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Looking for an appropriate monitoring design for Water Framework Directive priority substances targeting biota

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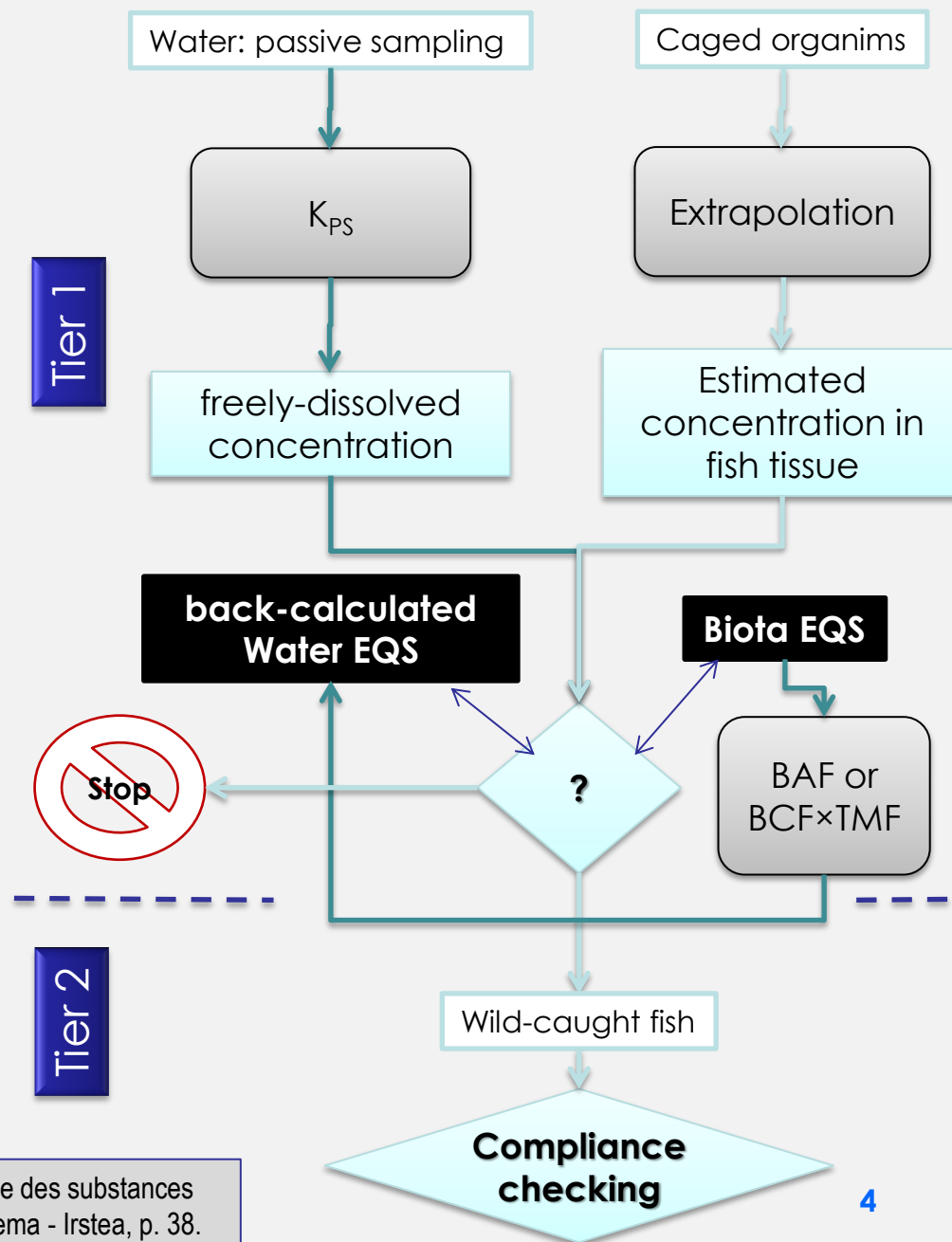
Introduction

- WFD chemical status – targets water, sediment, biota
 - No standard (EQS) for sediment
- Directive 2013/039 ⇒ 11 priority substances having biota-EQS
 - Likely to be found in sediment
 - Target mostly fish
- Guidance document N°32
 - Overarching goal and orientations
 - Flexibility – need for adaptations by Member States





- Two fish species
 - Barbus barbus*,
 - Squalius cephalus*
- Nevertheless, fish-based monitoring difficult and costly
- Alternative sampling matrices allowed by Dir. 2013/039
 - Proposal of a tiered approach using caged organisms at the first tier
- Need for predictive models
 - Might be TMFs ?



