JRC Scientific and Technical Reports

A general bioaccumulation DEB model for mussels

José-Manuel Zaldívar

EUR 23626 EN - 2008

The mission of the IHCP is to provide scientific support to the development and implementation of EU policies related to health and consumer protection.

The IHCP carries out research to improve the understanding of potential health risks posed by chemical, physical and biological agents from various sources to which consumers are exposed.

European Commission
Joint Research Centre
Institute for Health and Consumer Protection

Contact information
Address: Via E. Fermi 2749, TP 272
E-mail: jose.zaldivar-comenges@jrc.it
Tel.: +39-0332-789202
Fax: +39-0332-785807

http://ihcp.jrc.ec.europa.eu/
http://www.jrc.ec.europa.eu/

JRC 48848

EUR 23626 EN
ISBN 978-92-79-10943-0
ISSN 1018-5593
DOI 10.2788/36003

Luxembourg: Office for Official Publications of the European Communities

Printed in Italy

Cover picture (Blue mussel, Mytillus gallo provincialis) from: Picton, B.E. & Morrow, C.C., 2007. *[In] Encyclopedia of Marine Life of Britain and Ireland*
http://www.habitas.org.uk/marinelife/species.asp?item=W16510

CONTENTS

CONTENTS ..... **ii**
1. INTRODUCTION **1**
2. METHODS AND APPROACH **3**
2.1. STUDY AREA 3
2.2. BIOCONCENTRATION AND BIOACCUMULATION IN MUSSELS 4
2.3. MODEL DEVELOPMENT 7
2.3.1. The Dynamic Energy Budget (DEB) Approach 7
2.3.2. The bioaccumulation model 10
2.3.3. The estimation of the bioaccumulation model parameters 14
2.3.4. Forcing of the DEB-bioaccumulation model using 3D simulation runs 15
3. RESULTS AND DISCUSSION **18**
3.1. DEB GROWTH MODEL 18
3.2. BIOACCUMULATION MODEL 20
3.3. COMPARISON WITH EXPERIMENTAL DATA 22
4. CONCLUSIONS **24**
5. REFERENCES **25**

1. INTRODUCTION

Mussels are a common species that are frequently employed in contaminants monitoring programs in transitional, coastal and marine waters. For example, the US Mussel Watch program (Kimbrough et al, 2008) began monitoring trace metals and organic contaminants in mussels at several estuaries and coastal sites in US since 1986 and now it covers approximately 140 analytes. The OSPAR (OSPAR, 1999), HELCOM and MEDPOL conventions have included mussels as the species to analyze for assessing chemical contamination in coastal ecosystems (Roose and Brinkman, 2005), and there are also several European monitoring programmes in Member States, e.g. RINBIO (Réseaux Intégrateurs Biologiques, France).

Monitoring contaminants concentrations in mussels has some advantages, when compared with the measurement of total concentrations in the water column, principally for hydrophobic compounds that bioaccumulate in the food web. Data of organic contaminants accumulated in the tissues of mussels (or other biota) may provide an assessment of pollutant occurrence and distribution in aquatic ecosystems, acting as a time integrated measure (Goldberg, 1986; Pereira *et al.*, 1996). Specifically, in coastal ecosystems molluscs have been used as bioindicators of pollution because of their feeding behaviour and their scarce mobility, which make them particularly exposed to contamination both trough water column and sediment, directly or after resuspension. Among molluscs, mussels are farmed for human consumption and, if contaminated, might represent a potential risk for human health.

Although seafood represents a significant means of contamination of human diet, few legal thresholds have been established in order to protect human health from a number of toxic compounds and complex mixtures of chemicals. In particular the European Community introduced several laws in order to regulate the water quality parameters of bivalves farming zones (91/492/CEE) and to restrict farming, transport and purchase (79/923/CEE, 89/2886/CEE). However these rules refer only to microbiological contamination. In the last years several EC legislation already has been put in place concerning several families of organic contaminants like dioxins, dioxin-like PCBs, PAHs (Commission Regulation (EC) No 1881/2006 of 19 December 2006), and metals like lead, cadmium, mercury (Commission Regulation (EC) No 78/2005, amending Regulation 466/2001), etc. and for several aquatic species such as fish, molluscs, crustaceans and cephalopods. Furthermore, in the directive 2000/60/CEE, with reference to decision n. 2455/2001/CEE, European Countries, in the absence of agreement at European community level which is at the moment under discussion (COM (2006) 397), are requested to establish quality standard limits for priority hazardous substances in surface waters.

Along with field studies and monitoring activities, model tools are necessary to understand the fate and transport of contaminants and to assess their impacts on communities and ecosystems (Carafa *et al.*, 2006, 2009; Jurado et al., 2007; Bacelar et al., 2009; Dueri et al., 2009a,b; Marinov et al., 2008a,b).

In the management of hazardous chemicals the prediction of bioconcentration and bioaccumulation factors from water in aquatic organisms has become a very important tool for assessing the environmental and human health effects of a certain substance. The quantitative knowledge of uptake, metabolism, excretion and depuration processes of chemicals in the organisms is needed to predict the fate and bioaccumulation of contaminants along the food web (Moriarty and Walker, 1987). However, all these processes are strictly related to specific physiological characteristics, feeding behaviour and metabolism of the aquatic organism; to the particular chemical-physical features of the compound; and to the environmental conditions of the aquatic system in which the organisms resides. For these reasons it is difficult to make comparisons between different field studies and results can seem sometimes contradictory.

Consequently, it seems desirable to have a general modelling tool able to simulate field and laboratory toxicological experiments and integrate all the results into a predictive tool for the ecotoxicological behaviour of a certain substance.

This work has as objective to provide an evaluation tool for calculating the contaminant concentration values on mussels (*Mytilus galloprovincialis*) from the values in the water column. Specifically some compounds from PCBs (Polychlorinated Biphenyls) and PCDD/Fs (Polychlorinated dibenzo-dioxins and Furans) POPs (Persistent Organic Pollutants) families have been used to test the approach. However, the final objective is to develop a screening tool for predicting the bioaccumulation of a new chemical in mussels based on its physico-chemical properties that can be evaluated using QSAR techniques (Pavan et al., 2008). This will help in selecting candidate substances that have a potential to bioaccumulate in aquatic ecosystems as well as predicting which concentrations one could expect when analyzing mussel tissues.

For this reason a bioaccumulation model has been developed, implemented and calibrated using experimental data from Thau lagoon (France). The model uses input data from a 3D fate and biogeochemical model that provides chemical concentrations in the water column as well as in the sediments, and biomasses in the different compartments, i.e. phytoplankton, zooplankton and bacteria (Marinov et al., 2008a, 2008c; Dueri et al.,2009). The bioaccumulation model is based on the Dynamic Energy Budget approach (DEB) (Kooijman, 2000). The model predicts correctly the measured concentrations for several PCBs and PCDD/Fs congeners for which data were available. However improved data sets will be necessary to develop a generic tool for calculating bioconcentration factors (BCF) based on physicochemical properties of the selected compound. Concerning its possible implementation as a method to infer concentrations in the water column, from concentrations in

mussel tissues for monitoring purposes, it would be necessary to carry out a more detailed validation phase as well as QA/QC assessment if it is going to be used in compliance monitoring by MS in coastal areas.

2. METHODS AND APPROACH

2.1. STUDY AREA

The Thau lagoon is 25 km long, 5 km wide and on average 4 m deep. The lagoon is located on the French Mediterranean coast (Figure 1) and is sheltered with two narrow sea mouths. The catchment area is small (280 km²) and drained by numerous small streams with intermittent flows. The climate imposes a wide range of water temperatures and salinities with minima of 5° C in February and salinity near 27‰, and maxima of 29° C in August and a salinity of 40‰. Precipitation also shows large interannual variation (from 200 to 1000 mm per year). Wind is often strong with a mean of 118.5 days per year above Beaufort force 5 (data from Météo-France), particularly when it is blowing from the Northwest (the so called "Tramontane"). Thau lagoon hydrodynamics is heavily influenced by both meteorological forcing, i.e. wind and precipitation (Lazure 1992).

