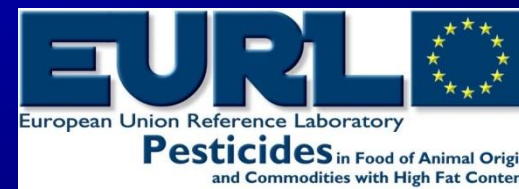




Midterm Workshop of the UN Environment/GEF project
'Continuing Regional Support for the POPs Global
Monitoring Plan under the Stockholm Convention'
in the Africa Region
Lusaka, Zambia, 23-25 July 2018

Proposal on including the analysis of other POPs beyond GMP2

Rainer Malisch



Project Cooperation Agreement (PCA), part II: analysis – compounds to be analysed in pooled national mother's milk samples

Compounds to be analysed in pooled national mothers milk samples by CVUA under this Agreement	
Initial POPs	
Aldrin	Aldrin
Chlordane	<i>cis</i> - and <i>trans</i> -chlordane; and <i>cis</i> - and <i>trans</i> -nonachlor, oxychlordane
DDT	4,4'-DDT, 2,4'-DDT and 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, 2,4'-DDD
Dieldrin	Dieldrin
Endrin	Endrin
HCB	HCB
Heptachlor	Heptachlor and heptachlorepoxide
Mirex	Mirex
PCB	Σ PCB ₆ (6 congeners): 28, 52, 101, 138, 153, and 180 PCB with TEFs* (12 congeners): 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189
PCDD/PCDF	2,3,7,8-substituted PCD/PCDF (17 congeners)
Toxaphene	Congeners P26, P50, P62
* PCB with TEFs (Toxic Equivalency Factors) assigned by WHO in 1998	
POPs listed at COP-4	
Chlordecone	Chlordecone
α -HCH	α -HCH
β -HCH	β -HCH
γ -HCH	γ -HCH
Hexabromobiphenyl	PBB 153
Pentachlorobenzene	PeCBz
c-penta BDE	BDE 47, 99, 153, 154, 175/183 (co-eluting)
c-octa BDE	Optional: BDE 100
POPs listed at COP-5	
Endosulfan	α -, β -endosulfan; and endosulfan sulfate
POPs listed at COP-6	
HBCD	α -HBCD, β -HBCD, γ -HBCD



UNITED NATIONS ENVIRONMENT PROGRAMME

Stockholm Convention on Persistent Organic Pollutants

اتفاقية استكهولم بشأن الملوثات العضوية الثابتة • 关于持久性有机污染物的斯德哥尔摩公约 • Convention de Stockholm sur les polluants organiques persistants
Convenio de Estocolmo sobre Contaminantes Orgánicos Persistentes • Стокгольмская конвенция о стойких органических загрязнителях



Expert meeting to update the Global Monitoring Plan guidance document

Brno, Czech Republic, 7-9 November 2017

2. Introduction and context:
 - (a) Outcomes of COP-7 and COP-8 relevant to the update of the global monitoring plan (GMP) guidance document;
 - (b) Mandate and process for updating the GMP guidance document;
3. Experiences from monitoring programmes in sampling and analyzing the newly listed POPs in core matrices and other media:
 - (a) Hexachlorobutadiene;
 - (b) Pentachlorophenol and its salts and esters;
 - (c) Polychlorinated naphthalenes;
 - (d) Decabromodiphenyl ether (BDE-209);
 - (e) Short-chain chlorinated paraffins;



Aim of CVUA Freiburg: inclusion also of voluntary POPs (COP 7, COP 8)
(*except PFAS, analysed at University Örebro*)

mandatory (according to PCA)

1) Initial POPs: aldrin, chlordane, DDT, dieldrin, endrin, HCB, heptachlor, mirex, toxaphene, PCB, PCDD, PCDF

2) POPs listed at COP-4: chlordecone, HCH (alpha, beta, gamma), hexabromobiphenyl (PBB 153), Pentachlorobenzene, PBDE (47, 99, 153, 175/183-co-eluting); optional: BDE 100; PFOS

3) POPs listed at COP-5: endosulfan

4) POPs listed at COP-6: HBCDD (alpha, beta, gamma)

voluntary:

5) POPs listed at COP-7: Hexachlorobutadiene (Annex A), pentachlorophenol + salts + esters, polychlorinated naphthalenes

6) POPs listed at COP-8: Decabromodiphenyl ether, SCCP, hexachlorobutadiene (Annex C)

7) possible candidates at COP-8: dicofol, pentadecafluorooctanoic acid (PFOA) and salts, perfluorohexane sulfonic acid (PFHxS)

- No multi-method for all compounds of interest
- Various methods necessary

Involved specialized laboratories at CVUA Freiburg

➤ Apolar pesticides/contaminants

- ✓ Extraction and clean up
- ✓ Various GC-MS techniques, GC-ECD, GC-NPD

➤ Polar pesticides/contaminants

- ✓ Extraction and clean up
- ✓ Various LC-MS techniques

➤ Dioxins (PCDD/PCDF, PCBs, PBDE + PCN [new])

- ✓ Extraction and clean up
- ✓ GC-HRMS, APGC-MS/MS

➤ Chlorinated Paraffins

- ✓ Extraction and clean up
- ✓ Various GC-MS techniques

COP Nr	Jahr	Parameter	Annex	Parent POPs	Transformation products	EURL	
	2003	1. Old POPs					
1		Aldrin	A	Aldrin		pesticides	OCP+
2		Chlordane	A	cis- and trans-Chlordane	cis- and trans-nonachlor, oxychlordane	pesticides	OCP+
3		DDT	B	p,p'- and o,p'-DDT	p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD	pesticides	OCP+
4		Dieldrin	A	Dieldrin		pesticides	OCP+
5		Endrin	A	Endin	endrin ketone	pesticides	OCP+
6		Heptachlor	A	Heptachlor	heptachlorepoixide	pesticides	OCP+
7		Hexachlorbenzene	A + C	Hexachlorbenzene		pesticides/hal. POPs	OCP+
8		Mirex	A	Mirex		pesticides	OCP+
9		PCB	A + C	PCB (6 indicator PCBs) *		hal. POPs	Diox
10		Toxaphene	A	Congeners P26, P50, P62		pesticides	OCP+
11		PCDD	C	PCDD *)		hal. POPs	Diox
12		PCDF	C	PCDF *)		hal. POPs	Diox
		Parameter		Parent POPs	Transformation products		
	COP-4	2009					
		2. New POPs					
1		alpha-HCH	A	alpha-HCH		pesticides	OCP+
2		beta-HCH	A	beta-HCH		pesticides	OCP+
3		gamma-HCH (Lindan)	A	gamma-HCH		pesticides	OCP+
4		Chlordecone	A	Chlordecone		pesticides	Quechers
5		Pentachlorbenzene	A + C	Pentachlorbenzene		pesticides/hal. POPs	OCP+
6		Hexabromobiphenyl (HBB)	A	Hexabromobiphenyl (HBB) mandatory: PBB153, optional-recommended: PBB138		hal. POPs	OCP+
7		Tetra- and pentabromodiphenyl ether	A	Tetra- and pentabromodiphenyl ether (mandatory 47, 99); recommended to add: 100) **)		hal. POPs	Diox
8		Hexa- and heptabromodiphenyl ether	A	Hexa- and heptabromodiphenyl ether (mandatory: 153, 154, 175/183 [co-eluting]) **)		hal. POPs	Diox
9		PFOS	B	PFOS (as anion); inclusion of linear and non-linear isomers		hal. POPs	PFOS
	COP-5	2011					
		3. new POPs					
1		Technical endosulfan and related isomers	A			pesticides	OCP+
	COP-6	2013					
		4. new POPs					
1		Hexabromocyclododecane (HCBDD)	A			hal. POPs	Quechers
	COP-7	2015					
		4. new POPs					
1		Hexachlorbutadiene	A			hal. POPs	OCP+
2		Pentachlorphenol + salts	A	zu bestimmen: nur Pentachloranisole (PCA)	pentachloranisole (PCA)	pesticides	OCP+
				Pentachlorphenol (und zusätzlich PCA)			Quechers
3		Polychlorinated naphthalenes	A			hal. POPs	Diox/PCN
	COP-8	2017					
		5. new POPs					
1		Decabrom diphenylether	A	commercial mixture			Diox/PBDE209
2		Short-chained chlorinated paraffins	A	C10-C13 chlorinated paraffins, reported as sum parameter (sum C10, sum C11 ...)			SCCP
3		Hexachlorbutadiene	C			hal. POPs	OCP+
		Possible Candidates at COP-8, 2017					
		Dicofol				pesticides	OCP+
		PFOA and salts					PFOS
		PFHxS					PFOS

