accounting for e-waste exports to developing regions. Environ. Sci. Technol. 50 (2), 798–805.

Cambridge dictionary, 2019. https://dictionary.cambridge.org/dictionary/english/megacity. (Accessed 9 July 2019).

Cao, J., Xu, H., Xu, Q., Chen, B., Kan, H., 2012. Fine particulate matter constituents and cardiopulmonary mortality in a heavily polluted Chinese city. Environ. Health Perspect. 120 (3), 373–378.

Chakraborty, P., Zhang, G., Cheng, H., Balasubramanian, P., Li, J., Jones, K.C., 2017. Passive air sampling of polybrominated diphenyl ethers in New Delhi, Kolkata, Mumbai and Chennai: levels, homologous profiling and source apportionment. Environ. Pollut. 231, 1181–1187.

Chung, Y., Dominici, F., Wang, Y., Coull Brent, A., Bell Michelle, L., 2015. Associations between long-term exposure to chemical constituents of fine particulate matter (PM2.5) and mortality in medicare enrollees in the eastern United States. Environ. Health Perspect. 123 (5), 467–474.

De la Torre, A., Sanz, P., Navarro, I., Martínez, M.Á., 2016. Time trends of persistent organic pollutants in Spanish air. Environ. Pollut. 217, 26–32.

Drage, D.S., Newton, S., de Wit, C.A., Harrad, S., 2016. Concentrations of legacy and emerging flame retardants in air and soil on a transect in the UK West Midlands. Chemosphere 148, 195–203.

Escher, B.I., Stapleton, H.M., Schymanski, E.L., 2020. Tracking complex mixtures of chemicals in our changing environment. Science 367 (6476), 388–392.

Gaga, E.O., Harner, T., Dabek-Zlotorzynska, E., Celo, V., Evans, G., Jeong, C.-H., Halappanavar, S., Jariyasopit, N., Su, Y., 2019. Polyurethane foam (PUF) disk samplers for measuring trace metals in ambient air. Environ. Sci. Technol. Lett. 6 (9), 545–550.

Gouin, T., Harner, T., Blanchard, P., Mackay, D., 2005. Passive and active air samplers as complementary methods for investigating persistent organic pollutants in the Great Lakes Basin. Environ. Sci. Technol. 39, 9115–9122.

Guigueno, M.F., Head, J.A., Letcher, R.J., Karouna-Renier, N., Peters, L., Hanas, A.M., Fernie, K.J., 2019. Early life exposure to triphenyl phosphate: effects on thyroid function, growth, and resting metabolic rate of Japanese quail (Coturnix