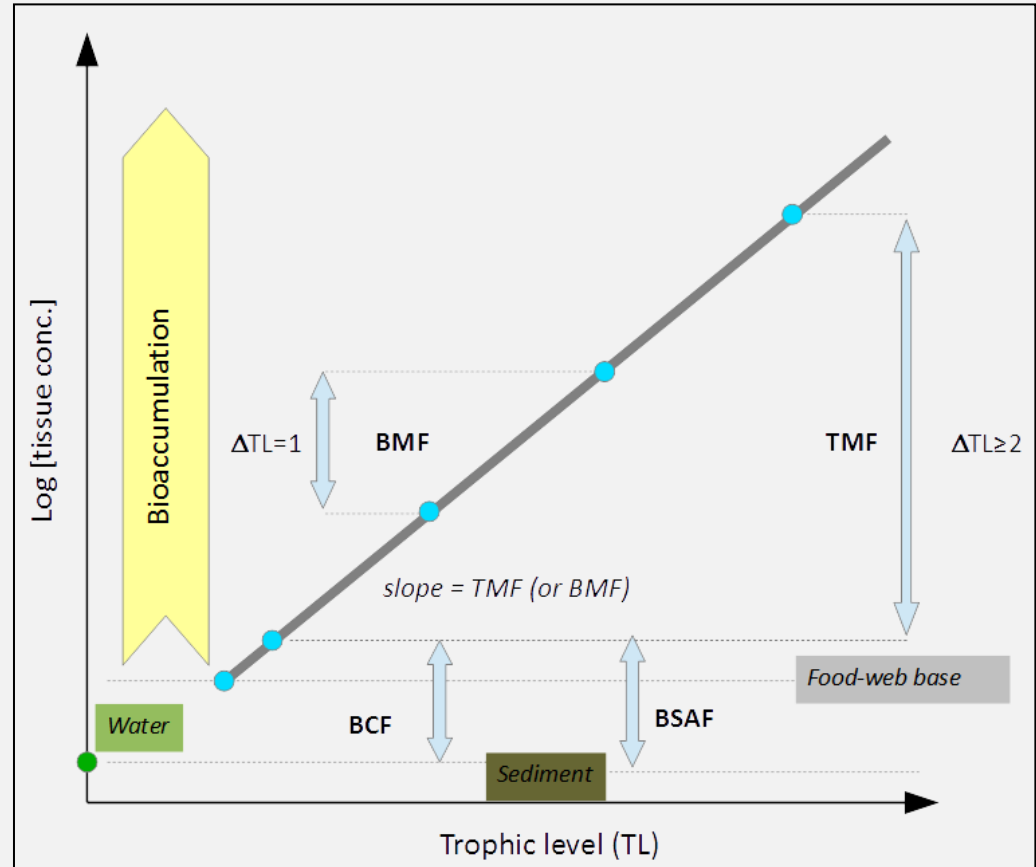
TMF concept

- TMF = diet-weighted average biomagnification factor (BMF) of chemical residues across food webs
- derived from the slope of a log-normal regression of chemical residues in organisms upon their corresponding trophic levels

