PS in support of fish monitoring – A new approach?

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Research centre
for toxic compounds
in the environment

GACR project

"Investigation of accumulation of persistent bioaccumulative toxic organic substances into aquatic organisms"

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To do this, a reference method is needed, that is not affected by trophic magnification, does not degrade substances, …

-- passive sampling --

GACR project

Get passive sampler equilibrium faster

Provide best quality polymer—water partition coefficients (K_{PW})

Polymer—lipid partition coefficient (K_{PL})

Validate passive sampling in tissue of biota

WATER by passive sampling

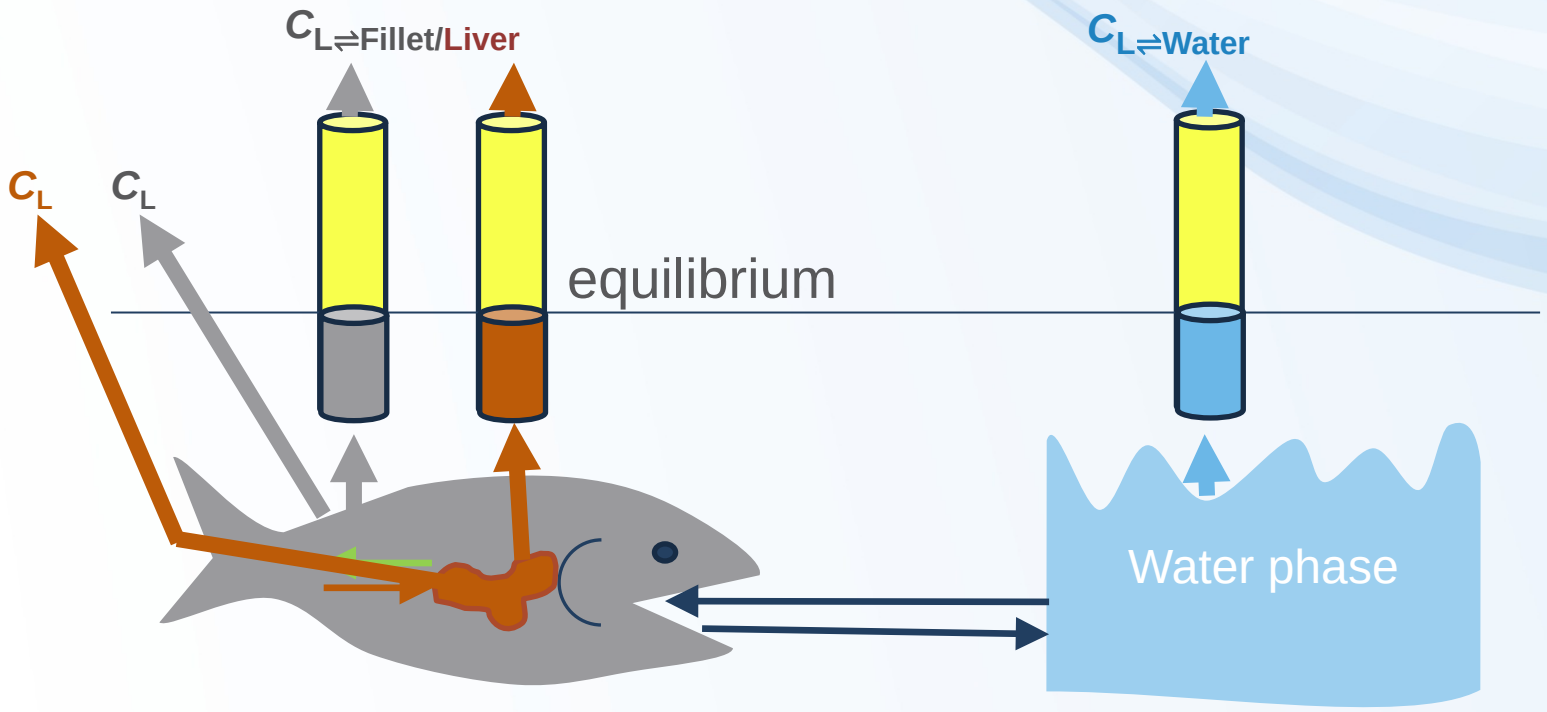
FISH : fillet – liver (classic and passive sampling)

Different: locations, species TROPHIC level

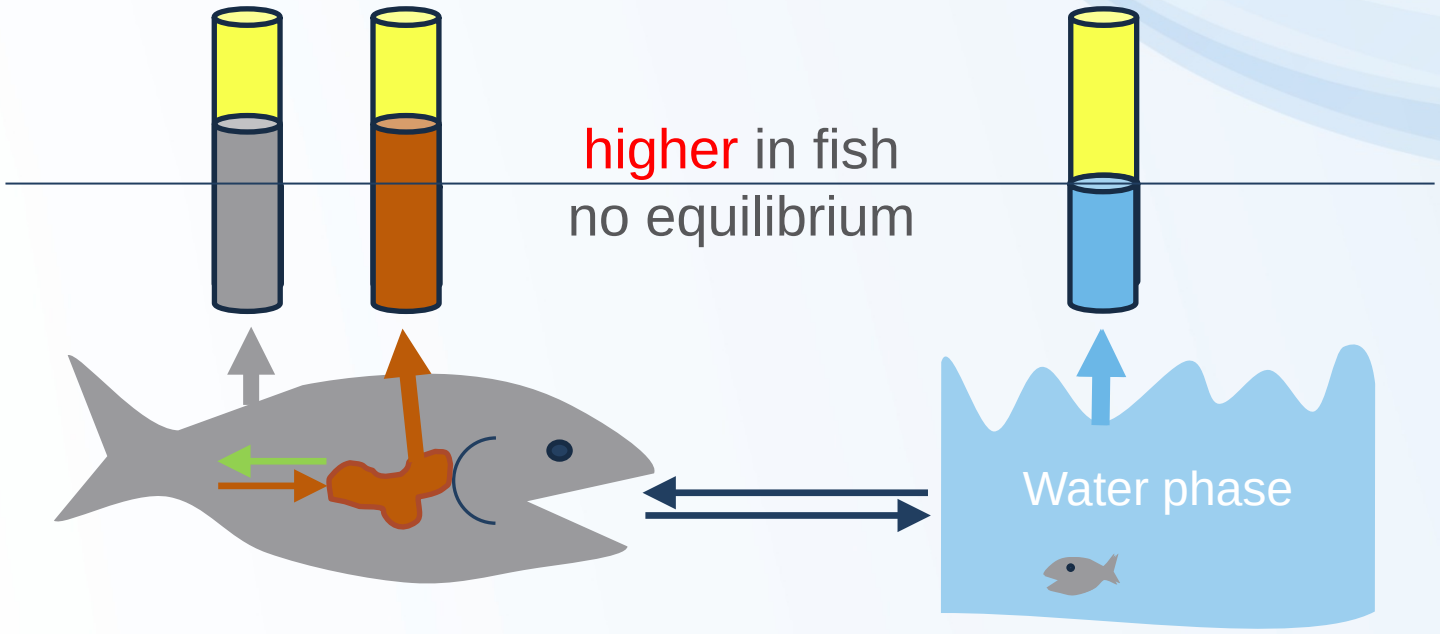
Comparison on lipid basis, PCB, OCP and BDE

