

NEW POPs IN AMBIENT AIR SAMPLES USING PASSIVE AIR SAMPLERS

Fiedler H¹, Abad E², Martrat G², van Bavel B³, Ericson I³, de Boer J⁴

¹UNEP/DTIE Chemicals Branch, 11-13, chemin des Anémones, CH-1219 Châtelaine (GE), Switzerland;

²Laboratory of Dioxins, Environmental Chemistry Department, IDÆA-CSIC, Jordi Girona 18-26, E-08034

Barcelona, Spain; ³Örebro University, Man-Technology-Environment Research Center (MTM), SE-701 82

Örebro, Sweden, ⁴VU University Amsterdam, Institute for Environmental Studies (IVM), De Boelelaan 1087, 1081 HV Amsterdam, The Netherlands.

Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs) is a dynamic legally binding instrument. Through a well-established and well defined process, new POPs can be added to any of the three annexes A, B, or C. The last three Conferences of the Parties (COP) agreed to list new POPs, so that at COP-4 (2009) nine new POPs were listed and at COP-5 (2011) and COP-6 (2013), one new POPs was listed at each. Accordingly, provisions in the Convention have to be updated or amended accordingly. With respect to the effectiveness evaluation as laid down in article 16 of the Stockholm Convention, the guidance document for the Global Monitoring Plan (GMP) on POPs has been amended to include the 11 new POPs. The United Nations Environment Programme's (UNEP) capacity building program is developing and testing methods for the analysis of new POPs in core matrices for recommendation of inclusion into the guidance document. A capacity building project is implemented from 2012 to 2014 together with partners and financed by the Global Environment Facility (GEF). Here we report on the approaches and results obtained for new POPs in ambient air using passive air samplers equipped with polyurethane foam disks (PUF disks) to capture and analyse new POPs, namely some chlorinated pesticides (hexachlorocyclohexanes (HCHs), endosulfan, chlordane and pentachlorobenzene), four brominated flame retardants (BFRs) (polybrominated diphenyl ethers (PBDE, *i.e.*, commercial penta and octa), hexabromocyclododecane (HBCD) and polybrominated biphenyls (PBB)), as well as perfluorinated alkyl substances (PFAS)^{1,2}. In some samples also toxaphene was analysed.

Materials and methods

The materials and procedures followed the established methods used in previous projects and in accordance with the specifications of the guidance for the GMP. Notably and based on the results by Ahrens *et al.*³, polyurethane foams could be used for all POPs analytes. Each country received six cleaned PUFs from CSIC. Briefly, the PUFs were cleaned up, first with water (ultrasonic bath) and secondly, the PUFs were Soxhlet extracted with acetone for 24 h. Finally, the PUFs were dried at room temperature. Five PUFs have been used for determining atmospheric concentrations of new POPs, as shown in the Table 1 below. One PUF was used as a field blank.

Table 1: Sampling and analysis scheme for the analysis of new POPs in PUFs.

Sampling period: Oct-Dec 2013		Analytes (new POPs only)	Country where sampler exposed				Analyzed by
Sampler 1:	PUF 1	pentachlorobenzene, endosulfans, HCHs, chlordane	MLI	KEN	FJI	URY	IVM VU
Sampler 2	PUF 1	pentachlorobenzene, endosulfans, chlordane	MLI	KEN	FJI	URY	CSIC
Sampler 3	PUF 1	8 PBDE, HBCD, PBB	MLI	KEN	FJI	URY	IVM VU
Sampler 4	PUF 1	6 PFAS	MLI	KEN	FJI	URY	MTM

Endosulfans include α -endosulfan, β -endosulfan, endosulfan sulfate; PBDE included the congeners PBDE-17, PBDE-28, PBDE-47, PBDE-99, PBDE-100, PBDE-153, PBDE-154, and PBDE-183, PFAS included PFOS,

PFOSA, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE, PBB consisted of congener PBB-153. HBCD was only screened by GC/MS (non-diastereomer-specific); isomer-specific determination was not performed.

