

# Investigating Variability in HBCDD Diastereomer Profile in the Environment

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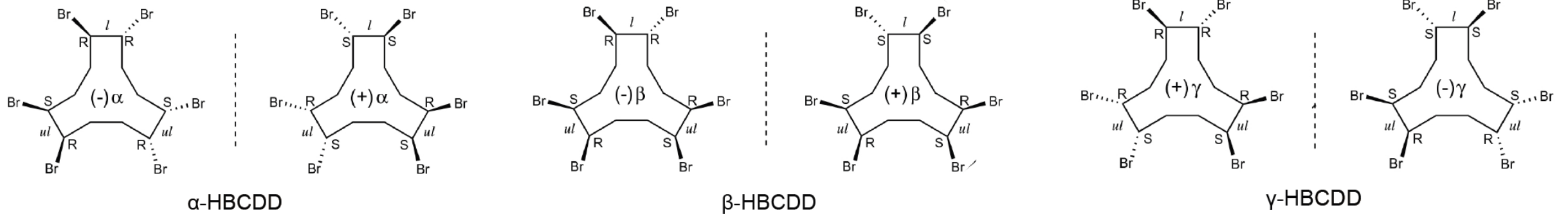
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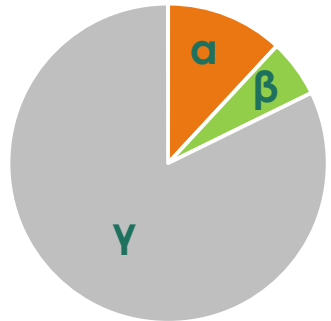
# Hexabromocyclododecane (HBCDD)

- Brominated flame retardant applied in polystyrene foams
  - Expanded polystyrene (EPS): insulation boards, packaging materials
  - Extruded polystyrene (XPS): insulation boards
- Included into the Stockholm Convention in 2013 for elimination
- Diastereomers



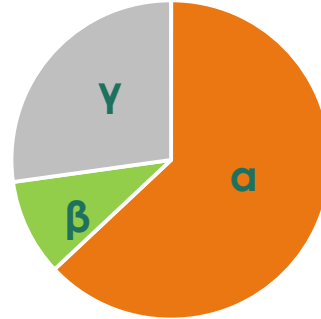
# Variability in HBCDD Diastereomer Profile

- Why can we observed diverse HBCDD diastereomer profile?

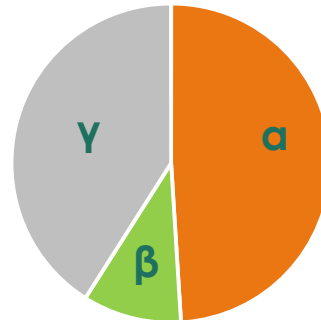


Technical HBCDDs  
(Heeb et al., *Chemosphere*, 2005)

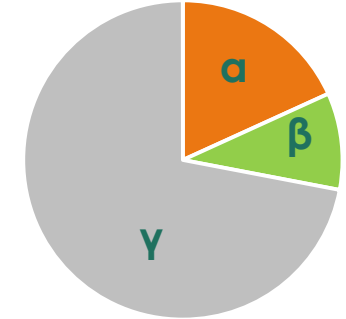
Isomerization →



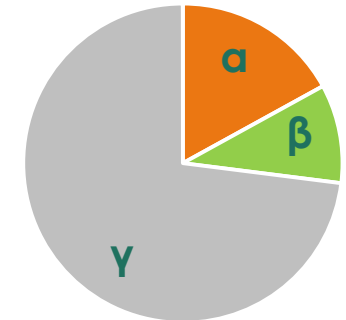
Guangzhou, urban air (n=32)  
(Yu et al., *ES&T*, 2008)



Shanghai, urban soil (n=27)  
(Wu et al., *Sci. Total Environ.*, 2005)



Svalbard, air (n=152)  
(Mano et al., NILU, 2010)



Tianjin, industrial soil (n=7)  
(Zhu et al., *Environ. Pollut.*, 2017)

