Overview of the outputs and outcomes of the UNEP/GEF POPs GMP project

Experts Presentations – Day 1



Final meeting of the UNEP/GEF POPs GMP projects in the Africa region

Casablanca, Morocco 28-30 November 2023

Facts and figures of dl-POPs and PFAS monitoring in air, national samples, human milk and water



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PAS/PUFs 1. dl-POPs (analyzed by CSIC, Barcelona) 2. PFAS

- Results were sent to national coordinators (and UNEP) for dl-POPs on 30 August 2020 and for PFAS on 30/31 August 2020
- Results for air were presented at on-line regional workshop in October 2020
- The PAS/PUF and AAS air results are contained in the UNEP regional report for Africa (HF sent to UNEP in March 2023, not yet published)
- A global report, summarizing air results (PAS/PUFs and active sampler) from four regional GMP2 projects are contained in a global report for air (HF sent to UNEP in December 2022, not yet published)
- A report presenting the results for all POPs of the UNEP/GEF GMP1 project was prepared and sent to UNEP in May 2020, not published
- The results are only partially contained in the dwh and not reflected in the global report for the COP.

Summary: dl-POPs in PAS/PUFs global

	Africa (N=89)	Asia (N=30)	PAC (N=23)	GRULAC (N=53)	Overall (N=195)
		TEQ_DF (p	g TEQ/PUF)		
Mean (SD)	13.3 (18.3)	<mark>13.6</mark> (12.6)	4.79 (7.34)	10.4 (6.98)	11.5 (14.2)
Median [Min, Max]	4.07 [0.055, 77.7]	9.80 [0.162, 40.3]	1.01 [0.0005, 27.0]	10.4 [0.141, 33.5]	6.41 [0.0005, 77.7]
		TEQ_PCB (p	og TEQ/PUF)		
Mean (SD)	<mark>3.53</mark> (3.78)	3.30 (2.55)	1.15 (1.23)	2.94 (2.16)	3.05 (3.07)
Median [Min, Max]	2.17 [0.0004, <mark>16.4</mark>]	3.10 [0.003, 8.57]	0.675 [0.002, 4.32]	2.62 [0.253, 11.0]	2.34 [0.0004, 16.4]





dl-POPs results by sample (n=89)



African samples have the widest range on regional basis Maximum for TEQ DF in Mali (77.7 pg TEQ/PUF), Maximum for TEQ_PCB in Egypt (16.4 pg TEQ/PUF)

Tunisia and Zambia have high shares of dl-PCB.

COD EGY ETH GHA 30 20 10 ETH (2017-III) ETH (2017-IV) (TH (2017-Q3) COD (2017-IV) ETH (2018-A) GHA (2017-I) COD (2017-III) COD (2018-A) OD (2019-H1) ETH (2017-II) 3HA (2017-A) GHA (2017-II) GHA (2017-III) EGY (2018-EGY (2018-EGY (2018-EGY (2018-1 EGY (2018-1 3HA (2018-**DD (2017** SHA (2017-MUS MAR 12 2.0 -1.5 50 Concentration (pg TEQ/PUF) (EN (2017-IV) ⁻ KEN (2018-A) ⁻ MLI (2018-A) MUS (2017-IV) MUS (2018-A) = (EN (2017-III) 1 = KEN (2017-I) ALI (2017-IV) MAR (2017-II) MAR (2017-III) MAR (2017-IV) MAR (2017-Q3) MLI (2017-A MLI (2017-I MUS (2017-III MUS (2017-1 MLI (2017-I MLI (2017-II KEN (2017-IUS (2017-(2018-0 NUS (201 SEN NGA TZA TGO 10.0 1.2 7.5 0.8 5.0 TGO (2017-III) TGO (2017-IV) (2019-A) A ZA (2019-H2) SEN (2017-A) SEN (2017-I) SEN (2017-II) (2017-11) SEN (2017-IV) EN (2018-Q3) ZA (2018-IV) TZA (2019-A) [ZA (2019-H1) TGO (2017-I) GO (2018-A) GO (2017-A (2018-GO (2017-UGA TUN JGA (2017-A) JGA (2017-IV) JGA (2017-Q3) (2018/2019) ZMB (2017-IV) ZMB (2017-I ZMB (2017-ZMB (2017

28-30 Nov

1GA

Sample_ID

Compounds

TEQ_DF

TEQ_PCB

PAS/PUFs: PFAS (n=317 global, 127 in Africa)

	Africa (N=127)	Asia (N=46)	PAC (N=43)	GRULAC (N=101)	Overall (N=317)
		PFOS			
Mean (SD)	<mark>1640</mark> (5940)	139 (122)	297 (219)	376 (497)	847 (3860)
Median [Min, Max]	110 [0, <mark>36000</mark>]	101 [27.3, 634]	266 [0, 827]	192 [0, 2260]	136 [0, 36000]
		PFOA			
Mean (SD)	<mark>305</mark> (464)	271 (194)	181 (86.5)	257 (125)	268 (313)
Median [Min, Max]	153 [0, <mark>3180</mark>]	183 [83.1 <i>,</i> 965]	165 [0, 417]	<mark>233</mark> [58.9, 655]	192 [0, 3180]
		PFHxS			
Mean (SD)	<mark>224</mark> (980)	13.4 (20.7)	41.6 (48.5)	9.72 (18.6)	101 (628)
Median [Min, Max]	0 [0 <i>,</i> <mark>7880</mark>]	0 [0, 96.1]	34.7 [0, 206]	0 [0, 101]	0 [0, 7880]
		FOSA			
Mean (SD)	132 (414)	24.6 (81.8)	68.5 (155)	138 (260)	112 (315)
Median [Min, Max]	0 [0, <mark>1890</mark>]	0 [0, 327]	0 [0, 669]	34.9 [0, 964]	0 [0, 1890]

