An experimental approach to examining correlation between external exposure and human body burdens

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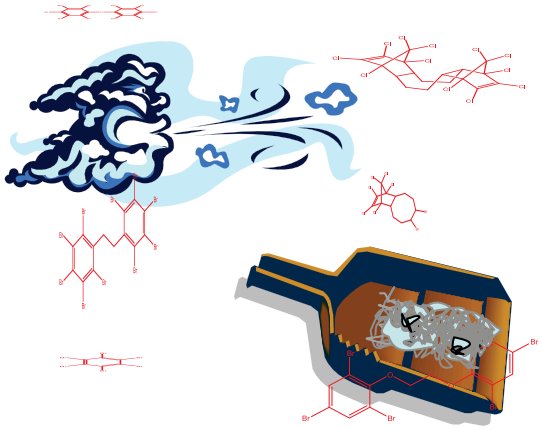
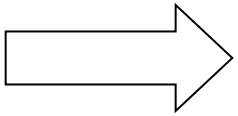
Outline

- ✓ Project overview
- ✓ Sampling campaign
- ✓ Chromatography and target flame retardants
- ✓ Extractions and recoveries
- ✓ Conclusions

Project overview

Assessing pathways for human exposure to emerging flame retardants by comparing external doses from measurements in indoor **air** and **dust** as well as **food** and **beverages** and compare these with internal doses obtained through bio-monitoring





$\sum$ FR in indoor air and dust $\approx$ $\sum$ FR in blood or urine ?

