SURVEILLANCE OF NEW PRIORITY CHEMICALS IN AIR UNDER THE GLOBAL ATMOSPHERIC PASSIVE SAMPLING (GAPS) NETWORK

Harner T[1]*, Schuster, J[1], Sverko, E[2], Jantunen, L[1], Lee, SC[1], Pozo, K[3,4]

[1]Environment Canada, Air Quality Processes Research Section, 4905 Dufferin St., Toronto, ON M3H 5T4 Canada; [2]Environment Canada, Water Science and Technology Directorate, Burlington, Ontario L7R 4A6; [3]RECETOX, Research Centre for Environmental Chemistry and Ecotoxicology, Masaryk University, Kamenice 3/126, 625 00 Brno, Czech Republic; [4]Facultad de Ciencias, Universidad Católica Santísima Concepción, Alonso de Ribera 2850, P.C. 407 01 29 Concepción..

Introduction

The Global Atmospheric Passive Sampling (GAPS) Network is the only global-scale air monitoring and surveillance program for legacy persistent organic pollutants (POPs) and new priority chemicals. A major component of the program involves the deployment of polyurethane foam (PUF) disk passive air samplers on a quarterly basis (every 3 months) across a global network of approximately 60 sites, to provide spatial and temporal (including seasonal) resolution in concentrations in air of target analytes[1]. These data help to develop and test emissions estimates and can be used to validate predictions from fate and transport models. The data also contribute to risk management both domestically (within Canada) and internationally (e.g. under the Stockholm Convention on POPs and the Global Monitoring Plan). In addition to monitoring legacy and newly listed POPs, the GAPS Network targets new priority chemicals, providing unique information on these candidate POPs to support risk assessments (e.g. work of the POPs Review Committee under the Stockholm Convention) and regulatory decisions.

We report on a retrospective analysis of GAPS sample extracts for three classes of priority chemicals and candidate POPs, including: short-chain chlorinated paraffins (SCCPs), organophosphate ester (OPE) flame retardants (FRs), and polychlorinated naphthalenes (PCNs).

Materials and methods

Details on the GAPS Network including information on sampling and analysis are given in Pozo et al.[1]. Archived sample extracts from the GAPS Network are stored in a sample bank at Environment Canada's Hazardous Air Pollutants Lab. The extracts undergo minimal clean-up and manipulation so that they are suitable for future analysis of new priority chemicals. In this study sample aliquots taken from the archive were analyzed separately for SCCPs, OPE FRs and PCNs. Information on selected samples is presented in Table 1.

SCCPs were analyzed according to the method of Tomy et al.[2] by a Thermo DFS GC/HRMS in electron capture negative ionisation mode. Samples were quantified by purified technical SCCP mixtures provided by Dr. Ehrenstorfer (Augsburg, Germany).

Analysis of the OPE FRs was done on an Agilent GC-MSD in electron impact (EI) and electron capture negative ionization (ECNI) modes using a DB-5 column (30-m x 0.25mm x 0.25um). Temperature program: initial 50^{o}C, hold 1min, 20^{o}C to 160^{o}C, 5^{o}C/min to 250^{o}C and 20^{o}C/min to 310^{o}C hold 10min. Injector temperature: 200^{o}C, transfer line 250^{o}C, source 150^{o}C (ECNI) or 230^o C (EI) and quad 150^{o}C. Target/qualifier ions: triphenyl phosphate (TPhP, EI 326/325), tris chloroethylpropyl phosphate (TCEP, EI 249/251), tris chloropropyl phosphate (TCPP, EI 99/125), tris dichloropropyl phosphate (TDCPP, ECNI 319/317), ethylhexyldipropyl phosphate (EHDPP, 251/252) and Mirex (ISTD ECNI: 404 and EI: 272): Peak purity criteria was +/- 20% of the standard target/qualifier ratio.

PCN analysis was performed by AXYS Analytical Services following an internal protocol. For PCN analysis an aliquot of the sample was cleaned on a gel permeation column and an alumina column. PCNs were analyzed by GC/HRMS in EI mode on a DB-5 capillary chromatography column (60 m,0.25 mm i.d. x 0.1 μm film thickness). Temperature program: initial 50^{o}C, hold 1min, 50^{o}C/min to 100^{o}C and 7^{o}C/min to 300^{o}C hold 2 min. Injector temperature: 200^{o}C, source 280^{o}C.