Besides its ecological interest as a recruitment zone for some sea fish species, the lagoon is of notable economic importance due to shellfish cultivation (about 15 000 tons per year, amongst the highest in the Mediterranean Sea). The Thau lagoon frequently undergoes, in summer, anoxia that can lead to important economic losses.

During the last twenty years, the Thau lagoon has been extensively studied, with investigations of the exchange between the water column and sediments, the oysters farming activities, the impact of the watershed and interactions with the Mediterranean Sea (Amanieu et al. 1989; Picot et al. 1990; Plus et al. 2006 and references therein). Various numerical models have been developed, focusing on hydrodynamics (Lazure 1992), nitrogen and oxygen cycles (Chapelle 1995; Chapelle et al. 2001), plankton ecosystem (Chapelle et al. 2000), impact of shellfish farming (Bacher et al. 1997; Gangery et al. 2004a, b) and macrophytes (Plus et al. 2003a,b). However, no model was developed having in mind the study of fate and effects of contaminants.

IFREMER has been coordinating a monitoring programme (RNO, Réseau National d'Observation de la qualité du milieu marin) with the objective of evaluating the levels and trends of chemical contaminants in the marine environment (http://www.ifremer.fr/envlit/surveillance/rno.htm).

Concerning Thau lagoon, there are temporal time series for PAHs, PCBs PBDEs, OCPs and PCDD/Fs in mussels and sediments during the last decades (Tronczyński, 2006; Munchy et al., 2008). All these contaminants show a decreasing trend with the exception of PBDEs. This decreasing trend has significantly slower rates in sediments than in mussels, for example $t_{1/2}$ for ΣPCBs is 8 years in mussels and 32 years in sediments (Tronczyński, 2006).

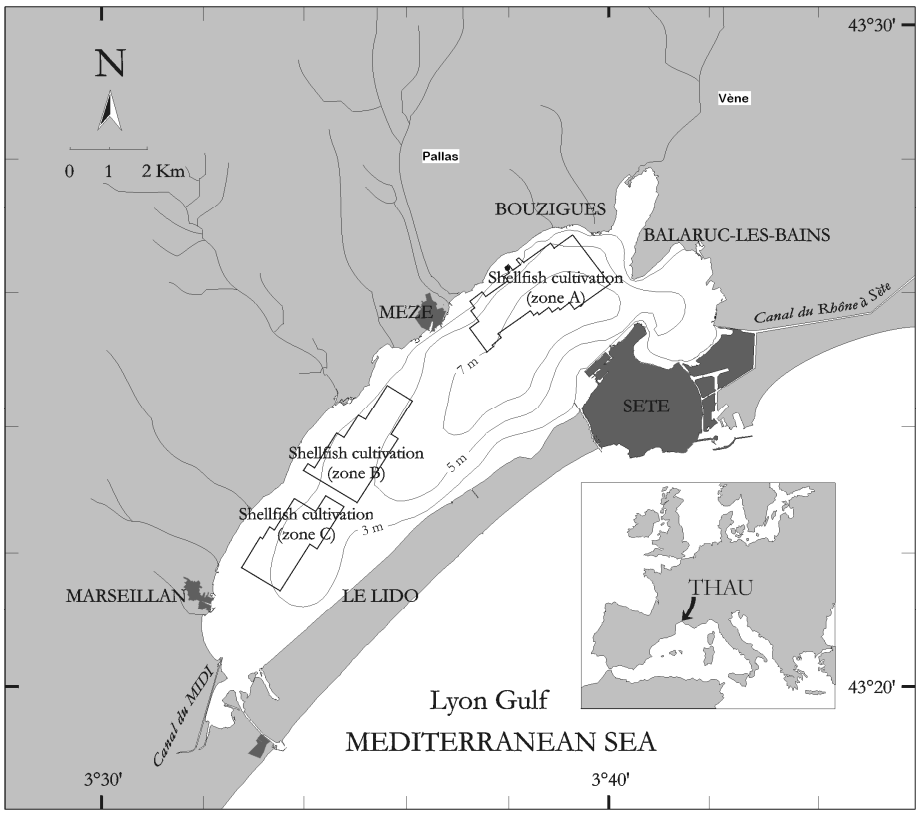

Figure 1. The Thau lagoon and its watershed. Connections with the Mediterranean Sea are located at the extremities: in the Sète city and near Marseillan village.

2.2. BIOCONCENTRATION AND BIOACCUMULATION IN MUSSELS

As an example, Figure 2 show some of the observed trends at two stations (in Zone A and Zone C) for several PCBs, whereas in Fig. 3 the decreasing trend of PCDD/Fs concentrations in mussels is shown.

Accumulation is a general term for the net result of absorption (uptake), distribution, metabolism and excretion (ADME) of a substance in an organism. Information on accumulation in aquatic organisms is vital for understanding the fate and effects of a substance in aquatic ecosystems. In addition, it is an important factor when considering whether long-term ecotoxicity testing might be necessary. This is because chemical accumulation may result in internal concentrations of a substance in an organism that cause toxic effects over long-term exposures even when external concentrations are very small. Highly bioaccumulative chemicals may also transfer through the food web, which in some cases may lead to biomagnification.

Bioconcentration refers to the accumulation of a substance dissolved in water by an aquatic organism. The bioconcentration factor (*BCF*) of a compound is defined as the ratio of concentration of the chemical in the organism and in water at equilibrium, normally C_w is the dissolved water concentration.

$$BCF = \frac{C_b}{C_w} \tag{1}$$

The existence of equilibrium between the concentration of the chemical in the organism and the concentration in the water is not easy to asses. For example, for rainbow trout Vigano *et al*. (1994) measured a time range between 15 and 256 days to reach equilibrium after exposure to different concentrations of PCBs.

