# Progress in Tracking Legacy and Emerging POPs in the Global Atmosphere under the GAPS Network

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## Introduction

The Global Atmospheric Passive Sampling (GAPS) Network was initiated in 2003 to explore persistent organic pollutant (POPs) levels and their long range transport in air. GAPS data supports domestic and international monitoring programs including the Chemicals Management Plan (CMP) and the Global Monitoring Plan (GMP) of the Stockholm Convention on POPs. In particular, the GAPS Network provides atmospheric data on legacy and newly listed POPs, emerging contaminants and candidate POPs being considered for listing by the POPs Review Committee of the Stockholm Convention. Currently, there are ~ 60 core sites (Figure 1) operating under the GAPS Network, using polyurethane foam (PUF) disk passive air samplers (PUF-PAS) deployed quarterly. In addition, since 2009, sorbent impregnated PUF (SIP) disk passive air samplers (SIP-PAS) have been deployed every 2nd year to assess the more volatile compounds. In addition to the core network activities, special regional studies have been supported by the GAPS Network and on-line tools have been developed to further simplify the application of the PUF disk samplers.

In this study we summarize the latest progress under GAPS in the following areas:
i.) flame retardants (FRs) (polybrominated diphenyl ethers (PBDEs), novel FRs and organophosphate ester (OPE) FRs) in air at the global scale.
ii.) poly- and perfluoroalkyl substances (PFASs) and volatile methyl siloxanes (VMS) in air at the global scale.
iii.) emerging POPs across the GRULAC (Group of Latin American and Caribbean Countries) region.
iv.) new guidance and tools for using PUF-PAS.

## Materials and Methods

Sample deployment, preparation, processing, analyte lists, shipping and storage procedures for the GAPS network are described in Rauert et al.[1-4] Field blanks are collected at all sampling sites for assessment of sampling/laboratory contamination and sample results were blank subtracted using the mean analyte concentration detected. Air concentrations (pg/m$^3$) were derived from the mass of the chemical (pg) collected on the sampler divided by an effective air sampling volume (m$^3$) determined using the GAPS Template.[5]

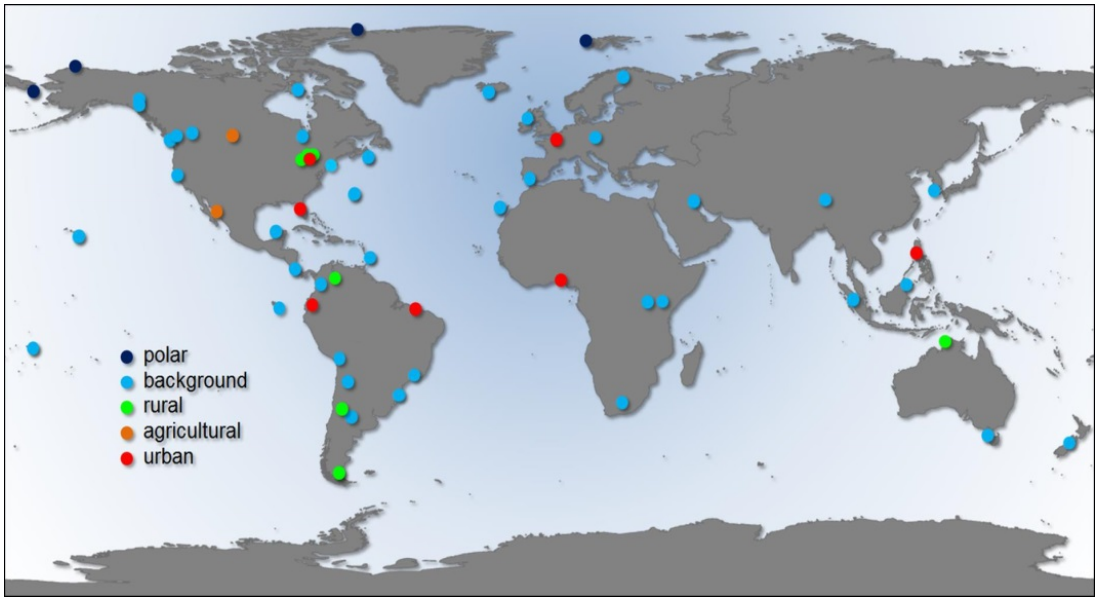

**Figure 1:** Map of the current global sites participating in the GAPS Network, with location type indicated by the colour of the site.

