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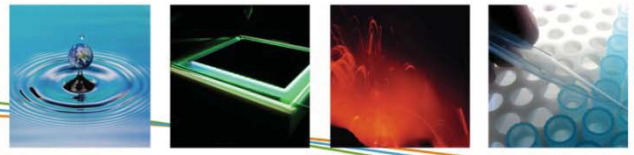

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Non-invasive bio-monitoring and exposure assessment of flame retardant chemicals

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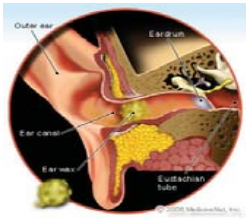
INFLAME

Non-invasive bio-monitoring and exposure assessment of flame retardant chemicals

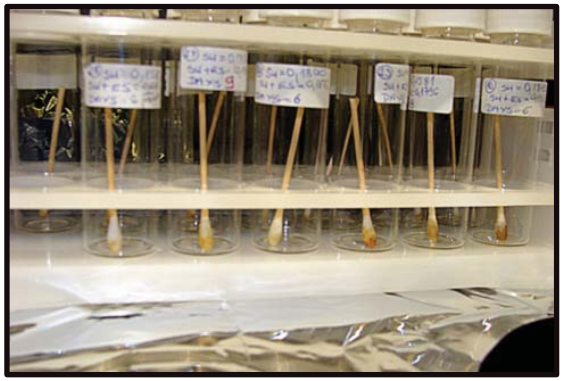
Objective

The development and validation of non-invasive methods for the monitoring of human body burdens; exploration of the utility of non-invasive matrices like hair, saliva, nails, earwax and urine as biomarkers of internal exposure to flame retardants (FR)

Earwax…



» 27 samples collected according to a well-defined protocol (Unit of Environmental Analysis and Technology at VITO)



» Average weight of the sample – 10-15 mg

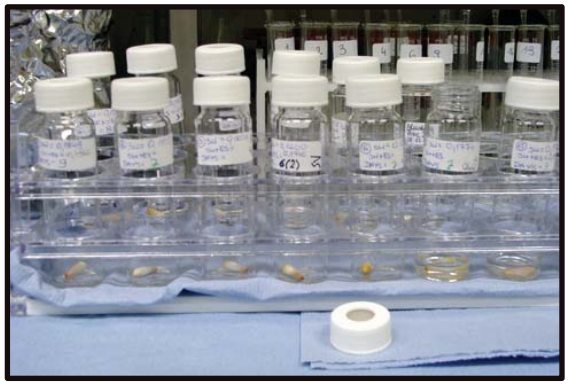
» Before earwax trial – oil test

» PBDEs (BDE-28, **-47**, **-99**, -100, -153, -154, -183, -209)

Extraction, clean-up and analysis…

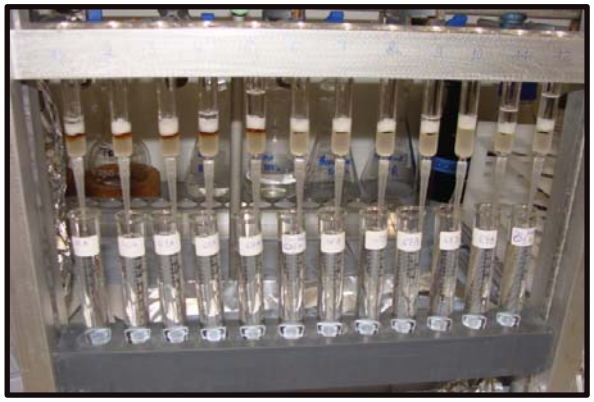
Extraction procedure

- Sample + 50 µl of IS (BDE-77, ^{13}C-BDE-209
- US assisted extraction with 4 mL of mixture of hexane:DCM (4:1 v/v)



Clean-up procedure

- On a polypropylene cartridge filled with acid silica gel + anhydrous Na_2SO_4
- Elution with 3x3 mL hexane and 1x3 mL DCM



- Reconstitution in 25 µL (iso-octane)

Analysis

- GC-**(ECNI)** MS; SIM mode ; column: DB-5HT 15m x 0,25 mm x 0,1 µm
- GC-(EI) HRMS; column: Rtx 1614 15m x 0,25 mm x 0,1 µm

Results…

BDE-47, BDE-99, BDE-209 (corelation with serum data)

- Most samples below LOQ
- Several samples BDE-47 and BDE-99 higher than in method blanks
- **1,4**, 1,1, 0,5, and 0,1 ng/g for **BDE-47** and 2 ng/g for **BDE-99**
- BDE-209 – 9, 53, 25, 24 ng/g

