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Atmospheric Concentrations of New Persistent Organic Pollutants and Emerging Chemicals of Concern in the Group of Latin America and Caribbean (GRULAC) Region

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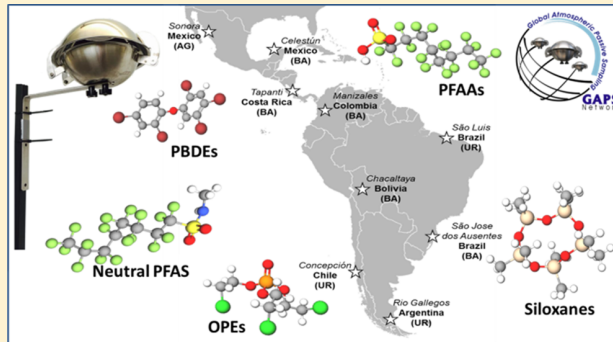
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Supporting Information

ABSTRACT: A special initiative was run by the Global Atmospheric Passive Sampling (GAPS) Network to provide atmospheric data on a range of emerging chemicals of concern and candidate and new persistent organic pollutants in the Group of Latin America and Caribbean (GRULAC) region. Regional-scale data for a range of flame retardants (FRs) including polybrominated diphenyl ethers (PBDEs), organophosphate esters (OPEs), and a range of alternative FRs (novel FRs) are reported over 2 years of sampling with low detection frequencies of the novel FRs. Atmospheric concentrations of the OPEs were an order of magnitude higher than all other FRs, with similar profiles at all sites. Regional-scale background concentrations of the poly- and perfluoroalkyl substances (PFAS), including the neutral PFAS (n-PFAS) and perfluoroalkyl acids (PFAAs), and the volatile methyl siloxanes (VMS) are also reported. Ethyl perfluorooctane sulfonamide (EtFOSA) was detected at highly elevated concentrations in Brazil and Colombia, in line with the use of the pesticide sulfuramid in this region. Similar concentrations of the perfluoroalkyl sulfonates (PFAS) were detected throughout the GRULAC region regardless of location type, and the VMS concentrations in air increased with the population density of sampling locations. This is the first report of atmospheric concentrations of the PFAAs and VMS from this region.



INTRODUCTION

The capacity for the Global Monitoring Plan (GMP) to evaluate the effectiveness of the United Nations Environment Programme's (UNEP) Stockholm Convention on persistent organic pollutants (POPs) is limited by the lack of monitoring information on POPs from developing regions. The GMP aims to provide comparable monitoring data from all United Nations (UN) regions;¹ however, there is a substantial gap from developing regions such as the Group of Latin American and Caribbean countries (GRULAC).^{2–4} This limits the informa-

tion provided to risk assessments on chemicals of concern; the ability to evaluate regional and global environmental transport^{2,5} and prevents global spatial and temporal trends being developed, thus limiting the ability to evaluate the effectiveness of restrictions.⁶

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Passive air sampling is a particularly useful methodology for atmospheric monitoring in developing regions^{7,8} because remote locations can be accessed with no electricity requirements, and they are cost-effective and easy to deploy. As such, a special initiative was implemented in 2012 by the Global Atmospheric Passive Sampling (GAPS) network, with support from UNEP, to address the lack of information on emerging contaminants and candidate, and new POPs in the GRULAC region. The GAPS network is a global passive sampling monitoring network that contributes unique atmospheric data on legacy and new and emerging POPs to the GMP.⁹ The GAPS network is run by a central laboratory at Environment and Climate Change Canada (ECCC) and contributes to international regulatory programs such as the Stockholm Convention and also contributes to domestic Canadian risk assessments and management programs under the Chemicals Management Plan (CMP).

The core GAPS sampling campaign includes a few sites in the GRULAC region,^{9,10} and in this special initiative, additional sites were added to provide a more-comprehensive monitoring reach. The first regional-scale monitoring data for polychlorinated dioxins and furans in the region has been reported from this initiative.¹¹ The second phase of this study has focused on emerging contaminants and candidate and new POPs. The first atmospheric data for organophosphate ester (OPE) flame retardants (FRs) in the GRULAC region has since been reported.² With the conclusion of the second phase of this special initiative, a wide range of new and emerging POPs have been monitored, including the polybrominated diphenyl ethers (PBDEs), OPEs, a range of other brominated and chlorinated alternative FRs (novel FRs), a range of poly- and perfluoroalkyl substances (PFAS), and the volatile methyl siloxanes (VMS).

PBDEs have been used historically as FRs in a range of consumer products including foam, electronic, and textile products. They are produced in three different commercial formulations: the PentaBDE, OctaBDE, and DecaBDE formulations, which contain different contributions of the PBDE congeners. Due to concerns over their persistency and toxicity, all three technical formulations have now been added to the Stockholm Convention for reduction with restricted uses.¹² With the restrictions imposed on the use of PBDEs, the use of alternative FRs has increased,^{13,14} including the OPEs and a range of other brominated and chlorinated novel FRs. These alternative FRs are also detected regularly in the environment^{13,15} and, due to concerns over its persistency and toxicity, hexabromocyclododecane (HBCD) was listed in Annex A of the Stockholm Convention in 2013.¹⁶ The OPEs have numerous applications other than as FRs, including as plasticizers, in hydraulic fluid and antifoaming agents.¹⁴ OPE atmospheric concentrations are often reported in levels that are at least an order of magnitude higher than the PBDEs.^{10,14} There are concerns over the persistency of the OPEs, and in Canada, tris(2-chloroethyl) phosphate (TCEP) is prohibited in foam products intended for children under the age of three.¹⁷ These alternative FRs are detected regularly in remote locations, thus showing their potential for long-range atmospheric transport.^{10,18–20}