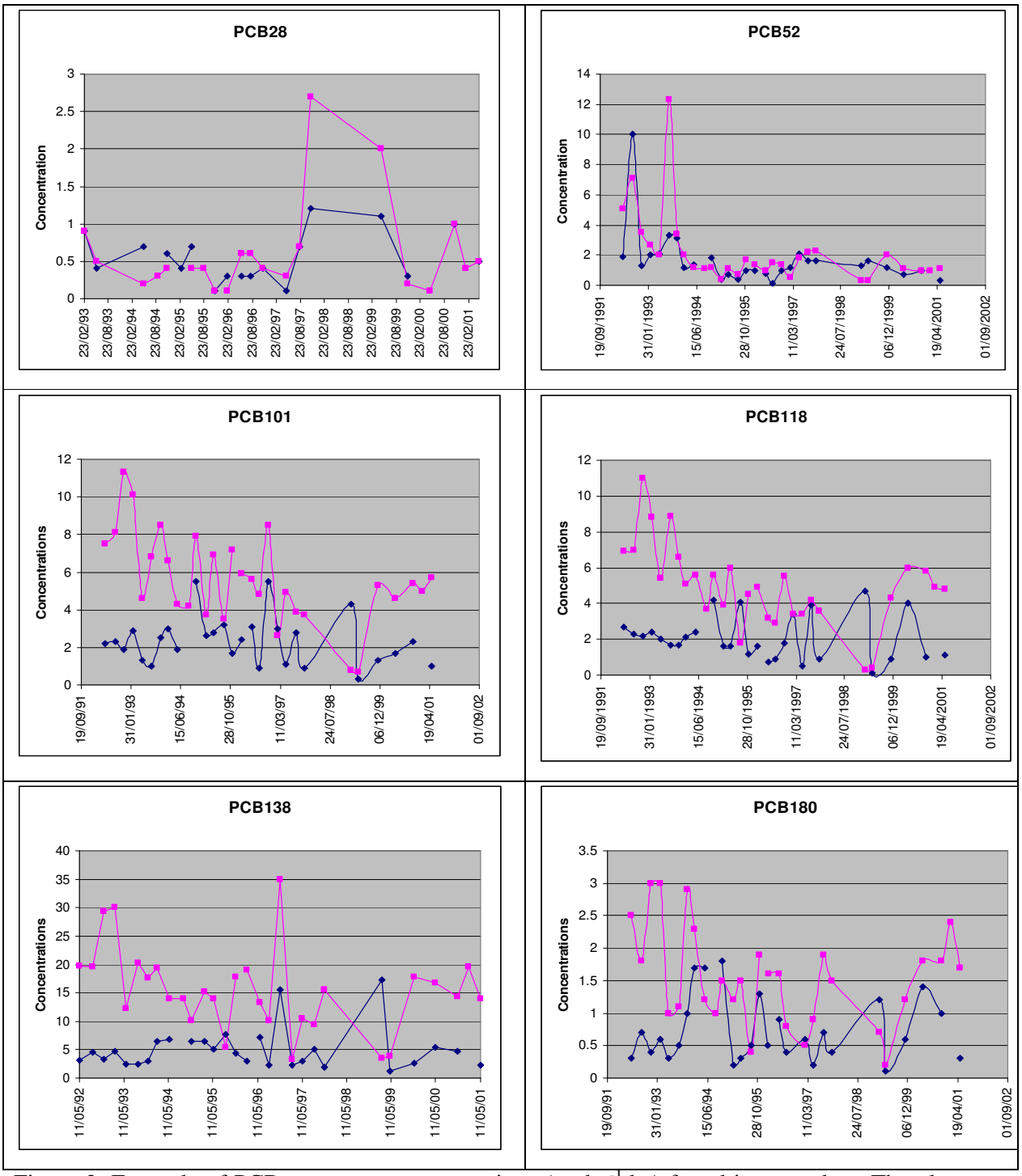

Figure 2. Example of PCB congeners concentrations (µg kg^{-1}dw) found in mussels at Thau lagoon at two sampling stations in Zone C (blue) and in Zone A (pink), see Fig.1, respectively.

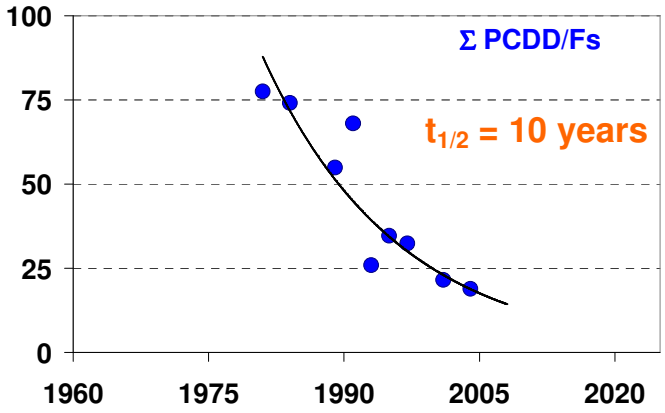

Figure 3. PCDD/Fs time trends in mussels (ng kg^{-1} dw) for Thau lagoon from 1980 to 2004 (data from Tronczyński, 2006).

Biomagnification refers to accumulation of substances via the food chain. It may be defined as an increase in the (fat-adjusted) internal concentration of a substance in organisms at succeeding trophic levels in a food chain. The biomagnification factor (*BMF*) can be expressed as the ratio of the concentration in the predator and the concentration in the prey:

$$BMF = \frac{C_b}{C_d} \tag{2}$$

where C_b is the steady-state chemical concentration in the organism (mg kg^{-1}) and C_d is the steady-state chemical concentration in the diet (mg kg^{-1}).

The term bioaccumulation refers to uptake from all environmental sources including water, food and sediment. The bioaccumulation factor (*BAF*) can be expressed for simplicity as the steady-state (equilibrium) ratio of the substance concentration in an organism to the concentration in the surrounding medium (e.g. water). Normally, it is evaluated using a multiplicative approach. Therefore, the Bioaccumulation Factor (*BAF*) may be calculated as:

$$BAF = BCF \cdot \prod_{i=1}^{n} BMF_i \tag{3}$$

where the number of biomagnifications factors depends on the trophic level or position of the organism in the food web.

For the case of mussels, we have calculated *BCF* based on measured concentrations data on the water column from Castro-Jiménez et al. (2008) and mussels measurements from Munschy et al. (2008)[1]. Concerning the bioconcentration and bioaccumulation factors for mussels in Thau lagoon, Tables 1 and 2 summarize the results for PCBs and PCDD/Fs, respectively. The value for BCF_{dw} was obtained by considering only dissolved concentrations, whereas the BAF_{dw} was calculated by considering total (dissolved+particulate) concentrations (Arnot and Gobas, 2006); the term dw refers to dry weight. For

PCDD/Fs there were no data available of dissolved concentrations –values bellow the Limit of Detection, LOD- so we have obtained only BAF_{dw} assuming that total concentration equals particulate concentration. It is important to notice that whereas water concentrations refer to 2005, mussel concentrations are from 2004.

Table 1. Experimental (mean and standard deviation) log BCF_{dw} and log BAF_{dw} (L kg^{-1}) for PCBs in mussels in Thau lagoon.

Compound (PCBs)	log K_{ow}	*log* BCF_{dw}	*log* BAF_{dw}
PCB28	5.67	5.57±0.93	4.92±0.21
PCB52	5.80	3.52±0.11	3.80±0.79
PCB101	6.40	3.95±0.34	3.95±0.28
PCB118	6.70	5.08±0.34	4.97±0.28
PCB138	6.83	5.58±0.30	5.52±0.30
PCB153	6.92	5.72±017	5.60±0.16
PCB180	7.40	4.65±0.28	4.53±0.17

Table 2. Experimental (mean and standard deviation) log BAF_{dw} (L kg^{-1}) for PCDD/Fs in mussels in Thau lagoon.

Compound (PCDD/Fs)	log K_{ow}	*log* BAF_{dw}
TCDD	6.9	-
PeCDD	7.4	-
HxCDD	7.8	7.72±0.25
HpCDD	8.0	7.62±0.25
OCDD	8.2	7.46±0.25
TCDF	7.7	-
PeCDF	7.6	-
HxCDF	7.7	7.50±0.14
HpCDF	7.5	7.52±0.24
OCDF	7.6	7.62±0.35

2.3. MODEL DEVELOPMENT

2.3.1. The Dynamic Energy Budget (DEB) Approach

The DEB theory (Kooijman, 2000) provides the basis for the description of the relations between feeding, maintenance, growth, development and reproduction in organisms. In DEB this description is carried out using mass and energy budgets normally expressed as ordinary differential equations. Following Kooijman (2000) the basic allocation pathways are shown in Figure 4. As it can be observed, structural body mass, reserves and maturity are the state variables. The assimilated food is added to the reserves compartment and then spited between the other compartments, whereas a fixed fraction is spent on somatic maintenance and growth and the rest on maturity maintenance and reproduction (or maturation). This theory has been extensively tested for different kind of organisms, e.g. mollusks, fish, birds, etc. (Kooijman, 2000).

During this report the notation and symbols follow those in Kooijman (2000), therefore:

[1] The interested reader is referred to the original papers for material and methods and QA/QC details

- Lower and upper case symbols are related via scaling;

- Quantities that refer to unit of volume are expressed within brackets []; those that refer to unit of biosurface area within braces {};

- Rates have dots.

