

How constant is the HCB/PeCB ratio in the aquatic environment at a regional level? what are the possible implications?

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Hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) – Sources/emissions

- On Stockholm Convention list of POPs
- Past uses of HCB: as a fungicide (1933-1980s)
- Up to 10^4 tonnes y^{-1} use of HCB in the 1980s
- National bans and restricted uses: 1960s-2000s
- Current HCB emissions through incomplete combustion processes, present as byproduct or impurity in solvents/pesticide formulations, re-mobilisation from soil to air
- PeCB used in PCB-based dielectric fluids, in the production of certain pesticides (e.g. quintozene)...

Characteristic and fate of HCB and PeCB in the environment

- Long half-lives: 2.7-6 years in air for HCB
- Enthalpies of air/surface phase change 1.9-37 kJ/mol → weak dependence of C_{air} on temperature for HCB
- “Multiple hoppers”



	PeCB	HCB
$\log K_{ow}$	5.0	5.5
$\log K_{AlteSil-w}$	4.6	5.06
H ($1/(\text{Pa m}^3 \text{ mol}^{-1})$)	0.014	0.019
$d \ln H/d(1/T)$ (K)	6000	5200
V_p (Pa)	0.88	0.245
S_w (mg L^{-1})	0.65	0.005
$\log K_{OA}$	6.5	6.8

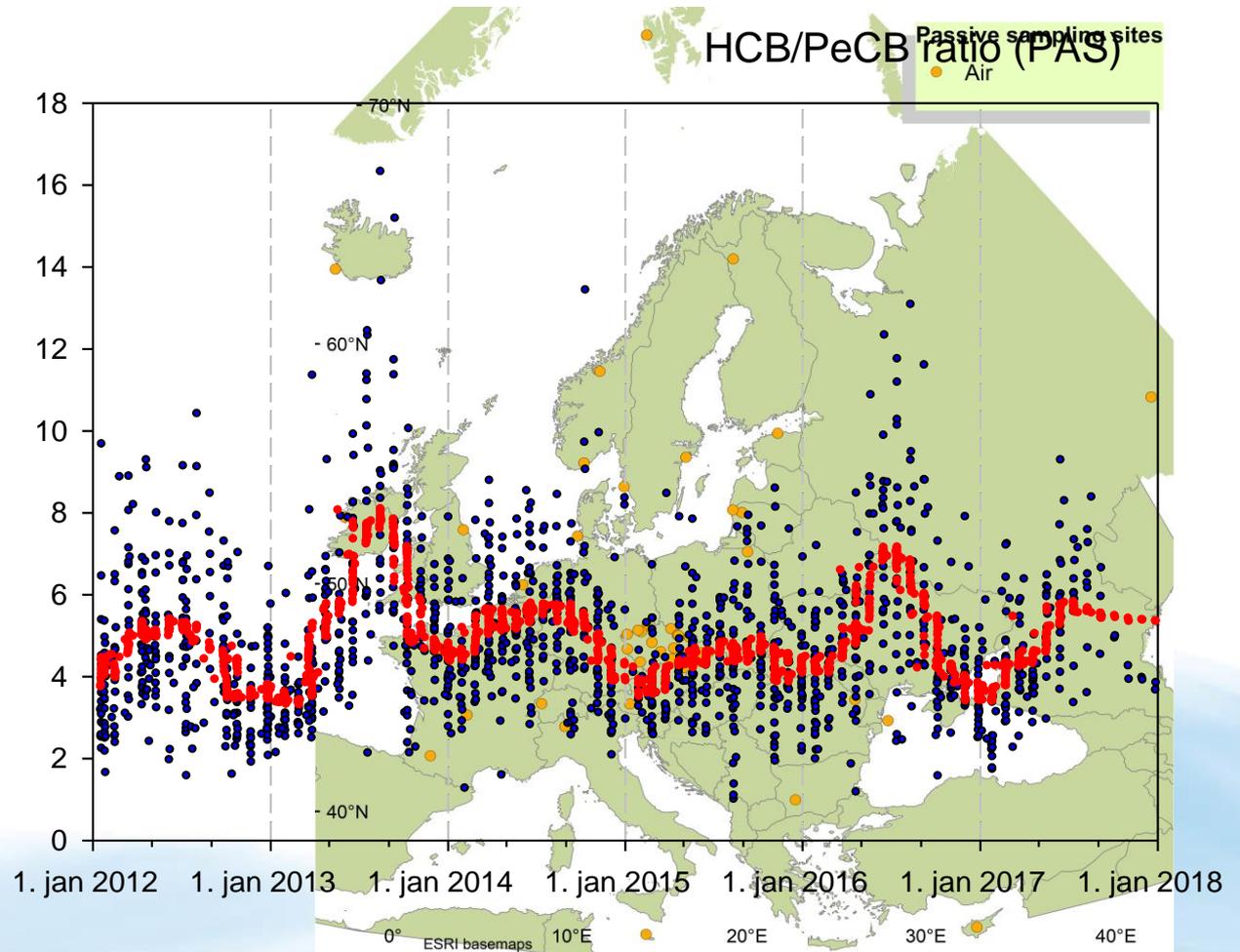
HCB and PeCB concentrations in air and water