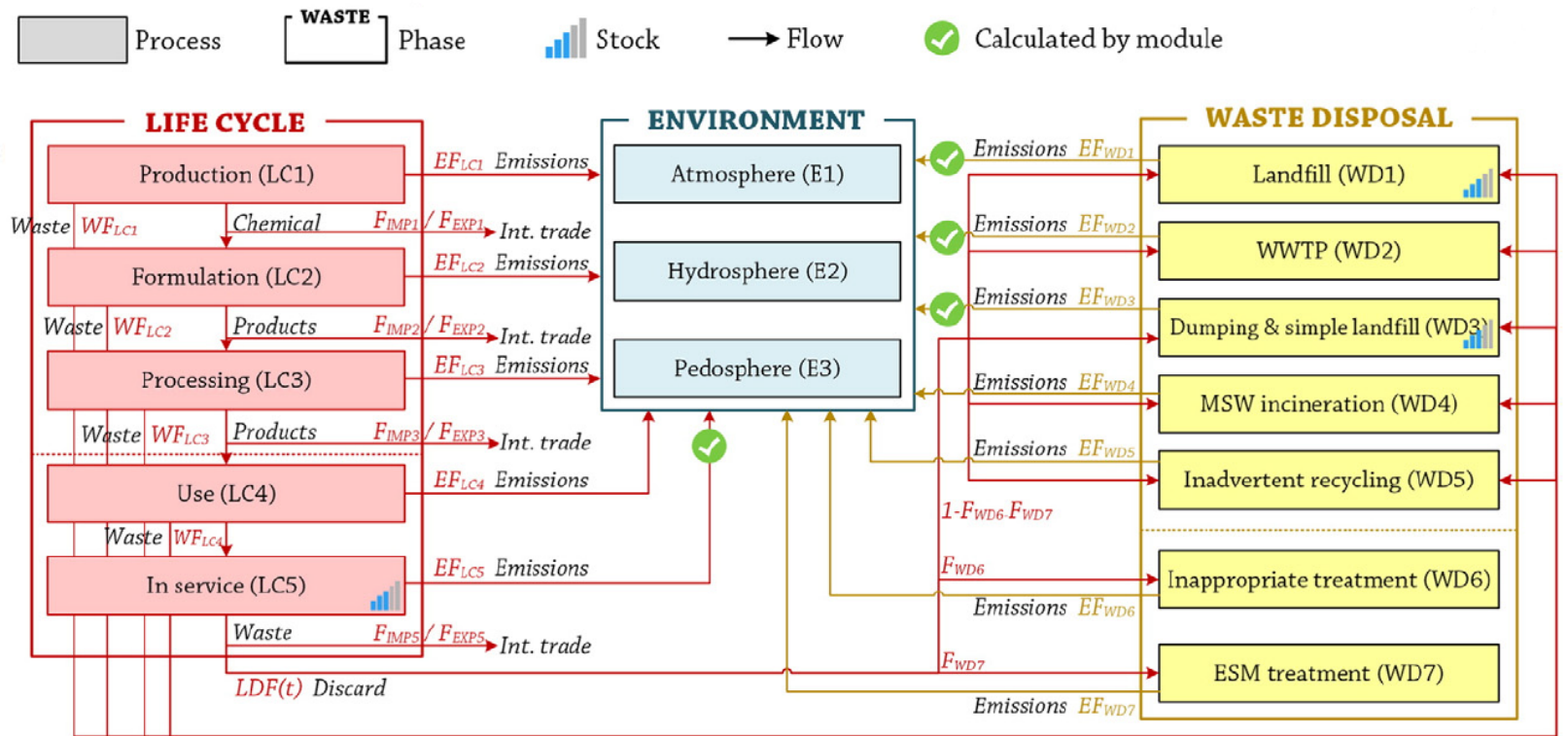
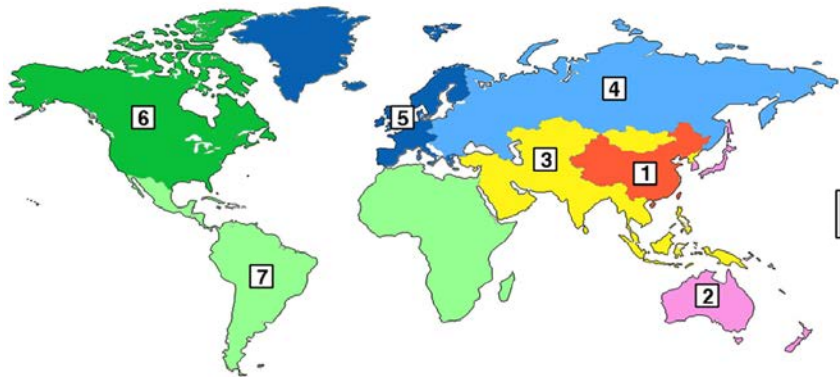
# Modeling Strategy



- A continuum from chemical production to concentration in environmental media
- Trace how diastereomer profile changes throughout the lifecycle of HBCDD-containing products

# CiP-CAFE Model

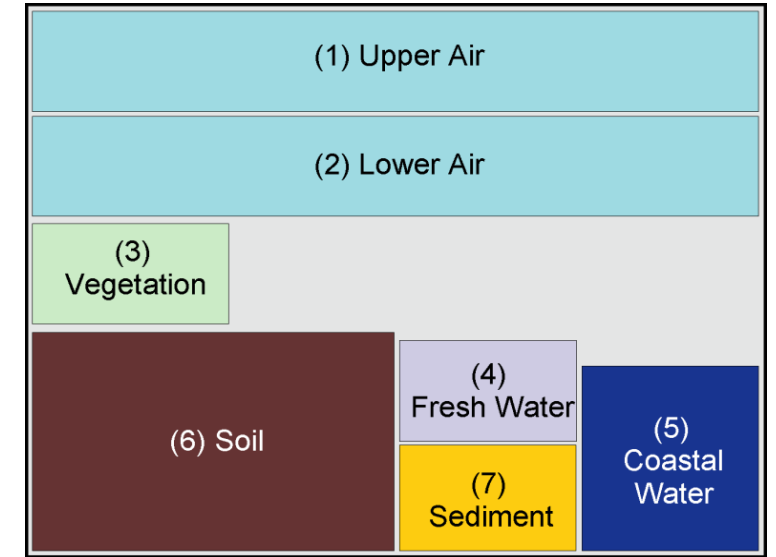
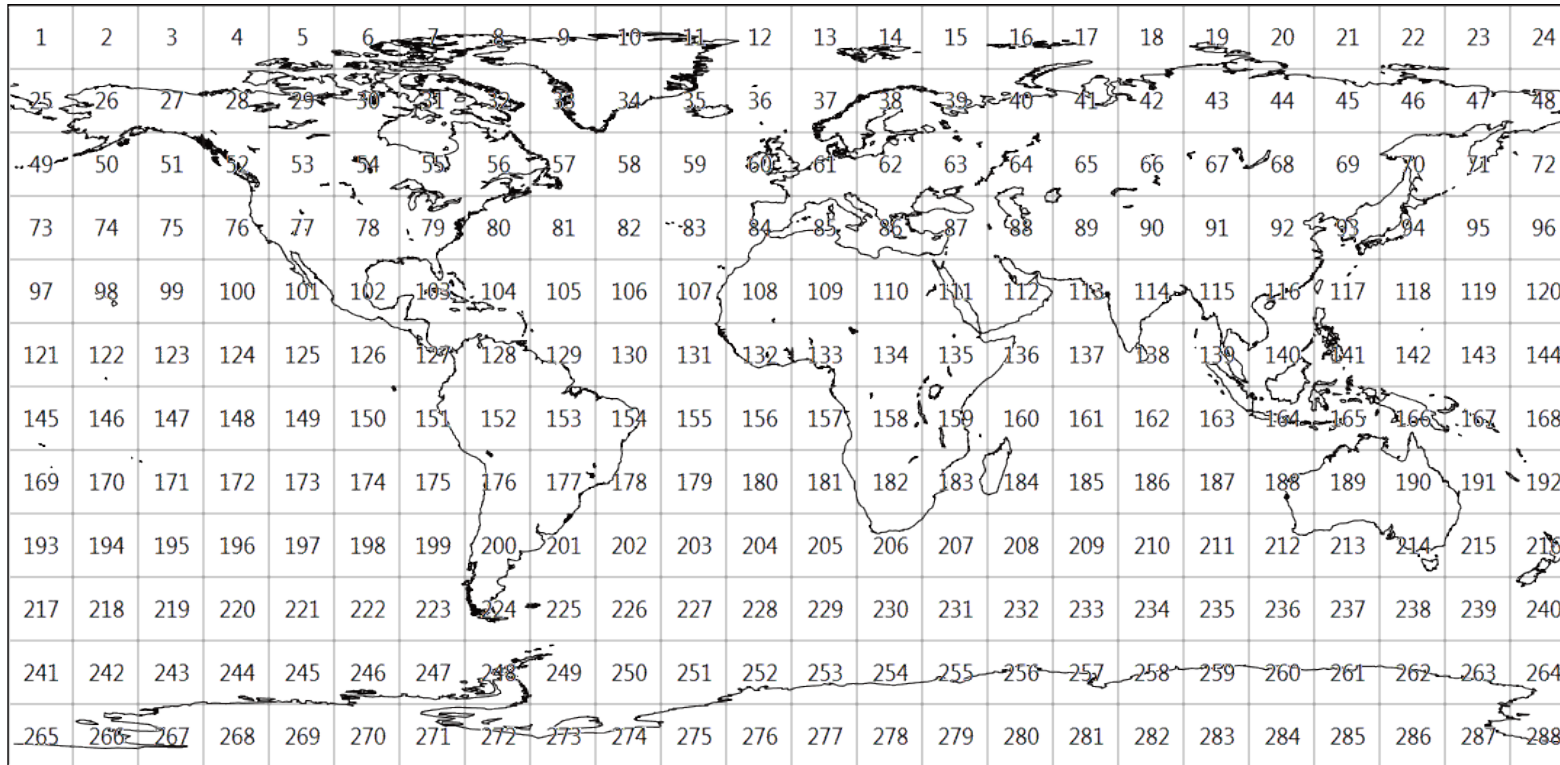
- CiP-CAFE: Chemical in Product – Comprehensive Anthropospheric Fate Estimation  
(Li and Wania, 2016; Li et al., 2017)