Sampling campaign

Sampling period: 24th January – 10th May

48 houses

Dust Air

Mother Children

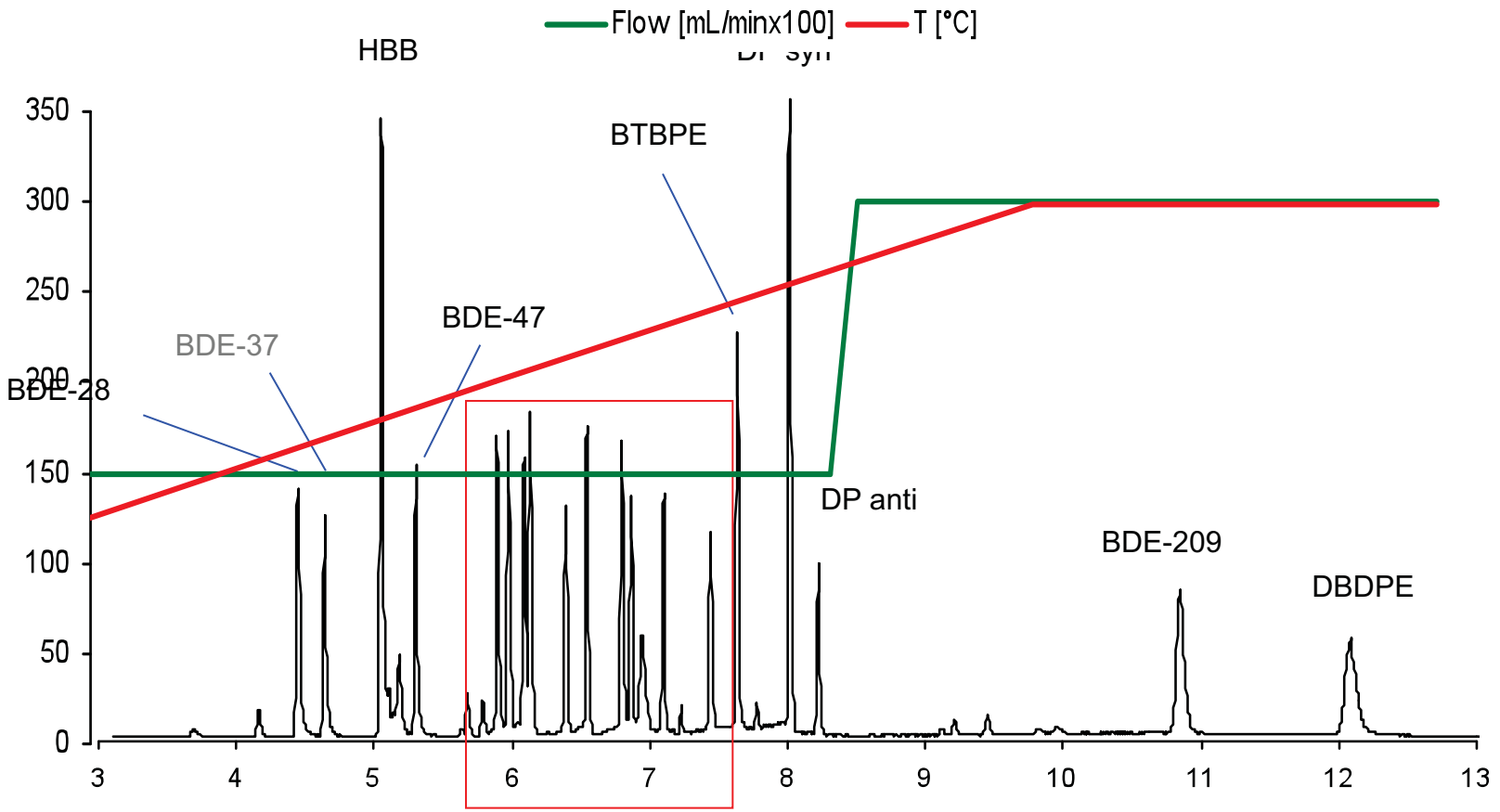
Blood Saliva Hair Urine

> 432 samples

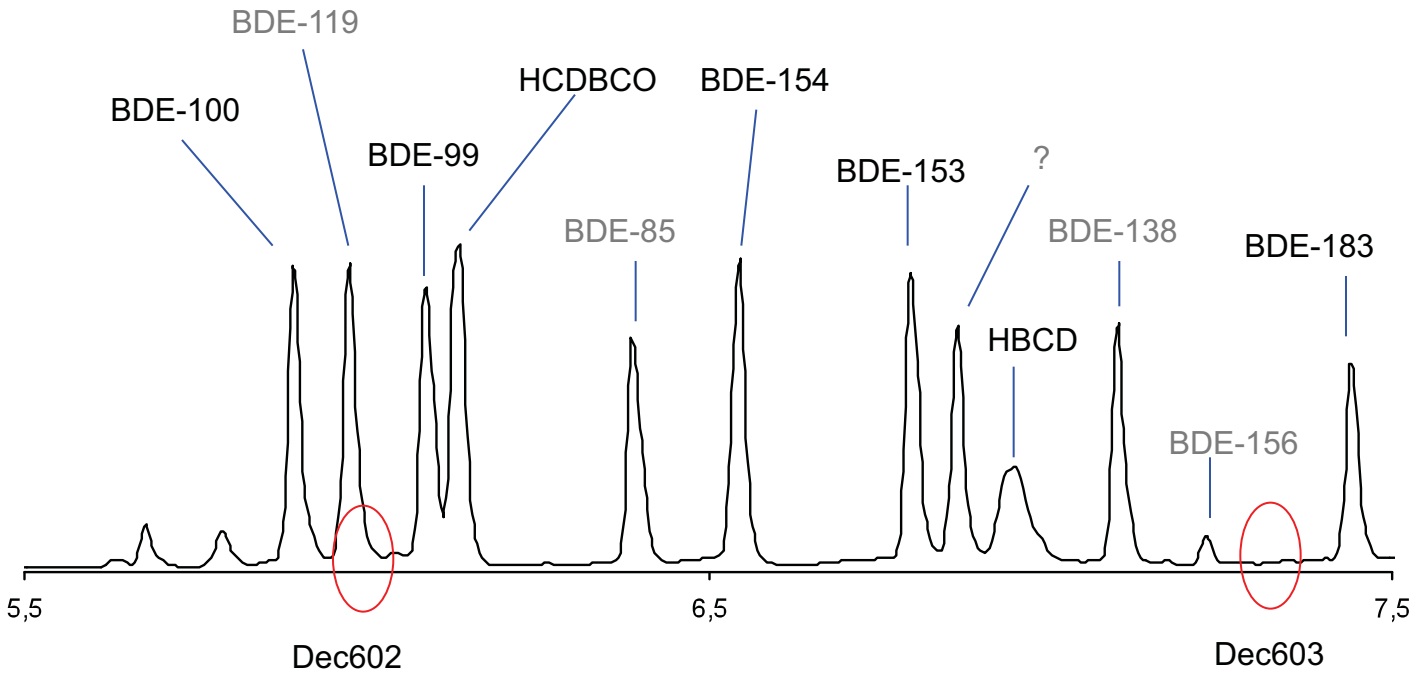
Chromatography

FR: BDE-28,47,99,100,153,154,183 and 209, DPsyn and anti; Dec602 and Dec603, HBB, HCDBCO, BTBPE and DBDPE

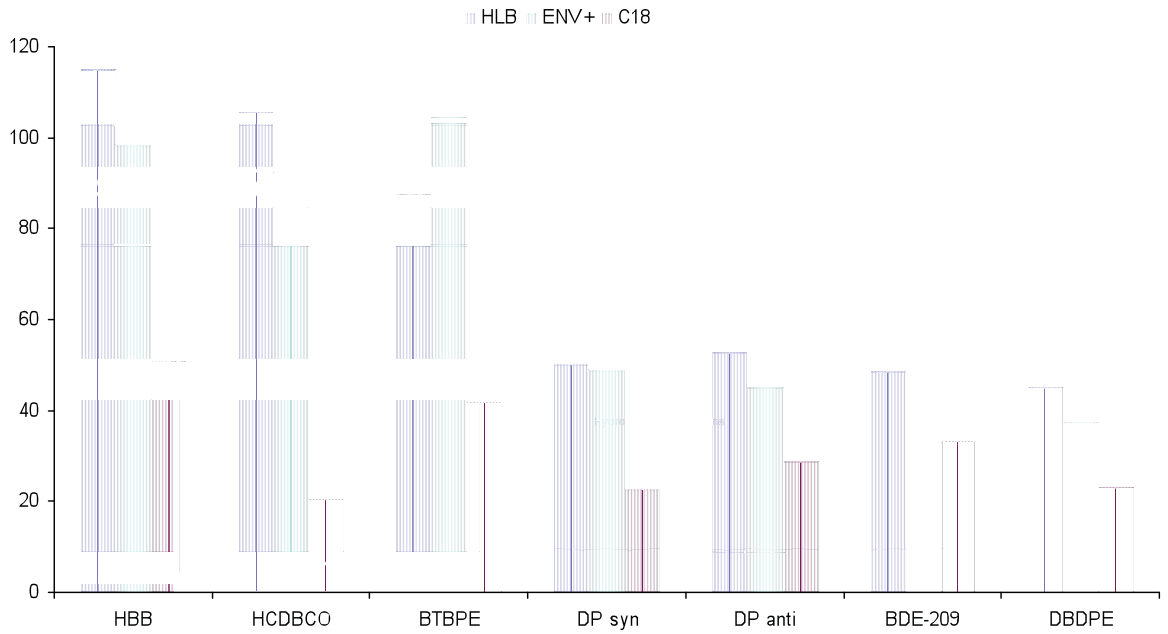
Column HP-5MS 15m x 0,25mm x 0,1µm



Chromatography



Solid phase extraction



Conditioning: 4mL DCM, MeOH and H_2O

Loading: 6mL (2mL serum + 2mL formic acid + 2 mL H_2O)

