Global Atmospheric Passive Sampling (GAPS) Study

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Introduction

The Global Atmospheric Passive Sampling (GAPS) study aims to investigate the atmospheric concentrations and transport of persistent organic pollutants (POPs) on a global scale. Air is being sampled for one year at 50 sites on seven continents. The main objective for GAPS is to demonstrate the usefulness of passive samplers for conducting global monitoring of POPs in the atmosphere. This study thus tests the feasibility of implementing the UNEP (United Nations Environment Program) Guidance document for Global POPs Monitoring[1],which advocated the use of passive air samplers. The simplicity of these samplers, which do not require electricity, makes it logistically and financially feasible to study the large scale spatial distribution of POPs in the atmosphere. A further objective of GAPS is to produce seasonally averaged air concentrations of POPs at background locations around the world. This will help to further develop and evaluate global transport models for POPs, and to assess their long range atmospheric transport. It is hoped that passive sampling approaches such as the ones tested in GAPS can be used to measure long term trends in global air concentrations of POPs. Such trends are instrumental in evaluating the effectiveness of control measures on POPs that are currently being implemented through international protocols such as the Stockholm Convention under UNEP and the POPs LRTAP Protocol under UN-ECE[2]. The success of GAPS relies heavily on existing infrastructure and participation of national and international collaborators and partners including many stations in the Global Atmosphere Watch (GAW) network of the World Meteorological Organization.

Material and methods

Two types of passive air samplers are used in GAPS. The first consists of a polyurethane foam (PUF) disk that is housed in a stainless steel chamber. The chamber consists of two stainless steel domes ('flying saucer' design) which protects the foam disks from direct precipitation, sunlight and coarse particle deposition. Air is allowed to flow over the sampling surface through a ~2.5 cm gap between the two domes. PUF disks are deployed on a seasonal basis with the sampling medium changed every 3 months. The uptake of POPs by PUF disks has been previously characterized[3,4,5]. The second sampler which is deployed for the entire year consists of an XAD resin-filled, stainless steel mesh tube placed in a cylindrical shelter that is open at the bottom[6,7]. Prior to exposure, PUF disks were pre-cleaned by Soxhlet extraction for 24h using acetone and then for another 24h using petroleum ether[4]. Before sending them to the study sites, PUF disks were fortified with depuration compounds covering a wide range of volatility (d_6-γ-HCH, polychlorinated biphenyl (PCB) congeners 3, 9, 15, 30, 107 and 198). The XAD, which had been cleaned as described in ref.[6], was similarly spiked with d-HCH and PCB-166. The loss of these substances, which typically do not occur in the atmosphere, over the sampling period can be used to assess sampling rate variability from site to site[4].

Samples and field blanks were deployed at ~50 sites around the world (Figure 1) starting in mid-December, 2004. PUF disk air samplers were and will be deployed on a seasonal basis - period 1, December 2004-March 2005; period 2, March-June 2005; period 3, June- September 2005; and period 4, September–December 2005. Samples and field blanks from period 1 have been collected and sent back to MSC for analysis. Target compounds initially include organochlorine pesticides (OCPs) and PCBs. Future work will investigate other 'emerging' POPs classes. PUF disks were individually extracted by Soxhlet for 24h using petroleum ether. Details of sample extraction, clean up and recovery tests are presented elsewhere[4]. So far, samples and field blanks from period 1 have been analyzed for

19 OCPs. These include: α-, β-, γ-, δ-HCHs, aldrin, heptachlor, heptachlor epoxide, *cis*-chlordane, *trans*-chlordane, *trans*-nonachlor, endosulfan I, endosulfan II, endosulfansulphate, *o,p'*-DDE*p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT (Ultra Scientific, North Kingstown, RI, USA). Analysis of PUF disk extracts was by gas chromatography-mass spectrometry (GC-MS) on a Hewlett-Packard 6890 GC-5973 MS. OCPs were determined in negative chemical ionization (NCI). Conditions for NCI analysis and selection of target/qualifier ions are described elsewhere[4].

Results

Air concentrations for OCPs for period 1 (Dec. 2004-March 2005) derived from PUF-disks samplers are given in Table 1 and in Figure 1. So far, results are available for more than half the sites where samples were deployed in period 1. Field blanks were below detection for all compounds so no blank correction was required. Volumetric air concentrations were derived by dividing the amount of chemical collected on the PUF disks by the product of the deployment period and an average PUF-disk sampling rate of 4.7 m^3/day previously derived by Pozo et al.[4] Eventually, site specific sampling rates will be used based on recoveries of depuration compounds and temperature information at each site (which partly controls the loss of depuration compounds).