➤ 4 different „main“ extraction and clean up methods combined with various detection methods need expansion and validation (apart from PFOS/University of Örebro)

Nr	Method	planned: g lipid/determination	
1	OCP+	1 x 0,5 g / 1 x 0,1 g	OCP (incl. Toxaphene, HCB, PentaCB), PBB153, Hexachlorbutadiene, Pentachloranisol [PCA]
2	Quechers	10 ml milk (0,3 g)	Chlordecone, HBCDD (alpha, beta, gamma), Pentachlorphenol (+Pentachloranisol)
3	Diox	1 g	PCDD/F (17) +PCB (12dl, 6 ndl)+PBDE (incl 209)
4	PCN	0,5	<i>polychlorinated naphthalenes</i>
5	SCCP	1 g	SCCP, MCCP
6	PFOS	Örebro-Aliquot	PFOS, PFOA
	sum:	3,5 g / single determination	

Samples are analysed with comprehensive quality control program to obtain confirmed results

Method 1 „organochlorine pesticides and contaminants - lipophilic analytes“



Laboratory for extraction and clean up of lipophilic pesticides and contaminants

Method 1 „organochlorine pesticides and contaminants - lipophilic analytes“

1. Extraction of lipophilic lipids, pesticides and POPs with organic solvents („Hot extraction“ more efficient and therefore faster than Soxhlet)



Sample + Na₂SO₄, filled into extraction thimble



After evaporation of solvent: determination of lipid amount

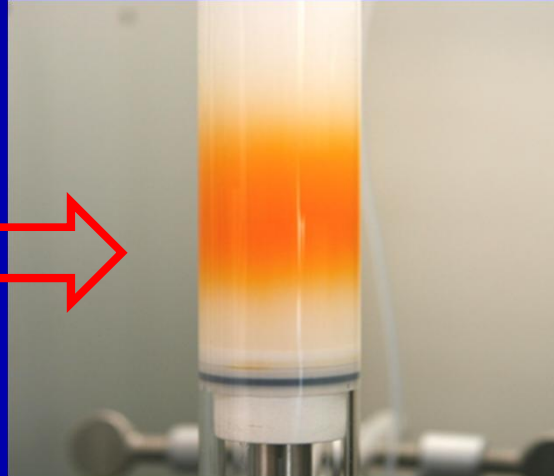


Alternative (manually): Twisselmann extraction

Method 1 „organochlorine pesticides and contaminants - lipophilic analytes“

2. Gel chromatography for separation of lipids from POPs

- Principe: separation based on molecular weight
- Bio-Beads S-X3 with cyclohexane/ethyl acetate (1:1 v/v)



Lipid + internal standard



Method 1 „organochlorine pesticides and contaminants - lipophilic analytes“

3. Column chromatography purification



Silica (1.5 % water); elution with toluene

Method 1 „organochlorine pesticides and contaminants - lipophilic analytes“

4. Detection / determination: various GC-ECD, GC-MS, GC-MS/MS

In parallel : 3 different GC columns, two different detection systems (e.g. ECD + MS/MS); confirmation by duplicate analysis



Method 1 „organochlorine pesticides and contaminants - lipophilic analytes“



Detection / determination with various GC-MS, GC-ECD, GC-NPD techniques:
Ultra high resolution MS (Orbitrap)

Method 2 „organochlorine pesticides and contaminants - polar analytes“



„QuEChERS“-based methods

Laboratory for extraction and clean up of polar pesticides and contaminants

Method 2 „organochlorine pesticides and contaminants - polar analytes“



Detection / determination with various LC-MS techniques

Method 2 „organochlorine pesticides and contaminants - polar analytes“



Laboratory with various LC-MS techniques: UHD Accurate-Mass Q-TOF LC/MS

Method 3 „PCDD/PCDF, PCB, PBDE“ (to be expanded for Method 4 „PCNs“)