The three expert laboratories used their validated in-house method for the analysis of the new POPs. Briefly, CSIC applied Soxhlet extraction with toluene for 24 h for PBDEs. Before extraction, the sample was spiked with known amount of labeled PBDEs. Clean up is based on silica/alumina solid liquid adsorption chromatography. Finally, analysis is performed by HRGC/HRMS (EI+) using the isotopic dilution as quantification method (by CSIC). Before instrumental analysis, a set of calibration curves composed by labeled and unlabeled compounds provided the relative response factors employed for quantification. IVM VU Amsterdam extracted the PUF samples over-night, roughly 16 h with dichloromethane in pre-cleaned Soxhlet glassware. Before extraction, internal standards were added (PCB 103, PCB 198 for chlorinated pesticides, ¹³C₁₀-Kepone, ¹³C₈-mirex for toxaphene and PBDE 58 for the brominated flame retardants. The extracts for the determination of pentachlorobenzene, HCHs and endosulfans were cleaned by applying alumina and silica gel column chromatography. The other analytes were determined in the second extract. Fractions were treated with sulphuric acid before measurement of BFRs and toxaphene. Pentachlorobenzene, HCHs, endosulfans were analysed by GC-ECD/ECD using CPSil8 and CPSil19 columns (60 m x 0.25 mm x 0.25 µm). The analysis of the BFRs and toxaphene were performed with GC-MS operating in the electron-capture negative ion mode using DB-5HT columns and chlordecone by GC-MS (ECI) using a CPSil8CB column (60 m x 0.25 mm x 0.25 µm). PFAS compounds have been analysed by GC-MS/MS.

Results and discussion

The sampling locations were located at sites already used in the 2010/2011 sampling^{3,4} as shown in Table 2 and are specified below. The geographic locations together with the results for HCHs and endosulfans are shown in Figure 1. The profiles of the three HCH and the three endosulfan congeners are displayed in Figure 2. In all samples, γ -HCH was the predominant congener within the HCHs, α -endosulfan was dominating within the three endosulfans.

Table 2: Sampling locations for the placement of 5 PAS in four continents and respective exposure periods

Country	Location	GPS	Exposure		Days of exposure
			from	To	
Fiji	Nausori airport	18°02'48.2"S 178°33'33.3"E	2-Oct-2013	2-Jan-2014	92
Kenya	Meteorological station, University of Nairobi, Upper Kabete Campus, Nairobi	01° 15' S 36° 44' E	1-Oct-2013	2-Jan-2014	93
Mali	Bamako, Mali	12°38.155' N, 008° 01.352' W	4-Oct-2013	7-Jan-2014	95
Uruguay	Facultat de Agronomia, Montevideo	34° 50' 13.1"S 56° 13' 20.8"N	8-Oct-2013	8-Jan-2014	92

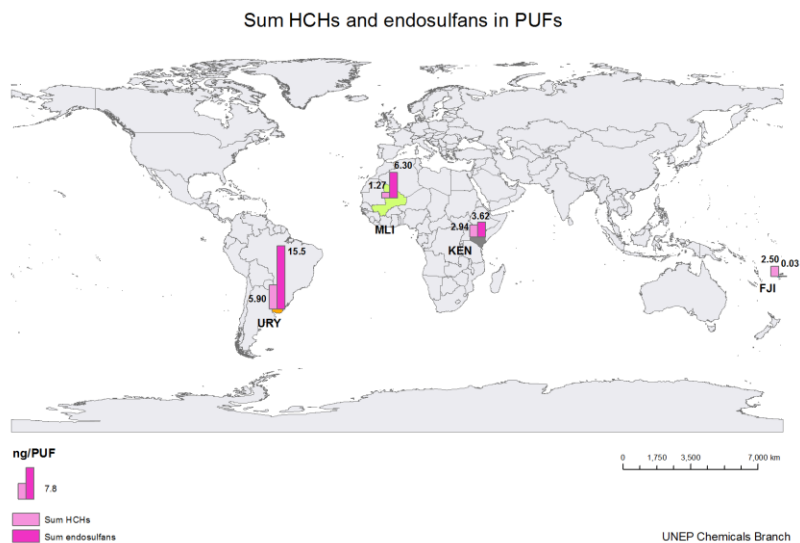


Figure 1: Concentrations of Σ HCHs and Σ endosulfans in PUFs after three months of exposure (Oct-Dec 2013)

