

New and emerging POPs in the Group of Latin America and Caribbean (GRULAC) Region

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Introduction

The Global Atmospheric Passive Sampling (GAPS) Network was established in 2005 to support domestic and international monitoring programs including the Global Monitoring Plan (GMP) of the Stockholm Convention on Persistent Organic Pollutants (POPs). The GAPS Network has had a strong relationship with researchers of the Group of Latin American and Caribbean (GRULAC) Region and along with established regional-scale passive sampling monitoring initiatives, has provided regional data on atmospheric levels of legacy POPs.¹⁻⁴ Although passive sampling campaigns in the GRULAC Region have increased there still exists an information gap on atmospheric levels of newly listed POPs, emerging contaminants and candidate POPs being considered for listing by the POPs Review Committee of the Stockholm Convention in the region. To address this information gap a special initiative under the GAPS Network was implemented in 2012, with focus to the new and emerging POPs since 2014, and the first data for atmospheric concentrations of the organophosphate flame retardants (OPFRs) in this region has since been reported.⁵

In this study we report the final results from this special project for a range of analyte classes including the OPFRs; brominated flame retardants (BFRs) including the polybrominated diphenyl ethers (PBDEs), novel BFRs and hexabromocyclododecane (HBCD); penta- and hexachlorobenzene (PeCB and HCB); volatile methyl siloxanes (VMS) and perfluoroalkyl substances (PFAS) including ionizable and neutral compounds.

Materials and methods

Nine sites in the GRULAC region were included in this special initiative and covered a range of location types, including background, agricultural, rural and urban sites, Figure 1. Polyurethane foam (PUF) disk samplers were deployed quarterly at all 9 sites during 2014 and 2015 to assess flame retardants including the OPFRs and BFRs. An additional sorbent impregnated PUF (SIP) disk was deployed for one quarter during 2015 at 7 sites (São Luis, Brazil and Concepción, Chile were not included) to assess the more volatile VMS, HCB, PeCB and the PFAS.

PUFs were extracted and processed for the analysis of target analytes using previously reported methods⁵ and samples were analysed for OPFRs using previously reported methods.⁵ Three HBCD diastereomers were analyzed (α -HBCD, β -HBCD, γ -HBCD) and were separated with a Waters HSS T3 reversed phase column (50 mm, 2.1 mm i.d., 1.6 μ m particle size) and detected using a Waters Acquity I-class Ultra Performance Liquid Chromatograph coupled with Xevo TQ-S tandem quadrupole Mass Spectrometer (UPLC-MS/MS, Waters, Boston, MS) using an Electrospray ionization (ESI) source operated in negative ion mode. The BFRs analysed included 14 PBDE congeners (BDE-17, 28, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190, 209) and 15 novel BFRs (Allyl-2,4,6-tribromophenyl ether (ATE), Beta tetrabromoethylcyclohexane (β -BDE-DBCH), 2-Bromoallyl-2,4,6-tribromophenyl ether (BATE), Beta 1,2,5,6 tetrabromocyclooctane (β -TBCO), 2,3-Dibromopropyl-2,4,6-tribromophenyl ether (TBP-DBPE), Hexabromobenzene (HBB), Dechlorane-602 (Dec 602), Dechlorane-604 (Dec 604), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-Bis(2,4,6-tribromophenoxy) ethane (BTBPE), Bis(2-ethyl-1-hexyl) tetrabromophthalate (BEH-TEBP), Octabromotrimethylphenylindane (OBIND), Syn- and Anti-Dechlorane (syn-DP, anti-DP) and Decabromodiphenyl ethane (DBDPE)). BFRs were separated with a Restek Rtx-1614 column (15m, 0.25mm i.d., 0.1 μ m film) and detected using an Agilent 7890B Gas Chromatograph coupled with an Agilent 7010 tandem quadrupole Mass Spectrometer (GC-MS/MS, Agilent, Santa Clara, CA) using an electron ionization (EI) source.

SIPs were extracted and analysed for the VMS and PFAS using previously reported methods.⁶ HCB and PeCB target ions were added to the VMS GC-MS methods for concurrent analysis of these analytes. Air concentrations (pg/m^3) were derived from the mass of the chemical (pg) collected on the PUF/SIP sampler divided by an effective air sample volume (m^3) determined using the GAPS Template.⁷

Figure 1: Map of the 9 sites participating in the GRULAC special initiative and listing of site type; BA = Background, AG = Agricultural, RU = Rural, UR = Urban.