## Results and Discussion

**Flame Retardants (FRs):** PUF-PAS were deployed at 48 global sites in 2014 to monitor a range of FRs. Mean concentrations of PBDEs and novel FRs at the sampling sites ranged from 0.097 to 93 pg/m$^3$ for $\Sigma_{14}$PBDEs and from below detection limits to 126 pg/m$^3$ for $\Sigma_{15}$novel FRs. For the PBDEs, the detected concentrations were similar to those previously reported from samples collected in 2005 at GAPS sites, suggesting global background atmospheric concentrations of PBDEs have not declined at these sites since regulatory measures were implemented. OPEs were detected at every GAPS site, with $\Sigma_{18}$OPEs ranging from 69 to 7770 pg/m$^3$ (Figure 2). OPE concentrations were at least an order of magnitude higher than the PBDEs. This study presents the first data on global distributions of OPEs in the atmosphere, obtained from a single passive sampling monitoring network.[2]

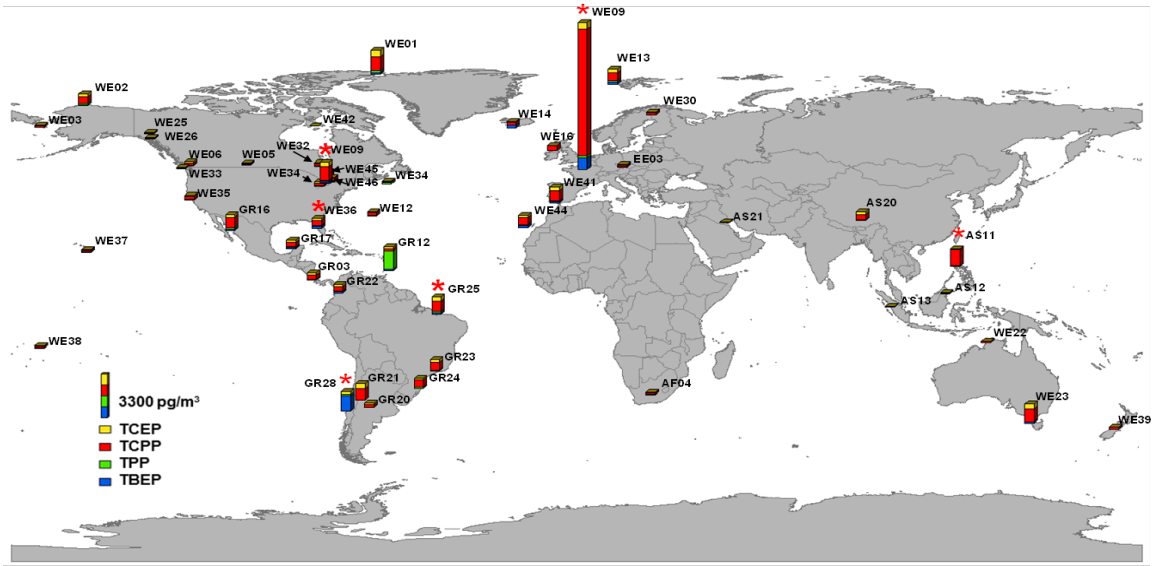


**Figure 2:** Global map of the mean profiles of TCEP, TCPP, TPP and TBEP determined at all GAPS sites in 2014. The 6 urban sites in this study are indicated with *.[2]

**Poly- and Perfluoroalkyl Substances (PFASs) and Volatile Methyl Siloxanes (VMS):** SIP-PAS were deployed at 21 GAPS sites in North America, Europe and Australia to monitor the PFAS and VMS. Atmospheric concentrations previously reported from 2009 [6] were compared to concentrations measured at these sites in 2013 and 2015, to assess trends over 7 years of monitoring. Concentrations of the fluorotelomer alcohols ($\Sigma_3$FTOHs) ranged 1.7 to 177 pg/m$^3$ in 2013 and <1 to 236 in 2015, while the fluorinated sulfonamides and sulfonamidoethanols ($\Sigma_4$FOSAs and FOSEs) ranged <0.7 to 7.3 and <0.7 to 8.2 pg/m$^3$ in 2013 and 2015 respectively. Concentrations of all the neutral PFAS were stable at these sites from 2009-2015 with no significant difference ($p > 0.05$) in concentrations. In both 2013 and 2015, elevated concentrations of all the neutral PFAS were detected at source regions (urban sites) as compared to the polar/background sites. Concentrations of the perfluorosulfonic acids ($\Sigma_3$PFSAs), including perfluorooctane sulfonate (PFOS), ranged 0.11 to 15 pg/m$^3$ in 2013 and <0.4 to 41 pg/m$^3$ in 2015, with concentrations significantly increasing ($p < 0.001$) from 2009-2015. The perfluorocarboxylic acids ($\Sigma_{11}$PFCAs), including perfluorooctanoic acid (PFOA), had concentrations of <1 to 25 pg/m$^3$ in 2013 and 0.63 to 72 pg/m3 in 2015. Although concentrations were also elevated in 2015, the difference was not statistically significant ($p > 0.05$). Concentrations of the PFSAs and the PFCAs were generally similar at all location types, showing the global reach of these persistent compounds.