japonica) chicks. Environ. Pollut. 253, 899–908.
Gullett, B.K., Wyrzykowska, B., Grandesso, E., Touati, A., Tabor, D.G., Ochoa, G.S., 2010. PCDD/F, PBDD/F, and PBDE emissions from open burning of a residential waste dump. Environ. Sci. Technol. 44 (1), 394–399.
Harner, T., Pozo, K., Gouin, T., Macdonald, A.M., Hung, H., Cainey, J., Peters, A., 2006. Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers. Environ. Pollut. 144 (2), 445–452.
He, C., Lin, C.-Y., Mueller, J.F., 2020. Organophosphate flame retardants in the environment: source, occurrence, and human exposure. In: Comprehensive Analytical Chemistry. Elsevier, Amsterdam, Netherlands, pp. 341–365.
Ionas, A.C., Dirtu, A.C., Anthonissen, T., Neels, H., Covaci, A., 2014. Downsides of the recycling process: Harmful organic chemicals in children's toys. Environ. Int. 65, 54–62.
Kalu, B., 2018. Landfill fury. Lancet Respir. Med. 6 (6), 419.
Kim, J.H., Park, H.Y., Bae, S., Lim, Y.H., Hong, Y.C., 2013. Diethylhexyl phthalates is associated with insulin resistance via oxidative stress in the elderly: a panel study. PloS One 8 (8), e71392.
Kurt-Karakus, P., Alegria, H., Birgul, A., Gungormus, E., Jantunen, L., 2018. Organophosphate ester (OPEs) flame retardants and plasticizers in air and soil from a highly industrialized city in Turkey. Sci. Total Environ. 625, 555–565.
Kurt-Karakus, P., Alegria, H., Jantunen, L., Birgul, A., Topcu, A., Jones, K.C., Turgut, C., 2017. Polybrominated diphenyl ethers (PBDEs) and alternative flame retardants (NFRs) in indoor and outdoor air and indoor dust from Istanbul-Turkey: levels and an assessment of human exposure. Atmos. Pollut. Res. 8 (5), 801–815.
Lam, J., Lanphear Bruce, P., Bellinger, D., Axelrad Daniel, A., McPartland, J., Sutton, P., Lisette, D., Natalyn, D., Saunak, S., Woodruff Tracey, J., 2017. Developmental PBDE exposure and IQ/ADHD in childhood: a systematic review and meta-analysis. Environ. Health Perspect. 125 (8), 086001.
Lelieveld, J., Pozzer, A., Pöschl, U., Fnais, M., Haines, A., Münzel, T., 2020. Loss of life expectancy from air pollution compared to other risk factors: a worldwide perspective. Cardiovasc. Res. 116 (7), 1334.
Li, Q., Yang, K., Li, K., Liu, X., Chen, D., Li, J., Zhang, G., 2017. New halogenated flame retardants in the atmosphere of nine urban areas in China: pollution characteristics, source analysis and variation trends. Environ. Pollut. 224, 679–688.
Liu, K., Li, J., Yan, S., Zhang, W., Li, Y., Han, D., 2016a. A review of status of tetrabromobisphenol A (TBBPA) in China. Chemosphere 148, 8–20.
Liu, L.-Y., Salamova, A., Venier, M., Hites, R.A., 2016b. Trends in the levels of halogenated flame retardants in the Great Lakes atmosphere over the period 2005–2013. Environ. Int. 92–93, 442–449.
Liu, Q., Liggio, J., Wu, D., Saini, A., Halappanavar, S., Wentzell, J.J.B., Harner, T., Li, K., Lee, P., Li, S.M., 2019. Experimental study of OH-initiated heterogeneous oxidation of organophosphate flame retardants: Kinetics, mechanism, and toxicity. Environ. Sci. Technol. 53 (24), 14398–14408.
Liu, X., Zhang, G., Li, J., Yu, L.L., Xu, Y., Li, X.D., Kobara, Y., Jones, K.C., 2009. Seasonal patterns and current sources of DDTs, chlordanes, hexachlorobenzene, and endosulfan in the atmosphere of 37 Chinese cities. Environ. Sci. Technol. 43 (5), 1316–1321.
Loganathan, B.G., Masunaga, S., 2009. Chapter 18 - PCBs, dioxins, and Furans: human exposure and health effects. In: Gupta, R.C. (Ed.), Handbook of Toxicology of Chemical Warfare Agents. Academic Press, San Diego, pp. 245–253.
Lyche, J.L., Rosseland, C., Berge, G., Polder, A., 2015. Human health risk associated with brominated flame-retardants (BFRs). Environ. Int. 74, 170–180.
Markovic, M.Z., Prokop, S., Staebler, R.M., Liggio, J., Harner, T., 2015. Evaluation of the particle infiltration efficiency of three passive samplers and the PS-1 active air sampler. Atmos. Environ. 112, 289–293.
Muñoz-Arnanz, J., Roscales, J.L., Ros, M., Vicente, A., Jiménez, B., 2016. Towards the implementation of the Stockholm Convention in Spain: five-year monitoring (2008–2013) of POPs in air based on passive sampling. Environ. Pollut. 217, 107–113.
Peverly, A.A., Ma, Y., Venier, M., Rodenburg, Z., Spak, S.N., Hornbuckle, K.C., Hites, R.A., 2015. Variations of flame retardant, polycyclic aromatic hydrocarbon, and pesticide concentrations in Chicago's atmosphere measured using passive sampling. Environ. Sci. Technol. 49 (9), 5371–5379.
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 (3), 796–803.
Pozo, K., Harner, T., Wania, F., Muir, D.C.G., Jones, K.C., Barrie, L.A., 2006. Toward a global network for persistent organic pollutants in air: results from the GAPS study. Environ. Sci. Technol. 40 (16), 4867–4873.
Qi, H., Li, W.-L., Liu, L.-Y., Song, W.-W., Ma, W.-L., Li, Y.-F., 2014. Brominated flame retardants in the urban atmosphere of Northeast China: concentrations, temperature dependence and gas–particle partitioning. Sci. Total Environ. 491–492, 60–66.
