

*Bioaccumulation of PBDEs,  
their replacement products  
(TBB, TBPH, BTBPE) and  
HBCD in freshwater mollusks  
from the Yadkin River  
(North Carolina, USA)*



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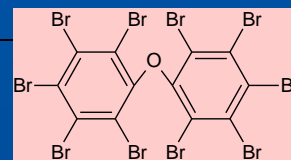
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College of William & Mary  
Gloucester Point, Virginia



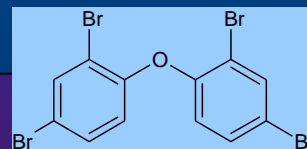
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# PBDEs, environment and human health

- Polybrominated diphenyl ethers (PBDEs)
  - **additive** brominated flame-retardants (BFRs)
    - formulations: Penta-, Octa-, Deca-BDEs
    - uses: polyurethane foam, electronics (e.g. casings, wires) and textiles
      - ubiquitous, persistent and bioaccumulative
      - endocrine disrupters



- Penta- & Octa-BDEs
  - 2004, production ended US, ban by EU
  - 2009, listed POP Stockholm Convention
- Deca-BDE
  - phased-out in Europe, 2008
  - to be phased-out in US, 2013



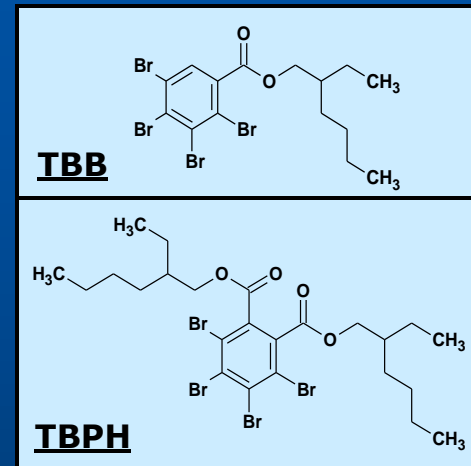
# Penta- and Octa-BDE replacement products

- *Penta- replacement*

- Firemaster 550 and BZ-54 (Chemtura Corp. CT. USA)
  - TBB (2-ethylhexyl 2,3,4,5-tetrabromobenzoate)
  - TBPH (di (2-ethylhexyl)-2,3,4,5-tetrabromophthalate)

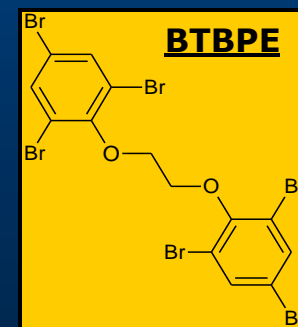
- *Octa- replacement*

- FF-680 (Chemtura Corp. CT. USA)
  - BTBPE (1,2-bis (2,4,6-tribromophenoxy) ethane)



- TBB, TBPH and BTBPE

- **additive** brominated flame-retardants (BFRs)
- TBB, TBPH: detected in sewage sludge<sup>1</sup>, household dust<sup>2</sup> and marine mammals<sup>3</sup> (**DNA damage exposed laboratory minnows<sup>4</sup>**)
- BTBPE: detected in sewage sludge<sup>1</sup>, dust<sup>2</sup>, air<sup>5</sup>, sediment<sup>5, 6</sup>, aquatic species<sup>6</sup> and bird eggs<sup>7</sup>



<sup>1</sup>La Guardia et al., ES&T 2010

<sup>2</sup>Stapleton et al., ES&T 2009

<sup>3</sup>Lam et al., ES&T 2009

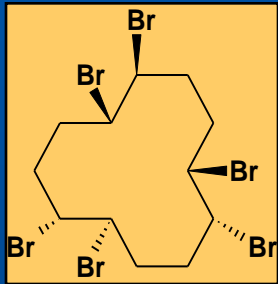
<sup>4</sup>Bearr et al., Environ.. Tox. Chem 2010

<sup>5</sup>Hoh et al., ES&T 2005

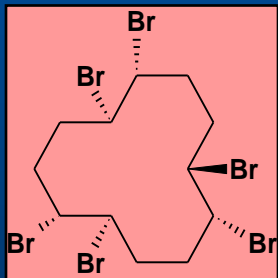
<sup>6</sup>Wu et al., ES&T 2010

<sup>7</sup>Gauthier et al., ES&T 2009

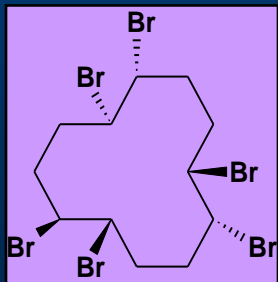
# Hexabromocyclododecane (HBCD)



$\alpha$ -HBCD

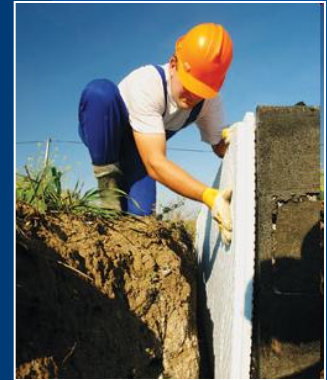


$\beta$ -HBCD



$\gamma$ -HBCD

- **additive** brominated flame-retardant (BFR)
  - polystyrene foam, electronics, **textiles**
  - 2001: 16,700 MT global demand
  - Technical product:  $\alpha$ -,  $\beta$ -HBCD (~20%),  $\gamma$ -HBCD (~80%)
- environmental exposure
  - ubiquitous contaminant
    - detected in sewage sludge<sup>1</sup>, house dust<sup>2</sup>, marine mammals<sup>3</sup> and birds<sup>4,5</sup>
    - human: breast milk<sup>6</sup> and blood<sup>7</sup>
- considered an endocrine disruptor
  - mimic thyroid hormone
  - developmental neurotoxin<sup>8</sup>
- usage/review
  - EU, phased-out by 2015
  - US, EPA action plan 2010
    - finalized by the end of 2011



