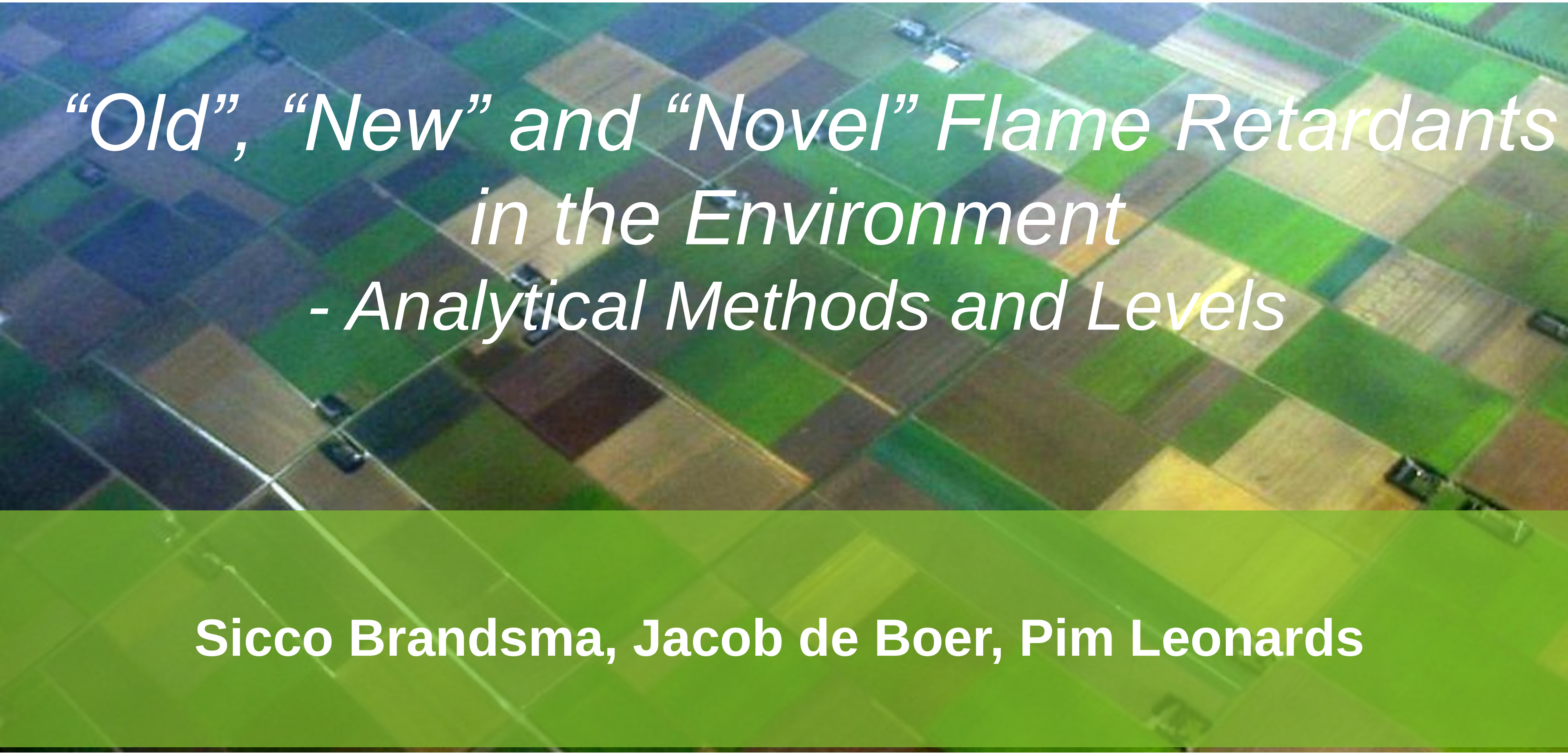

“Old”, “New” and “Novel” Flame Retardants in the Environment
- Analytical Methods and Levels

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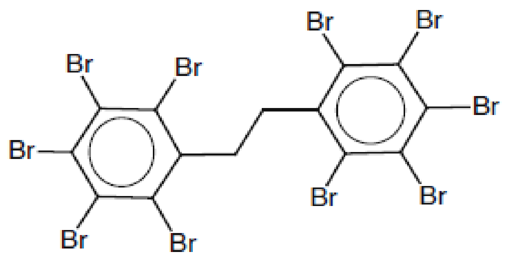
130 years

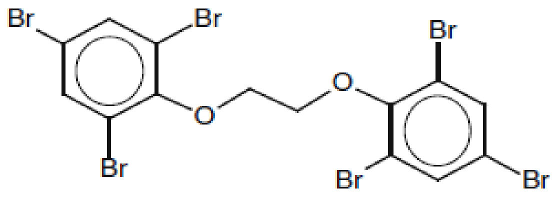
Outlines

- "Old" Brominated flame retardants
  - PBDEs, BDE209, TBBP-A and HBCD
- "New" Brominated flame retardants
  - BDBPE, DBDPE, TBB, TBPH and PBT
- "Alternative" Flame retardants
  - PFRs
- "Novel" Flame retardants
  - European research project ENFIRO

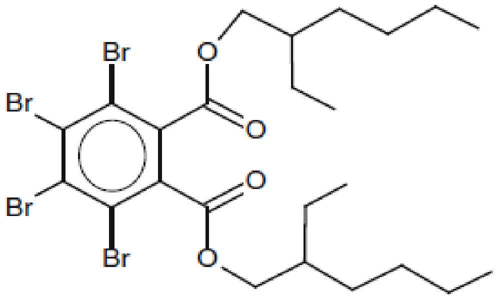
“New” brominated flame retardants



DBDPE (decabromodiphenylethane)

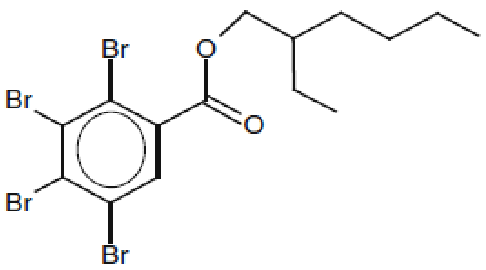


BTBPE (1,2 bis(2,4,6-tribromophenoxy)ethane)



TBPH

(bis-2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate)



TBB

(2-ethylhexyl-2,3,4,5-tertabromobenzoate)

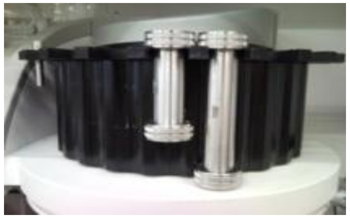
Analytical methods for "New" BFRs

- Analytical methods described in literature for different matrices

- Dust →Stapleton et al. (2008), Ali et al. (2011)
- Air →Sjordin et al. (2001) Takigami et al. (2009)
- Sediment →Hoh et al. (2005) , Lopez et al. (2011)
- S. sludge →Kierkegaard et al. (2004), Ricklund et al. (2008)
- Wastewater → Klosterhause et al. (2008), Zhou et al. (2010)
- Biota → Law et al. (2006), Luo et al. (2009)
- Blood → Karlsson et al. (2007)

Extraction of "New" BFRs

- Different extraction methods
  - Soxhlet
  - ASE
  - Ultrasonic extraction
  - SPE
- Wide range of solvent mixtures
  - Petroleum ether
  - Toluene
  - Dichloromethane
  - Hexane
  - Acetone



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Cleanup methods for “new” BFRs

- Cleanup methods for abiotic and biotic samples
  - Sulphuric washing
  - Deactivated or sulphuric acid impregnated silica column
  - Florisil column
  - SPE cartridges
  - Alumina column
  - Sulphur removal (activated copper, $AgNO_3$ on silica, TBA reagents and GPC)