$$\text{Log}[\text{contaminant}] = a + b \times \text{TL}$$



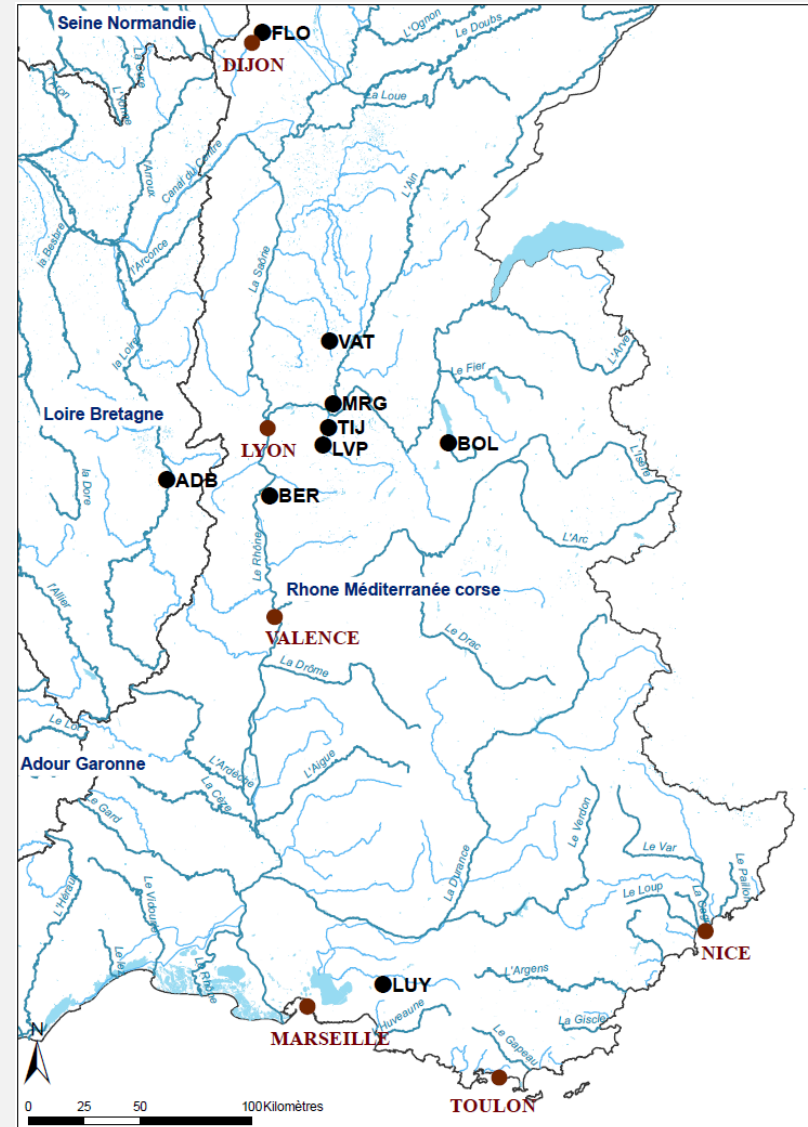
$$\text{TMF} = e^b$$



Adapted from Burkhard, L.P., Borgå, K., et al.. *Environmental Science & Technology* **47**, 1186–1187

