

GAPS NETWORK: AN UPDATE AND RECENT STUDIES IN THE GRULAC REGION

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Introduction

The Global Atmospheric Passive Sampling (GAPS) Network has been operating on all seven continents at more than 60 sites since 2005 to generate the only global-scale information on persistent organic pollutants (POPs) and priority chemicals in air.¹ These data are used for: i.) testing and improving emissions estimates for POPs, ii.) improving our understanding of their regional and global-scale transport and iii.) assessing spatial and temporal tendencies in air. Results from GAPS also contribute to the Global Monitoring Plan (GMP) of the Stockholm Convention on POPs and will help to evaluate the effectiveness of the Convention for protecting human health and the environment from the harmful effects of POPs. The GAPS Network has been particularly active in the Group of Latin American and Caribbean Countries (GRULAC) region, where 14 GAPS stations are currently supported by partner institutions and through the support of volunteers. Results from these stations have contributed to the 1st and 2nd GRULAC regional reports to the GMP. In addition there are numerous GAPS sub-projects and related studies carried out in the GRULAC region using the polyurethane foam (PUF) disk passive air sampler. These studies address local and national-scale issues related to POPs and priority chemicals.

We present an overview of recent, ongoing and new GAPS activities in the GRULAC region that are helping to address regional priorities and data gaps on POPs and emerging chemicals in air. This includes a special study carried out in 2011-2013 in collaboration with 14 institutes across the region to assess polychlorinated dibenzo dioxins and furans in air.² Building on this effort, a second special study is now underway to target 'new' POPs in air in the GRULAC region. In addition to the new studies being carried out in the GRULAC region, other recent developments in the application of GAPS-type PUF disk samplers will be presented including: i.) further characterization of the PUF disk sampler for a wide range of compound classes³, and ii.) field study results demonstrating that the PUF disk sampler effectively captures particle-phase chemicals in addition to gas-phase chemicals in air.⁴

Materials and methods

The PUF disk samplers used under the GAPS Network consists of a foam disk substrate that is protected in a stainless steel sampling chamber to prevent meteorological influences on the sampling of gas-phase and particle-phase compounds in air. The PUF disk is typically deployed for periods of 3 months to allow for determinations of seasonally resolved concentrations in air. Volumetric air concentrations (e.g. pg/m³) for target compounds are derived using the average PUF disk sampling rate (~4 m³/day).³ The sampling rate estimate can also be improved upon (e.g. to account for site specific effects such as high winds) by tracking the loss of depuration compounds added to PUF disks prior to exposure^{5,6} or through models that account for the wind influence on sampling rates (Petrich et al, 2013).⁶ For some of the more volatile compounds, the effective sample air volumes may depend on the chemical's approach to equilibrium with the PUF disk. In these cases, information on the puf-air partition coefficient and/or octanol-air partition coefficient, K_{oa}, are required to estimate the sample air volume.³ For the very volatile compounds, the sorptive capacity of the PUF disk is not adequate for time-integrated sampling. For these chemicals ground XAD resin is added to generate sorbent impregnated PUF or SIP disks that have a higher sorptive capacity.⁷

Results and discussion:

Listed POPs, New POPs and other priority air chemicals targeted under GAPS

The GAPS Network has been operating since 2005 and targeting legacy and emerging chemicals to support domestic and international chemical risk assessment and risk management efforts. Some compounds are monitored routinely while other compounds are targeted in special studies as shown in Table 1. Results from the GAPS Network are made openly available on the GENASIS database and visualization tool (<http://data.genasis.cz/data-browser/?lang=en>). Subsets of these results that are reported under regional reports of the global monitoring plan (GMP) are made available on a new GMP database (<http://www.pops-gmp.org/>) that includes other POPs monitoring data for air and human tissues.

Table 1: Stockholm Convention POPs, Candidate POPs, and other priority air chemicals investigated under GAPS.