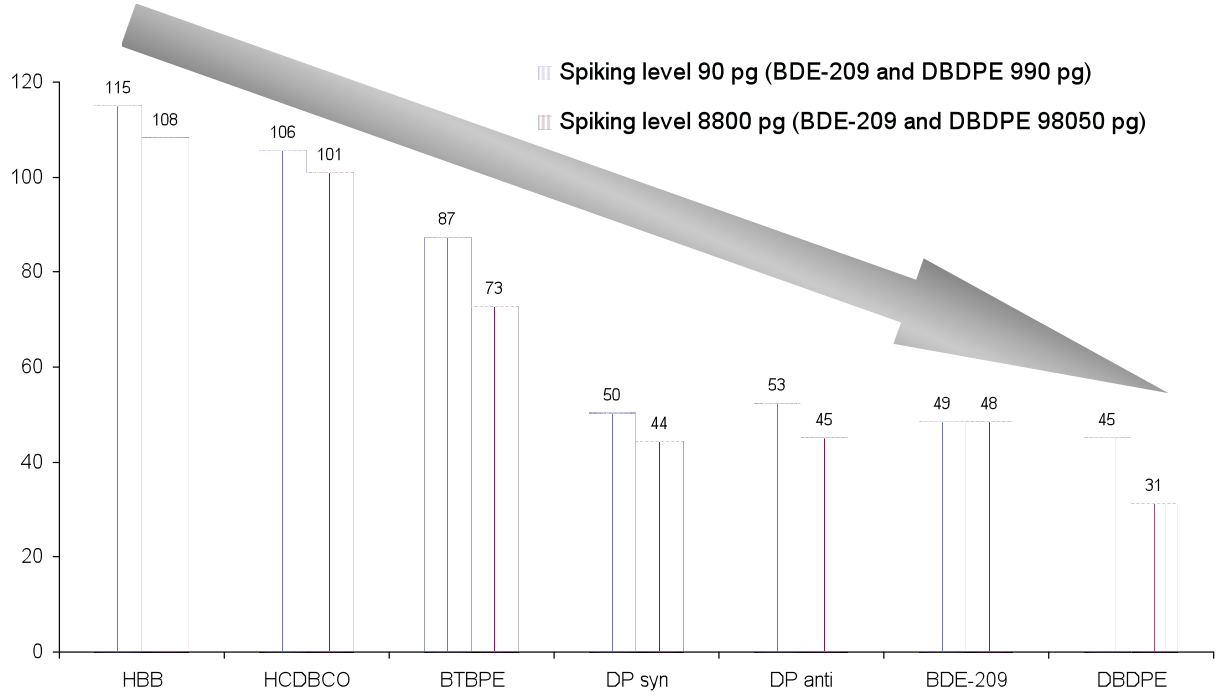
Washing: 4mL H_2O + 1mL MeOH

Eluting: 9mL DCM

Clean up (acid/silica 33% v/w): elution 8mL HEP/DCM 3:1

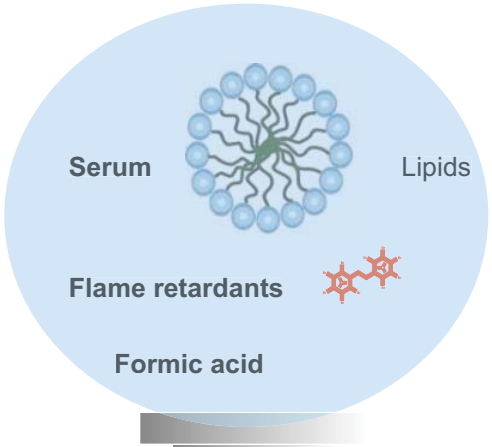
Recoveries

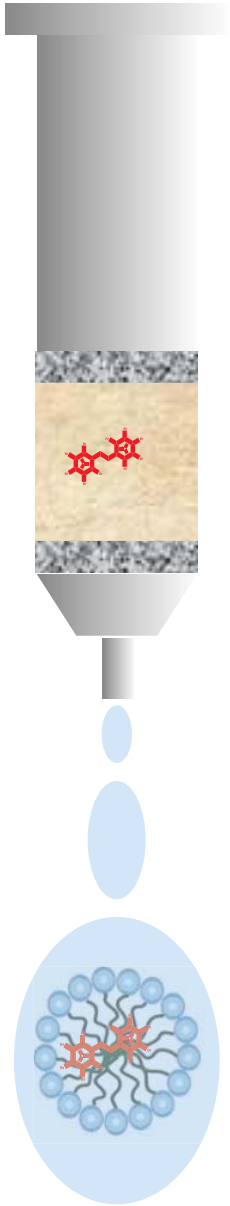
- SPE (HLB) recoveries spiking horse serum

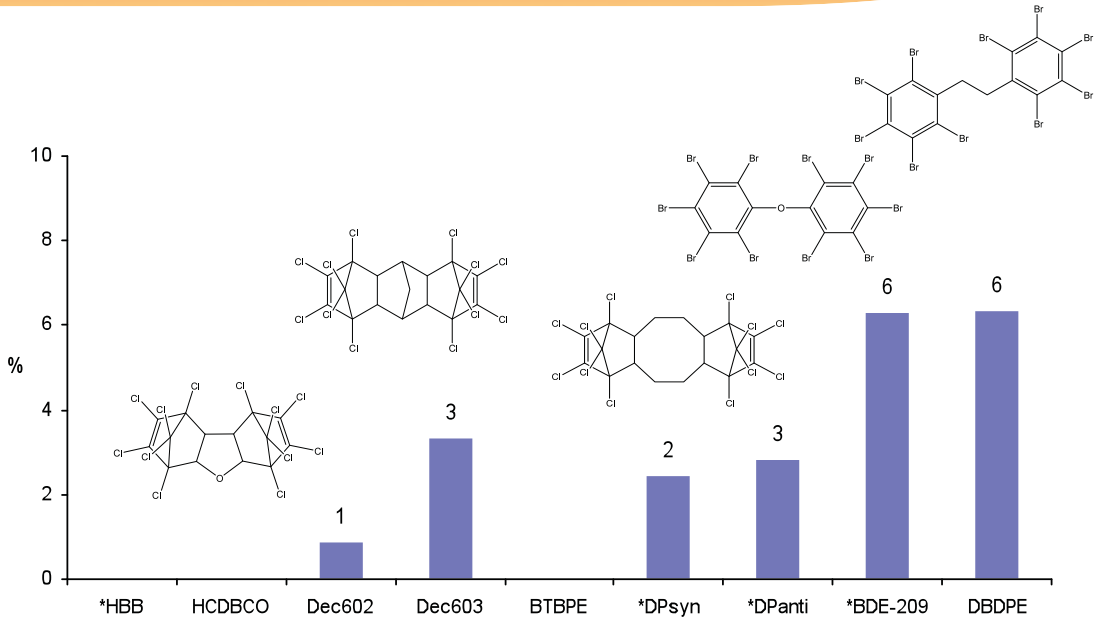


- Low spiking level (LL) recoveries range from 45 to 115% (n=4)
- High spiking level (HL) recoveries range from 31 to 108% (n = 2)
- Tendency to loose the highly hydrophobic analytes !!!