Li and Wania (2016) *Environ. Int.*, 94, 674-686  
 Li et al. (2017) *Environ. Sci. Technol.*, 51, 4461-4470

# BETR-Global Model

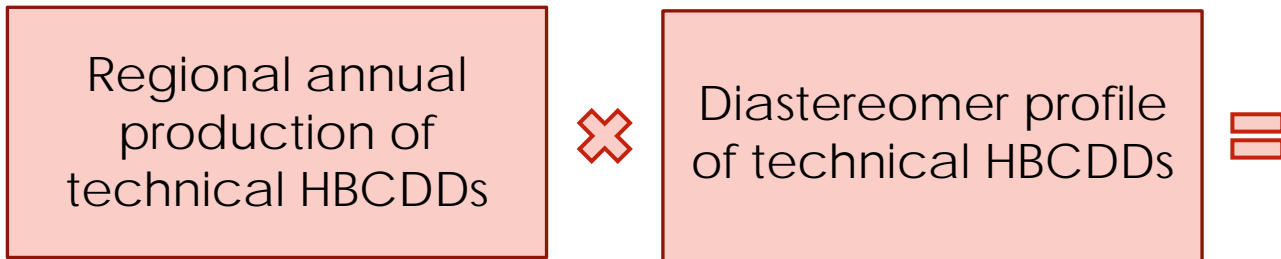
- BETR-Global: Berkeley-Trent Global (MacLeod et al., 2005, 2011)



MacLeod et al. (2005) *Environ. Sci. Technol.*, 39, 6749-6756  
 MacLeod et al. (2011) *Environ. Pollut.*, 159, 1442-1445

# Key Input Data

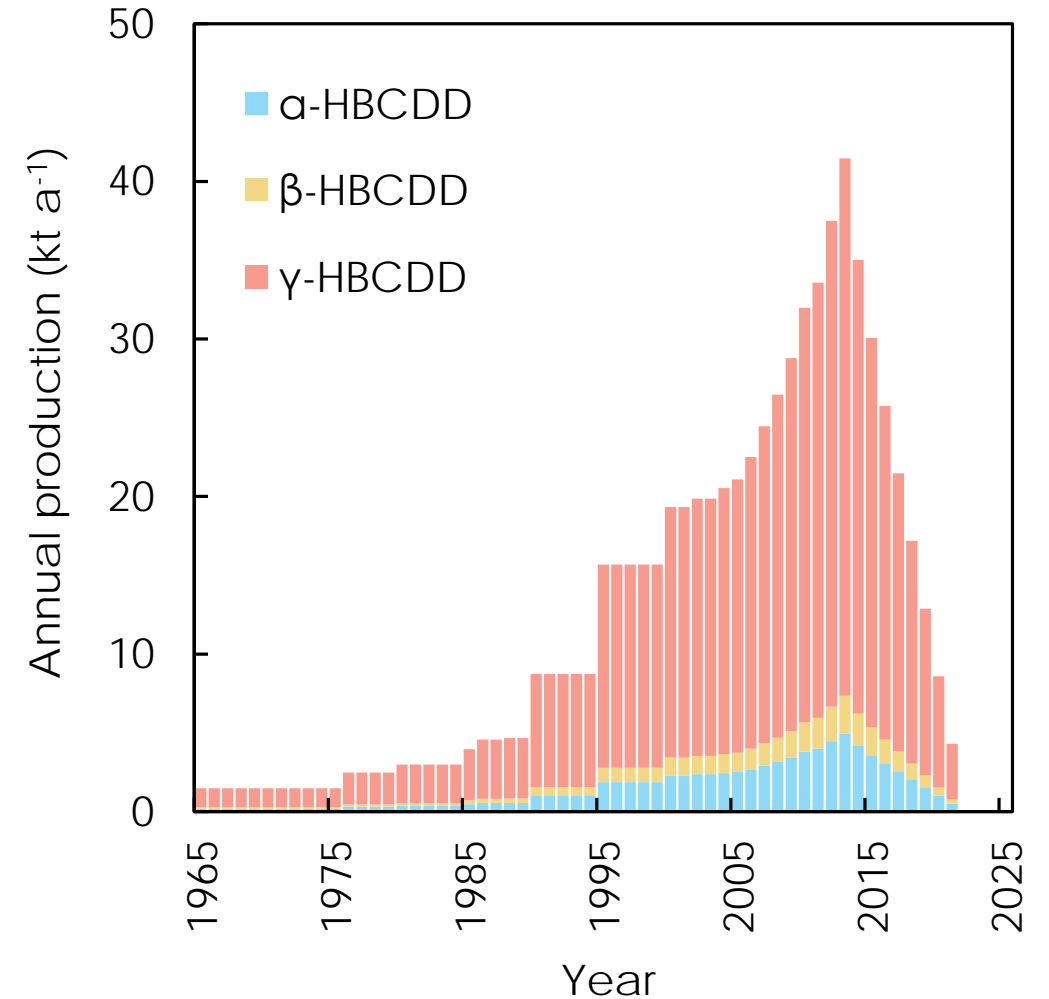
## Regional annual production/consumption of HBCDD diastereomers



