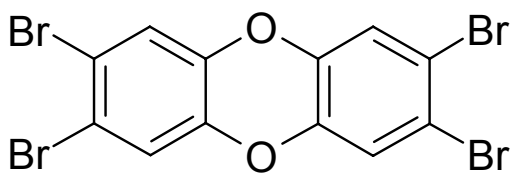
Brominated dioxins in plastic products

Emissions during fires and levels in sediments

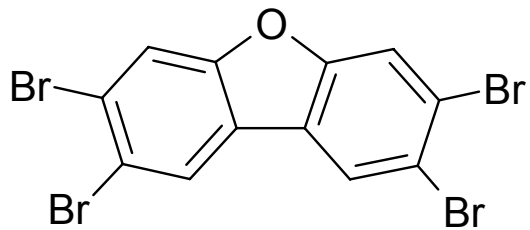
Staffan Lundstedt & Peter Haglund
Department of Chemistry
Umeå University

Brominated dioxins - PBDD/Fs

- **Analogous to the more well known chlorinated dioxins, but with bromine instead of chlorine, i.e. 75 PBDDs and 135 PBDFs.**
- **Also 4600 mixed bromo-chloro dioxins**
- **Seem to have similar toxicities**
- **PBDD/Fs are highly lipophilicand adsorb strongly to particles**
- **Debrominates easily in solution and in the atmosphere.**



2,3,7,8-tertabromo dibenzo-p-dioxin



2,3,7,8-tertabromo dibenzofuran

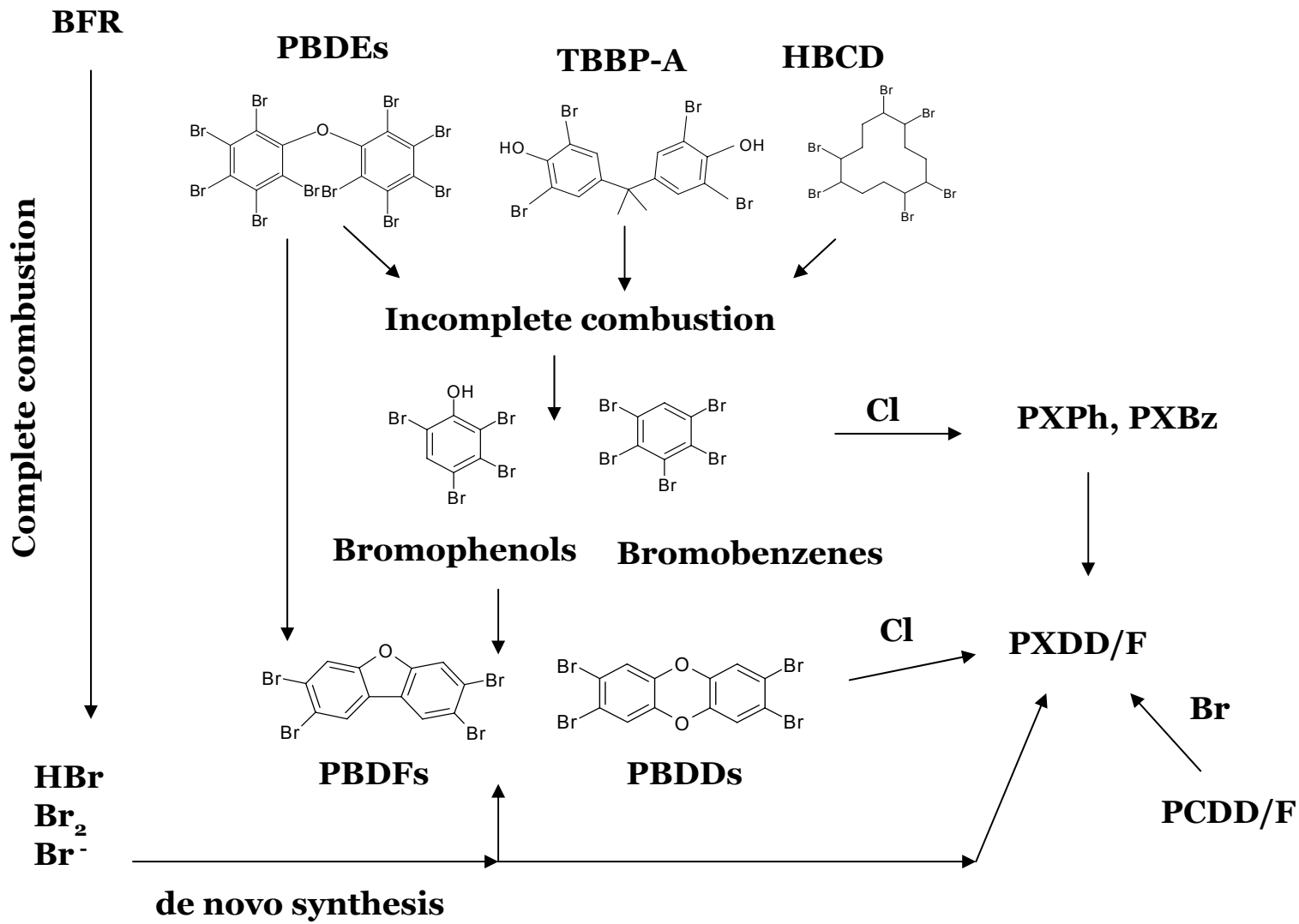
Why PBDD/Fs in plastics?

The PBDD/Fs originate from brominated flame retardants (BFR) that can be applied in plastic materials up to 20%.

- **Impurity in technical BFR-mixtures**
  (Hanari et al. 2006, Ren et al. 2011)
- **Formation of PBDD/Fs as BFR-containing materials are processed into refined products.**
  (Luijk et al. 1992, Weber & Kuch 2003)
- **Transformation of BFRs (e.g. PBDEs) into PBDD/Fs as the material or the product are exposed to heat or natural sunlight.**
  (Ebert & Bahadir 2003, Kajiwara et al. 2008)

Levels up to 1.3 mg/g (0.13 %) have been reported in PBDE-plastics. Much lower levels in plastics containing other BFRs

Formation of PBDD/Fs during combustion



PBDD/F-emissions during fires

- **To what extent are PBDD/Fs emitted during accidental fires in BFR-containing material?**
- **To what extent does this lead to environmental contamination?**

Typical for accidental fires like these:

✓ Poor and variable combustion conditions (oxygen supply and temperature)

✓ Bromine and PBDD/F-precursors highly available

Studied fires:

➢ Residental houses

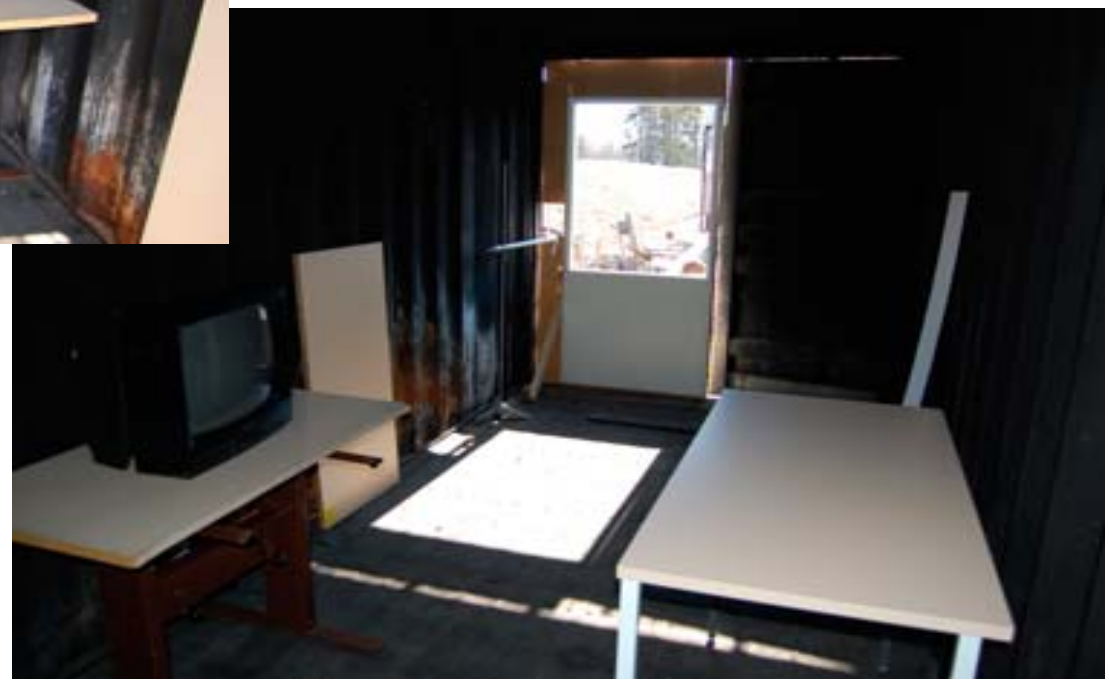
➢ A shopping mall and a big boat storage house

➢ Recycling plants for plastics and **electronic waste**

➢ **A simulated TV-fire**

Simulated TV-fire

Before the fire



Early during the fire

During the fire

After the fire

After the fire

Sampling after the fire

Levels of BFRs and dioxins in the TV and in the ash

ng/ g	Tv-cabinet	PC-board	Ash
Σ PBDE	18 000 000	18 000	370
TBBPA	1 900	2 600 000	3,4
Σ PBDD/ F	590 000	400	740
Σ PBCDD/ F	<0,05	<0,05	4,7
Σ PCDD/ F	1,0	3,8	1,6

- **1,8% PBDE in the TV-cabinet (3,4 kg), corresponding to 61 g pure PBDEs.**

- **0,26% TBBPA in the PC-board (230 g), corresponding to 0,61 g pure TBBPA.**

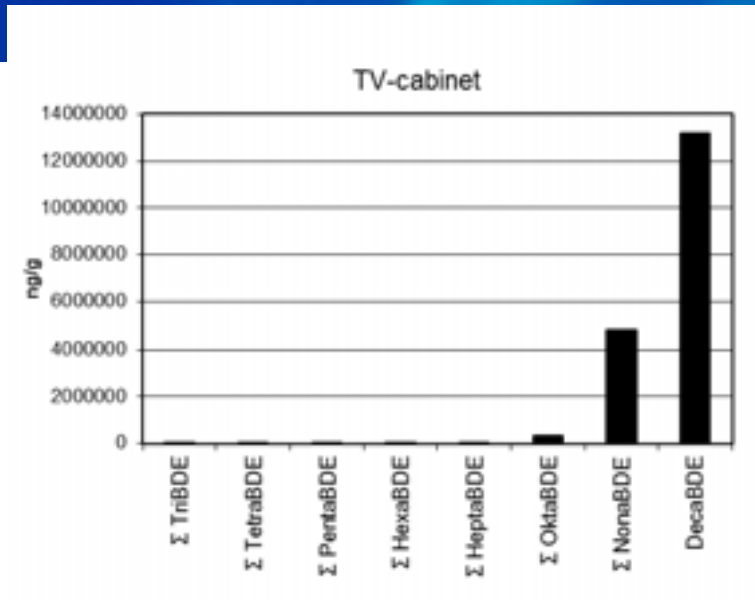
- **0,059% PBDD/F in the TV-cabinet, corresponding to 2 g pure PBDD/Fs.**

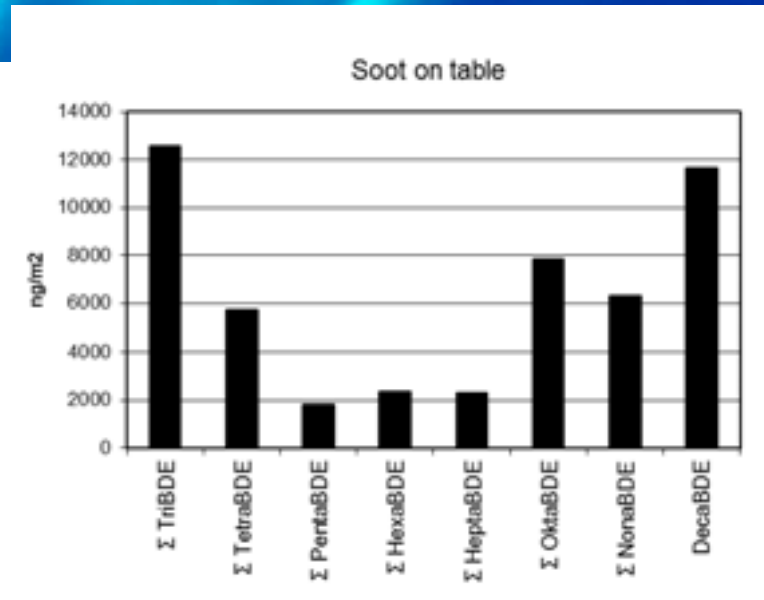
Amounts of BFRs and dioxins in the soot

ng/ m²	Table top	Table	Radiator	Plasterboard	Door	Glass [a]
Σ PBDE	14 000	51 000	1600	8700	730	480 000
TBBPA	440	1700	26	62	3,2	470
Σ PBDD/ F	95 000	370 000	21 000	110 000	14 000	610 000
Σ PBCDD/ F	220	660	26	140	15	2100
Σ PCDD/ F	3,7	17	1,6	4,4	10	-

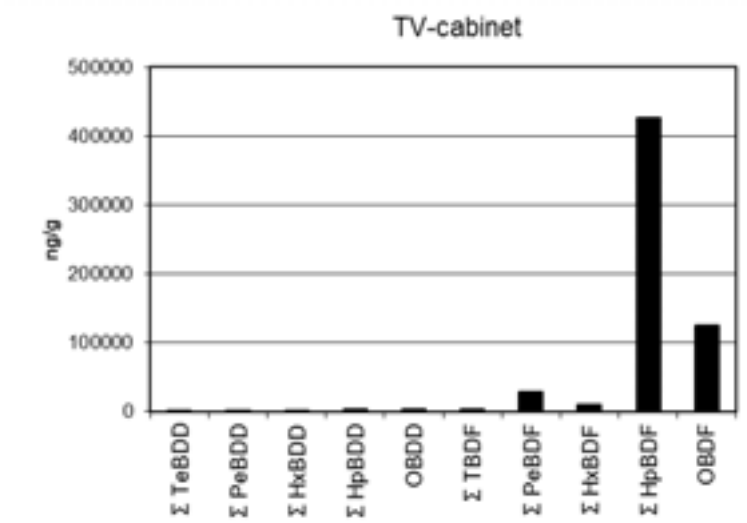
Congener profiles in TV-cabinet and soot for…