Results and discussion

Analyte amounts collected on the passive samplers were converted to air concentration units by estimating the effective air sample volume for the PUF disks for each sampling event. Previous calibrations of the PUF disks

samplers has shown that sampling rates are about 4 m^3/day and similar for both gas-phase and particle phase chemicals [3,4] . Most semivolatile chemicals experience this linear sampling rate over the entire 3-month seasonal deployment period of the PUF disks. In a small number of cases, for the more volatile compounds, sampling approaches equilibrium in the PUF disks and the effective air volume estimate needs to take into account the PUF-air partition coefficient so that the full uptake profile can be established. The PUF-air partition coefficient has been shown to be well correlated to a chemicals K_{OA} value. A calculation template used under the GAPS Network was applied to estimate sample air volumes for target compounds. For most compounds sample air volumes were on the order of about 350 m^3 of air.
(http://www.researchgate.net/publication/258363020_2013_Template_for_calculating_PUF_and_SIP_disk_sample_air_volumes_for_PCBs_PBDEs_OCPs_PCNs_PAHs_siloxanes_PFCs_PCDD_Fs_updated_November_2013).

Table 1. Information on selected GAPS Network samples collected during 2009 that were screened for OPE FRs, SCCPs and PCNs.

Site	Location	Country	Region	Site Type	Lat.	Long.
AS12	Danum Valley	Malaysia	Asia	Background	5.0	117.8
AS13	Bukit Kototabang	Indonesia	Asia	Background	0.2	100.3
EE03	Košetice	Czech Rep.	Europe	Background	49.6	15.1
WE01	Alert, Nunavut	Canada	North America	Polar	82.5	-63.5
WE02	Barrow, Alaska	United States	North America	Polar	71.3	-156.6
WE06	Whistler, BC	Canada	North America	Background	50.1	-122.9
WE09	Downsview, Ontario	Canada	North America	Urban	43.8	-79.5
WE12	Tudor Hill	Bermuda	Caribbean	Background	32.4	-64.7
WE13	Ny-Ålesund	Norway	Europe	Polar	78.9	11.9
WE14	Stórhöfði	Iceland	Europe	Background	63.4	-20.3
WE16	Malin Head	Ireland	Europe	Background	55.4	-7.3
WE17	Paris	France	Europe	Urban	48.9	2.4
WE25	Little Fox Lake	Canada	North America	Background	61.3	-135.6
WE32	Fraserdale, ON	Canada	North America	Background	49.9	-81.6
WE33	Ucluelet, BC	Canada	North America	Background	48.9	-125.5
WE34	Sable Island, NS	Canada	North America	Background	43.6	-60.0
WE35	Point Reyes, CA	USA	North America	Background	38.0	-122.8
WE36	Sydney, Florida	USA	North America	Urban	28.0	-82.2

Figures 1, 2 and 3 show global maps of concentrations in air for SCCPs, TDCPP and ΣPCN at selected GAPS sites from 2009 (see Table 1). Concentrations in air for the SCCPs were in the range of a few ng/m^3 with highest levels at the urban site WE09. The results from this study (obtained by high resolution GC/MS) are lower than recent literature values in other parts of the world, determined using low resolution GC/MS. This discrepancy may be partly due to analytical interferences by low resolution GC/MS that can lead to overestimation of the SCCPs [5].

TDCPP was the most abundant of the OPE FRs detected in the samples. Concentrations of TDCPP in air were in the range of about a hundred pg/m^3 and fairly constant across the GAPS sites and even among urban vs background sites. These data are consistent with the relatively high levels of TDCPP (mean of 59 pg/m^3) reported for the polar background site at Longyearben, Svalbard for 2012/13 [6]. Lastly, ΣPCN ranged from a few pg/m^3 to a few tens of pg/m^3 with highest values reported at the urban site WE17. These results are in the range of values reported during a survey of GAPS sites in 2004/05 [7]. A more detailed analysis of the PCN data will explore the relative contribution of combustion marker PCNs.

This screening study of archived GAPS samples provides unique and comparable global-scale data for these priority chemicals. Further analysis will explore temporal trends at selected sites.