LOQs

BDE-47	BDE-99	BDE-209
Min LOQ (ng/g)	Min LOQ (ng/g)	Min LOQ (ng/g)
0,2	**0,2**	**1,1**
Max LOQ	Max LOQ	Max LOQ
1,8	**2,3**	**12,4**

Further planning:

❑Higher exposed subjects

❑Novel FRs to be measured

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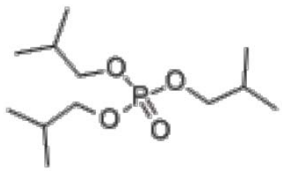
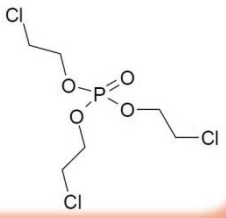
OPFRs – Organophosphate Flame Retardants

- 1st Interlaboratory Study on the analysis of PFRs organized by VUA (NORMAN network)
- Samples: dust, sediment and **fish oil**
- 10 PFRs included in the study:

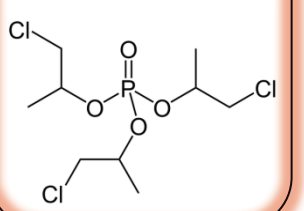
TiBP



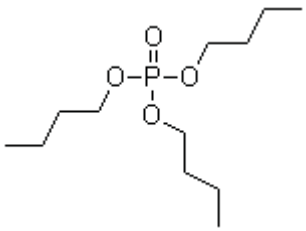
TCEP



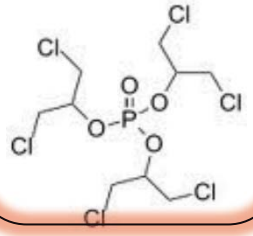
TCPP



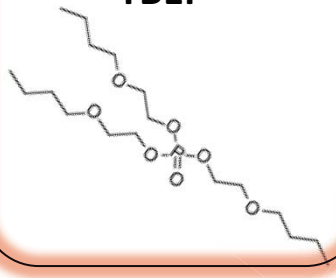
TnBP



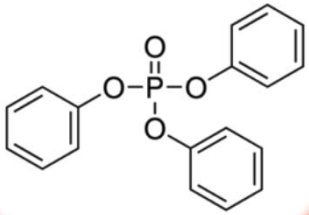
TDCPP



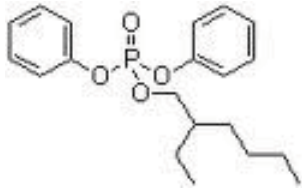
TBEP



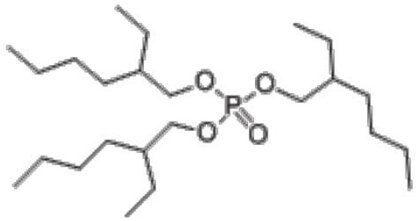
TPP



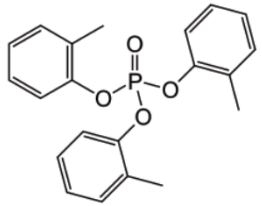
EHDP



TEHP



TCP



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OPEs - Several facts…

- Very high levels are measured (~ 10 µg/g lw)
- Increased worldwide production volume of PFRs
- Detected in various matrices e.g. water, air, sediment
- Limited information on PFRs in biota