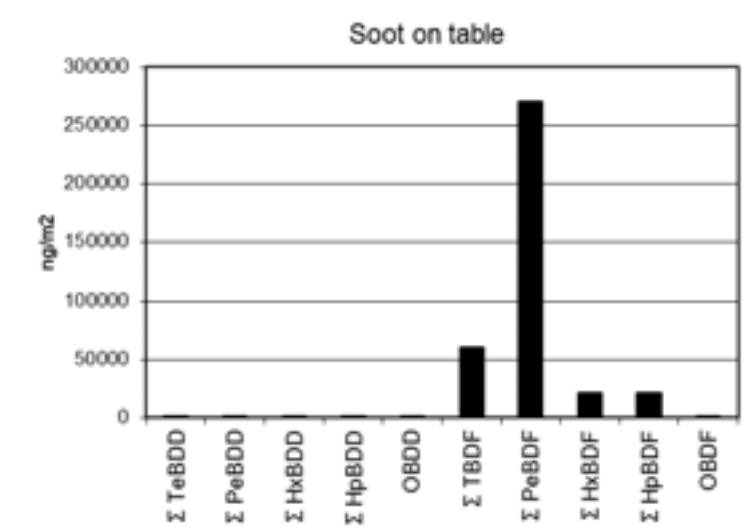
PBDEs





PBDD/Fs

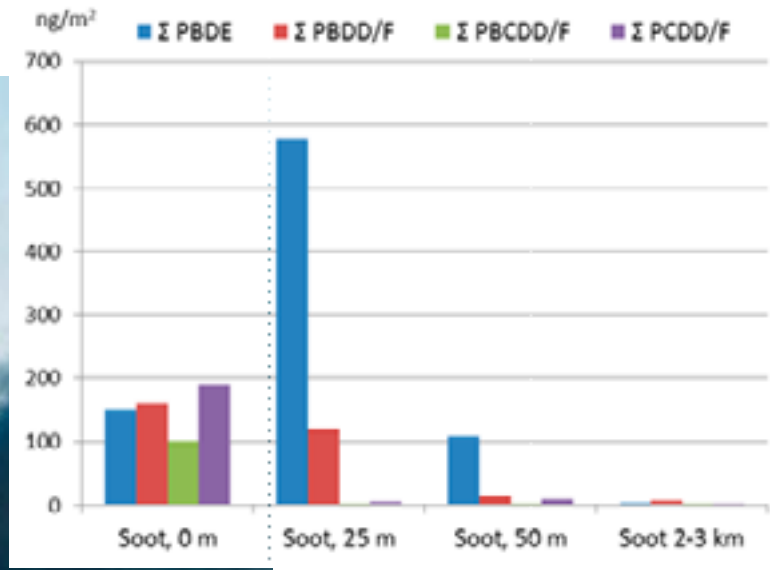




Fire at an e-waste recycling facility….

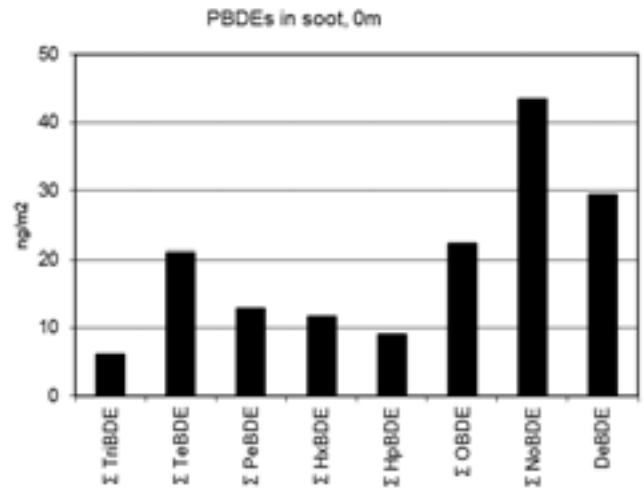
	E-waste ng/ g	Burnt e-waste ng/ g	Ash of e-waste ng/ g	Ash in office ng/ g
Σ PBDE	38000	2100	56	0,29
Σ PBDD/ F	1300	11000	28	0,44
Σ PBCDD/ F	33	15	110	0,47
Σ PCDD/ F	23	13	160	4,0

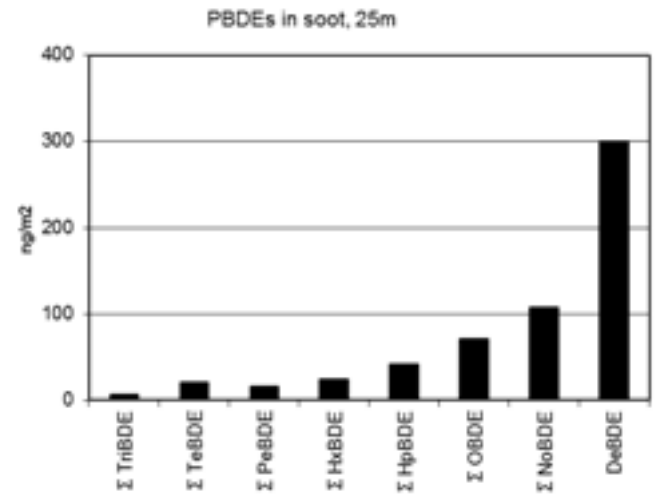
Emissions from the e-waste facility….