What passive sampling can show us

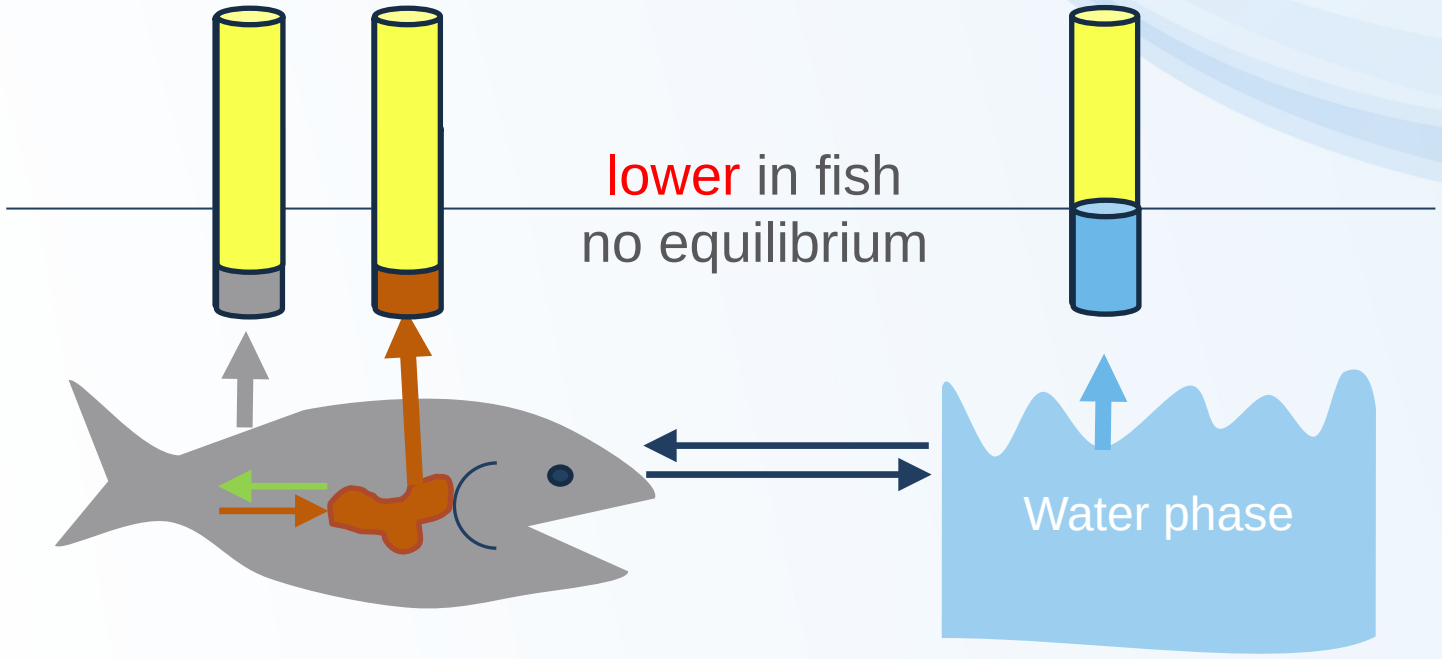
Levels in fish ← → water (1)



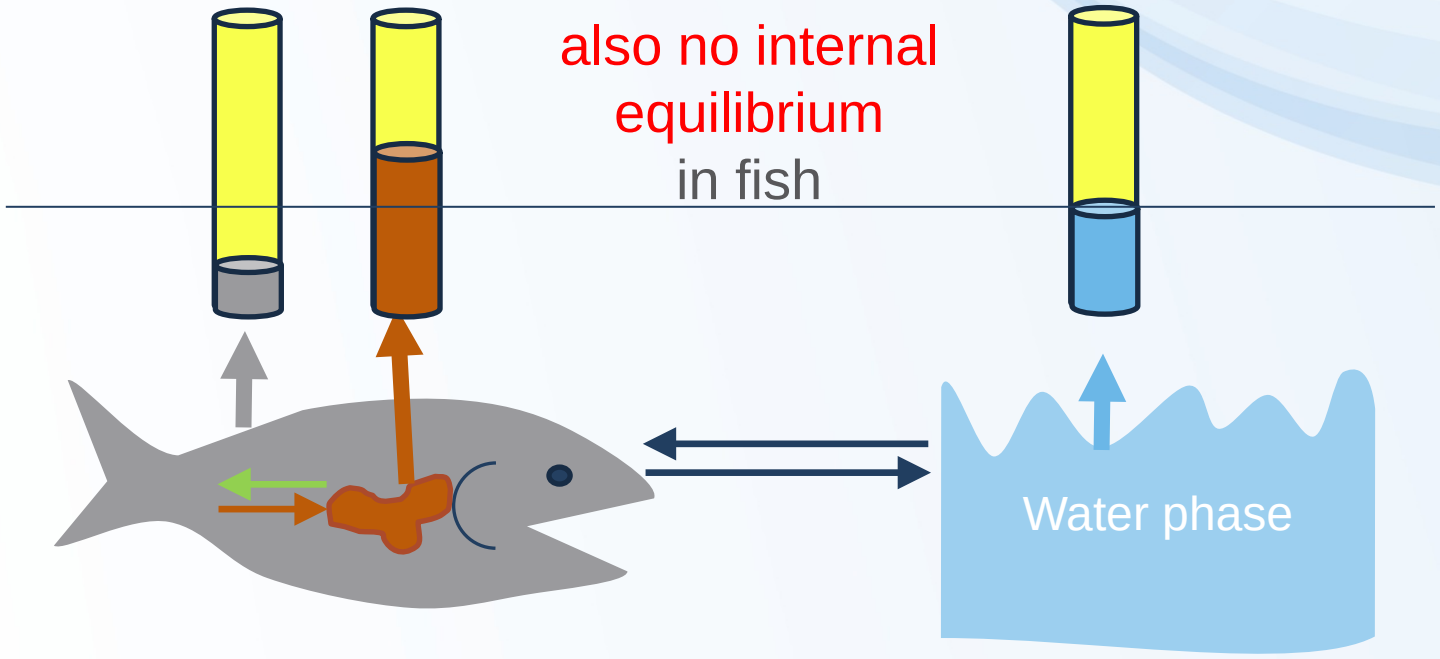
Levels in fish ← → water (2)



Levels in fish ← → water (3)



Levels in fish ← → water (4)



The practical activities

Sampling sites

European chub
Common nase
Common barbel

Wels catfish (2x4,5)
Ide (Orfe)
Common carp
Bronze bream
Grass carp

Asp (3)
Perch
European chub
Common bleak
Roach
Crucian carp
Common nase
Bronze bream
Common barbell (2)

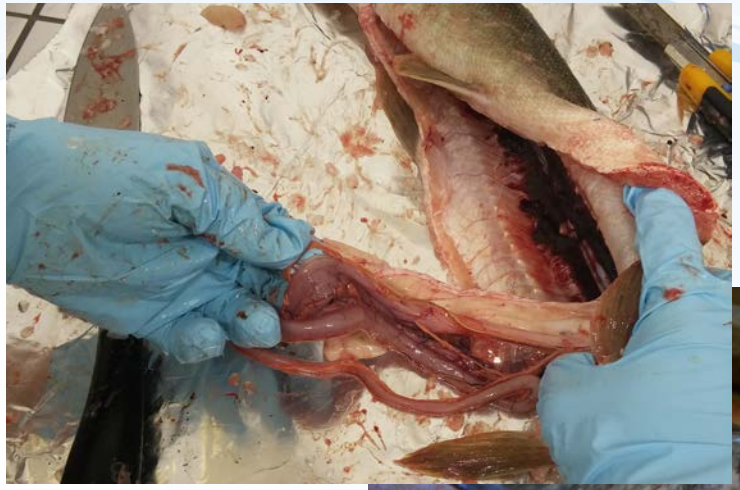
Trophic level

$$TL_{fish} = \{\delta^{15}N_{fish} - \delta^{15}N_{mussel}\}/3.4 + 2$$

3.4‰ change in δ15N per unit of TL (SD=1‰) ; Post D.; 2002

$\delta^{15}N$ baseline species e.g mussels; TL=2 by defintion

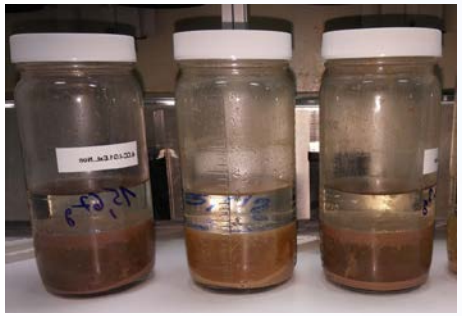
How does the fish handing look

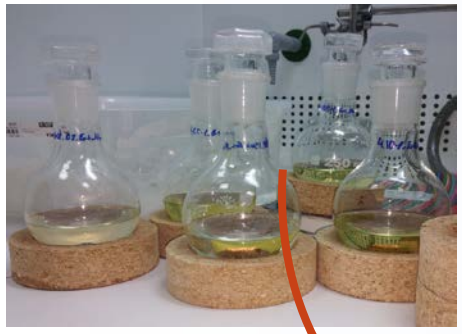


Classic solvent extraction

Equilibrium Passive Sampling in tissue (EPS)

Tissue extraction by partitioning





Cleanup – analysis

1. Lipid
2. PCB, DDx, BDE

C_L in liver

C_L in fillet

Passive samplers dosed with PRC were equilibrated with **fillet** and **liver**.

$$\frac{C_{P\rightleftharpoons\text{Liver}}}{K_{PL}} = C_{\text{L}\rightleftharpoons\text{Liver}}$$

$$\frac{C_{P\rightleftharpoons\text{Fillet}}}{K_{PL}} = C_{\text{L}\rightleftharpoons\text{Fillet}}$$