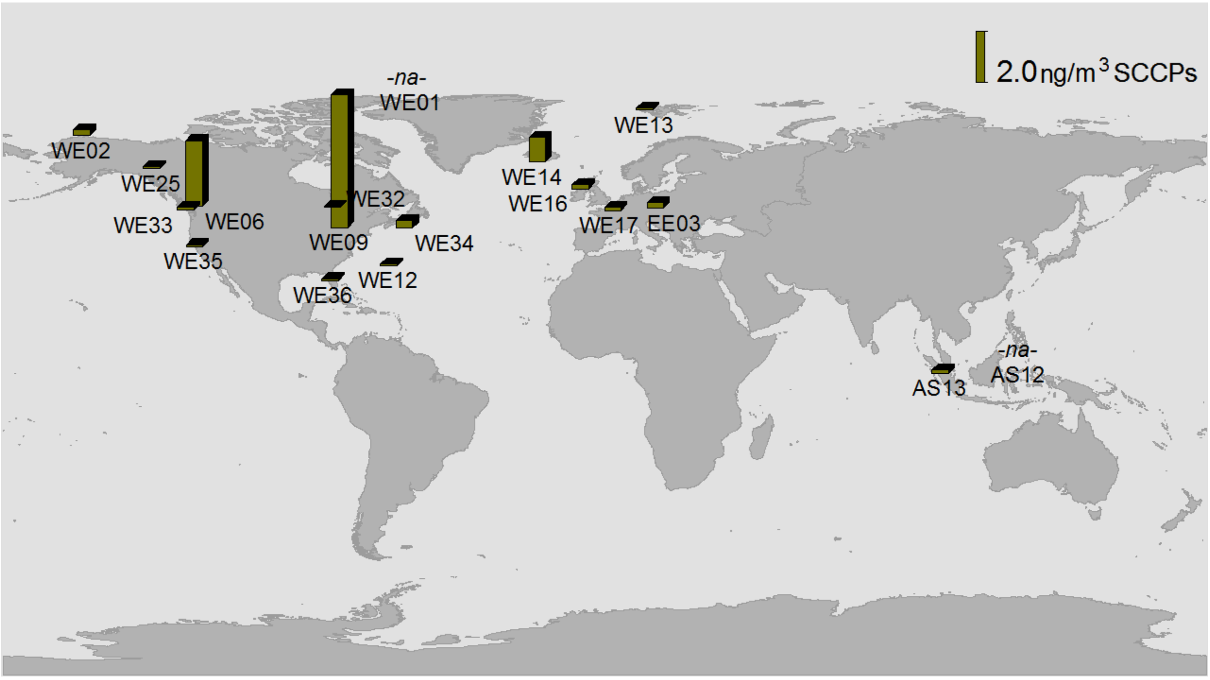

Figure 1. Global distribution of ΣSCPPs in air at selected GAPS Network sites in 2009.