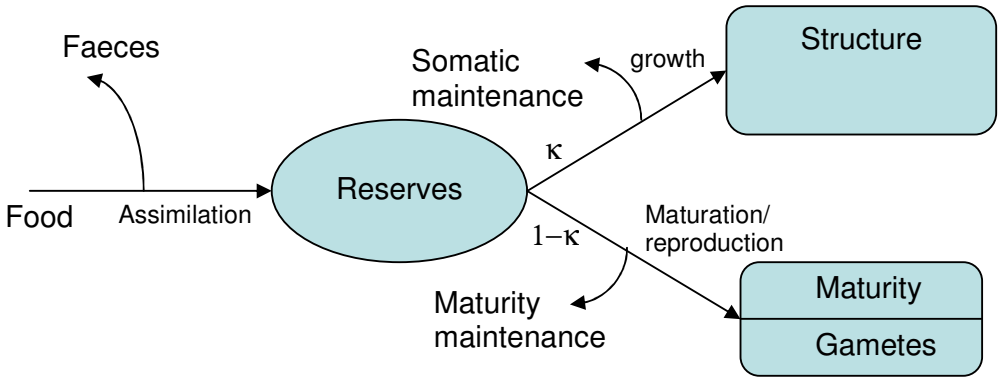

Figure 4. Representation of the energy fluxes following the DEB approach (Kooijman, 2000).

The state variables of the DEB model are: Structural Volume, V (cm^3), Energy reserves, E (J), and Energy allocated to development and reproduction, R (J). The model parameters and their values are summarized in Table 3.

The Energy reserves can be expressed as the difference between the assimilation energy rate ($\dot{p}_A$,J d^{-1}) and the energy utilization rate ($\dot{p}_C$, J d^{-1}):

$$\frac{dE}{dt} = \dot{p}_A - \dot{p}_C \tag{4}$$

where the assimilation energy rate may be expressed as:

$$\dot{p}_A = \{\dot{p}_{Am}\} f \cdot k(T) \cdot V^{2/3} \tag{5}$$

where $\{\dot{p}_{Am}\}$ is the maximum surface area-specific assimilation rate (J cm^{-2} d^{-1}) –see Table 3- and f is the functional response of assimilation to food concentration given by (Casas and Bacher, 2006):

$$f = \frac{[Chla]}{[Chla] + [Chla]_K} \tag{6}$$

where $[Chla]_K$ is the half saturation coefficient in μg l^{-1} (see Table 3) and k(T) is a temperature dependence defined as (Kooijman, 2000):

$$k(T) = \frac{\exp\left(\frac{T_A}{T_I} - \frac{T_A}{T}\right)}{\left[1 + \exp\left(\frac{T_{AL}}{T} - \frac{T_{AL}}{T_L}\right) + \exp\left(\frac{T_{AH}}{T_H} - \frac{T_{AH}}{T}\right)\right]} \tag{7}$$

The energy utilization rate, $\dot{p}_C$ (J d^{-1}), may be expressed as (Kooijman, 2000):

$$\dot{p}_C = \frac{[E]}{[E_G] + \kappa[E]} \left(\frac{[E_G]\{\dot{p}_{Am}\} \cdot V^{2/3}}{[E_m]} + [\dot{p}_M] \cdot V \right) \quad (8)$$

where $[E]$ is the energy density, $[E]=E/V$, $[E_G]$ is the volume-specific cost for structure (J cm^{-3}), $[E_m]$ is the maximum energy density in the reserve compartment (J cm^{-3}), κ is the fraction of energy utilization rate spent on maintenance plus growth, and $[\dot{p}_M]$ is the maintenance costs (J cm^{-3} d^{-1}) which is also function of the temperature, i.e. $[\dot{p}_M] = k(T) \cdot [\dot{p}_M]_m$.

According to Kooijman (2000) a fixed fraction of energy is allocated to somatic maintenance and growth while the rest is used for maturation reproduction (see Fig. 4). However, maintenance has priority over growth and when there is not enough food growth stops. Therefore, the change in structural volume, V, is given by:

$$\frac{dV}{dt} = \frac{\kappa \cdot \dot{p}_C - [\dot{p}_M] \cdot V}{[E_G]} \quad (9)$$

Concerning the energy allocated to development and reproduction, Kooijman (2000) showed that it can be expressed as:

$$\frac{dR}{dt} = (1-\kappa)\dot{p}_C - \left(\frac{1-\kappa}{\kappa} \right) \min(V, V_P)[\dot{p}_M] \quad (10)$$

where V_P, is a threshold value of the structural volume for the transition juvenile/adult (the subscript P refers to puberty). To simulate the loose of around 40-70% of mollusks wet weight at spawning (Van Haren et al., 1994), Pouvreau et al. (2006) introduced the following rule for oysters: when $V>V_P$, the ratio between gonad and total tissue mass is above 0.35 and water temperature, T>20 ºC the buffer R is completely emptied. Similar rule has been used by Casas and Bacher (2006) for mussels.

Table 3.Parameters of the mussel Dynamic Energy Budget (DEB) model.

Parameter	**Unit**	***Description***	***Value***	***Reference***
$\{\dot{p}_{Am}\}$	J cm^{-2} d^{-1}	Maximum surface area-specific assimilation rate	147.6	Van der Veer et al. (2006)
$[Chla]_K$	mg m^{-3}	half saturation coefficient	3.88	Casas and Bacher (2006)
T_A	K	Arrhenius temperature	5800	Van der Veer et al. (2006)
T_I	K	Reference Temperature	293	Van der Veer et al. (2006)
T_L	K	Lower boundary of tolerance range	275	Van der Veer et al. (2006)
T_H	K	Upper boundary of tolerance range	296	Van der Veer et al. (2006)
T_{AL}	K	Rate of decrease of lower boundary	45430	Van der Veer et al. (2006)
T_{AH}	K	Rate of decrease of upper boundary	31376	Van der Veer et al. (2006)
$[\dot{p}_M]_m$	J cm^{-3} d^{-1}	Volume specific maintenance costs	24	Van der Veer et al. (2006)
$[E_G]$	J cm^{-3}	Volume specific costs of growth	1900	Van der Veer et al. (2006)
$[E_m]$	J cm^{-3}	Maximum energy density	2190	Van der Veer et al. (2006)
κ	-	Fraction of utilised energy spent on maintenance / growth	0.7	Van der Veer et al. (2006)
V_P	cm^3	Volume at start of reproductive stage	0.06	Van der Veer et al. (2006)
δ_m		Shape coefficient	0.25	Casas and Bacher (2006)
d	g cm^{-3}	Specific density	1	Kooijman (2000)
μ_E	J g^{-1}	Energy content of reserves	6750	Casas and Bacher (2006)

Shell length, L (cm), and fresh tissue mass, W (g), may be obtained using the following correlations:

$$L = \frac{V^{1/3}}{\delta_m} \tag{11}$$

$$W = d\left(V + \frac{E}{[E_G]}\right) + \frac{R}{\mu_E} \tag{12}$$

where δ_m is the shape coefficient, d is the specific density (g cm^{-3}) and μ_E is the energy content of reserves (J g^{-1}).

2.3.2. The bioaccumulation model

Transfer mechanisms of persistent hydrophobic contaminants in aquatic organisms are essentially two: the first one is the direct uptake of dissolved phase from water trough skin or gills, named bioconcentration, the second one is the indirect uptake of bound contaminants to suspended particular matter and through consumption of contaminated food (biomagnification).

The bioaccumulation of pollutants may be an important source of hazard for the ecosystem, due to adverse effect not quickly evident (e.g. acute or chronic toxicity) but that became manifested after years in the higher levels of the trophic food web or in a later stage of life of organisms or after several generations (Van der Oost *et al*., 2003).