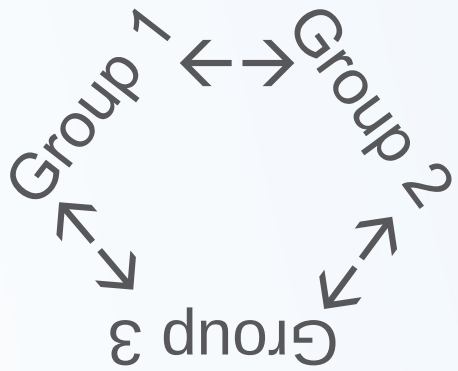
Polymer-lipid partition coefficient

Liver = liver or hepatopancreas

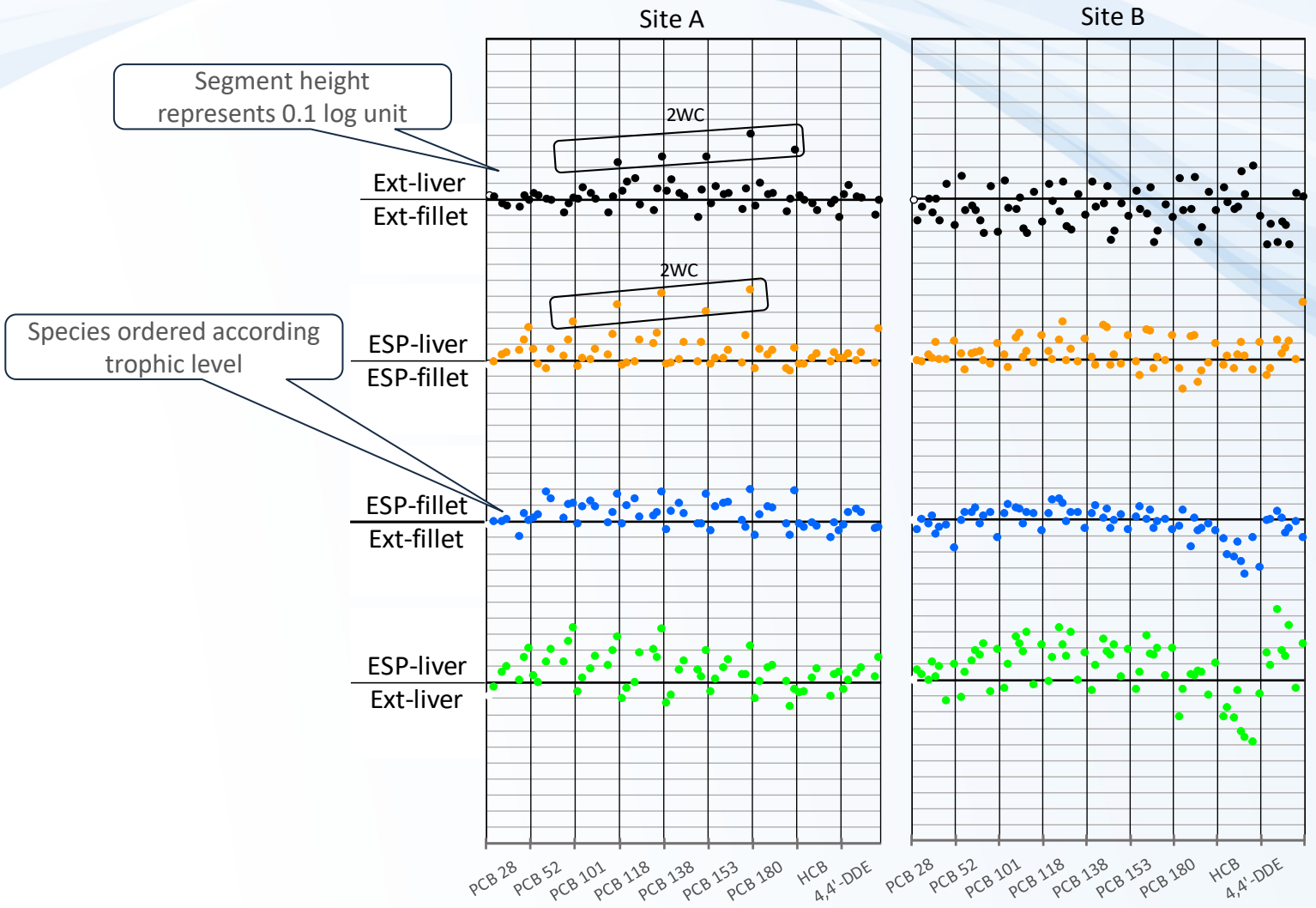
Method comparability and fish variability/repeatability

EPS ←→ extraction

liver ←→ fillet

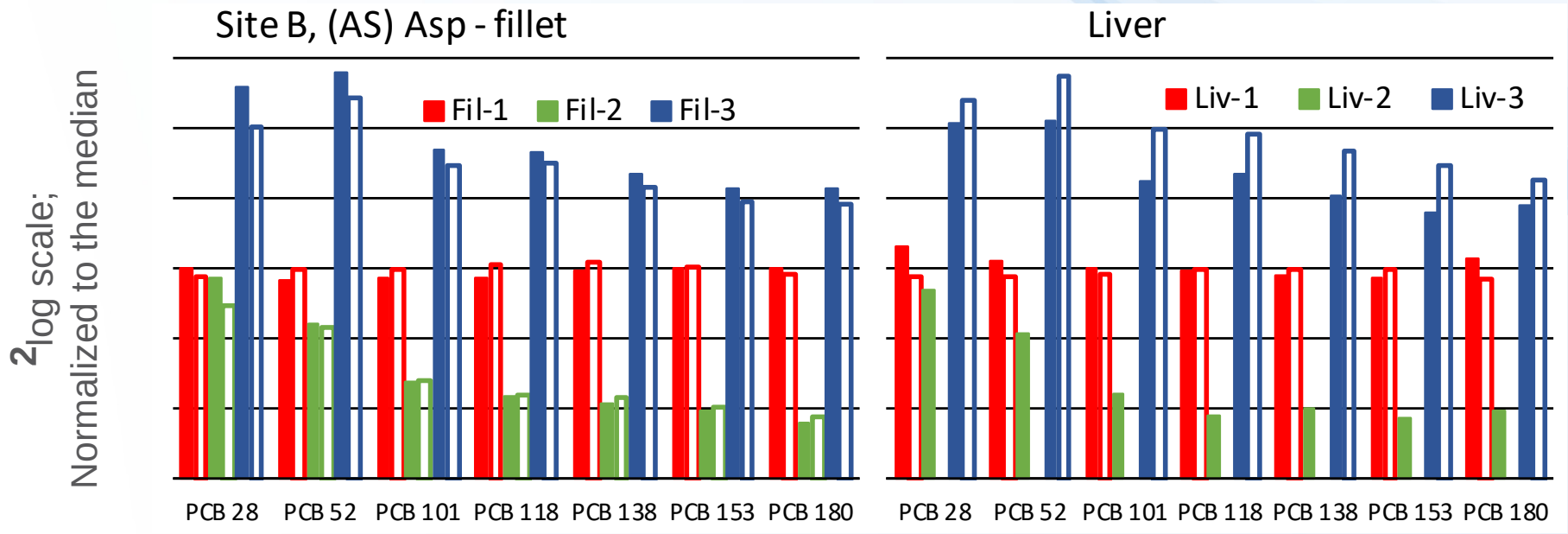


Comparing C_L determined by different method liver ←→ fillet and EPS ←→ extraction



Differences between fish–groupes
Fillet and liver as well; as well as direct and EPS show the same level

1. **Filled column is C_L by classic extraction — open column C_L via EPS**
2. **Overlay of left and right graph shows similarity between liver and filet**
3. **Different colors → different groups (1, 2, 3) of the same fish species (Asp)**



Variation between asp fish groups is substantial greater than liver versus fillet or direct extraction versus EPS

Aqueous passive sampling

From Passive sampling convert to lipid basis

Kinetic, C_W by PRC

equilibrium

$$\frac{C_W \times K_{PW}}{K_{PL}} == \frac{C_{P \rightleftharpoons Water}}{K_{PL}} == C_{L \rightleftharpoons Water}$$

$C_{L \rightleftharpoons Water}$

is here the abiotic lipid based concentration in thermodynamic equilibrium with the sampled habitat/medium

Trophic magnification – the calcs

Trophic magnification factor (TMF) is the factor HOC's lipid-based concentration $\{C_L^{TL(X)}\}$ increases per unit trophic level (TL)

