UNEP/GEF Pilot testing in air and water for new POPs

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Pilot testing of new POPs in air

Experiments undertaken in 2013/2104

- Air sampling with PAS / PUF in four countries:
  - Fiji, Kenya, Mali, Uruguay
- 3 months each (October-December 2013)
- Analysis for new POPs in expert laboratories for
  - POPs pesticides
  - Brominated flame retardants
  - PFAS
- Analysis of **retained samples** for polybrominated flame retardants
  - GRULAC and Africa

Analysis of PBDEs in Passive Air Samples to Support the Global Monitoring Plan under the Stockholm Convention on Persistent Organic Pollutants

- Martrat MG[1], Parera J[1], Adrados MA[1], Abalos M[1], Fiedler H[2]*, E. Abad[1]
- [1] IDAEA-CSIC, Barcelona, Spain, [2] UNEP/DTIE Chemicals Branch, Geneva, Switzerland

Organohalogen Compd. **74**, 1308-1311 (2012) Dioxin2011, Cairns-AUS

”New” POPs in African Air Samples – Chlorinated Pesticides Are Dominant

Heather Leslie and Jacob de Boer
IVM VU Amsterdam, Amsterdam, the Netherlands

Organohalogen Compd. **76**, 1533-1536 (2014)

Dioxin2014, Madrid

New POPs in Ambient Air Samples Using Passive Air Samplers

- H. Fiedler[1], E. Abad[2], G. Martrat[2], B. van Bavel[3], I. Ericson Jogsten[3], J. de Boer[4]
- [1] UNEP/DTIE Chemicals Branch, Geneva, Switzerland, [2] IDAEA-CSIC, Barcelona, Spain, [3]MTM Centre Örebro University, Örebro, Sweden, [3] IVM VU Amsterdam, Amsterdam, the Netherlands

Organohalogen Compd. **76**, 1533-1536 (2014)

Dioxin2014, Madrid

Analytes

- Endosulfans include α-endosulfan, β-endosulfan, endosulfan sulfate;
- $PBDE_8$ included the congeners PBDE-17, PBDE-28, **PBDE-47**, **PBDE-99**, PBDE-100, **PBDE-153**, **PBDE-154**, and **PBDE-183**;
- PBB consisted of congener PBB-153;
- HBCD (α, β, γ) was only screened by GC/MS (non-diastereomer-specific);
- PFAS included PFOS, PFOSA, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE.

Analysis of pesticides and BFR

- PUFs extracted over-night (ca. 16 h) with dichloromethane in pre-cleaned Soxhlet glassware;
- Before extraction, internal standards were added
  - PCB 103, PCB 198 for chlorinated pesticides,
  - $^{13}C_{10}$-Kepone, $^{13}C_{8}$-mirex for toxaphene , and
  - PBDE 58 for the brominated flame retardants
- For determination of pentachlorobenzene, HCHs and endosulfans, extracts were cleaned by applying alumina and silica gel column chromatography;
- Other analytes were determined in the second extract;
- Fractions were treated with sulphuric acid before measurement of BFRs and toxaphene;
- Pentachlorobenzene, HCHs, endosulfans: GC-ECD/ECD using CPSil8 and CPSil19 columns (60 m x 0.25 mm x 0.25 μm);
- BFRs and toxaphene: GC-MS operating in the electron-capture negative ion mode using DB-5HT columns, and
- Chlordecone by GC-MS (ECI) using CPSil8CB column (60 m x 0.25 mm x 0.25 μm)

Analysis of perfluoroalkyl substances

Extraction method

PUF + labeled IS

^{13}C labeled standards of PFASs (PFCAs, PFSAs and FASA/FASE)

MeOH extraction x 2

Ultrasonication

Centrifugation

SPE, Oasis WAX

Condition with water and MeOH.
Load sample.
Washing with 4 ml NaAc (pH 4), 4 ml 20% MeOH.
Eluate with 4 ml MeOH, 4 ml NH_4OH, combine extracts.

ENVI-carb

Centrifugation, split extracts

PFCA PFSA in 40 % MeOH	FASAs FASEs In 80 % MeOH	FTOH To be analyzed

Instrumental analysis
UPLC-MS/MS, ESI^-
Gradient separation of 10 µL injections
BEH C18 column (100 mm x 2.1 mm, 1.7 µm)