PFAS are surfactants with applications including as stain repellants in fabric and grease-proof paper, in fluoropolymer manufacture and in aqueous film-forming foams.²¹ The perfluoroalkyl acids (PFAAs) have raised concerns due to their persistency and toxicity, and perfluorooctanesulfonate (PFOS) and its salts and precursor compound (perfluorooctane

sulfonyl fluoride) were added to the Stockholm Convention in 2009 for restriction of production and use, with specific exemptions.²² Perfluorohexanesulfonate (PFHxS) and perfluorooctanoic acid (PFOA) are currently under review for addition to the Stockholm Convention.²³ Also of concern are the neutral PFAS (n-PFAS), which are known to degrade in the environment to the toxic PFAAs.²¹ In the GRULAC region, Brazil has registered the use of PFOS, its salts, and PFOSF in the Register of Acceptable purposes for the use as an intermediate in the production of the pesticide sulfluramid.²⁴ The active ingredient of sulfluramid is ethyl perfluorooctane sulfonamide (EtFOSA), a known precursor for PFOS.²⁵

The VMS are used in the manufacture of silicone polymers, as surfactants and lubricants, and also in a wide range of personal-care products.²⁶ They are classified as high-production-volume chemicals, and highly elevated concentrations (as compared with the FRs and PFAS) are detected regularly in the environment.^{27,28} Concerns arise over the toxicity of the VMS to aquatic organisms,²⁹ and more monitoring is required to understand their distribution in the environment. The PFAS and VMS are also regularly detected in remote locations, again demonstrating the persistency and potential for the long-range transport of these chemicals.^{28,30–32}

Previous atmospheric monitoring studies of these chemicals of concern tend to focus on North America and Europe, and more monitoring information is needed from developing regions to provide a complete picture of global distribution and transport. This special initiative provides unique regional monitoring data on emerging chemicals of concern and new and candidate POPs from the GRULAC region, and this is the first reporting of atmospheric concentrations of the PFAAs and VMS from across this region.

■ MATERIALS AND METHODS

Sample Deployment. This special initiative included 9 sites covering 7 countries: Mexico ($n = 2$), Costa Rica ($n = 1$), Colombia ($n = 1$), Brazil ($n = 2$), Bolivia ($n = 1$), Argentina ($n = 1$), and Chile ($n = 1$). The majority of sites were classified as background sites ($n = 5$), with 3 urban and 1 agricultural site included. Site classifications follow the guidelines under the guidance document for the global monitoring plan.³³ Rio Gallegos falls under the category of suburban following these guidelines and, in this study, is referred to as an urban site. Further site details are provided in Table S1, and Figure 1 maps the location of each sampling site. At each site polyurethane foam passive air samplers (PUF-PAS) were deployed for sampling periods of 3 months, providing 4 sampling quarters throughout a sampling year, referred to as Q1, Q2, Q3, and Q4. The PUF-PAS were deployed during 2014 and 2015, and the deployment details are listed in Tables S2–S5. Sorbent-impregnated PUF passive air samplers (SIP-PAS) were also deployed for one sampling quarter in 2015. The SIP-PAS have a greater uptake capacity than the PUF-PAS,³⁴ and for more-volatile compounds that form equilibrium quickly with the PUF-PAS, the SIP-PAS will continue to sample in the linear sampling phase, providing time-averaged concentrations of these analytes. The PUF-PAS and SIP-PAS at Tapanti (Costa Rica) were deployed for a full year (June 2015–June 2016) due to restrictions accessing the site. The SIP-PAS at Chacaltaya (Bolivia) was deployed in 2016 (not 2015) but was still deployed in Q2 (April–July). Deployment details of the SIP-PAS are listed in Table S6.



Figure 1. Location of the nine sites included in the GRULAC study. The location type is listed below the site name. BA, background; AG, agricultural; and UR, urban.

PUF-PAS and SIP-PAS were precleaned, stored in glass jars, and shipped to the sampling sites following previously published methods.^{11,27} The samples were deployed in double-domed sampling chambers (TE-200, Tisch Environ-

mental, Cleves, OH), and the deployment and collection followed procedures previously published.¹¹ After collection, the samples were shipped back to ECCC for analysis.

Extraction and Analysis. The PUF-PAS were extracted and analyzed for the PBDEs, novel FRs, and OPEs. Target analytes are listed in Table S7. The PUF-PAS were extracted and processed following previously reported methods.¹⁰ The sample extracts were analyzed for the PBDEs and novel FRs with gas chromatography–tandem quadrupole mass spectrometry (GC–MS/MS) and analyzed for the OPEs and the HBCD diastereomers using ultra-performance liquid chromatography–tandem quadrupole mass spectrometry (UPLC–MS/MS). Analysis details have been previously reported in Rauert et al.¹⁰

The SIP-PAS were extracted and analyzed for the n-PFAS, PFAAs, and VMS. Target analytes are listed in Table S8. The SIP-PAS were extracted and processed following previously reported methods.²⁸ The sample extracts were analyzed for the n-PFAS and VMS with GC–MS and analyzed for the PFAAs with UPLC–MS/MS. Analysis details have been reported previously in Rauert et al.²⁸