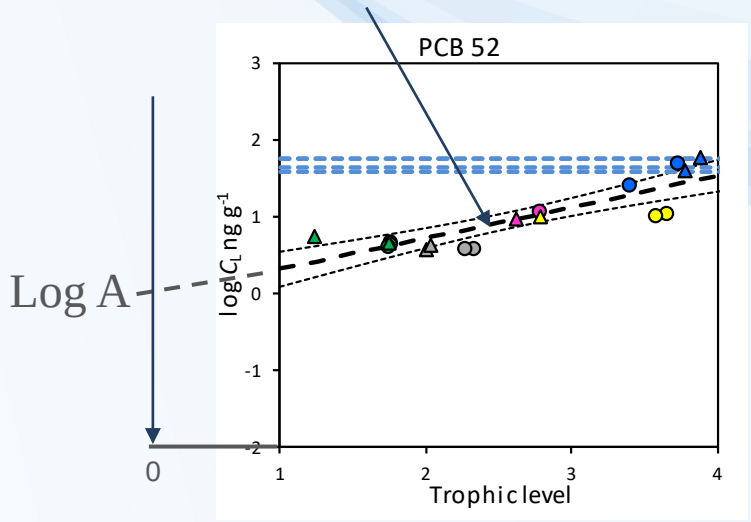
$$C_L^{TL(x)} = A \times TMF^{TL(x)}$$

$$\log C_L^{TL(x)} = \log A + TL(x) \log TMF$$

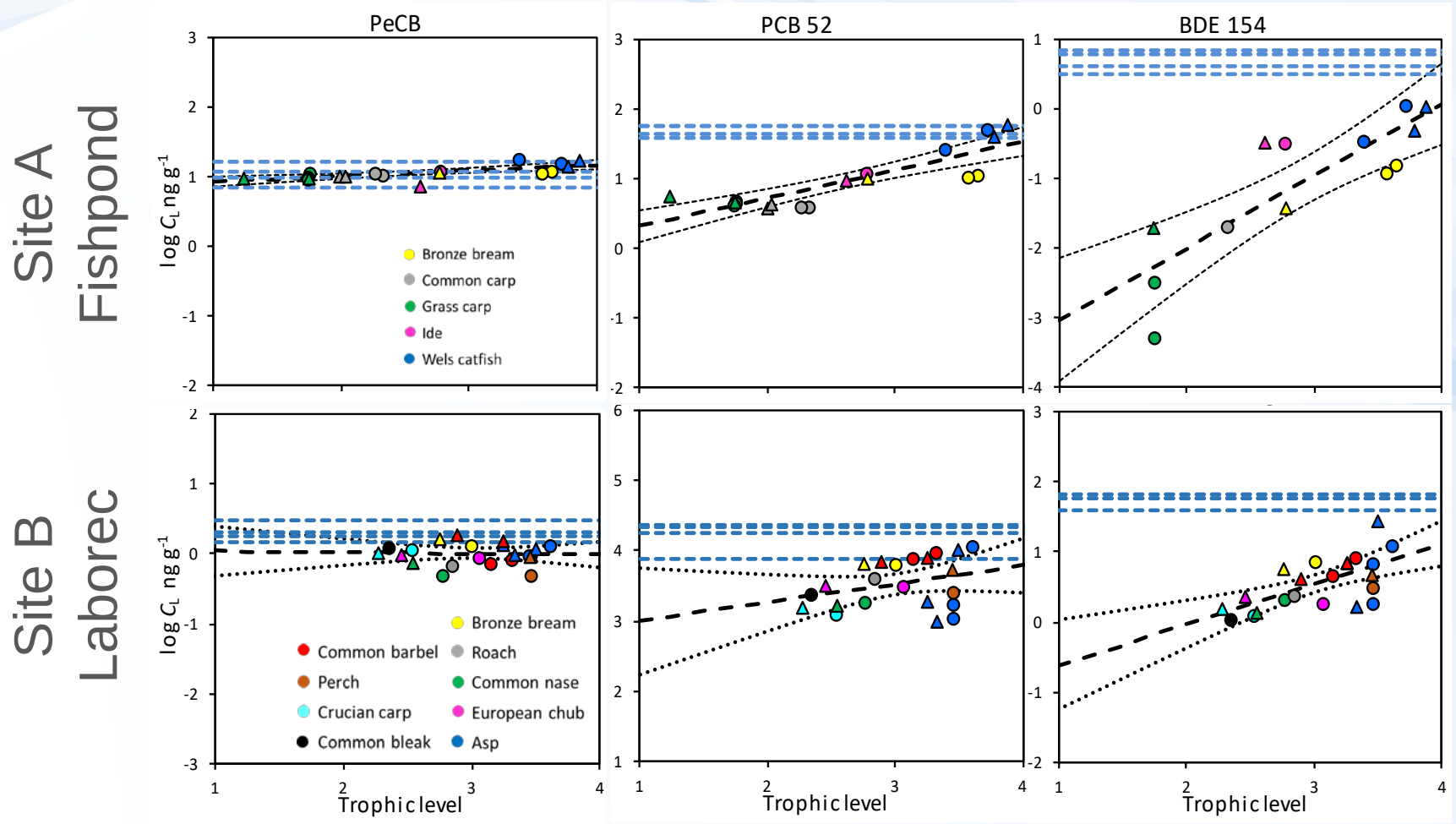
$$\log C_L^{TL(x)} = \log C_L^{TL=1} + \{TL(x)-1\} \log TMF$$