Sampling scheme

PUF Code	Country of origin	PAS site name	GPS coordinates of site	Sampler No.	Analytes	Actual exposure start date (d-mmm-yyyy)	Actual exposure end date (d-mmm-yyyy)	Effective days of exposure
URY-1	Uruguay	Facultat de Agronomia, Montevideo	34° 50´ 13.1"S 56° 13´ 20.8"N	1	New pesticides	8-Oct-2013	8-Jan-2014	92
URY-2	Uruguay			2	New pesticides	8-Oct-2013	8-Jan-2014	92
URY-3	Uruguay			3	BFR	8-Oct-2013	8-Jan-2014	92
URY-4	Uruguay			4	BFR	8-Oct-2013	8-Jan-2014	92
URY-5	Uruguay			5	PFAS	8-Oct-2013	8-Jan-2014	92
KEN-1	Kenya	Meteorological station, University of Nairobi, Upper Kabete Campus. Nairobi	01° 15' S 36° 44' E	1	New pesticides	1-Oct-2013	2-Jan-2014	93
KEN-2	Kenya			2	New pesticides	1-Oct-2013	2-Jan-2014	93
KEN-3	Kenya			3	BFR	1-Oct-2013	2-Jan-2014	93
KEN-4	Kenya			4	BFR	1-Oct-2013	2-Jan-2014	93
KEN-5	Kenya			5	PFAS	1-Oct-2013	2-Jan-2014	93
MLI-1	Mali	Mali Bamako ACI2000	12°38.155' N, 008° 01.352' W	1	New pesticides	4-Oct-2013	7-Jan-2014	95
MLI-2	Mali			2	New pesticides	4-Oct-2013	7-Jan-2014	95
MLI-3	Mali			3	BFR	4-Oct-2013	7-Jan-2014	95
MLI-4	Mali			4	BFR	4-Oct-2013	7-Jan-2014	95
MLI-5	Mali			5	PFAS	4-Oct-2013	7-Jan-2014	95
FJI-1	Fiji	Nausori airport	18°02'48.2"S 178°33'33.3"E	1	New pesticides	2-Oct-2013	2-Jan-2014	92
FJI-2	Fiji			2	New pesticides	2-Oct-2013	2-Jan-2014	92
FJI-3	Fiji			3	BFR	2-Oct-2013	2-Jan-2014	92
FJI-4	Fiji			4	BFR	2-Oct-2013	2-Jan-2014	92
FJI-5	Fiji			5	PFAS	2-Oct-2013	2-Jan-2014	92

Sampling sites (1)

Fiji, Nausori airport
18°02'48.2"S , 178°33'33.3"E
Exposure: 2 Oct 2013-2 Jan 2014

Mali, Bamako Centre
12°38.155' N, 008° 01.352' W
Exposure: 4 Oct 2013-7 Jan 2014

Sampling sites (2)