- Already in 2004-5, Jaward *et al.* and Barber *et al.* pointed out that in phase equilibrium, the ratio of concentrations of a chemical in air and water approaches unity:
- Barber *et al.* (2005) proposed that HCB would reach regional/global equilibrium faster than other POPs
- HCB/PeCB ratios in the range 2.5-5.6 in air in Estonia (Roho *et al.*, 2010). For the HCB/PeCB ratio, this means:
- Homogenous HCB and PeCB distribution in North Sea air (Mai *et al.*, 2016)

$$\frac{C_{w,HCB}}{C_{w,PeCB}} = \frac{C_{a,HCB}}{C_{a,PeCB}} \frac{H_{PeCB}}{H_{HCB}}$$
- Close to phase equilibrium for HCB in marine environments with continental influence (Lohmann *et al.*, 2009)

PAS concentrations from the GENASIS database

- Data for 2012-2018
- The average of all data is approx 4.90
- Slight seasonal effect



→ Can the HCB/PeCB concentration ratio in water be used to:

- I. Identify sites with elevated HCB or PeCB concentrations?
- II. Benchmark other chemicals?

This presentation

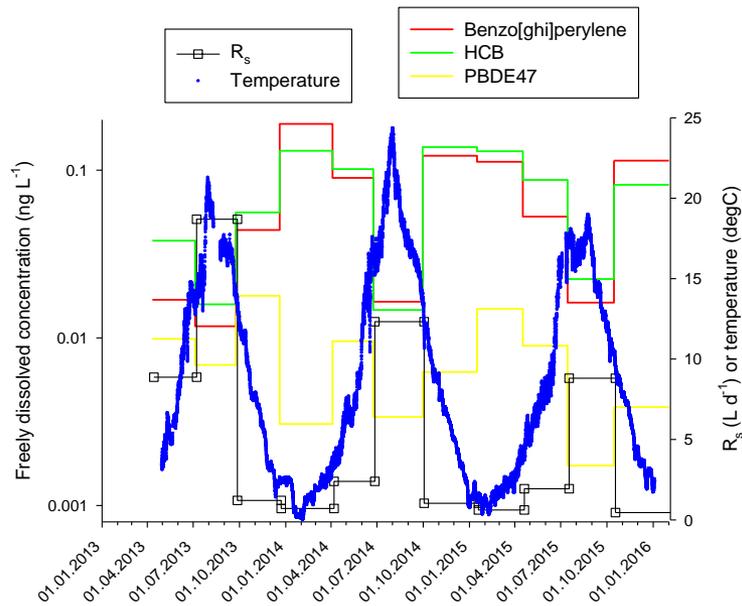
- Investigate data from two Norwegian rivers:
 - HCB/PeCB ratio
 - Benchmarking for other chemicals
- Expand the study to more sites across Europe:
 - HCB/PeCB ratio (freshwater and marine)
 - Benchmarking for other chemicals