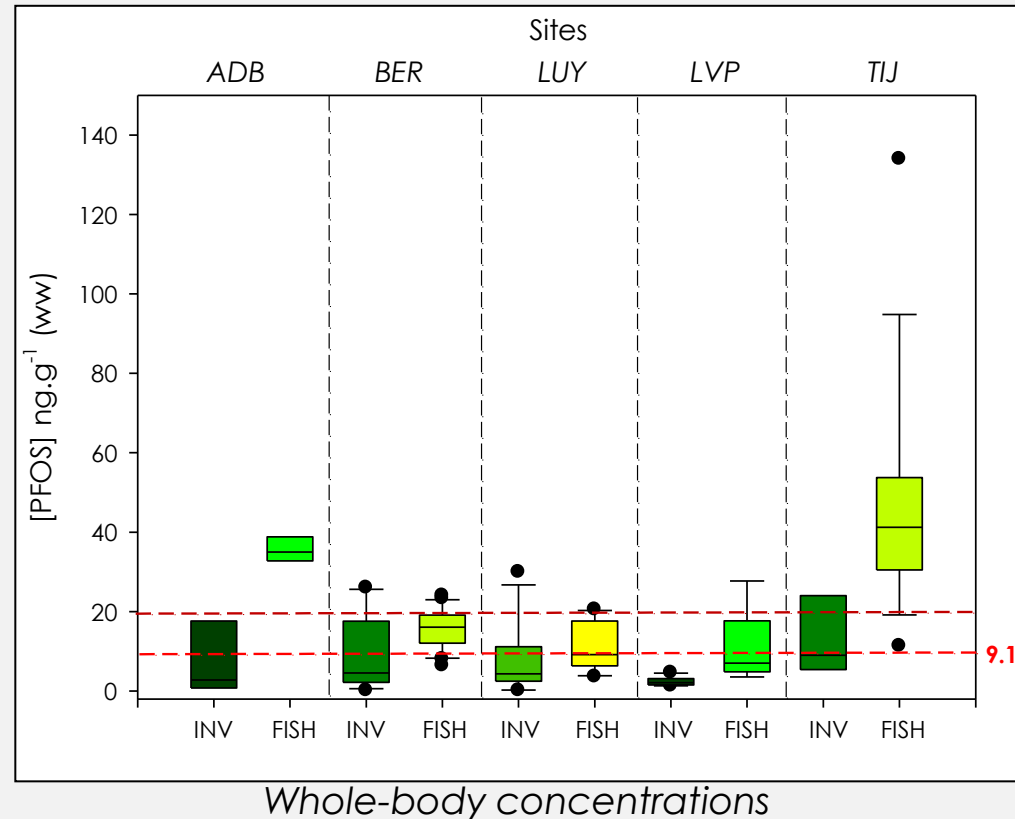
Study design

- Priority substances: PFOS, PBDEs (HBCDD)
- Riverine sites (N = 9)
 - Various hydrological contexts
 - Preliminary knowledge of contamination (PBDEs in sediment)
- Field sampling + caging
 - Fish spp. *B. barbus*, *S. cephalus*
 - Benthic invertebrates (wild)
 - Caged organisms: *C. riparius*, *Gammarus* spp.
- Analysis (PFOS, PBDEs, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, lipids)
- Statistical models: linear regression, Kendall regression, generalized linear mixed effect model (GLMM)



Results: PFOS

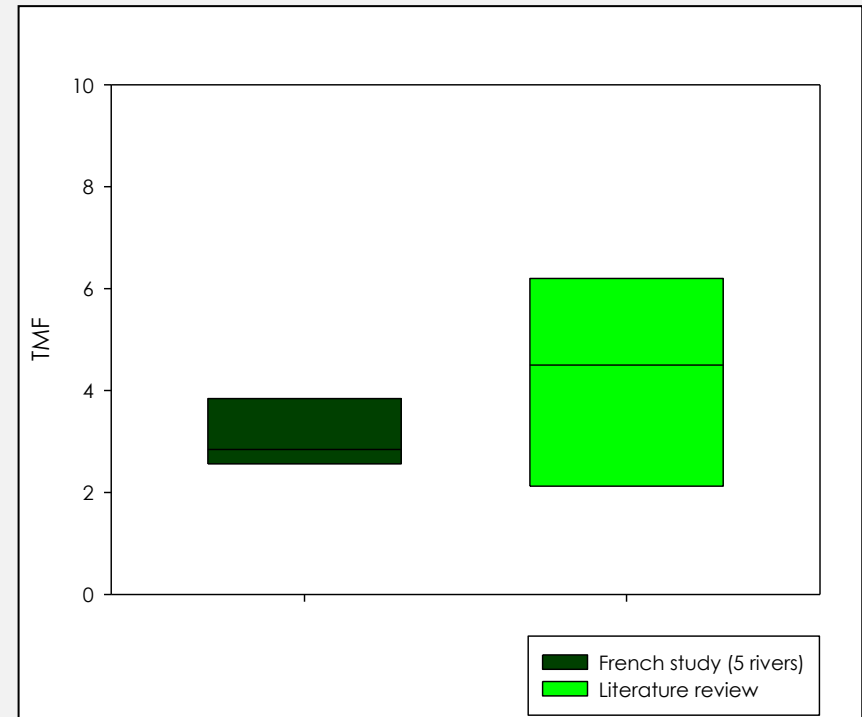
- INV:
 - <LD à 107.5 ng.g^{-1} (ww)
 - Difference among sites: not significant
- FISH:
 - 0 non-detect
 - Fillet $\approx 50\%$ of the whole-body concentration
 - EQS exceedance (geomean / fillet): 2/5 sites not compliant (ADB, TIJ)