Use of HBCDDs in five applications

- *EPS insulation*
- *XPS insulation*
- *textiles*
- *EPS packaging*
- *HIPS plastics*

\* Future production & new use: The Stockholm Convention allows 5-year "specific exemptions" for EPS and XPS in buildings needed to give countries time to phase-in safer substitutes.

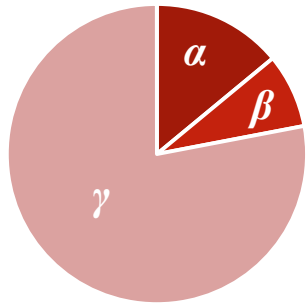


# Key Input Data

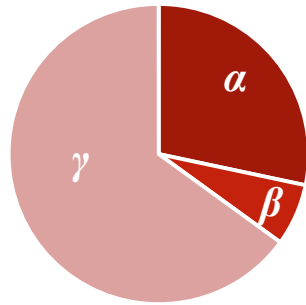
## ■ Isomerization factor (IF) during thermal processing

- Relative change of the abundance of a diastereomer

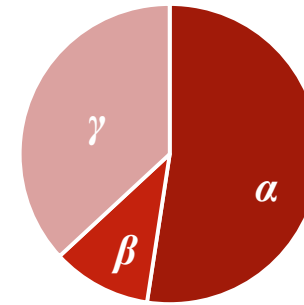
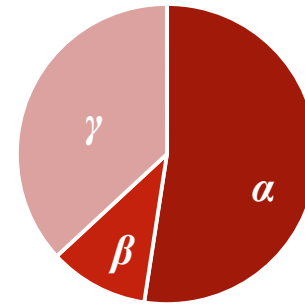
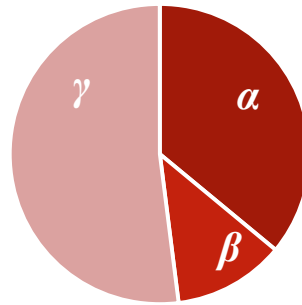
$$IF = \frac{\text{Abundance of a diastereomer after isomerization}}{\text{Abundance of a diastereomer before isomerization}}$$



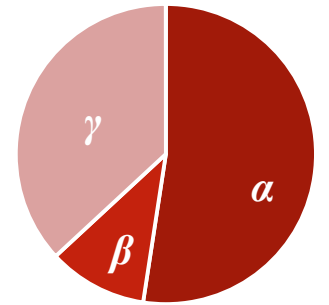
Technical HBCDDs .....



.....kinetic-controlled.....



.....thermodynamic-controlled



Increasing time at specific processing temperature



IF( $\gamma$ -HBCDD) keeps decreasing  
IF( $\alpha$ -HBCDD) keeps increasing

IF is a range:  $IF_{\text{minimum}} < IF < IF_{\text{maximum}}$



# Variability in Input Data

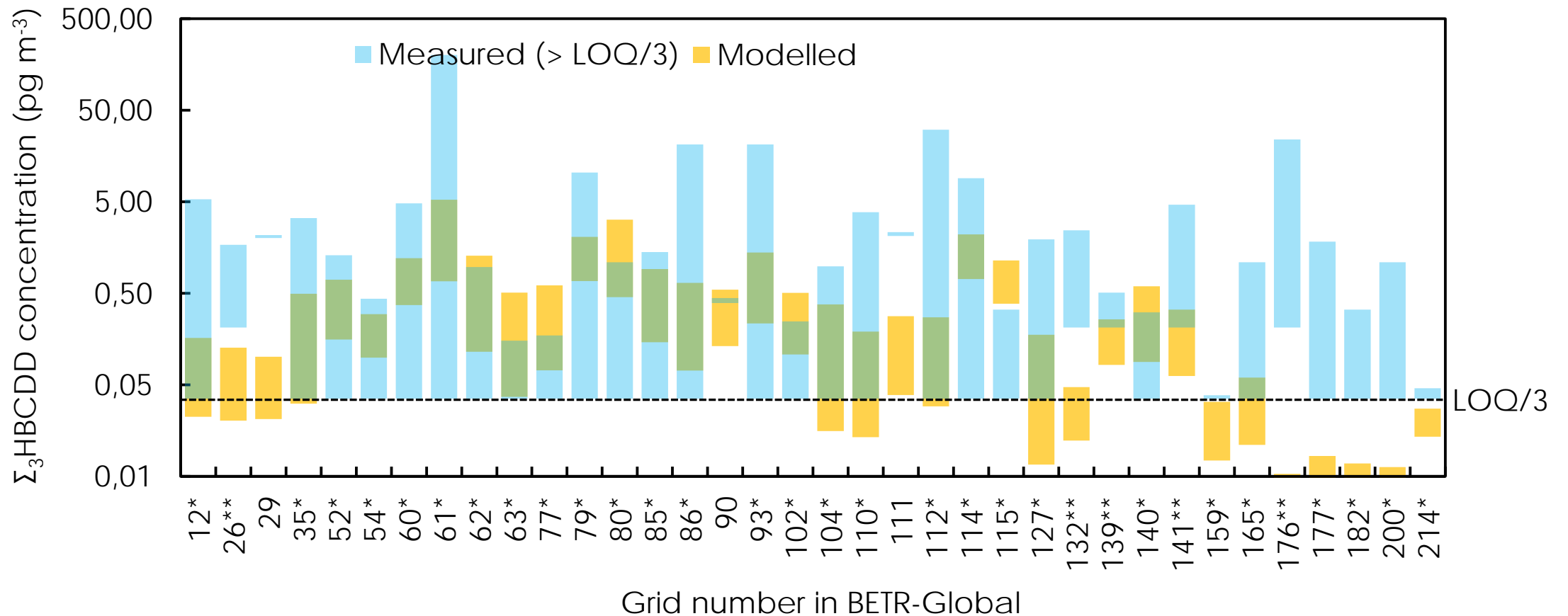
- Define 8 separate simulation scenarios
- Upper bound of the emission estimate: maximum of the 8 results  
Lower bound of the emission estimate: minimum of the 8 results