Concentrations of the cyclic VMS ($\Sigma_4$cVMS) ranged 9.4 to 541 ng/m$^3$ in 2013 and 0.33 to 307 ng/m$^3$ in 2015 and were at least an order of magnitude higher than the linear VMS (lVMS) and the PFAS. A mix of increasing or decreasing tendencies was observed in atmospheric concentrations from 2009-2015. Octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) significantly increased in concentrations from 2009-2013 ($p < 0.05$), however,

hexamethylcyclotrisiloxane (D3) significantly decreased in concentrations from 2009-2015 ($p < 0.01$).[3] These data provide a baseline against which future levels can be compared.

**Special study in the Group of Latin America and Caribbean Countries (GRULAC) region:** PUF-PAS were deployed at 9 sites in the GRULAC region in 2014 and 2015 (Figure 3a) to monitor the FRs and legacy POPs, and SIP-PAS were deployed at 7 sites in 2015 to monitor the PFAS and VMS. This is the first reporting of atmospheric concentrations of the OPEs, PFAAs and VMS from this region. Concentrations of the PBDEs were significantly lower ($p < 0.05$) than concentrations reported from North America/Europe in the core GAPS sampling campaigns. Meanwhile, the OPEs were significantly higher ($p < 0.03$) than the levels reported in North America/Europe. Monitoring is continuing in this region to provide more information on these tendencies. Of the neutral PFAS, ethyl perfluorooctane sulfonamide (EtFOSA) was detected at elevated concentrations in Brazil and Colombia (Figure 3b), which is in line with the manufacture of the pesticide Sulfluramid in Brazil and application in these two countries. Similar concentrations of the perfluoroalkyl sulfonates (PFAS) were detected throughout the GRULAC region (Figure 3c) and the VMS concentrations in air increased with population density of sampling locations.[4]

Some newly listed POPs were also identified for the first time in the GRULAC region including hexachlorobutadiene (HCBD), pentachloroanisole (PCA) and dicofol breakdown products. HCBD was detected at similar concentrations at all location types, ranging <20 - 120 pg/m$^3$. PCA saw elevated concentrations at the urban site Concepción (Chile), of 49 - 222 pg/m$^3$, and concentrations of <1 - 8.5 pg/m$^3$ at the other sites in this study. Dicofol breakdown products were detected at the agricultural site of Sonora (Mexico) at elevated concentrations ranging 30 - 117 pg/m$^3$. The study also showed a good comparability for the analysis of more volatile compounds from co-deployed PUF-PAS (acting as an equilibrium sampler) and SIP-PAS (acting as a linear phase sampler), Figure 4. This supports the use of the PUF-disk for a broader range of compounds and is incentive for directly measuring the PUF-air partition coefficient ($K_{PUF\text{-}Air}$) values for volatile target compounds.[7]

