Hexachlorobenzene, pentachlorobenzene and polychlorinated biphenyls monitoring in fish and with passive samplers

Ian J. Allan¹, Branislav Vrana², Norman W. Green¹ & Anders Ruus¹

¹Norwegian Institute for Water Research (NIVA, Oslo, Norway) ²RECETOX, Masaryk University (Brno, Czech Republic)



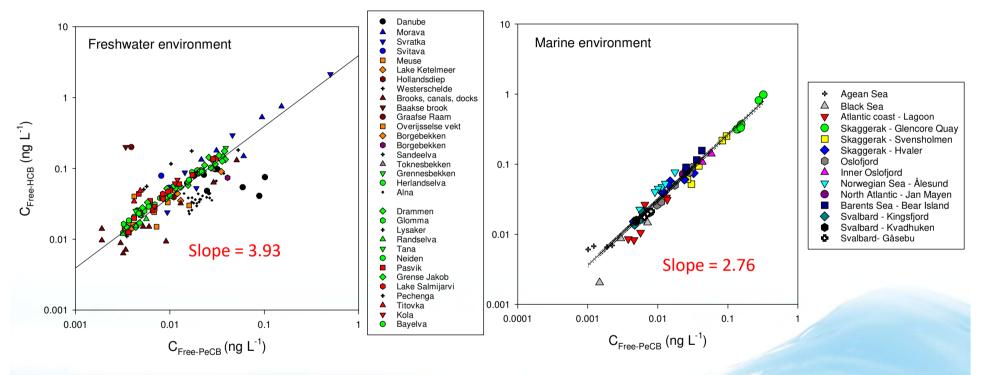
Objectives for this presentation

- Considerable amounts of data on contaminants in fish available in the Norwegian environmental contaminants database
- Extensive passive sampling (PS) done in rivers and along the coast in Norway
- \rightarrow How can we compare these data?
- \rightarrow Suitable chemicals for comparison:

NIVA

- Hexachlorobenzene (HCB), and pentachlorobenzene (PeCB), both are priority substances
- Polychlorinated biphenyls (PCBs)
- Q1: Is there evidence of biomagnification of HCB in fish?
- Q2: Are contaminant levels higher in fish than in water?

Passive sampling of HCB and PeCB in water*



- Correlation between freely dissolved HCB and PeCB concentrations in freshwater and in the marine environment.
- Constant C_{w-HCB}/C_{w-PeCB} in water at sites remote from point sources of either of the chemicals

NIVA

*Allan et al. (2021) Passive sampling and benchmarking to rank HOC levels in the aquatic environment. Scientific reports, 11(1), pp.1-12.

On the use of PS data to interpret biota data (i)

How can we investigate whether HCB biomagnifies?

• Some assumptions:

NIV

- Constant C_{w-HCB}/C_{w-PeCB} in water (remote from point sources of either of the chemicals)
- Hexachlorobenzene is a potential biomagnifier
- Pentachlorobenzene does not biomagnify
- Calculate lipid-based ("abiotic") bioconcentration factors from K_{lip-SR} and K_{SR-w}:

$$\frac{BCF_{lip,x}}{BCF_{lip,PeCB}} = \frac{K_{lip-w,x}}{K_{lip-w,PeCB}} = \frac{K_{lip-sr,x}K_{sr-w,x}}{K_{lip-sr,PeCB}K_{sr-w,PeCB}}$$

• Calculate hypothetical HCB/PeCB concentration ratio in fish:

$$\frac{C_{lip,equiv,x}}{C_{lip,equiv,PeCB}} = \frac{BCF_{lip,x}}{BCF_{lip,PeCB}} \frac{C_{free,x}}{C_{free,PeCB}}$$

Ratio of C_{Free} from passive sampling

4

On the use of PS data to interpret biota data (ii)

• The calculated ratio of bioconcentration factor – BCF_{lip}- is 3.4

Compound	logK _{sr-w}	K _{lip-sr}	logBCF _{lip}	BCFlip	BCFlip, x/BCFlip, PeCB		
	(L kg⁻¹)ª	(kg kg⁻¹)ª	(L kg⁻¹)	(L kg-1)			
PeCB	4.62	7.38	5.49	307650	1		
НСВ	5.05	9.35	6.02	1049087	3.4		
^a For AlteSil silicone rubber ¹⁴							

