

# Determination of BSAFs for freshwater fish and derivation of a sediment standard for PCBs: a case study of the Rhone basin

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# Context, study objectives

- Inventories of fish contamination by PCBs and dioxins since 2005-2006 in the Rhone basin
  - Bed sediments considered as the main source
- European policy on dioxin-related compounds – Directive 2006/13/EC
  - 8 pg TEQ.g<sup>-1</sup>(fresh weight) except eels, 12 pg TEQ.g<sup>-1</sup>
- Water Framework Directive (WFD) implementation:
  - A sediment standard for PCBs (or dioxins) would not be very relevant if only based on toxicity to benthic invertebrates
  - Trophic transfer from sediment to higher trophic level organisms not covered by the draft guidance on environmental quality standard (EQS) derivation
- Objectives
  - Develop robust biota to sediment accumulation factors (BSAFs) for freshwater fish species (basin-wide)
  - Derive a “trigger value” for sediment (SQG: sediment quality guideline)



# Background

- Most current definition
- Uncertainties, limitations
  - “connection” sediment – fish (spatially and temporally)
  - knowledge of distributions generally missing
- Availability of 2 large databases in the Rhone basin:
  - Fish contamination inventory (2005-2009, ca. 2000 samples)
  - Sediment contamination (monitoring since 1993)

$$BSAF = \frac{C_l}{C_{soc}} = \frac{C_{org}/f_l}{C_{sed}/f_{soc}}$$

- $C_{org}$  concentration in organism ( $\mu\text{g.kg}^{-1}$  wet weight),
- $C_{sed}$  concentration in sediment ( $\mu\text{g.kg}^{-1}$  dry weight),
- $f_l$  lipid fraction (g lipids / g ww),
- $f_{soc}$  organic fraction (g OC / g dw)



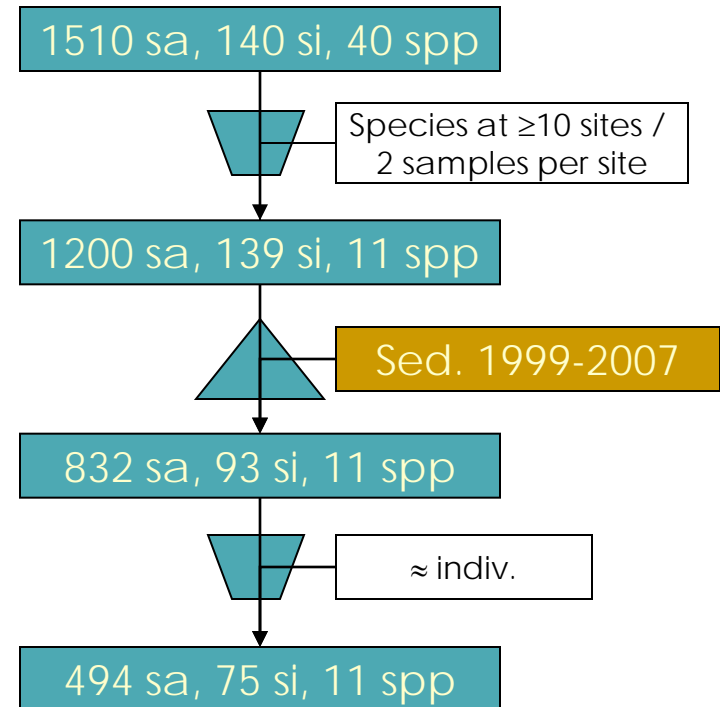
# Approach

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- Dataset: matching the 2 databases
- Data selection
  - Fish: sampling protocol, number of samples
  - Sediment ↔ fish exposure
- BSAF determination
  - Bootstrap method ⇒ BSAF variability
  - Site by site, 3 sets (fish, sediment – PCB and TOC)
- Threshold derivation: indirect approach
  - Regulatory threshold (RT) refers to dioxins and related compounds
  - Most sediment data cope with indicator congeners ( $\Sigma$ iPCB)
  - BSAF more appropriate when referring to a single compound