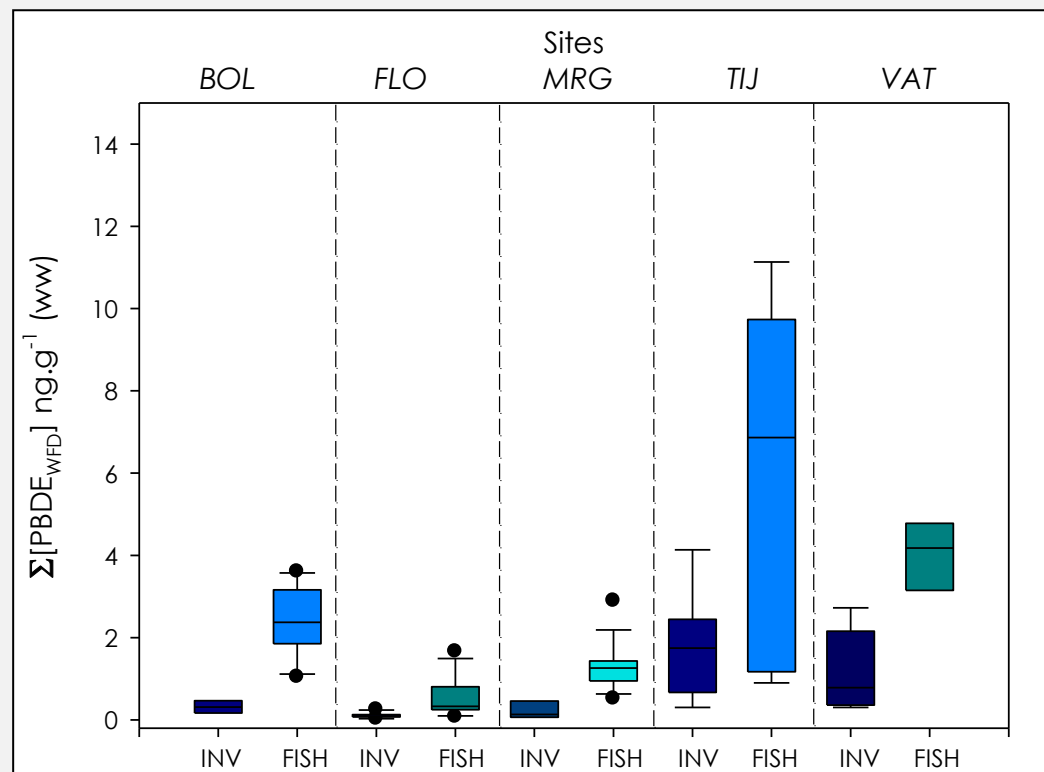
Results: TMFs for PFOS

- TL range ≥ 2 in 4/5 sites
- GLMM regression:
 - Slope non significantly different from 0 \Rightarrow 1/5 site
- TMF range:
 - 2.55 ± 0.18 to 4.09 ± 1.35
 - Comparable to the literature



Results: Σ PBDEs

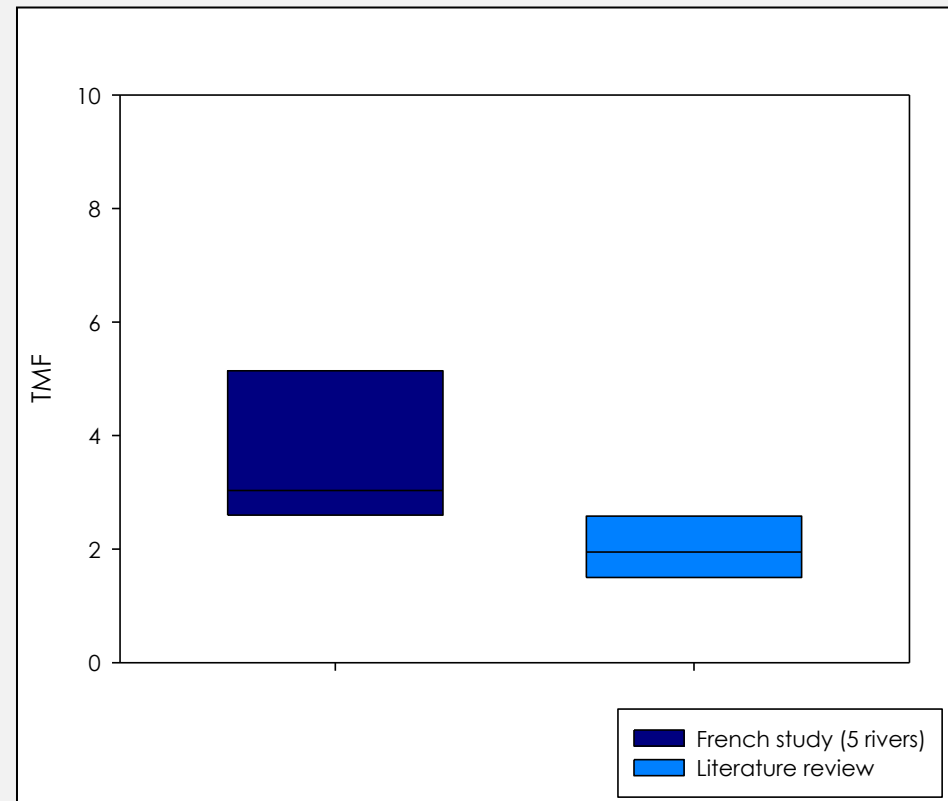
- Σ PBDEs: congeners 28, 47, 99, 100, 153, 154)
- INV
 - < LD – 4.14 ng.g⁻¹ (ww)
 - No apparent influence of lipid contents?
- FISH
 - 0.07 – 11.1 ng.g⁻¹ (ww)
 - Influence of lipid content (and site / fish species)
 - Fillet \approx 30 % of whole-body concentrations
 - EQS systematically exceeded





