'NEW' POPs IN AFRICAN AIR SAMPLES – CHLORINATED PESTICIDES ARE DOMINANT

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Introduction

The Stockholm Convention (SC) is a global treaty administered by the United Nations Environment Program (UNEP, Geneva, Switzerland) with the aim of protecting human health and the environment from persistent organic pollutants (POPs), which include pesticides, industrial chemicals and unintentional pollutants listed in the annexes of the SC text[1]. The Global Monitoring Plan (GMP) for POPs was established as a harmonized organizational framework for the collection of comparable monitoring data on the presence of POPs from all regions[2]. For a scientifically sound and meaningful evaluation of global distribution, time trends and regional and global transport of POPs must be based upon reliable, quality-controlled, analytical data and robust sampling schemes. The Conference of Parties (COP) of the SC selected air, human milk and human blood to be the matrices for POPs analysis for the GMP. These matrices provide data on both human exposure to POPs and long-range atmospheric transport of POPs, which is a key aspect in the global cycling of POPs. The GMP makes use of polyurethane foam discs (PUFs) for passive sampling of air. This study focused on the so-called new POPs, which were recently added to the already existing list of POPs. These new POPs were analysed in PUFs from Africa, which were sampled at the same time (in 2011) with PUFs that had already been analysed for the traditional POPs, so a comparison of concentrations could easily be made.

Materials and methods

Pre-cleaned PUFs ready for deployment were provided to ten African participants by Recetoc, Brno, Czech Republic. The deployment period was three months. After deployment, all PUFs were packed in sealed plastic bags and sent to our institute. Target compounds were pentachlorobenzene (QCB), hexachlorocyclohexanes (HCHs), α and β-endosulfan, endosulfan sulphate, total hexabromocyclododecane (HBCD), polybrominated biphenyl (PBB) 153 and the bromodiphenylethers (BDEs) 17, 28, 47, 99, 100, 153, 154 and 183. In addition to the new POPs, also toxaphene (the three chlorobornanes (CHBs) 26, 50, 62) was analysed. PUFs were Soxhlet extracted for 16h by dichloromethane using pre-cleaned glassware. Internal standards were added before extraction: polychlorobiphenyl (PCB) 103 and 198 for the organochlorine pesticides, ^{13}C mirex for toxaphene and BDE 58 for all BDEs and PBB. The extracts were split and the extracts used for the determination of QCB, HCHs and α-endosulfan were cleaned over alumina and silica gel. All other compounds were first separated from toxaphene by eluting over a DSC-NH2 cartridge using 8 mL hexane, 8 mL hexane-diethylether (8/2, v:v) and 10 mL acetone. After analysis, the two fractions of the second extract were combined, treated with sulphuric acid and analysed for the toxaphene and BDE congeners. QCB, HCHs and α and β-endosulfan were analysed by GC/ECD, using a CP Sil 8 and a CP Sil 19 column, both of 60 m length with an internal diameter of 0.25 mm and a film thickness of 0.25 μm. All other compounds were determined by GC/ECNI-MS, using a 15m DB 5HT column with an internal diameter of 0.25 mm and a film thickness of 0.1 μm. Two blank PUFs were analysed in parallel as well as one enriched PUF. The recoveries in the enriched sample varied between 61 and 106%, with only the recoveries of the CHBs and β-endosulfan below 70%. In the blanks all target compounds were absent apart from minor amounts of the BDEs 17 and 28 (0.12 ng/PUF) only in one of the two blanks. Two PUFs were analyzed from Mali and Kenya. The method used was not suitable to analyze chlordecone (kepone). CHB62 could not be determined due to an interference. HBCD was determined as total HBCD, only for screening. The POP levels are expressed in ng/PUF. Only after dividing the amount of chemicals by the corresponding air-sampling volume the concentration of POPs in air in ng/m^3 can be obtained. The volume of air passing the samplers may vary with weather conditions but is assumed to be in the order of 2–8 m^3/day, in most cases 3-4 m^3/day[3]. Bogdal et al. used 3.5 m^3/d as an average for all their PUFs[3]. Obviously, this calculation from ng/PUF

to ng/m^3 adds to the uncertainty in the data. Weather conditions may therefore influence the data produced, and should preferably be recorded.

Results and discussion

A number of clear observations can immediately be made when considering the results of the analyses shown in Tabel 1. HBCD is not detected at all in all samples. The same is true for PBB153, with exceptions for low levels in Ghana (0.24 ng/PUF) and Mali (0.03-0.1 ng/PUF). PBDEs are present but at relatively low levels, in the same order of magnitude as PCB levels in most of these countries, analysed before in PUFs sampled at the same time and locations a the PUFs analysed for the present study[4]. The highest PBDE concentrations were found in Ghana and Mali, the same countries in which also the PCB concentrations were the highest[4]. In Zambia, however, where also measurable PCB levels were reported in PUFs[3], PBDE concentrations are very low. These data suggest that the use of industrial mixtures such as brominated flame retardants and PCBs has been relatively limited in Africa and restricted to a few countries, mainly in West-Africa.

Table 1. POP concentrations in PUFs from Africa (ng/PUF).