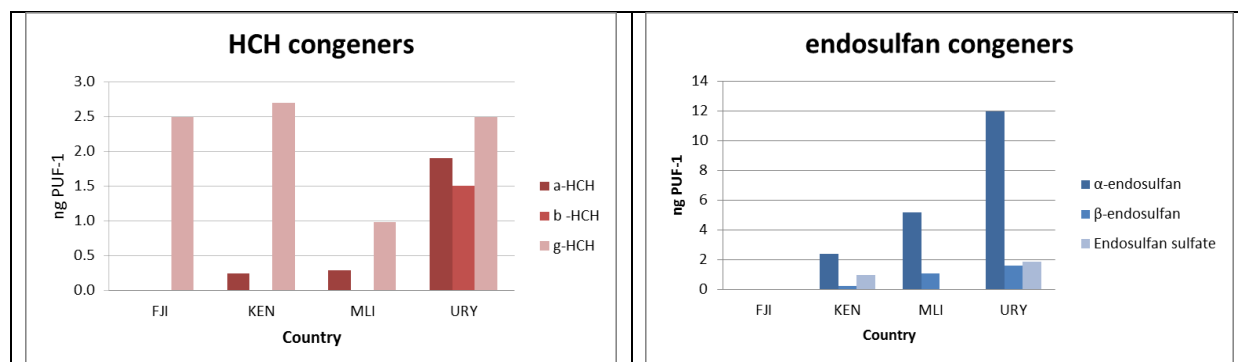


Figure 2: Profiles of HCH and endosulfan congeners in PUF disks

The results for BFRs are shown in Table 3. Whereas PBDE could be identified and quantified in all samples, HBCD was below the limit for detection using HRGC-HRMS using a EI+ source. The concentration of PBB-153 was close to the limit of quantification in all samples.

Table 3: Concentrations of BFR in PUFs after three months of exposure (ng PUF⁻¹)

Sample ID	FJI-BFR (2013-IV)	KEN-BFR (2013-IV)	MLI-BFR (2013-IV)	URY-BFR (2013-IV)
Unit	ng PUF ⁻¹	ng PUF ⁻¹	ng PUF ⁻¹	ng PUF ⁻¹
PBDE-17	0.17	0.21	0.880	0.53
PBDE-28	0.43	0.30	0.43	0.36
PBDE-47	3.50	0.40	1.40	1.20
PBDE-99	1.10	0.23	0.52	0.43
PBDE-100	0.33	0.12	0.47	0.21
PBDE-153	0.07	0.11	0.210	0.08
PBDE-154	0.11	0.12	0.120	0.08
PBDE-183	<0.12	<0.12	0.18	<0.12
Sum PBDE ₈	5.71	1.49	4.21	2.89
PCB-153	0.06	<0.03	0.03	<0.03

Discussion

Quantification of chlordecone was not possible due to the strong polar character of compound; it could not be separated from the matrix. Therefore, the analytical procedure needs to be modified. It was attempted to analyse endosulfans in the same extract together with chlordecone; however, the baseline was too high for a proper quantification.

The three HBCD congeners could not be quantified as sum parameter using LRMS detection at a detection limit of 0.33 ng PUF⁻¹. When using HRGC-HRMS with an EI+ source, the peaks were close to the LOD and could not be quantified; therefore, it is attempted to use HRGC-(APGC)-MS/MS.

The results for new POPs obtained in a sampling campaign in autumn 2013 can be compared with the results for initial POPs in autumn 2010 in the same countries⁵. Whereas the concentrations of the new POPs pesticides – HCHs and endosulfans – were up to 3 ng PUF⁻¹ for HCHs and 12 ng PUF⁻¹, concentrations of initial POPs such as the drins (aldrin, endrin, dieldrin) ranged from 21 ng PUF⁻¹ to 64 ng PUF⁻¹ and DDTs were close to 400 ng PUF⁻¹ for 3-month exposure periods. When the two groups of industrial POPs are compared, the concentrations of the PBDE (sum of 8 congeners) were very comparable to the concentrations of the indicator PCB (sum of 6 congeners): Kenya (Σ PBDE₈ = 2.0 ng PUF⁻¹, Σ PCB₆ = ND), Mali (Σ PBDE₈ = 22 ng PUF⁻¹, Σ PCB₆ = 20 ng PUF⁻¹), Uruguay (Σ PBDE₈ = 29 ng PUF⁻¹, Σ PCB₆ = 27 ng PUF⁻¹) and Fiji (Σ PBDE₈ = 5.7 ng PUF⁻¹, Σ PCB₆ = 5.1-29 ng PUF⁻¹).

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