Parameters with remarkable variability	Boundary 1	Boundary 2	# of cases
(A) Isomerization factor	$\alpha$ -dominant	$\gamma$ -dominant	2
(B) Emission factors of production & formulation	Literature reported value $\times 1$	Literature reported value $\times 10$	2
(C) Emission factors in non-open use of insulation boards	Literature reported value $\times 1$	Literature reported value $\times 0.5$	2
Total			8

# Model Performance

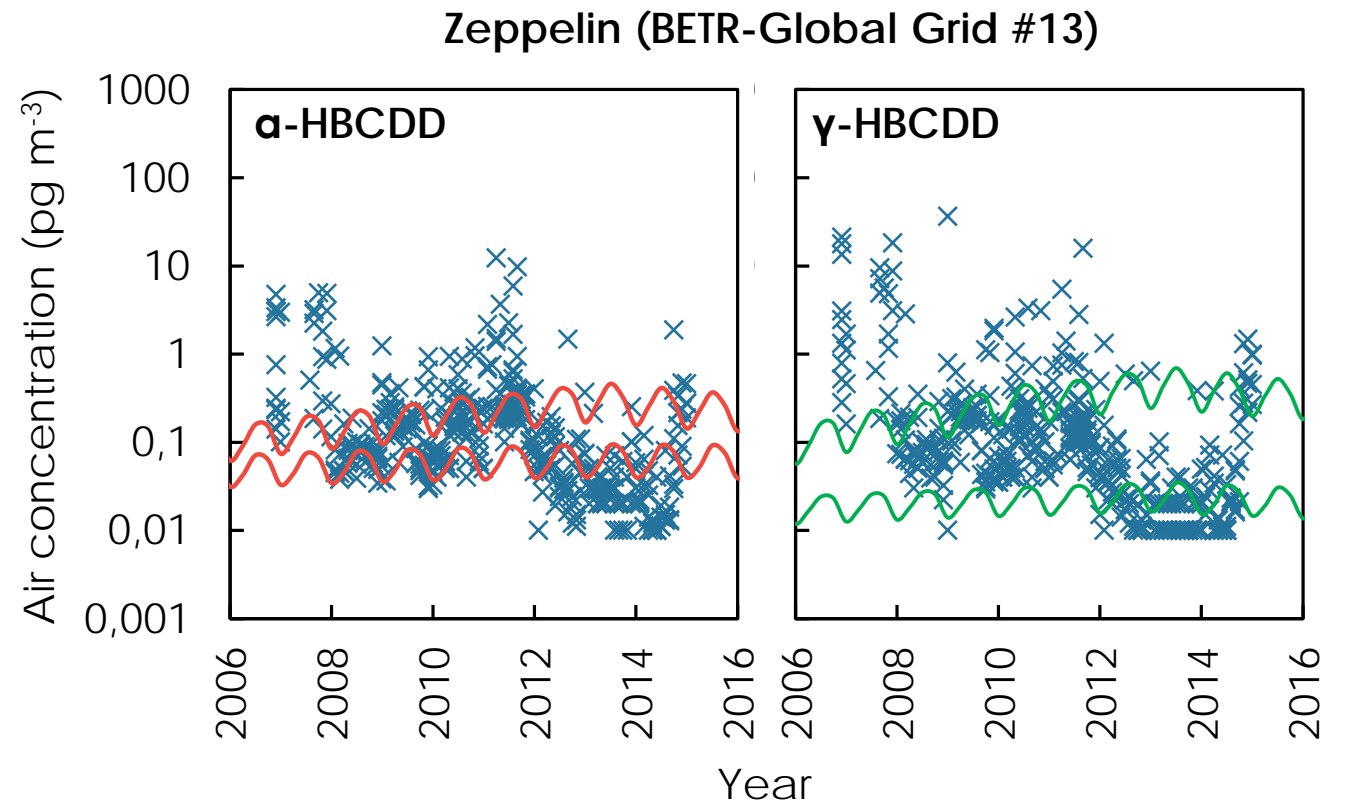
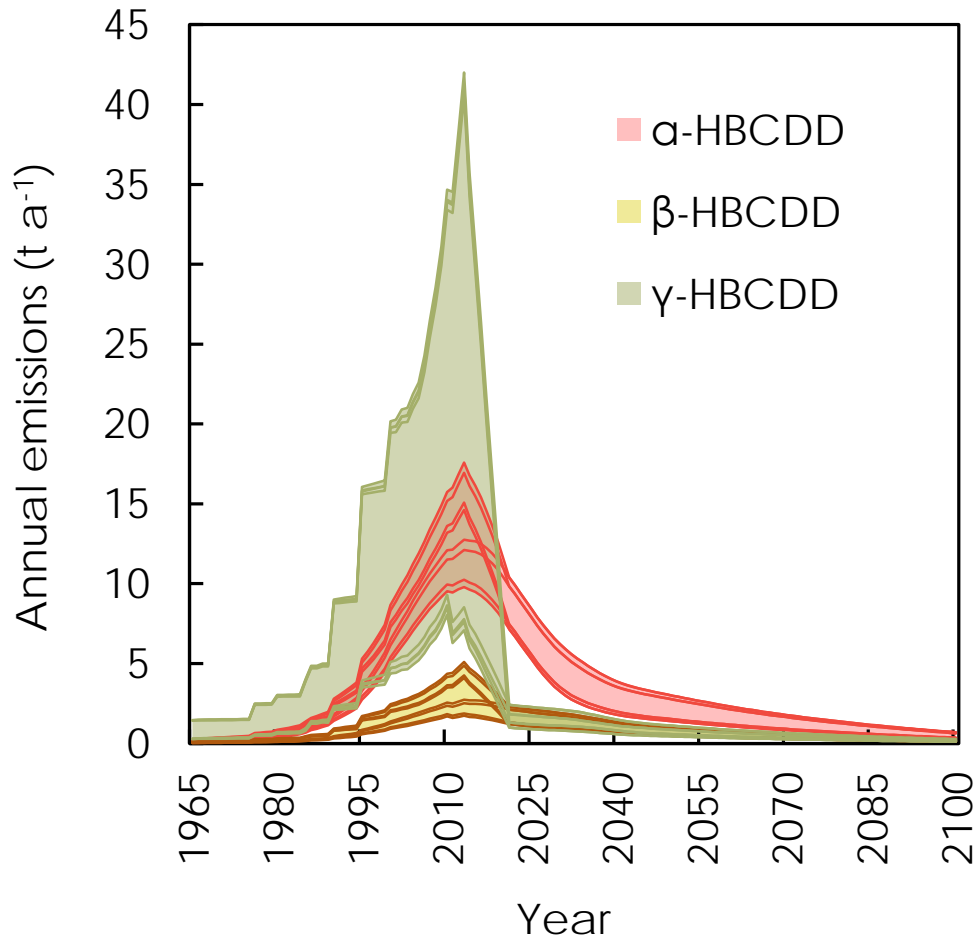
- Fed with the CiP-CAFE-derived emission estimate