Laboratory for extraction and clean up

Method 3 „PCDD/PCDF, PCB, PBDE“ (to be expanded for Method 4 „PCNs“)



Extraction and clean up – various manual or automated extraction procedures

Method 3 „PCDD/PCDF, PCB, PBDE“ (to be expanded for Method 4 „PCNs“)



Extraction and clean up – various manual or automated clean up procedures

Method 3 „PCDD/PCDF, PCB, PBDE“ (to be expanded for Method 4 „PCNs“)



GC-MS Laboratory

Method 3 „PCDD/PCDF, PCB, PBDE“ (to be expanded for Method 4 „PCNs“)



GC-MS Laboratory: 2x HRGC-HRMS (DFS),
1x APGC-MS/MS



Some PCNs with dioxin-like properties

- Elements of PCB analysis
(separation of dioxin-like and non-dioxin like PCBs resp. PCNs)

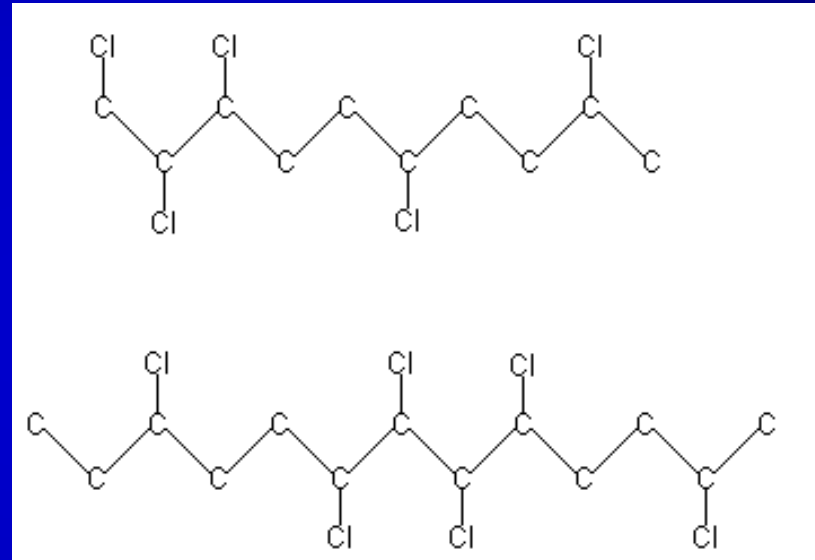
The Toxicological Effects of Halogenated Naphthalenes: A Review of Aryl Hydrocarbon Receptor-Mediated (Dioxin-like) Relative Potency Factors

Jerzy Falandysz^a, Alwyn Fernandes^b, Ewa Gregoraszczyk^c & Martin Rose^b

Journal of Environmental Science and Health, Part C, 32:239–272, 2014

Chlorinated Paraffins

- $C_{10}-C_{30}$, 30-70% Cl
- Three categories:
 - SCCP (C_{10-13})
 - MCCP (C_{14-17})
 - LCCP (C_{18-30})