<sup>1</sup>La Guardia et al., ES&T 2010

<sup>2</sup>Stapleton et al., ES&T 2009

<sup>3</sup>Lam et al., ES&T 2009

<sup>4</sup>He et al., ES&T 2010

<sup>5</sup>Fernie et al., ES&T 2010

<sup>6</sup>Shi et al., ES&T 2009

<sup>7</sup>Meijer et al., ES&T 2008

<sup>8</sup>van der Ven et al., Tox Letters 2009

# Yadkin River – outfall - samples

- Yadkin-Pee Dee River
  - 690 km/430 miles, Blue Ridge Mountains North Carolina, South Carolina to the Atlantic Ocean
- Elkin, NC (textile outfall)
  - 4MGD, wastewater treatment facility serves textile mills
  - US EPA's Toxics Release Inventory (TRI) 2001-2004 **5350 kg/ 11,800 lbs** deca-BDE released to surface water
- Sample Sites (collected 2009)
  - sediments and mollusks
  - 4-sites, Elkin (outfall) to Pilot Mountain State Park, NC
  - 45 km/28 river miles



# Mollusk samples - bivalves and gastropods

## Bivalve: *Corbicula fluminea* (Asian clam)

Native range: Asia and Africa

Nonindigenous species: North and South America and Europe

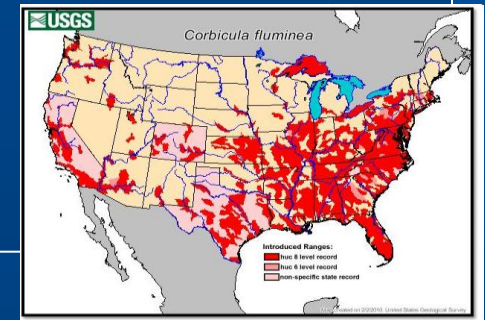
Life span: 1-4 years

Feeding: filter-feeder, phytoplankton

Reproduction: hermaphrodite, several yearly broods

Movement: relatively sessile

Predators: fish, birds, raccoons...



## Gastropod: *Elimia proxima*

Native range: North America (Virginia to Georgia)

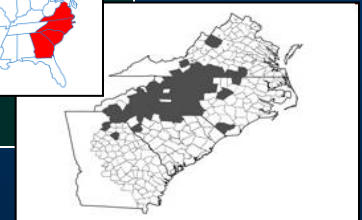
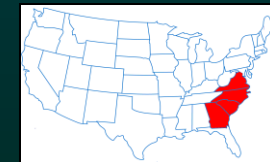
Life span: several years

Feeding: grazer, algae (attached) and detritus

Reproduction: egg layers, mate yearly

Movement: <20m yr<sup>-1</sup>

Predators: fish, crayfish, birds...