Kenya

Meteorological station, Nairobi

01° 15' S, 36° 44' E

Exposure: 1 Oct 2013-2 Jan 2014

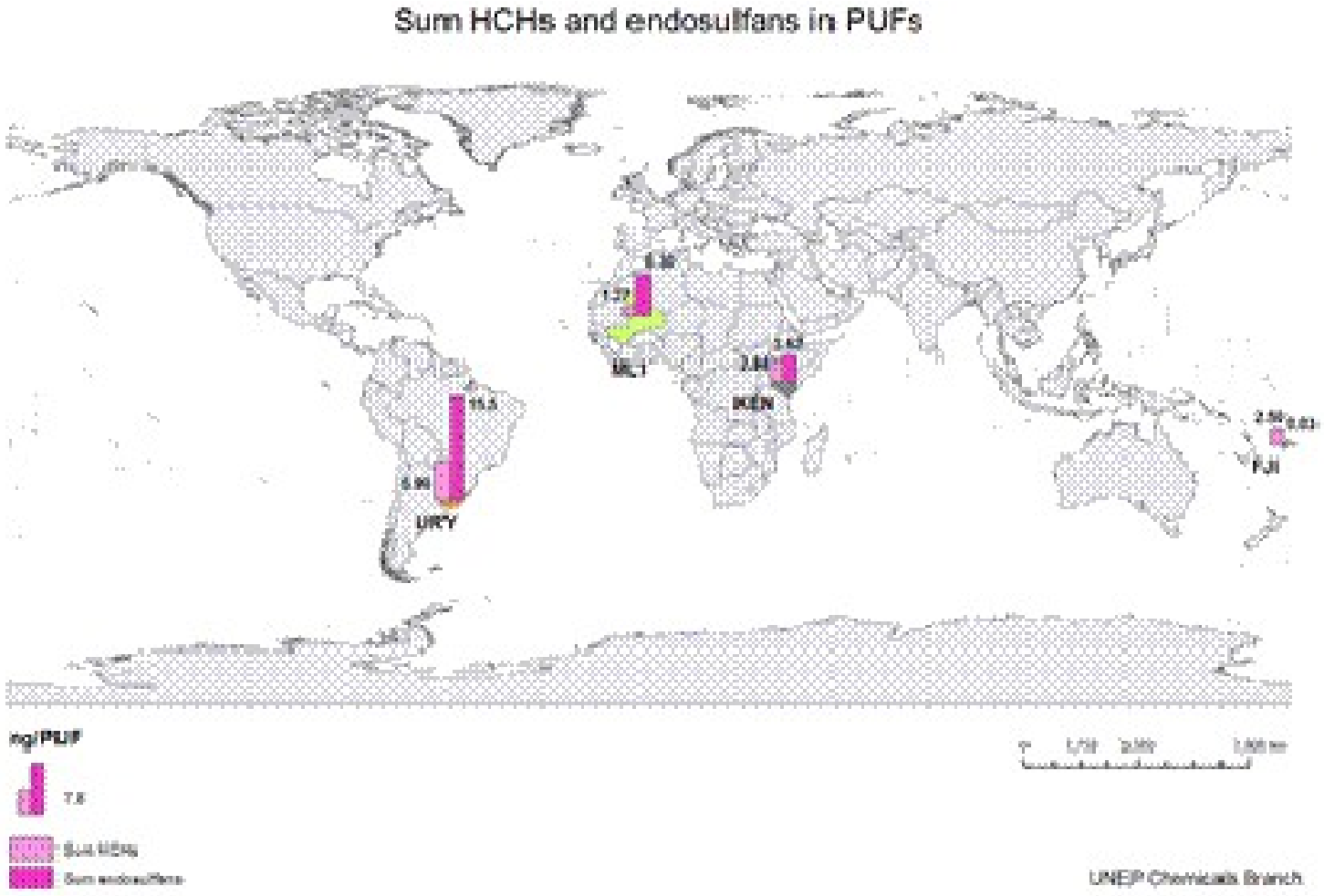
Uruguay

Facultat Agronómica, Montevideo

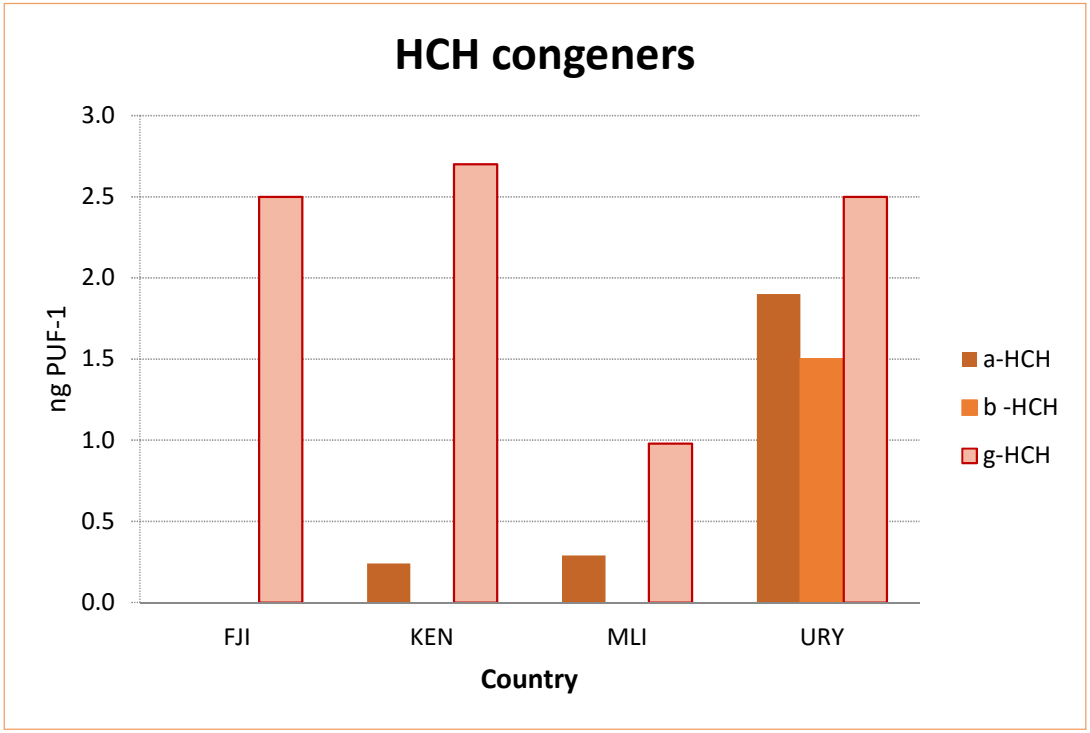
34° 50´ 13.1” S, 56° 13´ 20.8” W

Exposure: 1 Oct 2013-2 Jan 2014

GIS sketch of new POPs/PAS



HF, New POPs Tools, Hanoi, Jan 2016

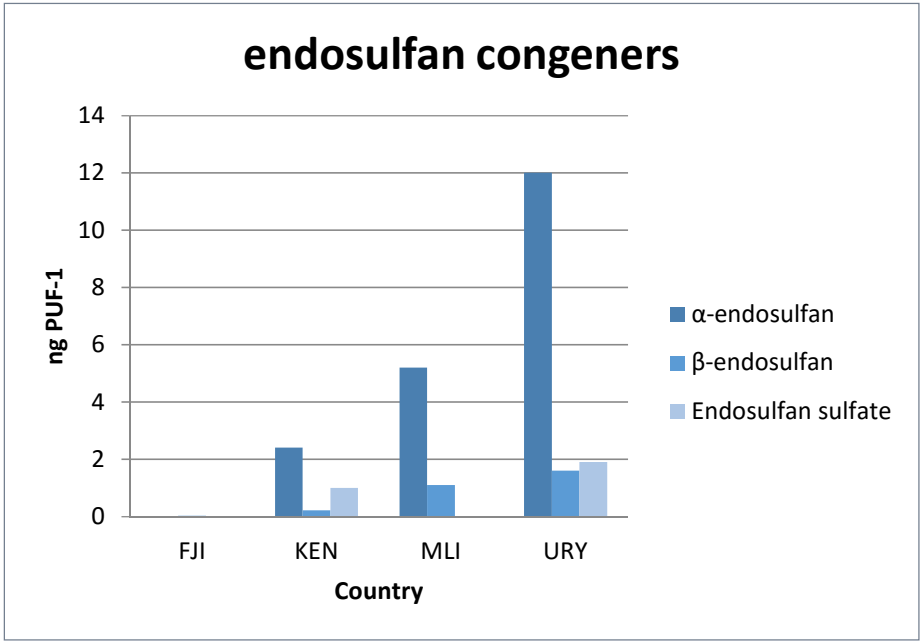


New POPs pesticides in PUFs

3 months exposure

In all samples, γ-HCH was the predominant congener within the HCHs

In all samples, α-endosulfan was dominating within the three endosulfans.