Quality Assurance and Quality Control. Air concentrations (pg/m^3) were derived from the mass of the target analyte detected on the sample (pg) divided by an effective air sampling volume. The air volume was determined using the GAPS template.³⁵ The OPEs and novel FRs 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 $4 \text{ m}^3/\text{day}$, as described in Rauert et al.¹⁰ Field blanks were sent to each site and consisted of an additional precleaned PUF-PAS in 2014 and 2015 and a SIP-PAS in 2015. The field blanks were collected following the same protocol as the sample deployment without actual deployment. Further details on field blanks and collection are provided in Schuster et al.¹¹ The field blanks

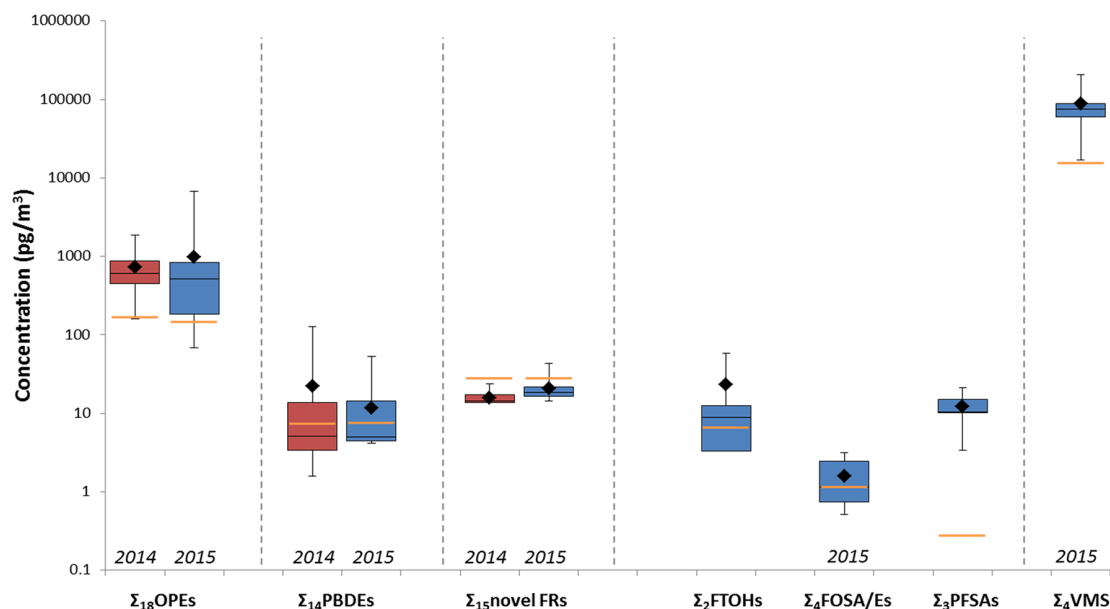


Figure 2. Box-and-whisker plots of target analyte concentrations (pg/m^3) in 2014 (red) and 2015 (blue) in the GRULAC region. The line indicates the median concentration; boxes correspond to the interquartile range with the upper and lower edges designating the 75th and 25th percentiles, respectively. The whiskers represent the maximum and minimum concentrations. The diamond indicates the mean concentration and the orange line indicates the MDL. $\Sigma_{18}\text{OPEs}$, sum of all OPEs; $\Sigma_{14}\text{PBDEs}$, sum of all PBDEs; $\Sigma_{15}\text{novel FRs}$, sum of all novel FRs; $\Sigma_2\text{FTOH}$, sum of 8:2 FTOH and 10:2 FTOH; $\Sigma_4\text{FOSA/Es}$, sum of all FOSA and FOSEs; $\Sigma_3\text{PFSA}$, sum of PFBS, PFHxS, and PFOS; and $\Sigma_4\text{VMS}$, sum of D3, D4, D5, and D6. Where an analyte was not detected, $1/2$ MDL was used.

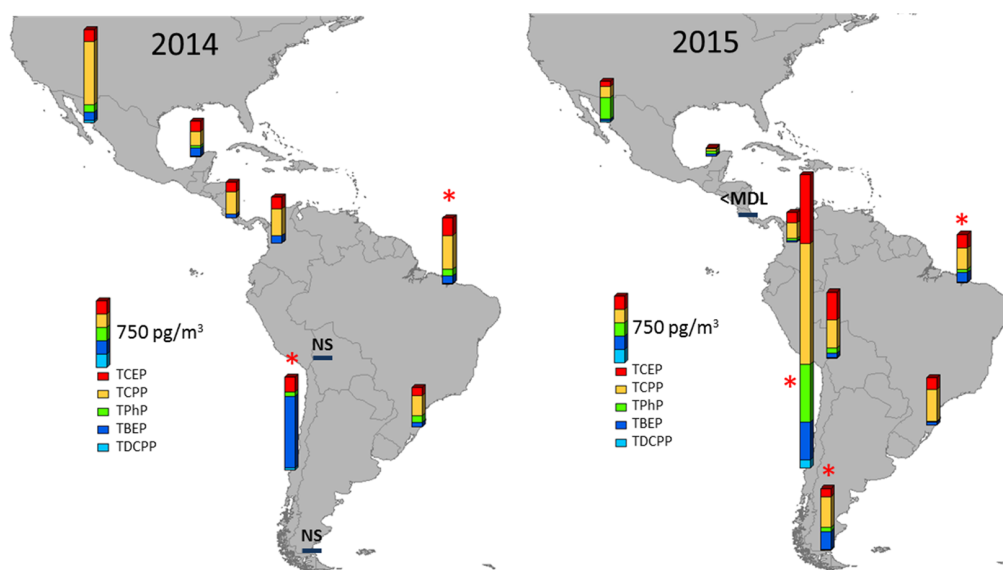


Figure 3. Map of mean concentrations (pg/m^3) of TCEP, TCPP, TPhP, TBEP, and TDCPP in the GRULAC region in 2014 and 2015. The three urban locations are marked with an asterisk. NS indicates that a sample was not deployed in that year. <MDL indicates that all analytes were below detection limits in that year.