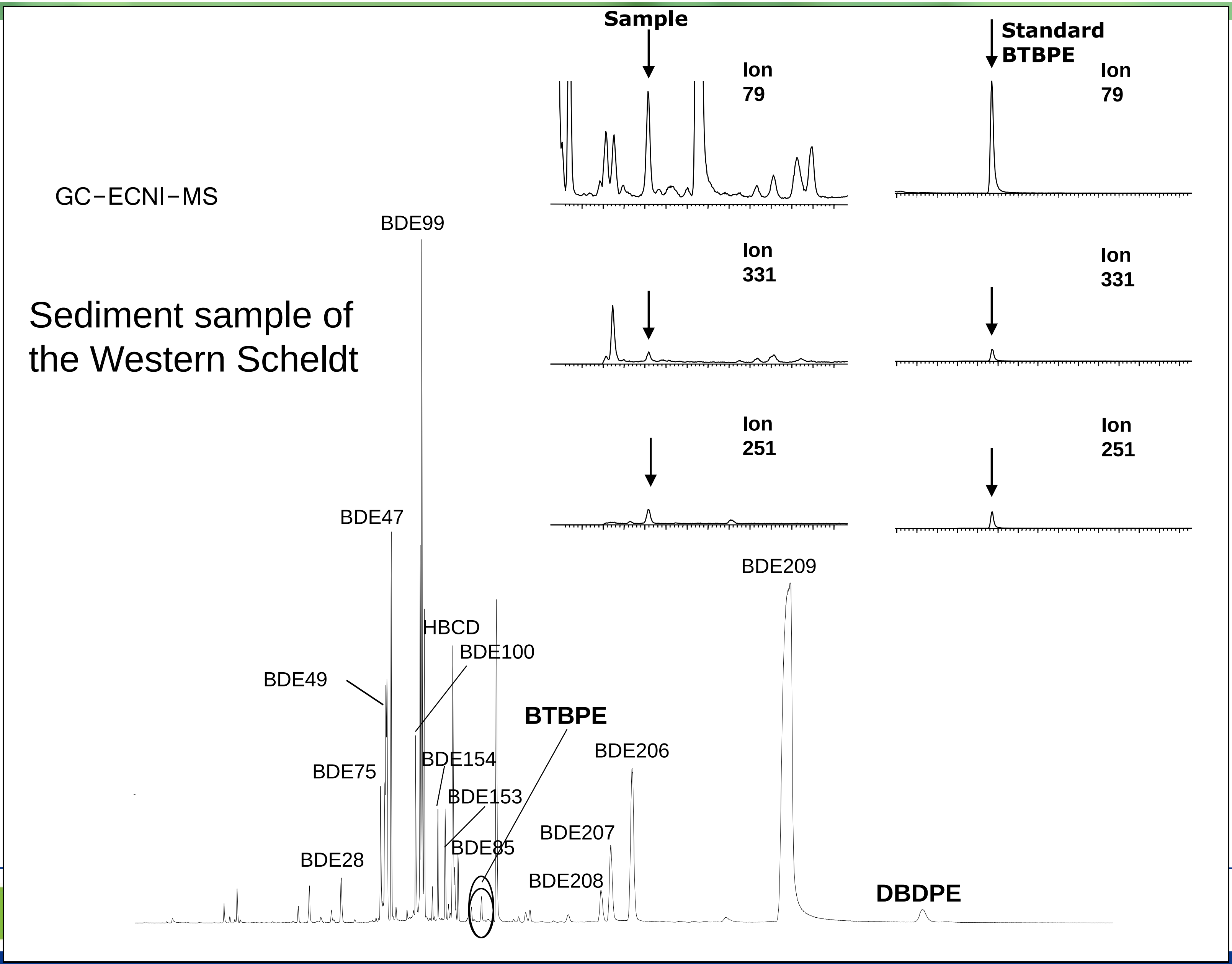
Critical parameters for “new” BFRs

- Sulphuric acid treatment can only be used for DBDPE
- Non-destructive cleanup methods needed for BDBPE, TBB and TBPH
- TBA reagents may caused debromination of DBDPE
- DBDPE, TBB and TBPH undergo photodegradation
- Difficulties encountered in the analysis of DecaBDE are also expected for DBDPE
    - Poorly soluble in organic solvent
    - Higher boiling point than DecaBDE
    - Thermally degrades to mainly bromotoluenes
    - Blank problems

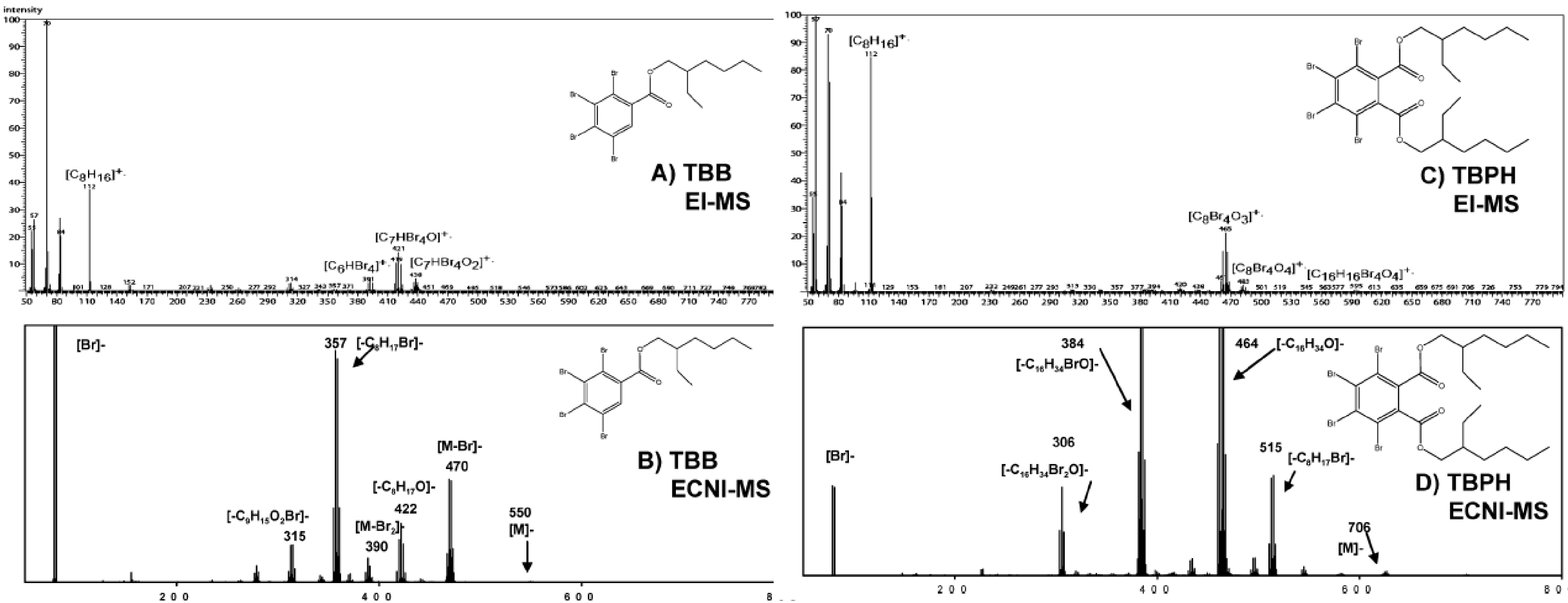
Instrumental analysis for DBDPE, BDBPE

- LR-ECNI-MS monitoring m/z 79/81 for DBDPE and 79/81 and 250.8/252.8 for BDBPE
- HR-EI-MS m/z 969/971 for DBDPE m/z 685/687 for BDBPE
- LR-ECNI-MS more sensitive then HR-EI-MS less specific
- Labeled DBDPE could not be used as IS for LR-ECNI-MS
- 13C BDE 209 used as alternative for LR-ECNI-MS
- DBDPE degrades on the GC column use column <15 meter

GC-ECNI-MS chromatogram of DBDPE, BDBPE



Instrumental analysis of TBB and TBPH



TBB was quantified using ion fragment (*m/z) 357 (Quant)* and 471 (Qual)