Results and discussion

OPFR levels and profiles in 2015 were comparable to that previously reported for 2014.⁵ Of the 18 OPFRs investigated, 12 were detected frequently and the chlorinated compounds (tris(2-chloroethyl) phosphate (TCEP) and tris(chloroisopropyl) phosphate (TCPP)) were present in the highest concentrations ($<\text{MDL}$ to $2800 \text{ pg}/\text{m}^3$), followed by triphenyl phosphate (TPP) and tris(2-butoxyethyl) phosphate (TBEP) ($<\text{MDL}$ to 1500 and $<\text{MDL}$ to $1200 \text{ pg}/\text{m}^3$ respectively). The urban site of Concepción, Chile, had the highest levels over the sampling campaign with $\Sigma_{12}\text{OPFRs}$ concentrations ranging $700\text{--}7000 \text{ pg}/\text{m}^3$. Concentrations at the other 8 sites ranged 2 orders of magnitude from 30 to $2200 \text{ pg}/\text{m}^3$ during the sampling campaign. Box whisker plots of $\Sigma_{12}\text{OPFRs}$ at the 8 sites and at Concepción are shown in Figure 2a.

11 PBDE congeners were detected frequently in the samples with the congeners associated with the PentaBDE formulation dominating the profiles. Concentrations ranged from $<\text{MDL}$ to 60 , 55 and $8.8 \text{ pg}/\text{m}^3$ for BDE-47, 99 and 100 respectively. BDE-153 and 154, commonly associated with the OctaBDE formulation, were detected at levels of $<\text{MDL}$ to 5.9 and 4.4 respectively. BDE-209 was also detected frequently at Sonora and Celestún in Mexico and Concepción, Chile at concentrations of 1.0 to $3.8 \text{ pg}/\text{m}^3$. $\Sigma_{14}\text{PBDEs}$ were similar at most sites ranging $<\text{MDL}$ to $20 \text{ pg}/\text{m}^3$ except for the agricultural site of Sonora, Mexico where levels ranged 20 to $130 \text{ pg}/\text{m}^3$ over the sampling campaign. Box whisker plots of $\Sigma_{14}\text{PBDEs}$ at the 8 sites and at Sonora are shown in Figure 2a. The PUF extracts were also analyzed for 15 novel BFRs with most analytes below detection limits. HBB, Dec 602, EH-TBB and BTBPE were detected frequently but at lower concentrations than the PentaBDEs, with concentrations ranging $<\text{MDL}$ to 0.8 , 0.7 , 3.7 and $1.9 \text{ pg}/\text{m}^3$ respectively. Of the HBCD diastereomers only γ -HBCD was detected at Concepción, Chile at levels ranging 0.7 to $180 \text{ pg}/\text{m}^3$ over the two sampling years.

The 7 SIP extracts were analysed for VMS with the cyclic compounds detected in all samples. D4 and D5 dominated the profiles at every site, except São Jose, Brazil where the D3, then D4, dominated the profile. Concentrations ranged from $<\text{MDL}$ to $220 \text{ ng}/\text{m}^3$ for the D3, 6.3 to 140 for the D4, 4.0 to 300 for the D5 and 1.0 to $7.6 \text{ ng}/\text{m}^3$ for the D6. HCB and PeCB were also detected in every sample at concentrations ranging 50 to 200 and 10 to $140 \text{ pg}/\text{m}^3$ respectively.

The ionizable PFAS showed similar profiles at all sites for the perfluoroalkyl sulfonic acids (PFASs) and perfluoroalkyl carboxylic acids (PFCAs). For the PFASs, perfluorooctane sulfonate (PFOS) dominated the profile, followed by perfluorobutane sulfonate (PFBS) and perfluorohexane sulfonate (PFHxS) at concentrations ranging 2.5 to 10, 0.9 to 8.2 and <MDL to 3.1 pg/m^3 respectively. The carboxylic acids were detected at three sites, Tapanti Costa Rica, Manizales Columbia and Rio Gallegos Argentina with perfluorooctanoic acid (PFOA) ranging in concentrations from <MDL to 7.9 pg/m^3 . The atmospheric levels of the priority POPs PFOS and PFOA are directly in line with levels previously reported in North America and Europe⁸⁻¹¹ (2.3 to 9.1 pg/m^3 for PFOS and 0.8 to 7.7 pg/m^3 for PFOA) and further demonstrate the long range atmospheric transport properties of these chemicals.

The fluorotelomer alcohols (FTOH) which are PFCA precursors were detected at most sites with 8:2 FTOH dominating at concentrations of <MDL to 50 pg/m^3 and the 10:2 FTOH present at concentrations ranging <MDL to 7.4 pg/m^3 . The urban site São Jose, Brazil displayed 4 times higher concentrations of the FTOHs than other 6 sites. The sulfonamides and sulfonamido ethanols (precursors of the PFASs) were also detected but at lower concentrations than the FTOHs with varying profiles between sites. The N-methyl and N-ethyl perfluorooctane sulfonamide (MeFOSA and EtFOSA) were detected at concentrations ranging <MDL to 0.5 and 2.3 pg/m^3 respectively. The N-methyl and N-ethyl perfluorooctane sulfonamido ethanols (MeFOSE and EtFOSE) were detected at concentrations ranging <MDL to 0.9 and 0.5 pg/m^3 respectively. Figure 2b presents box whisker plots of air concentrations of the PFAS (pg/m^3) and VMS (ng/m^3) from the 7 sites.