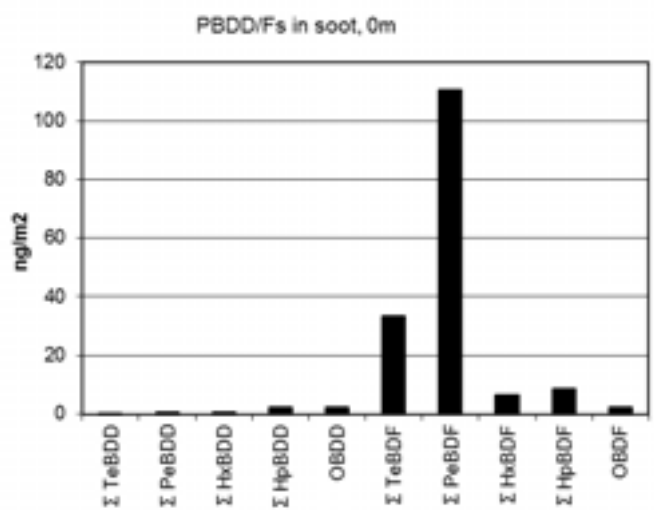
Congener profiles in the soot for…

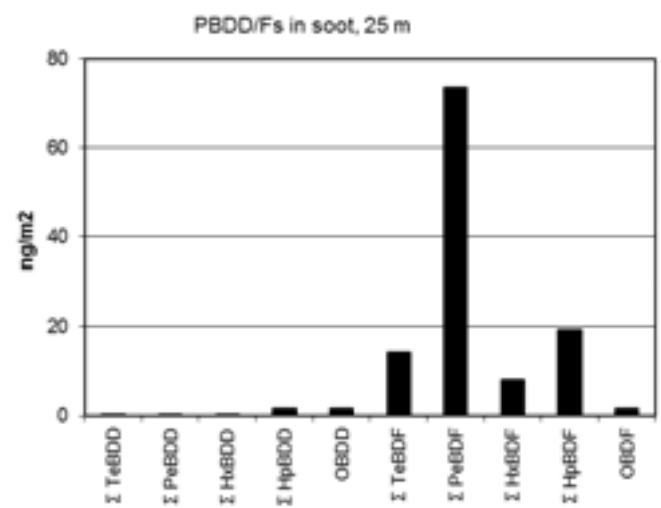
PBDEs



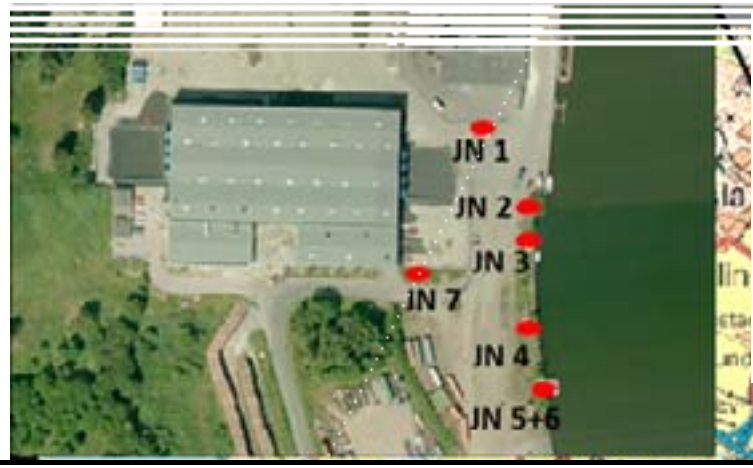


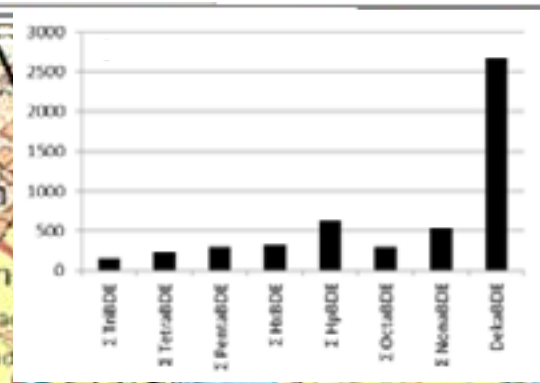
PBDD/Fs

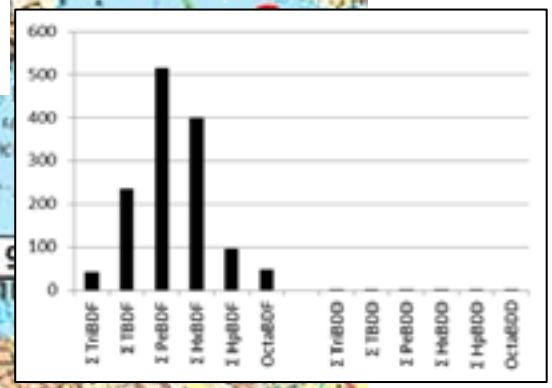


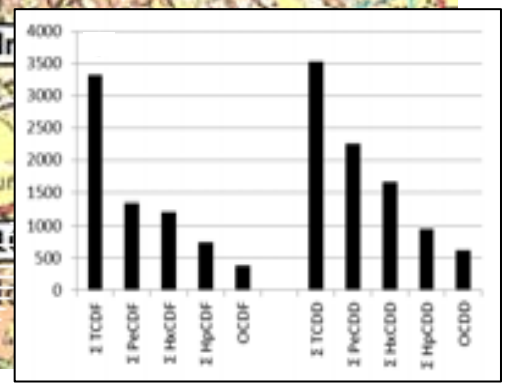


Samples of soil, sediment and fish at the e-waste recycling facility





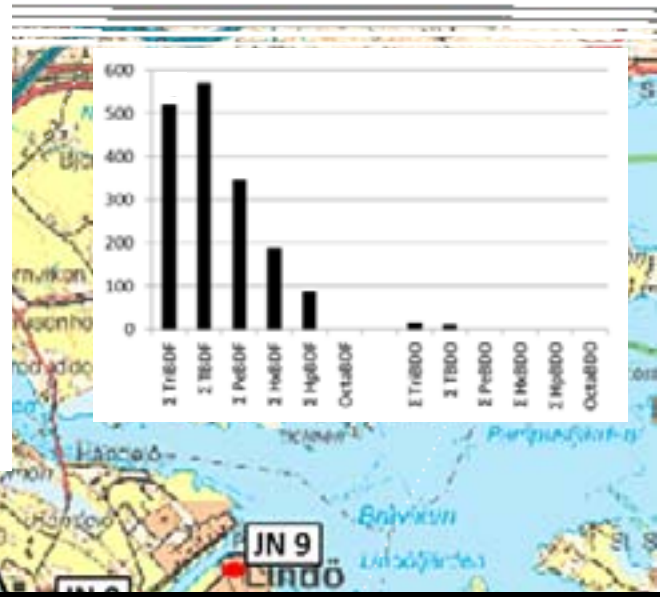


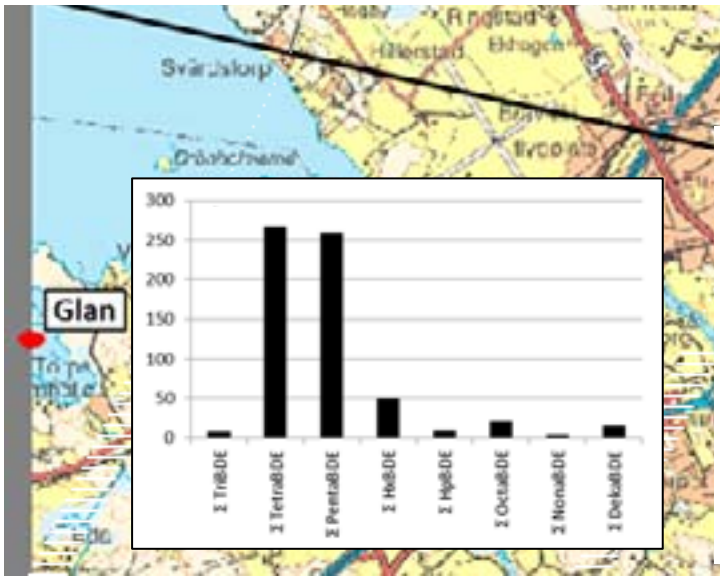


Soil samp	Fraction org.mtrl. (%)	ΣPBDE (ng g^{-1})	ΣPBDD/F (ng g^{-1})	ΣPCDD/F (ng g^{-1})	ΣPBDD/F (pg TEQ g^{-1})	ΣPCDD/F (pg TEQ g^{-1})
JN 1	23	5100	1300	16	5100	170
JN 2	20	1800	12	4,3	41	44
JN 3	8,9	930	33	7,5	110	82
JN 4	23	92	3,0	1,5	14	12
JN 5	9,9	17	0,54	1,7	3,7	12
JN 6	6,6	0,71	0,085	0,86	0,074	4,9
JN 7	9,9	30	0,54	0,65	3,5	6,0
JN 8	6,0	0,25	0,12	0,049	0,017	0,57
JN 9	1,2	0,36	0,040	0,024	0,048	0,27
JN 10	29	1,9	0,19	0,97	0,57	12

Samples of soil, sediment and fish at the e-waste recycling facility

Sediment samples	Fraction org.mtrl. (%)	ΣPBDE (ng g^{-1})	ΣPBDD/F (ng g^{-1})	ΣPCDD/F (ng g^{-1})	ΣPBDD/F (pgTEQ g^{-1})	ΣPCDD/F (pgTEQ g^{-1})
Glan 1	12	4.4	0,085	1,3	0,55	13
Glan 2	15	16	0,082	1,9	0,78	15
Strömsholmen	2,2	51	0,41	0,31	2,4	2,6
Blixholmen 1	20	55	0,63	2,0	3,3	12
Blixholmen 2	20	62	1,7	2,0	5,1	9,0
Händelö 1	14	33	0,46	1,7	2,2	7,1
Händelö 2	15	29	0,72	1,8	4,2	7,0