- PFAS in 38 PUFs could not be reported due to deterioration of the sample matrix (across all projects)
- FOSA could not be quantified in about 50% of the samples
- NMe-/NEtFOSA and NMe-/NEtFOSE are not reported due to only very few occurrences



Presence of PFAS by country in Africa (n=317)



- Extremely high values found in Zambia (point source = excavation work at Lusaka airport)
- Question: where to locate sampling stations in case of deviation from guidance document?
- PFOS, PFHxS, and FOSA order of magnitude higher in ZMB
- PFOA high but to lesser extend
- Tanzania did not send any PUF for PFAS analysis (reason: no MeOH-pretreated PUFs exposed)

PFAS4 by country

Diverse picture: FOSA not frequently quantified PFOA>PFOS (median) in COD, ETH, MUS, MAR, NGA, SEN, TGO, TUN, UGA Ratio PFOS:PFOA varied; sometimes between measurements in the sample country





PFAS4 in air

- 355 polyurethane foam disks analyzed for PFOS and precursors, PFOA and PFHxS
- PFOS (with wide range of values) and PFOA dominated over PFHxS and other PFAS
- Low sorption capacity of PUFs hampered analysis and quantification of PFAS





- Highest single PFAS values found in Africa;
- Driving high mean values;
- Median values were highest in GRULAC and not in Africa



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Trends for dl-POPs in air samples (PAS/PUFs) GMP1 vs. GMP2 (2010/2011 vs. 2017-2019)







- Trend analysis with 8-9 year interval could be made for PCDD, PCDF, and dl-PCB
- Global trends hardly seen since trends within the regions were different, and trends for countries within the same region were different.





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National samples

1. dl-POPs (analyzed by commercial laboratories) 2. PFAS

- Results were sent to national coordinators (and UNEP) for dI-POPs on 26 October 2020 and for PFAS on 14 November 2020
- Results for national samples and human milk were presented at on-line regional workshop in November 2021
- These results are not yet summarized, made available by UNEP



Summary dl-POPs in national samples (global)

	Afr	ica	Asi	Asia		PAC		GRULAC	
	abiotic (N=24)	biota (N=41)	abiotic (N=18)	biota (N=40)	abiotic (N=3)	biota (N=22)	abiotic (N=16)	biota (N=21)	
				TEQ_DF					
Mean (SD)	0.550 (0.971)	0.356 (0.904)	6.71 (10.5)	0.155 (0.245)	0.026 (0.022)	0.171 (0.460)	13.9 (40.3)	0.137 (0.352)	
Median [Min, Max]	0.005 [0, 3.37]	0.023 [0, <mark>5.29</mark>]	2.75 [0.011, 44.1]	0.059 [0, 1.26]	0.027 [0.004, 0.047]	0 [0, 1.64]	0.576 [0.012, 163]	0.065 [0.00002, 1.66]	
				TEQ_PC	3				
Mean (SD)	0.028 (0.062)	<mark>0.725</mark> (2.20)	0.541 (1.38)	0.254 (0.360)	0 (0)	0.179 (0.470)	1.10 (2.34)	0.292 (1.12)	
Median [Min, Max]	0.0004 [0, 0.235]	0.054 [0, <mark>11.8</mark>]	<mark>0.081</mark> [0, 5.91]	0.111 [0, 1.40]	0 [0, 0]	0.002 [0, 1.86]	0.022 [0.0007, <mark>8.32</mark>]	0.039 [0.0001, 5.17]	





Sediments as abiotic and fish/eggs have highest concentrations

National samples – dl-POPs by sample



National samples analyzed for PFAS

- Total of 238 national samples; of these: 71 abiotic samples and 167 biota samples
 - abiotic without air samples (317 PAS/PUFs, 18 from active air samplers) and without 144 samples from water network
 - biota without 44 human milk samples
- 76 samples (32% of total) were fish, 36 (15%) were egg (new matrix for PFAS)
- Africa contributed with 68 samples (29% of total)

	Afr	ica	As	ia	P/	AC	GRL	JLAC
	abiotic (N=25)	biota (N=43)	abiotic (N=21)	biota (N=41)	abiotic (N=3)	biota (N=27)	abiotic (N=22)	biota (N=56)
			PFO	S (pg/g f.w.)				
Mean (SD)	49.0 (91.8)	50.0 (67.5)	68.1 (98.7)	33.9 (52.6)	21.3 (36.9)	23.7 (33.5)	<mark>238</mark> (297)	<mark>139</mark> (360)
Median [Min, Max]	15.9 [0 <i>,</i> 409]	30.8 [0, 326]	22.4 [0, 303]	21.2 [0, 309]	0 [0, 63.9]	12.4 [0, 151]	173 [0, 1140]	25.3 [0, 1650]
			PFO	A (pg/g f.w.)				
Mean (SD)	18.6 (18.7)	11.2 (9.50)	20.9 (18.7)	7.48 (8.64)	6.63 (5.76)	10.4 (10.5)	<mark>46.9</mark> (52.6)	9.26 (22.8)
Median [Min, Max]	12.4 [0, 74.5]	8.74 [0, 43.9]	19.9 [0, 60.3]	6.92 [0, 44.4]	9.55 [0, 10.4]	9.36 [0, 48.5]	28.8 [0, 172]	4.15 [0, 160]
			PFHx	S (pg/g f.w.)				
Mean (SD)	13.3 (61.2)	1.87 (5.67)	0.827 (3.79)	1.31 (3.58)	0 (0)	0.641 (2.40)	7.80 (12.6)	1.64 (4.37)
Median [Min, Max]	0 [0, <mark>307</mark>]	0 [0, <mark>28.7</mark>]	0 [0, 17.4]	0 [0, 18.2]	0 [0, 0]	0 [0, 11.0]	0 [0 <i>,</i> 49.5]	0 [0, 22.9]

Scale of PFAS in national samples (global)



All values in pg/g f.w.)



Africa national samples: PFAS by sample





All values in pg/g f.w.)