$$\log C_L^{TL(x)} = \log C_L^{TL(y)} + \{TL(x)\text{-}TL(y)\} \log TMF$$

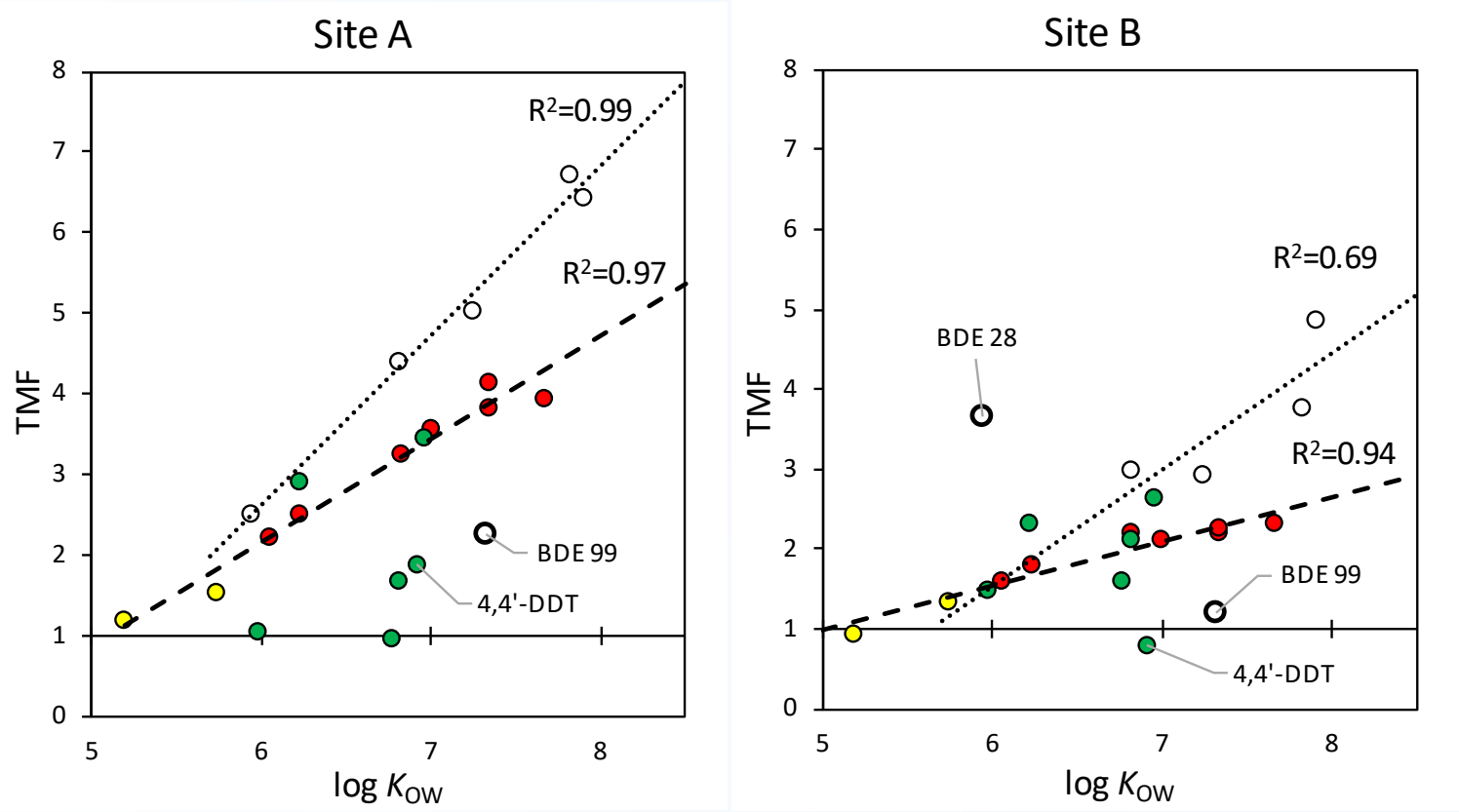
Slope is log *TMF*



Trophic magnification (1) and the aqueous phase

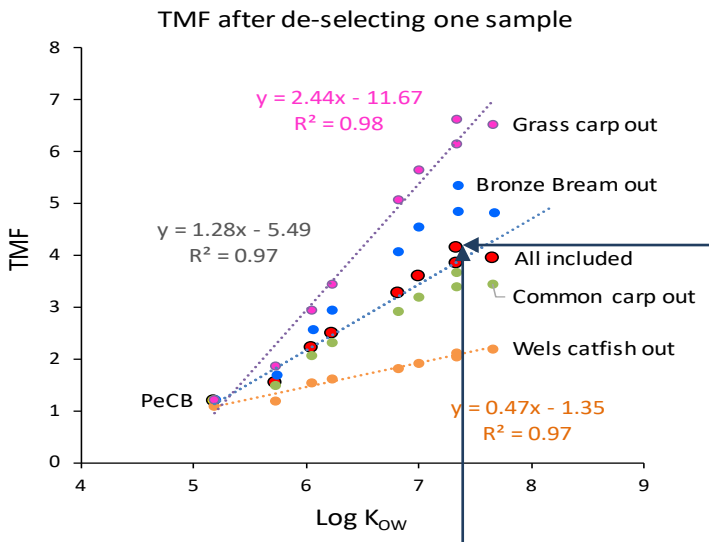


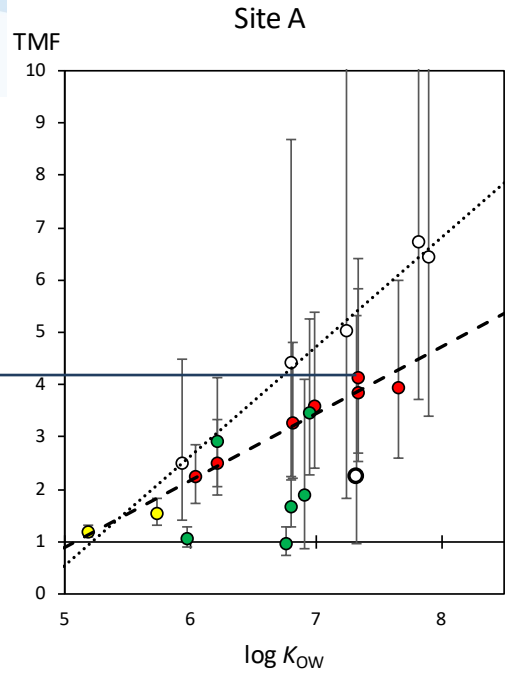
Trophic magnification (2)

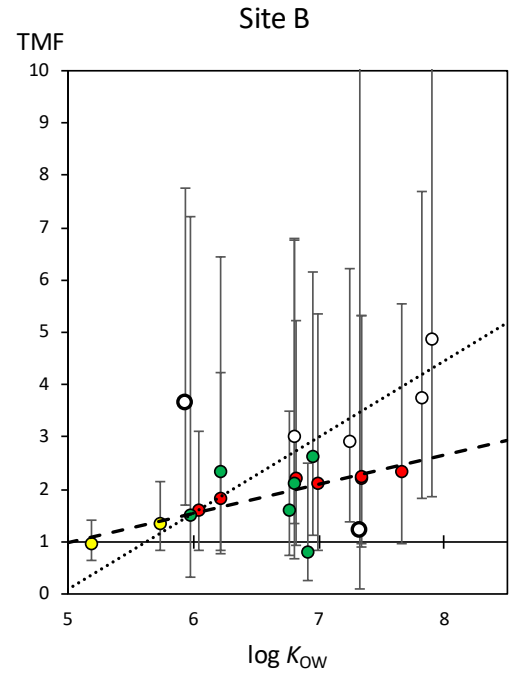


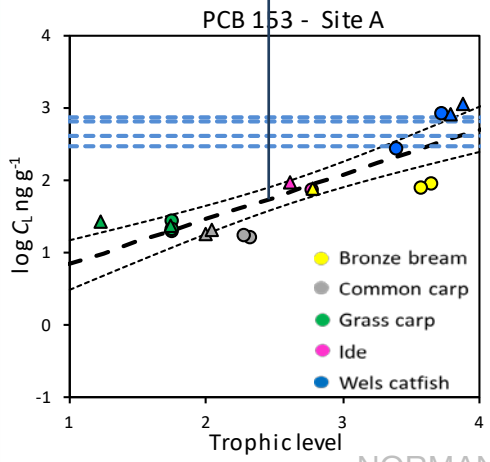
PeCB and HCB (●), PCB (●), DDx (●) and BDE (○)

Trophic magnification (2a)



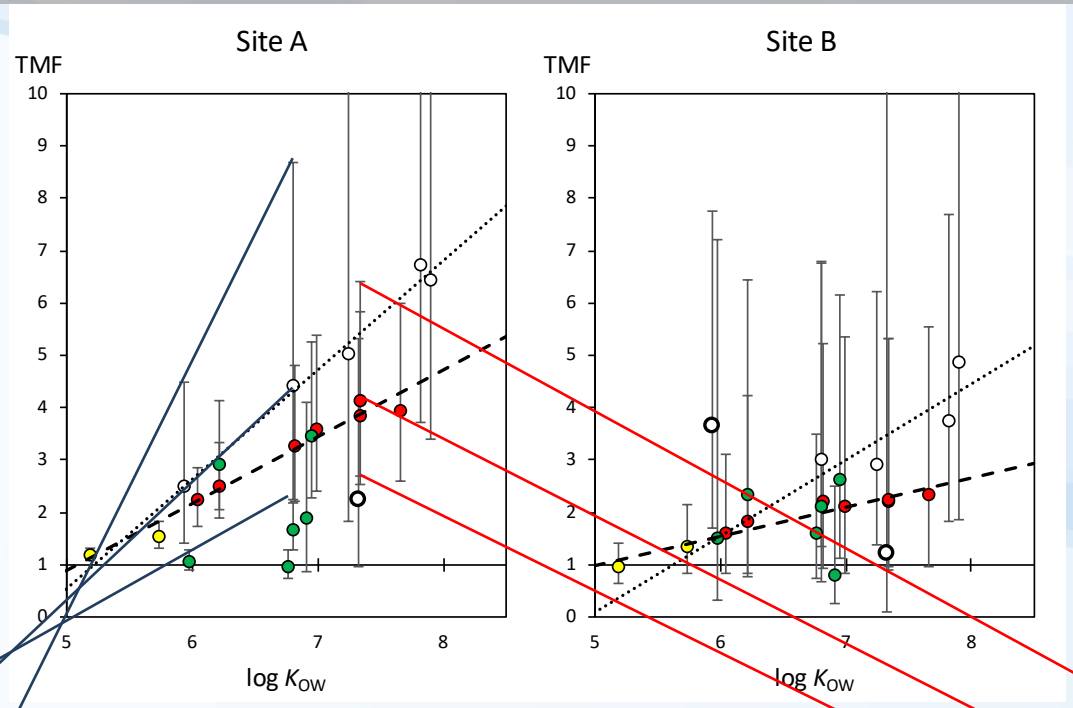






PeCB and HCB (●), PCB (●), DDx (●) and BDE (○)

Trophic magnification (3)



PeCB and HCB (●), PCB (●), DDx (●) and BDE (○)

	–95%CI	TMF	+95%CI
BDE 47	2.2	4.4	8.7

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PCB 153	2.7	4.1	6.4

Trophic magnification 4

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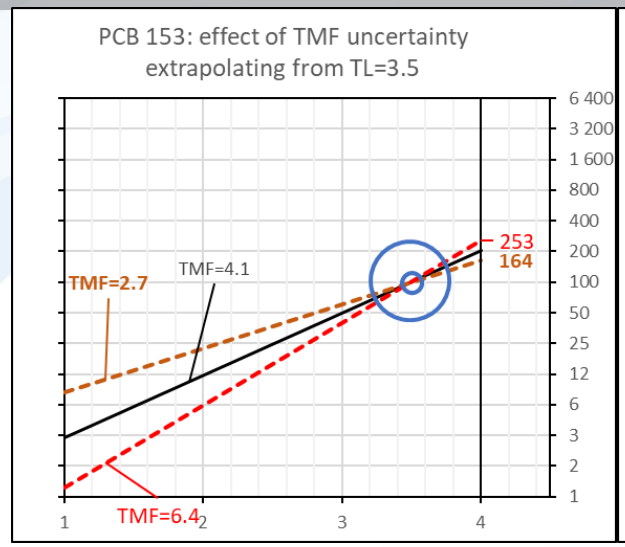