# Data selection

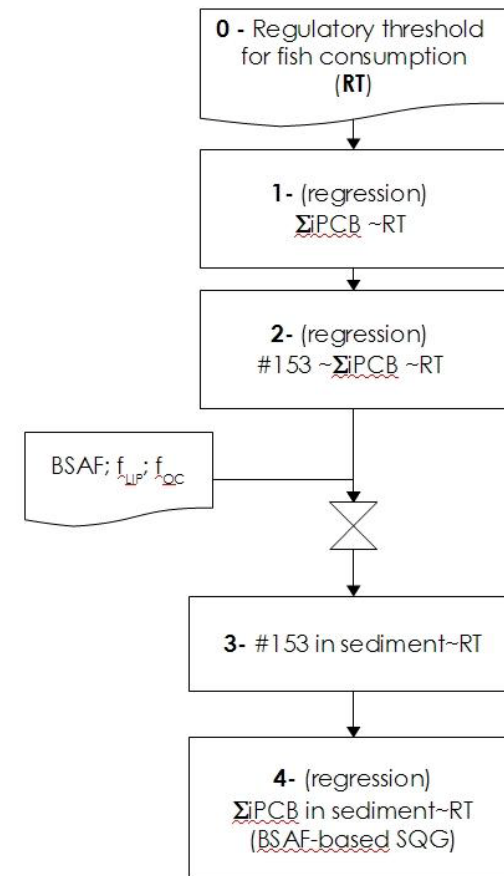
- Online fish database
  - Sites for which sediment data are available
  - Fish sampled 2007-2009
    - ✦ Spp present at  $\geq 10$  sites
    - ✦  $\geq 2$  samples / site
    - ✦ Individuals or pools (restricted to 2 individuals same size)
- Online sediment database
  - Sites for which fish data are available
  - 1999 – 2007 (according to fish size-age)



[http://www.rhone-mediterranee.eaufrance.fr/usages-et-pressions/pollution\\_PCB/basepcb](http://www.rhone-mediterranee.eaufrance.fr/usages-et-pressions/pollution_PCB/basepcb)

# Sediment threshold derivation

- TEQ correlated to  $\Sigma\text{iPCB}$ 
  - unless local dioxin sources
- More chlorinated congeners (e.g. #153) correlated to  $\Sigma\text{iPCB}$  in fish and sediment
- Uncertainty on the SQG
  - Confidence intervals for each parameter (slope and intercepts) of successive regressions



# Overview of fish data

- Consistent relationship size / weight
- Few non-detects (less chlorinated #)
- Concentration ranges
- Almost no relationship
  - weight / lipid content
  - weight / PCB
  - lipid content / PCB
- Distributions normal (gaussian) or log-normal
- ⇒ rather consistent dataset
- #153 correlated to  $\Sigma$ iPCB (whole set, each species)

*Pearson similarity matrix*

	Lip. Cont.	# 28	# 52	# 101	# 118	# 138	# 153	# 180
# 28	0.47							
# 52	0.56	<b>0.83</b>						
# 101	0.36	0.59	<b>0.84</b>					
# 118	0.45	0.54	<b>0.84</b>	<b>0.97</b>				
# 138	0.33	0.49	0.70	<b>0.89</b>	<b>0.87</b>			
# 153	0.31	0.43	0.65	<b>0.84</b>	<b>0.83</b>	<b>0.94</b>		
# 180	0.18	0.35	0.46	0.61	0.58	<b>0.87</b>	<b>0.83</b>	
$\Sigma$ iPCBs	0.33	0.49	0.71	<b>0.89</b>	<b>0.87</b>	<b>0.99</b>	<b>0.97</b>	<b>0.89</b>