• Estimate hypothetical HCB/PeCB ratio in fish to check if HCB biomagnifies With TMF = 1 for TL = 1, and TMFs of 3.4 (range of 2-4) for HCB**

		$C_{free,HCB}/C_{free,PeCB}^{a}$	BCF _{lip,HCB} / BCF _{lip,PeCB} b	$BAF_{lip,HCB}/BAF_{lip,PeCB}$		$C_{lip,HCB}/C_{lip,PeCB}d$		
			.,	TL=3	TL=4	TL=3	TL=4	11
	Freshwater	3.93	3.4	39 (14-55)	134 (27-218)	155 (53-214)	525 (107-855)	
	Marine	2.76	3.4	39 (14-55)	134 (27-218)	108 (37-150)	369 (75-600)	
NIV	**apply	ying range of trop	hic magnifi	cation fa	ctors (TMF)	found fro	m literature	5

On the use of PS data to interpret biota data (iii)

• Compare HCB/PeCB concentration ratio in fish from monitoring data* with hypothetic ratio to check for bioconcentration of the two chemicals

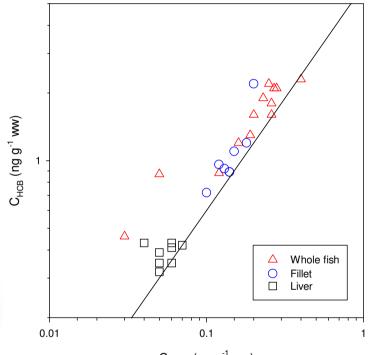
• Compare chemical activity in fish and in water for sampling locations where passive sampling and fish monitoring was conducted in parallel

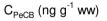
NIVA

$$\frac{A_{Fish}}{A_{water}} = \frac{C_{Fish,lip}}{C_{lip,equiv}} = \frac{C_{Fish,lip}}{K_{lip-sr}K_{sr-w}C_{free}}$$

*Fish data from the Norwegian environmental contaminants database <u>https://vannmiljo.miljodirektoratet.no/</u>

Caged brown trout in the river Alna (Oslo)*





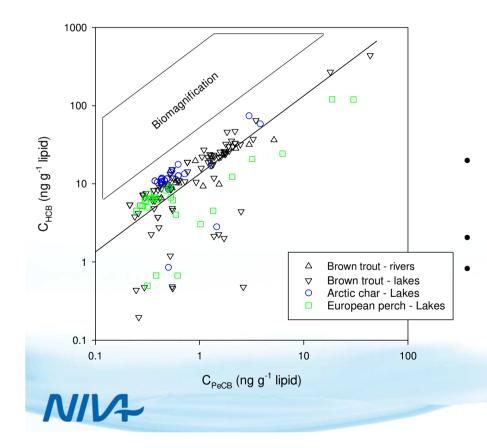
With caged fish not allowed to feed, bioconcentration of the two chemicals was expected

Excellent agreement between the HCB/PeCB concentration ratio in fish and the predicted HCB/PeCB concentration ratio using-BCF_{lip} and ratio of C_{free} (line)

*Allan et al (2013) In technology, 47(20), p

*Allan et al (2013) In vivo passive sampling of nonpolar contaminants in brown trout (Salmo trutta). *Environmental science & technology*, 47(20), pp.11660-11667.

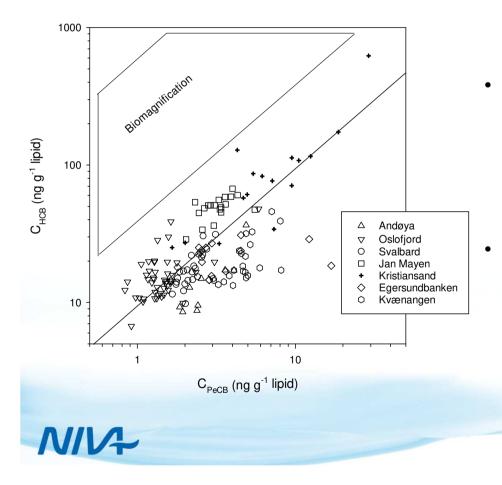
HCB and PeCB in freshwater fish of Norway