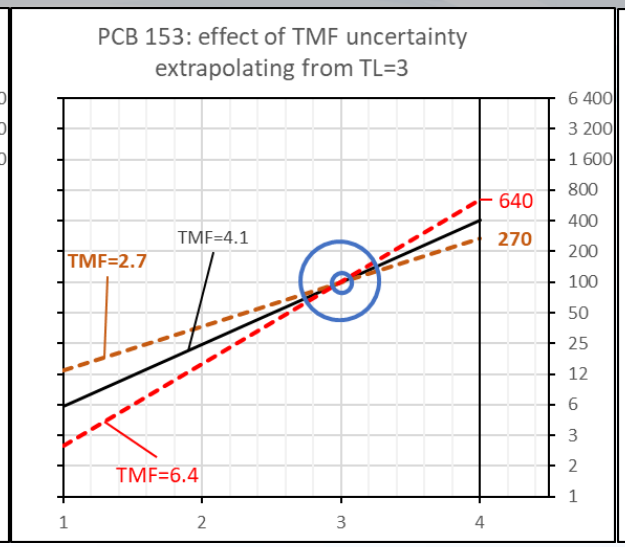

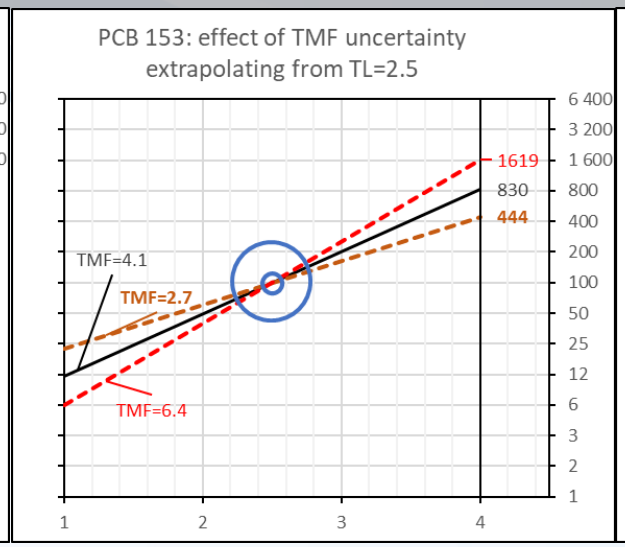

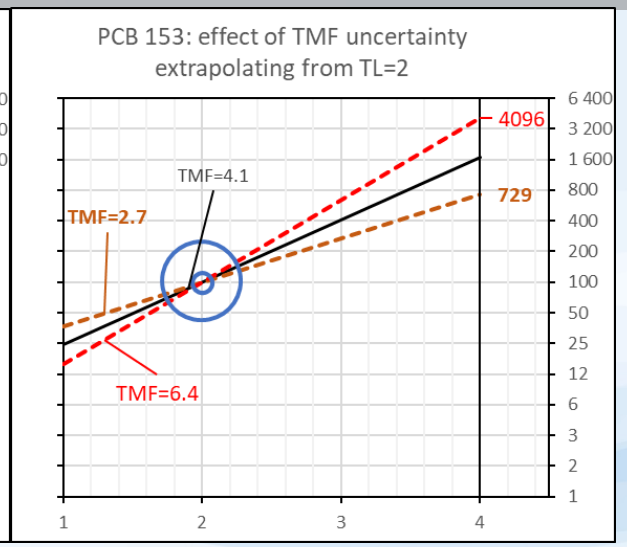

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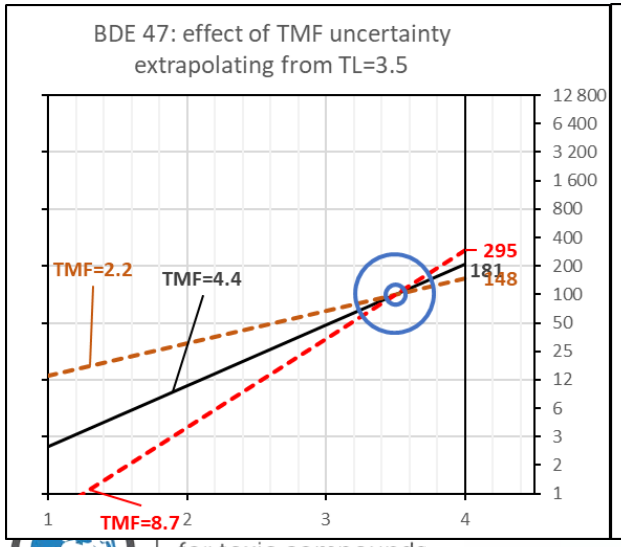
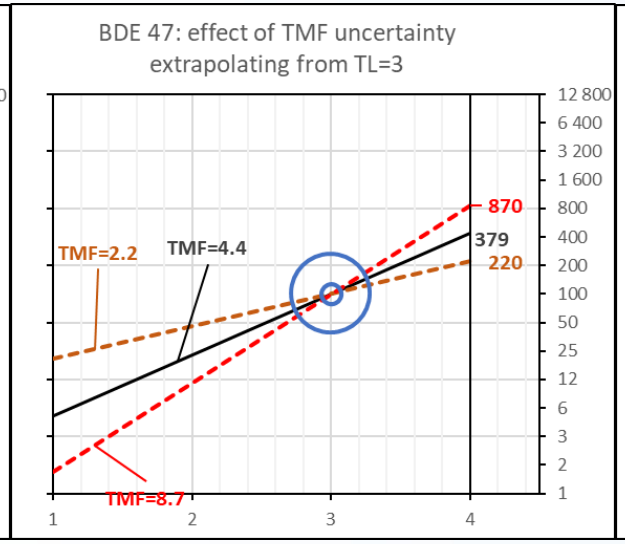
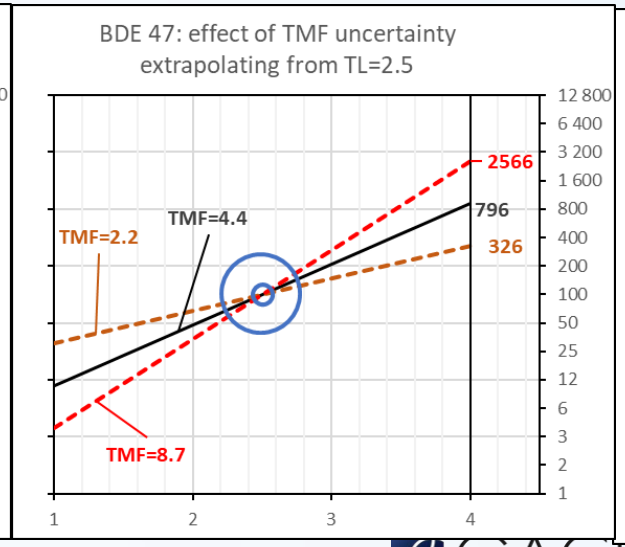
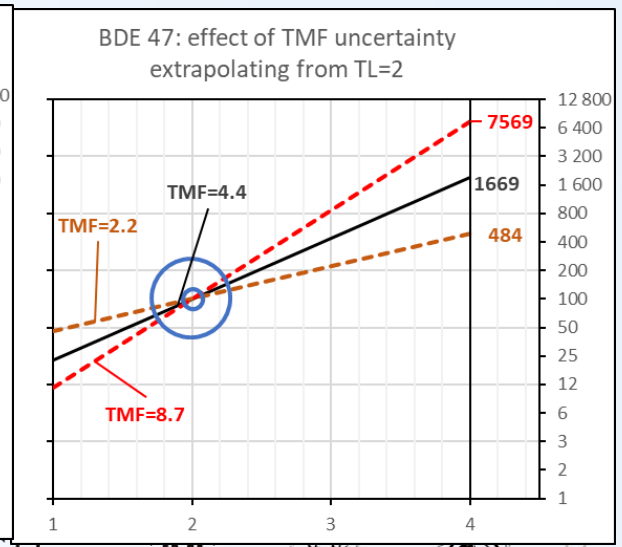