N = 457 samples – all #  $\geq$  LQ

# Overview of sediment data

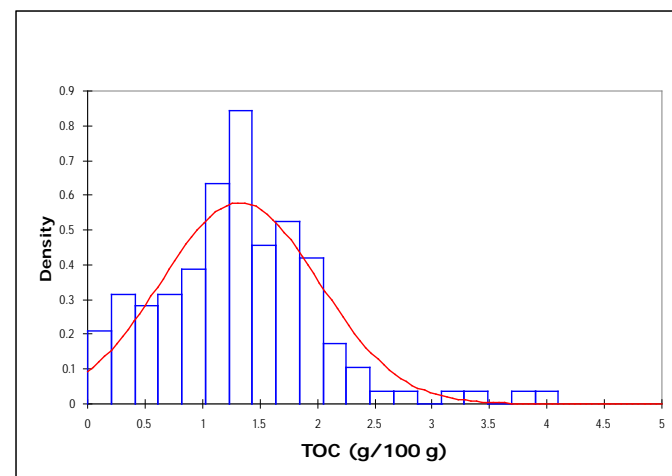
- 459 sets(75 sites)
  - ... 111  $\geq$  LQ
- Reliability?
- #153 correlated to  $\Sigma$ iPCB
- Some other congeners correlated to #153
- BSAF  $\Rightarrow$  #153
- Organic Carbon (TOC)
  - 157 samples (Rhône river)
  - 1<sup>st</sup> quartile 0.013 g.g<sup>-1</sup> (dw);
  - 3<sup>rd</sup> quartile 0.019 g.g<sup>-1</sup> (dw)

Each #  $\Rightarrow$   $\Sigma$

	N	adj R <sup>2</sup>	p
# 101	54	0.73	< 0.0001
# 118	49	0.15	0.003
# 138	88	<b>0.94</b>	< 0.0001
# 153	90	<b>0.95</b>	< 0.0001
# 180	68	<b>0.90</b>	< 0.0001