were extracted and analyzed following the same procedures as the samples. Concentrations (ng/PAS) of target analytes detected in each field blank are listed in Tables S9–S15. Instrument detection limits (IDLs) were calculated as the concentration of a peak that would produce a signal-to-noise ratio of 3:1. Method detection limits (MDL) were calculated as the mean mass in the field blanks plus three times the standard deviation. For the OPEs, PBDEs, and novel FRs, MDLs were calculated as the mean concentration in field blanks, to keep data sets comparable with the global FR data from Rauert et al.¹⁰ Where a target analyte was detected regularly in field blanks, samples were blank corrected by subtracting the mean mass (in nanograms) from all the field blanks; hence, it is possible for reported concentrations to be below the MDLs. Limits of quantitation (LOQ) were calculated as the concentration of a peak that would produce a signal-to-noise ratio of 10:1 and inserted for MDLs where an analyte was not detected in the field blanks. For calculating average values, $1/2$ MDL or $1/2$ LOQ were inserted when an analyte was not detected. To convert MDLs and LOQs to pg/m^3 , the average air sampling volume (m^3) was applied.

All analytes, except for the novel FRs, were surrogate recovery corrected and the mean recoveries are listed in Table S16. As described in Rauert et al.¹⁰ an enhancement in the surrogate recoveries was observed for the PBDEs and hence they were not used to recovery correct the novel FRs. To improve this methodology, future analyses in the GAPS network will use mass labeled versions of the novel FRs (and the PBDEs) and adopt surrogate recovery correction for the novel FRs. However, for these samples, this option was not available, and we note that this increases the uncertainty with the analysis of the novel FRs. Statistical analyses (two-sample t tests assuming unequal variances) were conducted using Microsoft Excel 2010.

RESULTS AND DISCUSSION

PUF-PAS. The PUF-PAS were analyzed for the three FR classes. Concentrations of OPEs, PBDEs, and novel FRs from

the 2014 deployment have been reported previously,^{2,10} and this is the first reporting of atmospheric concentrations of these analyte classes from 2015. Concentrations from each sample (2014 and 2015) are listed in Tables S17–S22. Figure 2 depicts box and whisker plots of concentrations of all the analyte classes monitored (including the PFAS and VMS monitored with SIP-PAS), showing the variation in atmospheric concentrations between the different classes.

Organophosphate Esters. Total OPE concentrations ($\Sigma_{18}\text{OPEs}$) were similar between both sampling years (Figure 2), with $\Sigma_{18}\text{OPE}$ concentrations in each sample ranging 90–1850 pg/m^3 in 2014 and 60–2200 pg/m^3 in 2015, and were not significantly different between the two years ($p > 0.05$). The urban site of Concepción (Chile) was the exception, where elevated concentrations were detected in 2015 of 730–7050 pg/m^3 (Figure 3). The other two urban sites of São Luis (Brazil) and Rio Gallegos (Argentina) had concentrations in line with the background sites in both sampling years.

In this GRULAC study five OPEs were detected the most frequently and in the highest concentrations (TCEP, tris(chloroisopropyl) phosphate (TCPP), triphenyl phosphate (TPhP), tris(2-butoxyethyl) phosphate (TBEP), and tris(1,3-dichloro-2-propyl) phosphate (TDCPP)). Figure S1 presents box and whisker plots of the concentrations of the five dominating OPEs in 2014 and 2015. The mean profiles of the five dominating OPEs at each site are mapped in Figure 3.

The profiles of the OPEs were similar at most sites in both 2014 and 2015, although variations were observed at Concepción and Celestún (Mexico). At Concepción, elevated concentrations of TBEP were detected in 2014; however, in 2015, the profile was similar to the other sites, although it is noted only two PUF-PAS were deployed in 2014. At Celestún (Mexico), tri-*n*-butyl phosphate (TnBP) was detected at elevated concentrations in Q1 of 2015 but was not detected at this site in 2014. The other OPEs at Celestún were in line with concentrations detected at the other background sites. As discussed later, one challenge of passive air sampling studies is

deployment at a location that avoids possible point sources, which may be an influence at these sites.

Seasonal differences in OPE levels in air were not observed in 2014 or 2015. This is in line with other global regions monitored in the regular GAPS sampling campaign, in which seasonal differences were not observed in 2014.¹⁰ The concentrations of OPEs in the GRULAC region in 2014 were significantly higher than concentrations seen in North America and Europe in 2014 in the core GAPS network ($p < 0.03$), as discussed in more detail in Rauert et al.¹⁰ Further monitoring is needed in the GRULAC region to determine if this is a trend or influenced by the high variability in concentrations at the sampling sites.