# BFR extraction and analysis



**Samples**  
*(sediment and mollusks)*

**Freeze-dry**



**Enhanced Solvent Extraction**  
ASE 200 (Dionex)

**Size Exclusion Chromatography**  
Envirosep-ABC, 350 x 21.1 mm  
(Phenomenex)

exchange to  
hexane

**Solid Phase Extraction**  
Glass column, 2 gm silica

**Fraction #1**  
3.5mL (hexane)

**Fraction #2**  
6.5mL (hexane/DCM, 60:40)

**Fraction #3**  
8mL (DCM)

**Fraction #4**  
5mL (DCM/Ace, 50:50)

**UPLC/ESI-NI MS/MS**  
 $(\alpha-, \beta-, \chi\text{-HBCD})$

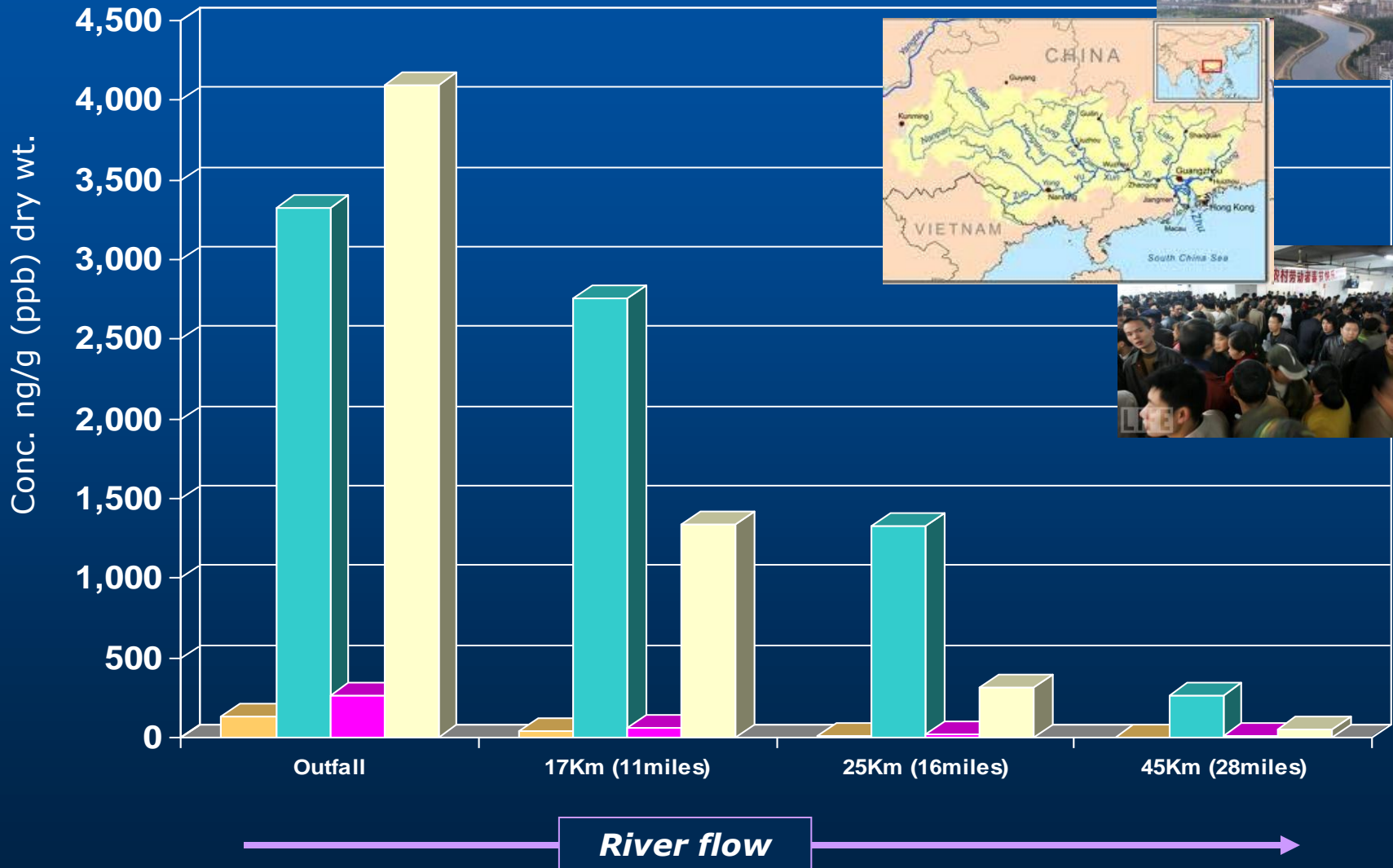
reduce  
volume

**Solvent exchange**





# BFRs – river sediments



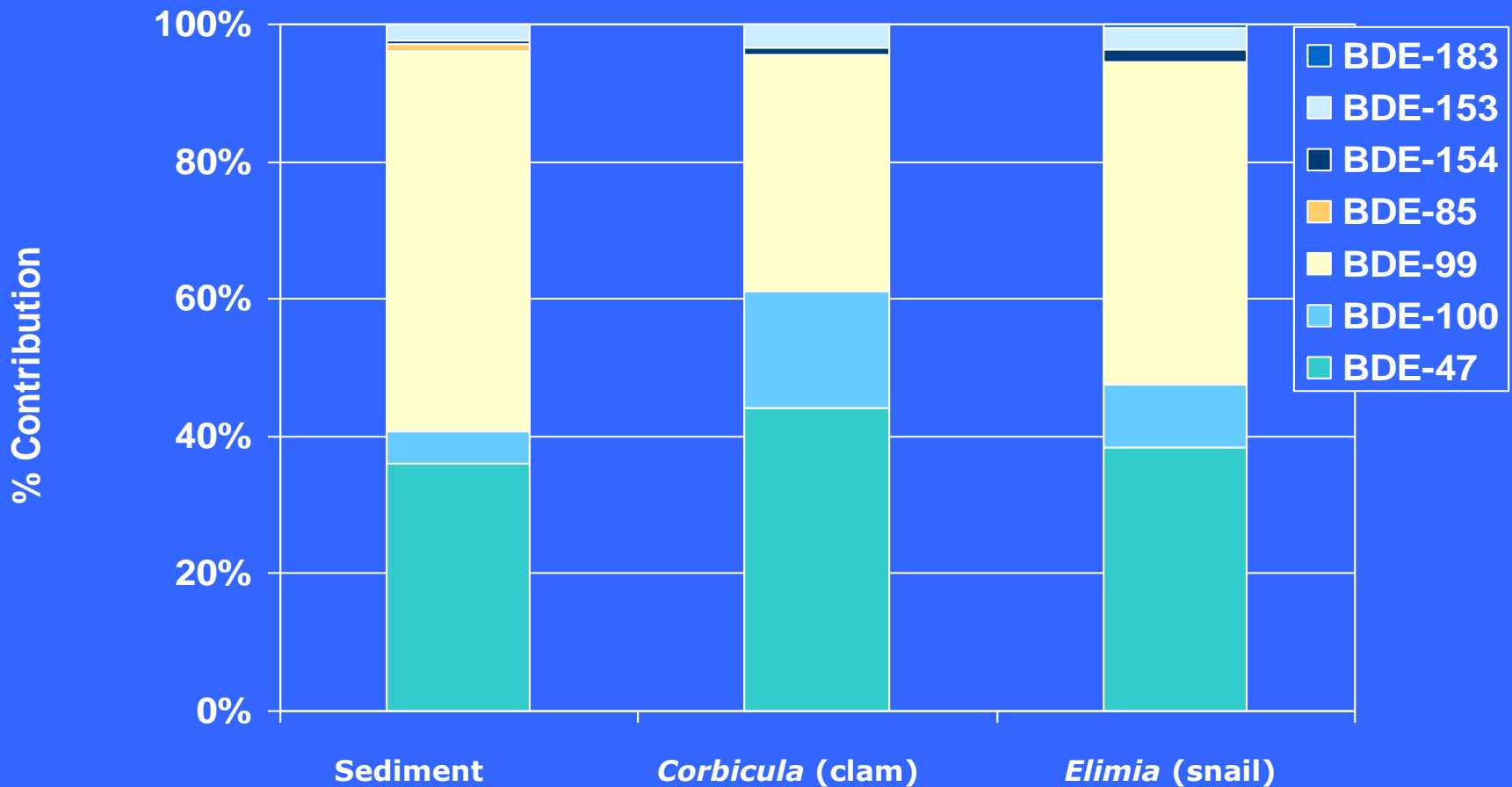




# BFRs – sediment and mollusks (outfall)

(TOC or lipid normalized)

## Penta- & Octa-BDEs

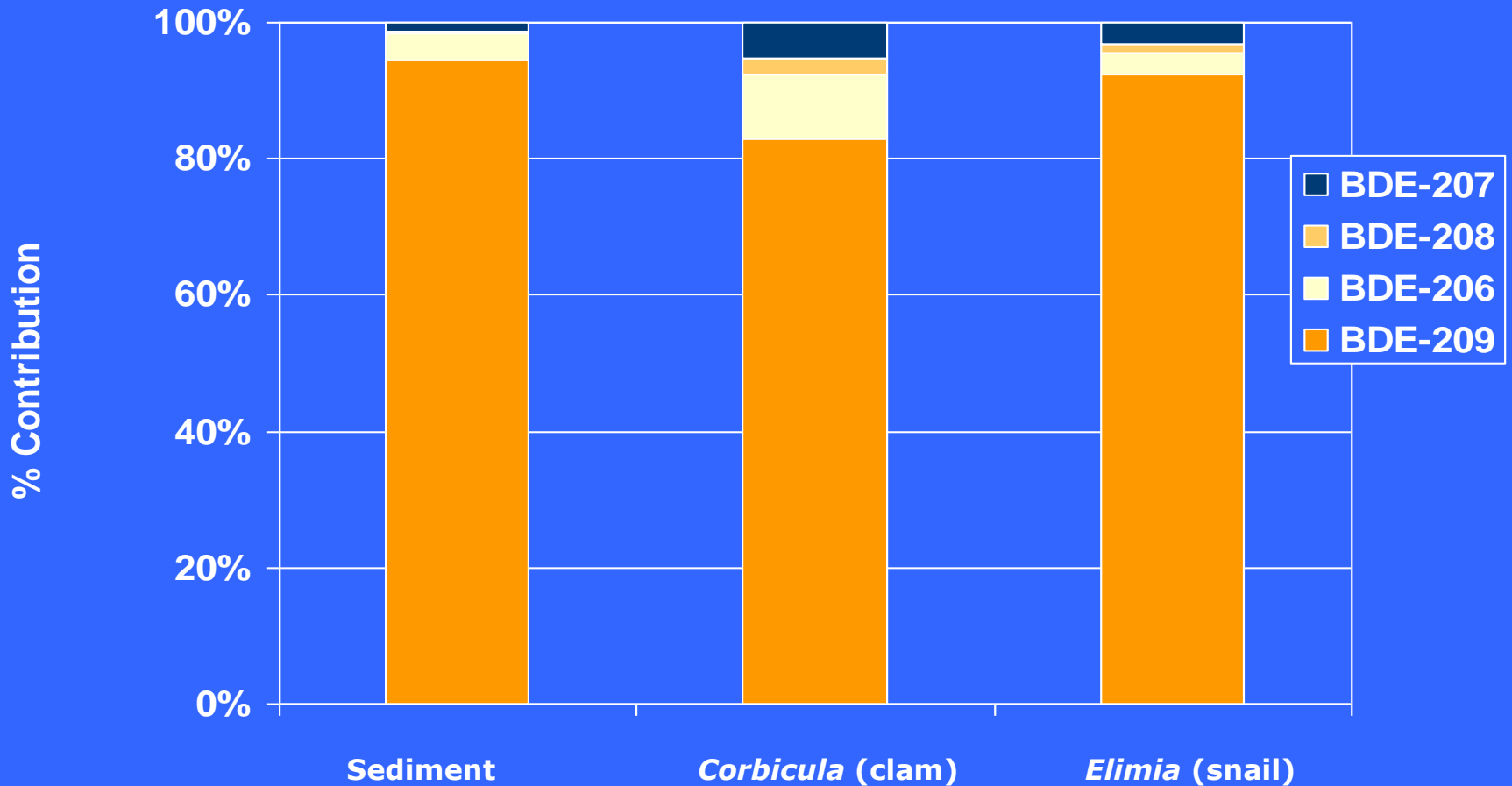




# BFRs – sediment and mollusks (outfall)

(TOC or lipid normalized)