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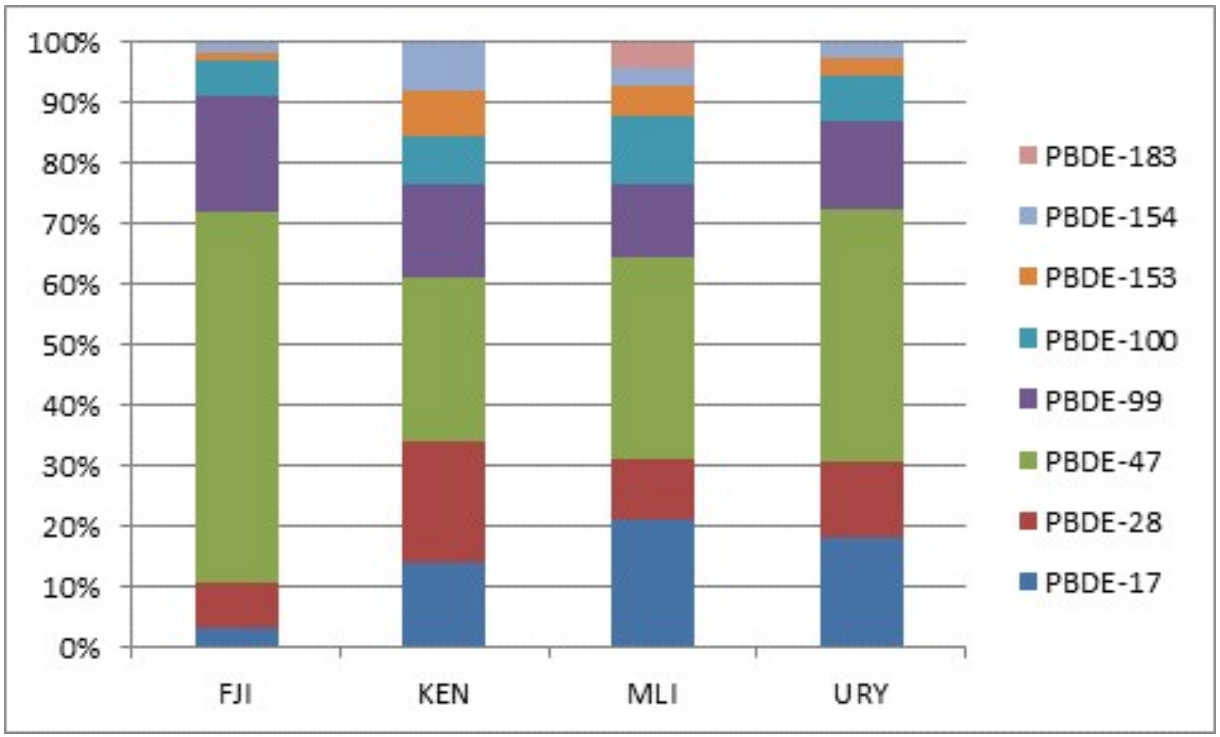
Endosulfans in PUFs

Sample ID	FJI	KEN	MLI	URY
Unit	ng PUF^{-1}	ng PUF^{-1}	ng PUF^{-1}	ng PUF^{-1}
α-endosulfan	<0.10	2.40	5.20	12
β-endosulfan	0.03	0.22	1.1	1.6
Endosulfan sulfate	<0.1	1.0	<0.1	1.9
Σendosulfans	0.03	3.62	6.30	15.5

	FJI	KEN	MLI	URY
Unit	ng PUF^{-1}	ng PUF^{-1}	ng PUF^{-1}	ng PUF^{-1}
∑PBDE(8)	5.71	1.49	4.21	2.89
PBB-153	0.06	<0.03	0.03	<0.03