Rauert, C., Harner, T., Schuster, J.K., Quinto, K., Fillmann, G., Castillo, L.E., Fentanes, O., Ibarra, M.V., Miglioranza, K.S.B., Rivadeneira, I.M., Pozo, K., Puerta, A.P., Zuluaga, B.H.A., 2016. Towards a regional passive air sampling network and strategy for new POPs in the GRULAC region: Perspectives from the GAPS Network and first results for organophosphorus flame retardants. Sci. Total Environ. 573, 1294–1302.
Rauert, C., Schuster, J.K., Eng, A., Harner, T., 2018. Global atmospheric concentrations of brominated and chlorinated flame retardants and organophosphate esters. Environ. Sci. Technol. 52 (5), 2777–2789.
Reemtsma, T., Quintana, J.B., Rodil, R., García-Lópe, M., Rodríguez, I., 2008. Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. Trac. Trends Anal. Chem. 27 (9), 727–737.
Rodgers, T.F.M., Truong, J.W., Jantunen, L.M., Helm, P.A., Diamond, M.L., 2018. Organophosphate ester transport, fate, and emissions in Toronto, Canada, estimated using an updated multimedia urban model. Environ. Sci. Technol. 52 (21), 12465–12474.
Rotterdam Convention, 2019. http://www.pic.int/TheConvention/Overview/tabid/1044/language/en-US/Default.aspx. (Accessed 12 August 2019).
Saini, A., Clarke, J., Jariyasopit, N., Rauert, C., Schuster, J.K., Halappanavar, S., Evans, G.J., Su, Y., Harner, T., 2019. Flame retardants in urban air: a case study in Toronto targeting distinct source sectors. Environ. Pollut. 247, 89–97.
Salamova, A., Ma, Y., Venier, M., Hites, R.A., 2014. High levels of organophosphate flame retardants in the Great Lakes atmosphere. Environ. Sci. Technol. Lett. 1 (1), 8–14.
Schreder, E.D., Uding, N., La Guardia, M.J., 2016. Inhalation a significant exposure route for chlorinated organophosphate flame retardants. Chemosphere 150, 499–504.
Schuster, J.K., Harner, T., Fillmann, G., Ahrens, L., Altamirano, J.C., Aristizabal, B., Bastos, W., Castillo, L.E., Cortes, J., Fentanes, O., Gusev, A., Hernandez, M., Ibarra, M.V., Lana, N.B., Lee, S.C., Martinez, A.P., Miglioranza, K.S., Puerta, A.P., Segovia, F., Siu, M., Tominaga, M.Y., 2015. Assessing polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in air across Latin American countries using polyurethane foam disk passive air samplers. Environ. Sci. Technol. 49 (6), 3680–3686.
Stockholm Convention, 2008. Global Monitoring Plan. http://chm.pops.int/Implementation/GlobalMonitoringPlan/Overview/tabid/83/Default.aspx. (Accessed 17 July 2019).
Stockholm Convention, 2019. Proposal to List Dechlorane Plus (CAS No: 13560-89-9) and its Syn- Isomer(CAS No:135821-03-3) and Anti-isomer (CAS No:135821-74-8) in Annexes A, B And/or C to the Stockholm Convention on Persistent Organic Pollutants. Persistent Organic Pollutants Review Committee. 2019. UNEP/POPS/POPRC.15/3. http://chm.pops.int/TheConvention/ThePOPs/ChemicalsProposedforListing/tabid/2510/Default.aspx. (Accessed 6 September 2019).
Sullivan, J., 2014. Trash or treasure: global trade and the accumulation of E-Waste in Lagos, Nigeria. Afr. Today 61 (1), 89–112.
Takigami, H., Suzuki, G., Hirai, Y., Sakai, S.-I., 2009. Brominated flame retardants and other polyhalogenated compounds in indoor air and dust from two houses in Japan. Chemosphere 76 (2), 270–277.
United Nations, 2018. https://www.un.org/development/desa/en/news/population/2018-revision-of-world-urbanization-prospects.html. (Accessed 17 July 2019).
Van der Veen, I., de Boer, J., 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. Chemosphere 88 (10), 1119–1153.
Wang, D.-G., Yang, M., Qi, H., Sverko, E., Ma, W.-L., Li, Y.-F., Alaee, M., Reiner, E.J., Shen, L., 2010. An Asia-specific source of dechlorane plus: concentration, isomer profiles, and other related compounds. Environ. Sci. Technol. 44 (17), 6608–6613.
WHO, 2016. Air Pollution. https://www.who.int/sustainable-development/cities/health-risks/air-pollution/en/. (Accessed 17 July 2019).
Wong, F., de Wit, C.A., Newton, S.R., 2018. Concentrations and variability of organophosphate esters, halogenated flame retardants, and polybrominated diphenyl ethers in indoor and outdoor air in Stockholm, Sweden. Environ. Pollut. 240, 514–522.
Wyzga, R.E., Rohr, A.C., 2015. Long-term particulate matter exposure: Attributing health effects to individual PM components. J. Air Waste Manage. 65 (5), 523–543.
Yang, J., Zhao, Y., Li, M., Du, M., Li, X., Li, Y., 2019. A review of a class of emerging contaminants: the Classification, distribution, intensity of consumption, synthesis routes, environmental effects and expectation of pollution abatement to organophosphate flame retardants (OPFRs). Int. J. Mol. Sci. 20 (12), 2874.
Zhu, J., Feng, Y.-l., Shoeib, M., 2007. Detection of dechlorane plus in residential indoor dust in the city of Ottawa, Canada. Environ. Sci. Technol. 41 (22), 7694–7698.