

How can passive sampling be used to help understand POP bioaccumulation in fish?

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Introduction & theory

- Passive sampling (PS) enables the estimation of freely dissolved concentrations (C_{free}) of bioaccumulative substances in water
- Lipid-silicone rubber partition coefficients (K_{lip-sr}) allow to express contaminant levels in water (activity, A) on a lipid basis ($C_{lip-equiv}$) to facilitate comparison with levels in biota (also expressed on a lipid basis)

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

- Ratios of hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) in water are very constant (Allan et al., 2021). HCB is expected to biomagnify while PeCB is not. Trophic magnification factors (TMF) in the range of 2-4 (median 3.4) have been reported for HCB.
- Benchmarking of HCB levels against those of PeCB and calculation of expected ratio in fish in the case of bioconcentration of both chemicals:

$$\frac{C_{lip,equiv,HCB}}{C_{lip,equiv,PeCB}} = \frac{C_{sr,equiv,HCB} K_{lip-sr,HCB}}{C_{sr,equiv,PeCB} K_{lip-sr,PeCB}} = \frac{K_{lip-w,HCB} C_{free,HCB}}{K_{lip-w,PeCB} C_{free,PeCB}}$$

with $K_{lip-w} = K_{lip-sr} \times K_{sr-w}$.

AIMS OF THIS STUDY

- Evaluate whether HCB biomagnification in fish used for chemical monitoring in biota in Norway can be observed based on HCB/PeCB benchmarking ratios
- Assess fish-water activity ratios on a lipid basis for HCB, PeCB and PCBs where silicone rubber was conducted alongside cod (Gadus morhua) biomonitoring

Methodology

- Contaminant levels in fish from: <https://vanmiljo.miljodirektoratet.no/>
- Calculation of ratio of $K_{lip-w,HCB}/K_{lip-w,PeCB}$:

Compound	$\log K_{sr-w}$ (L kg ⁻¹) ^a	K_{lip-sr} (kg kg ⁻¹) ^a	$\log K_{lip-w}$ (L kg ⁻¹)	K_{lip-w} (L kg ⁻¹)	$K_{lip-w,HCB}/K_{lip-w,PeCB}$
PeCB	4.62	7.38	5.49	307650	
HCB	5.05	9.35	6.02	1049087	3.4

^aFor AlteSil silicone rubber¹⁵

- Calculation of expected ratio in case of biomagnification of HCB with

$$\frac{C_{lip,equiv,HCB}^{TL}}{C_{lip,equiv,PeCB}} = \frac{K_{lip-w,HCB} C_{free,HCB} TMF^{TL-1}}{K_{lip-w,PeCB} C_{free,PeCB}}$$

- Calculated expected HCB/PeCB ratio for TMFs of 3.4 for fish species with trophic levels (TL) of 3 or 4:

	$C_{free,HCB}/C_{free,PeCB}$ ^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
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)

REFERENCES

- Allan et al. (2021). Passive sampling and benchmarking to rank HOC levels in the aquatic environment. Scientific reports, 11(1), 1-12.
 Smedes et al. (2020). Unraveling the relationship between the concentrations of hydrophobic organic contaminants in freshwater fish of different trophic levels and water using passive sampling. Environmental science & technology, 54(13), 7942-7951.

ACKNOWLEDGEMENTS

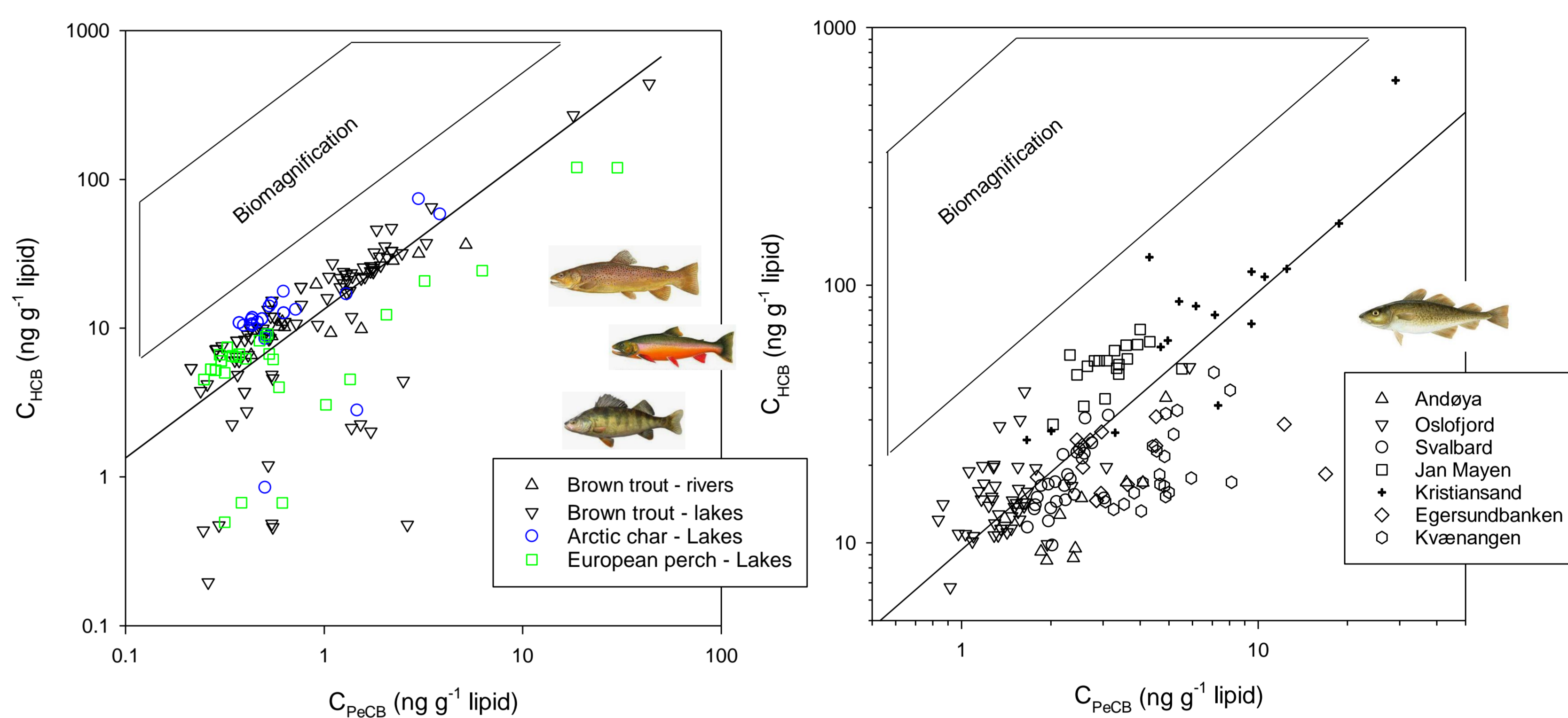
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Results