AlteSil™ silicone rubber exposures

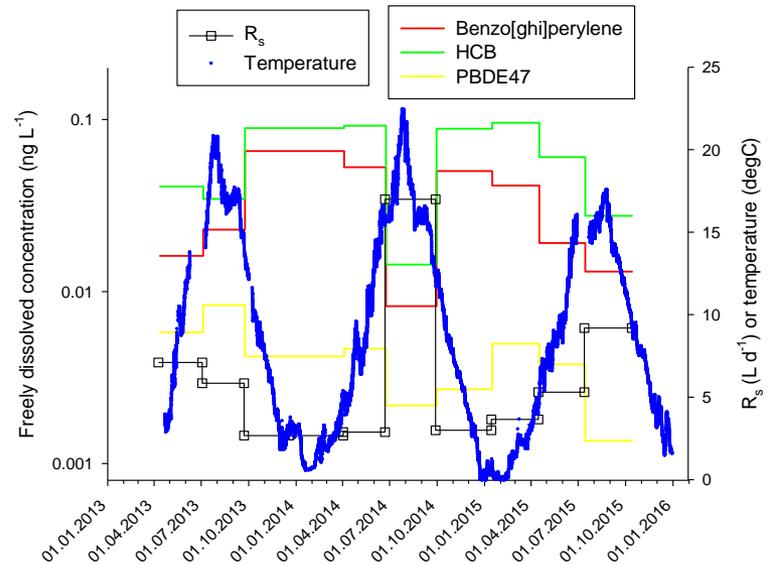
NIVA	
Mass of SR (g)	28-34 g (1000 cm ²)
Exposure time (d)	14-365
Exposures	SPMD cages, glider
PRCs	Deuterated PAHs
Analysis	GC/MS for PAHs GC/MS or ECD for OCPs

RECETOX	
Mass of SR (g)	22-27
Exposure time (d)	1.5-164
	Cages, mobile dynamic
PRCs	PCBs
Analysis	GC/MSMS

