Long-Range Transport of Various BFRs: non-PBDEs in Comparison to PBDEs

Martin Scheringer, Sebastian Strempel, Carla Ng, Konrad Hungerbühler

ETH Zürich, Zürich, Switzerland

Norman Workshop on "New" Flame Retardants Stockholm, Sweden, November 23–24, 2011

General Main Points

Many non-PBDE BFRs have properties similar to those of PBDEs

- intended: effective as flame retardants unwanted effects (smoke)?
- unintended: POPs and PBT properties
- Based on screening exercises using estimated physicochemical properties and degradation half-lives

Key question:

What level of detail do we need to reach in our research into non-PBDE BFRs before they can be regulated / banned?



San Antonio Statement on Brominated and Chlorinated FR

Editorial

San Antonio Statement on Brominated and Chlorinated Flame Retardants

doi:10.1289/ehp1003089

Joseph DiGangi,¹ Arlene Blum,^{2,3} Åke Bergman,⁴ Cynthia A. de Wit,⁵ Donald Lucas,⁶ David Mortimer,⁷ Arnold Schecter,⁸ Martin Scheringer,⁹ Susan D. Shaw,¹⁰ and Thomas F. Webster¹¹ ¹International POPs Elimination Network, Berkeley, California, USA; ²Department of Chemistry, University of California, Berkeley, California, USA; ³Green Science Policy Institute, Berkeley, California, USA; ⁴Department of Materials and Environmental Chemistry, and ⁵Department of Applied Environmental Science, Stockholm University, Stockholm, Sweden; ⁶Lawrence Berkeley National Laboratory, Berkeley, California, USA; ⁷Food Standards Agency, London, United Kingdom; ⁸University of Texas School of Public Health, Dallas, Texas, USA; ⁹Institute for Chemical and Bioengineering, ETH Zürich, Zürich, Switzerland; ¹⁰Marine Environmental Research Institute, Center for Marine Studies, Blue Hill, Maine, USA; ¹¹Department of Environmental Health, Boston University School of Public Health, Boston, Massachusetts, USA

The statement is signed by the individual scientists and other professionals listed separately below. Please note that the views expressed are those of the authors and signatories; institutional affiliations are provided for identification purposes only. Abbreviations and an Annotated Statement are available as Supplemental Material (doi:10.1289/ehp.1003089).

We, scientists from a variety of disciplines, declare the following:

1. Parties to the Stockholm Convention have taken action on three brominated flame retardants that have been listed in the treaty

Therefore, these data support the following:

- 11. Brominated and chlorinated flame retardants as classes of substances are a concern for persistence, bioaccumulation, long-range transport, and toxicity.
- 12. There is a need to improve the availability of and access to information on brominated and chlorinated flame retardants and other chemicals in products in the supply chain and throughout each product's life cycle.
- 13 Consumers can play a role in the adoption of alternatives to

Environmental Health Perspectives 118 (2010), A516–A518

PBT Screening Exercise (I)

- How many chemicals exceed P, B, and T thresholds of REACH?
- ◆≈ 3% PBT chemicals among 100,000 chemicals on the market



PBT Screening Exercise (II)

Properties estimated with EpiSuite:

- half-life of aerobic biodegradation (BIOWIN3)
- BCF (BCFBAF)
- ➡ LC₅₀, EC₅₀, NOEC for aquatic species (ECOSAR)

Four hazard classes:

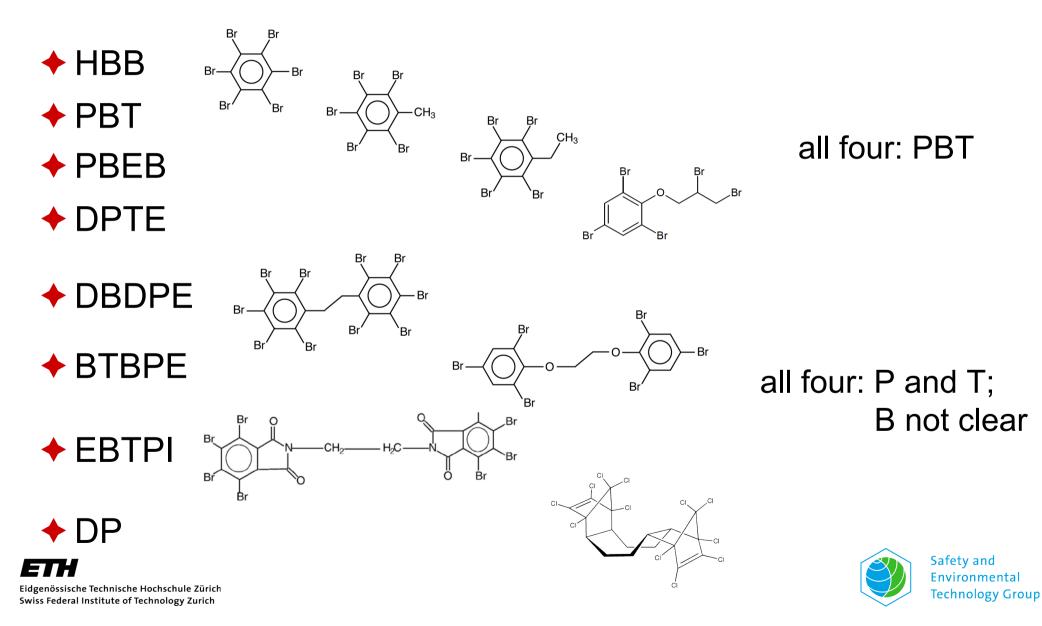
- all three REACH thresholds exceeded: PBT
- two thresholds exceeded: nonPBT2
- one threshold: nonPBT1
- no threshold exceeded: nonPBT0

Calculate a PBT score



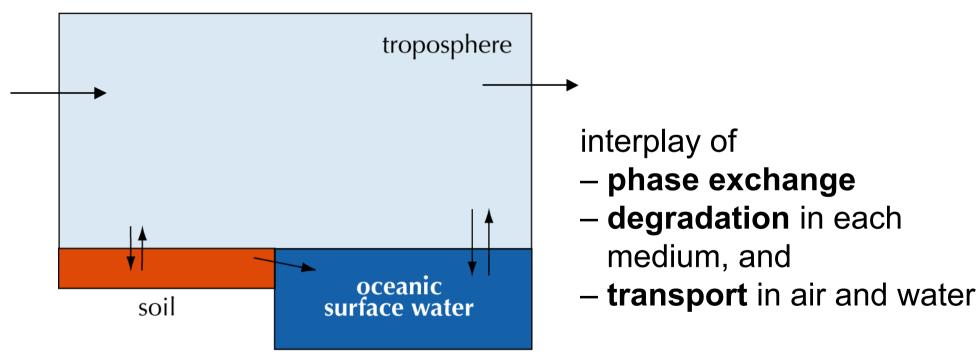
part 1

Results for non-BDE BFRs and DP



Pov and LRTP Screening Exercise

 Calculate overall persistence (Pov) and long-range transport potential (LRTP) with the OECD Tool





part 2

The OECD P_{ov} and LRTP Tool

- Multi-compartment model for the assessment of overall persistence and long-range transport potential
- Developed by ETH Zurich with a mandate by OECD
- Endorsed by a larger group of model developers
- Available from OECD website: <u>http://tinyurl.com/66q47j</u>
- Now a standard tool for Pov and LRTP assessments
- Described in a journal paper by Wegmann et al., Environmental Modeling & Software 24 (2009), 228–237.

The Tool: User Interface and Input Data

NECD Pov & LRTP

- Left: databases
- Right: single chemical
- Color code: quality of input data
- Chemical property data required:
 - $\log_{10} K_{aw}$
 - $\rightarrow \log_{10} K_{\rm ow}$
 - degradation half-lives air water

soil

Eidgenössische Technische Hochschule Zürich Swiss Federal Institute of Technology Zurich