Compound	MUS	TGO	NIG	GHA	SEN	UGA	KEN	KEN	ZMB	MLI	MLI	ETH
QCB	0.44	0.72	0.62	0.46	<0.25	0.49	0.50	0.39	0.43	1.2	0.80	1.5
α-HCH	0.41	<0.2	<0.3	<0.25	11	0.89	0.74	0.24	<0.45	0.59	0.29	0.83
β-HCH	<0.3	3.5	<2.1	<0.3	13	<0.9	<0.8	<0.2	<1.1	<2.4	<0.9	<1.1
γ-HCH	8.7	6.8	3.9	2.8	2.7	1.3	4.1	2.7	4.1	1.1	0.98	1.9
α−Endosul.	4.1	11	29	12	4.2	14	26	2.4	25	12	5.2	14
β-Endosul.	0.05	0.7	5.4	3.8	0.23	0.20	0.94	0.22	4.7	3.9	1.1	2.2
Endosul. S	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CHB26	<5	<5	<5	<5	<5	<5	12	<6	<5	<5	<2.5	<5
CHB50	<5	<5	<10	<7	<5	<7	9.4	<10	5.2	<5	<2.5	<5
BDE17	<0.1	0.14	0.24	1.1	<0.07	0.08	0.24	0.21	0.10	1.1	0.88	<0.1
BDE28	1.6	0.18	0.44	0.74	<0.07	0.12	0.32	0.30	0.18	1.1	0.43	0.32
BDE47	1.5	0.68	1.2	7.4	0.22	0.42	0.52	0.40	0.22	3.1	1.4	0.36
BDE99	0.96	0.30	0.44	3.2	0.14	0.20	0.24	0.23	0.10	1.5	0.52	0.26
BDE100	0.28	0.12	0.16	1.6	<0.07	0.12	0.14	0.12	<0.05	0.08	0.47	<0.08
BDE153	0.10	0.08	0.10	0.42	<0.07	<0.07	<0.08	0.11	<0.05	0.32	0.21	0.08
BDE154	0.10	<0.08	0.08	0.64	<0.06	<0.07	<0.08	0.12	<0.06	0.33	0.12	<0.06
BDE183	0.30	<0.3	<0.3	0.86	<0.3	<0.3	<0.3	<0.1	<0.3	<0.3	0.18	0.30
HBCD	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.3	<0.7	<0.7	<0.3	<0.3
PBB153	<0.05	<0.05	<0.05	0.24	<0.05	<0.05	<0.05	<0.1	<0.05	0.10	0.03	<0.1

MUS: Mauritius, TGO: Togo, NIG: Nigeria, GHA: Ghana, SEN: Senegal, UGA: Uganda, KEN: Kenya, ZMB: Zambia, MLI: Mali, ETH: Ethiopia.

The highest concentrations in this study were found for endosulfan. In particular α-endosulfan concentrations are found in PUFs from all countries with peaks of 25-29 ng/PUF in Nigeria, Kenya and Zambia. This clearly points to the use of endosulfan at this continent. β-endosulfan is always lower than α-endosulfan, in most cases ca. 5-30% of α-endosulfan, but sometimes lower. Endosulfan sulphate was non-detectable in all samples. Another interesting observation is the ratio of the HCH isomer concentrations in Senegal. Whereas normally, and also in this study in all ther samples, γ-HCH is the highest of the three isomers in concentration, in Senegal clearly higher α and β-HCH levels are found. This may be related to old stocks of HCHs. Similar ratios were for example found in fish from the Netherlands in the 1980s[5]. Toxaphene concentrations were often not detectable but present in Kenya. QCB levels were measurable but not particularly high and comparable in most countries, although somewhat elevated in Ethiopia (1.5 ng/PUF).

Clearly the concentrations of these 'new' POPs are in general not higher than those of total DDT. Leslie et al.[4] reported p,p'-DDE concentrations of up to 400 ng/PUF in Mali and 140 ng/PUF in Zambia. On top of that in

Zambia even higher p,p'-DDT concentrations were found (310 ng/PUF), strongly suggesting recent use of DDT. Also in Ethiopia p,p'-DDT was higher than p,p'-DDE[4]. These data show that recent DDT spraying, although benefical against malaria, immediately initiated higher DDT concentrations in air, and higher than the levels of other POPs, including endosulfan and dieldrin.

We conclude that PUFs, provided thoroughly precleaned and handled with care to prevent contamination, are excellent tools to analyse air pollution of POPs. In addition to Africa, they were also successfully applied in other continents[4]. The effect of calculation, from ng/PUF to ng/m^3 air, should not be underestimated but the value of these PUFs as a cheap screening tool is high. Furthermore, although already on the first POPs list, toxaphene needs to be analysed more often, as very little data are available, while these PUFs allow its determination. More difficult is the situation for chlordecone. Due to its polar character, a proper method for its analysis in air is still lacking.

Of all POPs analysed in this study and in the one reported by Leslie et al.[4], total DDT, dieldrin, lindane and endosulfan emerge as priority contaminants in Africa, emphasising that pesticides are more important contaminants in Africa until now than contaminants from an industrial origin.

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