ANALYSIS

- GC-MS/ LC-MS
- Sample prep → Clean-up – the most robust step

The Analytical Dilemma

❑OPEs are "easilly" hydrolyzed

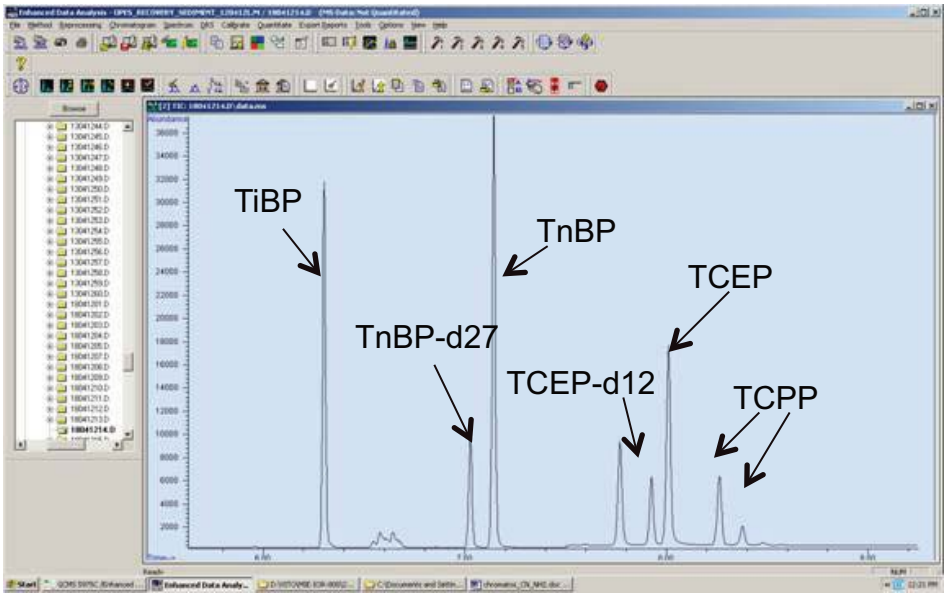
❑Large difference in polarity

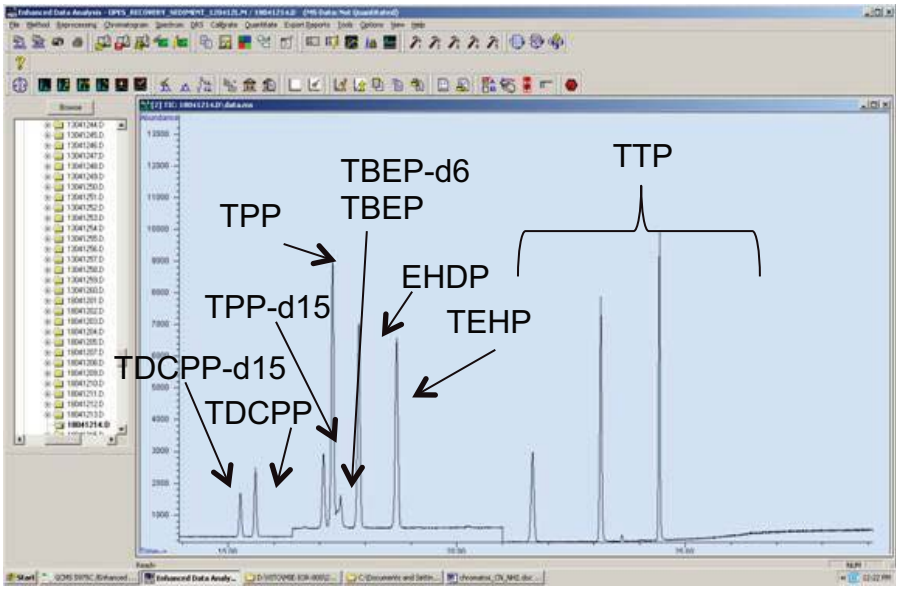
❑Large difference in size

Organophosphate Flame Retardants

GC – EI/MS (low sensitivity; high fragmentation)

Capillary column – DB5-MS (30m x 0,25mm x 0,25 µm)





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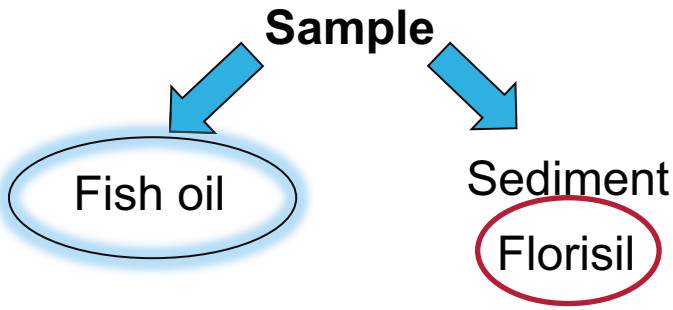
INFLOME

Clean-up method development



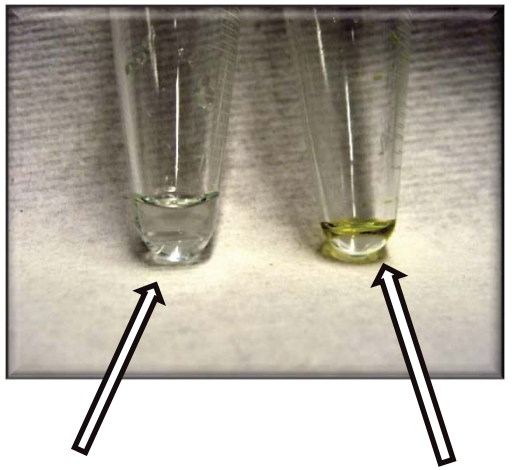
Methods used:

➢GPC (Envirogel ™ Clean-up; DCM for elution; time range 13:30-18:30 min.)