Occurrence of other PFAS in national samples



38% of the results had PFAS >LOQ

Detection frequencies:

- PFOS = 80%
- PFOA = 73%
- PFHxS =24%
- PFNA = 55%

These informations, as well as results for air and water samples, have not been taken into considerations in other groups such as POPRC or inventories (include POPs under evaluation for listing; PFOA-2019, PFHxS-2022, LC_PFAS-2023ff)

Water for PFAS and active sampling only

- Results from water network were sent to national coordinators (and UNEP) on 29 August 2020
 Other water results were sent as part of the national samples
- Results for water and air samples were presented at the on-line regional workshop in October 2020
- The water results are contained in the UNEP regional report for Africa (HF sent to UNEP in March 2023, not yet published)
- A global report, summarizing PFAS results from all water samples are contained in a global report for water (HF sent to UNEP in January 2023, not yet published)

PFAS in water overview

- 168 water samples were analyzed for PFAS, of these:
 - 144 were from GMP2 water network
 - 24 samples were submitted as national samples
- In comparison, the amounts were low
- Maximum values from GMP2 were in Africa (PFOA) and PAC (PFOS and PFHxS)



	Afr	rica	A	sia	PAC	GRU	ILAC	Ov	erall
	GMP2 (N=44)	Nat (N=6)	GMP2 (N=14)	Nat (N=9)	GMP2 (N=46)	GMP2 (N=40)	Nat (N=6)	GMP2 (N=144)	Nat (N=21)
				PFOS (ng	g/L)				
Mean (SD)	0.64 (0.64)	0.23 (0.20)	0.11 (0.11)	1.07 (0.95)	1.04 (1.85)	<mark>1.61</mark> (1.35)	0.86 (0.89)	0.99 (1.39)	0.77 (0.83)
Median [Min, Max]	0.45[0, 2.64]	0.22 [0.03, 0.45]	0.07 [0, 0.44]	0.94 [0.04, 2.68]	0.07 [0, <mark>6.23</mark>]	1.35 [0.04, 5.32]	0.47 [0.30, 2.63]	0.37 [0, 6.23]	0.44 [0.03, 2.68]
				PFOA (ng	g/L)				
Mean (SD)	<mark>0.73</mark> (0.85)	0.52 (0.68)	0.176 (0.12)	1.24 (0.97)	0.16 (0.30)	0.62 (0.40)	0.83 (0.99)	0.46 (0.60)	0.92 (0.91)
Median [Min, Max]	0.38 [0.05, 4.02]	0.24 [0.11, 1.86]	0.13 [0, 0.46]	1.51 [0, <mark>2.33</mark>]	0.05 [0, 1.51]	0.55[0.05 1.44]	0.25 [0.08, 2.20]	0.23 [0, 4.02]	0.26 [0, 2.33]
				PFHxS (n	g/L)				
Mean (SD)	0.22 (0.40)	0.05 (0.06)	0.01 (0.02)	0.17 (0.14)	0.55 (1.05)	<mark>0.31</mark> (0.30)	0.26 (0.30)	0.33 (0.67)	0.16 (0.19)
Median [Min, Max]	0.06 [0, 1.63]	0.04 [0, 0.13]	0 [0 <i>,</i> 0.05]	0.16 [0, 0.41]	0.01 [0, 3.51]	<mark>0.17</mark> [0, 0.95]	0.11 [0, 0.74]	0.06 [0, 3.51]	0.10 [0, 0.74]



Scale and pattern by sample

Pattern: stable

Scale: large variation





- Water sampling approach with 4 samples per year successfully tested and recommended for future monitoring projects
- VUT, ARG: stable scale and pattern at measurable concentrations, incl. PFHxS.
- KEN, KIR: larger differences between measurements; quite stable pattern
- BRA: change of sampling location -> difference in scale



Human milk (PFAS)

- Results of GMP2 samples were sent to national coordinators (and UNEP) on 8 August 2020
- Results for national samples and human milk were presented at on-line regional workshop in November 2021
- All human milk results for listed substances are contained in the UNEP regional report for Africa (HF sent to UNEP in March 2023, not yet published)
- Stored human milk samples, prior to 2016, were re-analyzed by MTM Örebro University and published in a peer-reviewed journal (2022). Includes sub-samples from Brazil (2012)
- These samples are referenced as WHO milk in the dwh and not according to performing laboratory or donor



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RESEARCH ARTICLE

Perfluoroalkane acids in human milk under the global monitoring plan of the Stockholm Convention on Persistent Organic Pollutants (2008–2019)

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SC PFAS in human milk (GMP2)

	Africa (N=14)	Asia (N=13)	GRULAC (N=9)	WEOG+CEE (N=8)	Overall (N=44)
		PFC)S		
Mean (SD)	9.55 (7.34)	<mark>32.0</mark> (54.8)	12.5 (12.1)	22.3 (13.2)	19.1 (31.6)
Median [Min, Max]	10.3 [0, 21.9]	17.2 [0, <mark>212</mark>]	11.8 [0, 40.5]	17.8 [12.2, 51.4]	13.2 [0, 212]
		PFC	A		
Mean (SD)	12.7 (3.75)	16.9 (6.67)	14.3 (4.19)	28.6 (7.66)	17.2 (7.87)
Median [Min, Max]	12.5 [6.20, 18.1]	14.6 [9.98, 31.8]	15.9 [7.81, 19.0]	31.0 [17.7, <mark>37.4</mark>]	15.8 [6.20, 37.4]
		PFH	xS		
Mean (SD)	0	<mark>9.11</mark> (30.7)	0	3.24 (6.46)	3.28 (16.9)
Median [Min, Max]	0	0 [0, 111]	0	0 [0, 17.4]	0 [0, 111]



- High PFOS and PFHxS values for Kiribati drive mean values for Asia
- PFHxS not quantified in Africa and GRULAC