Listed POPs	GAPS core target list	GAPS special studies list	Special Notes
Aldrin	<input type="checkbox"/>		
Endrin	<input type="checkbox"/>		
Mirex			Not detected in air and removed from target list
Chlordane	<input type="checkbox"/>		
Heptachlor	<input type="checkbox"/>		
Toxaphene			Not included due to analytical challenges
Dieldrin	<input type="checkbox"/>		
Hexachlorobenzene (HCB)	<input type="checkbox"/>		
PCBs	<input type="checkbox"/>		
DDTs	<input type="checkbox"/>		
Dioxins		<input type="checkbox"/>	GRULAC special study 2010-2012
Furans		<input type="checkbox"/>	GRULAC special study 2010-2012
a-HCH	<input type="checkbox"/>		
b-HCH	<input type="checkbox"/>		
Chlordecone			Not included. Not detected in air.
Hexabromobiphenyl (HBB)		<input type="checkbox"/>	Detected in archived PUF disk samples
Commercial octa-BDE	<input type="checkbox"/>		Blank issues
Commercial penta-BDE	<input type="checkbox"/>		Blank issues
PFOS		<input type="checkbox"/>	Detected in PUF and SIP disk samples
Pentachlorobenzene		<input type="checkbox"/>	Requires SIP disk due to high volatility
Endosulfan	<input type="checkbox"/>		
Hexabromocyclododecane (HBCD)		<input type="checkbox"/>	Detected in some archived samples (retrospective analysis). Challenging due to low levels in air.
Candidate POPs			
Deca-BDE	<input type="checkbox"/>		Is being added to core target list
Dicofol		<input type="checkbox"/>	Analytical challenges. Not yet reported.
Short-chain chlorinated paraffins (SCCPs)		<input type="checkbox"/>	Analyzed in retrospective analysis. Will be screened in GRULAC special study samples.
PCNs		<input type="checkbox"/>	Reported in PUF disk samples.
Hexachlorobutadiene			Not included
Pentachlorophenol			Not included
Other Priority Chemicals			
Siloxanes		<input type="checkbox"/>	Easily detected in SIP disk special study samples..
Current-Use pesticides		<input type="checkbox"/>	Reported in both PUF and SIP disk samples.
Dechlorane and DP		<input type="checkbox"/>	Detected in archived PUF disk samples.
'New' flame retardants		<input type="checkbox"/>	Detected in archived PUF disk samples
OP flame retardants		<input type="checkbox"/>	Detected in archived PUF disk samples

Special study on Dioxins/Furans in air in the GRULAC region

During the period 2010-2012, a UNEP-funded study was carried out with the support of numerous institution and colleagues in the GRULAC region to provide the first comparable concentrations of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) (i.e. PCDD/Fs) in air across the region (Schuster et al., 2015) (Figure 1). A highlight of the study was the evaluation of these unique measurements in a framework that includes emissions and model estimates generated by the Global European Monitoring and Evaluation Programme (EMEP) Multi-media Modeling System (GLEMOS). The good agreement between measurements and model results contributes to the validation of the EMEP global chemical fate model that uses the latest UNEP Stockholm Convention inventory of dioxins and furans emissions.