➢SPE cartriges (polar sorbents)

Florisil

SiOH OH **CN** **NH_2**



“transparent layer” “yellowy layer”

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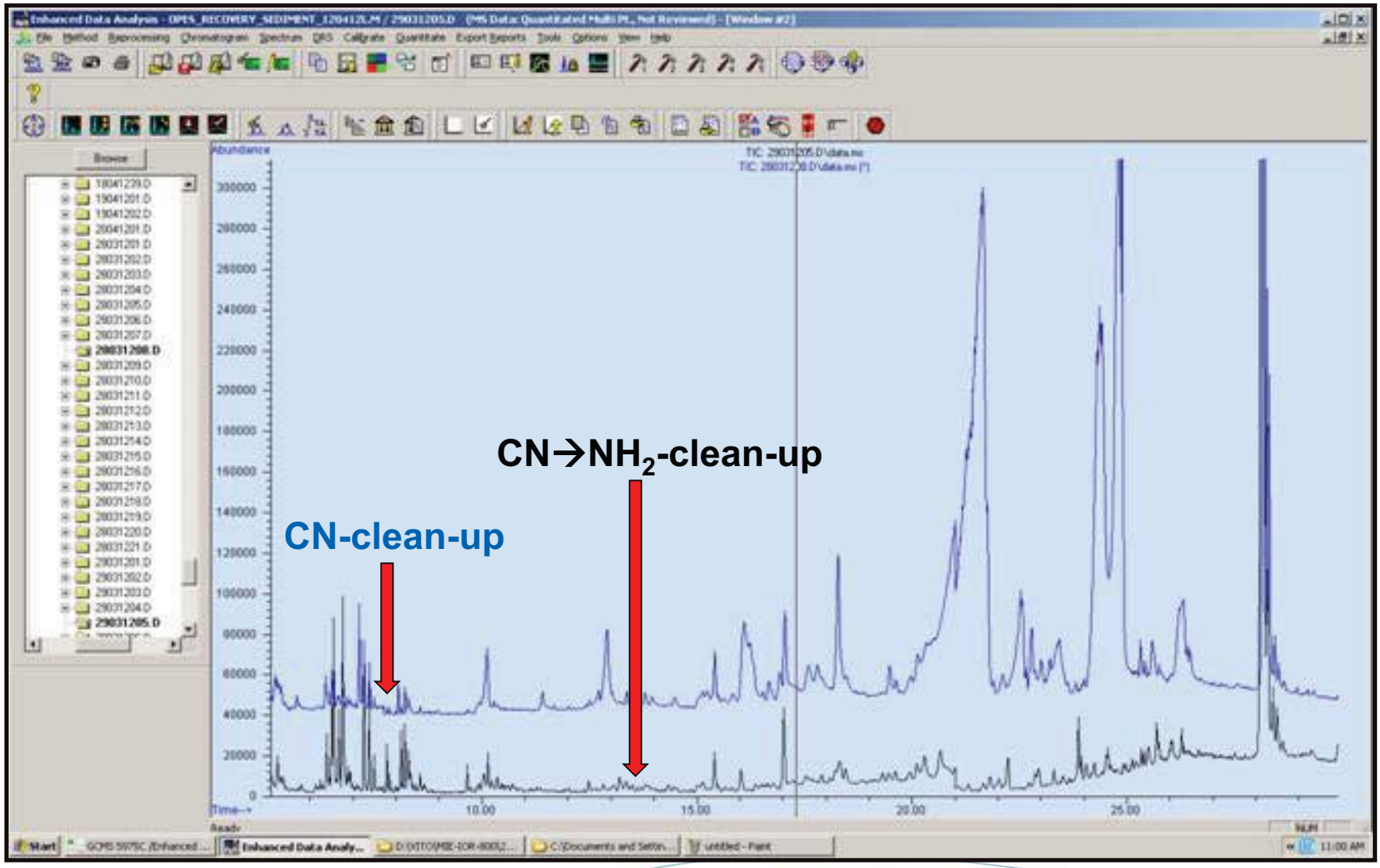
INFLOME



Planning…

- Secondment – Sampling Campaign in Norway (NIHP)
- Method validation for 1st ILS on PFRs
- OPEs in serum samples; earwax – method validation (Florisil, NH_2, CN)
- OPEs and metabolites (mono- and di-esters) in urine → LC/MS

Thank you ☺