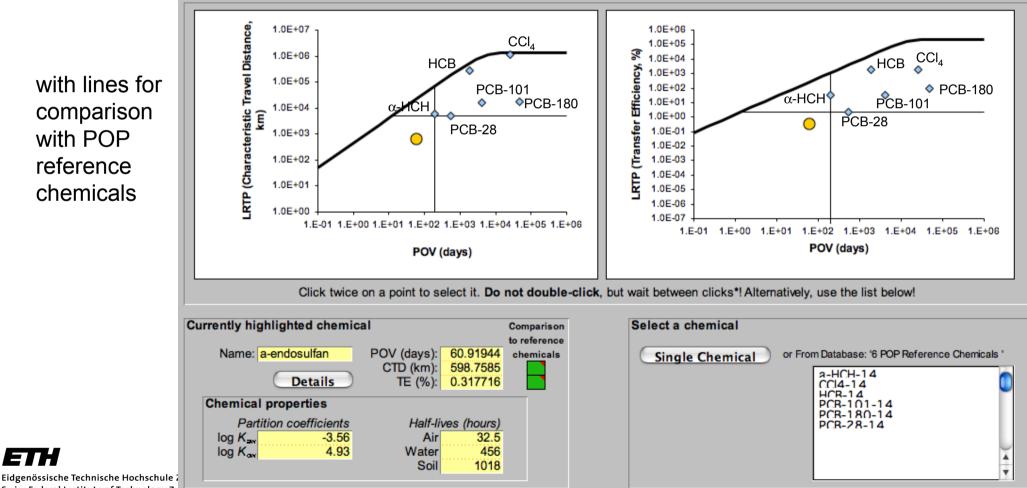
Screening Tool*	Main M	CNU Help	Preferences
		cals to evaluate ase and one chemical are	possible.
Reference Chemicals Generic PCR Homologues History	0	Single Chemical Name Molecular mass Log K _{av} Log K _{ov} Half life in air (h)	a-endosulfan -3.56 4.93 3.25E+01
Deselect Manage Database Statu		Half life in water (h) Half life in soil (h)	4.56E+02 1.02E+03 Clear Chemical Status:
Color C	Calcu	ulate 🗌 🗆 Inclu	ude Monte Carlo Analys
	Res	sults already present	
		Warnings: calculation pos	sible
		· ·	
	W/2	rnings: calculation still pos	ssible
		prs: calculation impossible	

* A manual describing this software is provided on the Help page.

part 2 The Tool: Presentation of Results

+ Left graph: Characteristic Travel Distance vs. P_{ov}

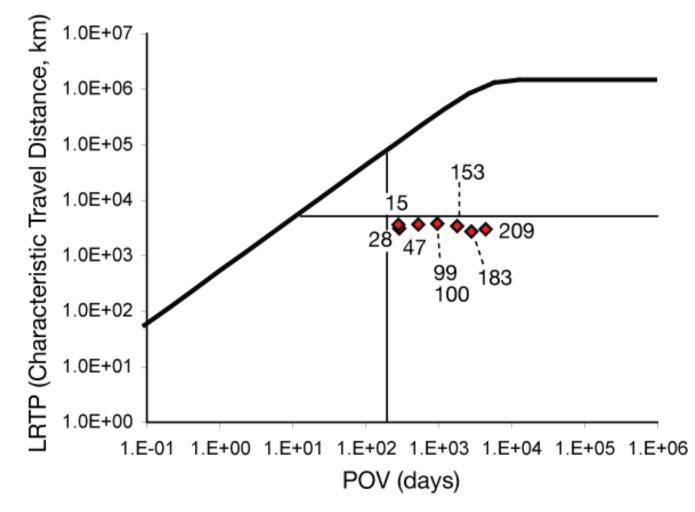
 \bullet Right graph: Transfer Efficiency vs. P_{ov}



Swiss Federal Institute of Technology Zu

The Tool: Results for PBDEs

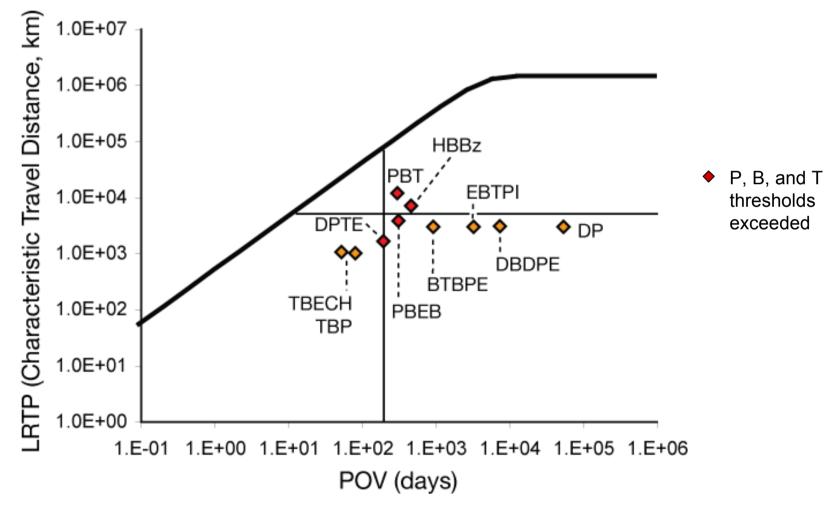
+ Similar CTDs; Pov varies because of $t_{1/2}$ in soil.