Drammen and Glomma rivers



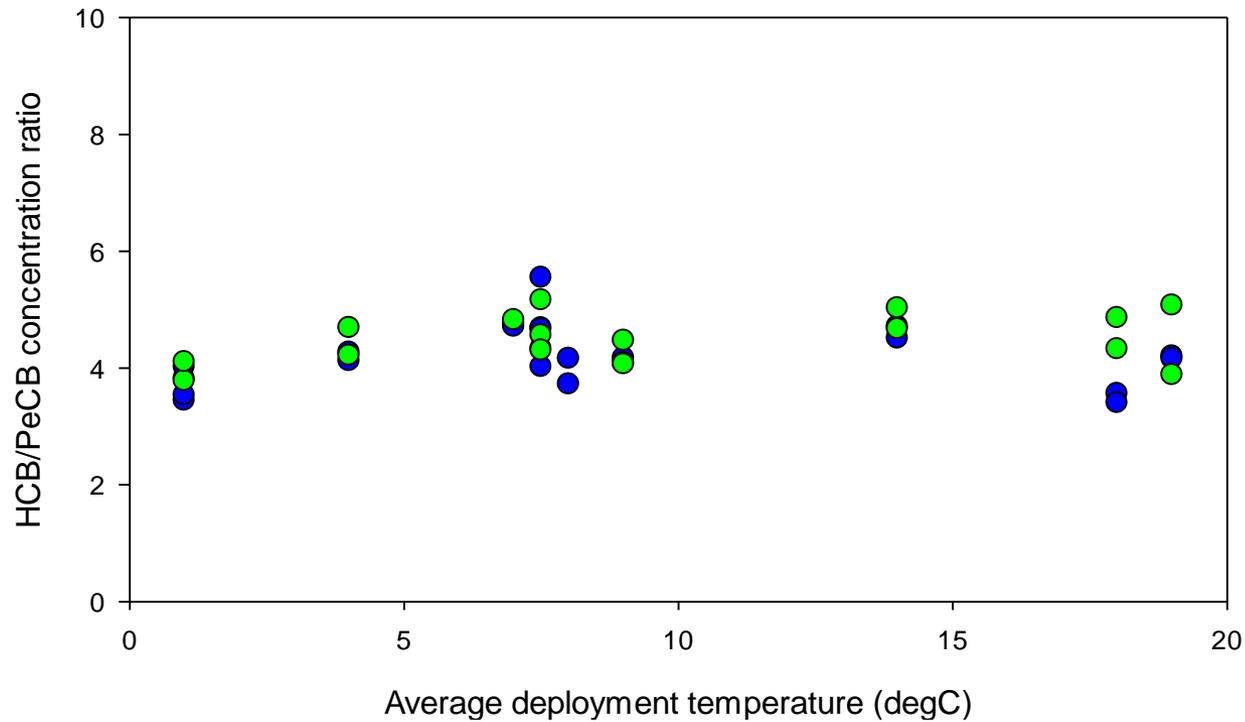
Drammen



Glomma

Wide amplitude in R_s linked to water temperature

HCB/PeCB ratio in the Drammen and Glomma rivers

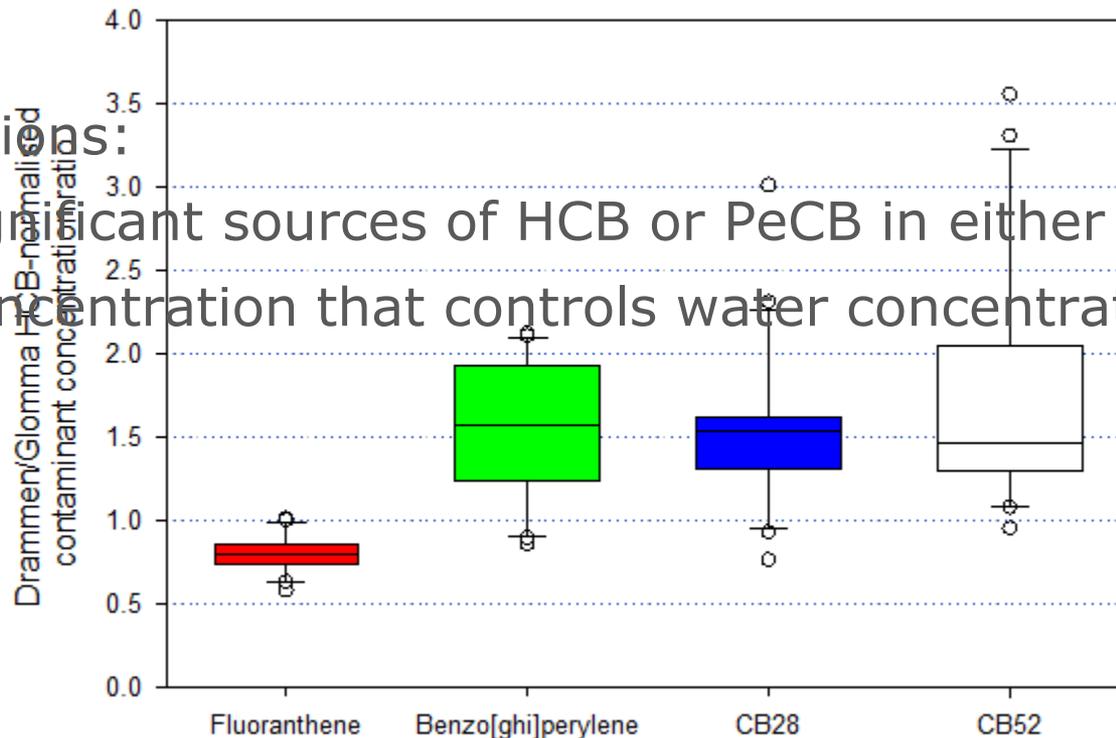


Relatively constant HCB/PeCB ratio and similar for the two rivers

Benchmarking for PAHs and PCBs

Assumptions:

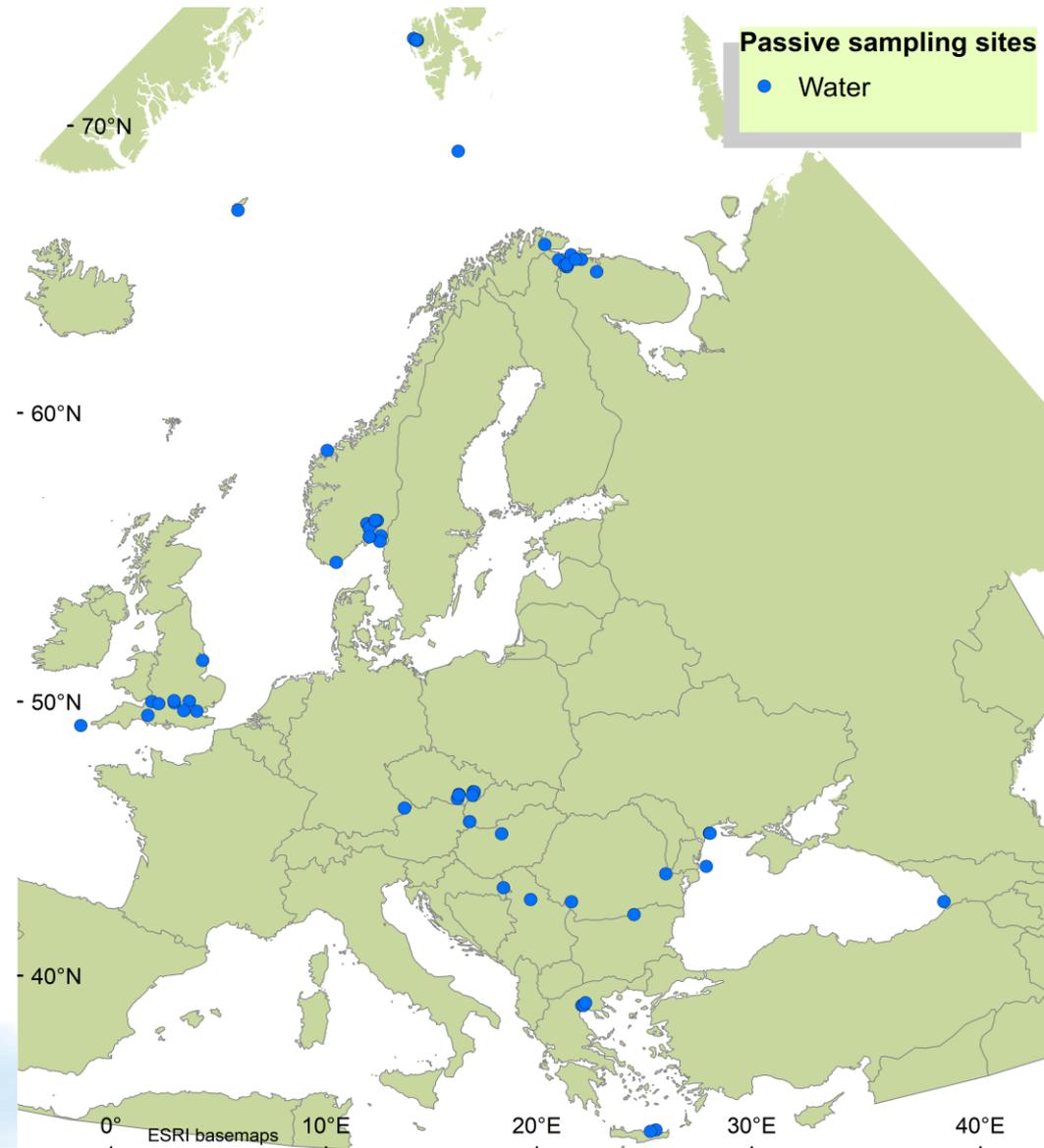
- No significant sources of HCB or PeCB in either of the rivers
- Air concentration that controls water concentration?