TBPH was quantified using ion fragments (*m/z) 463 (Quant) and 515 (Qual)*

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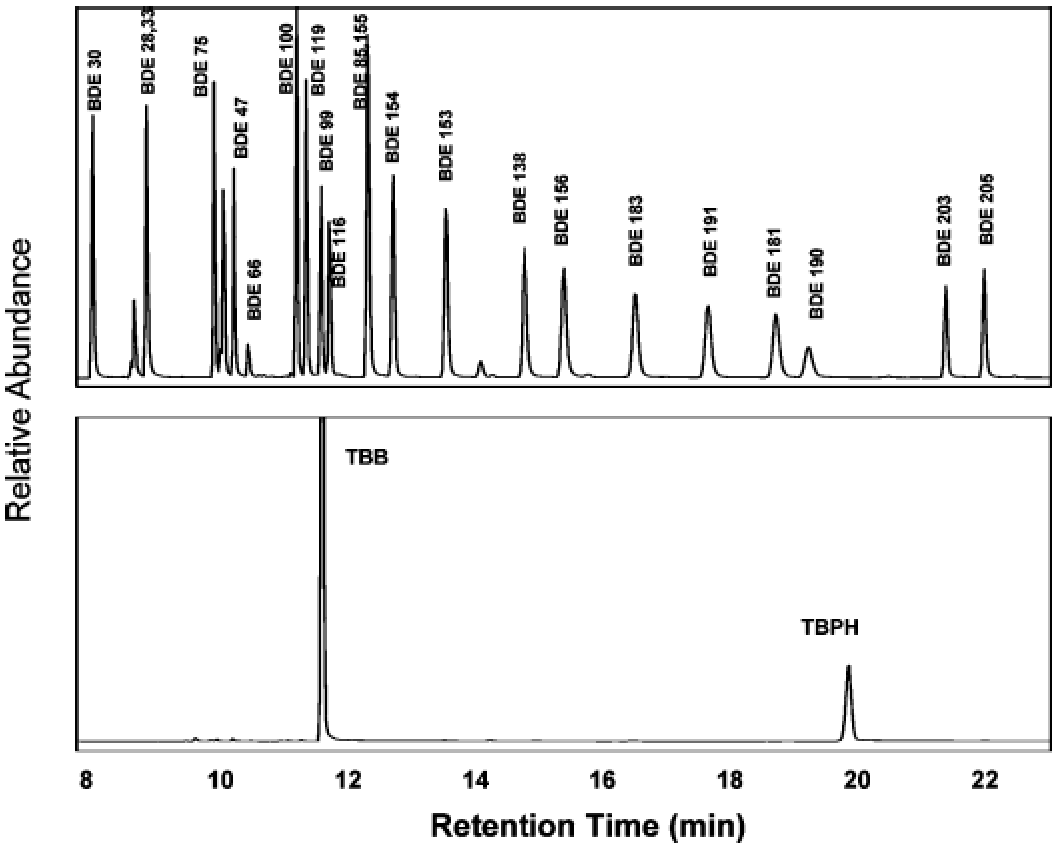
Stapleton et al, (2008)Environ. Sci. Technol. ***42, 6910–6916***

GC-ECNI-MS chromatogram

GC/ECNI-MS chromatograms revealing the relative retention times of the primary BDE congeners, TBB and TBPH on a 15 m DB5-MS column



Stapleton et al, (2008)Environ. Sci. Technol. ***42, 6910–6916***

LC-MS/MS

- LC-APPI-MS/MS in negative mode developed by Abdallah et al. (2009) for analyzing 14 PBDEs in house dust
- LC-MS/MS (APPI/APCI) in negative mode was also used by Zhou et al. (2010) to measure the “new” BFRs in combination with the PBDEs HBCD and TBBP-A

Advantages

- no thermal degradation
- use of 13C labeled standards
- Measuring al compounds in one run no column changes

	GC/LR-ECNI-MS	LC-MS/MS
LOD	30 fg - 1.7 pg*	12 - 30 pg*
Sensitivity	+ +	- -
Selectivity	No	yes
Labeled standards	No (only for BDE209)	yes
Thermal degradation	yes	no
Expensive	+ -	+
Expert training	-	+
Libary search	No	No
	*Eljarrat et al, (2002) J Mass Spectrom 37: 76-84	*Abdallah et al, (2009) Anal. Chem., 81, 7460–7467

Disadvantages

- Less sensitive then GC-ECNI-MS

Levels in the environment (I)

Matrix	DBDPE concentrations	Range DBDPE	BTBPE concentrations	Range BTBPE
Air	1916 pg/m³ (Shi et al., 2009). 1–22 pg/m³ (Venier and Hites, 2008) up to 120 pg/m³ (Hoh et al., 2005)	1–1916 pg/m³	0.1–10 pg/m³ (Hoh and Hites, 2005) 30.7 pg/m³ (Shi et al., 2009) 0.5–1.2 pg/m³ (Venier and Hites, 2008)	0.1–30.7 pg/m³
Air (e-waste)	0.6 ng/m³ (Kierkegaard et al., 2004) 7 ng/m³ (Karlsson et al., 2006a,b)	0.7–77 ng/m³	<0.6–39 ng/m³ (Pettersson-Julander et al., 2004) 5.6–67 ng/m³ (Sjödin et al., 2001) 30 ng/m³ (Karlsson et al., 2006b)	5.6–67 ng/m³
Dust	Average 47 µg/kg in Swedish house dust (Karlsson et al., 2007) Average 270, 170, and 400 µg/kg in UK homes, offices, and cars respectively (Harrad et al., 2008) <10 to 11070 µg/kg dw, median 201 µg/kg dw (Stapleton et al., 2008). 353 µg/kg dw (Sawal et al., 2008)	<10 to 11070 µg/kg dw	Average 4.8 µg/kg in Swedish house dust (Karlsson et al., 2007) Average 120, 7.2, and 7.7 µg/kg in UK homes, offices, and cars respectively (Harrad et al., 2008) 1060 µg/kg dw (Sawal et al., 2008) 1.6-789 µg/kg dw (Stapleton et al., 2008)	4.8–1060 µg/kg dw
Dust e-waste	<2.50 to 139 µg/kg dw (Shi et al., 2009)	<2.50 to 139 µg/kg dw	14.6 to 232 µg/kg (median 107 µg/kg) dw (Shi et al., 2009).	14.6–232 µg/kg dw
Sewage sludge	100 µg/kg dw (Kierkegaard et al., 2004) 266 to 1995 (median 1183) µg/kg dw (Shi et al., 2009). - DBDPE range 57–220 µg/kg dw (mean 81 µg/kg dw Europe, 31 µg/kg dw North America); ratio DBDPE/BDE-209 = 0.0018–0.83 (Ricklund et al., 2008a,b) - DBDPE digested sludge 66–95 µg/kg dw (mean 81 µg/kg dw), BDE-209 digested sludge 650–1100 µg/kg dw (mean 800 µg/kg dw) (Ricklund et al. 2008)	266 to 1995 µg/kg dw	0.31 to 1.66 µg/kg dw (Shi et al., 2009).	0.31–1.66 µg/kg dw
Sediment	24 µg/kg dw (Kierkegaard et al., 2004) 38.8 to 364 µg/kg (mean 247) µg/kg dw (Shi et al., 2009).	24–364 µg/kg dw	0.05 to 2.07 µg/kg dw (Shi et al., 2009) 6.7 µg/kg dw (Qiu et al., 2007)	0.05–6.7 µg/kg dw
Soil	28.1 µg/kg dry wt (Shi et al., 2009).	28.1 µg/kg dw	0.05 µg/kg dw (Shi et al., 2009).	0.05 µg/kg dw
Birds	Muscle: 9.6–16.3 µg/kg dw (mean 12.7), Liver: 13.7–54.6 µg/kg dw (mean 34.4), Kidney: 24.5–124 µg/kg dw (mean 64.5) (Shi et al., 2009) ND to 1.7 µg/kg lw (Gao et al., 2009). Range 4–800 µg/kg lw in various tissues (Luo et al., 2009)	ND-800 µg/kg lw	Muscle: 0.07–0.39 µg/kg dw (median 0.19), Liver: 0.27–2.41 µg/kg dw (median 1.23), Kidney: 0.12–0.89 µg/kg dw (median 0.45) (Shi et al., 2009)	0.07–2.41 µg/kg dw
Fish	< 0.03–3.7 µg/kg lw (K. Law et al., 2006)	<0.03 to 3.7 µg/kg lw		
Bird egg	1.3 to 288 µg/kg ww (Gauthier et al., 2007)	1.3 to 288 µg/kg ww	0.11 µg/kg (Karlsson et al., 2006a,b) 0.96 µg/kg lw in egg yolk (Verreault et al., 2007)	0.11–0.96 µg/kg
Tree bark	ND to 0.73 µg/kg dw (Qiu and Hites, 2008; Zhu and Hites, 2006)	ND to 0.73 µg/kg dw		
Panda tissue	ND to 863 µg/kg lw (Hu et al., 2008).	ND to 863 µg/kg lw		
Childrens' toys	5540 µg/kg (Chen et al., 2009)	5540 µg/kg	101 µg/kg (Chen et al., 2009)	101 µg/kg

Covaci et al, (2011) Environ. Internat. ***37, 532–556***

Levels in the environment (II)