Note: y-axis in log scale

Human milk PFAS3 – GMP2 n=44

- KIR extrem values for PFOS + PFHxS
- PFHxS only quantified in KIR, THA, CHE, SWE
- No sample from Egypt received



Sample_ID





Sample_ID

Human milk: PFAS re-analysis of all samples

Re-analysis of PFAS in historic pools PFAS necessary: (1) more substances, and (2) improved analytical method



Fiedler H, Sadia M, Krauss T, Baabish A, Yeung L W Y (2022). Perfluoroalkane acids in human milk under the global monitoring plan of the Stockholm Convention on Persistent Organic Pollutants (2008-2019). Frontiers of Environmental Science & Engineering, 16(10): 132

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Human milk: 3 PFAS (N=86)



PFHxS: African samples - quantified in Mali (2009) and Togo (2010), but not in subsequent years

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Trends for PFAS3



Heidelore Fiedler^{a,*}, Xue Li^b, Jin Zhang^c













Summary and conclusions

- Sampling and analysis programme generated a wealth of quantitative data as to the scale of POPs present in 42 countries and other metadata. Analytical methods have been modified and adapted to reach high performance.
- Assessment as to significance for regional interpretation or usefulness of the data not known.
- It is of outmost importance to implement the sampling and analytical protocols to achieve coherent datasets for further assessment. Long time for execution of the project considered to be the biggest draw-back.
 - The water sampling implementation must be valuated as success and according to the GMP guidance document.
 - Gaps in PAS/PUF sampling when wrong PUFs were exposed so that not all POPs could be determined. Sampling frequency (as to years) needs to be agreed.
- Component of national samples with mirror analysis disappointing: only 28 of 42 countries sent national samples, 33% did not have have samples of their national interest analyzed in an expert laboratory. Further, the majority of POPs labs did not take the opportunity to test their own chemical analytical capacities in these mirror samples.
 Africa=11 of 15 participating countries sent samples, Asia=4 of 7, Pacific Islands=4 of 9, GRULAC=9 of 11.
- Component with active air sampler only punctual implementation.
- Missed opportunity: POPs under consideration for listing in the Stockholm Convention have been analyzed and data from developing countries became available.
- Monitoring results for PFAS and dI-POPs of UNEP/GEF GMP2 projects were not included in the global report (and regional reports) prepared for the COP.

Final meeting of the UNEP/GEF project "Continuing Regional Support for the POPs Global Monitoring Plan under the Stockholm Convention in the Africa Region"

> 28-30 November 2023 Casablanca, Morocco

Key findings on POPs monitoring in the Africa Region: Human milk survey

Rainer Malisch CVUA Freiburg, Germany



WHO/UNEP-coordinated human milk studies on POPs

- Starting point: participation of 15 countries from Africa in the 2016-2019 study
- Discussion of these results in a wider context

Coordinator	Round	Period	N (countries)	Coverage of POPs
wно	1	1987-1988	19	PCB, PCDD/PCDF
wно	2	1992-1993	19	PCB, PCDD/PCDF
wно	3	2000-2003	26	21 POPs
Joint WHO/UNEP	4	2005-2007	13	21 POPs
Joint WHO/UNEP	5	2008-2012	45	22 POPs
UNEP	6	2014-2015	17	22 POPs
UNEP	7	2016-2019	43	30 listed + 2 proposed POPs

2000-2019:

- 82 countries (19 from Africa)
- Increasing number of analytes of interest

Comprehensive results available for samples of the 2016-2019 period

		COP No	Year	Parameter	Parent POPs	Transformation products	No of analy
			2001	1. Initial 12 POPs			
1	1			Aldrin	Aldrin		1
2	2			Chlordane	cis- and trans-chlordane	cis- and trans-nonachlor,	5
3	3			DDT	p,p'-DDT, o,p'-DDT	p,p'-DDE, o,p'-DDE, p,p'-	6
4	4			Dieldrin	Dieldrin	000, 0,p-000	1
5	5			Endrin	Endrin	Endrin ketone	2
6	6			Heptachlor	Heptachlor	Heptachlorepoxide	2
7	7			Hexachlorbenzene (HCB)	Hexachlorbenzene		1
8	8			Mirex	Mirex		1
9	9			Polychlorinated biohenvils (PCB)	ΣPCB6 (6 "indicator congeners"): 28, 52, 101,		6
-	-				138, 153, and 180 PCB with TEFs* (12 congeners): 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and		12
10	10			Toxaphene	189 Congeners P26, P50, P62		3
- 11	11			Polychlorinated dibenzo-n-dioxins (PCDD)	2.3.7.8-substituted PCDD (7 conceners)		7
12	12			Polychlorinated dihenzofurans (PCDF)	2.3.7.8-substituted PCDE (10 congeners)		10
				8 DCB with TEEs (Toxis Emissions Easters) assis	end by WHO is 1000		10
Í			V	Pells with TEPS (Toxic Equivalency Factors) assign	D	T	
			10000	Parameter	Patent POPs	Transformation products	
		001-4	2009	2. New POPS			
13	1			Alpha hexachlorocyclohexane (alpha-HCH)	alpha-HCH		1
14	2			Beta hexachlorocyclohexane (beta-HCH)	beta-HCH		1
15	3			HCH), common name: Lindane	gamma-HCH		1
16	4			Chlordecone	Chlordecone		1
17	5			Pentachlorobenzene	Pentachlorbenzene		1
18	6			Hexabromobiphenyl (HBB)	PBB 153		1
19	7			Tetra- and pentabromodiphenyl ether	PBDE 47, 99; optional: PBDE 100		2
20	8			Hexa- and heptabromodiphenyl ether	PBDE 153, 154, 175/183 (co-eluting)		3
21	9			Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulforivl fluoride (PFOSF)	PFOS (linear and branched isomers)		
		COP-5	2011	3. new POPs			
22	1			Technical endosulfan and related isomers	alpha-, beta-endosulfan, endosulfan sulfate		4
		COP-6	2013	4. new POPs			
23	1			Hexabromocyclododecane (HBCD)	alpha-, beta-, gamma-HBCD		3
		COP-7	2015	4. new POPs			
24	1			Hexachlorobutadiene	HCBD		1
25	2			Pentachlorophenol + salts		[Pentachloranisole (PCA)]	2
26	3			Polychlorinated naphthalenes	[PCN (congeners to be decided)]		21
		COP-8	2017	5. new POPs			
27	1			Decabromodiphenylether (DecaBDE)	PBDE-209		1
28	2			Short-chained chlorinated paraffins (SCCPs)	[SCCP] *)		thousan
24)	3			Hexachlorbutadiene	HCBD		(1)
		COP-9	2019	6. new POPs			
29	1			Dicofol	[Dicofol]		1
30	2			PFOA and salts	PFOA		
				Proposed for listing			
31				Medium-chained chloringted paraffirs (MCCPs)			thousan
20			_	Dediterteres enferis seid	DELLO		uiousalli
32				Periodinexane suffonic acid	Prnxs		