part 2

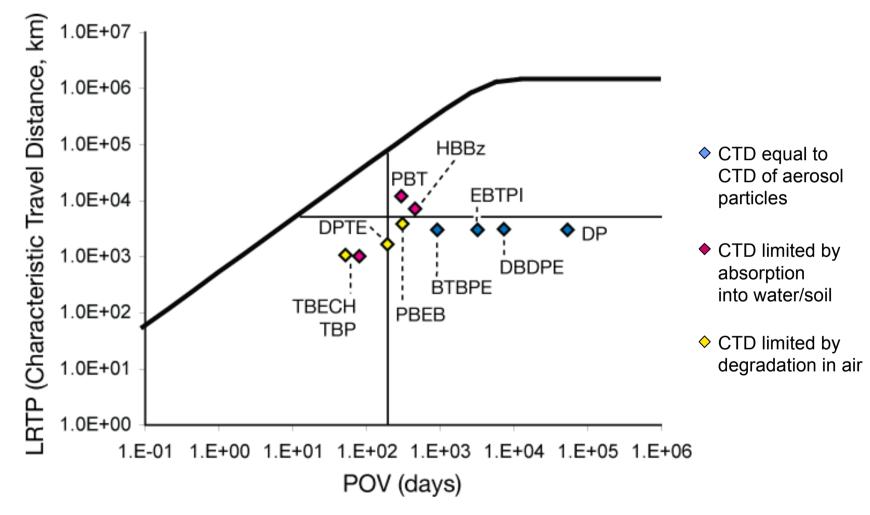
The Tool: Results for non-BDE BFRs

TBECH and TBP lower; others like PBDEs



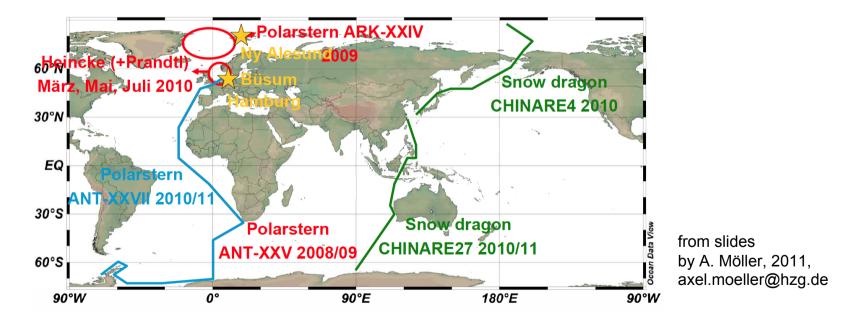
The Tool: Results for non-BDE BFRs

TBECH and TBP lower; others like PBDEs



Eidgenössische Technische Hochschule Zürich Swiss Federal Institute of Technology Zurich part 3 Recent Field Data on Emerging FRs

- Measurements in air and water by Axel Möller et al., Helmholtz Research Center Geesthacht, Germany:
 - HBB, DPTE, DP present in all samples from Arctic to Antarctic
 - ♦ other non-PBDEs present in some samples: PBT, TBPH, BTBPE, TBB, ...
 - concentrations similar to or higher than for PBDEs



A. Möller et al., Environ. Pollut. 159 (2011) 1577–1583; A. Möller et al., Environ. Sci. Technol. 44 (2010), in press
A. Möller et al., Environ. Sci. Technol. 45 (2011), in press; A. Möller et al., Atmos. Environ. (2011), in press;
^h Z. Xie et al. Environ. Sci. Technol. 45 (2011), 1820–1826

Eidgenössische Technische Hochschule Zürich Swiss Federal Institute of Technology Zurich

Are We On the Wrong Track?

- M. Zennegg, "Novel" Brominated Flame Retardants in New Products of the Swiss Market¹
- 2023 new products controlled by XRF (market survey 2008/09)
- ◆ 26% (*n* = 529) with bromine above 500 ppm
- 254 analyzed with GC/MS, LC/MS or GC/ECD for target compounds: PBDEs, HBCD, TBBPA, PBB
- ♦ 58 (23%) contained target compounds
- 196 (77%) contained bromine in unknown compounds

Swiss Federal Laboratories for Materials Testing and Research (Empa), Laboratory for Analytical Chemistry, Dübendorf, Switzerland, markus.zennegg@empa.ch

General Main Points

Many non-PBDE BFRs have properties similar to those of PBDEs

intended: effective as flame retardants - unwanted effects (smoke)?

unintended: POPs and PBT properties

 Based on screening exercise using estimated physicochemical properties and degradation half-lives

Key question:

What level of detail do we need to reach in our research into non-PBDE BFRs before they can be regulated / banned?

Current scheme of substitution needs to be changed