- PBB and TBPH
- TBPH and TBB sewage sludge of WWTP San Francisco, US (*Klosterhaus et al. 2008*)
  - TBB: 40 to 1412 ng/g dw
  - TBPH: 57 to 515 ng/g dw
  - In the same ranges or higher than HBCD and decaBDE

- In finless porpoises from Hong Kong and China (*Lam et al. 2009*)
  - TBB: <0.4 -70 ng/g lw
  - TBPH: <0.04-3859 ng/g lw

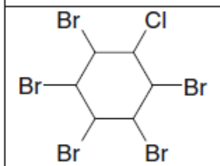
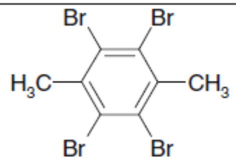
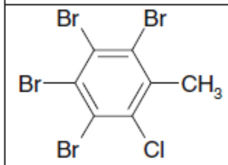
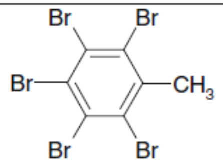
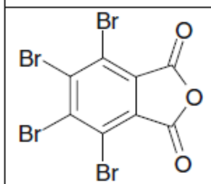
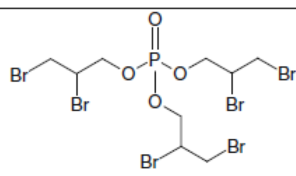
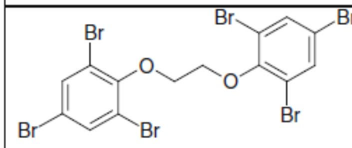
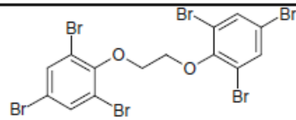
- In house dust form Boston, US (*Stapleton et al. 2008*)
  - TBB: <6.6 to 15,030 ng/g (median 133 ng/g)
  - TBPH:1.5 to 10,630 ng/g (median 142 ng/g)

Conclusions

- GC-ECNI-MS sensitive method to measure BDBPE, DBDPE, TBB and TBPH
- The ‘new’ BFRs can be analyzed in the same run as PBDEs
- GC column < 15 meter (degradation of DBDPE)
- Use of non-destructive cleanup methods is needed (no acids)
- Combine cleanup with PBDEs
- LC-MS/MS in APPI/APCI mode good alternative
- Detected in the environment (limited data)

More "new" BFRs

- Determination of new brominated flame retardants and PBDEs in sediment and SPM from the Western Scheldt (Lopez et al. 2011)

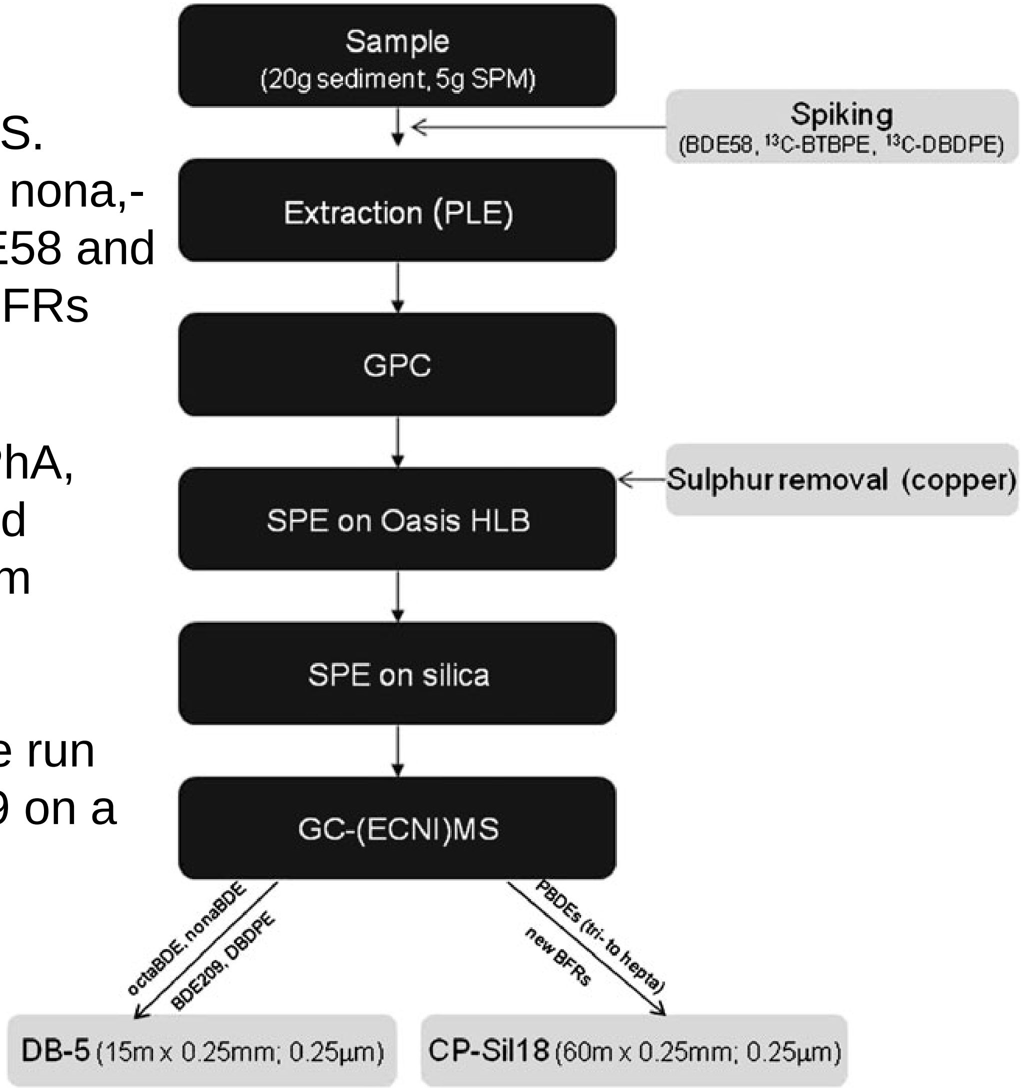
Molecular structure	Compound	Molecular structure	Compound
	Pentabromochlorocyclohexane PBCCH (isomers A, B, C and D) CAS [87-84-3] [a]MW = 513.09 [b]S_{water} =0.055 mg/L [c]Log $P_{octanol\text{-}water}$ = 4.72		2,3,4,5,6-Tetrabromo-*p*-xylene *p*TBX CAS [23488-38-2] MW = 421.75
	Tetrabromo-*o*-chlorotoluene TBoCT CAS[39569-21-6] MW = 422.19		2,3,4,5,6-Pentrabromotoluene PBT CAS [87-83-2] MW = 486.62 S_{water} =0.000935 mg/L Log $P_{octanol\text{-}water}$ = 6.99
	Tetrabromophthalic anhydride TBPhA CAS [632-79-1] MW = 463.7 S_{water} =0.016 mg/L Log $P_{octanol\text{-}water}$ = 5.63		Tris(2,3-dibromopropyl)phosphate TDBPP CAS [126-72-7] MW = 697.64 S_{water} =8 mg/L Log $P_{octanol\text{-}water}$ = 4.29
	1,2-bis(2,4,6-tribromphenoxy)ethane BTBPE CAS [37853-59-1] MW = 687.64 S_{water} =0.2 mg/L Log $P_{octanol\text{-}water}$ = 9.15		Decabromodipheylethane DBDPE CAS [84852-53-9] MW = 971.2 S_{water} =0.00072 mg/L Log $P_{octanol\text{-}water}$ = 11

Cleanup method

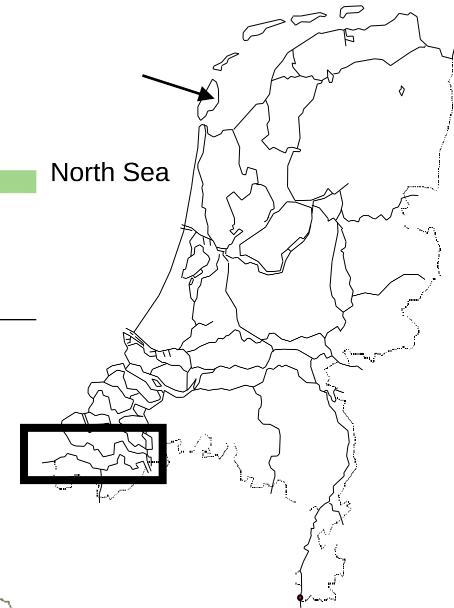
- Quantification was conducted by IS. ^{13}C BDE209 was used for octa-, nona,- and decaBDE and DBDPE. BDE58 and ^{13}C BDBPE was used for the other BFRs