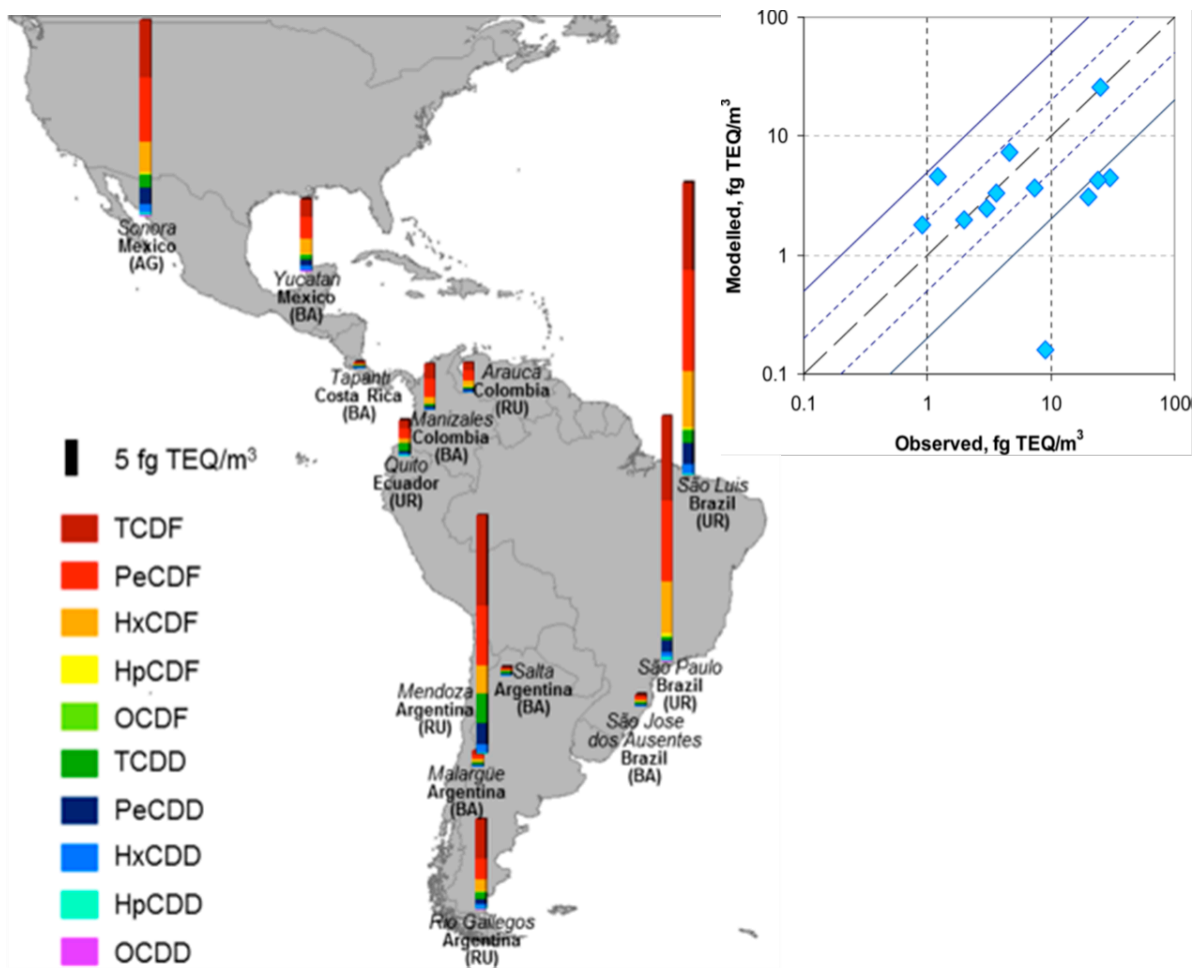


Figure 1. Concentrations of 2,3,7,8-substituted PCDDs and PCDFs in air in the GRULAC region (femtograms of TEQ per cubic meter of air) and comparison against GLEMOS model estimates. The black large dashed line is the 1:1 ratio. Blue dashed lines denote the area of agreement within a factor of 2 and solid lines the area of agreement within a factor of 5 (modified from Schuster et al., 2015).²

Special study on 'new' POPs in the GRULAC region

In 2014 a new GAPS Network special study was initiated with partners in Latin America to address the lack of information on new POPs in air across the GRULAC region. This special study led to an expansion of GAPS Network sites (Figure 2). Compounds analyzed will include the core GAPS target list as well as many of the new POPs listed in Table 1, SIP disk samplers are also deployed alongside PUF disks at each site to capture more volatile chemicals such as the linear and cyclic volatile methyl siloxanes