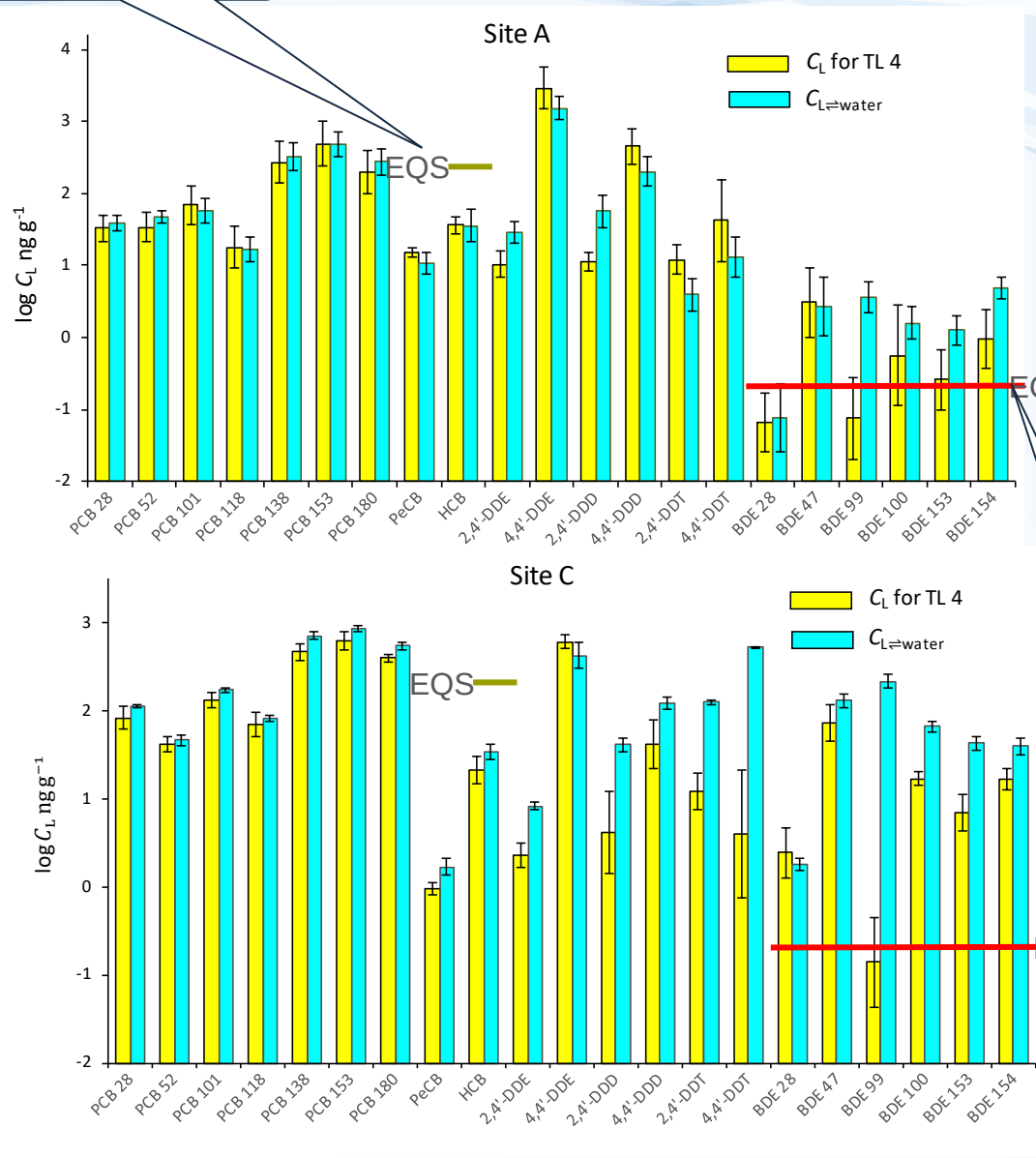




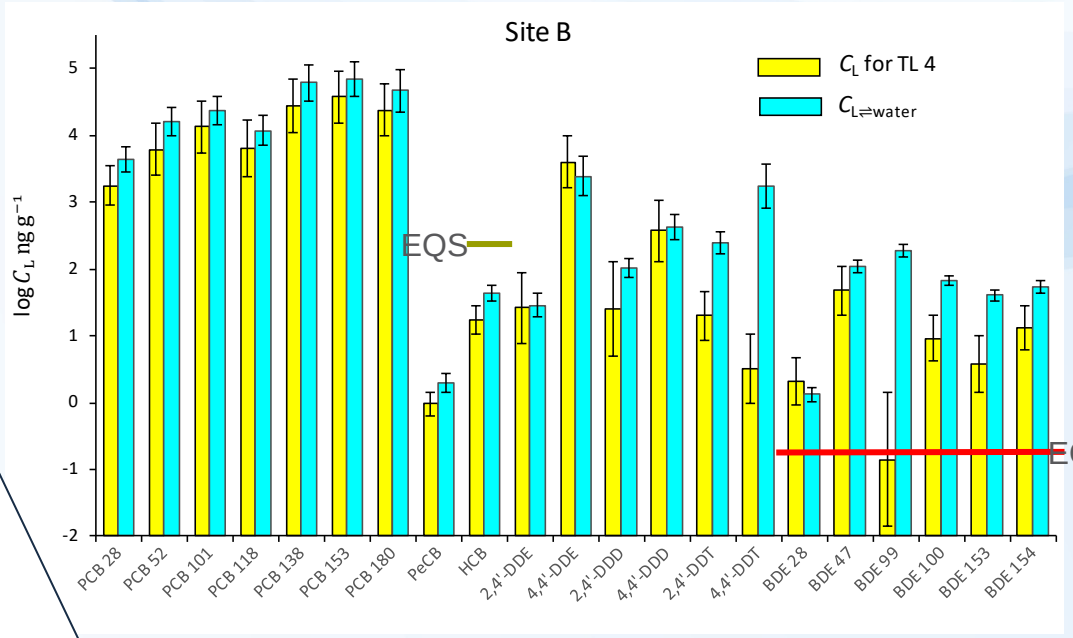


Log $C_{AL \rightleftharpoons WATER}$ log $C_{(A)L}$ biota at TL=4

EQS$_{Lipid}$= WFD-EQS*20

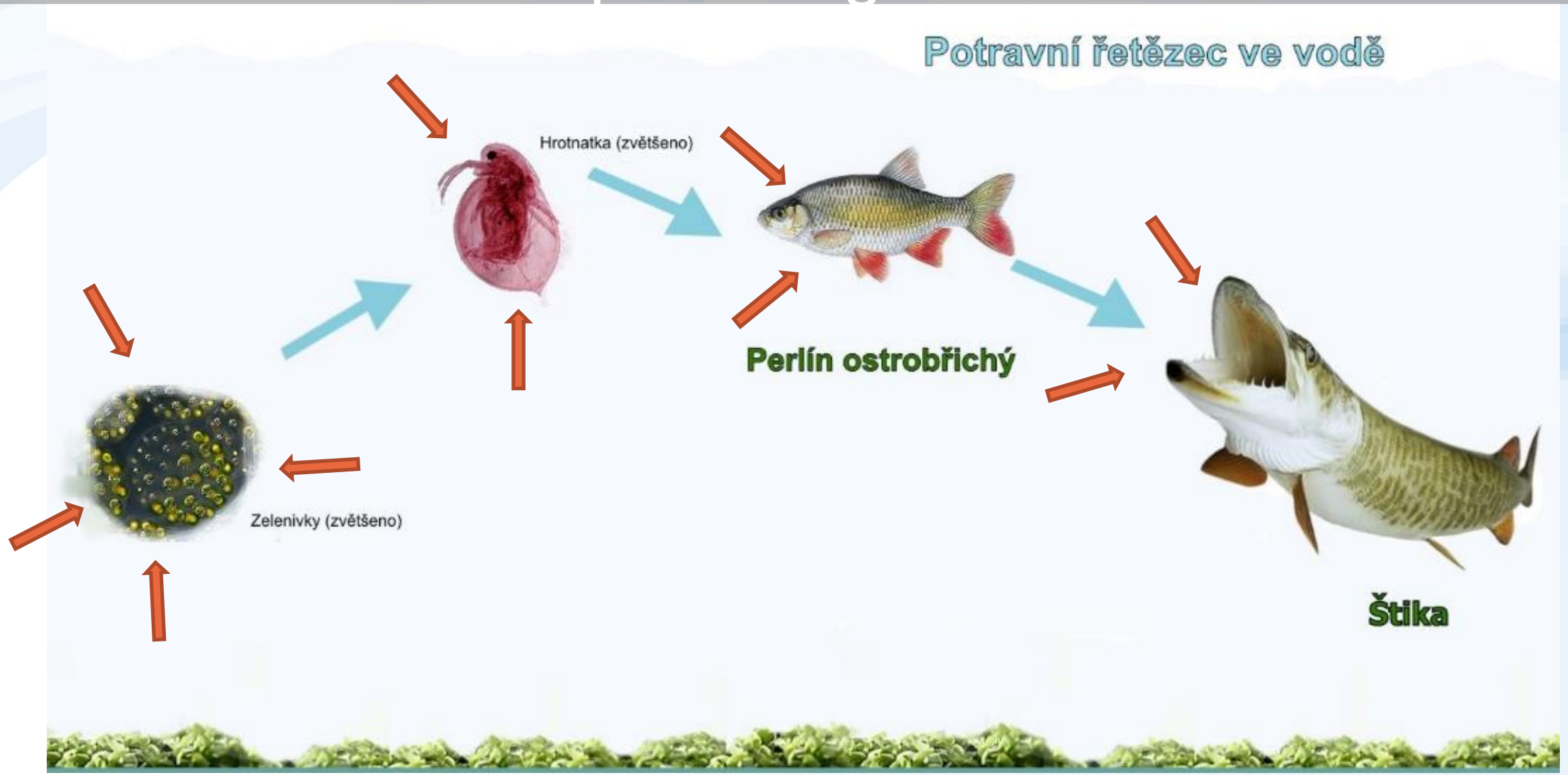


Confidence limits of C_L by PS (n=4) are two times lower than by fish sampling (n=20)