BETR-Global succeeds in reproducing most  $\Sigma_3$ HBCDD concentrations observed in GAPS

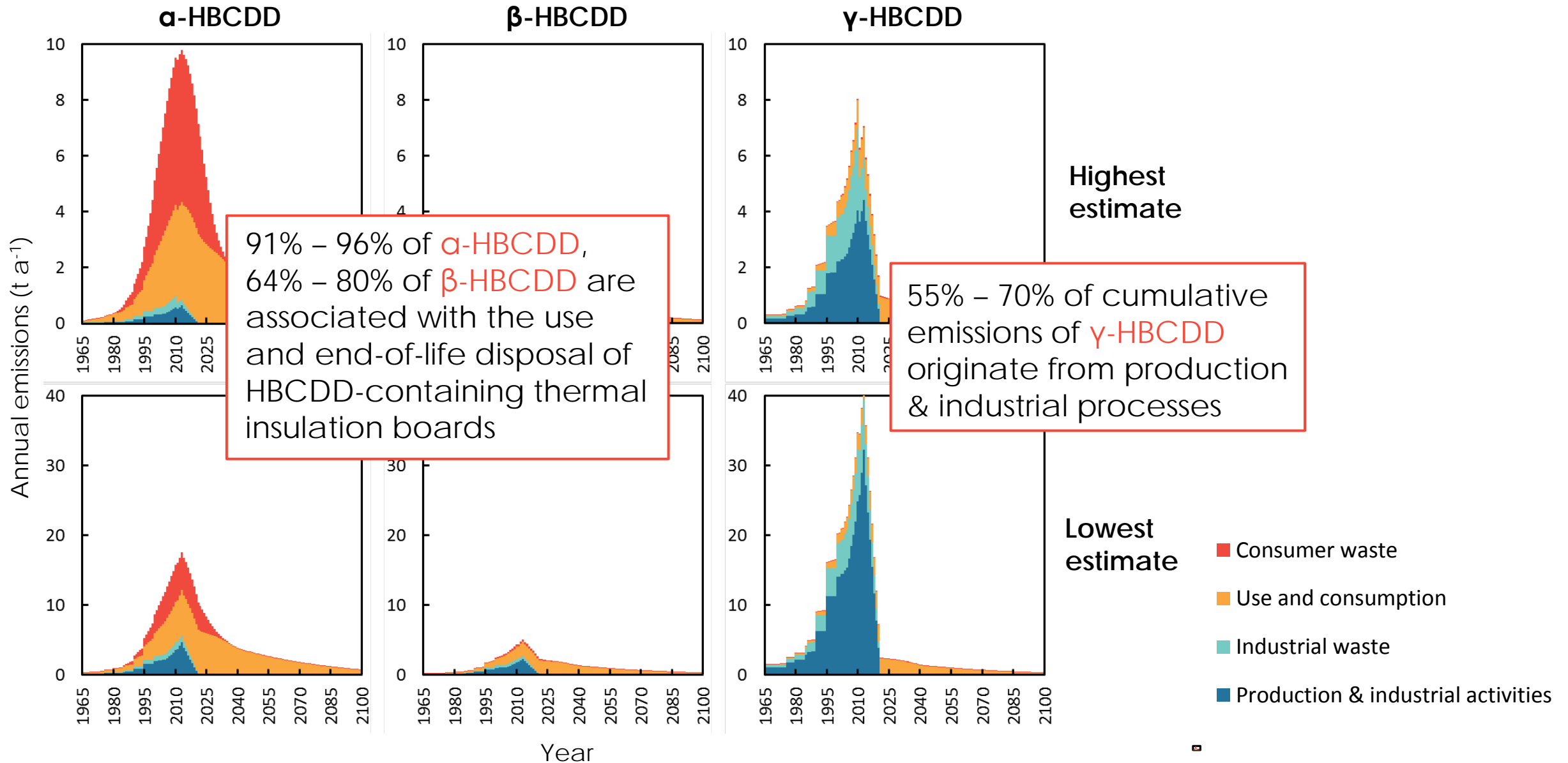


# Global Emissions of HBCDD Diastereomers

- On the global scale,  $\alpha$ -HBCDD and  $\gamma$ -HBCDD are almost similarly abundant



