Determination of thresholds in marine molluscs as an alternative to the Environmental Quality Standards in marine water defined in the Water Framework Directive

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Introduction

The European Commission's Water Framework Directive (WFD) lays down Environmental Quality Standards (EQS) in marine water for 34 priority substances. Among these substances, 25 (table 1) are hydrophobic and bioaccumulable (2 metals and 23 organic compounds). For these 25 substances, monitoring in the water matrix is inappropriate and an alternative matrix should be developed. Bivalve molluscs and particularly mussels (*Mytilus edulis, Mytilus galloprovincialis*) have been used by Ifremer as a quantitative biological indicator since 1979 in France to assess marine water quality through the French chemical contaminant monitoring network (ROCCH and RINBIO).

The aim of this study is to determine thresholds for mussels at least as protective as EQS for these 25 substances

Three following steps were defined:

❶ Provide an overview of knowledge on the relations between contaminant concentrations in marine water and mussels through BAF and BCF.

❷ Compare concentrations in wild and caged mussels (respectively ROCCH and RINBIO) and concentrations in marine water for the determination of BAF.

❸ Select BCF or BAF in order to recommend molluscs thresholds.

BCF - Bioconcentration factor is the ratio of the concentration of a chemical in the tissue of an aquatic organism from water only (by breathing or direct skin contact).

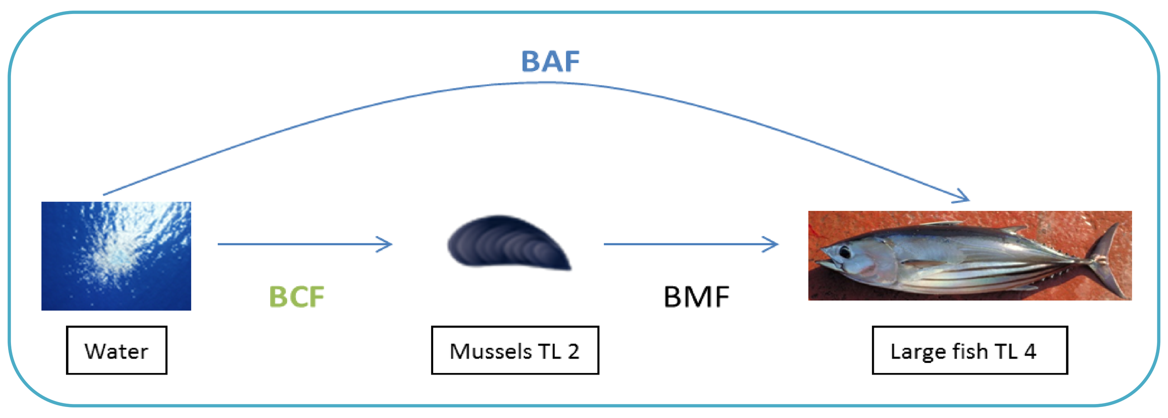
$$BCF\ [L.kg_{-1}\ P.H.] = \frac{C_{organism}}{C_{dissolved\ water}}$$

Methodology

Using conversion factors (figure 1), the European Technical Guidance for Deriving Environmental Quality Standards (TGD-EQS) proposes an equation for converting water concentrations to equivalent biota concentrations:

$$QS_{biota}\ [\mu g.Kg^{-1}] = QS_{water} \times BAF$$

$$QS_{biota}\ [\mu g.Kg^{-1}] = QS_{water} \times BCF \times BMF$$



BAF: bioaccumulation factor
BCF: bioconcentration factor
BMF: biomagnification factor

Figure 1 : *Illustration of conversion factors*

For molluscs, the BMF process is very low or non-existent (figure 1). So we can say that: BAF ≈ BCF. This equation is available for trophic levels lower than TL 3.

BAF – The Bioaccumulation Factor is the ratio of the concentration of a chemical in the tissue of an aquatic organism from all surrounding media (water, food, sediment) to its concentration in water.

BAF [L.kg$_{-1}$ P.H.]= BCF x BMF

BMF : biomagnification factor (amplification through food web, from prey to predator)

❶ How can BCF and BAF be determined?

BCF can be determined experimentally (according to US EPA or ASTM standards), or by Quantitative Activity-Structure Relationship models (QSAR) using Log Kow of the chemicals: out of four equations applicable to molluscs, two are specific to *Mytilus edulis* (figure 2).