This study presents, to the authors' knowledge, the first atmospheric data for PFAS and VMS in the GRULAC region and provides further data and evidence of the presence of OPFRs and BFRs in this region, also providing a baseline of background atmospheric concentrations for future passive sampling studies to expand on.

Figure 2a: Box Whisker plots showing concentrations in air (pg/m^3) of Σ_{12} OPFRs and Σ_{14} PBDEs from PUFs deployed at GRULAC sites during 2014 and 2015. The boxes show median concentrations and the 25th and 75th percentiles, and 10th and 90th percentiles as indicated by the whiskers.

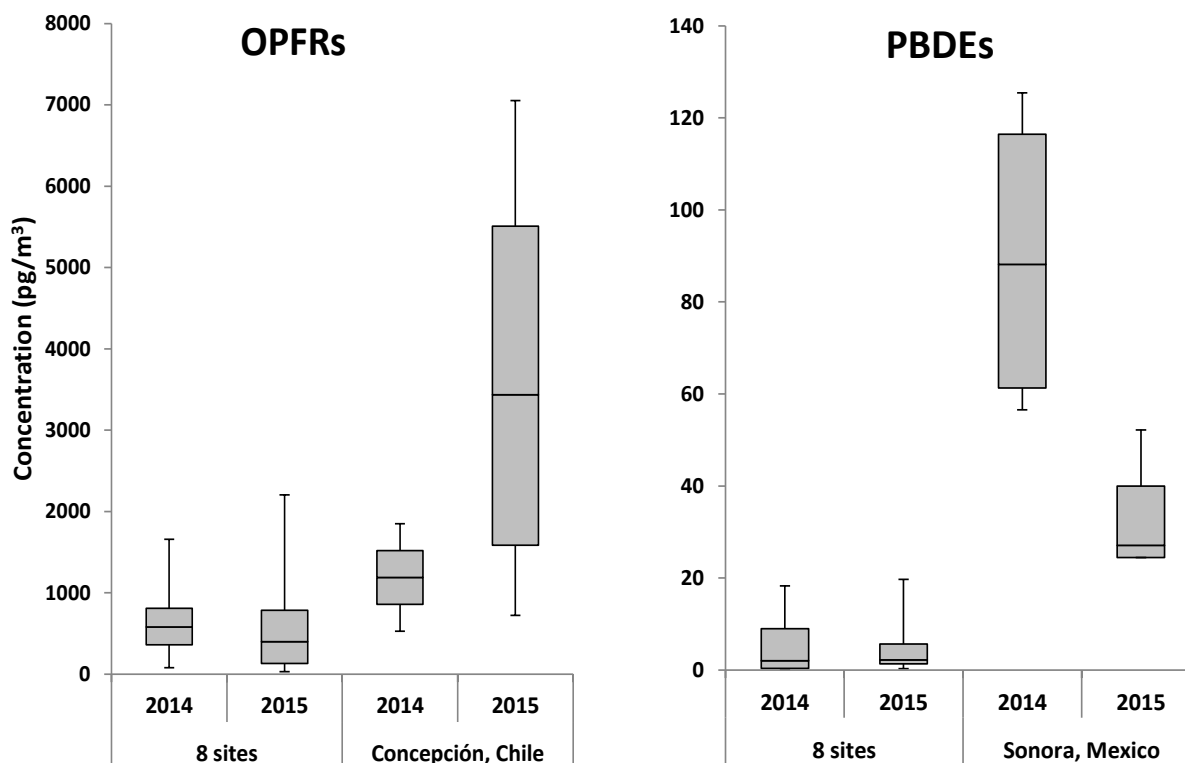
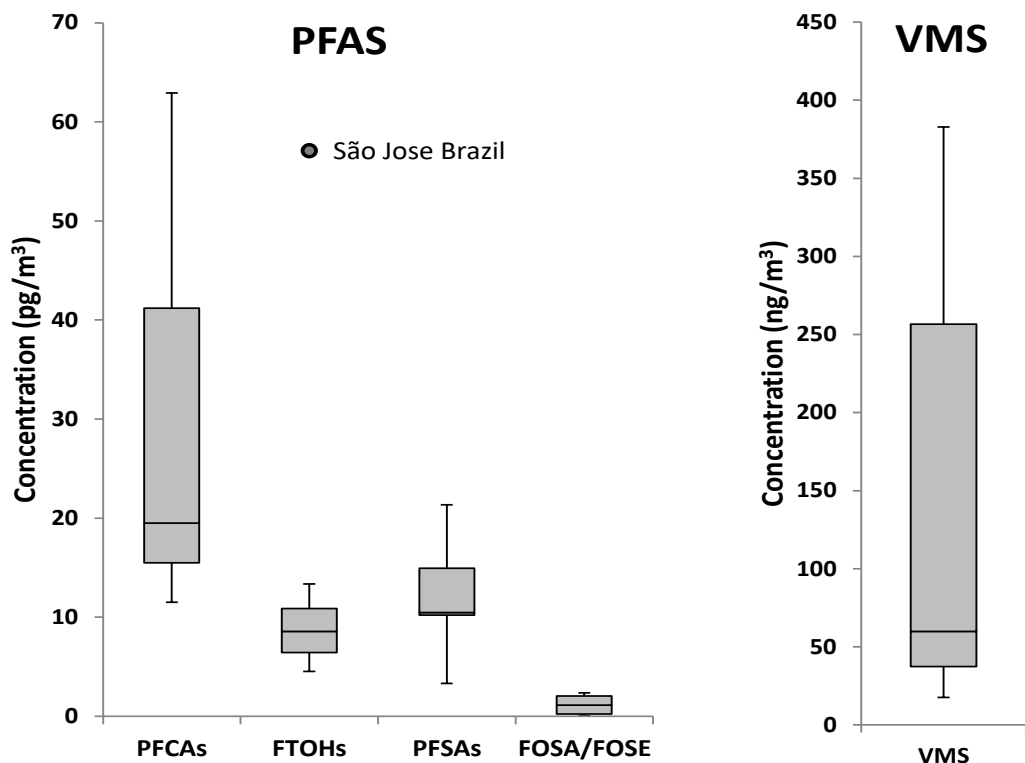