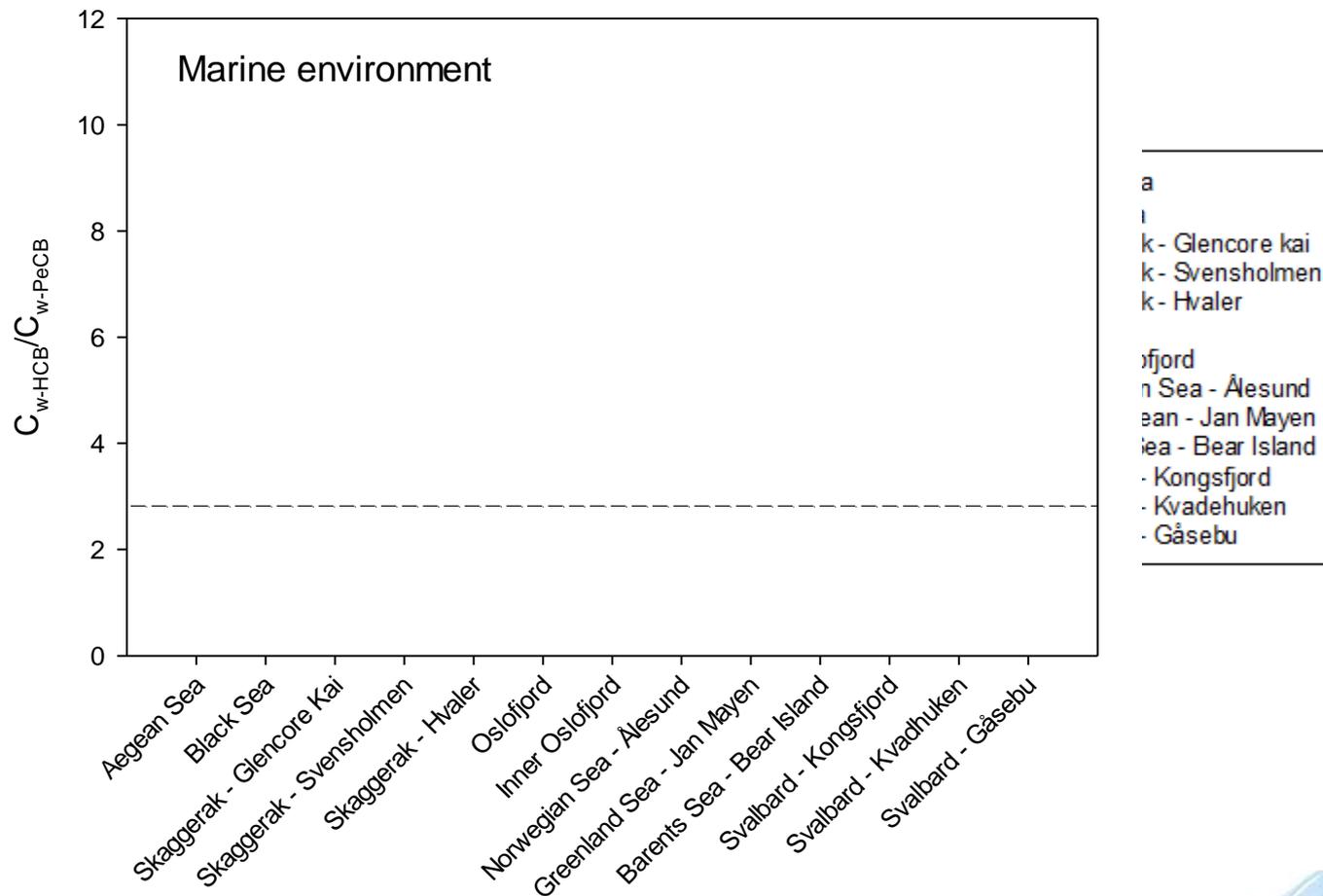
Ratios of paired HCB-normalised concentrations of fluoranthene, benzo[ghi]perylene, CB28 and CB52 estimated for simultaneous passive sampling exposures in the Rivers Drammen and Glomma for the period 2013-2016 (n = 11)