Polybrominated Diphenyl Ethers. The atmospheric concentrations of the PBDEs were at least an order of magnitude lower than the OPEs (Figure 2). The Σ_{14} PBDE concentrations were not significantly different ($p > 0.05$) between the two sampling years and ranged 0.40–18 pg/m³ in 2014 and 0.86–20 pg/m³ in 2015. The agricultural site of Sonora (Mexico) was the exception with highly elevated concentrations in both years (ranging 24 to 125 pg/m³), possibly associated with inputs from buildings near the sampling site.¹⁰ This will be evaluated in future sampling campaigns at this site.

Figure S2 presents box-and-whisker plots of the concentrations of the sum of the PBDE congeners that dominate in the PentaBDE, OctaBDE, and DecaBDE formulations, and the main congeners in the PentaBDE formulation (BDE28, 47, 99, 100) dominated the profiles at all 9 sites. The mean profile of the congeners in the PentaBDE formulation at each site is mapped in Figure S3. BDE209 was detected at three sites in this study, Sonora in 70% of samples, Celestún (Mexico) in 1 out of 8 samples, and Concepción (Chile) in 33% of samples. BDE209 has a higher detection limit than the other congeners, which contributes to the lower detection frequency of this congener, although the detected concentrations were lower than seen in North America in the core GAPS samples from 2014.¹⁰

PBDEs have been reported previously by Pegoraro et al.³⁶ from atmospheric samples collected in 2014 at Mar del Plata (Argentina) and off the coast of Argentina. Levels of PBDEs measured in air during this cruise were lower than in the GRULAC study and enriched in BDE209 (70% contribution). The lower levels of PBDEs in the off shore samples reflect their greater distance from point sources of PBDEs, whereas the higher proportion of BDE209 indicates a different source type. PBDEs have also been reported from PUF-PAS deployed in three Chilean cities in 2008–2009, including Concepción. Total PBDE concentrations at Concepción were similar between this Chilean study³⁷ (0.5–20 pg/m³) and this GRULAC study. BDE-209 was the dominant congener at the urban and industrial sites, suggesting there may be different sources between the sampling locations in the respective studies.

Seasonal differences of the PBDEs were not observed at these sites, which is in line with observations at other global regions sampled in the GAPS Network.¹⁰ As discussed in Rauert et al.¹⁰ concentrations of PBDEs in the GRULAC region in 2014 were significantly lower than concentrations from the core GAPS sites in North America in 2014. This is not surprising considering the higher historical use of PBDEs in North America,³⁸ as compared to developing regions.

Novel Flame Retardants. The novel FRs were detected less frequently and in generally lower concentrations than the

PBDEs in both 2014 and 2015 (Figure 2). The profiles varied between sites and years, although 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), hexabromobenzene (HBB), and dechlorane 602 (Dec 602) generally dominated the profiles. Figure S4 presents box-and-whisker plots of the concentrations of EH-TBB, HBB, and Dec 602 in 2014 and 2015, also highlighting that the detected concentrations were in the same range as the MDLs. Total novel FR (Σ_{15} novel FR) concentrations (excluding HBCD) ranged <0.1–13 pg/m³ in 2014 and <0.1–30 pg/m³ in 2015 except for an anomalously high concentration of EH-TBB and bis(2-ethyl-1-hexyl) tetrabromophthalate (BEH-TEBP) at Concepción (Chile) in Q4 of 2015 (2880 and 2890 pg/m³, respectively). This sample may have been contaminated during processing and is removed from further discussion. The Σ_{15} novel FR concentrations in 2015 were significantly higher than in 2014 ($p = 0.01$), primarily due to the higher detection frequencies of both EH-TBB and HBB in 2015 (86–93% in 2015 and 14–24% in 2014). Figure S5 maps the average concentrations of EH-TBB, HBB, and Dec 602 at the GRULAC sites, clearly showing the elevated concentrations of EH-TBB in 2015. Due to the low detection frequencies of the novel FRs, and the uncertainty due to detected concentrations being close to the detection limits, more monitoring is required to determine if an increasing trend of EH-TBB is being observed in this region.

Concepción was the only site where HBCD was detected, and only the γ -HBCD diastereomer was detected. Concentrations at this site in 2014 were the highest of all the 44 global sites in the GAPS network monitored in 2014.¹⁰ Concentrations in 2015, meanwhile, were an order of magnitude lower than in 2014. Figure S6 graphs the concentrations of γ -HBCD detected in 2014 and 2015, the diastereomer profile expected in the HBCD technical formulation and the profile expected after thermal rearrangement of the diastereomers.³⁹ There is no obvious explanation for why only the γ -HBCD diastereomer was detected and further monitoring will be conducted at this site.

Seasonal differences of the novel FRs were not observed at these sites in either 2014 or 2015. This is again in line with other global regions monitored in the regular GAPS sampling campaign, where seasonal differences were not observed in 2014.¹⁰ The low detection frequencies of these compounds, however, make comparisons difficult, and this is a challenge that should be addressed in future passive air sampling campaigns, as discussed further in Rauert et al.¹⁰

Flame-Retardant Summary. As the GRULAC region is developing, it is expected to become a major e-waste and waste electrical and electronic equipment (WEEE) producer in the next 10 years.^{38,40} Brazil in particular has a rapidly expanding market and is undergoing a “boom” in e-waste generation.⁴¹ The importation of e-waste is prohibited in Brazil under Brazil’s National Solid Waste Policy;⁴² however, Mexico is expected to receive significant quantities of e-waste, exported from developed countries.⁴⁰ Electronic equipment can contain high percentage levels of FRs, and the dismantling of e-waste (whether produced domestically or imported) is a major contributor of FRs to the surrounding environment as well as to the workers and the surrounding communities.⁴⁰ Limited controls over the disposal of e-waste in developing regions, where the majority of disposal areas are open area dumping sites, also contributes to environmental levels. Therefore, the GRULAC region is a key region for future monitoring studies