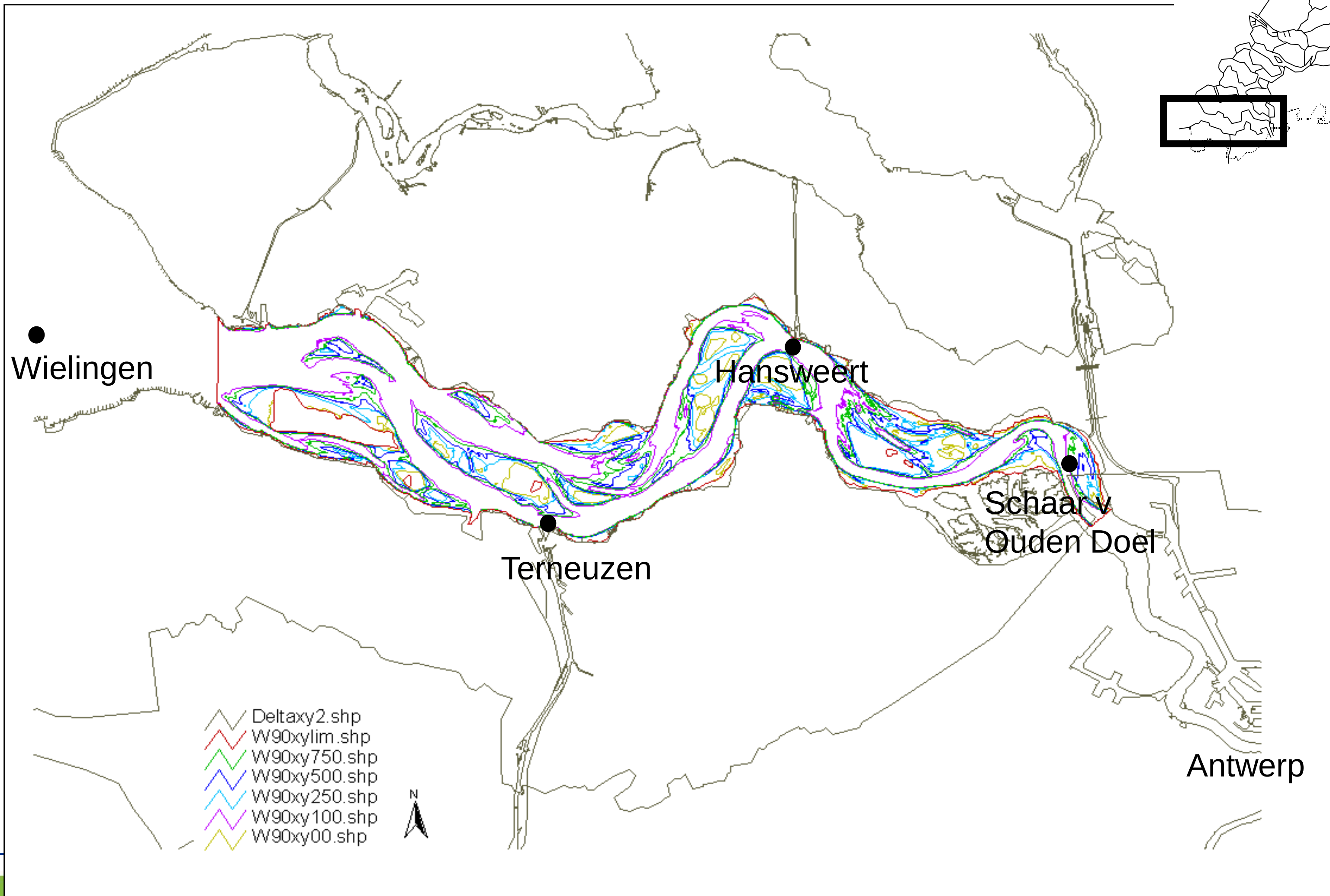
- PBCCH, TBoCT, pTBX, PBT, TBPhA, TBDPP and BTBPE were analysed together with the PBDEs on a 50 m column

- DBDPE was analysed in the same run as octa-, nona-BDEs and BDE209 on a short column to avoid on-column degradation

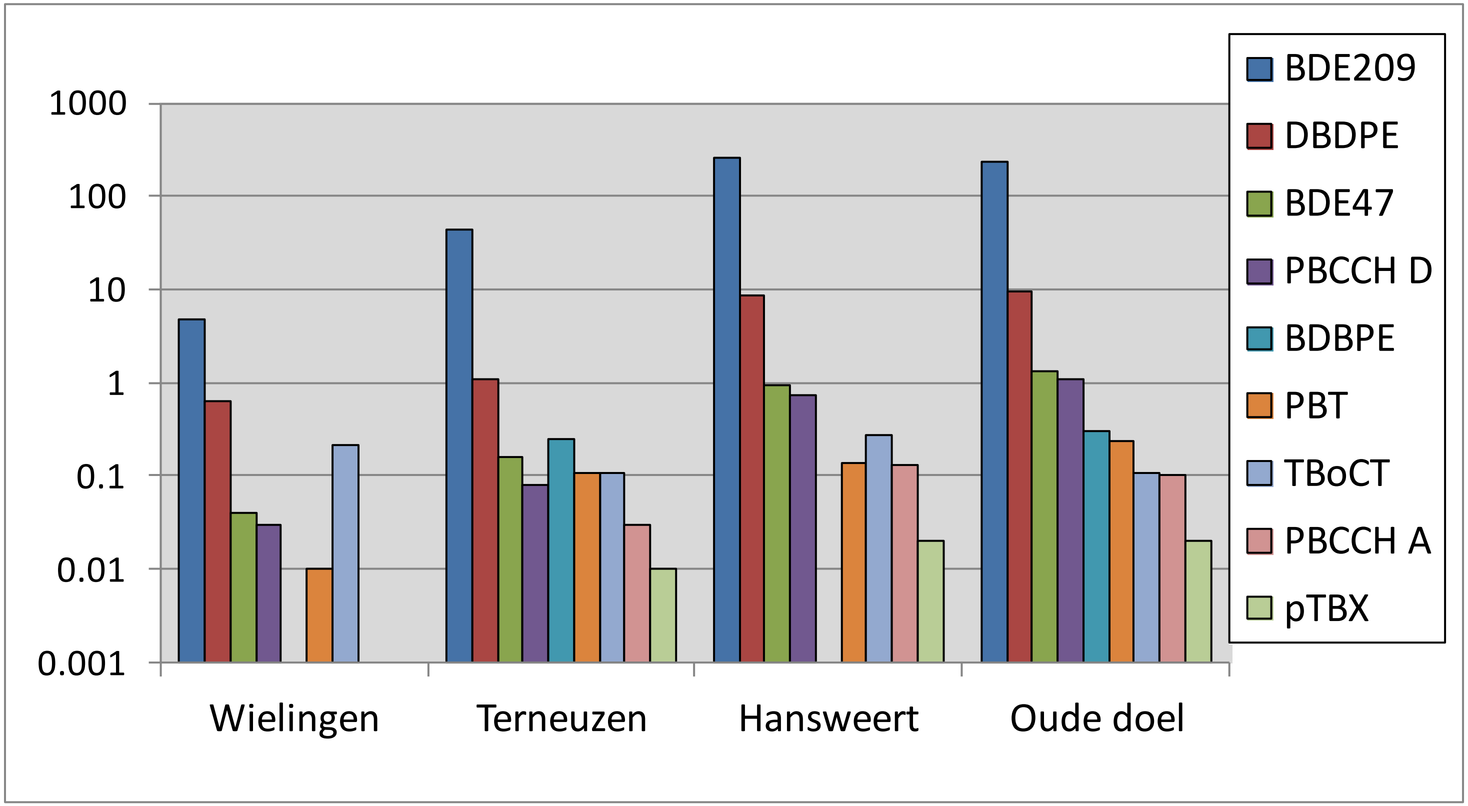


Spatial distribution sediment





Concentrations in sediment (ng/g dw)