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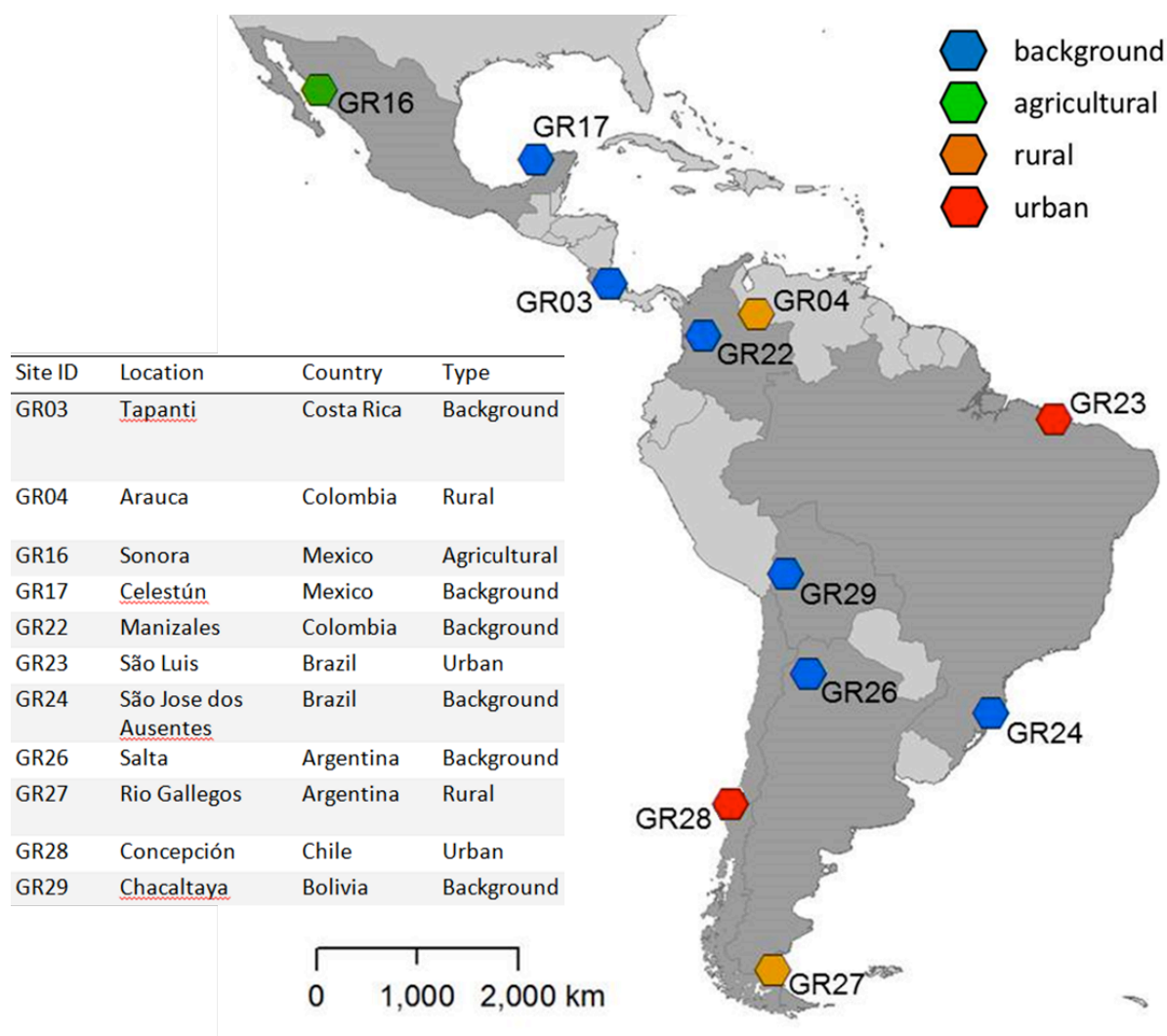


Figure 2. Map of sampling sites in GAPS-GRULAC special study on new POPs.

References: (Example) Use Times New Roman, pt 10

1. Pozo K, Harner T, Lee SC, Wania F, Muir DG, Jones KC. (2009); *Environ Sci Technol.* 43: 796–803.
2. Schuster, J.K., et al. (n=19) (2015) *Environ. Sci. Technol.* 2015, 49, 3680-3686.
3. Harner, T., 2014_GAPS Template for calculating PUF and SIP disk sample air volumes_November 6 2014, *ResearchGate*. Retrieved date? www.researchgate.net/profile/Tom_Harner?ev=hdr_xprf
4. Markovic, M., Prokop, S., Staebler, R.M., Liggio, J., Harner, T. (2015) *Atmos. Environ.* (in press)
5. Pozo, K., Harner, T., Shoeib, M., Urrutia, R., Barra, R., Parra, O., Focardi, S. (2004) *Environ. Sci. Technol.* 2004, 38, 6529-6537.
6. Gouin, T., Harner, T., Blanchard, P., Mackay, D. (2006) *Environ. Sci. Technol.* 2005, 39, 9115-9122.
7. Ahrens, L., Harner, T., Shoeib, M. (2014) *Environ. Sci. Technol.* 2014, 48, 9374-9381.