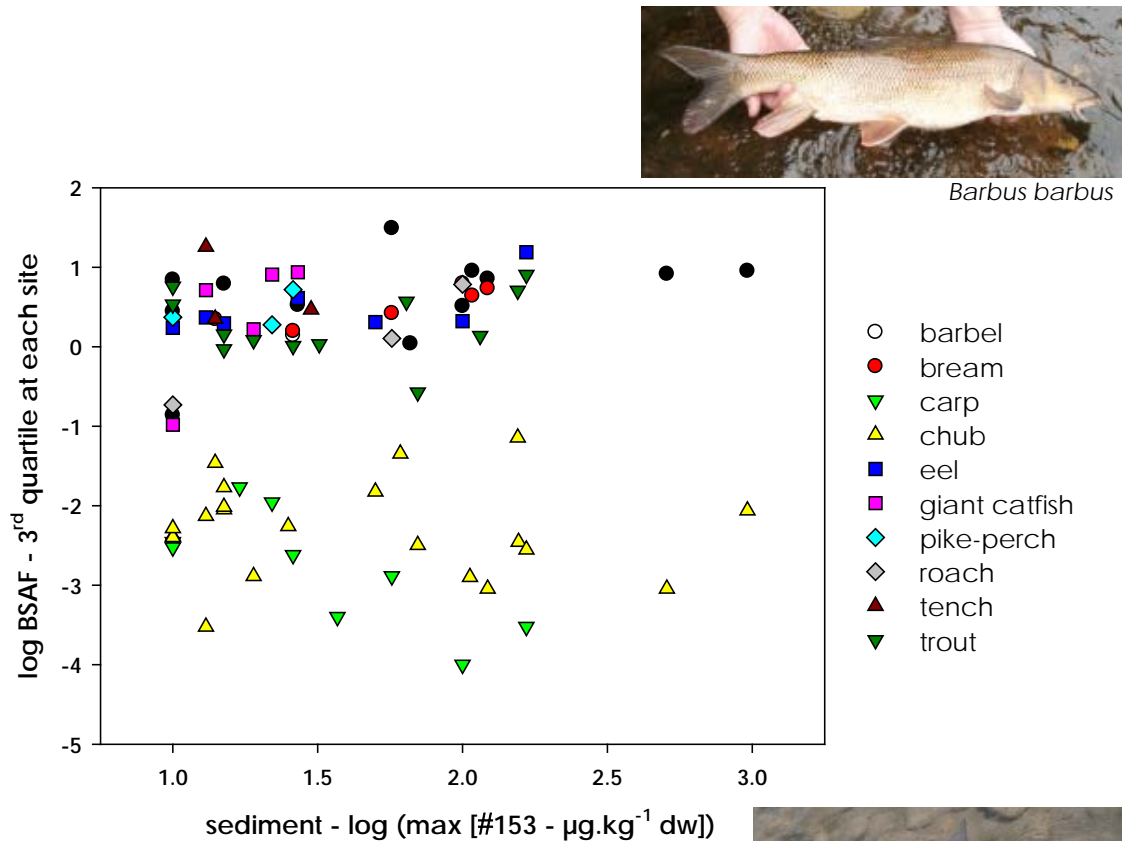
#i  $\Rightarrow$  #153

	N	adj R <sup>2</sup>	p
# 101	54	0.62	< 0.0001
# 138	83	<b>0.89</b>	< 0.0001
# 180	68	<b>0.95</b>	< 0.0001





# BSAFs distribution



*Barbus barbus*



*Squalius cephalus*

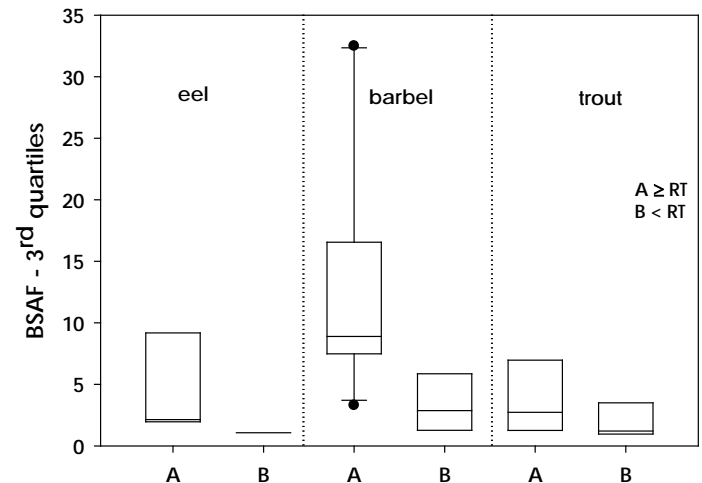
- No direct relationship with sediment concentrations
- Roughly 2 groups
  - carp, chub
  - giant catfish, roach, bream, pike-perch, tench, trout, eel, barbel
- Low BSAFs in chub related to food regime
- Low BSAFs in carps may be related to physiology and habitat
- Highest BSAFs (3<sup>rd</sup> quartile)
  - eel 1.7 – 15.5
  - barbel 0.14 - 31