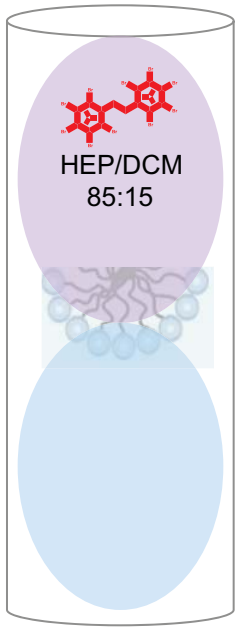
Recoveries - Horse serum





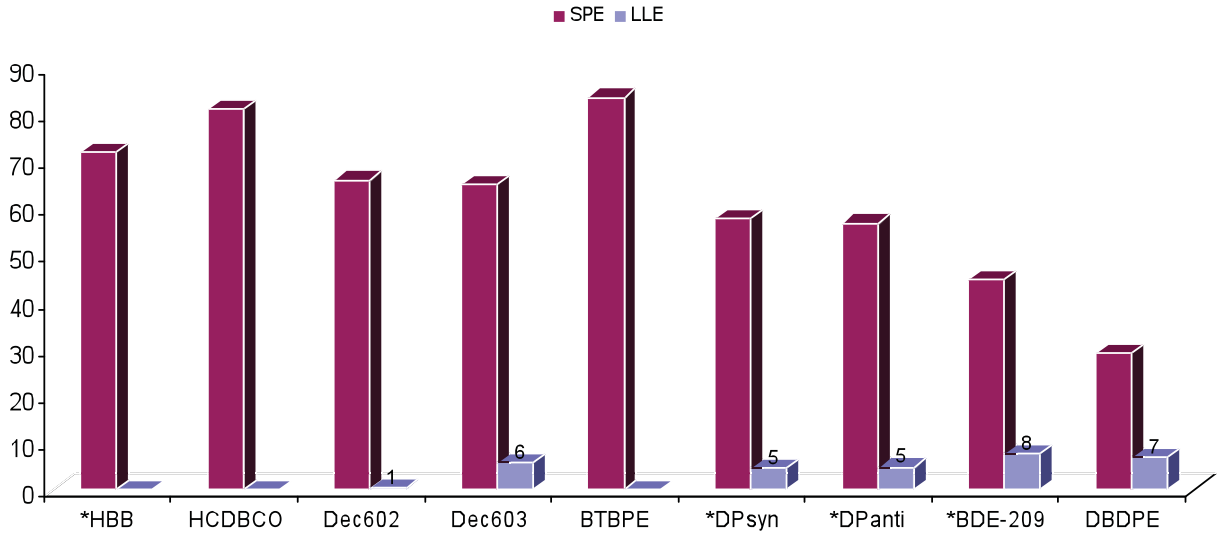


LLE



Recoveries - Human serum

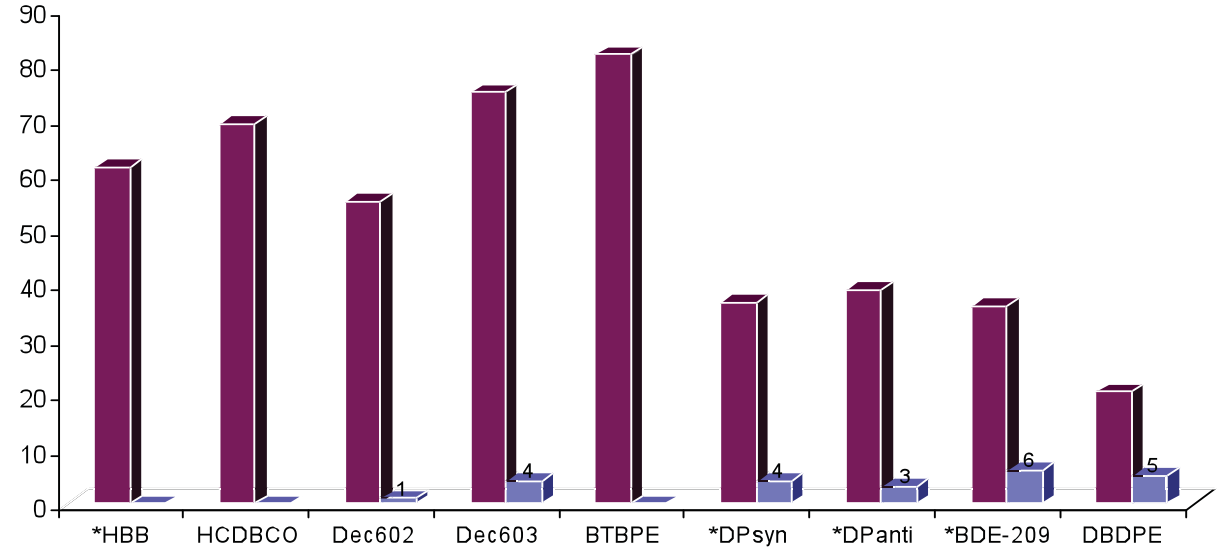
High level spiking (~3ng; 5ng BDE-209; 24ng DBDPE)



HL spiking

	SPE	LLE
n	5	4
RSD [%]	4-22	18-42

Low level spiking (~100pg; 500pg BDE-209; 3ng DBDPE)