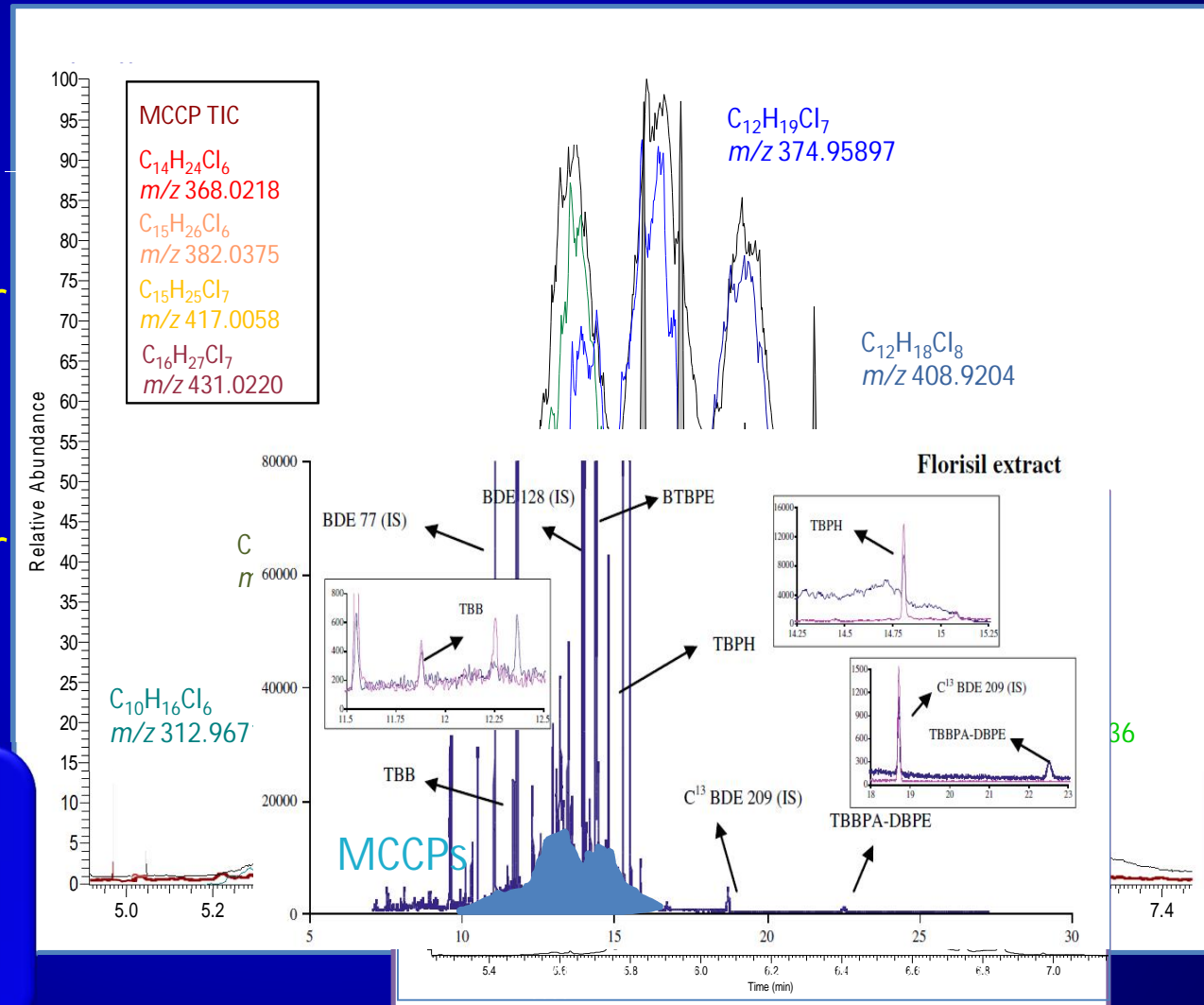


Annual production 2012: > 1.1 mio t
(PCBs 1929 – 2001: 1.4 mio t)

Analytical Challenge: instrumental analysis

- ✓ complex mixtures
- ✓ coelution of SCCPs and MCCPs
- ✓ coelution with other POPs like PCBs
- ✓ low response in comparison to other POPs often leads to dismissal as noise

Compensation through HRMS and/or statistical models: GC-Orbitrap-HRMS



Comprehensive analytical requirements and permanent quality control

- ✓ EU regulation for official food control: Legally binding analytical performance criteria and guidance documents, including for Measurement Uncertainty and LOQs
- ✓ accredited
- ✓ validated methods
- ✓ reagent blanks
- ✓ various quality control samples – control charts for long-time variation
- ✓ Participation in PTs
- Most important: permanent practical experience

Proposal:

- ✓ Start of analyses with established methods
- ✓ Ongoing optimization and validation to cover also voluntary POPs (second half 2018)
 - Analytically demanding expansion of multi-methods: validation with full established spectrum plus new POPs
- ✓ Then inclusion also of these voluntary POPs as far and fast as possible
 - This would be the most efficient way of inclusion of these POPs already in the ongoing study / not waiting some years for another round of studies
 - Results would allow to draw conclusions from a very comprehensive picture including “newest” POPs at earliest possible time

Thank you !