BAF can be determined using the Dynamic Budget Model, but this model is very complex to use and requires a lot of thematic data, which must be acquired prior to evaluation. BAF can also be determined using QSAR or experimentally, but these methods are considered invalid for molluscs. Only field experiments are adapted to molluscs, but no standards exist for determining BAF in the field (figure 2).

❷ Determination of BAF using field data

Concentration data in marine water (C_{water}) was collected from both scientific literature (Web of Science, Science Direct, Google scholar) and studies and monitoring programmes (RINBIO, bioaccumulation studies, Seine Aval programme – map 1). This data was then compared to concentrations in wild mussels ($C_{mussels}$) obtained from the French chemical contaminant monitoring network (ROCCH) and concentrations in caged mussels obtained from the biological integrator network (RINBIO). If large amounts of data were available, the median concentrations in water and in mussels were calculated, providing a BAF median for each substance.

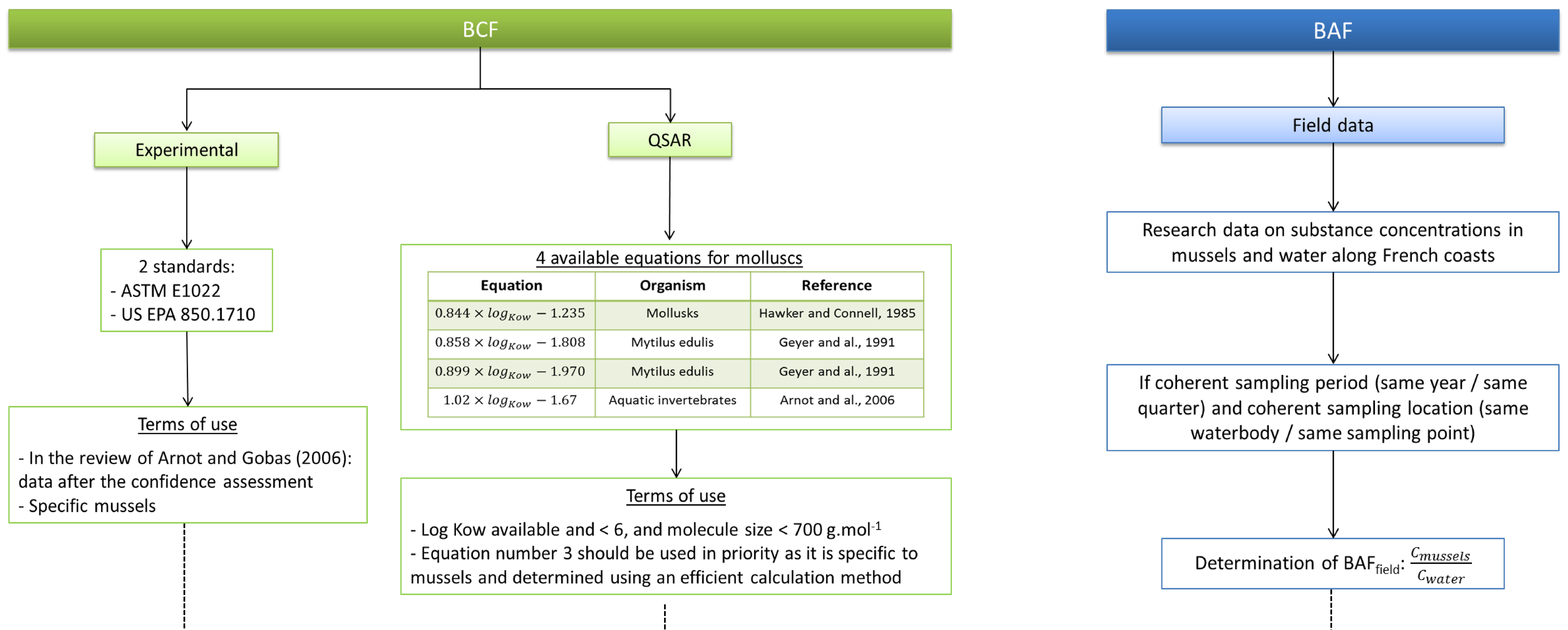
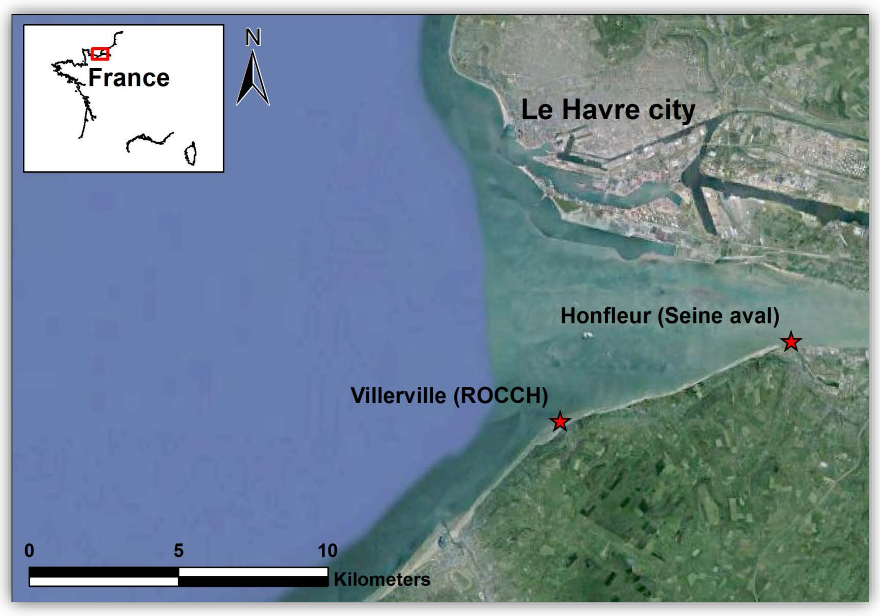