Upstream Scheldt estuary

Results and Conclusions

- Analytical procedure to determine PBCCH, TBoCT, pTBX, TBPhA, PBT, BDBPE, and DBDPE together with PBDEs in sediments and in suspended particulate matter
- First identification of PBCCH, pTBX and TBoCT in sediment and SPM
- The concentrations of these new flame retardants ranged from 0.05 to 0.30 µg/kg dry weight

Organophosphorus Flame Retardants (PFRs)

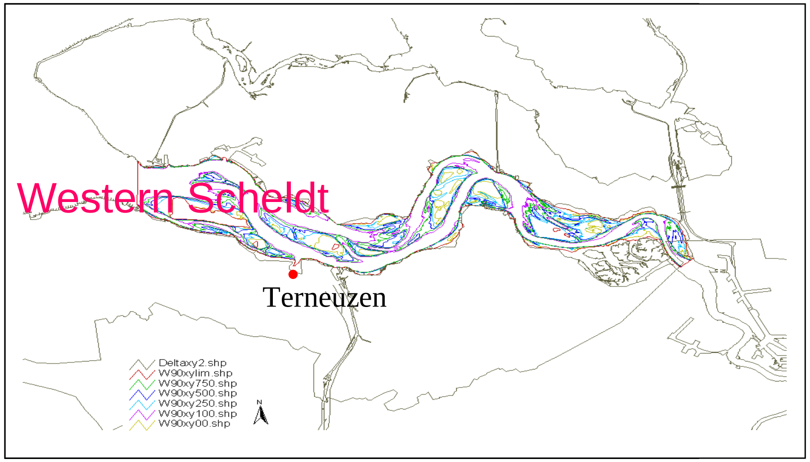
Introduction

- Phase-out production and use of PBDEs
- Increased use of alternative FRs (e.g. PFRs)
- Worldwide production volume of FRs
  - 14% PFRs compared to 21% for BFRs*
- Detected in various matrices e.g. water, air sediment
- Limited information on PFRs in biota

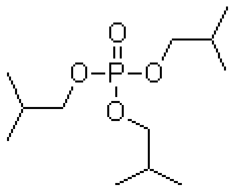
*(www.cefic/efra.com)

Objectives

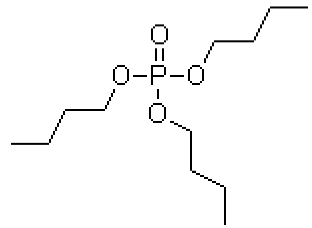
- Determination of PFRs in the pelagic and benthic food web of the Western Scheldt