# Refined approach

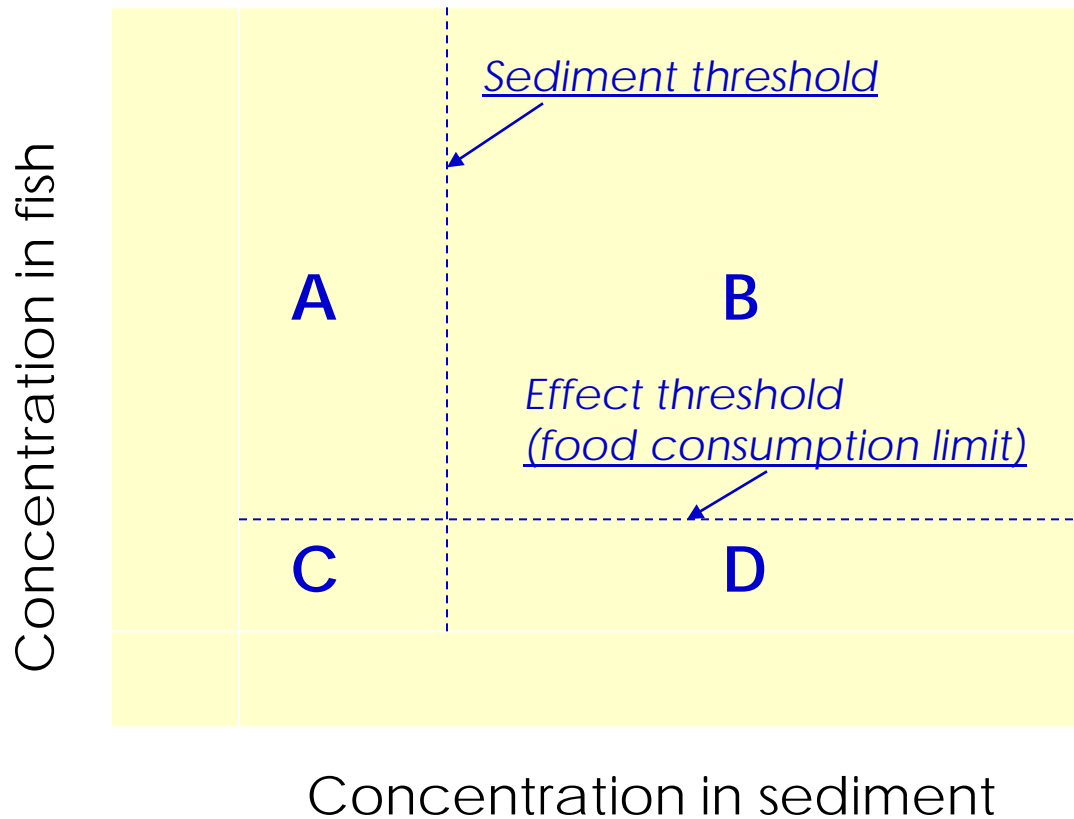
- 2 groups according to RT exceedence
  - G1 = fish  $\geq$  RT (A)
  - G2 = fish  $<$  RT (B)
  - Some sites belong to both groups
- Statistics = Kaplan-Meier for left-censored data for calculating quartiles in sediment
- Refined bootstrap - BSAFs higher in G1 (A) than in G2 (B)

Sediments  
( $\mu\text{g.kg}^{-1}$  dw)

	G1	G2
N sites	33	69
N sites > LQ / N sites	64%	48%
1 <sup>st</sup> quartile	10	10
median	15	10
mean	80.1	29.7
std deviation	32.4	8.2
3 <sup>rd</sup> quartile	66	22
max	963	507