# Different Diastereomers, Different Dominant Sources

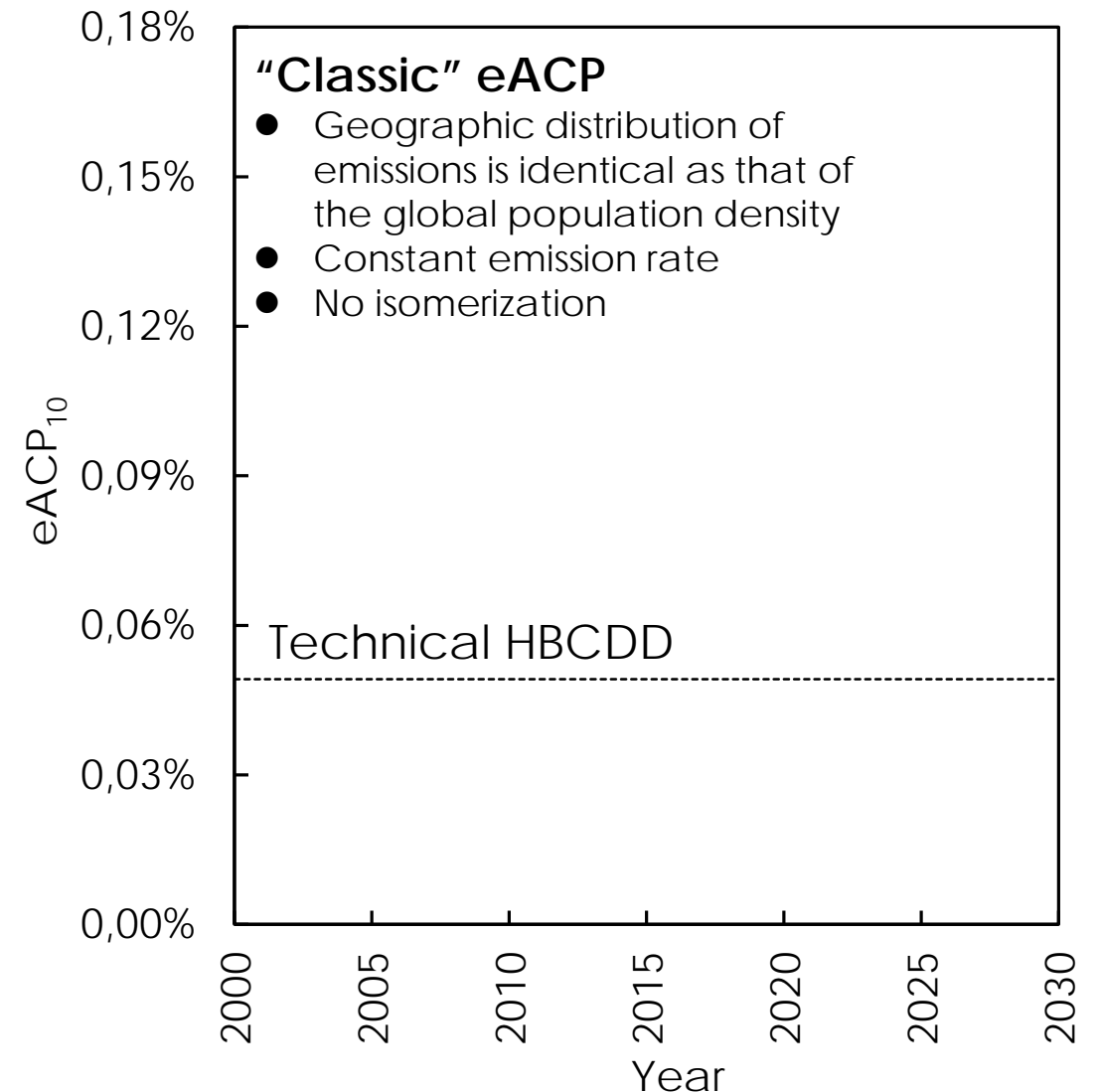


# Enrichment of Diastereomers in the Arctic

## Absolute Arctic Contamination Potential

- Percentage of enrichment of HBCDD diastereomers in Arctic (BETR-Global cells #1 – 48) surface media after a decade of emissions

$$eACP_{10} = \frac{\text{Amount present in Arctic surface media}}{\text{Cumulative global emissions over the decade}}$$