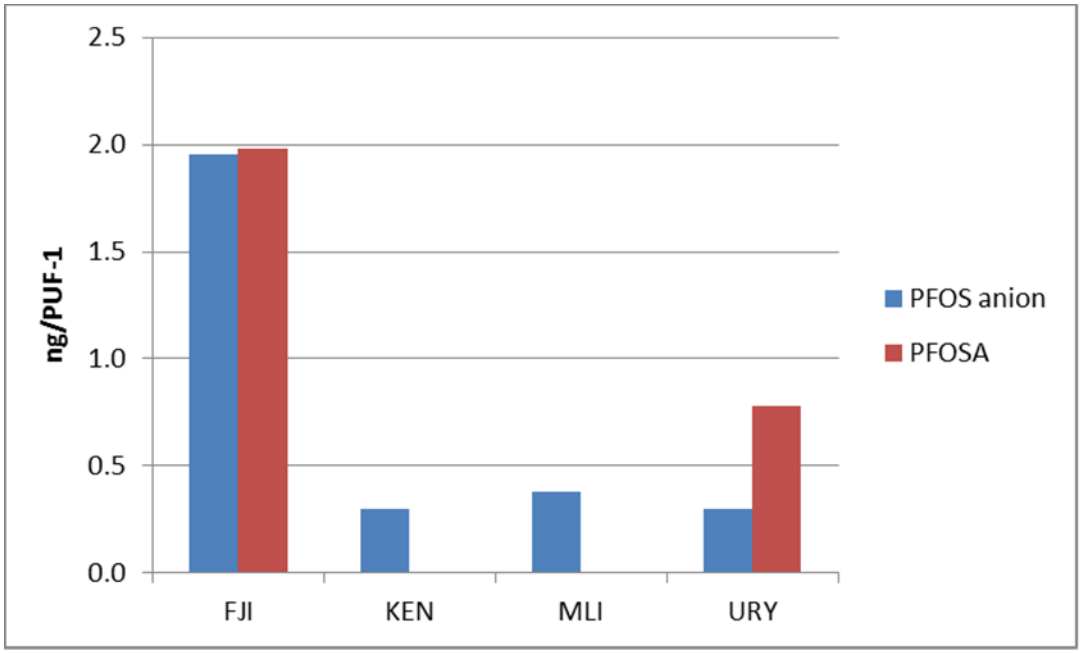


$PBDE_8$ and PBB in PUFs

3 months exposure

- ∑$PBDE_8$ were at similar concentrations in all four countries;
- In all samples, PBDE-47 was the predominant congener

PFASs in PUFs



Samples from Mali and Uruguay needed additional clean-up steps; therefore, poor recoveries.

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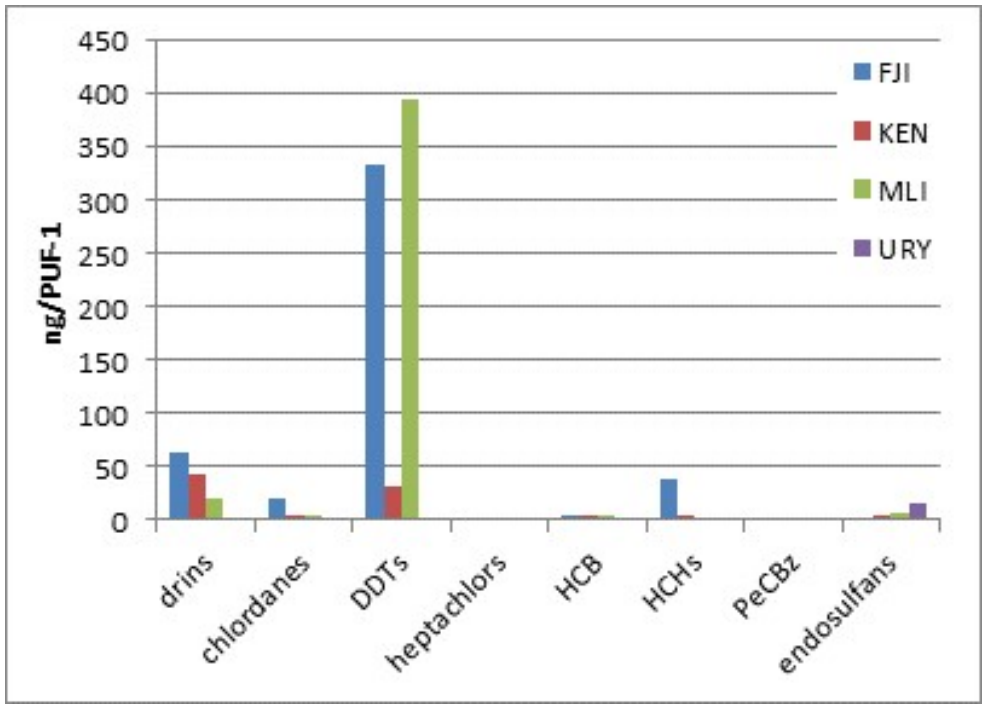
	FJI	KEN	URY	MLI
PFOS	1.95	0.30	0.30	0.38
FOSA	1.98	<0.386	0.78	<0.386
NMeFOSA	0.16	<0.031	<0.031	<0.031
NEtFOSA	0.10	0.03	<0.023	<0.023
NMeFOSE	2.70	0.64	<0.15	<0.15
NEtFOSE	0.69	0.53	<0.003	<0.003



Comparison: Initial POPs (2010) *vs.* new POPs (2013)

"Snapshot" measurement (3 m):

Pesticides: Endosulfans lower concentrations than DDTs and drins;

Industrial chemicals: Pentachlorobenzene similarly low as HCB;

