On how passive sampling refers to chemical monitoring of HOC in biota under the Water Framework Directive

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Monitoring environmental quality for HOC

High K_{OW} - accumulative substances

→ very low aqueous concentrations

→WFD choose for monitoring in biota

→EQS were set for biota at

trophic level 4 for fresh- and 5 for marine-water

OUR OBJECTIVES

First bleu print of the project originates from 2012 and was funded by GACR in 2014

- Objective: investigate the relation between

  levels in biota ← → passive samplers

  to assess PS as alternative to biota monitoring

Building on the work driven by Mayer, Jahnke, et al: various necessary partition coefficients were estimated and methods developed to derive lipid based concentrations from PS

The WFD biota monitoring procedure[1)]

- Select/catch appropriate fish species/size and numbers
- Apply lipid normalisation
- Determine the trophic level (TL)

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

3.4‰ change in δ15N per unit of TL

- Measured concentrations are then converted to TL=4

$$C_{TL=4} = C_{TL(x)} \times TMF^{\{4-TL(x)\}}$$

Tropic Magnification Factor
the factor C_{fish} increases per unit TL.
Substance specific

- Guidance does not provide TMF values

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

C is lipid normalised

1) Deutsch et al, 2014, Guidance document no. 32 on biota monitoring (the implementation of EQS biota) under the water framework directive. https://doi.org/doi:10.2779/833200

WFD about water phase to check compliance?

- Conversion of EQS_{Biota} to EQS_{Water} needs BAF
  but BioAccumulationFactor needs BCF and TMF

$$\log BAF_{(TL=4)} = \log BCF + 3 \times TMF$$

What water phase do BAF or BCF apply?

All unknown or unreliable!

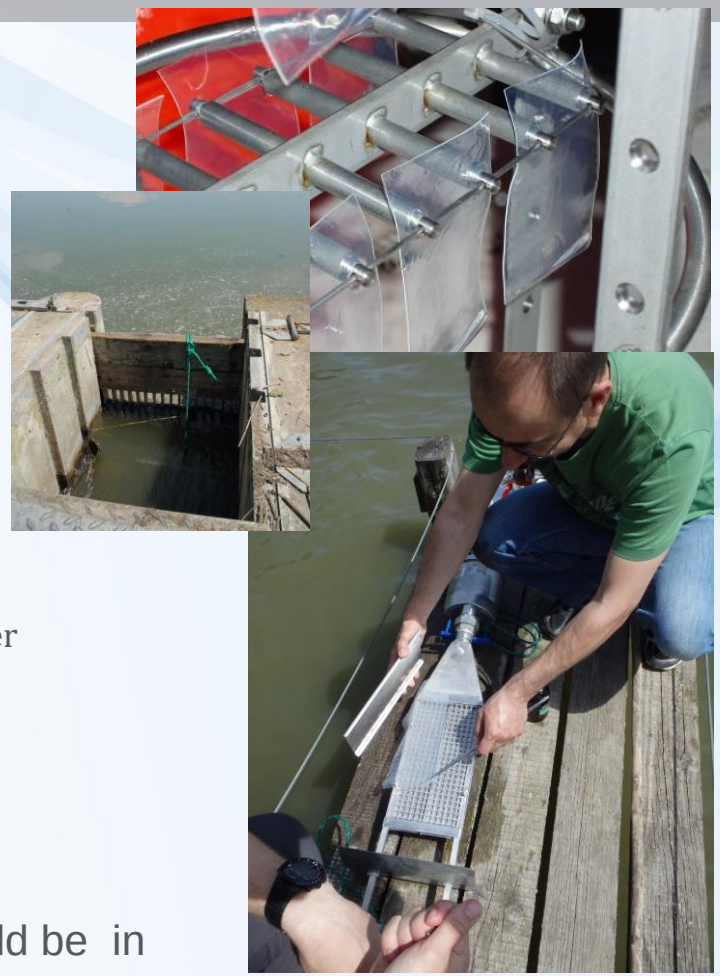
We did NOT try to plug-in water phase concentrations

(I) Lipid based via aqueous passive sampling?

From Passive sampling convert to lipid basis

Kinetic, C_W by PRC

equilibrium

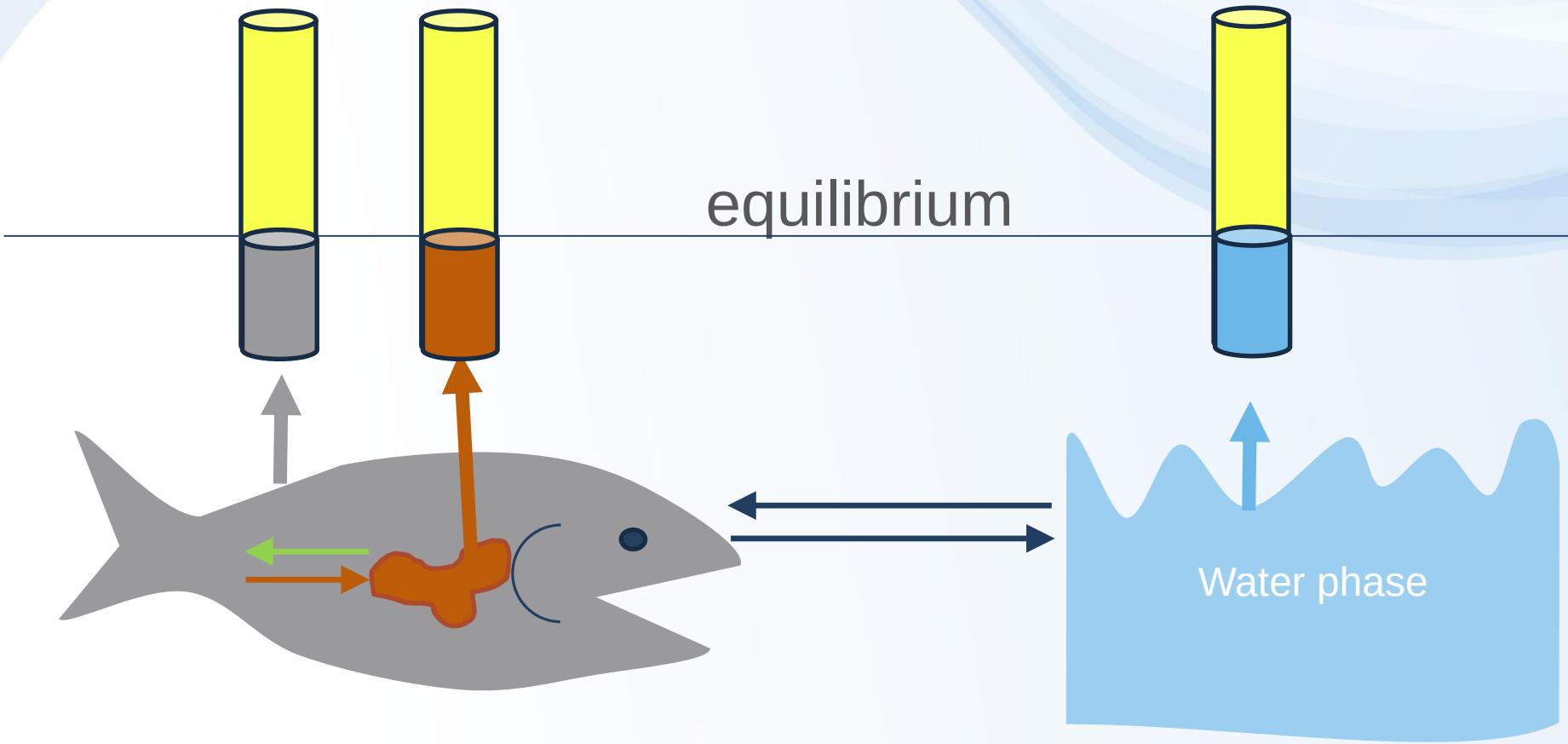


$$\frac{C_W \times KP_W}{K_{PL}} = C_{\mathrm{AL}\rightleftharpoons\mathrm{Water}} \qquad \frac{C_{\mathrm{P}\rightleftharpoons\mathrm{Water}}}{K_{PL}} = C_{\mathrm{AL}\rightleftharpoons\mathrm{Water}}$$