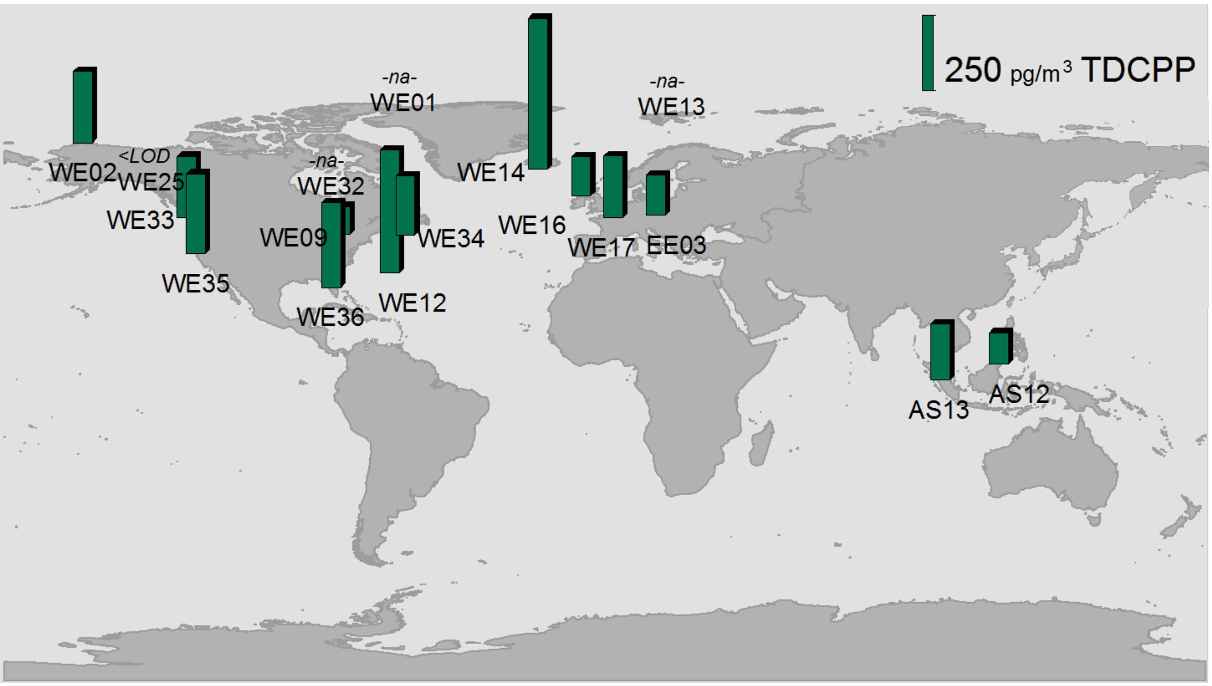

Figure 2. Global distribution of TDCPP in air at selected GAPS Network sites in 2009.

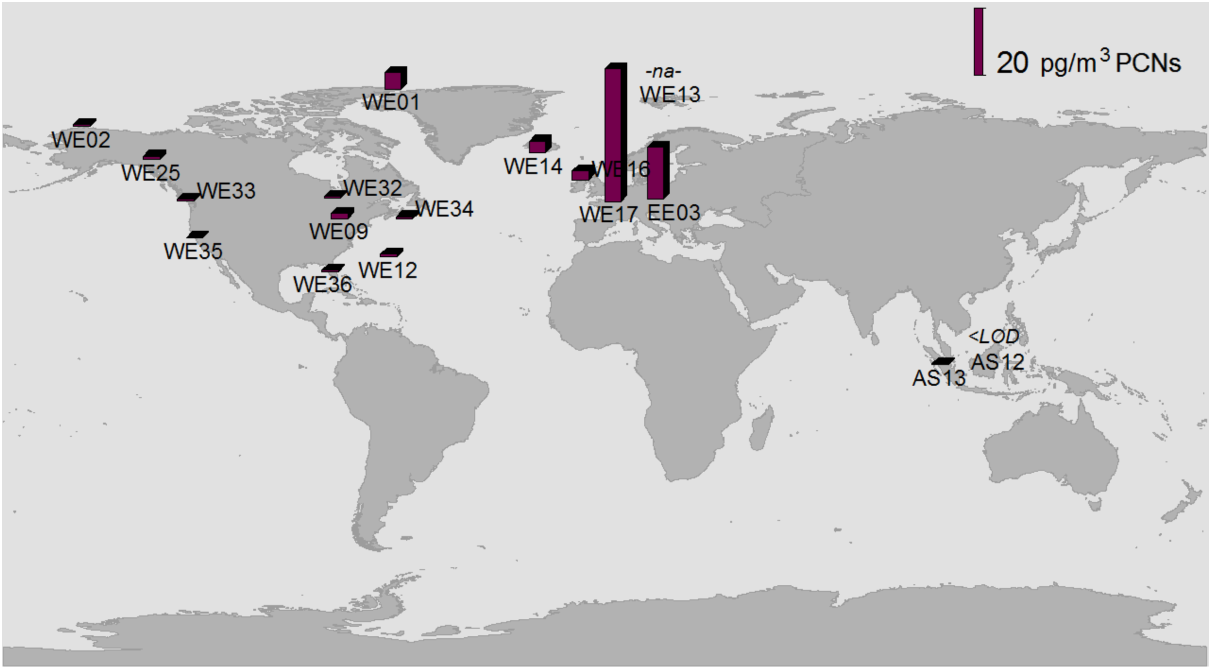

Figure 3. Global distribution of ΣPCN in air at selected GAPS Network sites in 2009.

Acknowledgements

Funding provided by the Chemicals Management Plan, the Northern Contaminants Program, and UNEP. We are especially grateful to all GAPS Network partners who assist with sample collection.

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