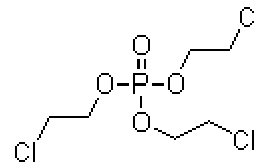
PFRs



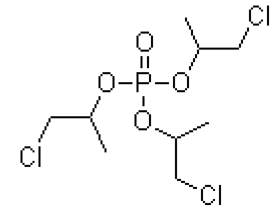
TiBP



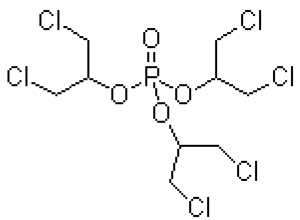
TBP



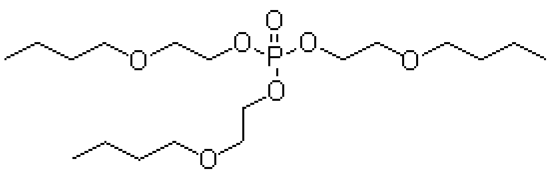
TCEP



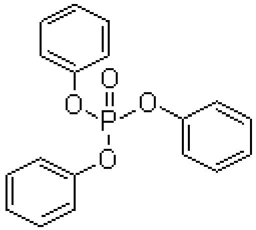
TCPP



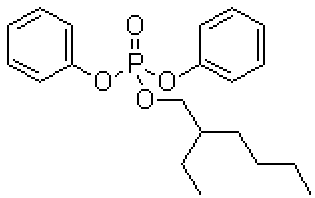
TDCPP



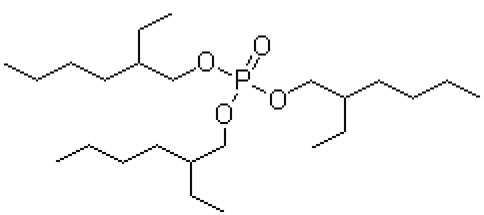
TBEP



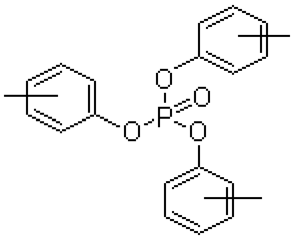
TPP



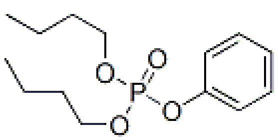
EHDP



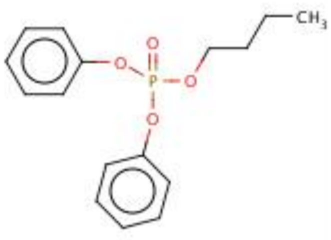
TEHP



TCP

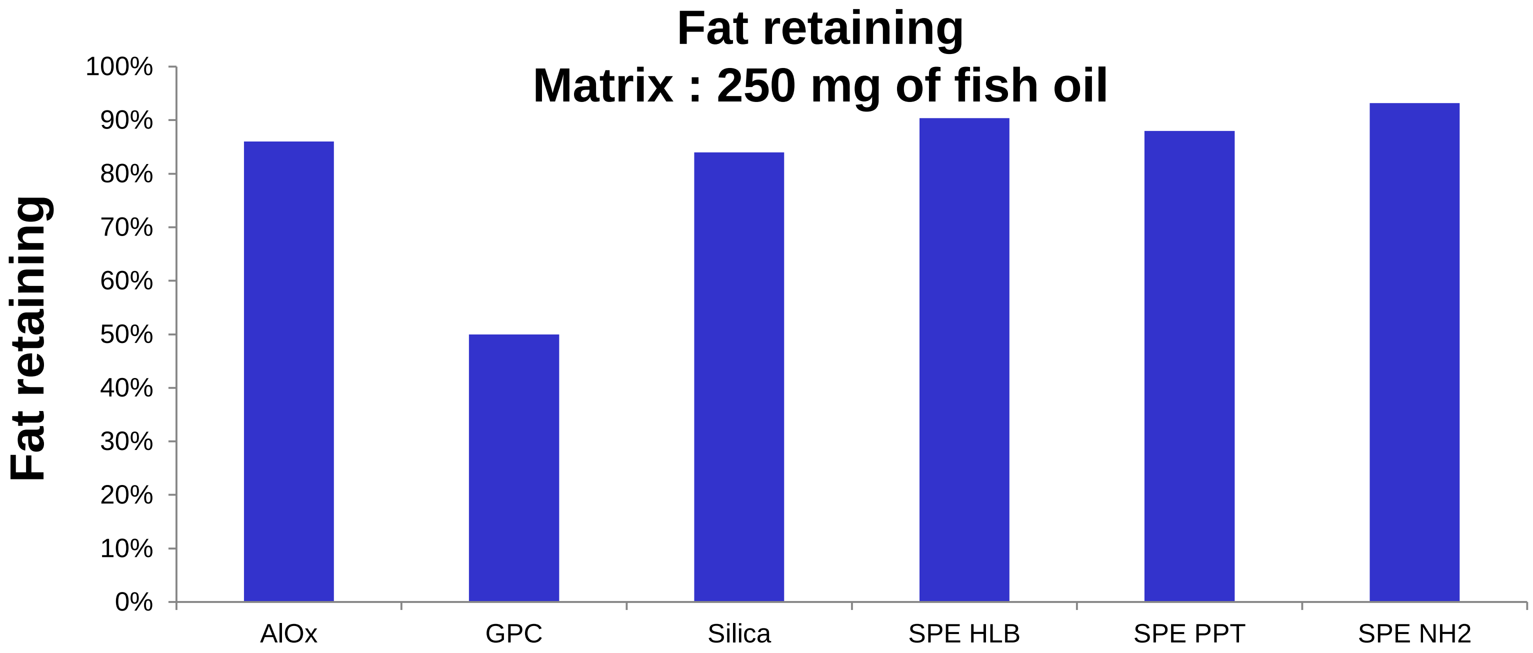


DBPhP



DPhBP

Cleanup

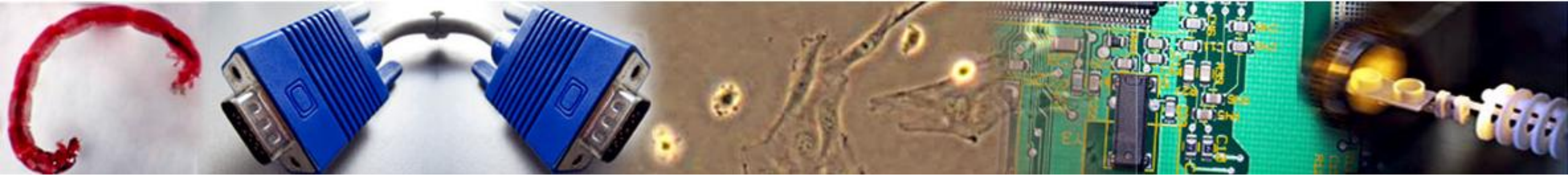


	AlOx	GPC	Silica	SPE HLB	SPE PPT	SPE NH2
Recovery PFRs	**18-125%**	**86-115%**	**75-120%**	**48-238%**	**10-164%**	**68-128%**
Summary	**No cyclic**	**Too much matrix**	**Too much matrix**	**Poor recovery**	**No cyclic**	**Best solution**

PFRs in Belgian home dust (n=33) µg/g

	House dust samples ($n=33$)				
FRs	DF (%)[a]	Mean	Median	P95[b]	Range
OPFRs					
TEP	0	<0.05	<0.05		
TiBP	100	4.20	2.99	8.81	0.70–15.6
TnBP	100	0.25	0.13	0.63	0.03–2.70
TCEP	86	0.49	0.23	1.72	<0.08–2.65
TCPP	100	4.82	1.38	14.5	0.19–73.7
TBEP	100	6.58	2.03	23.1	0.36–67.6
TPP	100	2.02	0.50	7.28	0.04–29.8
TDCPP	97	0.57	0.36	0.99	<0.08–6.64
TCP	97	0.44	0.24	1.10	<0.04–5.07
∑OPFRs		19.4	13.1	70.3	1.92–94.7
BFRs[c]					
BDE-209	98	0.59	0.31	0.92	<0.001–5.30
∑PBDEs		0.70	0.36	1.14	0.003–6.33
∑HBCDs		1.74	0.13	2.46	0.010–42.70
TBBPA	85	0.04	0.01	0.09	0.002–0.42

Van den eede et al, (2011) Environment International 37 454–461



Life Cycle and Risk Assessment of Environmental Compatible Flame Retardants
Prototypical case study

ENFIRO

EU research project FP7: 226563

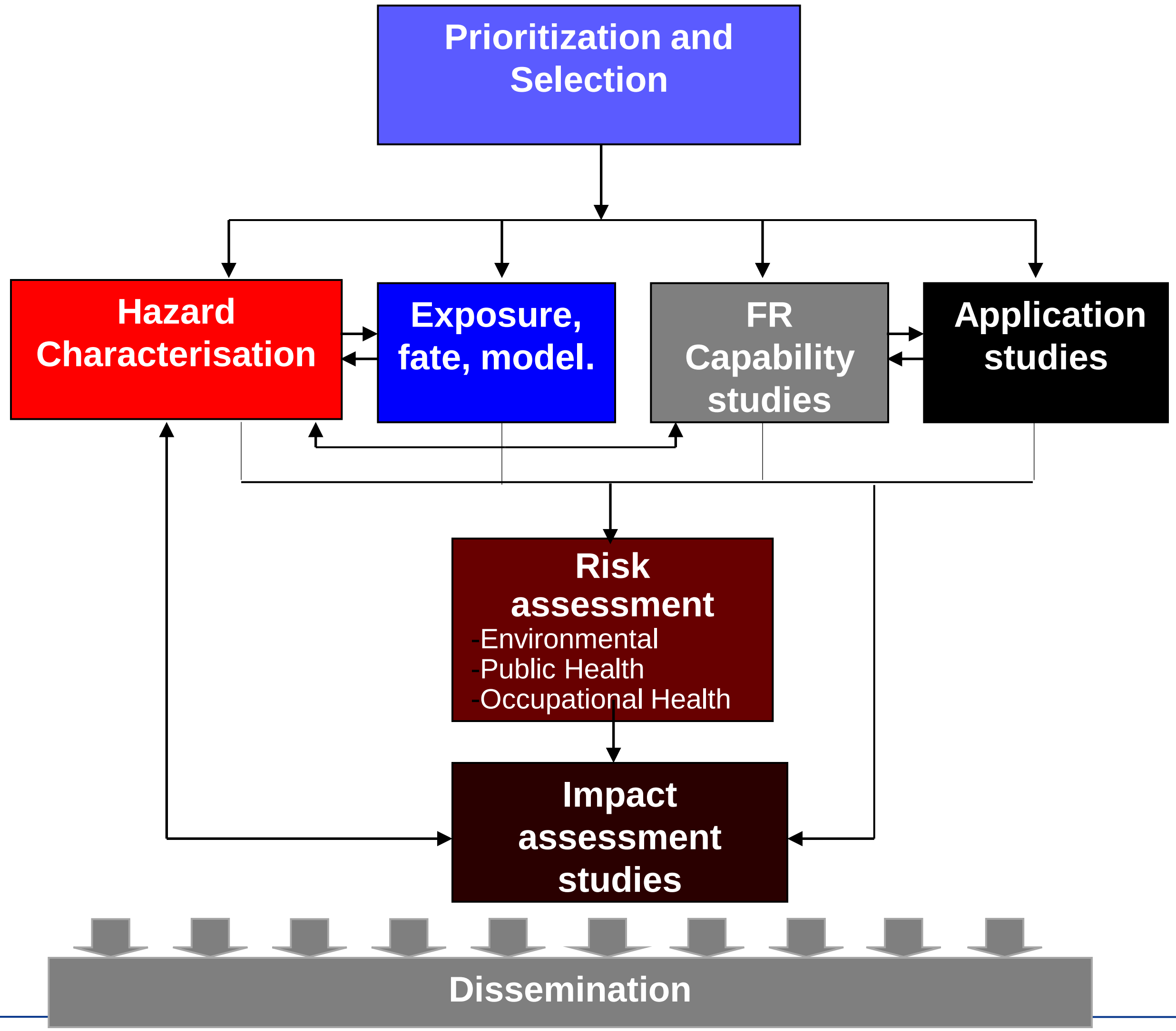
IVM Institute for
Environmental Studies

Objectives ENFIRO

- To study the substitution options for some BFRs

- ENFIRO delivers:
  - Comprehensive dataset on the viability of production, application
  - Risk assessment
  - Life cycle assessment (LCA)

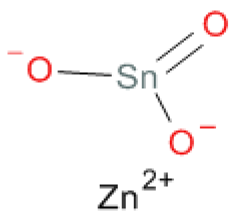
Work plan

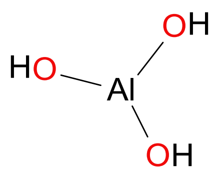


Prioritization and Selection
Hazard Characterisation
Exposure, fate, model.
FR Capability studies
Application studies
Risk assessment
-Environmental
-Public Health
-Occupational Health
Impact assessment studies
Dissemination

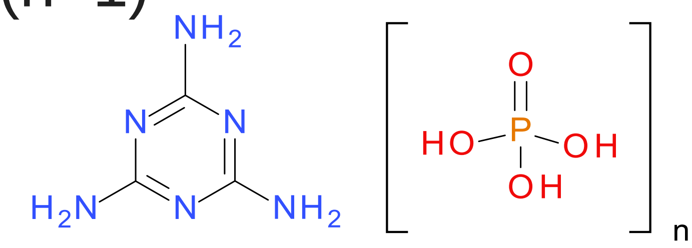
ENFIRO: HFFRs for screening study

Inorganic FRs (n=7)