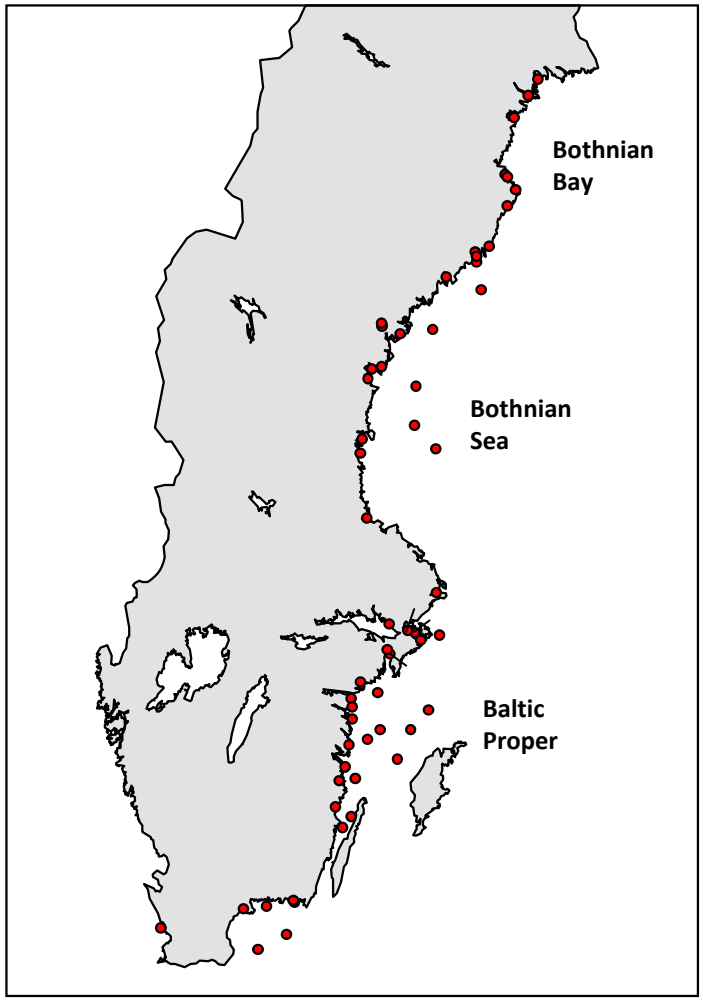


Fish samples	Fat cont. (%)	ΣPBDE (pg g^{-1})	ΣPBDD/F (pg g^{-1})	ΣPCDD/F (pg g^{-1})	ΣPBDD/F (pgTEQ g^{-1})	ΣPCDD/F (pgTEQ g^{-1})
Glan	0,57	170	<10*	19	<0,5*	0,27
Strömsholmen	0,60	340	<10*	13	<0,5*	0,17
Blixholmen	0,64	640	<10*	9,8	<0,5*	0,15
Händelö	0,67	560	<10*	13	<0,5*	0,22
Esterö, Bråviken	0,74	110	<10*	5,4	<0,5*	0,14

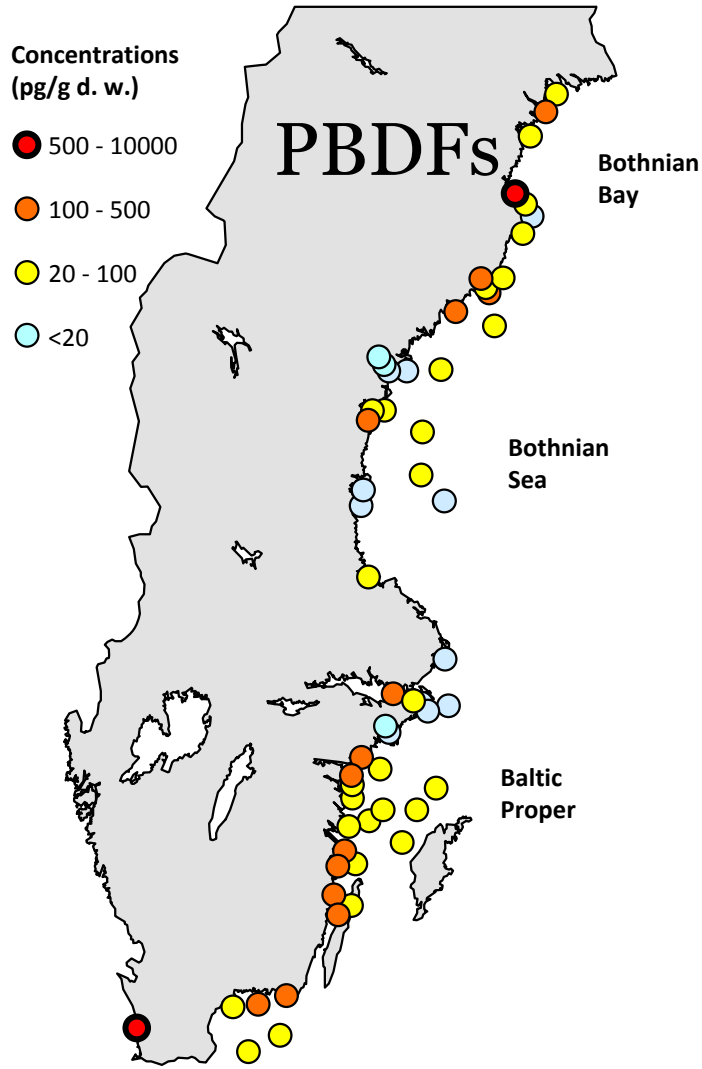
How far do the the PBDD/Fs get?

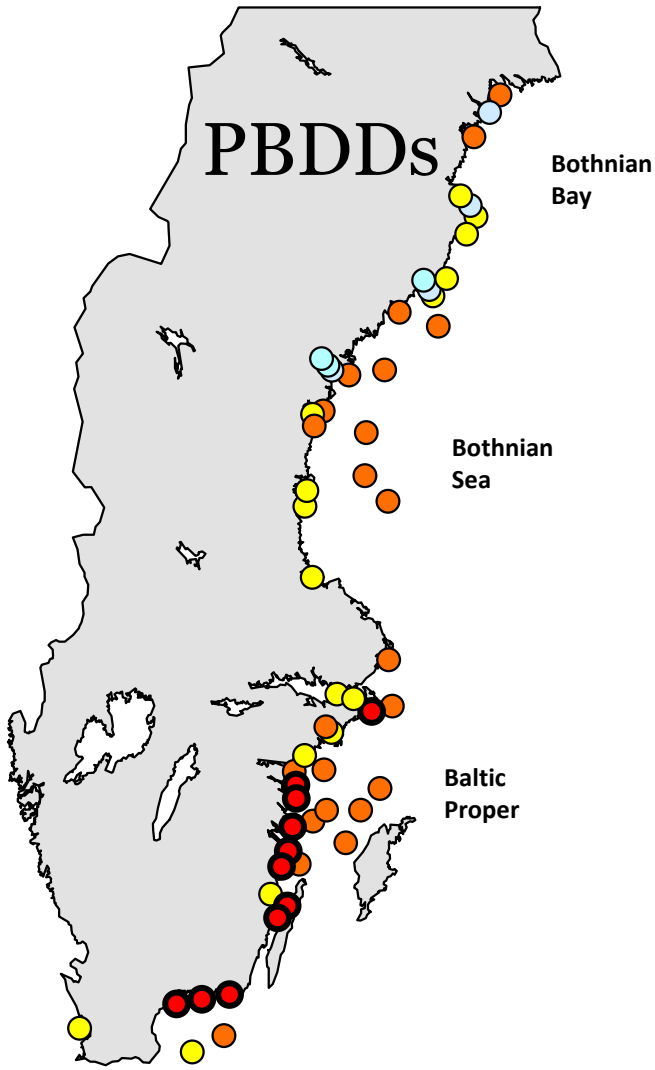
- Screening of PBDD/Fs in marine sediments from the Baltic Sea
- Measuremens of PBDD/Fs in human milk
- Are there other sources?