Results: TMFs for PBDEs

- TL range > 2 in 2/5 sites, slightly < 2 in 3/5 sites
- GLMM-based TMF range:
 - 1.7 ± 1.4 to 5.7 ± 2.6
 - 2.9 ± 0.5 when adjusted to lipid content
 - Higher than TMFs from literature





Results: caged organisms

- PFOS
 - Chironomids 0.5 – 1.2 ng.g⁻¹ (ww)
 - Gammarids 0.8 – 5.8 ng.g⁻¹ (ww)
- Σ PBDEs
 - Chironomids 0.05 – 0.8 ng.g⁻¹ (ww)
 - Gammarids 0.05 – 1.1 ng.g⁻¹ (ww)
- Somewhat difficult to compare to wild invertebrates
 - Different exposure conditions
 - Same site ranking
- Protocol under revision (gammarids)
 - Exposure duration

Extrapolation from caged organisms to fish tissues



- C_{inv} : measured concentrations in caged organisms
- TL_{inv} : mean trophic level of the corresponding wild taxon
- TL_{fish} : mean TL per site (each spp.)
- TMF: GLMM-based TMF values (each site)

$$C_{fish} = C_{inv} \times TMF^{(TL_{fish} - TL_{inv})}$$

Prediction correct if:

- Same range as observed concentrations
- or
- Same position compared to EQS

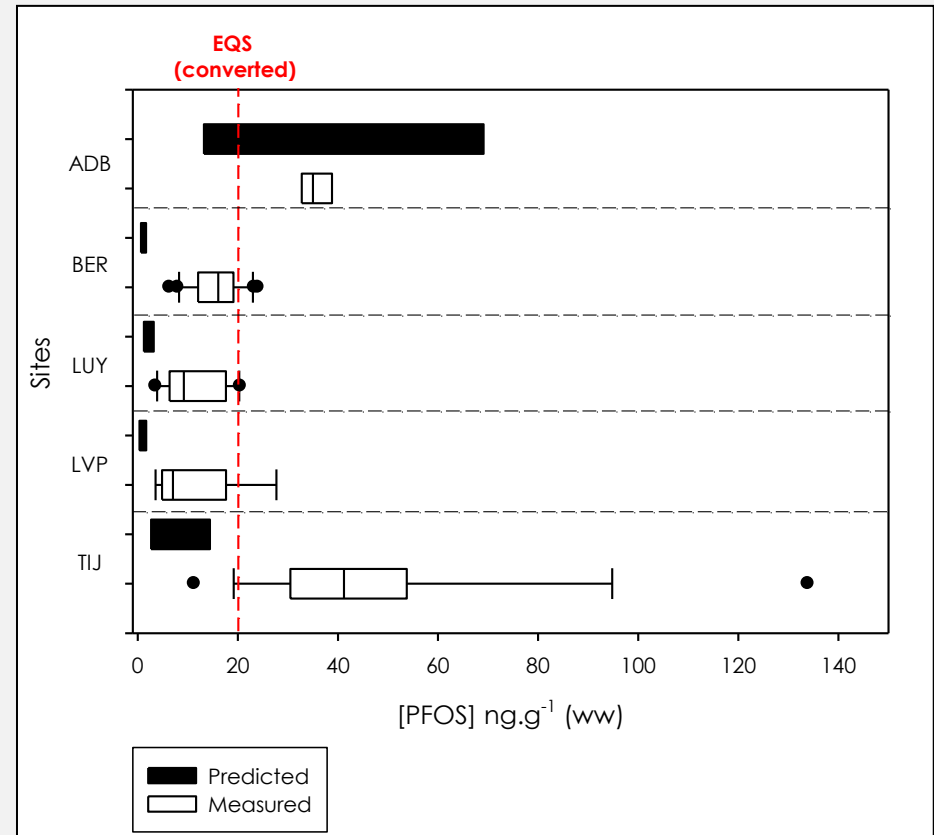


Common Implementation Strategy for the Water Framework Directive (2000/60/EC) - Guidance Document No. 32 on Biota monitoring