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30 listed POPs

2 proposed POPs

- 101 chlorinated/ brominated analytes without CPs; thousands for CPs
- PFOS (linear and branched), PFOA, PFHxS

No multi-method for simultaneous determination – about half a dozen of different analytical methods necessary

Unique characteristic among the core matrices of the GMP: results for the full set of 32 POPs of interest available for samples of the 2016-2019 period

including

- decabromodiphenyl ether [PBDE-209] and short-chain chlorinated paraffins [SCCP] as listed in 2017
- dicofol and perfluorooctanoic acid [PFOA] as listed in 2019,
- medium-chain chlorinated paraffins [MCCP] and perfluorohexane sulfonic acid [PFHxS] as proposed for listing

Three pillars



- 30 listed POPs
- 2 proposed POPs

- Countries
- UN-RegionsGlobal

Art. 16: Effectiveness evaluation

Presentation of results for the three pillars

- Presentation of concept, analysis, results and discussion of these global studies for these POPs: complex task which cannot be fulfilled in one presentation/publication
- Therefore, a series of publications as chapters to five parts of compendium "Persistent organic pollutants in human milk"

Content

- I Introduction
- II Analytical methods and quality control
- III WHO/UNEP-coordinated exposure studies 2000-2019: results of chlorinated and brominated POPs and discussion
 - (i) PCB, PCDD and PCDF;
 - (ii) chlorinated pesticides and industrial chemicals;
 - (iii) polybrominated substances;
 - (iv) chlorinated paraffins;
 - (v) polychlorinated naphthalenes.
- IV Assessments
 - ✓ time trends:
 - PCB, PCDD/PCDF,
 - Selected chlorinated pesticides
 - PFAS
 - ✓ risk-benefit analysis for dioxin-like compounds
- V Summary and conclusions

- > Open access
- Supported by UNEP and CVUA Freiburg

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26	Witt	Ana
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https://link.springer.com/book /10.1007/978-3-031-34087-1

Key message A – Efficient and effective tool with global coverage as key contributor to the Global Monitoring Plan (GMP)

Concept of the WHO- and/or UNEP-coordinated exposure studies:

- ✓ collection of (usually 50) individual samples from mothers fulfilling protocol criteria;
- ✓ preparation of **pooled** (physically averaged) **samples considered to be representative for a country/subgroup**;
- ✓ analysis of the pooled samples in reference laboratories contributes to reliability and reduces uncertainty
- Cost-effective concept: Analysis of one or few pooled representative human milk samples is far less expensive than the analysis of a high number of individual samples, particularly for PCDD/PCDF or CPs



Global coverage 2000 – 2019: 82 countries

Key message B – Relative importance ("ranking") of chemicals

		COPIN	Year	Parameter	Parent POPs	Transformation products	No of analytes
			2001	1. Initial 12 POPs			
1	1			Alorin	Aldrin		. T
2	2			Chiordane	cie- and trans-citionitane	do- and trans-nonachtar,	5
3	3			DOT	p#/001, e.p-007	8,0-006, s.p-006, p.p-	.6
4	4			Delto	Detre	Mar. S.F. Sher	1
				lixain	tican	Endiritietore	3
0				Heladia	Fectación	Hecladiliceboilde	2
7	7	-	-	Headleterrere (107)	Hexatériterrere		
B			-	Hims	Vires		1
0	-		-	Paivchierinated balters to (PCB)	EPC86 (6 "Indicator congenera") 28, 52, 101,		
					138, 153, and 180 PCB with TEES' (12 congeneral) 77, 61, 165, 134, 145, 122, 129, 156, 157, 187, 169, and		12
10	10			Toxophene	Congenera P26, F50, P52		3
11	11		1	Preventermated ditienza-o-dicsing (PCDCs	2.3.7.8 extrattuted PCDD (7 congressm	-	2
12	12		-	Polychematec deeracturane (PCDF)	2.3.7.8 substituted PCOF (10 congeneral)		10
-	1125			1975 mit Tille (Ter a Dependence)	matine (ULIP) in 1998		
1		COP No.	Year	Parameter	Pawi POPi	Transformation products	
		007-4	2009	Z. New POPs			
13	1			Albhe Instactionocyclohexene (albhe-HCH	alpha-HOH		<u></u>
14	2			Bela hexachiorocyclohexane (Sela-HOH)	bdaHCH		3
15	4			Garana Nexachlorocycloherane (garrinte- HD-0, common neme: Lindene	pamma-HOH		1
16	4			Chiordecone	Oriendecone		1
17				Percantectoriana	Persaction because		
18	. 6			His absorrcclipterigit (HBB)	P58 153		1
15	7			Tetra- and pertabromolipheral effer	PEDE 47. 99. optional PEDE 100		
20.	8		-	Hima- and heptabronic dipletest ether	PRDE 153, 154, 179/183 (co-eluling)		5
21				Performance reformation and 6-4 OGL its mate	PFO8 (linear and brandhed isomers)		
		COP-5	2011	3. sow POPs			
22	1			Technical endorullari and related increas	alpha-, bela-endo sullan, endo sullan sullate		4
		00P-6	2013	4. new POPs			
23	+	-		Hexatesmocy.dode.declane & BCC)	abhe, bite, gammeHBCD		3
	_	COP-7	20%	4. BOW POPE			
24	1			Histachfortobutadiana	HCED		1
22	3			Pertactorophenor - salts		Pertachoranece (PCA)	2
26	3			Payottemated regitifuleres	(PCN accorganeers to be decided)		21
	-	COP-8	2017	5. sew POPs			
27	1			Decisionnelisten letter (Decision)	P707-203		
26	2			Short-shared stionated parafina (CCCP+)	190071 1		thought
245	1	-	-	Herachtstadione	HCBD		CD
- 7		(CORD)	2040	6 app(0)(r		-	10
		SUT-9	40.00	Desta	Destal		
	-			Here and state	MAN AN A		
-41	1	-	-		1.04		-
			_	Proposes for Using		-	-
31				Heaun chared chicrinaled paraffire (HCOPs)			Thousands
22				Perfusitience sulfonic add	PTHIS		
		POPt t	te did	ded. Precently, the analytical methods still need	lutter development before analytics can be reco	mmunded.	101
		Reference	e isbord	toriaz			