Table 1. Air concentrations (pg/m^3) of OCPs at 29 GAPS sites derived from PUF-disk samplers[a].

Country	Site		α-HCH	γ-HCH	Endo I	Endo II	TC	CC	TN	pp'DDE
Antarctica	Italian Base	remote	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Argentina	Bahia Blanca	rural	1	3	11200	3150	0.9	BDL	0.4	BDL
Australia	Darwin	rural	BDL	0.3	14	BDL	7	3	2	BDL
Australia	Cape Grim*	remote	BDL	0.3	45	BDL	0.1	0.12	0.14	BDL
Bermuda	Bermuda	rural	15	6	57	3.2	1.6	3	2.2	BDL
Canada	Bratt's Lake*	rural	12	6	34	BDL	0.4	0.4	0.3	BDL
Canada	Toronto	rural	8	4	28	BDL	1.4	2	2	BDL
Canada	Dorset	remote	1	0.5	5.8	BDL	0.2	2	BDL	BDL
Canada	Alert	remote	36	7	45	BDL	0.4	1.4	1.1	BDL
Canary Isl	Las Palmas[b]	rural	2	43	4700	1813	2	1.1	2	555
China	Chengdu	urban	73	32	20	BDL	2.5	BDL	0.2	BDL
China	Quingcheng	mountain	15	11	10	BDL	1	3	BDL	BDL
Colombia	Sede Arauca	remote	BDL	3	265	88	BDL	BDL	BDL	2
Czech Rep	Košetice	rural	18	26	29	BDL	0.4	0.7	0.8	BDL
Finland	Hollola[c]	remote	8	114	36	7	1.6	1.2	2	2
Iceland	Stórhöfði	remote	20	17	87	BDL	3	7	6	7
Ireland	Malin Head	remote	8	7	57	3.2	0.4	2.2	1.7	8
Italy	Marettimo	remote	2.3	3	38	1.2	1.2	1.5	1.2	110
Kuwait	Kuwait	rural	3	10	53	BDL	2	2.5	1.2	29.2
Philippines	Philippines	rural	BDL	BDL	27	BDL	60	43	30	9
Poland	Gdańsk	rural	4	6	12	0.7	BDL	0.3	0.2	10
Russia	Danki	remote	13	5	10	BDL	2	0.2	BDL	BDL
South Africa	De Aar	remote	126	74	390	28	0.4	0.3	0.1	BDL
Spain	Barcelona	urban	7	38	148	32	8	4	2.1	31
Turkey	Izmir	rural	15	6	86	16.3	0.02	0.5	0.3	34
USA	Barrow, Alaska*	remote	71	14	91	4	2	3	2	BDL
USA	Athens, GA	rural	67	11	62	BDL	0.2	1.6	0.9	BDL

*Stations that are part of the Global Atmosphere Watch (GAW) network operated by WMO; Abbreviations: BDL, below detection limit; IDL, instrumental detection limit; HCH, hexachlorocyclohexane; HEPT, heptachlor; HEPX, heptachlor epoxide; TC, trans-chlordane; CC, cis-chlordane; TN, trans-nonachlor; Endo, Endosulfan. The IDL for OCPs present the following values (pg): α-HCH: 0.07; γ-HCH: 0.02; *pp'*DDE: 0.09; CC: 0.03; TC: 0.01; TN: 0.01; Endo I: 0.11; Endo II: 0.11. [a]Aldrin, β-HCH, and δ-HCH, were not detected in any of the samples analyzed and due to interferences. Heptachlor and heptachlor epoxide were detected but not reported here.[b]Telde coastal zone (10 Km

South Las Palmas), [c]10 Km North from Lahti City.