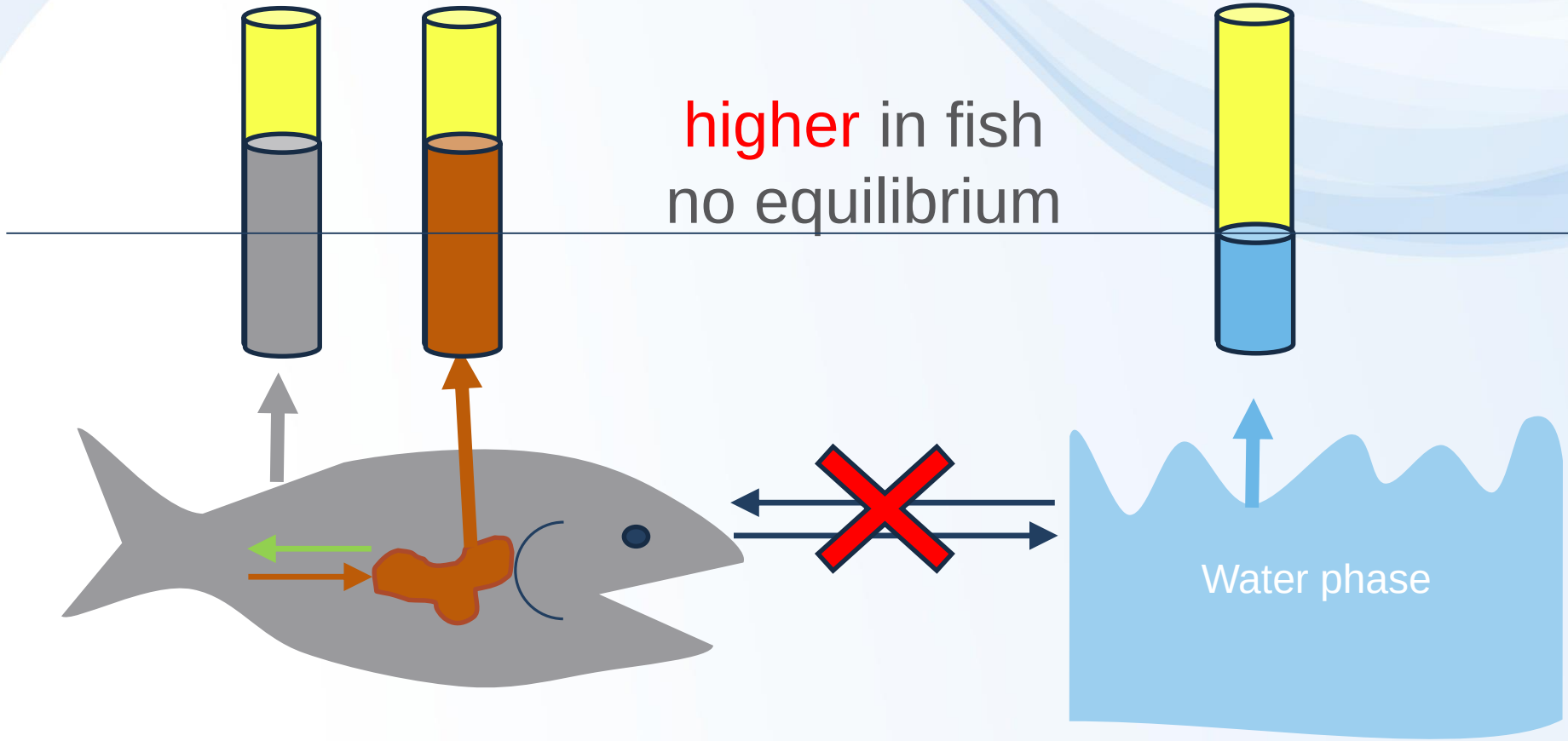
K_{PL}= Polymer-lipid partition coefficient

$C_{\mathrm{AL}\rightleftharpoons\mathrm{Water}}$ is here an abiotic lipid based concentration representing C_L contained in biota that would be in thermodynamic equilibrium with sampled habitat/medium

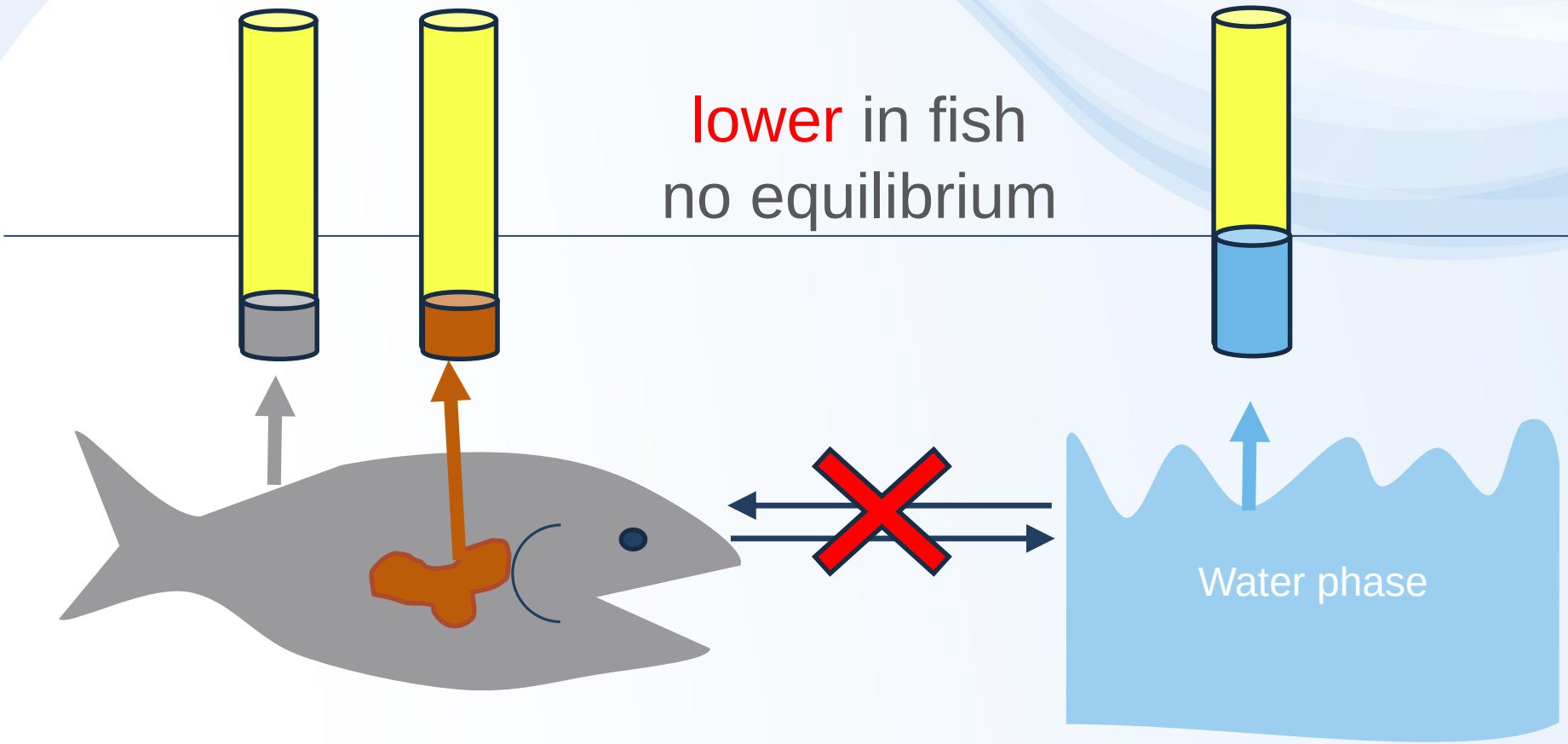
Passive sampling in different matrices (1)