The mass balance of a contaminant (A) in the tissue of an aquatic organism, C_b (mg kg^{-1}), can be defined as (adapted from Thomann, 1989 and Thomann *et al*., 1992):

$$\frac{dC_b}{dt} = k_u C_w + k_f C_p - k_d C_b - k_m C_b - k_g C_b \tag{13}$$

where the first two terms indicate the uptake (u) of contaminant from water (w) and predation (p), respectively, and the third, fourth and fifth terms indicate losses of contaminants through depuration (d) (release from gill membranes or excretion through feces), metabolism (m) and dilution effect of growth (g), respectively.

Removal of chemicals in an aquatic organism is realized essentially through two main pathways: the contaminant is either eliminated by depuration/excretion in the original chemical form (parent molecule) or bio-transformed by the organism. The latter process leads in general to the formation of more hydrophilic compounds. In this case the metabolites are rapidly excreted after a detoxification reaction. These compounds are normally less harmful than the parent compound. However, in some cases the parent compound can be "bioactivated" through metabolic reactions and lead to formation of a metabolite more toxic than the former molecule (Van der Oost, *et al.,* 2003).

The velocity and efficiency of metabolic clearance have been demonstrated to be a function of several species-specific characteristics: presence of enzymes, feeding status, stage of life, spawning period (Van der Oost *et al.*, 2003).

Using this model and assuming steady-state conditions, i.e. $dC_b/dt = 0$, then it is possible to calculate the bioconcentration factor (*BCF*) as:

$$BCF = \frac{k_u}{(k_d + k_m + k_g)} \tag{14}$$

In addition, the biomagnification factor (*BMF*) defined as the ratio between the uptake of a contaminant from food and its removal by depuration/excretion (*d*), metabolism (*m*) and growth (Sijm *et al*., 1992) is given by:

$$BMF = \frac{k_f}{k_d + k_m + k_g} \tag{15}$$

This simple model, Eq. (13), considers the organisms as a single compartment. Kooijman and van Haren (1990) and van Haren et al. (1994) proposed based on the Dynamic Energy Budget (DEB) approach a more complete model that takes into account changes in lipid contents and size of the animal. Their approach is represented in Fig. 5. In this approach the chemicals, once taken up by the organism partition instantaneously over four compartments (Kooijman and van Haren, 1990): one aqueous fraction and three non-aqueous fractions: the structural component of the body, the stored energy reserves and the energy reserves set apart for reproduction. In addition, they assumed that uptake and elimination are assumed to be proportional to the surface area, $V^{2/3}$, of the organism.

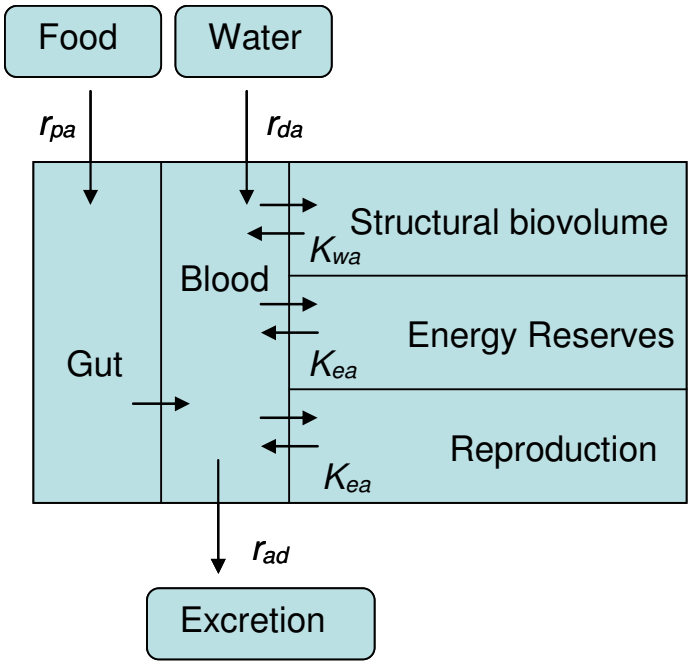

Figure 5. Schematic representation of the chemical partitioning in the body compartments of an individual organism.

The total number of moles of a compound in the organism can be divided as the sum of them in the different compartments:

$$n_{tot} = n_{aq} + n_V + n_E + n_R = (V_{aq} \cdot C_{aq} + V_V \cdot C_V + V_E \cdot C_E + V_R \cdot C_R) \cdot 10^{-3} \quad (16)$$

where the V_i's refer to the compartment volumes (cm^3) and the C_i's refer to the compartments concentrations (mol l^{-1}). Also, the total number of moles of a chemical can be expressed as: $n_{tot} = W \cdot C_b \cdot 10^{-6} / MW$, where W is the organisms weight (g), C_b is the contaminant concentration in aquatic organism (mg kg^{-1}) and MW is the molecular weight of the chemical (g mol^{-1})[2].

The chemical is assumed to be in equilibrium between the different compartments with fixed values partition coefficients: $K_{wa}=C_V/C_{aq}$; $K_{ea}=C_E/C_{aq}$ and $K_{ea}=C_R/C_{aq}$.

The time evolution of this amount can be calculated by a simple mass balance, assuming that uptake (via water and food) and depuration are proportional to the surface are of the organism, and only the aqueous compartment communicates directly with the environment (Kooijman, 2000), as:

$$\frac{dn_{tot}}{dt} = V^{2/3}\left(r_{da} \cdot C_w + r_{pa} \cdot f \cdot C_p \cdot 10^{-6} / MW - r_{ad} \cdot C_{aq}\right) \quad (17)$$

where the r_i's indicate the transport rates between the compartments (see Fig. 5), r_{da} and r_{ad} are the uptake and depuration rates (l cm^{-2} d^{-1}), r_{pa} is the intake via food consumption (g cm^{-2} d^{-1}), C_w and C_{aq} refer to the concentration in the dissolved fraction in the water column (mol l^{-1}) and in the aqueous compartment of the organism (mol l^{-1}), respectively, and f is given by Eq. (6). C_p refers to the concentration in the prey (mg kg^{-1})[1]. However, it is more convenient to express the mass balance as a function of the organism's concentration, C_b (mg kg^{-1}). Therefore, applying the chain rule of derivation we have:

$$\frac{dn_{tot}}{dt} = \frac{10^{-6}}{MW}\left(W\frac{dC_b}{dt} + C_b\frac{dW}{dt}\right) \quad (18)$$

and rearranging terms we obtain:

$$\frac{dC_b}{dt} = \frac{MW \cdot 10^6 \cdot V^{2/3}}{W}\left(r_{da} \cdot C_w + r_{pa} \cdot f \cdot C_p \cdot 10^{-6} / MW - r_{ad} \cdot C_{aq}\right) - \frac{C_b}{W}\frac{dW}{dt} \quad (19)$$

In this case, the last term represents the dilution due to growth of the organism. This is a more realistic assumption that the linear-constant function assumed by Thomman (1989), see Eq. (13). Since the concentration in the aqueous fraction, C_{aq}, is not a value that is measured, then we have to convert it in terms of C_b using the partitioning approach.

The wet weight, W, can also be expressed as a function of the volumes of the different compartments times the density (1 g cm^{-3}):

$$W = d\left(V_{aq} + V_V + V_E + V_R\right) \quad (20)$$

According to Kooijman and Van Haren (1990) the following relationships can be written:

$$V_V = \alpha_V \cdot V \quad (21)$$

[2] 10^{-6} is a conversion factor

$$V_E = \alpha_e \cdot e \cdot V \tag{22}$$

$$V_R = \alpha_e \cdot r \cdot V \tag{23}$$

$$V_{aq} = (1-\alpha_V)\cdot V + \alpha_e (1-e)\cdot V \tag{24}$$

where α_V and α_e are the non-aqueous fraction of the body size and the maximum volume of energy reserves as a fraction of body size, respectively; e is the energy reserves density (e = [E]/[E_m]) and r is the fraction of energy reserves allocated for reproduction. For mussels Van Haren et al. (1994) found α_e =0.95.