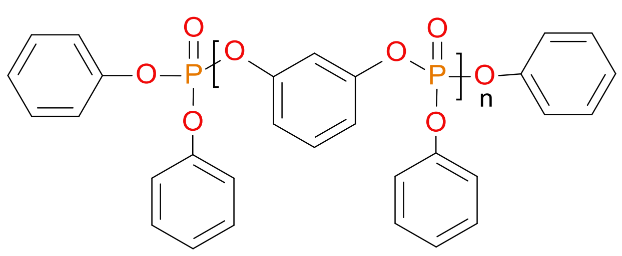


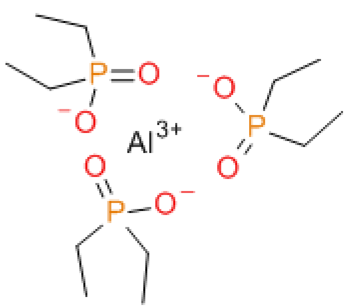


Nitrogen based organic FR (n=1)



Organophosphorus & salt FRs(n=5)



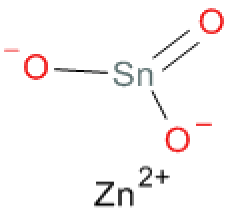


Intumescent systems (n=2)

Nanoclay (n=1)

Three level assessments

FR



Risk assessment
- Environment
- Human health

Material

Technological assessment
- Application
- Fire performance

•Leaching behaviour

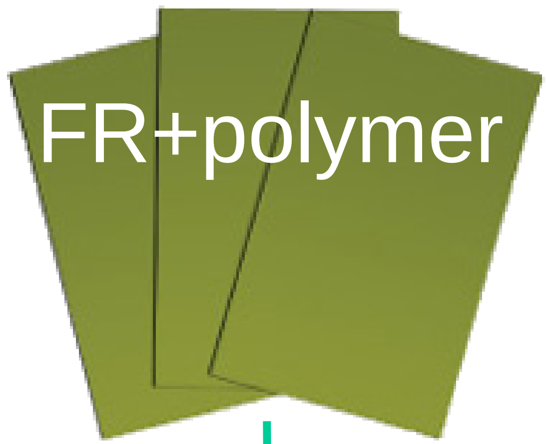
Product

Impact assessment studies
- Life cycle assessment
- Life cycle costing
- Social life cycle assessment

Assessment of FR/polymer material

Leaching FR
to air
(off-gassing)

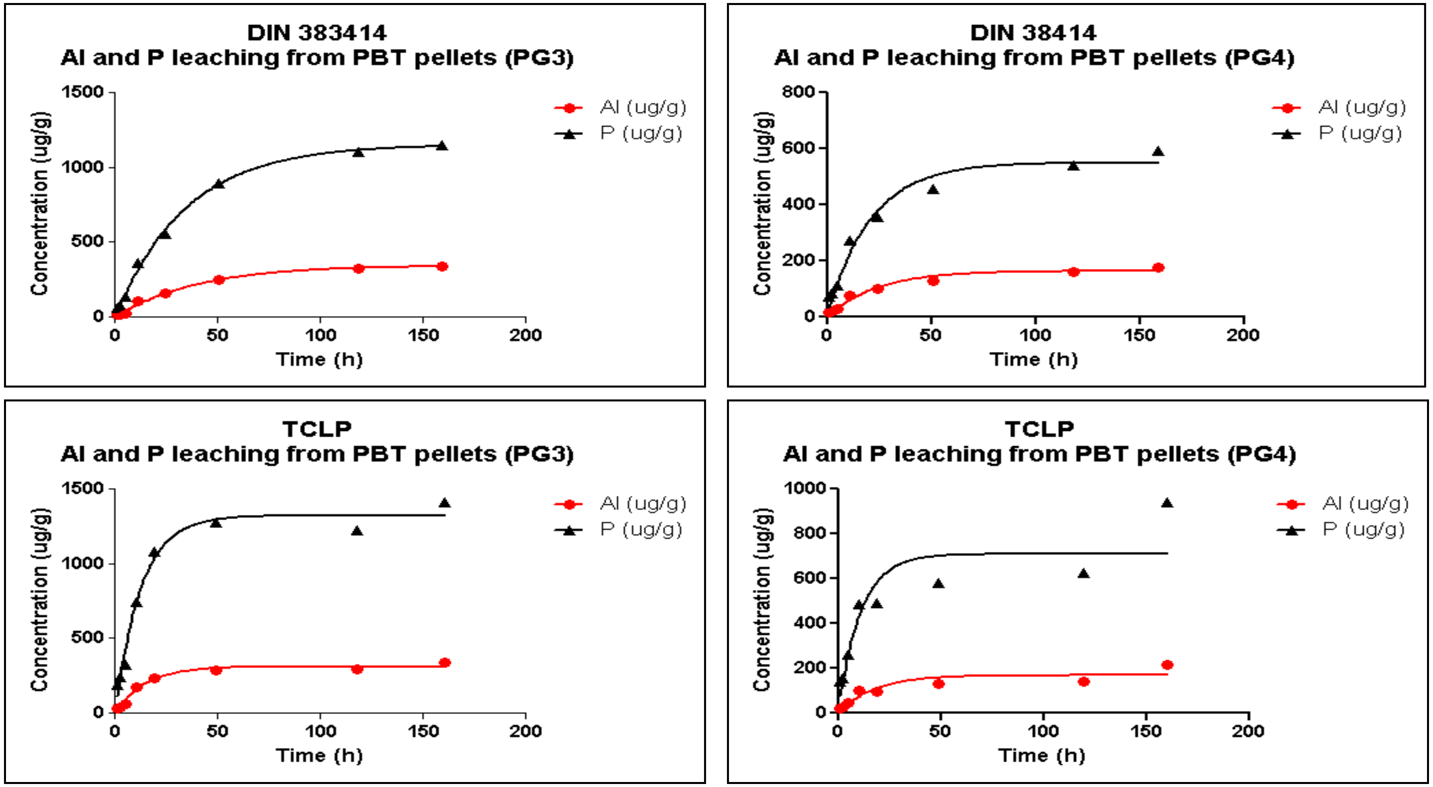
Leaching FR
to water
(concentrations and
toxicity)

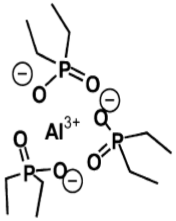


Toxic gasses
after fire tests

Weathering

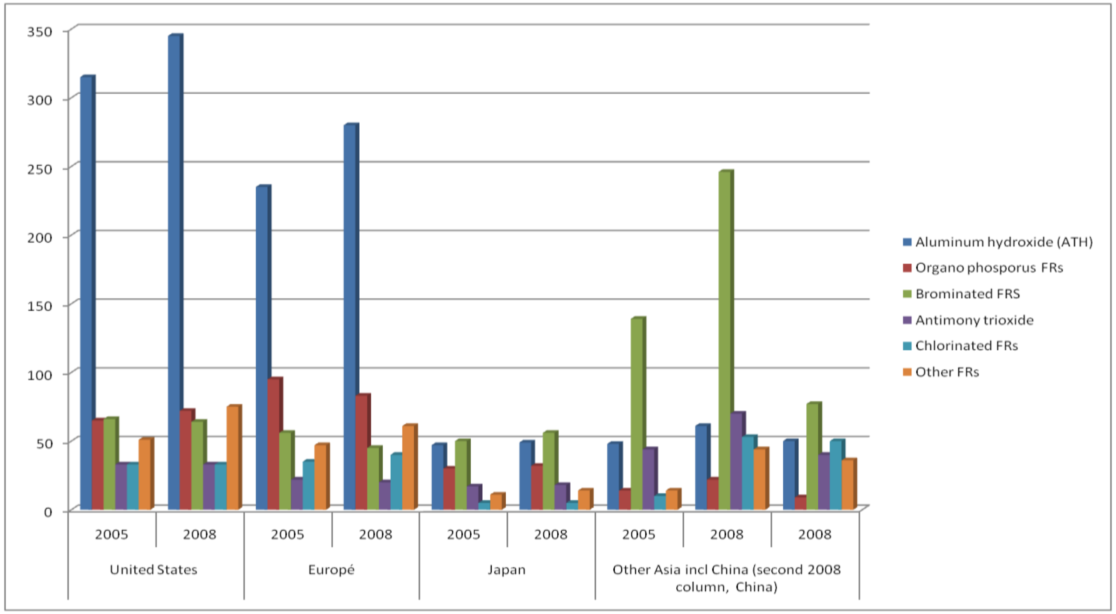
AlPi leaching from PBT pellets and moulded plates





Final conclusion

- New BFRs can be analysed by LC versus GC → Both
- Alternative flame retardant → only brominated or include PFRs
- What if we only use metal based FRs like ATH → problem solved?



Source: SRI Consulting 2005 and 2008

Acknowledgement

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