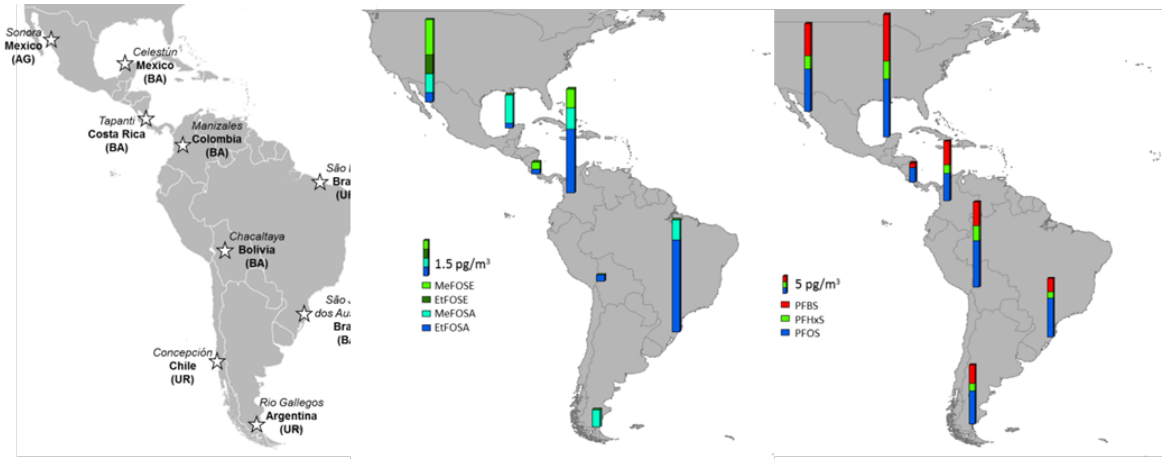


**Figure 3**: Map of a) the 9 sampling sites included in this special study b) concentrations (pg/m$^3$) of FOSA/FOSEs and b) concentrations (pg/m$^3$) of PFSAs in the GRULAC region from SIP-PAS deployed in 2015. Note the different scales on the two maps.[4]

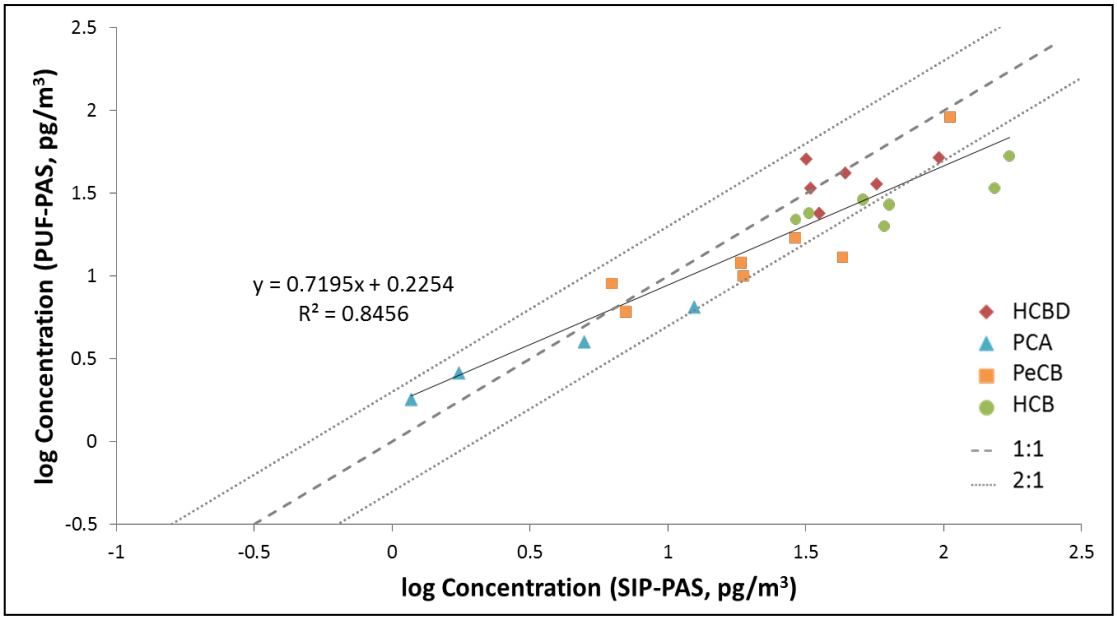


**Figure 4:** Regression of PUF-PAS derived and SIP-PAS derived air concentrations (pg/m$^3$) of the more volatile OCs (hexachlorobutadiene (HCBD), pentachloroanisole (PCA), pentachlorobenzene (PeCB) and hexachlorobenzene (HCB)). The PUF-PAS is operating as an equilibrium phase sampler and the SIP-PAS as a linear uptake sampler. The 1:1 dashed line represents perfect agreement and the 2:1 dashed line agreement within a factor of two.

**New Guidance:** In addition to new information on emerging POPs in the GRULAC region and globally, the GAPS Network has also been updating its strategy and tools for assessing POPs in air. New recommendations also stem from reporting under the GMP and will be summarized. Of particular interest to users of the PUF-PAS is a new on-line, user friendly model developed by Herkert et al.[8] (http://s-iihr41.iihr.uiowa.edu/pufpas_model/) which generates site-specific sampling rates for PUF-PAS samplers.

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