Replacing Eqs. (21)-(24) into Eq. (20), we obtain:

$$W = d\left[1+\alpha_e(1+r)\right]V \tag{25}$$

In addition, if we replace Eqs. (21)-(25) and the partition coefficients into Eq. (16) we have:

$$n_{tot} = C_{aq}\cdot V\cdot\alpha_e\left[\alpha_e^{-1}+1+\frac{\alpha_V}{\alpha_e}\left(K_{wa}-1\right)+\left(K_{ea}-1\right)\cdot e+K_{ea}\cdot r\right]\cdot 10^{-3} \tag{26}$$

Following Kooijman and Van Haren (1990) we will define:

$$\gamma = \alpha_e^{-1}+1+\frac{\alpha_V}{\alpha_e}\left(K_{wa}-1\right) \tag{27}$$

which is a constant value and it was estimated for mussels by Van Haren et al. (1994) considering PAHs and PCBs compounds as γ =10, and h as

$$h = \gamma + \left(K_{ea}-1\right)\cdot e + K_{ea}\cdot r \tag{28}$$

Therefore, we obtain

$$n_{tot} = C_{aq}\cdot V\cdot\alpha_e\cdot h\cdot 10^{-3} \tag{29}$$

and hence,

$$C_{aq} = \frac{W\cdot 10^{-3}}{MW\cdot V\cdot\alpha_e\cdot h}C_b \tag{30}$$

replacing this term in Eq. (19) and rearranging, we obtain a similar equation to the one proposed by Thomann (1989) and Thomann *et al.* (1992), i.e. Eq. (13):

$$\frac{dC_b}{dt} = \left(\frac{MW\cdot V^{2/3}\cdot 10^6}{W}r_{da}\right)C_w + \left(\frac{f\cdot V^{2/3}}{W}r_{pa}\right)C_p - \left(\frac{10^3}{V^{1/3}\cdot\alpha_e\cdot h}r_{da}\right)C_b - \left(\frac{1}{W}\frac{dW}{dt}\right)C_b \tag{31}$$

However in this case uptake and depuration rates are not constant but depend on the status of the organisms, the food availability, the evolution of its lipid content and its growth.

The variation of the wet weight, W, as a function of the state variables: E, V and R of the DEB model can be obtained applying the chain rule of derivation to Eq. (25). In this case, we obtain:

$$\frac{dW}{dt} = d\left[1+\alpha_e(1+r)\right]\frac{dV}{dt} + d\cdot V\cdot\alpha_e\frac{dr}{dt} \tag{32}$$

Since $r = R/([E_m]\cdot V)$ we have:

$$\frac{dr}{dt} = \frac{1}{[E_m]\cdot V}\frac{dR}{dt} - \frac{R}{[E_m]\cdot V^2}\frac{dV}{dt} \tag{33}$$

Replacing Eq. (33) in Eq. (32) and rearranging the terms we have:

$$\frac{dW}{dt} = d\left(1+\alpha_e\right)\frac{dV}{dt} + d\,\frac{\alpha_e}{[E_m]}\frac{dR}{dt} \tag{34}$$

Introducing Eq. (34) into Eq. (31), we finally obtain the evolution of the internal contaminant concentration in mussels:

$$\frac{dC_b}{dt} = \left(\frac{MW\cdot V^{2/3}\cdot 10^6}{W} r_{da}\right)C_w + \left(\frac{f\cdot V^{2/3}}{W} r_{pa}\right)C_p - \left(\frac{10^3}{V^{1/3}\cdot\alpha_e\cdot h} r_{ad}\right)C_b - \frac{d}{W}\left(\left(1+\alpha_e\right)\frac{dV}{dt} + \frac{\alpha_e}{[E_m]}\frac{dR}{dt}\right)C_b \tag{35}$$

This model has five parameters that need to be evaluated: the uptake rates for water and food, r_{da} and r_{pa}, the elimination rate, r_{ad}, and the partition coefficients, K_{wa} - in h, see Eqs.(27) and (28)- and K_{ea}.

2.3.3. The estimation of the bioaccumulation model parameters

To use Eq. (35) and the DEB growth model, Eqs. (4), (9)-(10), as a general tool for assessing bioaccumulation potential in mussels for new chemicals, we have to develop some general correlations that will allow us, based on the physico-chemical properties of the compound, to estimate these five parameters (r_{da}, r_{pa}, r_{ad}, K_{wa}, K_{ea}). For this reason, we have used experimental data on several Persistent Organic Pollutants (POPs) and tried to assess, as a first approach, if available correlations were able to produce adequate results.

Van Haren et al. (1994) developed a linear correlation between log K_{ow} and log K_{ea} for several PAHs and PCBs compounds as:

$$\log K_{ea} = 0.48\cdot\log K_{ow} + 1.72 \tag{36}$$

K_{wa} is only needed in the calculation of γ, Eq. (27), which was already estimated by Van Haren et al. (1994) for mussels and using data from PAHs and PCBs. Even though γ will depend on the species and the chemical compound, following Van Haren et al. (1994), we will assume that it is constant, γ=10.

Uptake ($m^3 \cdot kg^{-1} \cdot d^{-1}$) and depuration ($d^{-1}$) constants can be parameterized as function of bioconcentration factors of the chemical, permeability (P, m h^{-1}) of the cell membrane and specific surface area (S_p, m^2 kg^{-1}) (Del Vento and Dachs, 2002):

$$k_d = \frac{S_p\cdot P}{BCF}$$
$$k_u = S_p\cdot P \tag{37}$$

Furthermore, it has been demonstrated (Swackhamer and Skoglund, 1993; Stange and Swackhamer, 1994) that, for many organic compounds, the logarithm of the bioconcentration factor plotted against

the logarithm of the octanol/water partition coefficient gives two linear correlations (with a plateau in correspondence to log $K_{ow} \approx 6.5$. The same considerations can be made for the estimation of permeability of cell membrane and similar regressions have been proposed (Del Vento and Dachs, 2002). Geyer et al (1982) obtained the following correlation between *BCF* and K_{ow} (between 1.5 and 7) for mussels (*Mytilus edulis*):

$$\log BCF = 0.90 \cdot \log K_{ow} - 1.06 \quad (38)$$

A similar approach has been proposed by Booij et al (2006) where they developed two correlations for calculating the uptake constant (via water and food, k_{uf}) and the depuration plus metabolization plus growth constant (k_{dmg})as a linear function of K_{ow} values. They found that the uptake constant for *Mytilus edulis* could be modeled by a linear correlation like:

$$\log k_{uf} = -0.149 \cdot \log K_{ow} - 0.58 \quad (39)$$

whereas the bioaccumulation factor, $BAF = k_{uf}/k_{dmg}$, could be correlated with

$$\log BAF = 0.840 \cdot \log K_{ow} - 0.49(\pm 0.41) \quad (40)$$

Following these considerations, we have tried to estimate the values of r_{da} and r_{ad} as a function of the octanol/water partition coefficient. With this approach we would have a more general bioaccumulation model that, once validated, could be used for other families of chemical compounds.

Several values concerning the intake via food consumption, r_{pa}, has been presented by Van Haren et al. (1994) and Casas and Bacher (2006). Even though the values are for metals, this value probably does not depend on the chemical but only on the species; for this reason, we have adopted the mean value reported, $r_{pa} = 1.28 \pm 0.3 \cdot 10^{-3}$ g cm^{-2} d^{-1}.