- Fish data collection*:
 - Use of most paired HCB/PeCB data available in the database for the last 5-10 years
 - Single fish & composite fish datasets (fillet and/or whole fish)
 - Data from lakes and rivers
 - Few values below LOD/LOQ
 - Most data in agreement with ratio indicating bioconcentration of the two compounds when comparing with water
 - No indication of biomagnification of HCB
 - For the entire fish dataset (n=167), the HCB/PeCB concentration ratio is 17.4, corresponding to:
 - A C_{free,HCB}/C_{free,PeCB} ratio of 5 rather than 3.93
 - A TMF of 1.1 for a fish at TL = 4 and 1.15 for a fish at TL = 3.

*https://vannmiljo.miljodirektoratet.no/,

HCB and PeCB in cod from the Norwegian coast



Fish data gathering*:

• Use of most paired HCB/PeCB data available in the database for the last 5-10 years

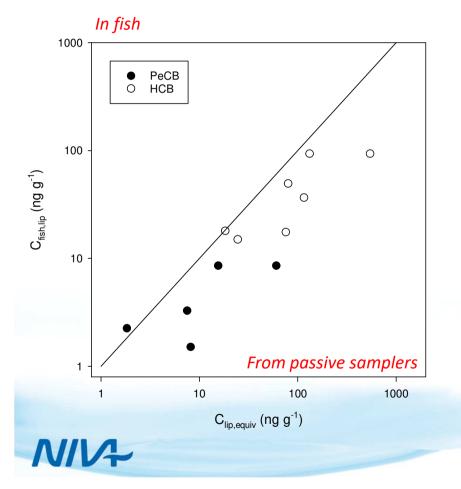
- Single fish & composite fish datasets
- Extraction and analysis from cod liver
- Few values below LOD/LOQ
- No fish data indicating biomagnification of HCB in cod when comparing with water



HCB and PeCB in cod from the Norwegian coast

.

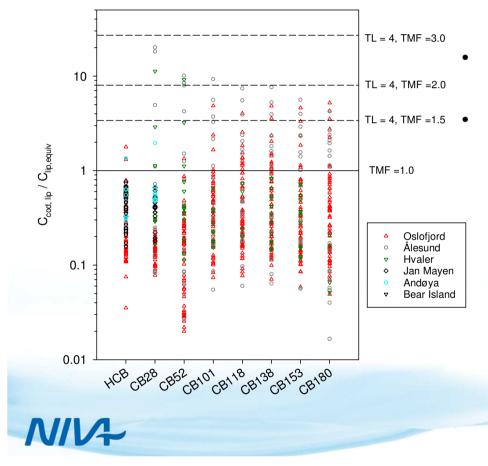
.



- Cod and PS data from Andøya, Bear Island, Jan Mayen, Kristiansand, Oslofjord and Svalbard (2009-2017)*
- Lipid-based cod liver concentrations of HCB and PeCB ($C_{fish-lip}$) at or below HCB and PeCB concentrations in lipid at equilibrium with the water ($C_{lip,equiv}$) estimated from passive sampling
- No fish data indicating biomagnification of HCB in cod with TMFs for HCB reported in the literature

^{*}https://vannmiljo.miljodirektoratet.no/,

PCBs in cod from the Norwegian coast



- Cod expected to have a Trophic level (TL) of 3-4
- Most data indicating PCB levels in cod (liver) not higher than in water



Conclusions

• No apparent biomagnification of HCB in Norwegian freshwater fish commonly used for WFD monitoring (when comparing with water)

ightarrow Fish data strongly connected to levels in water

- No apparent biomagnification of HCB in cod from Norwegian coastal areas
- Lipid-based cod liver concentrations of HCB and PeCB hardly ever above concentrations in lipids that would be at equilibrium with the water estimated from passive sampling (C_{lip,equiv})
- Most PCB concentrations in cod do not exceed C_{lip,equiv} calculated from PS data for contiguous measurement