$PBDE_8$ lower than PCB_6

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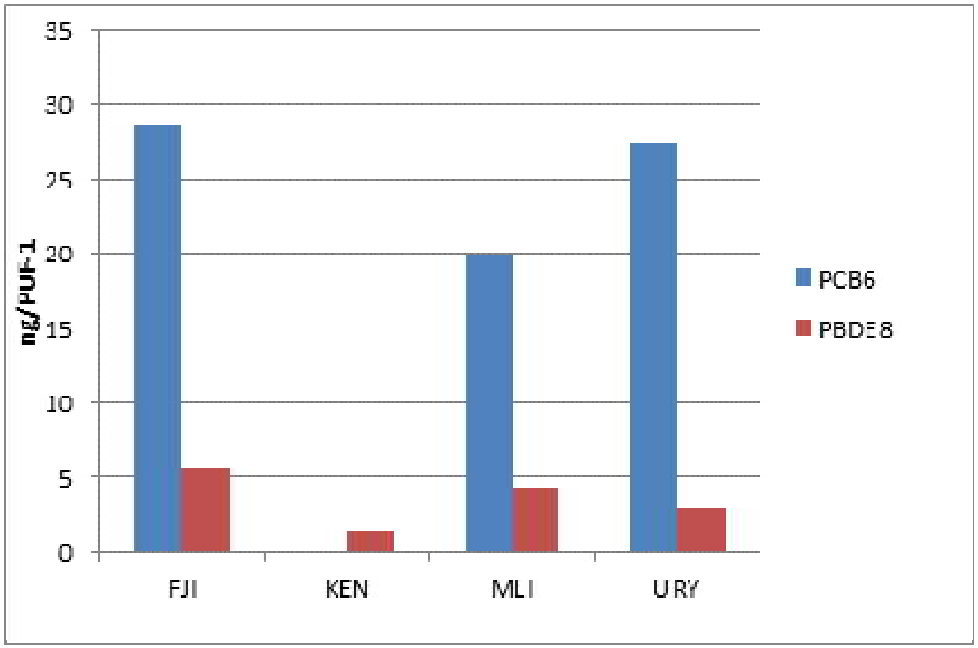

HBCD

- HBCD was screened in all four samples but was not quantifiable;
- Isomer-specific determination (α, β, γ) was not performed.

Conclusions air testing (1)

- The pilot testing of a proposed sampling and analysis scheme was very helpful – and necessary;
- PUF-PAS suitable to sample for all POPs presently listed in annexes of the Stockholm Convention;
- Clean-up of PUFs for analysis of PFOS/PFASs needs modification;
- Quantification of chlordecone was not possible due to the strong polar character of compound; it could not be separated from the matrix;
- Analysis of endosulfans and chlordecone in the same extract was not possible (baseline too high for proper quantification);
- The experiences did feed into the guidance document for the Global Monitoring Plan and UNEP/GEF GMP2 projects.

Conclusions air testing (2)

HBCD analysis

- Tiered approach
  - Screening step for the sum of three congeners (α, β, γ) with GC/(HR)MS as part of the PBDE analysis;
  - If positive, isomer-specific analysis with LC/MS-MS in expert laboratory (IVM VU Amsterdam)
- Analysis of sum HBCD:
  - The three HBCD congeners could not be quantified as sum parameter using LRMS detection at a detection limit of 0.33 ng PUF^{-1}.
  - Using HRGC-HRMS with an EI+ source, the peaks were close to the LOD; therefore, APGC-MS/MS developed

Proposed PAS/PUF sampling scheme

Assignment of samplers, PUFs, and analytes according to laboratory per country)			No. analyses per year
Sampler 1:	PUFs 1-4:	For basic POPs pesticides in expert back-up laboratory	4
		drins, chlordanes, DDTs, HCHs, heptachlors, mirex, HCB, pentachlorobenzene, endosulfans,	
		toxaphenes, chlordecone	toxaphene, annual sample only
Sampler 2:	PUFs 1-4:	For basic POPs in national POPs laboratory	4
		drins, chlordanes, DDTs, HCHs, heptachlors, mirex, HCB, pentachlorobenzene, endosulfans,	
		toxaphenes, chlordecone	toxaphene, annual sample only
Sampler 3:	PUFs 1-4:	For indicator PCB in expert back-up laboratory	4
		6 indicator PCB	
Sampler 4:	PUFs 1-4:	For indicator PCB in national POPs laboratory	4
		6 indicator PCB	
Sampler 5:	PUFs 1-4:	For dioxin-like POPs in expert back-up laboratory (combined into one extract as annual average)	1
		17 PCDD/PCDF, 12 dl-PCB	
Sampler 6:	PUFs 1-4:	For dioxin-like POPs in national dioxin laboratory (combined into one extract as annual average)	1
		17 PCDD/PCDF, 12 dl-PCB	
Sampler 7:	PUFs 1-4:	For dioxin-like POPs in expert back-up laboratory (each exposure to generate one seasonal data point; total of 4 per year and country)	4
		17 PCDD/PCDF, 12 dl-PCB	
Sampler 8:	PUFs 1-4:	For dioxin-like POPs in national laboratory (each exposure to generate one seasonal data point; total of 4 per year and country)	4
		17 PCDD/PCDF, 12 dl-PCB	
Sampler 9:	PUFs 1-4:	For PBDE in expert laboratory	4
		8 PBDE, HBCD, PBB	
Sampler 10:	PUFs 1-4:	For PBDE in national laboratory	4
		8 PBDE, HBCD, PBB	
Sampler 11:	PUFs 1-4:	For PFOS in expert laboratory	4
		6 PFAS	
Sampler 12:	PUFs 1-4:	For PFOS in national laboratory	4
		6 PFAS	

Color codes:

Green Analysis in expert back-up laboratory

No Fill Analysis in national laboratory

Yellow Groups of chemicals recommended for analysis

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Pilot testing of new POPs in water