"Ranking" based on increasing or decreasing <u>concentrations</u> possible for chlorinated/brominated POPs (ng/g lipid)

> Separate:

- Dioxin-like compounds: pg/g lipid;
- PFAS: pg/g fresh weight or ng/L

> Risk assessments need to consider potential adverse effects

✓ 30 listed POPs
✓ 2 proposed POPs
Key message B – Relative importance ("ranking") of chemicals



Chlorinated and brominated POPs (1):

- By far highest concentrations found for DDT and chlorinated paraffins
 - Maximum found for DDT (7100 ng/g lipid) a factor of 10 higher than for CPs (700 ng/g lipid for the sum of SCCP and MCCP)
 - However, median of CP concentrations (116 ng ∑ SMCCP/g lipid) comparable to median of DDT concentrations (125 ng/g lipid)
 - High CP concentrations caused predominantly by MCCPs (median 66 ng/g lipid; maximum 536 ∑ SMCCP ng/g lipid), with SCCP concentrations of 61 ng/g lipid as median and 188 ng/g lipid as maximum.
- PCB as next following group in the ranking of decreasing levels on average an order of magnitude lower concentrations than the CP concentrations (median 12.7 ng NDL-PCB /g lipid, maximum 109 ng/g lipid)

Range of concentrations of lipophilic chlorinated and brominated POPs in human milk (ng/g lipid) from 43 countries in the period 2016-2019 (median with error bars indicating the minimum and maximum) (without dioxin-like chemicals [pg TEQ/g lipid])

Key message B – Relative importance ("ranking") of chemicals



Chlorinated and brominated POPs (2):

- ➤ Nonachlor, ∑ PBDE₆ (and ∑ PBDE₇ including BDE-209, dieldrin, beta-HCH, HCB: median between 1 ng/g and 10 ng/g lipid, maximum up to 110
- Range below 5 ng/g lipid: seen as background concentrations
- Concentrations of many POPs frequently below LOQ (0.5 ng/g lipid)

Range of concentrations of lipophilic chlorinated and brominated POPs in human milk (ng/g lipid) from 43 countries in the period 2016-2019 (median with error bars indicating the minimum and maximum) (without dioxin-like chemicals [pg TEQ/g lipid])

Key message B – Relative importance ("ranking") of chemicals



- SCCPs and MCCPs dominated the share of POPs grouped as industrial chemicals and by-products in most areas
- Cause for follow-up studies and for further (or, in the case of MCCPs, any) regulatory efforts



Median sum of all POPs in pooled human milk samples 2015-2019

- Pesticides: aldrin, chlordane, chlordecone, DDT, dicofol; dieldrin, endosulfan, endrin, heptachlor, α-HCH, β-HCH; γ-HCH; mirex, pentachlorobenzene, pentachlorophenol (including pentachloroanisole) and toxaphene;
- (Other) Industrial chemicals and by-products: hexabromobiphenyl (HBB), HBCDD, HCB, hexachlorobutadiene; PBDE; PCB, PCDD, PCDF and PCN.

- Countries assigned to one of the five UN regions
- Concentrations can vary between UN regions
- For some POPs a wide range found **between countries in UN regions**





> Concentrations have to be seen in context with sampling period (time trends)



- > Upper third of frequency distribution might give more reason for follow-up studies than lower third
- > Comprehensive data sets available for assessments of individual POPs in a certain country/region at a certain time



African group: widest variation in contamination of human milk with total TEQ

Ethiopia () with the lowest levels of total TEQ of all countries in the 2000-2019 studies
 (1.29 pg total TEQ/g lipid in 2019, 1.54 pg total TEQ/g lipid in 2019)

• Egypt (\)

- 2001/2002: high levels comparable to levels in Europe at that time (median of 23.0 pg total TEQ/g lipid for 9 pooled samples; max 49 pg total TEQ/g lipid)
- > 2019: decreasing to 9 pg total TEQ/g lipid
- Côte d'Ivoire and DR Congo (↓) in the upper third of frequency distribution



PCDD/PCDF patterns - indication of possible sources

- PCDD-dominated patterns in Côte d'Ivoire and DR Congo mirror patterns found in certain clays with high PCDD/PCDF concentrations and hint at consumption of such clays ("geophagy") by pregnant women
- PCDD/PCDF pattern in **Egypt (2000-2002)** could indicate *combustion and drying processes*

Malisch, R., Schächtele, A., van Leeuwen, F.X.R., Moy, G., and Tritscher, A. 2023. WHO- and UNEP-coordinated exposure studies 2000-2019: Findings of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. In: Persistent organic pollutants in human milk (eds. Malisch, R., Fürst, P. and Šebková, K.), Springer Nature, Part III