SR deployments in water

- Deployments from 2009-2017
- Passive water sampling sites or transects (blue dots)

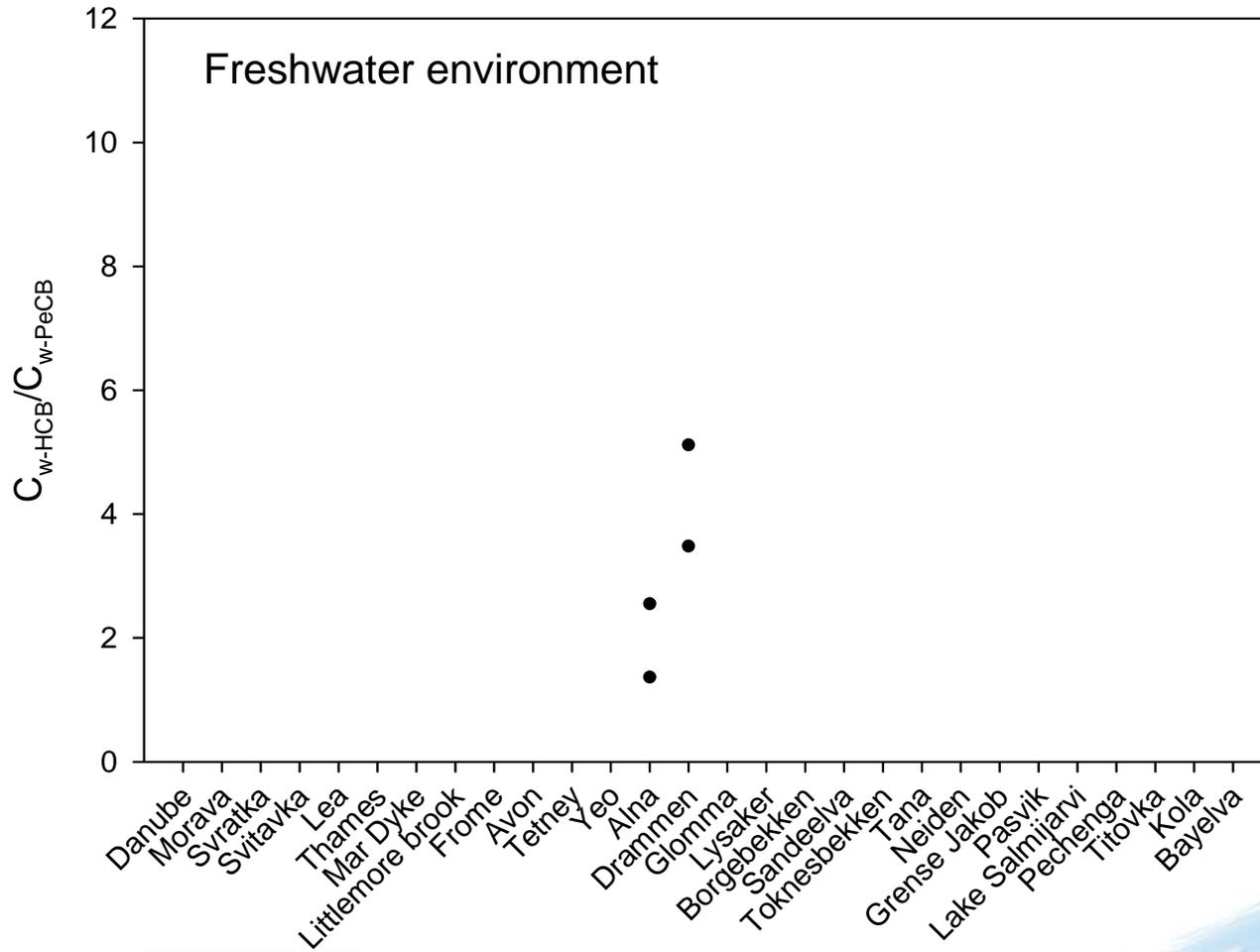


HCB/PeCB ratio in seawater



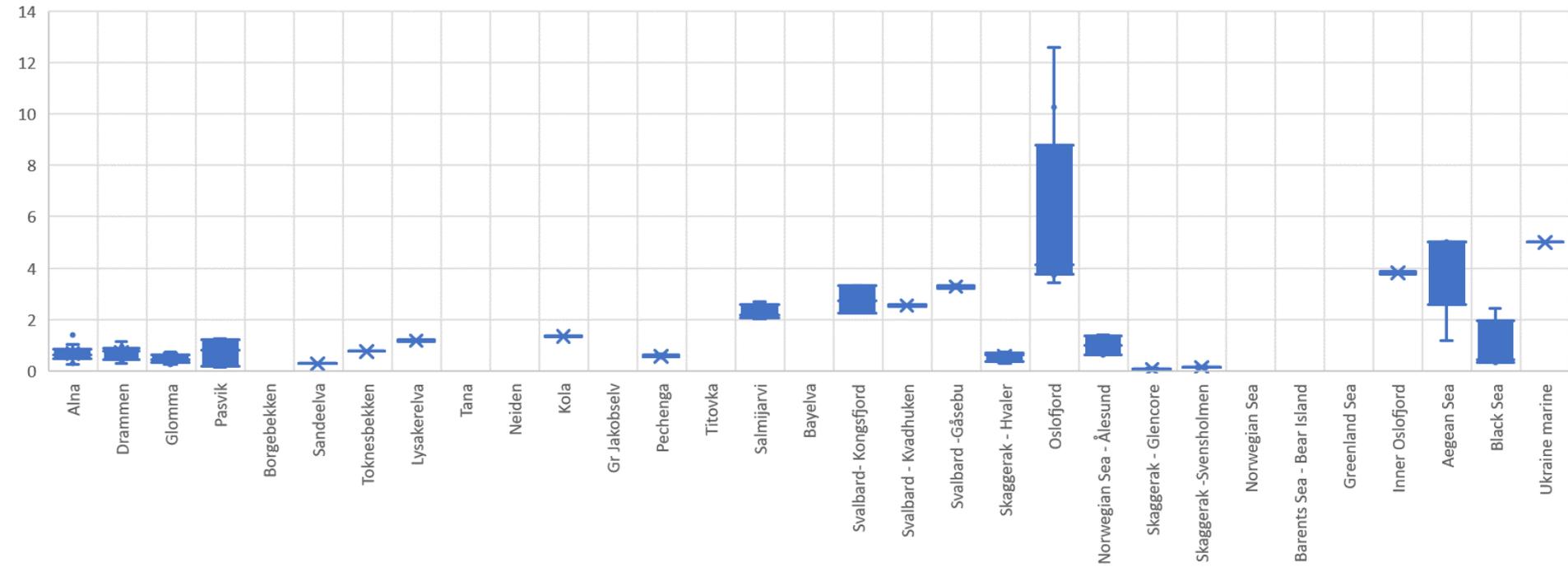
- Site
- The regression line: $y = 2.76$ (se = 0.06) $x + 0.0003$ (se = 0.003); $R^2 = 0.978$, $n = 60$

HCB/PeCB ratio in freshwater



Benchmarking of other chemicals

CB52/PeCB



Conclusions

- HCB/PeCB ratio appears to distinguish sites with contamination with either compounds
 - Confirmation, validation
 - Procedure to develop
 - Thresholds and scale?
- Benchmarking seems promising
 - Applicability?
- Changes in ratio will probably occur over time depending on the sources, strength of emission to atmosphere or water, or differences in loss rates
- What does it translate to for other matrices? Li *et al.* (2013) found HCB/PeCB ratios of 3.4-7.7 in carp livers

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