Figure 2: *Available methods for determining BCF and BAF in molluscs*



Map 1 : *Location of monitored points for the Seine Aval programme and ROCCH*

For example, on map 1, the "Seine Aval" programme measured cadmium concentrations data in water in the Seine estuary (Honfleur). This data was compared to cadmium concentrations found in wild mussels at the "Villerville" sampling point measured by the ROCCH monitoring network.

❸ Determined BCF and BAF values and proposed thresholds

Median $BCF_{experimental}$ was determined for 3 substances: chlorpyrifos (4 data sets), lindane (21 data sets), pentachlorobenzene (6 data sets).

BCF_{QSAR} was determined for 20 substances using the equation number 3.

N° CAS	Substance	EQS_{water} ($\mu g.L^{-1}$)	Conversion factor used ($L.Kg^{-1}$ P.H.)	Thresholds for molluscs proposed ($\mu g.Kg^{-1}$ P.H.)
120-12-7	Anthracene	0.1	BCF_{QSAR} = 1738	173.8
			BAF = 3065	306.5
7440-43-9	Cadmium and its compounds	0.2	BAF = 2861	572.2
85535-8438	C_{10-13} Chloralkanes	0.4	BCF_{QSAR} = 955 - 26301 (49% Cl)	382 - 10520.4 (49% Cl)
470-90-6	Chlorfenvinphos	0.1	BCF_{QSAR} = 309 (isomer Z) - 661 (isomer E)	30.9 (isomer Z) - 66.1 (isomer E)
2921-88-2	Chlorpyrifos	0.03	$BCF_{experimental}$ = 344	10.32
309-00-2	Aldrin	Σ = 0.005	-	-
60-57-1	Dieldrin		BCF_{QSAR} = 7586	37.93
72-20-8	Endrin		BCF_{QSAR} = 81	0.4
465-73-6	Isodrin		-	-
-	DDT	0.025	BAF = 51300	1282.5
117-81-7	DEHP	1.3	-	-
115-29-7	Endosulfan	0.0005	BCF_{QSAR} = 1778	0.89
58-89-9	HCH (lindane)	0.002	$BCF_{experimental}$ = 141	0.28
7439-92-1	Lead and its compounds	1.3	BAF = 4341	5643.3
91-20-3	Naphtalene	2	BCF_{QSAR} = 107	BCF_{QSAR} = 214
			BAF = 5671	BAF = 11342
84852-15-3	4-Nonylphenol branched	0.3	BCF_{QSAR} = 1148	344.4
140-66-9	Para-tert-Octylphenol	0.01	BCF_{QSAR} = 229 - 6166	2.29 - 61.66
608-93-5	Pentachlorobenzene	0.0007	$BCF_{experimental}$ = 3273	2.29
87-86-5	Pentachlorophenol	0.4	BCF_{QSAR} = 104	41.6
36643-28-4	Tributyltin cation	0.0002	BCF_{QSAR} = 66 - 525	0.013 - 0.105
120-82-1	1.2.4 Trichlorobenzene	0.4	BCF_{QSAR} = 468	187.2
1582-09-8	Trifluralin	0.03	BCF_{QSAR} = 3890 - 6761	116.7 - 202.83
124495-18-7	Quinoxyfen	0.015	BCF_{QSAR} = 1659	24.88
74070-46-5	Aclonifen	0.012	BCF_{QSAR} = 912	10.94
42576-02-3	Bifenox	0.0012	BCF_{QSAR} = 199	0.24
28159-98-0	Cybutryne (Irgarol)	0.0025	BCF_{QSAR} = 380	0.95
52315-07-8	Cypermethrin	0.000008	-	-
886-50-0	Terbutryn	0.0065	BCF_{QSAR} = 144	0.94