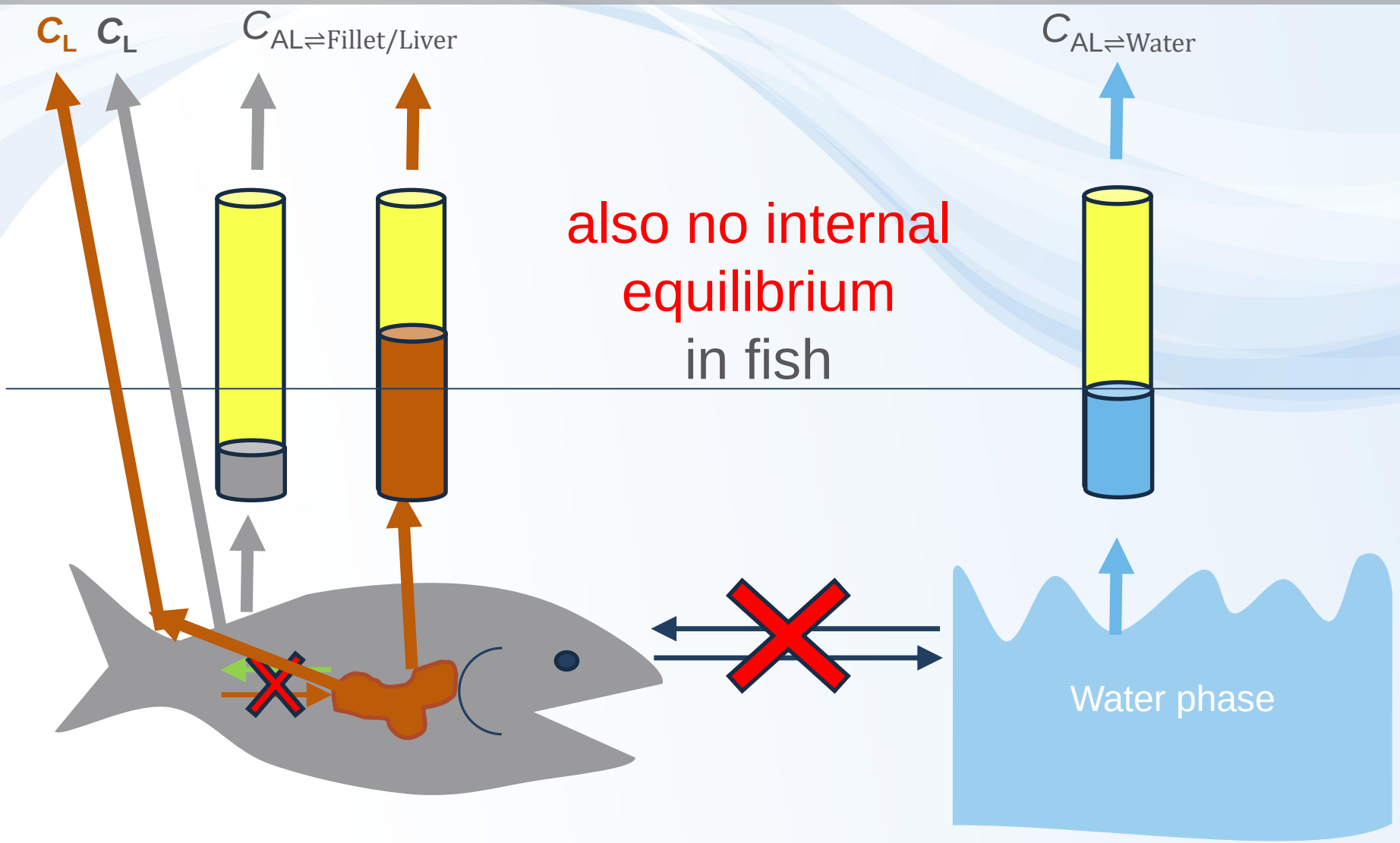
Passive sampling in different matrices (2)



Passive sampling in different matrices (3)

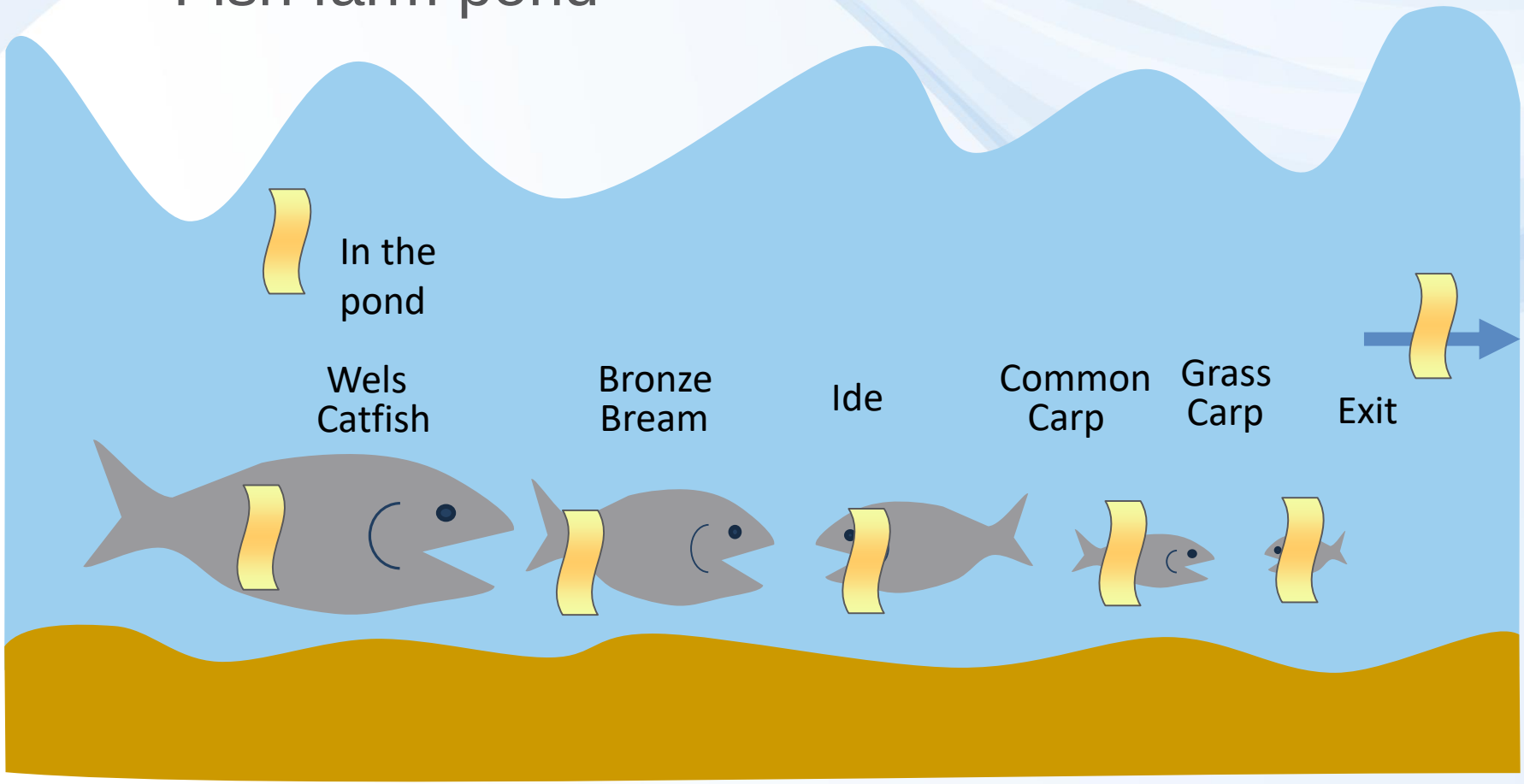


Passive sampling in different matrices (3)