2.3.4. Forcing of the DEB-bioaccumulation model using 3D simulation runs

To provide spatio-temporal data of the forcing parameters on the DEB and the bioaccumulation model, we have used a similar approach as in Carafa et al. (2009). A hydrodynamic 3D model of Etang de Thau has been developed and implemented (Marinov et al., 2008c) using COHERENS (Luyten et al., 1999). Coupled with COHERENS, a biogeochemical and a fate model have been introduced. All these three modules produce the forcing parameters that are being used in the DEB-bioaccumulation model as depicted in Fig. 6.

The values of [*Chla*] produced by the biogeochemical module and the temperatures obtained by the simulation with COHERENS for two of the three sampling stations in Zones A and C (see, Fig. 1), where mussels samples are periodically collected by Ifremer for assessing the level of contamination in shellfish, see figs. 2-3 are represented in Fig. 7. There is a good agreement between observations and numerical results for temperature, R^2=0.95, with results inside ±15% error zone or into ±2.5 °C deviation range (Marinov et al. 2008c). Furthermore, the biogeochemical model is able to simulate the average value of [*Chla*] in the lagoon over the last years.

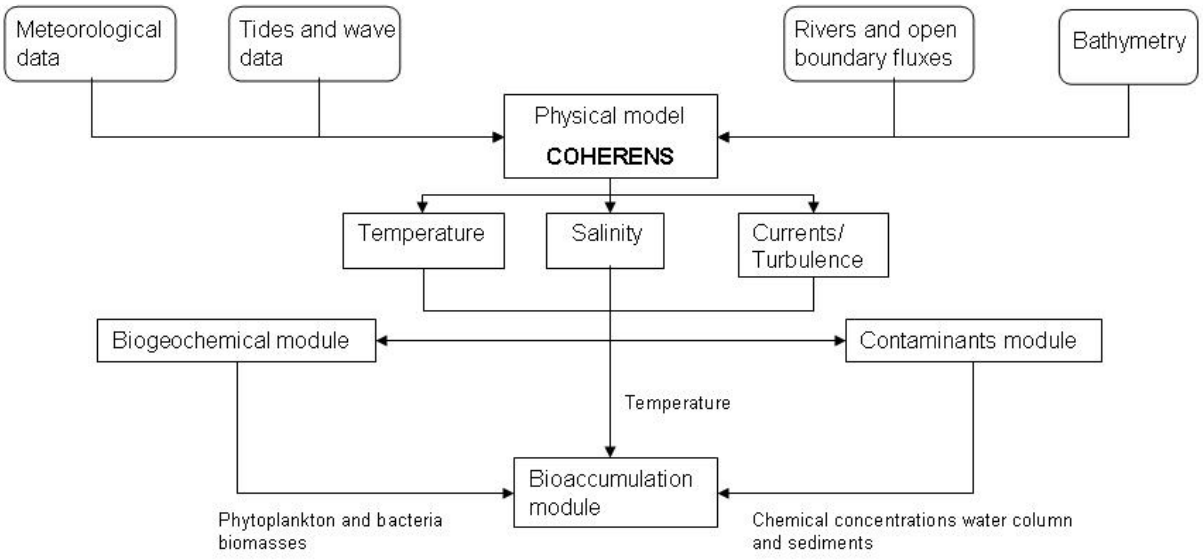

Figure 6. Integrated modelling approach using COHERENS.

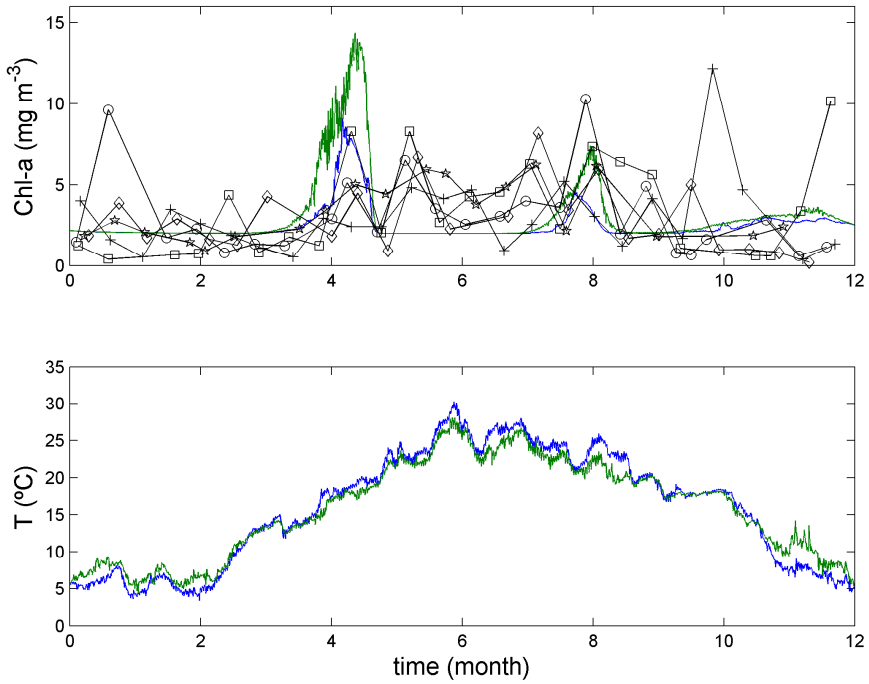

Figure 7. Simulated [Chla] (mg m^{-3}) and Temperature (ºC) (continuous line; green: Station in Zone A blue: Station in Zone C) used as forcing function for the mussels' model. Exprimental data from REPHY (Ifremer) Central Station from 1998 to 2002 (1998 –plus sign-, 1999 –square-, 2000 -circle-, 2001 –diamond-, 2002 –pentagram-).

[*Chla*] and temperature are parameters necessary to force the DEB model to simulate the growth of mussels. Concerning the bioaccumulation model, Fig. 8 represents, as an example, the concentrations of PCB153 in the water column (only the dissolved, phase) and in the phytoplankton compartment in the stations in Zones A and C, whereas in Fig. 9 the values for OCDD are presented. These values

provide the concentration in the water column, C_w, and the concentration in the food, C_p, necessary to force with realistic values the bioaccumulation module. The comparison between experimental and simulated results shows (Marinov et al., 2008c) that the model is able to produce reasonably good results for PCBs and PCDD/Fs. However, it is necessary to point out the model was forced during all the year, with constant air and river concentration values obtained during one experimental campaign in November 2005 (Castro-Jiménez et al., 2008) as well as validated with the water data obtained during the same campaign; therefore, there is not enough data to assess in detail model performances.

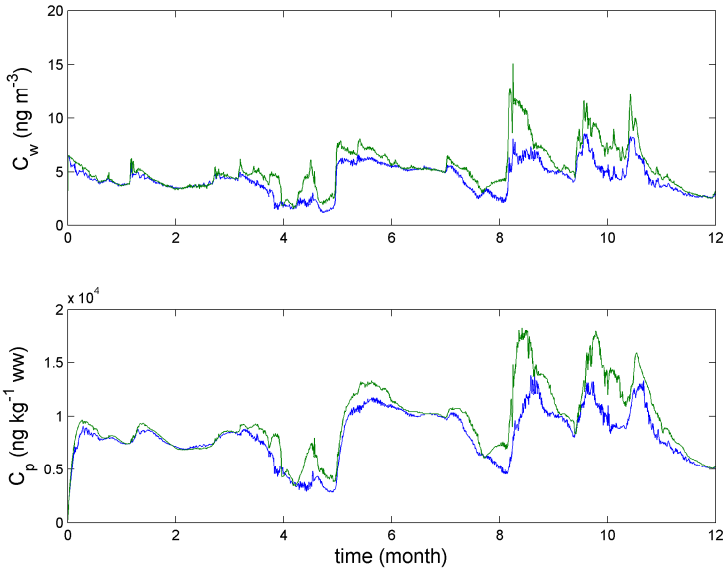

Figure 8. Simulated dissolved phase concentrations for PCB153 in the water column (top) and in phytoplankton (bottom) during one year (green line: Station in Zone A, blue line: Station in Zone C) used as forcing function for the bioaccumulation model.