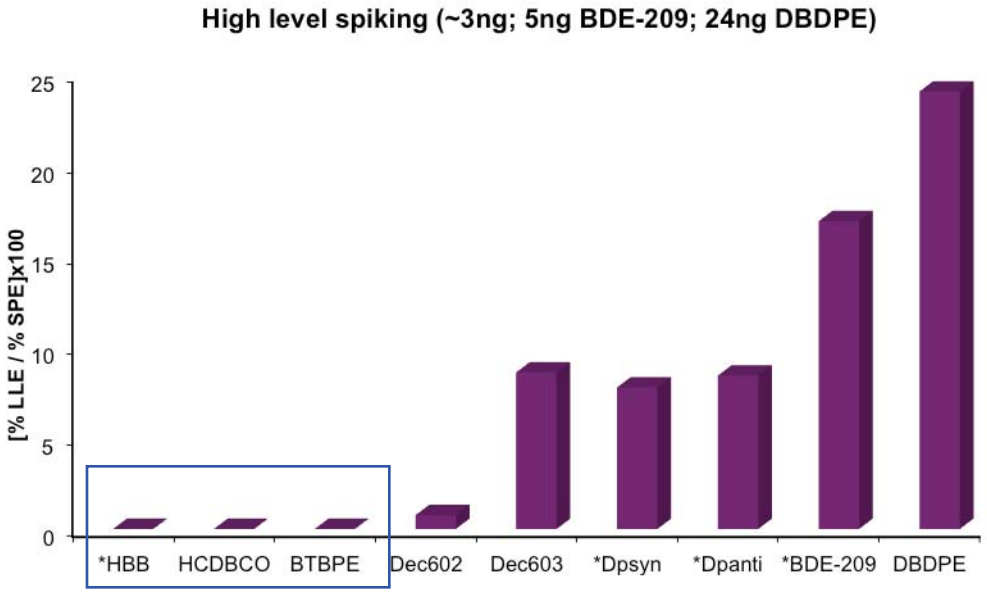


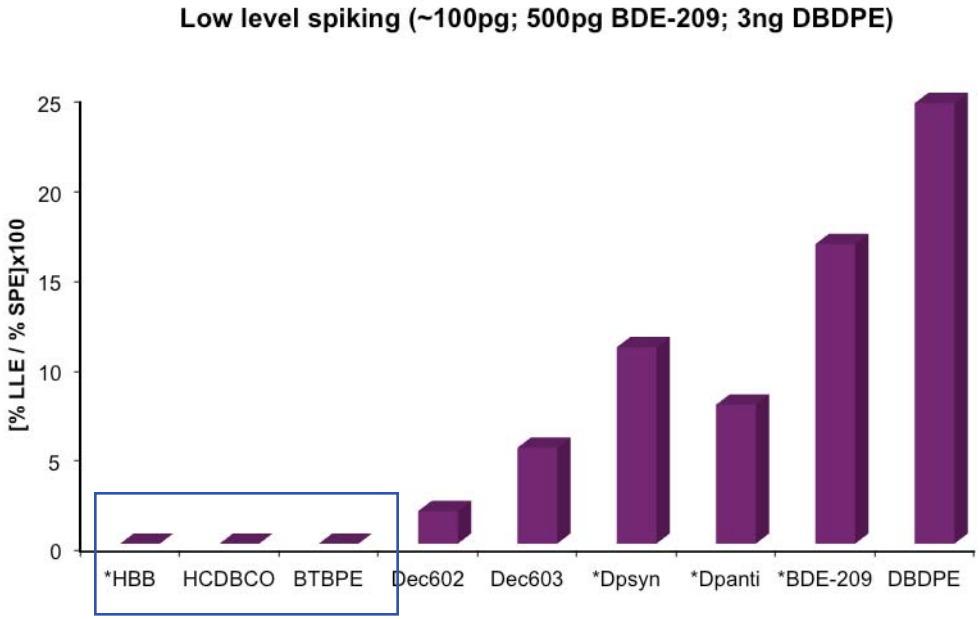
LL spiking

	SPE	LLE
n	5	4
RSD [%]	11-28	27-67

Recoveries - Human serum

Log K_{ow}	Flame retardant
5,6	*HBB
7,9	HCDBCO
7,9	BTBPE
	Dec602
	Dec603
9,1	*Dpsyn
9,1	*Dpanti
9,9	*BDE-209
11,1	DBDPE





Covaci, A.; Harrad, S.; Abdallah, M. A. E.; Ali, N.; Law, R. J.; Herzke, D.; de Wit, C. A. *Environment International*. **2011**, *37* (2), 532-556

Sverko, E.; Tomy, G. T.; Reiner, E. J.; Li, Y. F.; McCarry, B. E.; Arnot, J. A.; Law, R. J.; Hites, R. A. *Environ. Sci. Technol*. **2011**, *45* (12), 5088-5098

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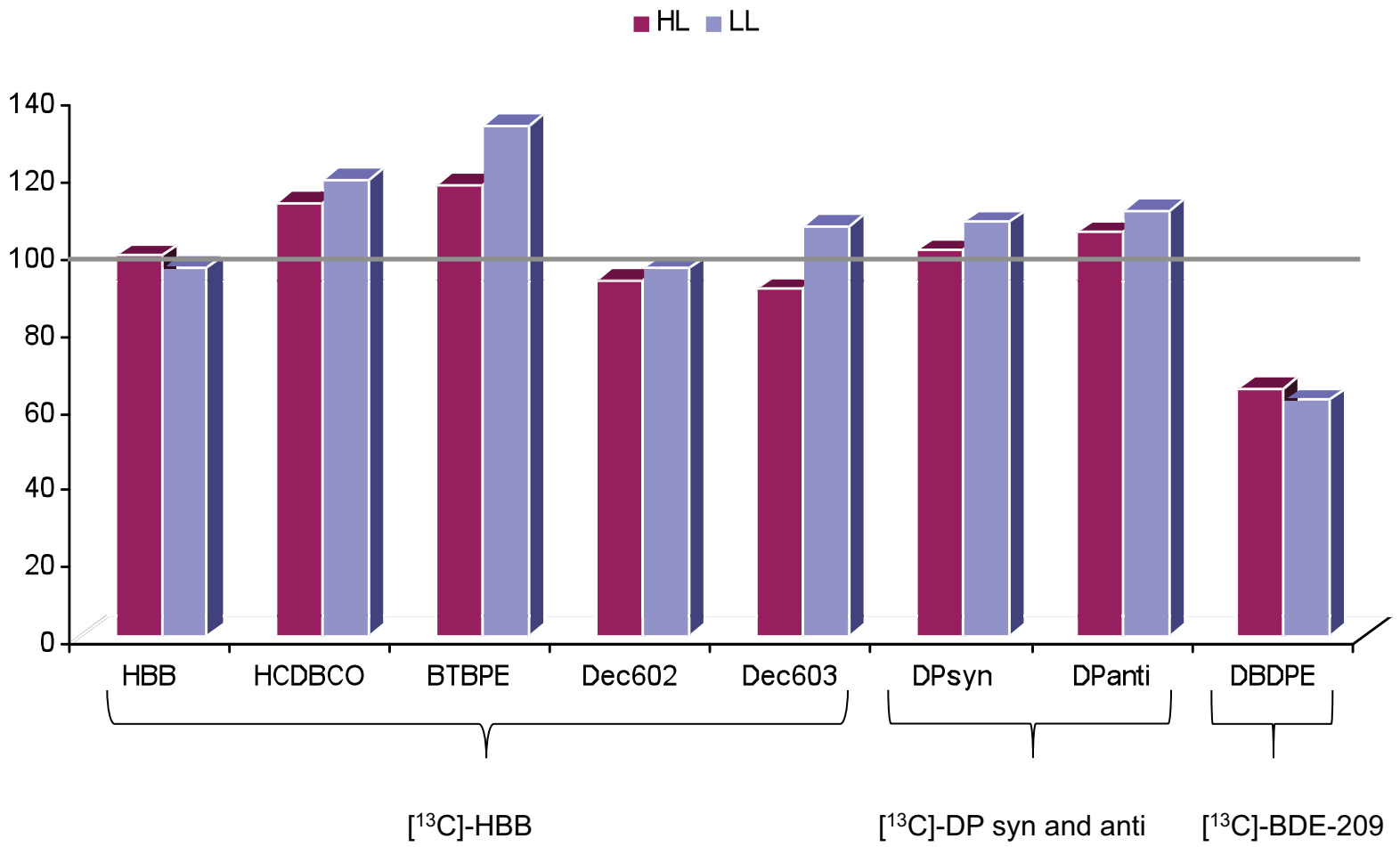
SPE accuracy - Human serum



Conclusions

- Satisfactory separation of target flame retardants in 15 meters column
- When working with serum, lower recoveries in SPE must be expected for compounds with high K_{ow}
- Highly halogenated FR have been found in water after SPE process

…and outlook

- Is LLE efficient enough to release flame retardants completely from the theoretical micelle formation?
- Can this effect occur also in organisms?