TEST EXPERIMENT

Fish farm pond



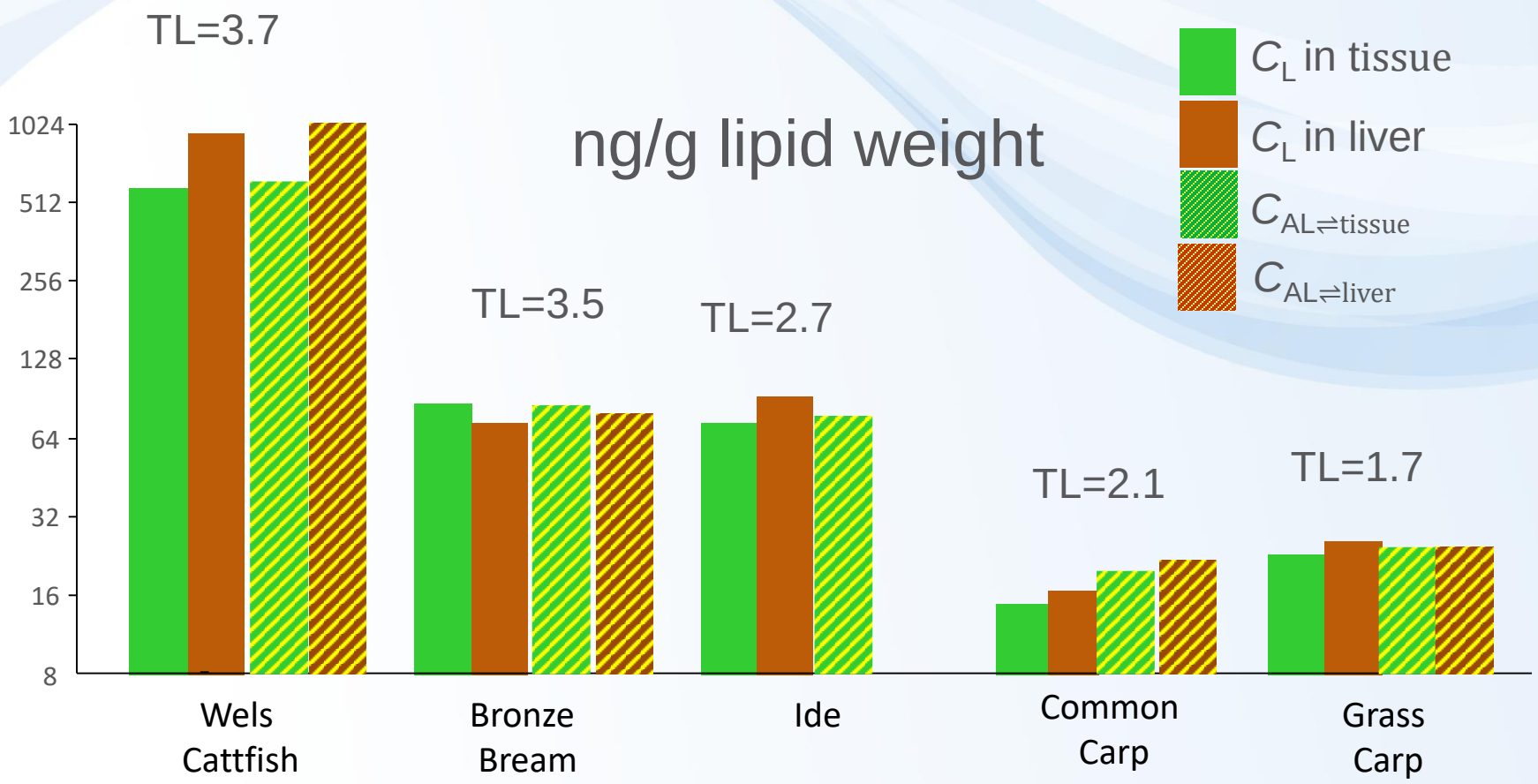
The obtained parameters

For 5 fish species, PCBs OCPs, lipid fraction

- N-isotope ratio → δ_N → TL
- Raw concentrations and f_L=lipid fraction
- Lipid normalized → C_L for fillet
  → C_L for liver
- A-Biotic lipid - in-tissue PS → $C_{AL \rightleftharpoons Fillet}$
  → $C_{AL \rightleftharpoons Liver}$
- A-Biotic lipid - aqueous PS → $C_{AL \rightleftharpoons WATER}$

Allows comparison of matrices in equal units !!
In this case ng/g of biotic or abiotic lipid

PCB 153 in various fish species



Conversion of C_L to TL=4

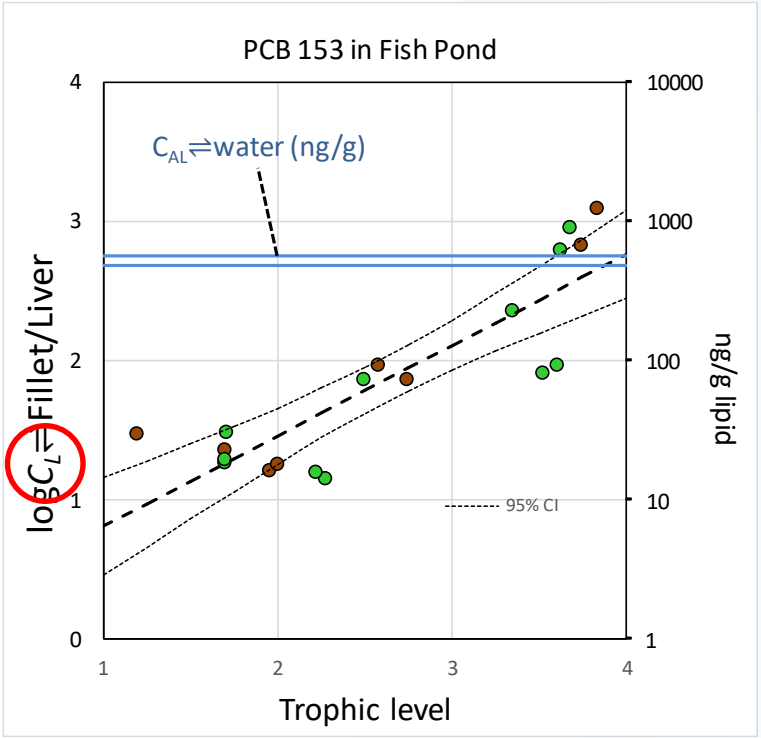
- TMF unknown
- So regression necessary

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

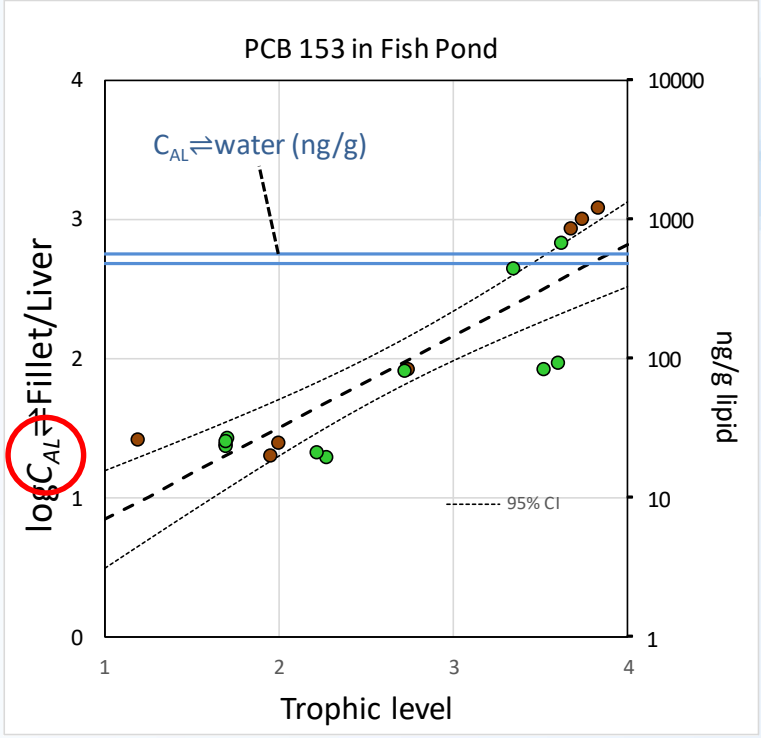
PCB153 - Log Lipid based versus TL

Blue lines show lipid based from aqueous passive sampling ($C_{AL \rightleftharpoons WATER}$) on the same scale