Sampling sites

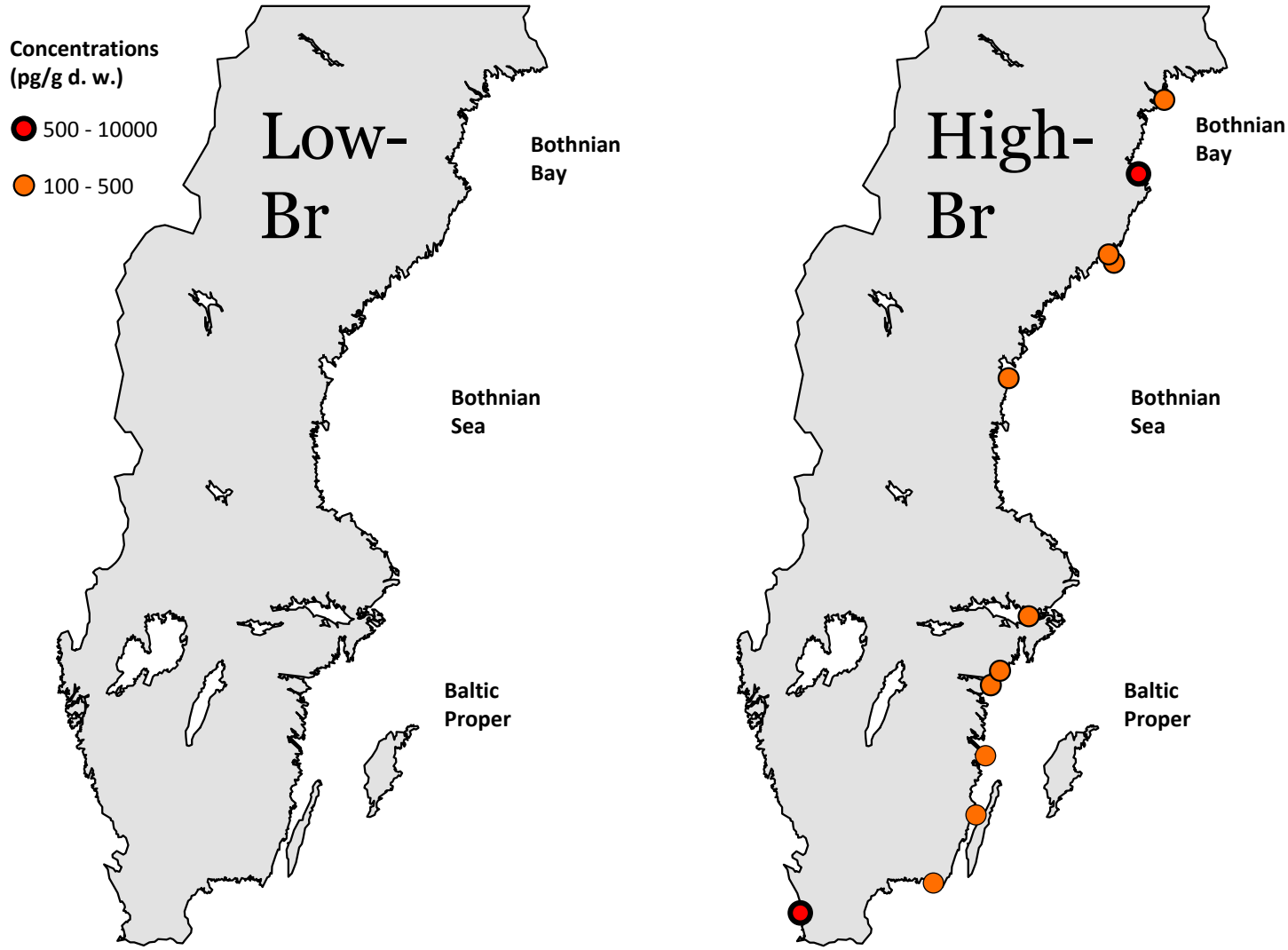


Total concentrations

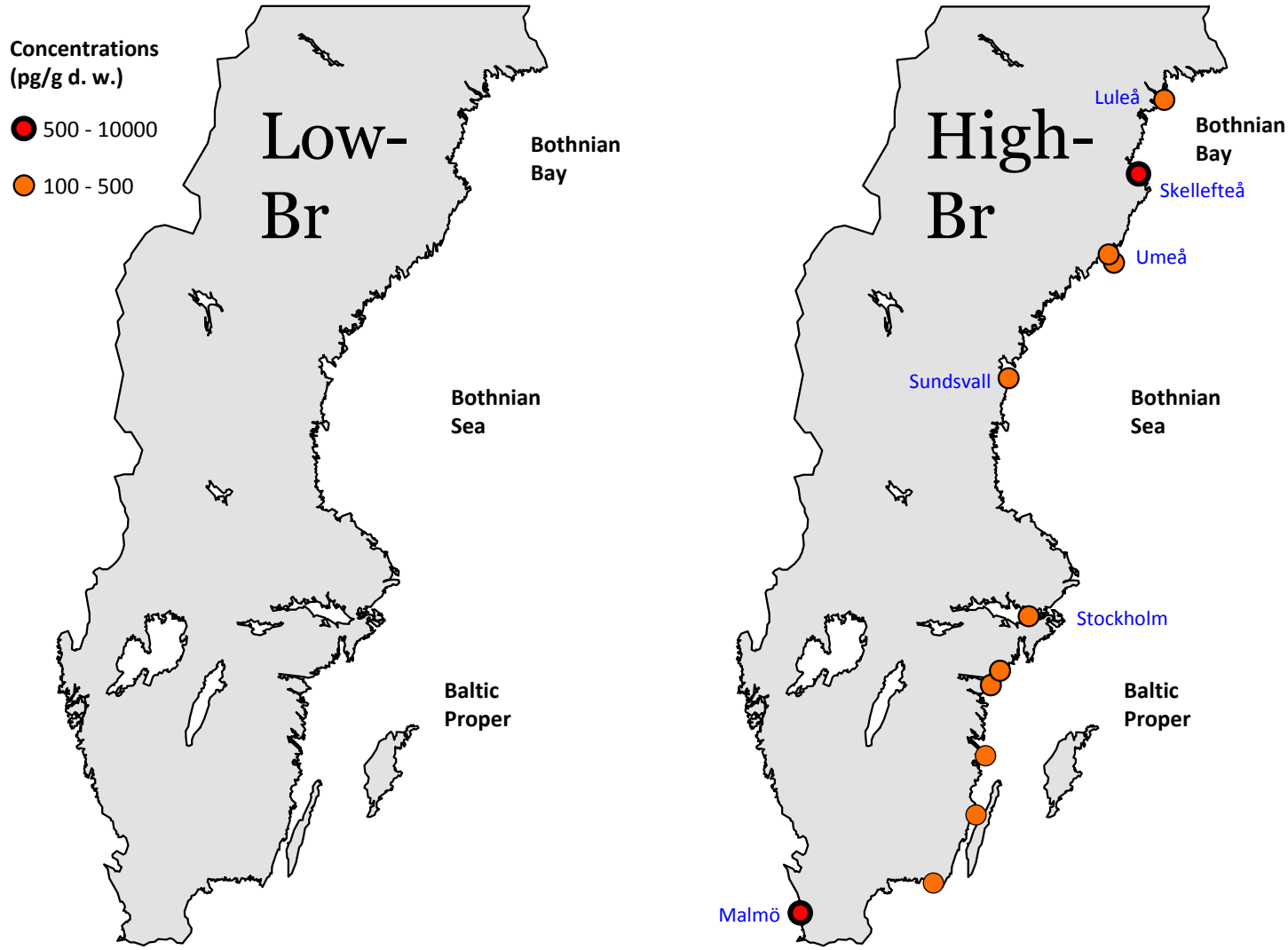




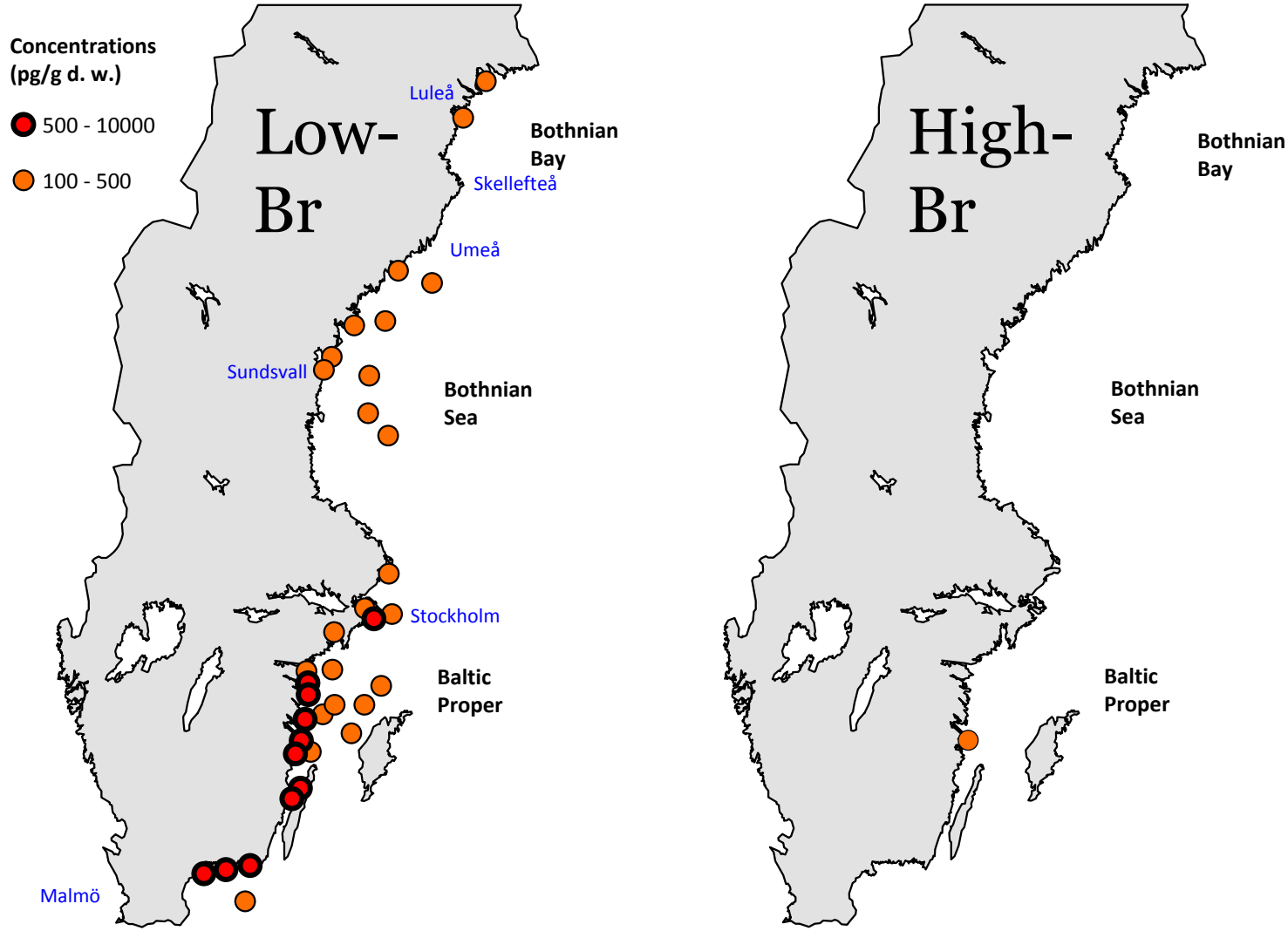
”Furan” concentrations



”Furan” concentrations



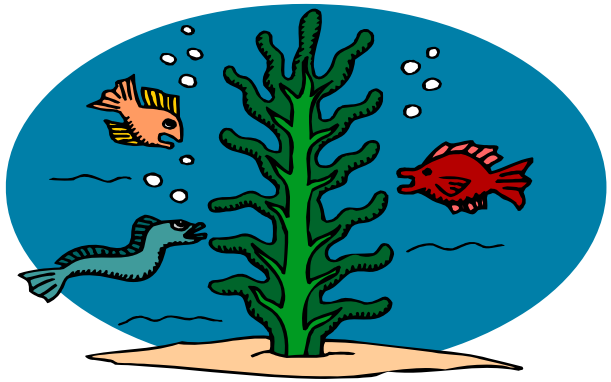
”Dioxin” concentrations

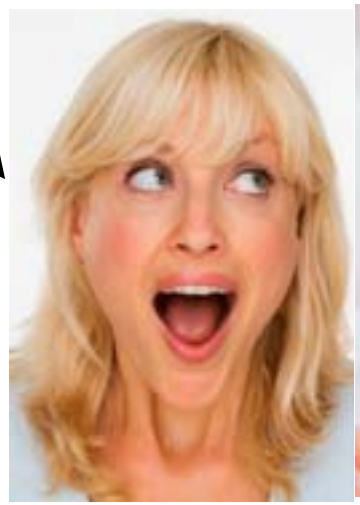


Sources - Exposure

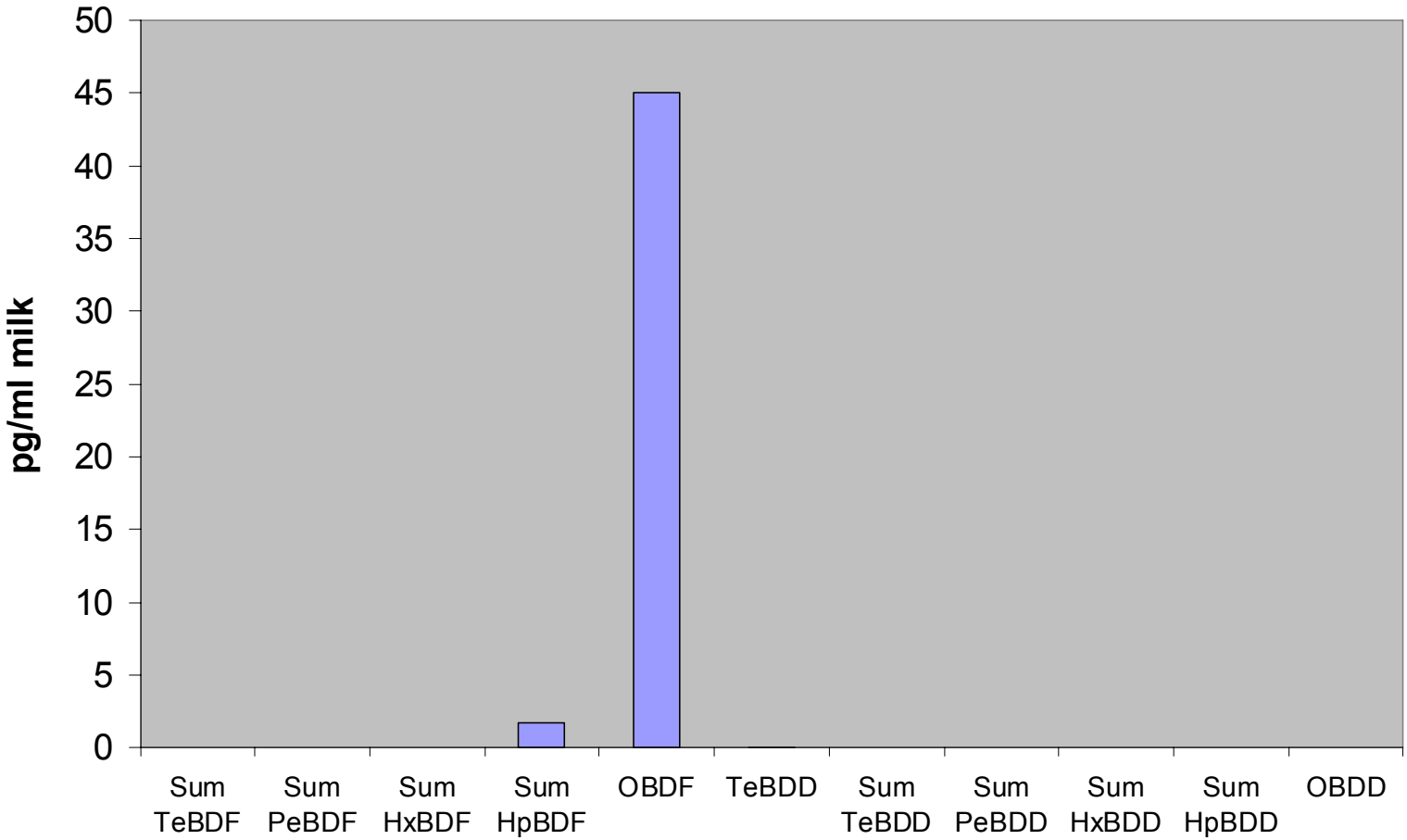
Higly-Br furans

Low-Br dioxins

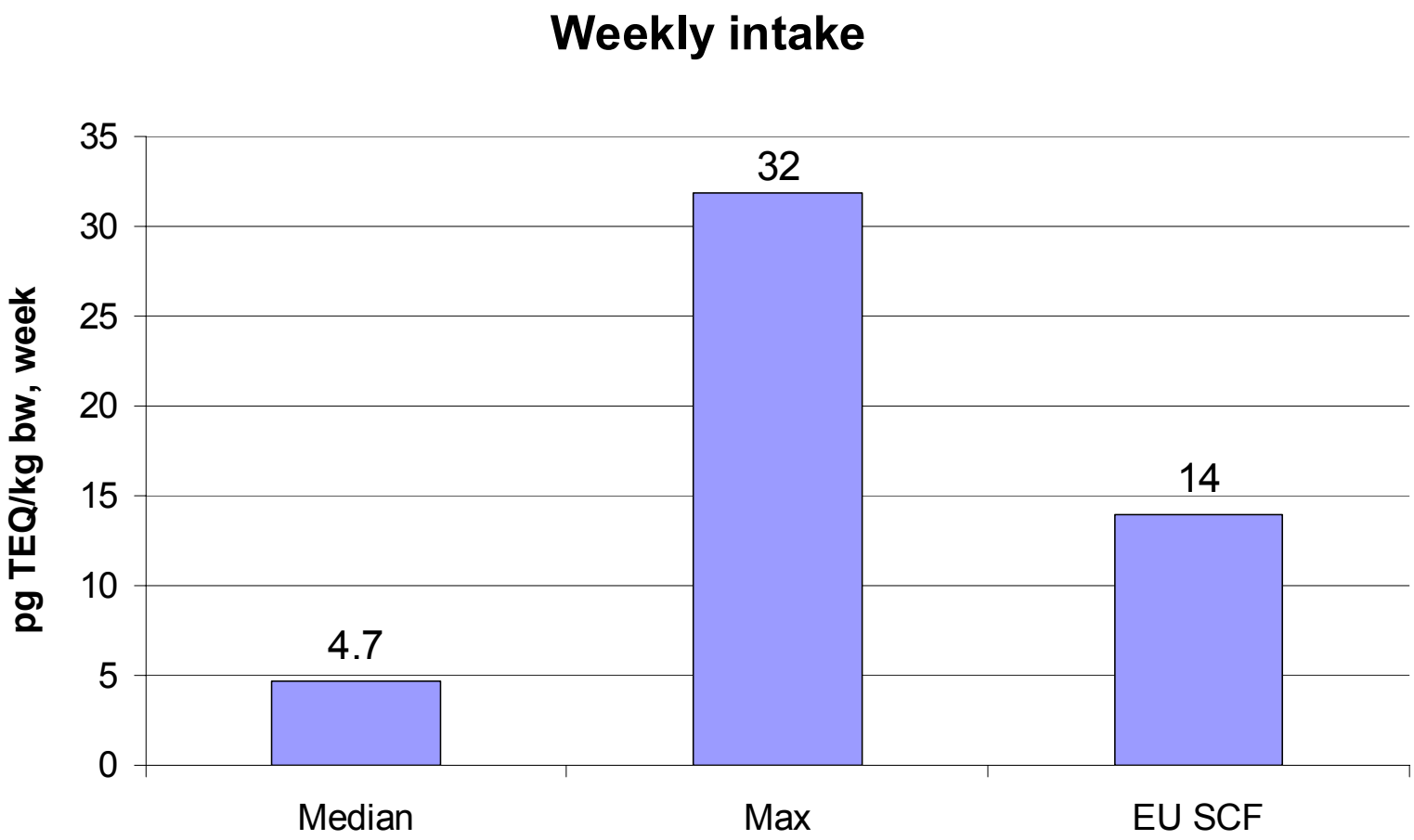




PBDD/F profile in human milk



Infant PBDD/F exposure



Conclusions

- Plastics and other materials containing BFRs may also contain significant amounts of PBDD/Fs, particularly if the BFRs are composed of PBDEs
- During accidental fires the PBDD/F-emission may be great.
- The emissions may lead to significant contamination of the surroundings
- Emissions and leakage from PBDE-containing material is probably a major source of PBDD/Fs to the environment (although not only from fires).

- PBDF levels in sediment are correlated to urbanization/industialization
- PBDD levels in sediment are correlated to primary production

- Infants are exposed to relatively high levels of PBDD/Fs
- TEFs for PBDD/Fs needs to be established

Thank you!

Staffan Lundstedt & Peter Haglund
Department of Chemistry
Umeå University

E-mail and phone:

staffan.lundstedt@chem.umu.se

+46-90-786 6654

peter.haglund@chem.umu.se

+46-90-786 6667