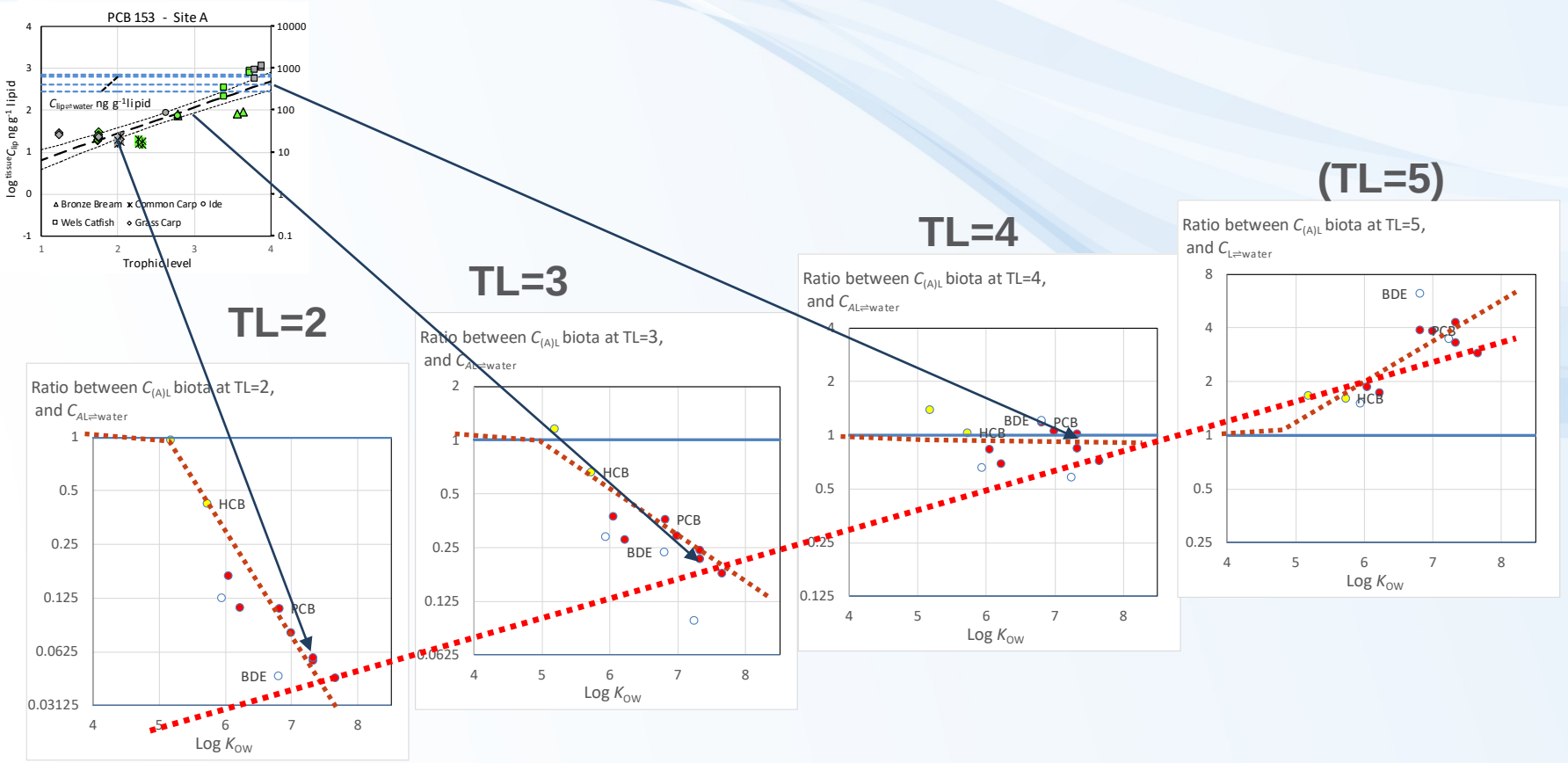


EQS$_{Lipid}$= WFD-EQS*20
Level is for sum BDE

Trophic magnification



Profiles of the ratios of C_L in biota and water for TL 2 to 5



Hypothesis: the start of the food chain is not in equilibrium with the water phase!?

Phytoplankton grows on CO_2 and nutrients → Start at C_L=0

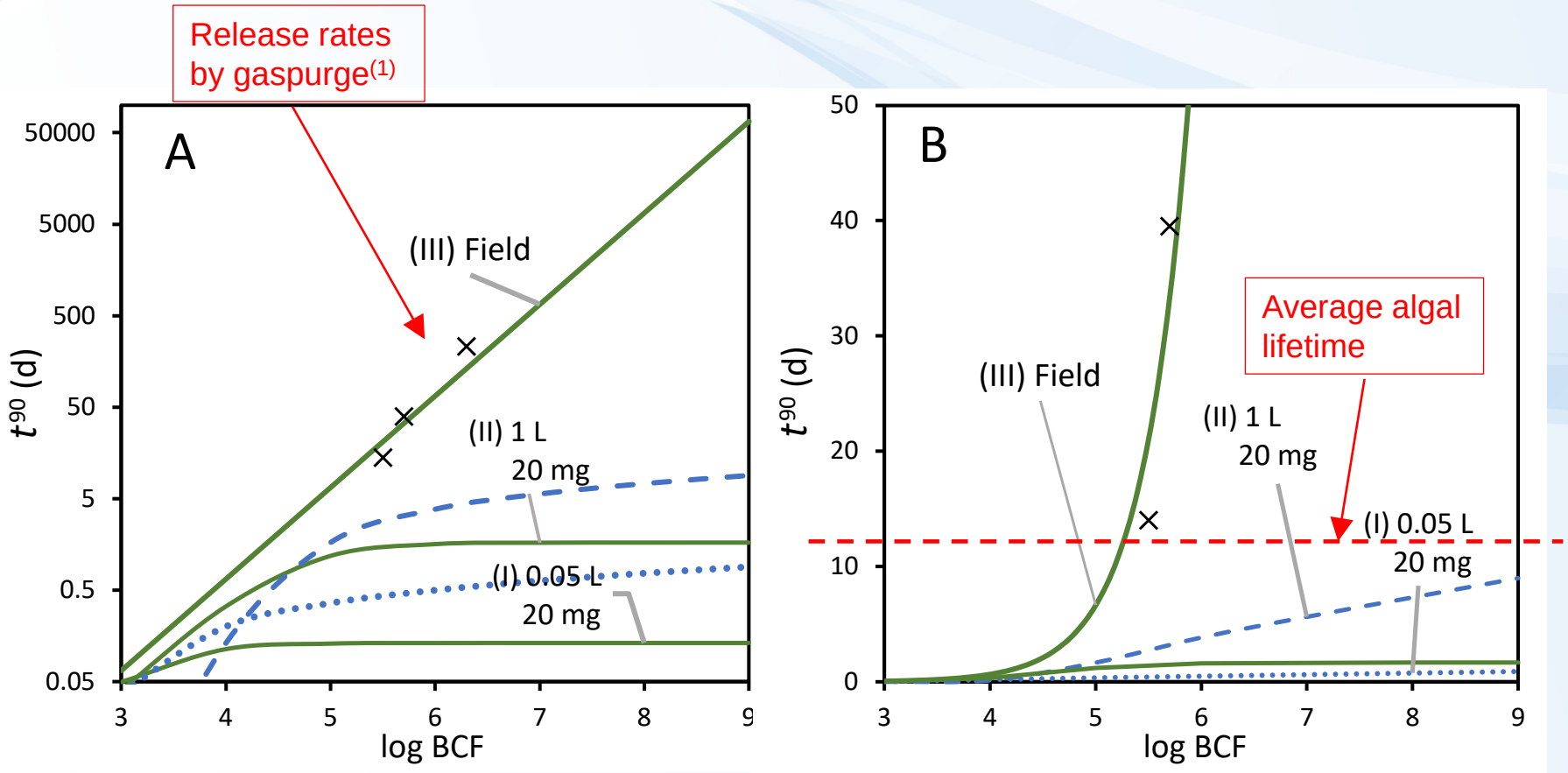
Uptake towards equilibrium is by diffusion through the WBL

This process is slow and becomes 10 times slower with each log unit K_{OW}

While the algae continues with growing, they are consumed before equilibrium

Passive samplers also do not reach equilibrium for over log K_{OW} =6

Algae equilibrium time depends on hydrophobicity
Longer in field than laboratory



(1) Koelmans et al. Environ. Toxicol. Chem. 1999, 18, 1164–1172.
(2) Sijm, et al. Toxicol. Chem. 1998, 17,1695–1704

Smedes et al, Unraveling the relationship between concentrations of hydrophobic organic contaminants in freshwater fish of different trophic levels and water using passive sampling, ES&T 2020 http://dx.doi.org/10.1021/acs.est.9b07821

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Thank you for your attention