Classical solvent extraction (C_L)



Sampler equilibration with tissue $C_{AL \rightleftharpoons fillet/liver}$



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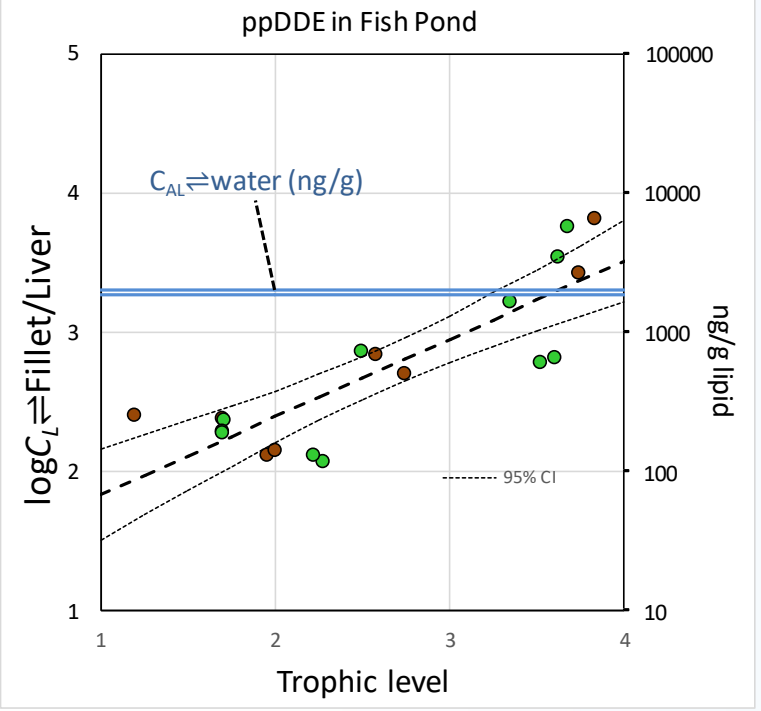
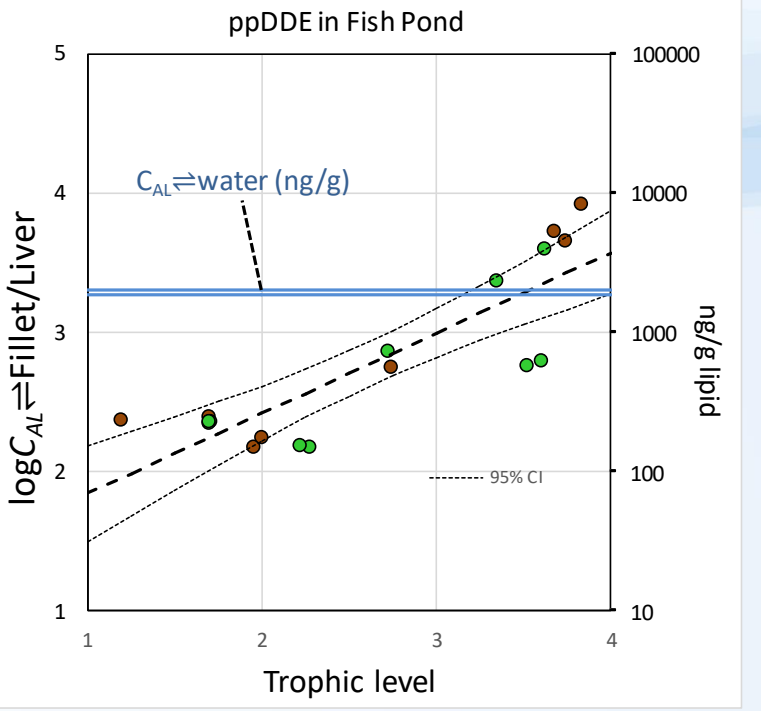
Same graphs for ppDDE

Blue lines show lipid based from aqueous passive sampling ($C_{AL \rightleftharpoons WATER}$) on the same scale

Classical solvent extraction (C_L)



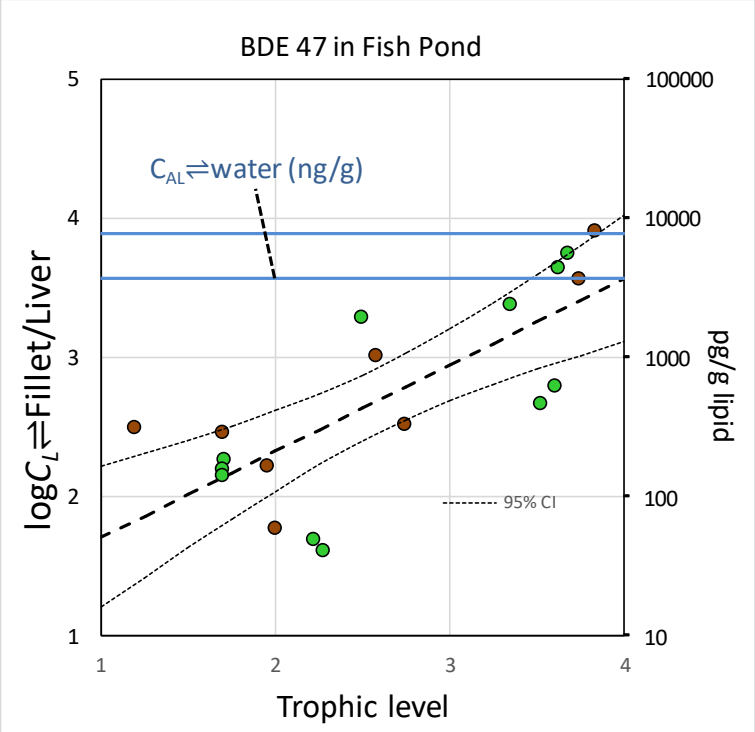
Sampler equilibration with tissue $C_{AL \rightleftharpoons fillet/liver}$



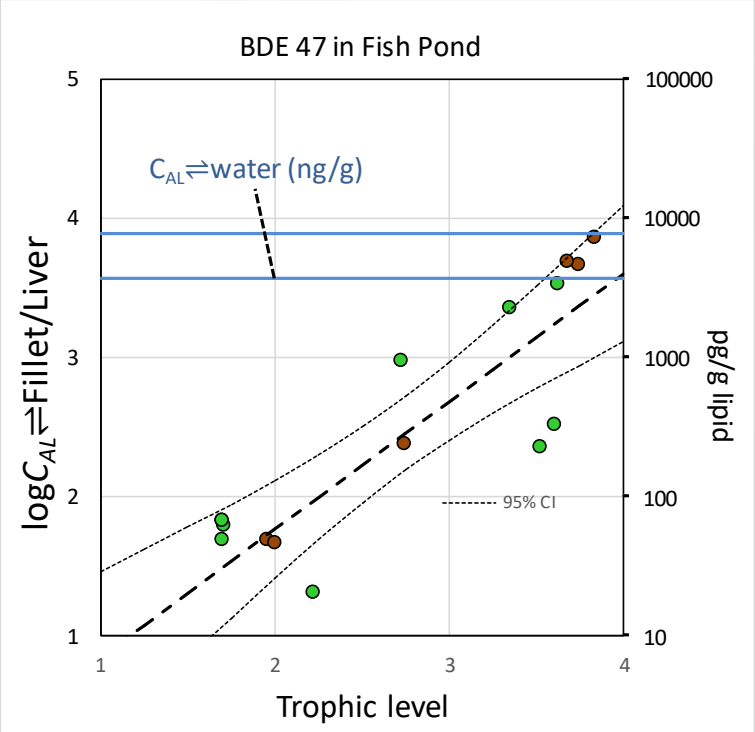
And the last such graphs is for BDE 47

Blue lines show lipid based from aqueous passive sampling ($C_{AL \rightleftharpoons WATER}$) on the same scale