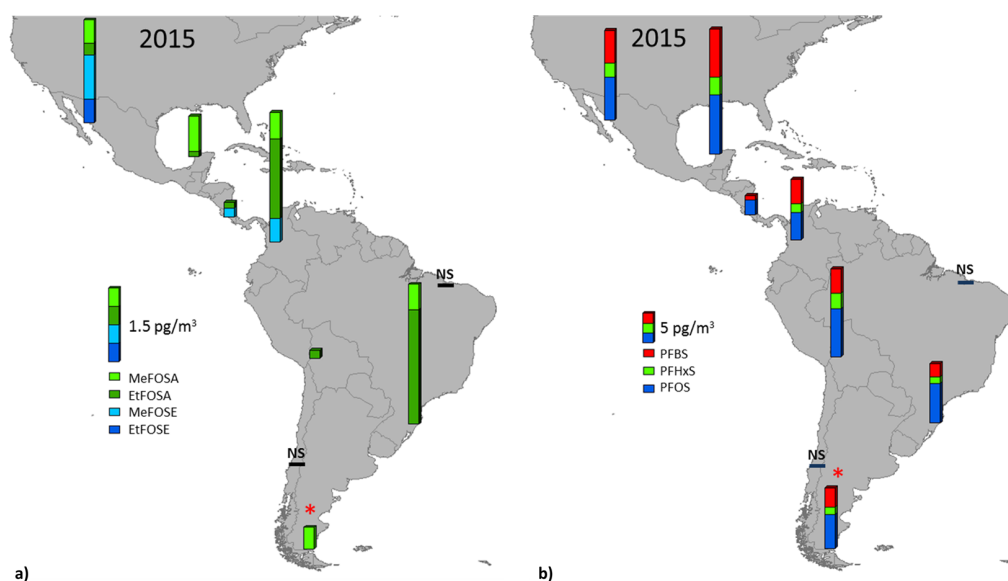


Figure 4. Map of detected concentrations (pg/m^3) of (a) FOSA and FOSEs and (b) PFASs in the GRULAC region from SIP-PAS deployed in 2015. Note the different scales on the two maps. The one urban location is marked with an asterisk. NS indicates that a sample was not deployed at that site.

for the assessment of a change in environmental FR levels with development.

SIP-PAS. SIP-PAS were deployed for one sampling quarter in 2015, at 7 sites. The SIP-PAS were only deployed at one urban site (Rio Gallegos, Argentina) and all of the background and agricultural sites. Concentrations of n-PFAS, perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs), and VMS from each sample are listed in [Tables S23–S26](#).

Neutral Poly- and Perfluoroalkyl Substances. The fluorotelomer alcohols (FTOHs) dominated over the perfluorooctane sulfonamides and sulfonamido ethanols (FOSA and FOSEs) at the sites where they were detected ([Figure 2](#)). The 8:2 FTOH concentrations were 2–7 times higher than the 10:2 FTOH, while the 6:2 FTOH was below the MDL in all samples. The FOSAs were detected at all seven sites, and the FOSEs were only detected at three sites with concentrations close to method detection limits. [Figure S7](#) presents box-and-whisker plots of individual n-PFAS.

[Figure 4](#) maps the profiles of concentrations of the FOSA/FOSEs over the GRULAC region, and [Figure S8](#) maps concentrations of the FTOHs. EtFOSA was detected at the highest concentrations at São Jose dos Ausentes (Brazil) and Manizales (Colombia) where concentrations were at least an order of magnitude higher than the other GRULAC sites ([Figure 4](#)). The concentrations at these two sites were also an order of magnitude higher than concentrations detected in North America and Europe in the core GAPS sampling campaign in 2015²⁸ ([Table S23](#)). EtFOSA is still produced and in use in Brazil as the active ingredient in the pesticide sulfluramid²⁵ and is exported from Brazil to other GRULAC countries for use, including Argentina, Colombia, and Costa Rica.²⁵ In Colombia, there are no specific regulations on the production or use of sulfluramid, and it is acknowledged in the Colombian National Implementation Plan of the Stockholm Convention that its use and registered sales have continued to at least 2015.⁴³ As such, the elevated atmospheric concentrations of EtFOSA detected in Brazil and Colombia are in line with the production and use of this pesticide.

Global n-PFAS levels (ng/PAS) have been previously reported from XAD-PAS deployed at up to 46 GAPS sites, including 8 GRULAC sites, in 2006–2011⁴⁴ ([Table S23](#)). The rural site of Indaiatuba (Brazil) and the background site of Saint Peter (Brazil) saw elevated concentrations of EtFOSA, which were also an order of magnitude higher than at the other GRULAC and global sites sampled in 2006–2011. A calibration study was also conducted at the suburban site of San Antonio de Belen (Costa Rica). Elevated levels of EtFOSA (similar to the levels at Brazil) were again seen, which is in line with known export of sulfluramid to Costa Rica.²⁵ In this 2015 GRULAC study, concentrations of EtFOSA were not elevated at the background site of Tapanti (Costa Rica), indicating different use patterns of EtFOSA in suburban and background (national park) areas of Costa Rica.