Key message D – Time Trends

Aim of WHO/UNEP-coordinated exposure studies: providing data for effectiveness evaluation of Stockholm Convention

Minimization of sources of variation

- Sampling design (harmonized protocol for representative pooled samples)
- Analysis of pooled samples by Reference Laboratories

Global Monitoring Plan (GMP) guidance document:

- <u>Temporal trend studies</u> should be able to detect a 50% decrease in the levels of POPs within a 10-year period
- However, no stipulation of a quantitative goal for reduction / decrease in POPs levels in countries / regions
- Convention's objectives:
 - either to eliminate or to reduce production, use and releases, depending on annex where chemical listed, but rate of decline is nowhere specified or required

With regard to participation of different countries in different rounds, conclusions on time trends cannot easily be drawn from the general data base using means or medians for certain periods



General estimation of time trends based on all results of the 2000-2019 period – example DDT

- Decrease observed from 2000-2003 period to 2016-2019 period in all regions
- Considerable differences among regions and a great variation among the rounds
 - In Africa: variation caused by results of Ethiopia in comparison to other countries in two periods:
 - 2012-2015: 23.500 μg/kg lipid,
 - 2016-2019: 7.100 μg/kg,

Time trends for mean concentrations of DDT in human milk (expressed as μg DDT complex /kg lipid)

Key message D – Time Trends



5000

2005

2010

2015

Time [year]

2020

2025

More precise approach: estimation of time trends based on results of countries with repeated participation over time

DDT in Africa: In all countries, decrease observed in comparison to previous surveys

Reduction rates should be seen also in context with the concentration range (differentiation of levels above or in the range of the background contamination):

- If **high levels** are found, **sources** might be detected which could be eliminated.
- However, at low background levels, other factors, e.g. contamination of feed and food by air via long-range transport and subsequent bioaccumulation, cannot be influenced locally.

GMP guidance document recommends to apply simple linear regression or Theil-Sen estimator for power analysis of statistical trends

Important:

- <u>Trends</u> can be derived if trend test (significance of Theil-Sen estimator) is positive on 95% confidence level of significance (i.e. p-values < 0.05).
- As Theil-Sen p is never below 0.05 for less than 5 data points and for most countries only less than 5 data points were available, statistically significant trends could be derived only for regions (combining data from countries) and few countries.
- For many countries, only two or three data points are available. In these cases, the observed changes of the concentrations are statistically not significant and indicate <u>tendencies</u>.

UN Regional Groups	N of countries	Overall decrease rate (%) per 10 years (Theil-Sen method)			
		DDT	beta-HCH	НСВ	
Africa	13	74	83	11	
Asia-Pacific	8	80	98	67	
Latin America and Caribbean	9	50	52	31	
Eastern Europe	6	39	63	47	
Western Europe and Others	8	39	63	45	
Global / median of 5 UN Regional Groups	44	58	84	57	

countries with repeated participation

Key message D – Time Trends



Time trends of ΣPCB₆ concentrations between 1987 and 2019 in 25 EEG and WEOG countries with repeated participation

- Significant reductions were already achieved in the 1990s
- > Decrease between 85% and 95% between end of 1980s and 2019 in countries with highest levels

For time trend analysis of ΣPCB₆ between 1987 and 2019: results of 247 pooled samples On a global level, decrease rate of PCB <u>over 10 years was 71%</u> calculated by the Theil-Sen method

UN Regional Groups	N of countries	Overall decrease rate (%) per 10 years (Theil-Sen method)
Africa	13	50
Asia-Pacific	10	65
Latin America and Caribbean	9	34
Eastern Europe	11	53
Western Europe and Others	14	63
Global / median of 5 UN Regional Groups	57	71

countries with repeated participation



Time trends of dioxin-like compounds between 1987 and 2019:

- Significant reductions were already achieved in the 1990s
- ✓ Global decrease rate per 10 years:
 - > WHO-PCDD/PCDF-TEQ: 48%
 - Total TEQ (WHO₂₀₀₅-TEQ): 50%

Countries with repeated participation

Key message D – Time Trends



Worldwide	N of countries	Overall decrease (%) per 10 years	p-value overall
All countries	59	48.3	<0.001
Countries with repeated participation	24	52.2	<0.001

Median decrease per 10 years:

- 58% for DDT,
- 84% for beta-HCH,
- 57% for HCB,
- 32% for PBDE
- 48% for PFOS
- 70% for PCB
- 48% for PCDD and PCDF (expressed as TEQ)

Decrease / Increase (%) of total CP

Table 7: Overall decrease (%) of total CP concentrations in the 5 UN Regional Groups and worldwide (computed using all individual samples). Negative decreases are to be read as increase. (n = number of samples)

UN Regional Groups	n	Overall decrease per 10 years [%]	p-value
African	27	-6.3	0.663
Asia-Pacific	15	-179	0.009
Latin American and Caribbean	21	9.5	0.737
Eastern European	11	-197	0.007
Western European and Others	10	63	0.001
global	84	-29	< 0.001

In contrast to decrease for various POPs, <u>CP</u> as "emerging POP" increasing tendencies in some UN Regional Groups.

On a <u>global</u> level, statistically significant **increase** of total CP concentrations in human milk of 30% over 10 years

Key messages - Conclusions



URL: https://link.springer.com/book/10.1007/978-3-031-34087-1

Key messages – Acknowledgement



Editors, authors and co-authors

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- WHO
- UNEP
- Countries
- National coordinators
- Funding bodies (GEF, others)
- Laboratories









Results of the GMP2 study on POPs in African Air

Jacob de Boer, Rianne van Dijk

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Persistent organic pollutants in air from Asia, Africa, Latin America, and the Pacific

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Overview

Countries:

- DRC
- Egypt
- Ethiopia
- Ghana
- Kenya
- Mali
- Mauritius

- Morocco
- Nigeria
- Senegal
- Tanzania
- Togo
- Tunesia
- Zambia

- 2017
- 2018
- 2019

- 1 PUF per 3 monthsPCB, OCPs, BFRs
- Toxaphene

PCBs and Pesticides - Comparison Continents



IVM Institute for Environmental Studies

BFRs in Air – Comparison Continents



IVM Institute for Environmental Studies

PCBs and Pesticdes in Africa

Environmental Studies



PBDEs in Air



Africa

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PBDE '

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HBCD.