Classical solvent extraction (C_L)



Sampler equilbtration with tissue $C_{AL \rightleftharpoons fillet/liver}$



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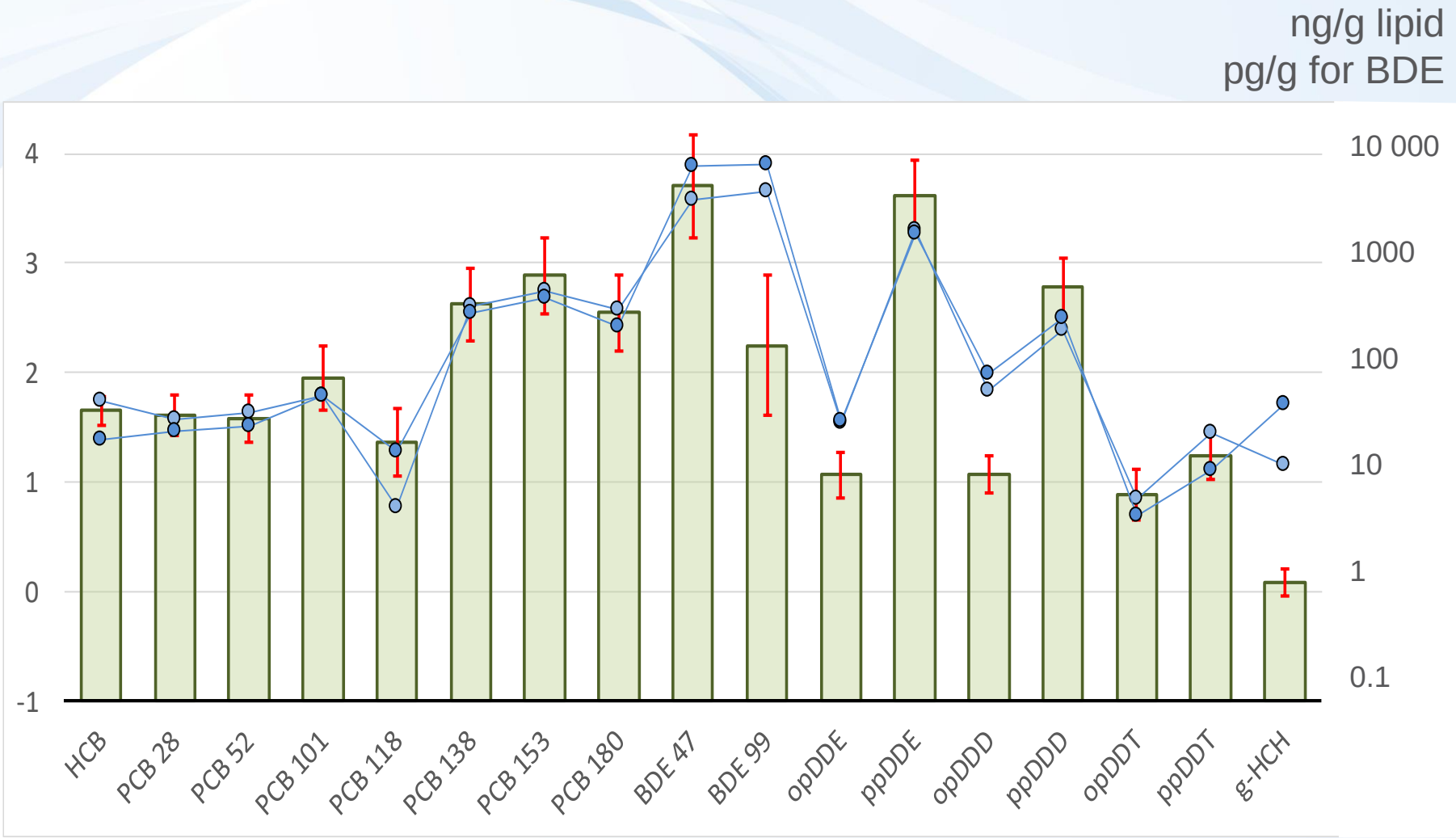
Comparing C_L for TL=4 with $C_{AL \rightleftharpoons WATER}$



Observations

Thermodynamic levels:

- similar in liver and fillet
- similar for classic extraction and in tissue sampling similar
- $C_{AL \rightleftharpoons WATER}$ levels similar to TL=4 fish!

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Should we conclude ?

that passive sampling……..

converted to lipid basis (actually 5%) is …

applicable for compliance testing versus EQS?

Acknowledgements:

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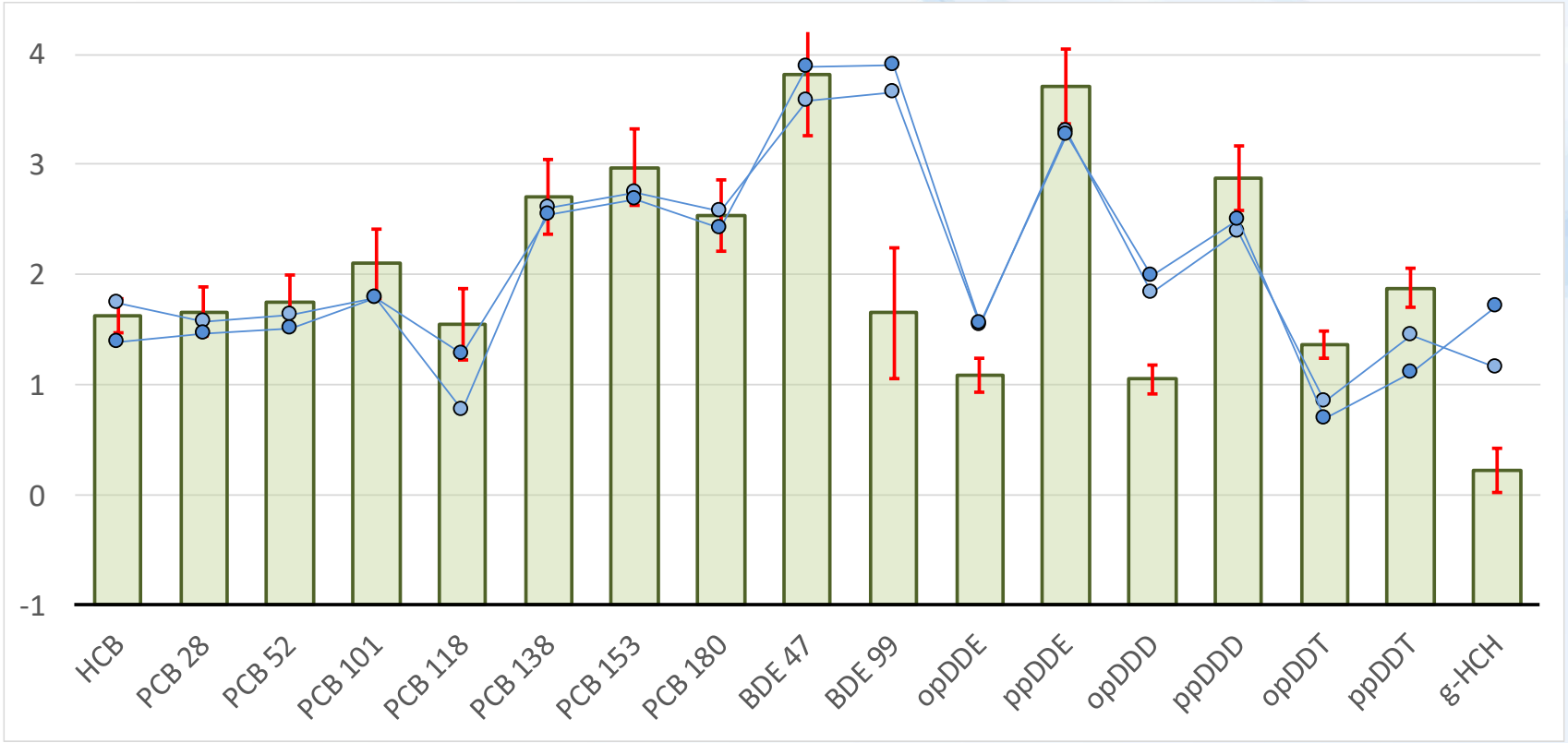
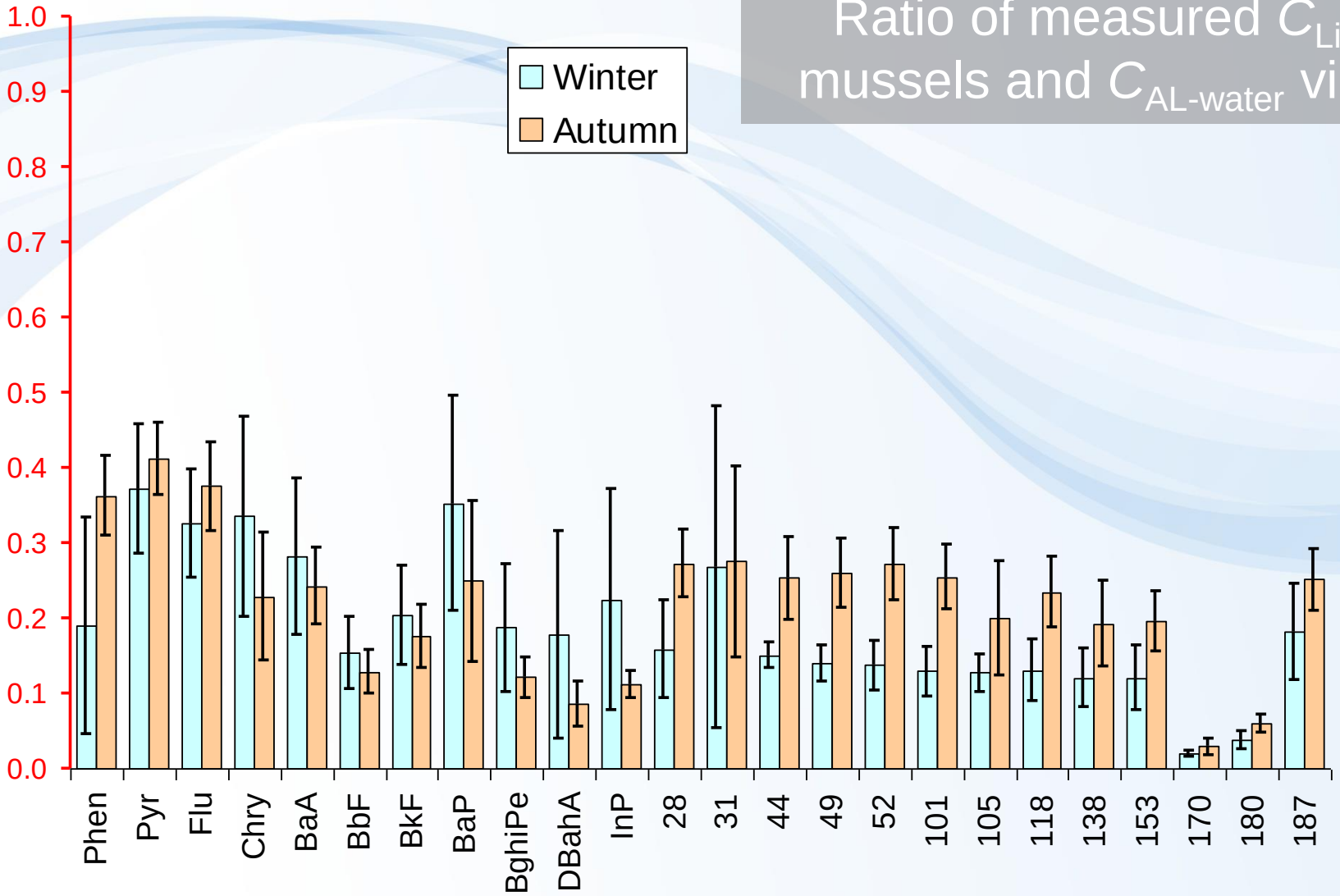
The end

Thank you for you attention

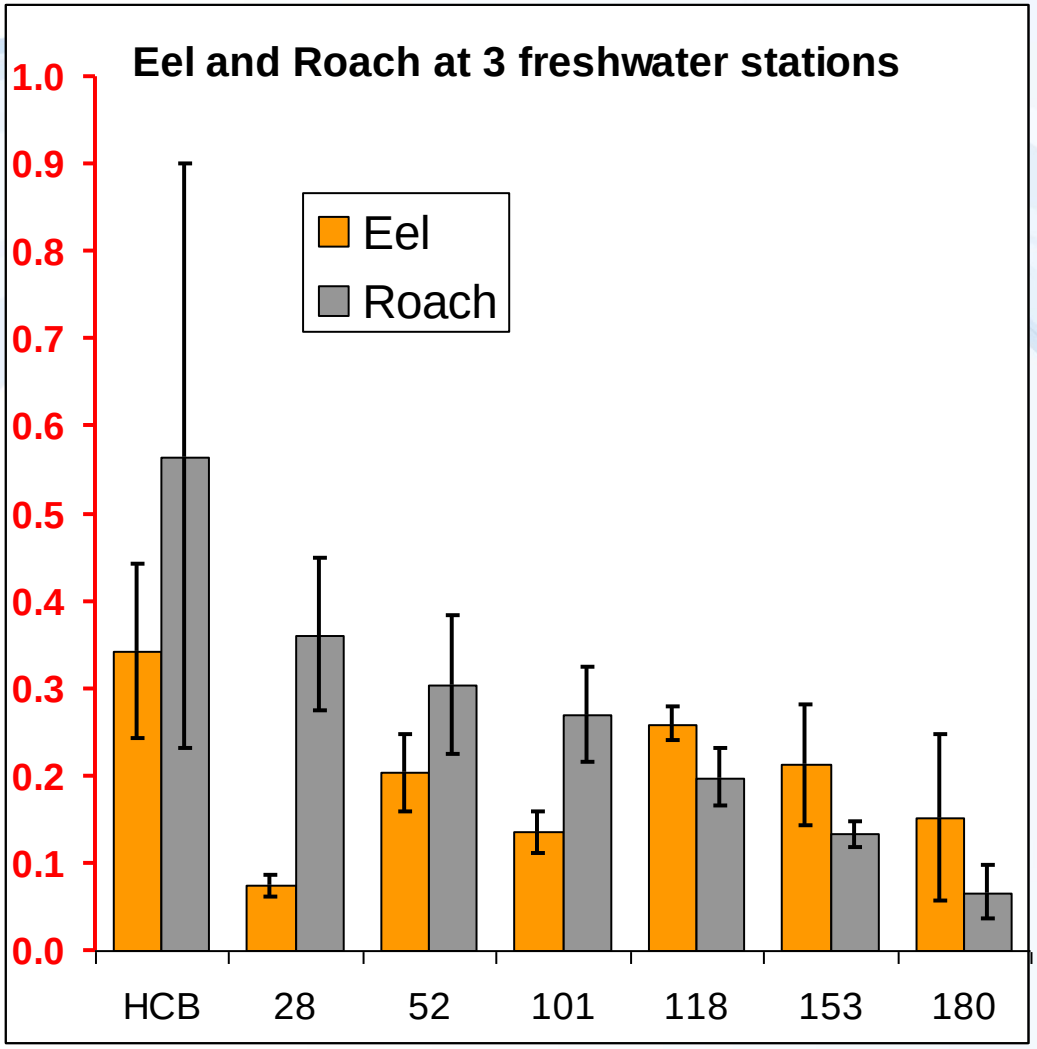
Comparing C_{AL} for TL=4 with $C_{AL \rightleftharpoons WATER}$