Future work

Short term

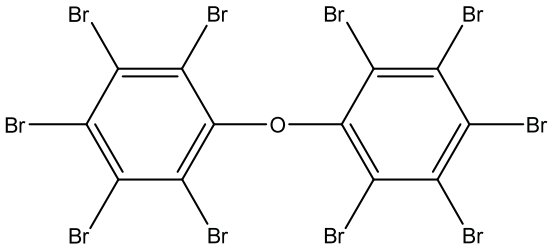
- Determine efficiency of LLE on SPE waste
- Validate GC/MS method (PBDEs and NFR)
- Analyze serum samples

Long term

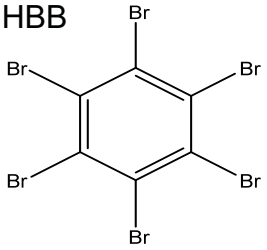
- Secondment in ITM for analyzing dust and air samples
- Develop LC/MS/MS method for metabolizable flame retardants
- Analyze urine samples

Flame retardants structures

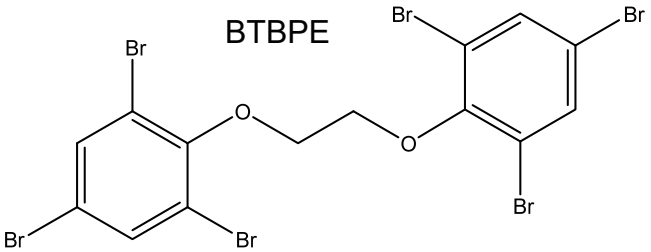
BDE-209



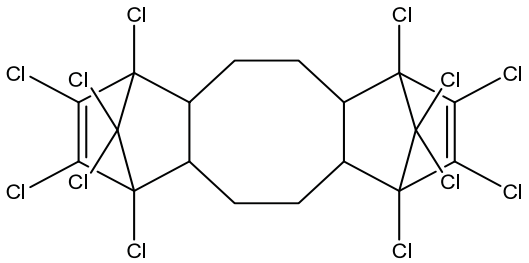
HBB

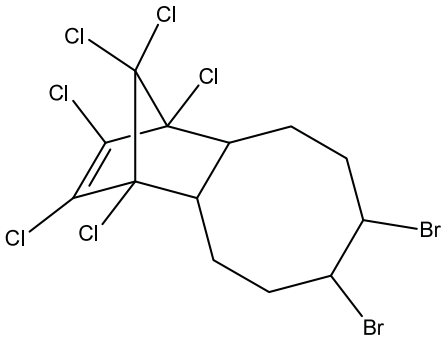


BTBPE

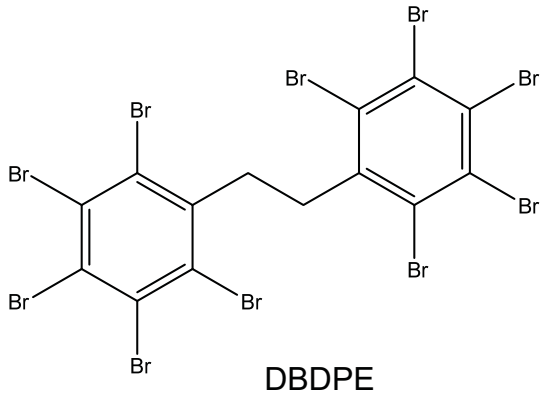


DP syn and anti

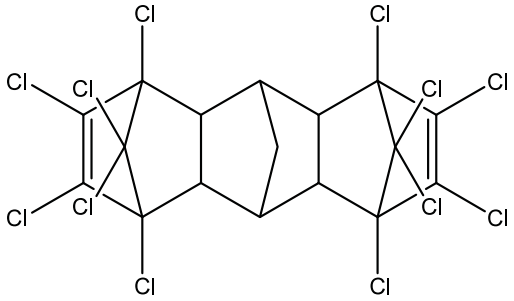




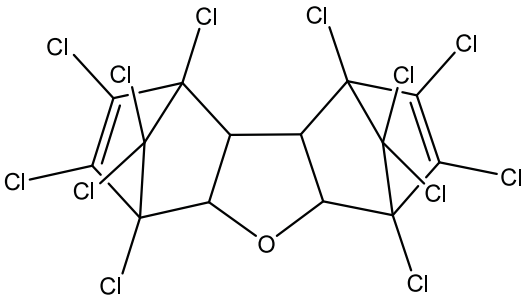
HCDBCO



DBDPE



Dec603



Dec602

Background

- Flame retardants are used to reduce or resist the spread of fire in a wide range of commercial and household products.
- Dechlorane plus, DBDPE, BDE-209 and BTBPE are manufactured in a high production volumes (>1000 tons/year).
- Long-range atmospheric transport (they have been found in the Arctic).
- Persistent, toxic and can accumulate in biota and humans.
- Detected in air, dust, soil, sewage sludge, animal tissues and human blood (DP, HBB and BDE-209).