## Deca-BDEs

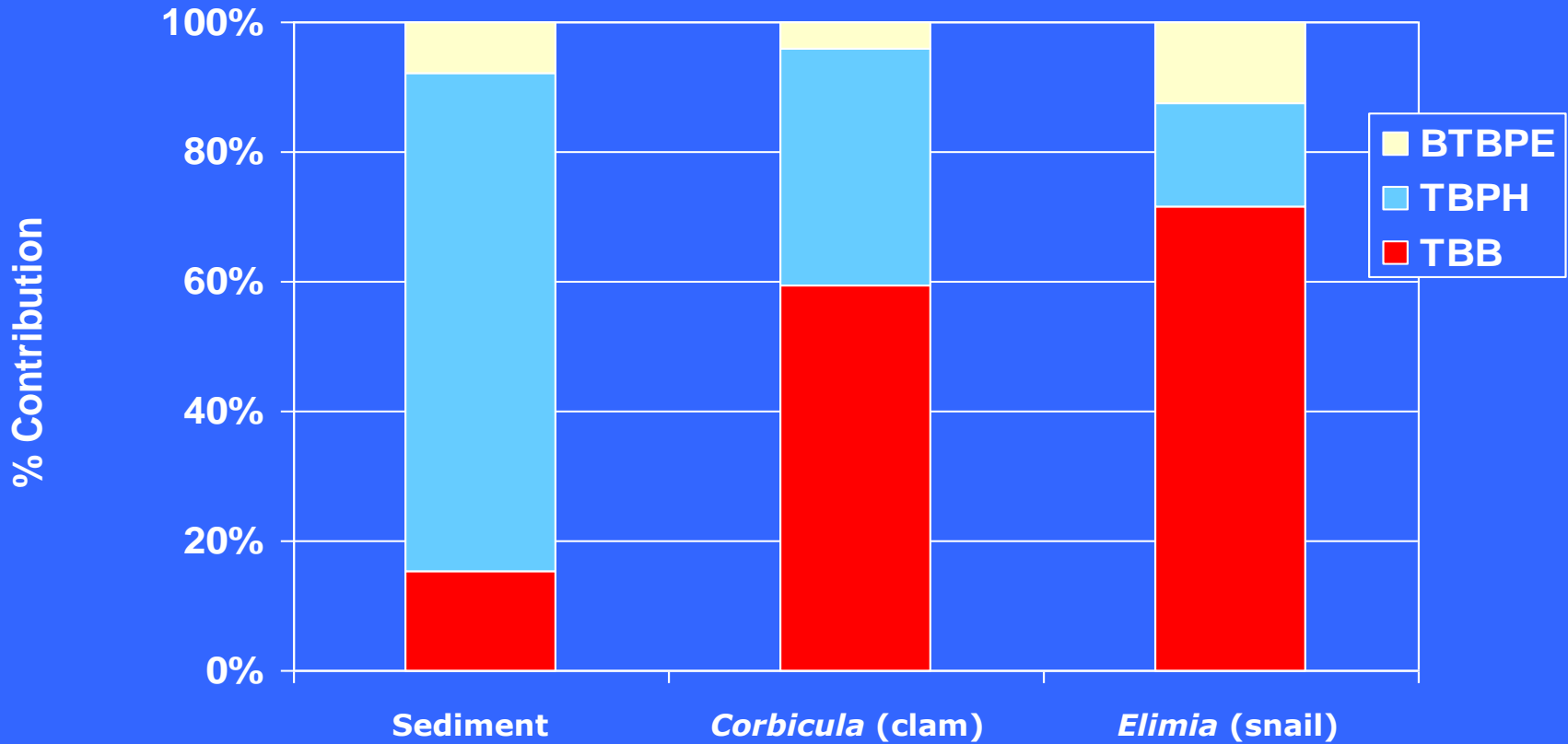




# BFRs – sediment and mollusks (outfall)

(TOC or lipid normalized)