Few studies have reported n-PFAS from the southern hemisphere, namely over the Atlantic and Southern Oceans, and are summarized in [Table S23](#). Janke et al.,⁴⁵ Dreyer et al.,⁴⁶ and Wang et al.⁴⁷ reported concentrations of n-PFAS in 2005, 2007–2008, and 2010–2011, respectively, that were in line with concentrations seen in the GRULAC region. All three ship-based studies reported a strong concentration gradient with significantly lower concentrations in the southern hemisphere than the northern hemisphere. This concentration gradient was not observed at the sites sampled in the GAPS Network. As mentioned previously, the n-PFAS have been reported from North America and Europe in 2015 from the regular GAPS sampling campaign.²⁸ Concentrations of the FTOHs and the FOSA and FOSEs at the GRULAC sites (with the elevated EtFOSA concentrations at São Jose dos Ausentes and Manizales removed from the comparison) were in line with concentrations at the background and polar sites in North America and Europe in 2015²⁸ ([Table S23](#)). The concentrations between the GRULAC region, North America and Europe were not significantly different ($p > 0.05$), although there is a small data set for the European ($n = 4$) and the GRULAC sites ($n = 7$), reducing the statistical reliability. The similar concentrations of the n-PFAS detected in the

developing and developed regions (where use and production is higher) demonstrates the global reach of these chemicals of concern and the long-range atmospheric transport properties of these volatile precursors of the PFAAs.^{48,49}

Perfluoroalkyl Acids. The PFSAAs were detected at every site with PFOS dominating, followed by perfluorobutanesulfonate (PFBS) and PFHxS. PFDS was not detected in the GRULAC region. Figure S7 presents box-and-whisker plots of the individual PFSAs. The PFCAs had elevated concentrations in the field blanks, as described further in Rauert et al.,²⁸ with target PFCAs only detected above MDLs at Tapanti (Costa Rica) (Table S24). Hence, the PFCAs are not included in the figures due to the low detection of these analytes.

PFSA concentrations were similar at all sites, including the urban site of Rio Gallegos (Argentina), except for Tapanti (Costa Rica), where lower concentrations were observed (Table S25). Figure 4 maps the profiles of atmospheric concentrations of the PFSAs. The concentrations of the PFSAs were 10 times higher than the precursor FOSAs/FOSEs, which is in line with observations at other global regions sampled in the GAPS Network.²⁸

PFOS is listed in the Stockholm Convention for reduction of production and use, but acceptable purposes are also listed, including the production of sulfuramid.^{22,24} Although elevated EtFOSA concentrations were detected in Brazil and Colombia, atmospheric concentrations of PFOS were similar in all countries in the GRULAC region (Figure 4). The numerous sources of PFOS to the atmosphere in this region, including the transformation of precursors, long-range transport, and localized emissions, all contribute to the similar regional background atmospheric concentrations observed.

PFAAs have been previously reported from a few atmospheric studies in the southern hemisphere, namely ship-based studies, summarized in Table S24–S25. Janke et al.⁴⁵ reported concentrations of PFOS in 2005 that were up to 2 orders of magnitude lower than the concentrations seen in the GRULAC region in 2015. Only the particulate phase was analyzed, and so concentrations may be underestimated. Dreyer et al.⁴⁶ also reported lower concentrations of the PFAS in 2007–2008 than in the GRULAC region in 2015. There are different sources to atmospheric samples from ship (marine)-based locations and land-based sites, with an increased number of potential local sources at land-based locations. The differences between these studies demonstrate that more monitoring is required from the southern hemisphere to determine the environmental fate and regional trends of the PFAS.

Similar concentrations of the PFSAs were seen between the North American and European sites in the GAPS Network and the GRULAC sites. PFSAs and PFCAs have been reported from North America and Europe in 2015 from the core GAPS sampling campaign²⁸ (Table S24–25). Concentrations of the PFSAs were not statistically different between the GRULAC region, and the background and polar sites in North America or Europe ($p > 0.05$). This again demonstrates the global reach of the PFAAs and long-range transport properties.^{49–51}

Volatile Methyl Siloxanes. The SIP-PAS from São Jose (Brazil) had unacceptably low surrogate recoveries (<5%), and this sample has been removed from the data set. The following text compares the remaining six SIP-PAS that were deployed around this region.

Dodecamethylpentasiloxane (L5) was the only linear VMS (IVMS) detected, and concentrations were close to the

detection limit. The cyclic VMS (cVMS), meanwhile, were detected at every site and had the highest concentrations of all of the analyte classes monitored (Figure 2). Figure S9 presents box-and-whisker plots of the individual cVMS. The urban site of Rio Gallegos (Argentina) had higher concentrations of the cVMS than the background and agricultural sites by at least a factor of 2. The elevated concentrations at this urban site are in line with other studies that have reported increasing cVMS atmospheric concentrations with increasing population density.^{28,52} Figure 5 maps the profiles of atmospheric concentrations of the cVMS in the GRULAC region.