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Sverko, E.; Tomy, G.T.; Reiner, E.J.; Li,Y.; McCarry, B.E.; Arnot, J.A.; Law, R.J.; Hites, R.A.; Environ. Sci. Technol. **2011**, *45*, 5088–5098

Chromatography

GC/LRMS Method only NBFR

Agilent 6890 (GC) 5973 (MS, single quadrupole)

Column **DB5**-MS (**15 m** x 0,25 mm x 0,1 µm) + retention gap

Injection volume 1µL

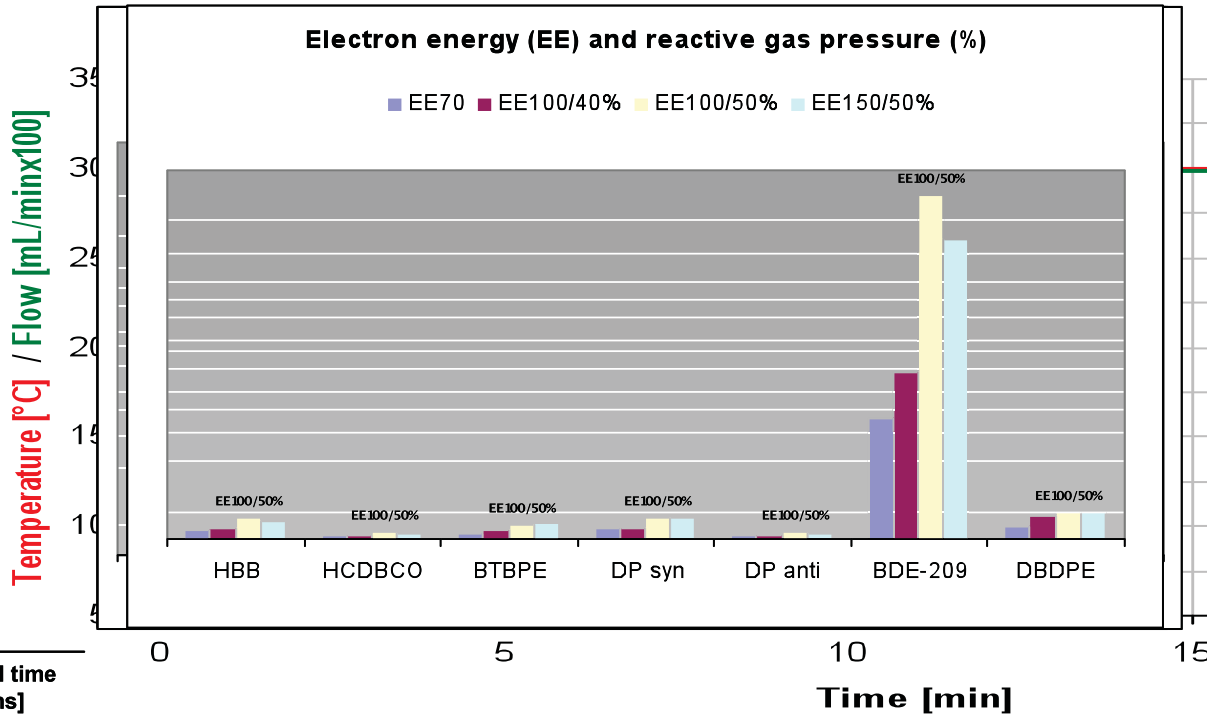
Injection/aux temperature 300 °C

Pulsed splitless 55psi@2min

Temperature and flow program

MS source 200°C

Reagent gas: CH_4 (50%; 2,2x10^{-4}Torr)
Ionization **ECNI** Detection **SIM**

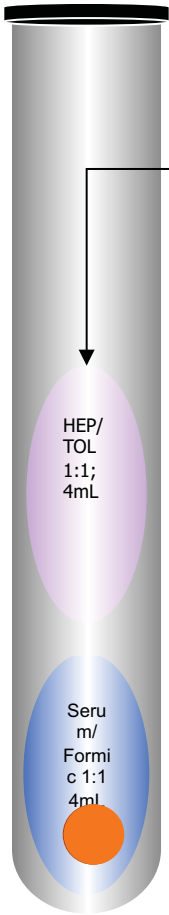


	Ions [m/z]	Dwell time [ms]
HBB	471,6 / 479,5 / 551,5 / 559,6	50
HCDBCO	537,5 / 541,7	50
BDE-139	160,8 / 414,9 / 573,8	50
BTBPE	79 / 251,8	100
DP syn/anti	651,8 / 653,8	100
BDE-205	573,5 / 653,7	100
BDE-209	486,6 / 488,7 / 494,6 / 496,6	50
DBDPE	79 / 81	100

selective **sensitive**

Liquid-Liquid Extraction (LLE)