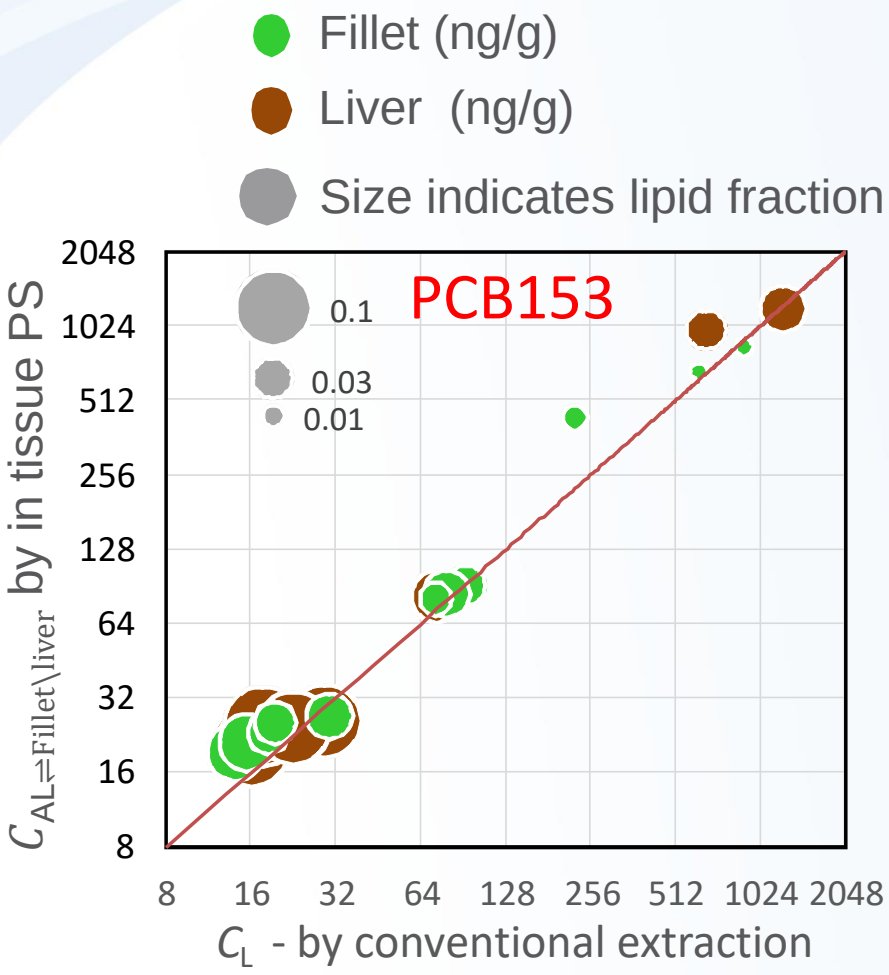
Ratio of measured C_{Lip} in mussels and $C_{AL\text{-}water}$ via PS

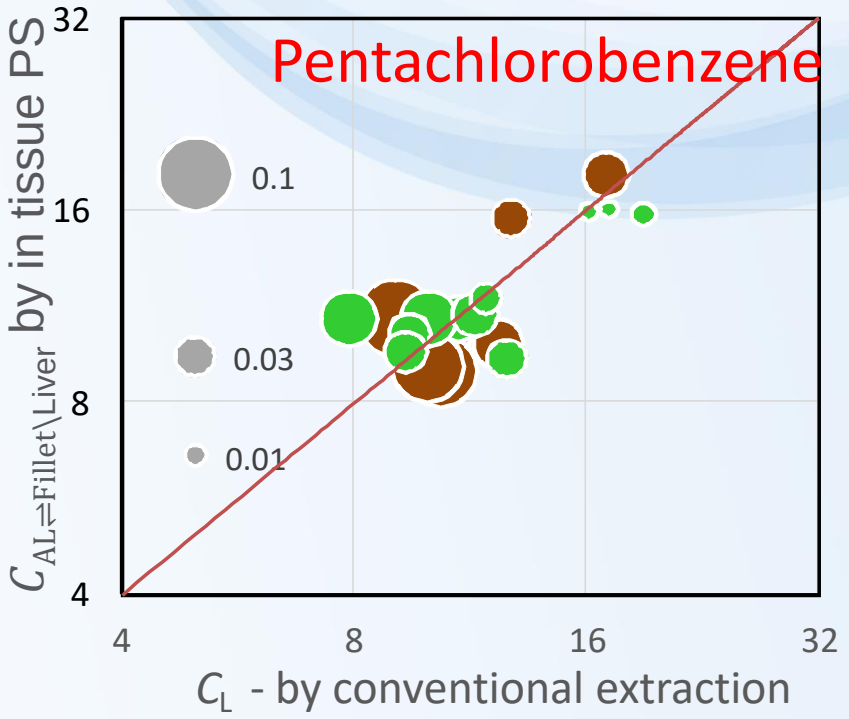


Ratio of measured C_L and $C_{AL\text{-}water}$ uit PS for Eel and Roach



In-tissue PS ($C_{AL \rightleftharpoons Tissue}$) versus lipid normalized (C_L)





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Passive sampling in fish

TH093

Various approaches to equilibrium passive sampling of POPs in lean and lipid rich fish tissue

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[1] Masaryk University, Faculty of Science, Research Centre for Toxic Compounds in the Environment (RECETOX) , Brno, Czech Republic. [2] Norwegian Institute for Water Research (NIVA), Tromsø office, Tromsø, Norway
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Introduction

Equilibrium passive sampling (EPS) in habitat water, sediment and organism's tissue helps to estimate the degree of thermodynamic equilibrium for POPs between these media, which is important for understanding bioaccumulation[1].

PDMS samplers are applied for in–tissue EPS and results, converted to model-lipid basis (C_{LipPS}), agree with lipid normalized

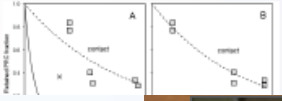
The problem

Static contact EPS in lean tissue does not achieve equilibrium before decay of the tissue (<7d).

Equilibrium conformation needs multiple measurements over time or thicknesses

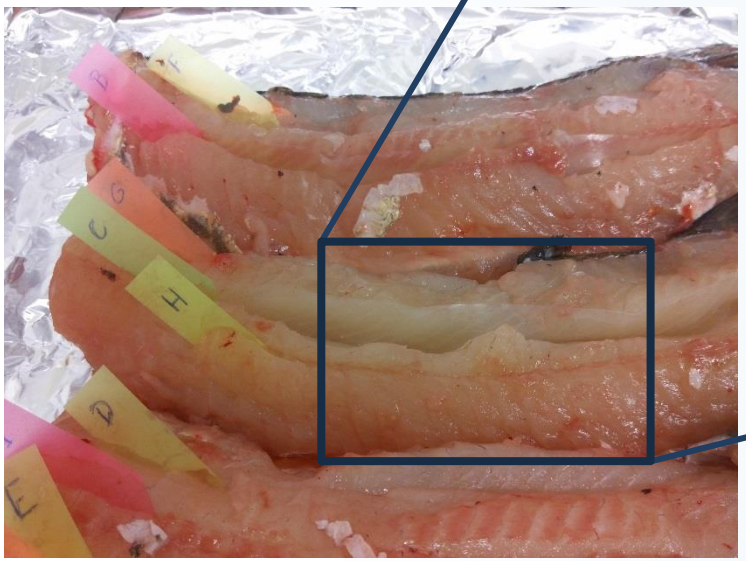
Method

PDMS samplers (0.125 mm thick, ~15 cm² surface area) dosed with PRCs were exposed to excess tissue in three ways:



Four R's towards equilibrium

- Reduce sampler thickness
- Relocate samplers to fresh tissue
- Roll samplers with tissue cubes
- Release of sampler dosed PRCs[3] for monitoring equilibriation progress



PCB 153 on wet weight basis