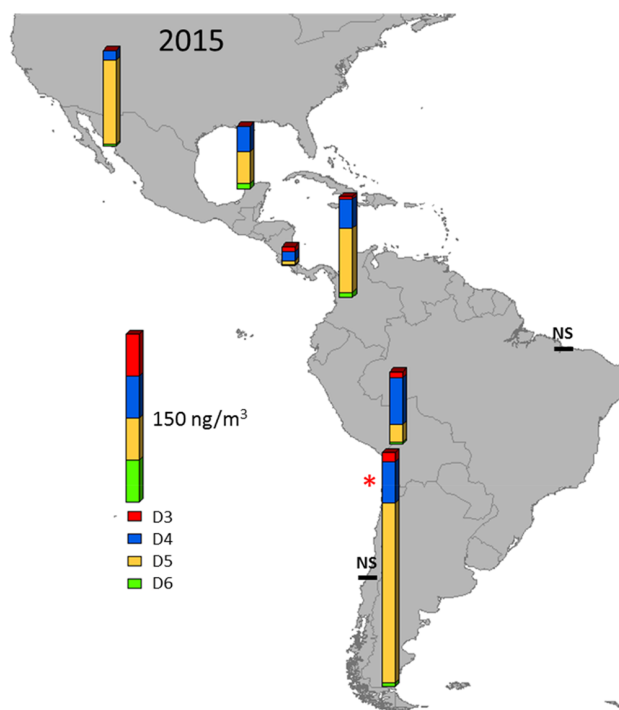


Figure 5. Map of detected concentrations (ng/m^3) of the cVMS in the GRULAC region from SIP-PAS deployed in 2015. The one urban location is marked with an asterisk. NS indicates that a sample was not deployed at that site.

This is the first report of VMS atmospheric concentrations from the GRULAC region as well as from the southern hemisphere (to the author's knowledge). The VMS have been reported previously from North America and Europe from the core GAPS sampling campaign in 2015.²⁸ Concentrations of the cVMS in the GRULAC region were not statistically different ($p > 0.05$) to the concentrations in North America or Europe, summarized in Table S26. The profiles were also similar between the three regions with octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) dominating. It is estimated that Europe, North America, and China account for about one-quarter each of the world consumption market of the VMS.²⁶ The similar atmospheric concentrations in the developed regions (with higher production and use of the VMS) and the developing GRULAC region, highlights that long-range atmospheric transport is a significant contributor to atmospheric concentrations in developing regions and also shows the global coverage of these chemicals as shown in modeling studies.^{32,53,54}

To further investigate long-range transport as a source to the atmosphere at these sites, the ratio of D5 to D4 was investigated as an indicator of atmospheric inputs of cVMS to a location.^{28,52} A higher ratio (>2) indicates that local sources, such as emissions from wastewater treatment plants,²⁷ are the main contributors to atmospheric concentrations and a lower ratio (<2) indicates long-range atmospheric transport is the main input.²⁸ At the GRULAC sites, the highest ratios were seen at the urban site of Rio Gallegos and the agricultural site of Sonora (Mexico) of 4.4 and 8.6, respectively, suggesting that local inputs are a primary contributor to the air mass at these areas. The background site of Manizales (Colombia) had a ratio of 2.2 indicating a mix of sources to this location, and the other sites all had ratios of <2, indicating that long-range atmospheric transport is the main contributor to atmospheric concentrations. All ratios are listed in Table S26.

Implications. The time series of newer POPs (and emerging chemicals of concern) from long-term monitoring programs in North America and Europe are still too short to distinguish trend changes from annual fluctuations.⁶ The time-series data from developing regions is even shorter or nonexistent. This study highlights the importance and need for monitoring data from developing countries, providing regional-scale monitoring data of the OPEs, PBDEs, novel FR, and n-PFAS and the first atmospheric data of the PFAAs and VMS from the GRULAC region. Further monitoring is required to investigate the tendencies observed in this study, such as the significantly higher concentrations of OPEs in the GRULAC region, as compared to North America and Europe, and the elevated concentrations of EtFOSA in Brazil and Colombia.

As discussed in Rauert et al.,¹⁰ there are a number of challenges that passive air sampling monitoring networks may face. In this GRULAC study, we have observed anomalous results at select sites in which certain compounds were elevated during one sampling year but not the next or over the entire study. This highlights the need to conduct longer term sampling and to exercise caution when deploying samplers to avoid possible point sources such as indoor air from ventilation systems. Placement of samplers should take advantage of the electricity-free nature of PAS, with the samplers deployed well away from buildings, electrical equipment and other potential sources of target analytes. Furthermore, to obtain representative results for urban areas, which tend to be more heterogeneous in terms of sources compared to background sites, it is advisable to deploy at multiple sites. Another uncertainty occurs with the use of an average sampling rate (4 m³/day) instead of site-specific sampling rates. The use of models of global sampling rates, currently being developed, may improve the accuracy of this measurement in future studies.⁵⁵

Another challenge, highlighted further in this GRULAC study, is that for some compound classes (e.g., the PBDEs and novel FRs), detection in air at background sites is difficult, as shown in Figure 2. The concentrations at these sites are in the same range as the MDLs, resulting in a lower confidence in the data and trends produced. Higher MDLs can be partly attributed to contamination issues and should be explored through improved laboratory practices, although this can be difficult and costly. Another option is to focus on representative urban sites, with higher air concentrations, to help overcome limitations related to MDLs and to develop meaningful regional and temporal trends.

Lastly, the study highlights the versatility of the PUF disk and SIP disk samplers for conducting region-scale sampling in a

simple and cost-effective way. These samplers are capable of sampling multiple target chemical classes that span an enormous range of volatilities. The GAPS-type sampler allows for both gas-phase and particle-phase chemicals to be sampled at similar rates,⁵⁶ which allows for the comparison of data against results obtained using conventional high-volume samplers.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b00995.

Tables showing site and sampling information, target analyte information, and concentrations of target analytes in each sample. Figures showing box and whisker plots of target analytes and maps of target analytes over the GRULAC region. (PDF)

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Notes

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