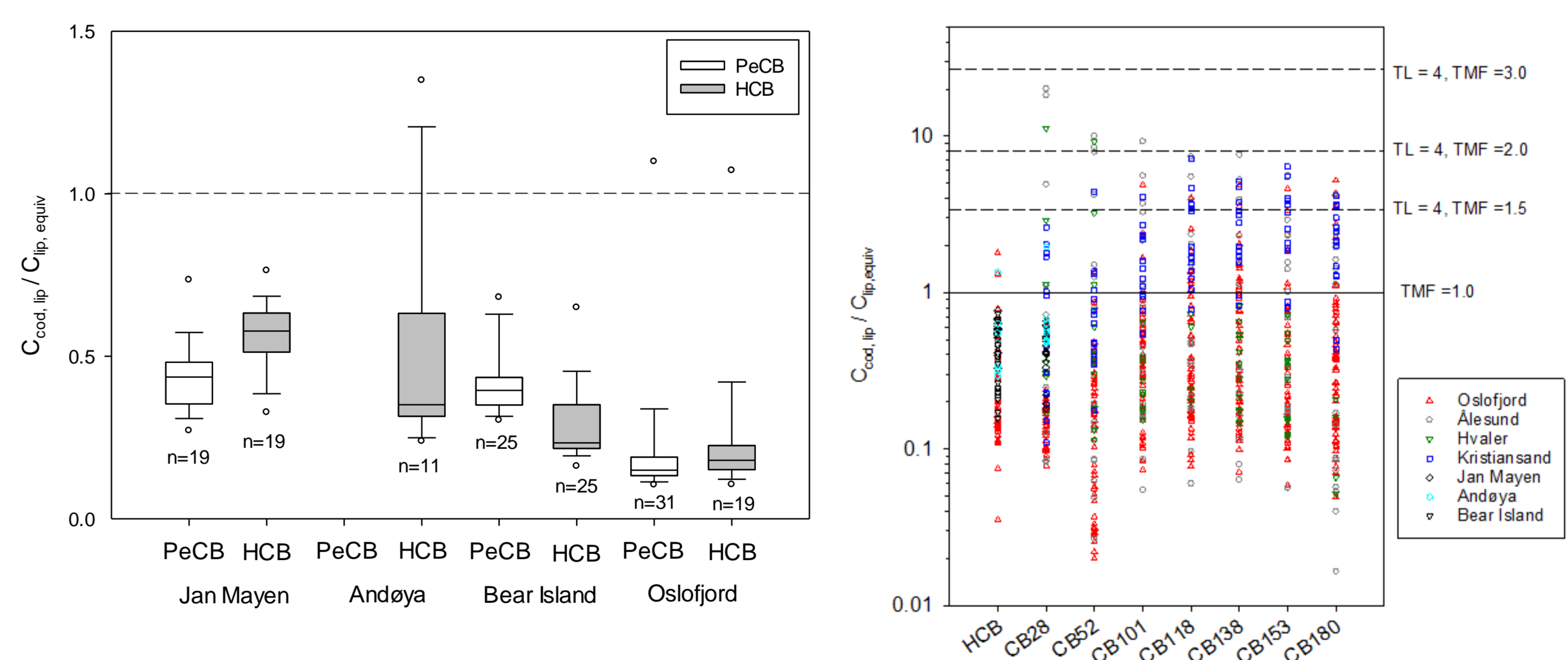
BENCHMARKING WITH PeCB IN FRESHWATER AND SEAWATER FISH

- Data for brown trout, Arctic char and European perch consistently close to the reference line indicative of bioconcentration of HCB
- HCB/PeCB ratios in freshwater fish far from showing biomagnification of HCB
- More spread of the data for cod on the coast of Norway, but still not demonstrating any biomagnification



ACTIVITY RATIOS FOR HCB, PeCB & PCBs IN COD

- Ratios consistently < 1 for HCB and PeCB
- Most sites showing activity ratios for PCBs < 1
- Data from Kristiansand showing ratios > 1; the area presents contamination with chlorinated compounds and fish and PS may not be representative of the same area/depth of water
- Activity ratios < 1 indicating contaminant level in fish lower than those in water



Conclusions

- No firm indication of HCB biomagnification in fish used for chemical monitoring in Norway:
- HCB/PeCB ratios << those expected in case of biomagnification of HCB
- Fish-water activity ratios < 1 for HCB in cod
- Fish-water activity ratios for PCBs in cod < 1 supporting previously published data for freshwater fish (Smedes et al., 2020)