Experiments undertaken in 2014

- Water sampling in six countries:
  - Fiji, Kenya, Mali, Uruguay, and
  - the Netherlands and Sweden
- Sampling procedure:
  - 1 day sampling;
  - Several grab samples merged into one;
- PFOS analysis:
  - Analysis for PFOS in expert laboratory

Guidance for Global Monitoring Plan

UNITED NATIONS

UNEP

SC

UNEP/POPS/COP.6/INF/31

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Stockholm Convention on Persistent Organic Pollutants

Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants
Sixth meeting
Geneva, 28 April–10 May 2013
Item 5 (i) of the provisional agenda*

Matters related to the implementation of the Convention: effectiveness evaluation

Guidance on the global monitoring plan for persistent organic pollutants

Water as a core matrix for PFOS/PFOSA

POPs listed at COP-4				
	Air	Human Milk	Human Blood	Water
Chlordecone	Chlordecone	Chlordecone	Chlordecone	
α-HCH	α-HCH	α-HCH	α-HCH	
β-HCH	β-HCH	β-HCH	β-HCH	
γ-HCH	γ-HCH	γ-HCH	γ-HCH	
Hexabromobiphenyl	PBB 153	PBB 153	PBB 153	
Pentachlorobenzene	PeCBz	PeCBz	PeCBz	
c-penta BDE c-octa BDE	BDE 47, 99, 153, 154, 175/183 (co-eluting) Optional: BDE 17, 28, 100	BDE 47, 99, 153, 154, 175/183 (co-eluting) Optional: BDE 100	BDE 47, 99, 153, 154, 175/183 (co-eluting) Optional: BDE 100	
PFOS[7]	PFOS, PFOSA, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE	PFOS, PFOSA	PFOS, PFOSA	PFOS, PFOSA

HF, New POPs

Pilot testing for PFOS in water (2014)

Matrix	Surface water	Surface water	Surface water	Surface water
Sampler				
Lab				
Date of analysis				
Sampler No.	1	1	1	1
Year	2014	2014	2014	2014
LAB code	xx	xx	xx	xx
Year-season	2014-xx	2014-xx	2014-xx	2014-xx
Exposure season				Sep
Original Sample-ID				
Full country name	Fiji	Kenya	Mali	Uruguay
Country ISO-3	FJI	KEN	MLI	URY
Sample ID	FJI-xx-1	KEN-xx-1	MLI-xx-1	URY-xx-1
Unit	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}
PFOS anion				

Sampling site and sampling - Fiji

Water site name	GPS coordinates of site
Waimanu River	18.026698°S 178.368659°E

Samplers and instructions were sent bu IVM VU Amsterdam and MTM Research Centre Örebro University

Sampling site and sampling - Kenya

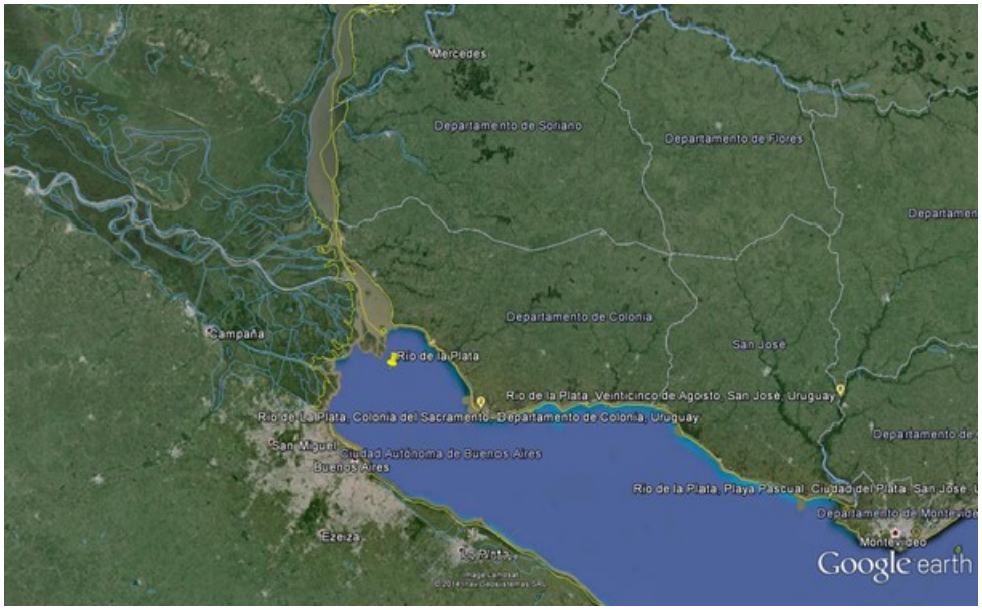
Water site name	GPS coordinates of site
Sabaki River Mouth	3° 09’ 41.0" S
close to Indian Ocean	40° 07’ 50.0" E

Figure 14: Water collection at Sabaki River mouth

Sampling site and sampling - Mali

Water site name	GPS coordinates of site
Sotuba/Mali	12°40.095’ N
Sotuba/Mali	
Sotuba/Mali	007°55.0034' W