## TBB, TBPH & BTBPE

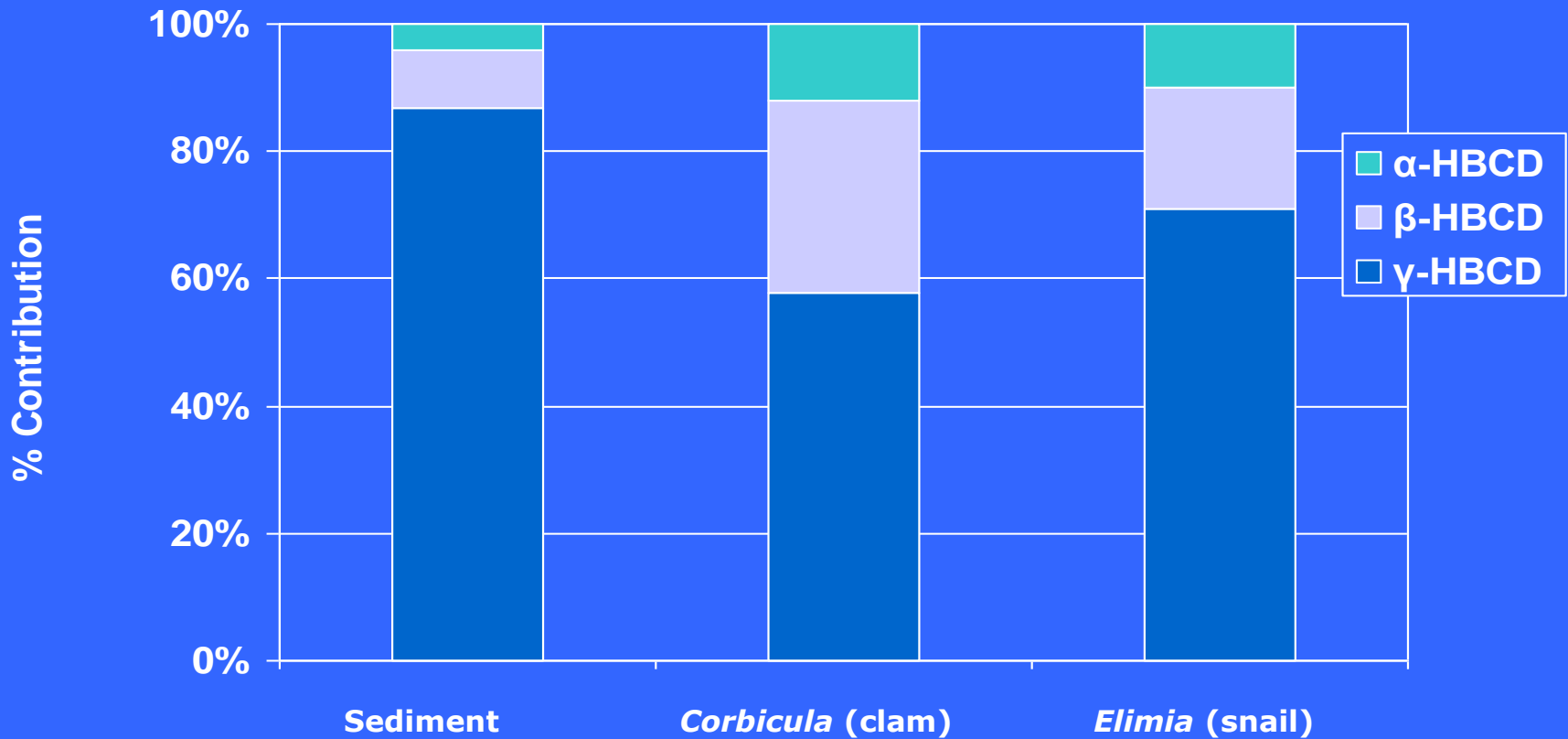




# BFRs – sediment and mollusks (outfall)

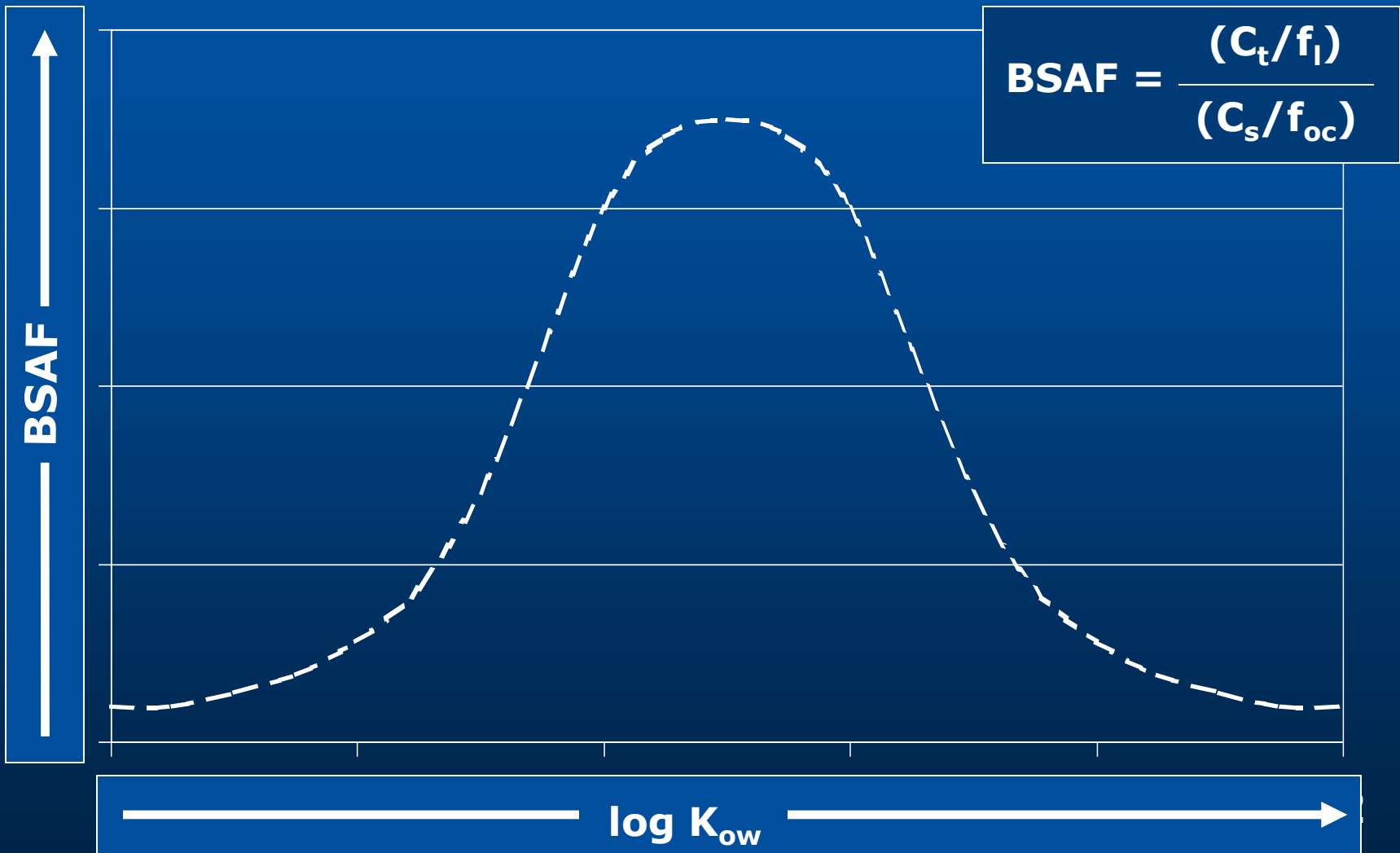
(TOC or lipid normalized)