Figure 2b: Box and Whisker plots showing concentrations in air (pg/m^3) of PFAS (Σ_7 PFCAs, Σ_2 FTOHs, Σ_3 PFASs, Σ_4 FOSA/Es) and concentrations (ng/m^3) of Σ_4 VMS from SIPs deployed at 7 GRULAC sites during 2015. The boxes show median concentrations and the 25th and 75th percentiles, and 10th and 90th percentiles as indicated by the whiskers.



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References

- Pozo, K., Harner, T., Shoeib, M., Urrutia, R., Barra, R., Parra, O and Focardi S (2004) *Environmental Science & Technology* **38**(24) 6529-6537.
- Estellano, V. H., Pozo, K., Harner, T., Franken, M and Zaballa, M (2008) *Environmental Science & Technology* **42**(7) 2528-2534.
- Meire, R.O., Lee, S.C., Yao, Y., Targino, A.C., Torres J.P.M., and Harner T (2012) *Atmospheric Environment* **59** 108-116.
- Schuster, J. K., Harner, T., Fillmann, G., Ahrens, L., Altamirano, J.C., Aristizábal, B., Bastos, W., Castillo, L.E., Cortés, J., Fentanes, O., Gusev, A., Hernandez, M., Ibarra, M.V., Lana, N.B., Lee, S.C., Martínez, A.P., Miglioranza, K.S.B., Padilla Puerta, A., Segovia, F., Siu, M., Tominaga M.Y and Zuluaga B.H.A (2015) *Environmental Science & Technology* **49**(6) 3680-3686.
- Rauert, C., Harner, T., Schuster, J.K., Quinto, K., Fillmann, G., Castillo, L.E., Fentanes, O., Villa Ibarra, M., Miglioranza, K., Moreno Rivadeneira, I., Pozo, K., Padilla Puerta, A., Aristizabal Zuluaga, B.H. (2016) *Science of the Total Environment*, **573** 1294-1302.
- Shoeib, M., Schuster, J., Rauert, C., Su, K., Smith, S-A., Harner, T. (2016) *Environmental Pollution*, **218** 595-604.
- Harner, T (2014) "2016_v1_3_Template for calculating PUF and SIP disk sample air volumes_March 11_2016".
- Kim, S-K and Kannan, K (2007) *Environmental Science and Technology*, **41** 8328-8334.
- Dreyer, A and Ebinghaus, R (2009) *Atmospheric Environment*, **43** 1527-1535.
- Ahrens, L., Harner, T., Shoeib, M., Lane, D.A and Murphy, J.G (2012) *Environmental Science and Technology*, **46** 7199-7206.
- Müller, C.E., Gerecke, A.C., Bogdal, C., Wang, Z., Scheringer, M and Hungerbühler, K (2012) *Environmental Pollution*, **169** 196-203.