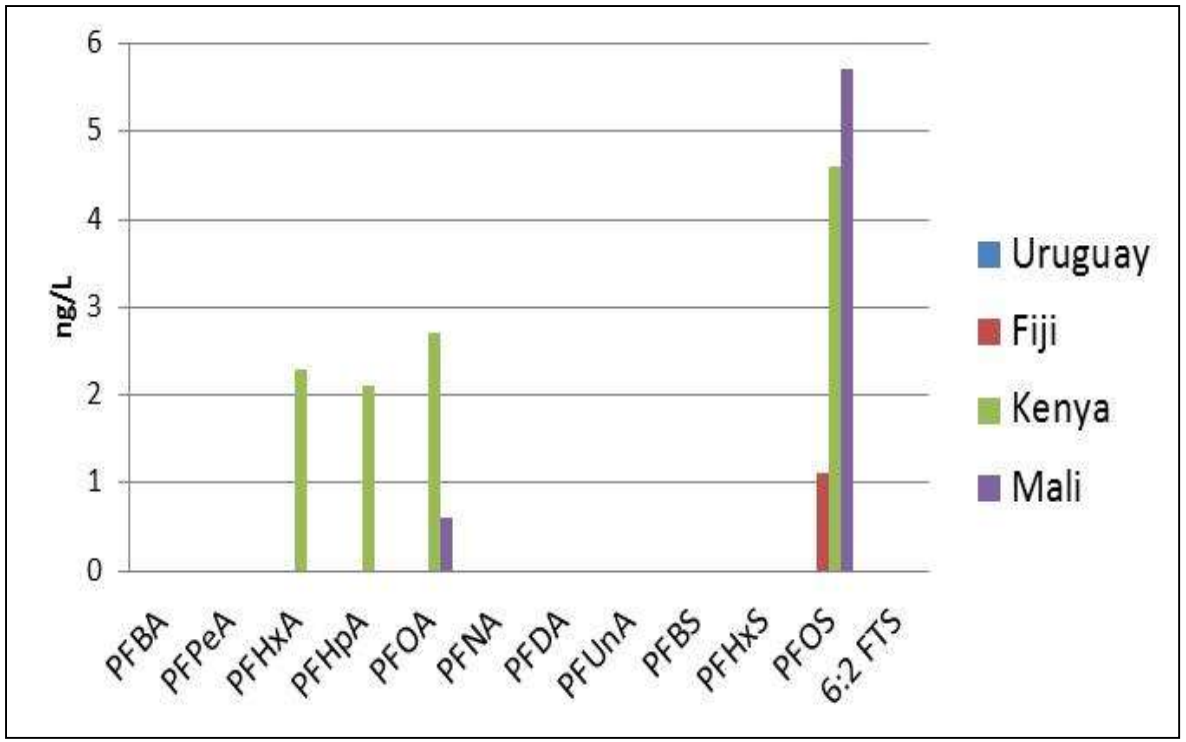
Sampling site and sampling - Uruguay



Water site name	GPS coordinates of site	Sampler origin	sampling depth (m)	Distance from shore (m)
Río de la Plata	34° 12´ 22.29"S	1	6	50
Río de la Plata	58° 04´ 38.32"W	2	6	50

GMP pilot monitoring

- Fiji, Mali, Kenya and Uruguay were invited to participate
- Background samples, rivers
- LOD ~1 ng/mL
- 100 mL/analysis
- HDPE bottles
- Duplicate analysis
- Reference material



By IVM VU Amsterdam

Results PFOS in water

Workshop
for UNEP/GEF Project "Establishing the tools and methods to include the nine new POPs into the Global Monitoring Plan"

UNEP GLOBAL MONITORING PLAN EXPERT WORKSHOP ON PFAS IN WATER

27-28 October 2014
VU University, Amsterdam, The Netherlands

Prepared by:
Institute for Environmental Studies (IVM)
for
Chemicals Branch
United Nations Environment Programme/DTIE
December 2014

Expert workshop held in Amsterdam to discuss amendments to the guide on POPs monitoring to include PFOS and precursors

Sampler type	Grab IVMVU	Grab IVMVU	Grab IVMVU	Grab IVMVU	Grab IVMVU	Grab IVMVU
Year-season	2014-W-IVM	2014-W-IVM	2014-W-IVM	2014-W-IVM	2014-W-IVM	2014-W-IVM
Start	30/04/2014		30/04/2014	04/09/2014	11/05/2014	
Country name	Fiji	Kenya	Mali	Uruguay	Netherlands	Netherlands
Latitude	18° 026.698' S	3° 09’ 41.0" S	12°40.095’ N	34° 12´ 22.29" S	52° 33'45.53'' N	51°01.05''N
Longitude	178° 368.659' E	40° 07’ 50.0" E	007°55.0034' W	58° 04´38.32" W	5° 54'39.95'' E	E4°29'00.70''
Site name	Waimanu River	Sabaki River Mouth	Sotuba/Mali	Río de la Plata	Kampen, IJssel	Rotterdam, Nieuwe Maas
Sample ID	FJI-W-IVM-1	KEN-W-IVM-1	MLI-W-IVM-1	URY-W-IVM-1	NLD-W-IVM-1	NLD-W-IVM-1
Unit	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}
PFOS anion	**1.1**	**4.6**	**5.7**	**<1.0**	**9.9**	**11**