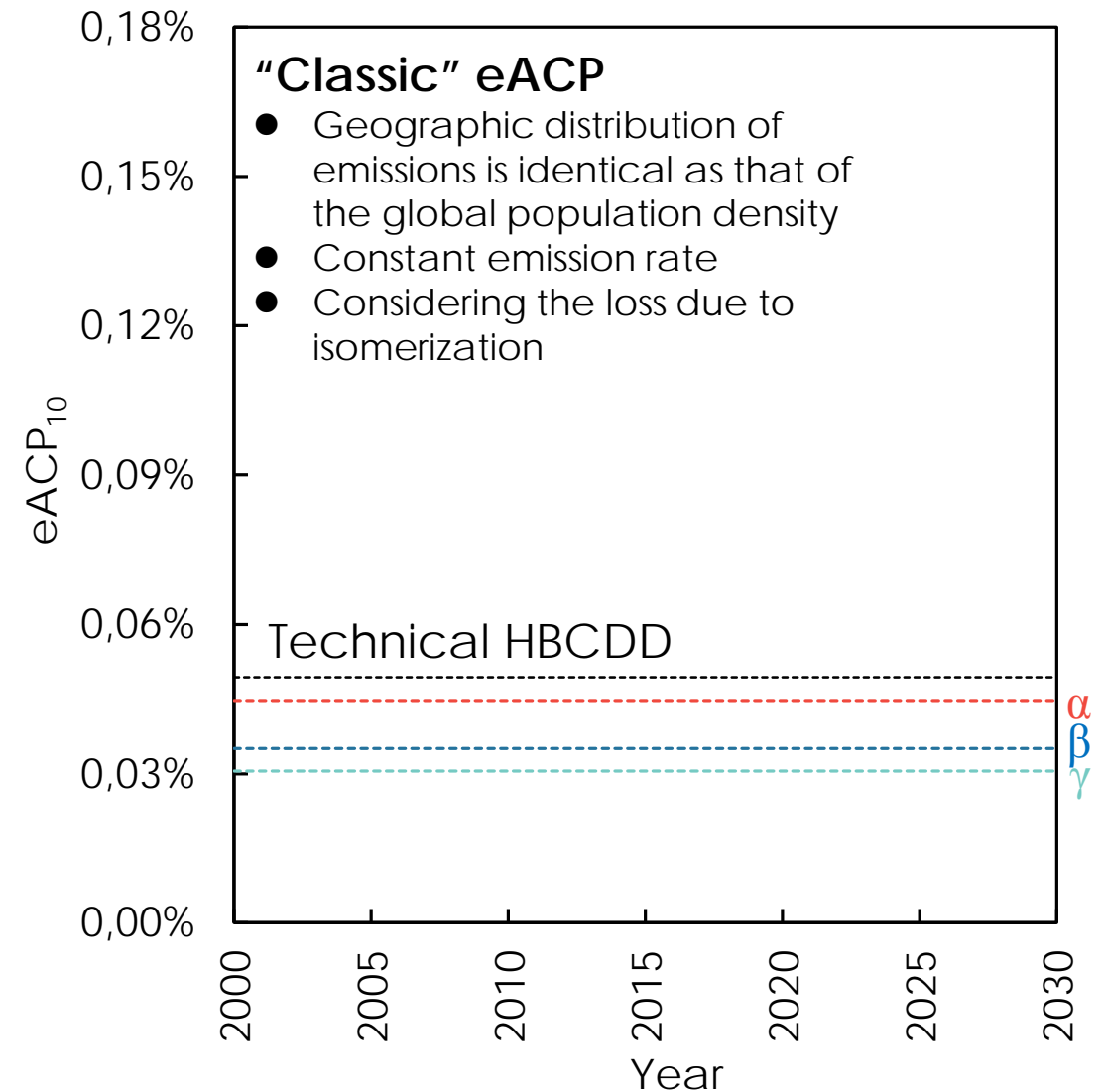


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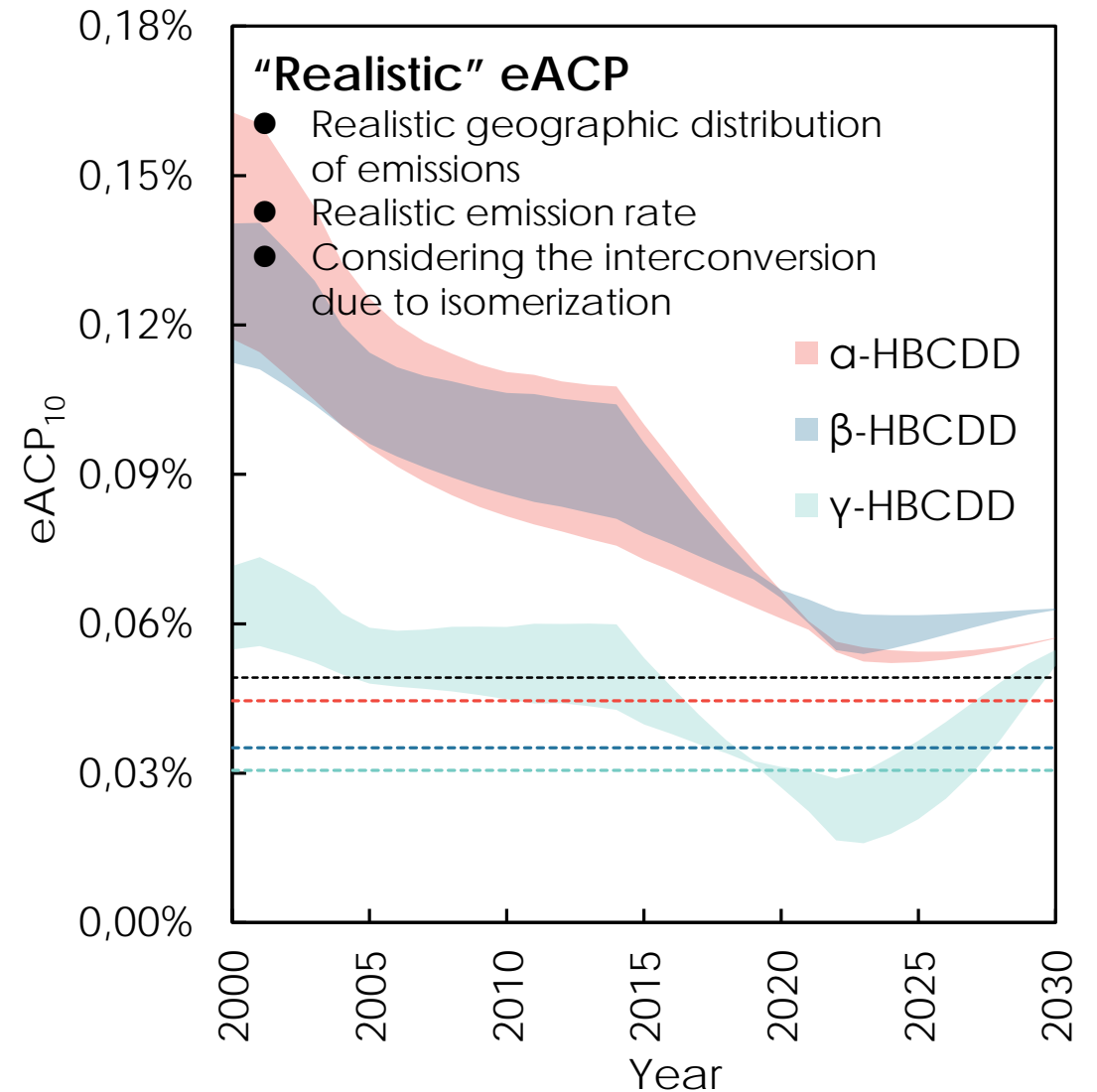


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# ■ Concern: $\alpha$ -HBCDD is More “Risky” in the Environ.

## ■ Example: In vitro biotransformation assay (Zegers et al., 2005)

- Laboratory rats and harbor seal: microsomal preparations of liver
- $\alpha$ -HBCDD is hardly metabolized by cytochrome P450 enzymes
  - “ $\alpha$ -HBCDD was not significantly biotransformed after 90 min of incubation”.
- $\beta$ - and  $\gamma$ -HBCDD are quickly metabolized by cytochrome P450 enzymes
  - $69 \pm 16\%$  of  $\beta$ -HBCDD and  $60 \pm 10\%$  of  $\gamma$ -HBCDD disappeared within 90 min.

## ■ Due to isomerization:

- The HBCDD mixture in the emission flow or in the environment, may be of more environmental concern than the mixture being produced.



## Implications

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- It is not appropriate to treat interconvertible mixtures as a unit in environmental fate studies.
- Environmental risk assessment of HBCDD is recommended to be conducted on a diastereomer-specific basis.

# Thanks for Your Attention Questions

## Acknowledgement

Scholarships from the China Scholarship Council &  
the Shanghai Tongji Gao Tingyao Environmental Science and Technology Development Foundation

## Related work

15:30 Abbasi et al. Global Inventory of PBDEs; from Production, Use and Waste to Environment  
Helga Engsthus, Auditorium 3