Table 1 : *Conversion factors and proposed thresholds for 25 study substances*

11 median BAF_{field} for 6 substances

12 data sets from the literature (anthracene, naphtalene, cadmium and lead), 11 data sets from the "Seine aval" programme (cadmium and lead), 12 data sets from RINBIO (cadmium and lead), 8 data sets from bioaccumulation studies (cadmium, lead, DDT and HCH).

The TGD-EQS recommendation for the conversion of EQS water to biota thresholds is to use prior field BAF; if unavailable, experimental BCF can be used and, lastly, QSAR BCF.

The majority of substances had a BCF value calculated using QSAR. However, several conversions factors were available for 8 substances: 2 metals (cadmium and lead) had several BAF values, 3 substances (anthracene, naphtalene, lindane) had both BAF and BCF values, and 4 substances (chlorpyrifos, lindane, pentachlorobenzene, pentachlorophenol) had both experimental BCF and BCF calculated by QSAR. In each case, the substance was examined carefully in order to choose the most pertinent value. Although the TGD-EQS recommends the priority use of BAF values this was not always the case, as the BAF could not be considered as sufficiently valid due to a lack of data.

Concerning metallic compounds for instance, BCF appeared to be inappropriate and QSAR calculation is unsuitable for metals; therefore, a BAF value is required.

This study pinpoints two major elements:

- **The highly variability of conversion factors values** and, in particular, BAF values. Interpretation of BAF values is difficult and must be performed cautiously, as BAF values are obtained by calculating ratio between integrated measurements in mussels and periodic measurements in dissolved water. Also, BAF variability is dependent on molluscs physiology (nutrition, growth, reproduction, etc.), environmental variability (substance concentration in water, salinity, trophic conditions, etc.) and the substance's physicochemical characteristics (bioavailability, hydrophobicity, etc.).
- **The absence of a methodology for the acquisition of field BAF**, hence lack of criteria for assessing BAF validity. A BAF is considered valid when it is calculated once a steady state is reached. For a given substance concentration in water, the steady state is considered as reached once uptake and depuration in an organism are equal.

Molluscs thresholds were proposed for 23 substances (table 1): 5 substances based on BAF values, 3 substances based on experimental BCF and 18 substances based on QSAR BCF. No thresholds were determined for DEHP, aldrin, dieldrin or cypermethrin.

Conclusions & prospects

This study allowed 23 thresholds to be proposed for mussels as an alternative to EQS in marine water, and highlighted some important points:

- a lack of data for comparing concentrations in water and mussels;
- the high existing variability of values for one conversion factor;
- the absence of a methodology for field BAF acquisition for mussels in the marine environment (no available standard).

For this purpose, the next step will be to develop a methodology to obtain a valid field BAF, in order to obtain reliable and operational thresholds for the WFD. In the framework of this methodology, it will be interesting to study the acquisition of concentrations in water, both by conventional methods and passive samplers, together with concentrations in wild and caged mussels.

Sire A., Amouroux I., 2015. Détermination de Valeurs Guides Environnementales (VGE) mollusques alternatives aux Normes de Qualités Environnementales (NQE) eau définies dans la DCE. Rapport Ifremer RBE/BE/ARC/2016.01, janvier 2016, 81 p..