60” vortex



Heptane

Heptane / toluene 1:1

Toluene

Heptane / MTBE 1:1

Centrifuge 3000rpm ; 2 min

Organic phase

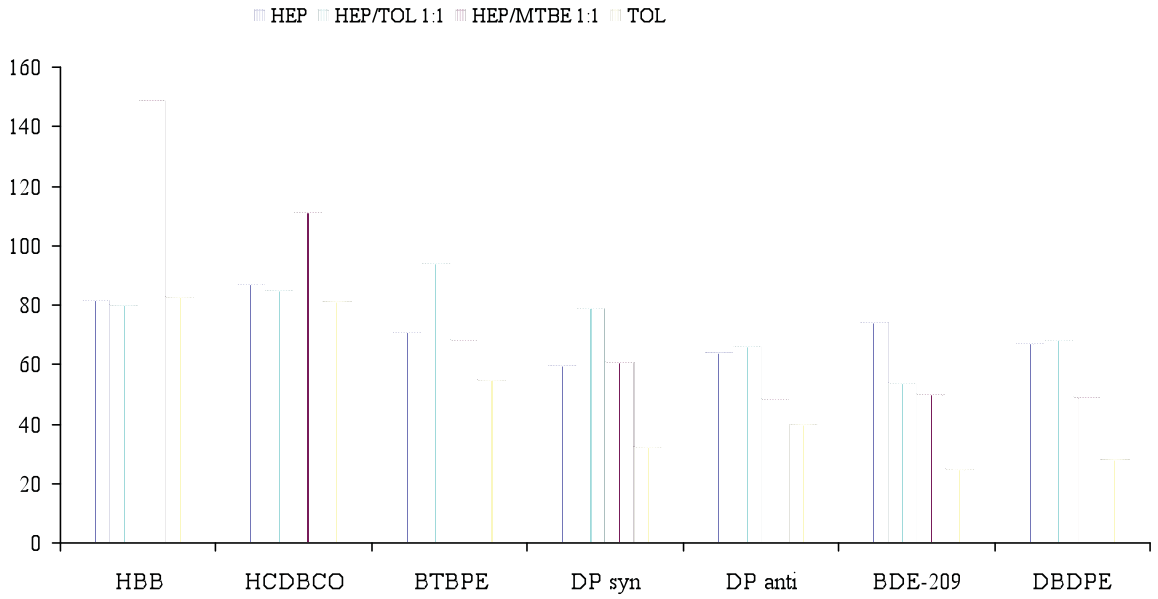
x3

Final Volume

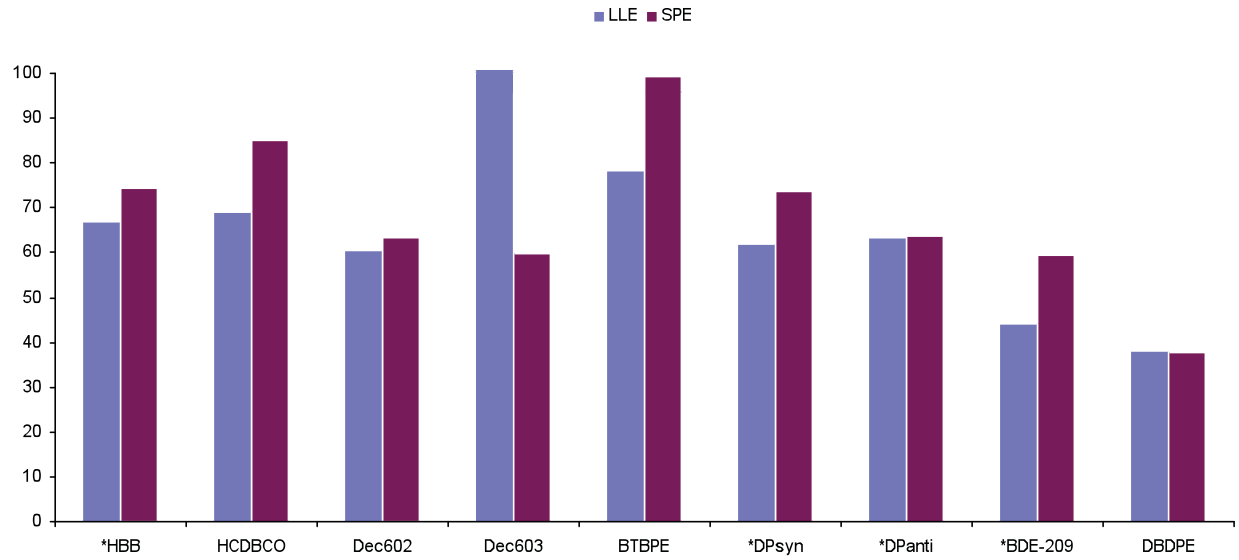
12 mL (Hep/Tol 1:1)

LLE recoveries

Horse serum

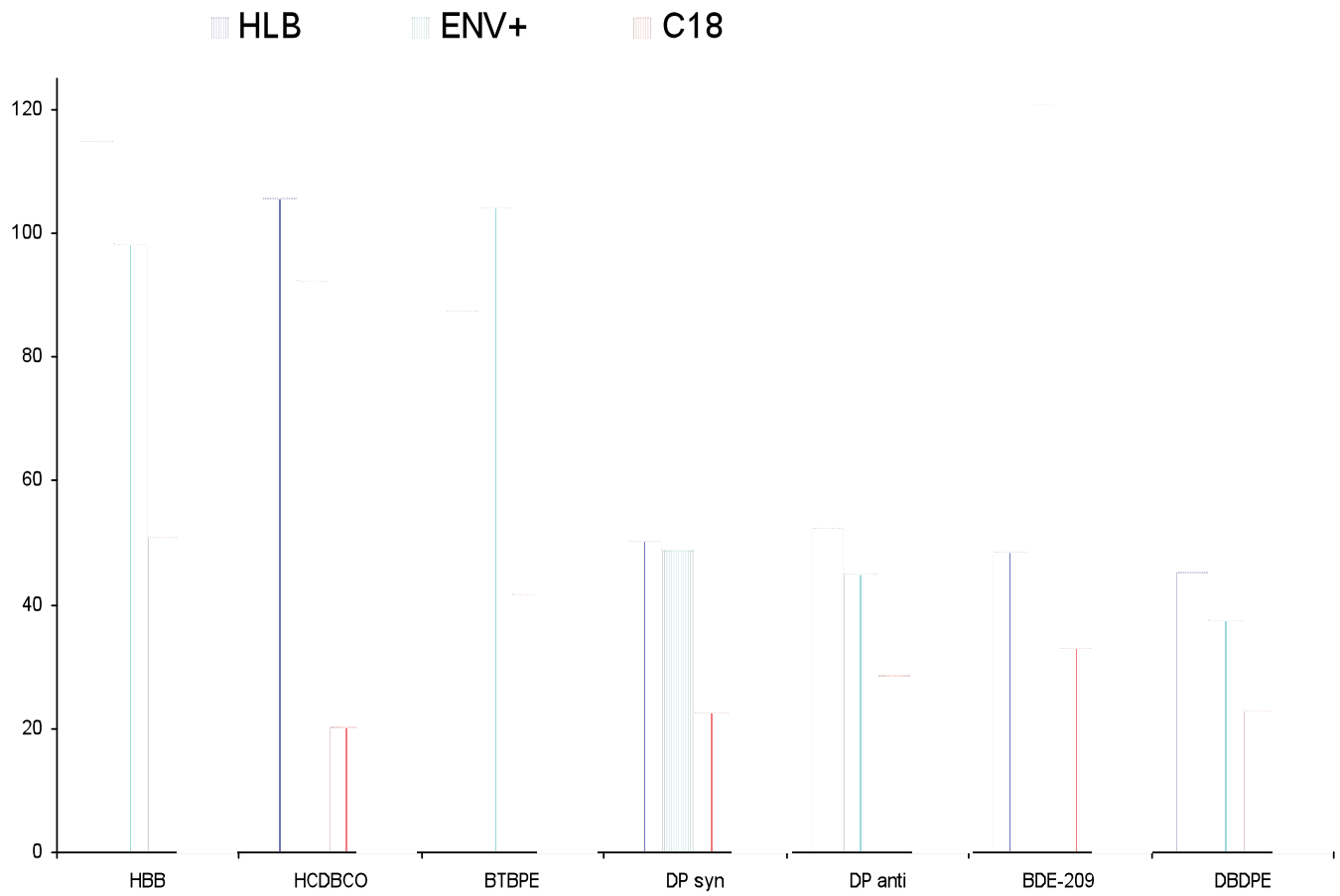


Human serum



Recoveries

- Comparing SPE (and LLE) recoveries in horse serum



- SPE (**HLB**) RSD ranged from 8 to 22 % (n=3).
- LLE (**Hep/Tol 1:1**) RSD ranged from 4 to 11 % (n=3).