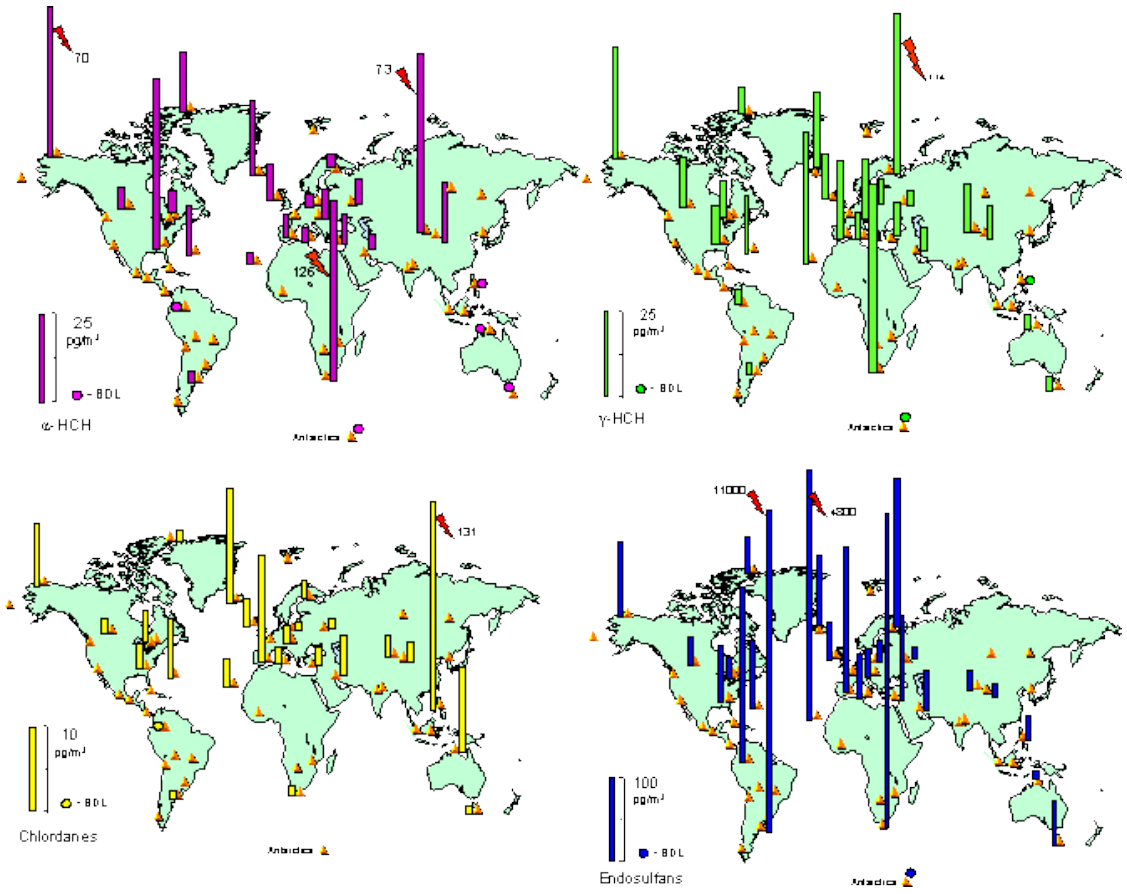

Figure 1.Air concentrations (pg/m^3) of selected OCPs during period 1 (December 2004 to March 2005) at GAPS sites.Endosulfans (sum of Endo I, Endo II and Endosulfan Sulfate); α-HCH (hexachlorocyclohexane), γ-HCH and chlordanes (sum of trans-chlordane, cis-chlordane and trans-nonachlor).

For reasons of brevity, the sampling sites and air concentration will not be discussed in detail. a-HCH is a banned pesticide that is globally distributed because of its volatility and persistence. Air concentrations of a-HCH were fairly uniform and in the expected range at most sites (10-50 pg/m^3) (Fig. 1). Some high values were observed in De Aar (South Africa), Chengdu (China) and at Barrow (Alaska). g-HCH is the main ingredient of lindane which is still used in some countries. g-HCH concentrations at most sites were between 10-50 pg/m^3 with some elevated values at De Aar (South Africa) and Hollola (Finland). Chlordane is another banned pesticide. Low concentrations were observed at most sites (2-15 pg/m^3) with an elevated value in the Philippines. Of all the OCPs investigated, endosulfans showed the highest levels in the range of tens to hundreds of pg/m^3. Very high values in the range of ng/m^3 were observed in Bahia Blanca (Argentina) and Las Palmas (Canary Islands). Endosulfan is a current-use pesticide that is widely used in many parts of the world. These high air concentrations of endosulfans may reflect regional application during period 1. Lastly, of the DDT family, only p,p'-DDE was detected and only at some sites (Table 1). An unusually high concentration of 555 pg/m^3 was observed at Las Palmas (Canary Islands).

In summary, these preliminary results from Period 1 of GAPS show promise for the use of passive samplers as a global air monitoring tool. Results from future sampling periods under GAPS are expected to provide information on the seasonal variability of OCP air concentrations. They will also allow for the comparison of PUF and XAD-based passive air samplers. Furthermore, results for other target compound classes, e.g. PCBs and polybrominateddiphenyl ethers (PBDEs), should provide more insight into POP sources and transport on a global scale.

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