PBDE209







Africa

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PBDE209













PBDE209



IVM Institute for Environmental Studies

7

Comparison GMP 1 and 2





PCB Patterns in Air







DRC and Egypt – PCB/OCP



■ EGY-1 (2018-I) ■ EGY-1 (2018-II) ■ EGY-1 (2018-III) ■ EGY-1 (2018-IV)

Ethiopia and Ghana - PCB/OCP



■ GHA-1(2018-I) ■ GHA-1(2018-II) ■ GHA-1(2018-III) ■ GHA-1(2018-IV)

Mauritius and Morocco - PCB/OCP



MAR-1 (2018-I) MAR-1 (2018-II) MAR-1 (2018-III)

Africa, 2018 – Sum 6 PCBs

Sum 6 PCBs 2018 (ng/PUF)



Africa, 2018, sum DDT

Sum DDTs 2018 (ng/PUF)



Africa, 2018 – Sum PBDEs

Sum PBDEs 2018 (ng/PUF)



Africa, 2018 – DecaBDE

DecaBDE 2018 (ng/PUF)



Africa 2018, HBCD

Sum HBCDs 2018 (ng/PUF)




- POP data in air from 43 countries worldwide were collected
- □ 14 African countries included
- □ Worldwide, DDT/DDE and PCBs are dominant, decreasing slightly
- In Africa DecaBDE and HBCD are higher than on other continents and tend to increase
- A substantial number of OCP concentrations have decreased to non-detectable values
- DRC: relatively high pollution with DDT/E, PCBs and BFRs
- □ Zambia : relatively high decaBDE and HBCD contamination
- Ugnada: relatively high HBCD contamination



Results of the UNEP Worldwide Monitoring of Persistent Organic Pollutants in Sediments, Biota and Food Products

Jacob de Boer, Manuela Abalos, Manuel Heinzelmann, Rianne van Dijk, Heidelore Fiedler, Esteban Abad



- Generate POPs data from samples relevant for and chosen by the participating countries
- Compare the analytical capability of the participating laboratories with that of the reference laboratories



Overview study

Asia/Pacific	Africa	GRULAC
Mongolia	Egypt	Antigua&Barbuda
Thailand	Ethiopia	Argentina
Vietnam	Ghana	Barbados
Fiji	Kenya	Brazil
Samoa	Mauritius	Chile
	Morocco	Colombia
	Nigeria	Jamaica
	Senegal	Uruguay
	Tanzania	
	Tunisia	
	Uganda	
	Zambia	

Faculty of Science

Matrices	Matrices	Target Compounds
Fish	Shellfish	PCBs
Sediment	Soil	OCPs
Eggs	Chicken	Toxaphene
Butter	Sugar	PBB
Cow milk	Beef	PBDEs
Maize	Flax seeds	HBCD
Beef	Pork	
Olive oil	Pulse	
Honey	Bananas	
Indoor air	Horse meat	
Sea buckthorn	Mutton	
Tomatoes	Kale	
Guinea fowl		



VU

1222

A detailed 15 page protocol was provided. Details included:

Scope, suggestions for samples, sampling details, instructions for splitting the sample in two parts for the mirror study, use of tools, details on dispatch, permits for transport, use of dry ice, labelling, and courier and customs information





Transport problems...





VU VIJE UNIVERSITEIT AMSTERDAM

Σ 6 PCBs in fish





Σ 6 PCBs and other POPs in fish





POPs in sediment





POPs in butter





Mirror Study Results

Country	РОР	Matrix	Total (n)	Acceptable (n)	Comments
Vietnam	PBDE	Sediment	64	34	DecaBDE often too high; acceptable values often <lod< td=""></lod<>
Tunisia	PCB	Fish, eggs, butter, olive oil	24	8	Acceptable values all <lod< td=""></lod<>
	OCP	Fish, eggs, butter, olive oil	66	14	Acceptable values all <lod< td=""></lod<>

A few countries delivered results after the deadline



Example of comparison

РСВ	Results Expert Lab μg/kg dw	Results Country μg/kg dw		Results Expert Lab μg/kg dw	Results Country μg/kg dw
Matrix	Fish	Fish	2,4'-DDT	<0.08	NA
28	2.4	<9.375	4,4'-DDT	*0.19	53.48
52	3	<1.59	2,4'-DDD	<0.05	NA
101	6.2	<1.71	4.4'-DDD	0.69	9.490
153	55	<3.33		*0.05	
138	36	<2.00	2,4'-DDE	*0.05	NA
180	27	<10.52	4,4'-DDE	2.3	<0.508

* Between LOD and LOQ; NA: not analysed



Concluding remarks

- No samples at all received from four countries
- Disappointing participation in mirror study
- Challenges in sending samples
- Many countries experience huge difficulties due to the <u>lack of a well-working GC/MS and</u> <u>unavailability of ¹³C labeled standards</u>
- **DDT and PCBs** are the major POPs in most countries
- Occasional high values for HBCD, penta- and hexachlorobenzene, HCHs
- Levels of most other POPs (e.g., mirex, PBB, toxaphene, chlordanes, heptachlor epoxide, endosulfan, drins) are low <LOD</p>
- Further reading: *Chemosphere*, Special Issue on:

Analysis of Persistent Organic Pollutants for the Stockholm Convention's Global Monitoring Plan

Chemosphere