# How efficient is the threshold?

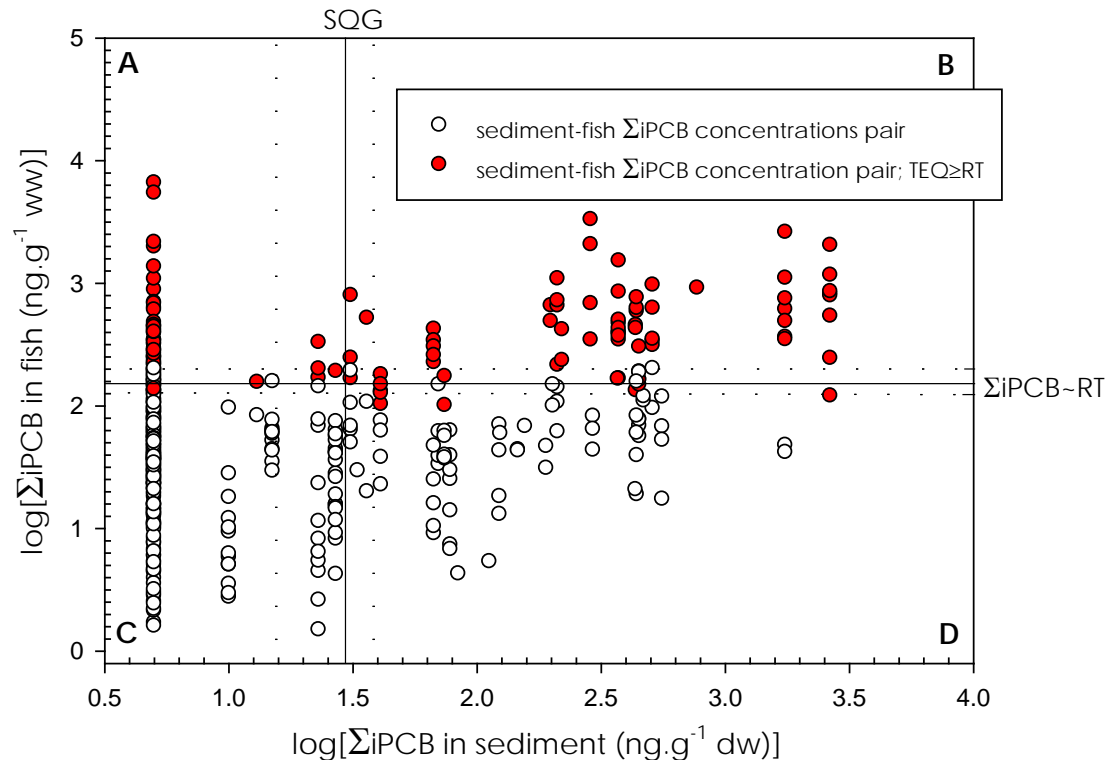


- Sensitivity =  $B/(A+B)$
- Specificity =  $C/(C+D)$
- Type I % =  $(D/(D+B)) \times 100$
- Type II % =  $(A/(A+C)) \times 100$
- Overall efficiency =  $(B+C)/(A+B+C+D)$

Adapted from Shine J.P. & al. (2003) *Envir. Toxicol. Chem.* 22/7 1642-1648

# Calculation results / efficiency

- 26.6 ng. g<sup>-1</sup> dw  
[15.8 – 38.6]
  - based on 3<sup>rd</sup> quart. of barbels BSAF
- 62 % fishes correctly classified according to RT
- Sensitivity (B/A+B)
  - 0.50
- specificity (C/C+D)
  - 0.71
- overall efficiency (B+C/A+B+C+D)
  - 0.65





# Discussion

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- Method consistency
  - Fish exposure “window”
- BSAF consistent with literature
  - Except for the carp
- Why BSAFs are different in G1 and G2?
  - Fatter fish specimens in G1
  - More contaminated sediments in G1
  - BSAF higher, but not correlated to sediment contamination
    - ✘ Bioavailability (among others?)
- Sediment threshold
  - Comparable to some extent to “co-occurrence” SQGs
  - ± comparable to Great Lakes *fca-SQT* (Bhavsar et al., 2010), but more robust / adaptable to varying local conditions

Bhavsar S.P., Gewurtz S.B. et al. (2010) *Integ. Environ. Assess. Manag.* 6/4 641-652



# Conclusions & perspectives

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- SQG applicability?
  - Not an environmental quality standard (EQS)!
  - SQG (screening): is the efficiency high enough?
    - ✘ Test on another dataset (nationwide)
- Compliance monitoring: towards a tiered approach?
  - Sediments at the first step (if possible)
  - Biota if sediment screening level exceeded
- Management guideline?



# Thank you for attention

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- study supported by a grant from DREAL Rhône-Alpes