## HBCD

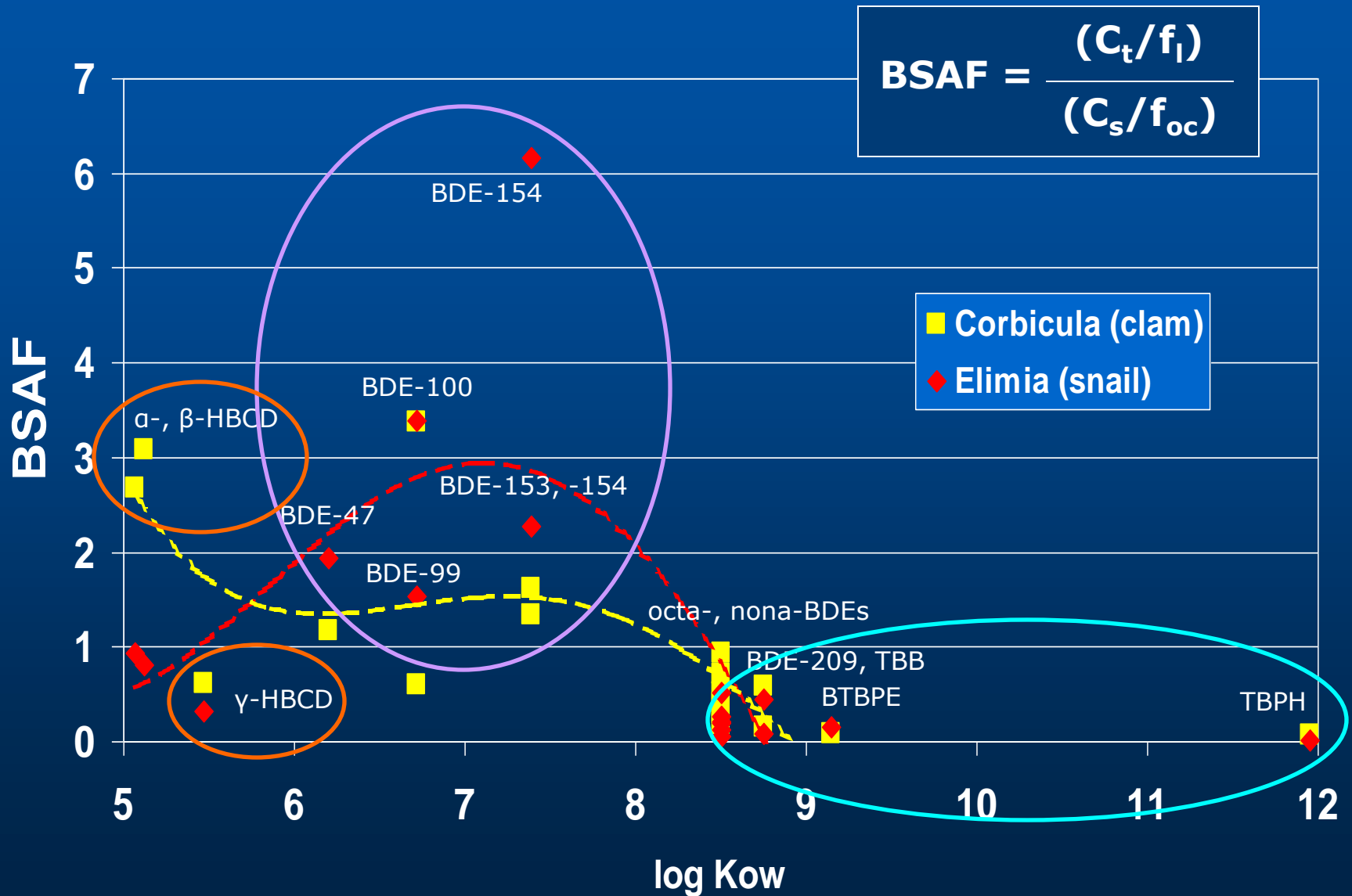


# Biota Sediment Accumulation Factors (BSAFs)

(Bioaccumulation at  $BSAF > 1$ ,  $BSAF = \text{lipid normalized tissue conc.} / \text{organic carbon normalized sediment conc.}$ )