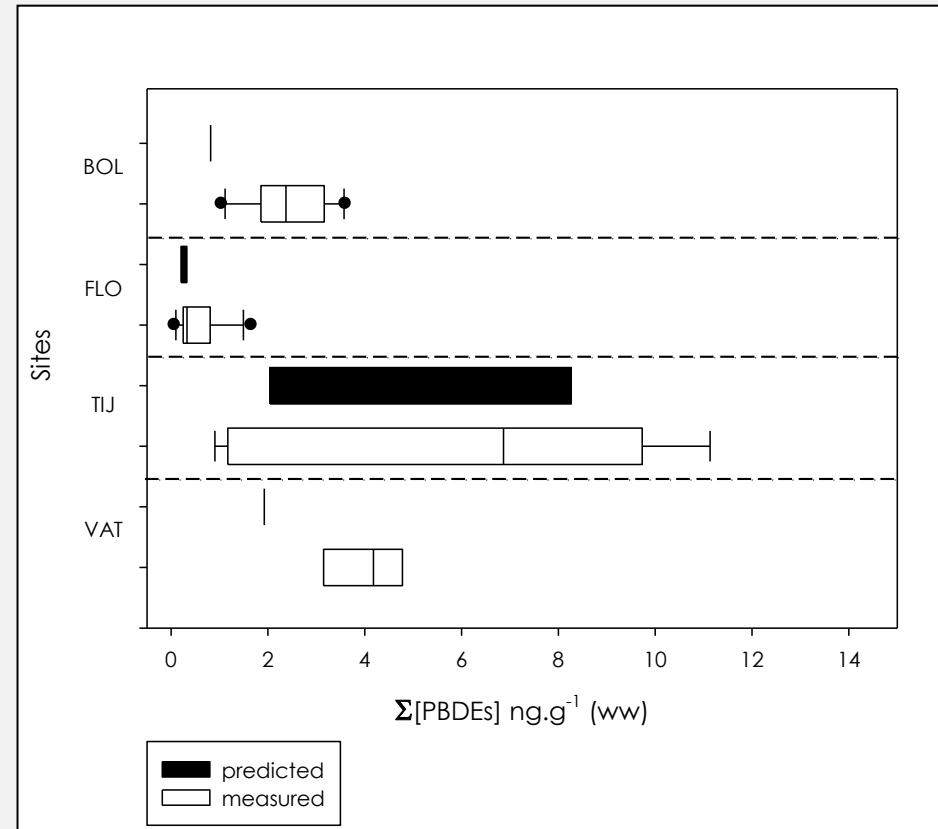
Observed vs predicted [PFOS] in fish tissues

- Predicted [PFOS] – 5 sites
 - underestimated 4/5 sites
- Site ranking vs EQS
 - Prediction correct at 4/5 sites
- If use of a single TMF value (e.g. 75th percentile of TMFs):
 - underestimated [PFOS] 3/5, correct 1/5, overestimated 1/5
 - EQS match 5/5



Observed vs predicted [Σ PBDEs] in fish tissues

- Predicted [Σ PBDEs] – 4 sites
 - underestimated: 2/4 sites
 - similar : 2/4 sites
- EQS match: not relevant
- If use of a single TMF value for all sites (e.g. 75th percentile of TMFs):
 - Reduced differences
 - Still underestimated 2-3/5 sites





Conclusions and perspectives

- Proof of concept: positive (for 3 priority substances)
 - Need to improve the prediction reliability
- TMF = not the only source of uncertainty:
 - TL assigned to caged organisms
 - TL_{fish} - variability
 - Exposure duration – steady state achievement
- TMF selection
 - Minimize type II error rate
 - Use of values from the literature \Rightarrow section criteria (HESI)
- Upcoming study
 - Better characterize uptake in caged organisms and apparent TL