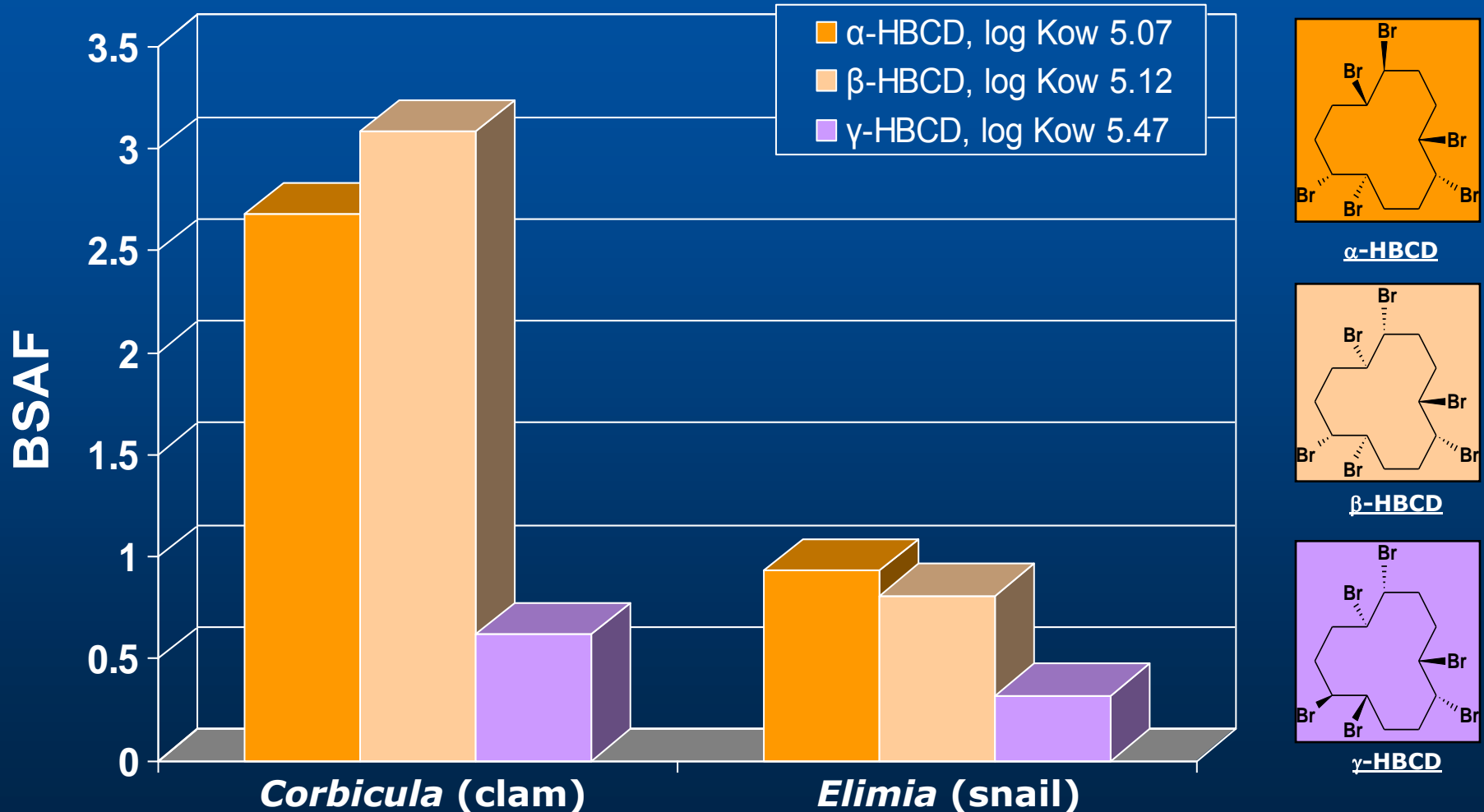


# BFRs BSAFs – Corbicula and Elimia



# Bioaccumulation or bioisomerization\*

(\*Law et al., Environ. Tox. Chem. 2006)





# Conclusions



- **PBDEs, TBB, TBPH, BTBPE and HBCD**
  - enter the aquatic environment (via treated effluent)
  - persistent, ***all*** detected 45Km (28 miles) downstream from outfall
  - bioavailable, detected in *Corbicula* and *Elimia*
- **BSAFs: TBB, TBPH and BTBPE (Penta- & Octa-replacement products)**
  - < Penta- & Octa-BDEs
  - BDE-209  $\approx$  TBB, TBPH, BTBPE
- **HBCD**
  - $\alpha$ -,  $\beta$ -HBCD BSAFs  $\approx$  Penta-BDEs
  - $\alpha$ -,  $\beta$ -HBCD BSAFs 3 to 6-times  $\gamma$ -HBCD
    - indicates bioisomerization in low tropic organisms

## Transformation products

- methoxy and hydroxy-BDEs
- debrominate
  - deca-BDE to more toxic lower brominated PBDEs
  - TBB and TBPH
    - TBPH to DEHP (di(2-ethylhexyl) phthalate)
- isomerization of  $\gamma$ -HBCD