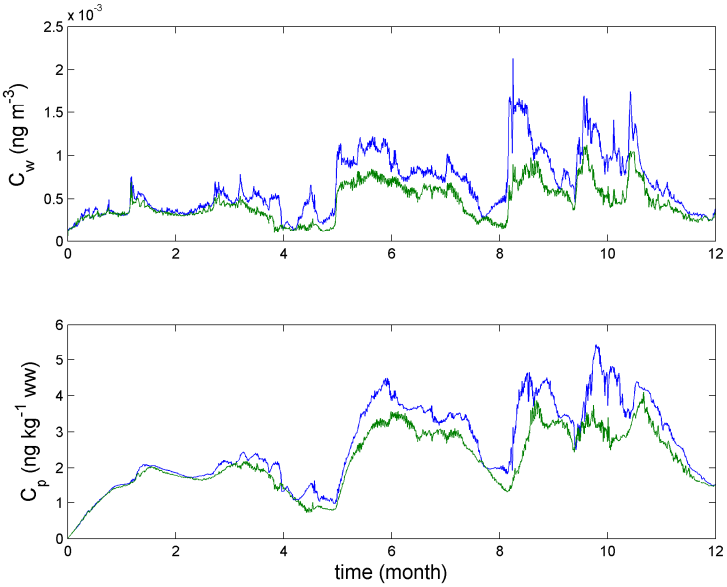

Figure 9. Simulated dissolved phase concentrations for OCDD in the water column (top) and in phytoplankton (bottom) during one year (green line: Station in Zone A, blue line: Station in Zone C) used as forcing function for the bioaccumulation model.

3. RESULTS AND DISCUSSION

3.1. DEB GROWTH MODEL

A long term simulation, ten years, with constant food, 5 μg l^{-1} [*Chla*], and sinusoidal temperature dependence: $T(°C) = 12.3 + 9.76 \cdot \sin\left(2 \cdot \pi \frac{t(d) - 114.74}{365}\right)$, is depicted in Fig. 10. For this example, reproduction has been fixed once every year at the beginning of November according with data from Casas and Bacher (2006) for Thau lagoon. The reproduction period is observed by a sharp drop in the R (Energy for development and reproduction) and by a decrease in the fresh tissue biomass (*W*). The model stabilizes around a shell length of 10 cm which is in agreement with the maximum observed values (between 10-15 cm) for *Mytilus* (Tebble, 1976). This value depends on several environmental parameters, i.e. temperature, and on the food availability, for example, by doubling the amount of [*Chla*], *L* moves to 12.4 cm.

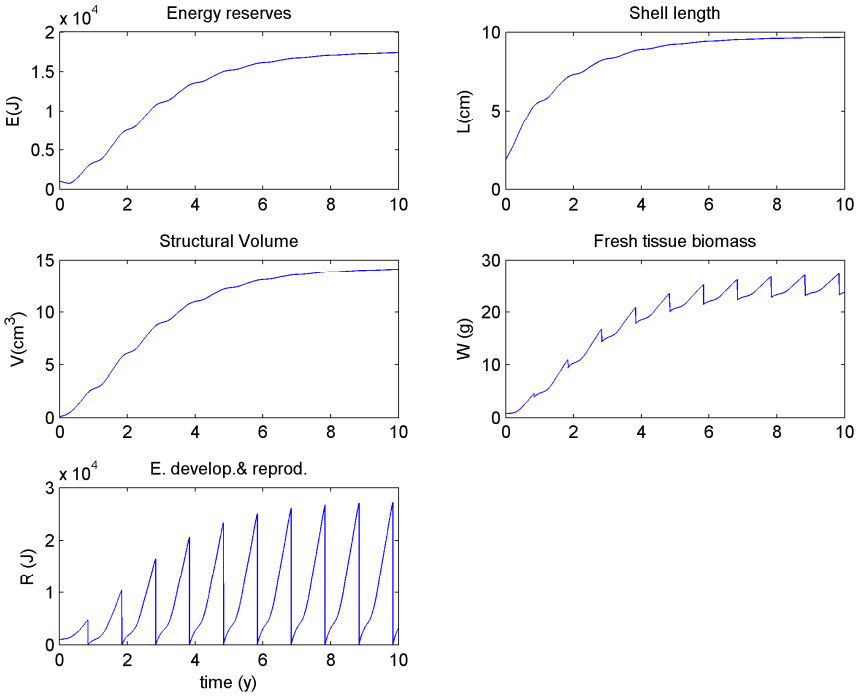

Figure 10.Temporal evolution of the three state variables (E, V and R), the shell length (L) and the fresh tissue biomass (W) during a ten years period.

A more realistic ten year simulation with temperature and [*Chla*] provided by the 3D model of Thau lagoon (Marinov et al., 2008c), see Fig.7, is depicted in Figs. 11-12 for two of the three sampling stations in Zones A and C (see, Fig. 1), where mussels samples are periodically collected by Ifremer for assessing the level of contamination in shellfish, see figs. 2-3. As it can be observed in Figs. 10 and 11, there are several differences on the evolution of mussels in both stations, which are due to the

slightly different forcing that both places experience. Considering only long time trends, energy reserves (E), structural volume (V) and energy for development and reproduction (R) are higher in the station in Zone A and, consequently, shell length and fresh tissue biomass are also higher in this station. This is mainly due to the differences in [*Chla*] concentrations but also small temperature differences may have influence over long term simulation times. However, one has to take into account that we have maintained the same forcing every year and, therefore, we have increased these differences.

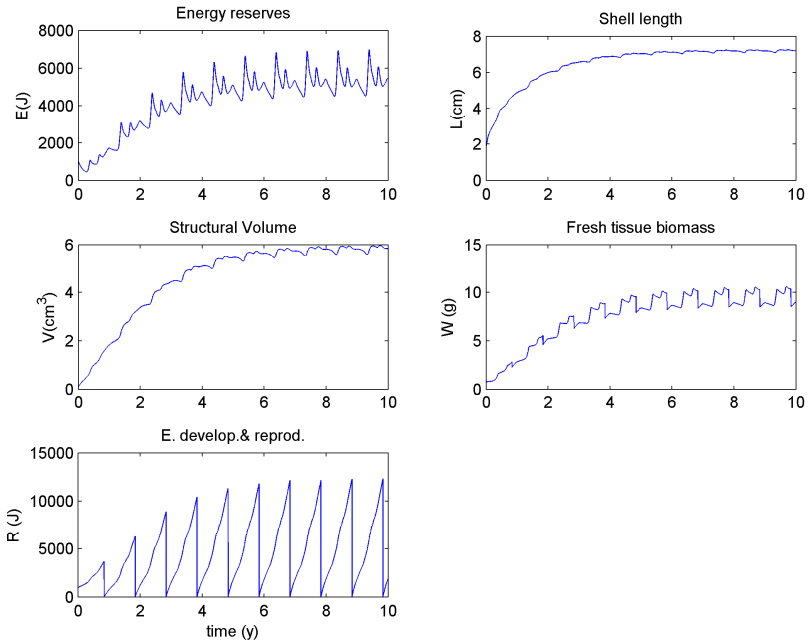

Figure 11. Ten years temporal evolution in Zone A using every year the same forcing from Fig. 7.

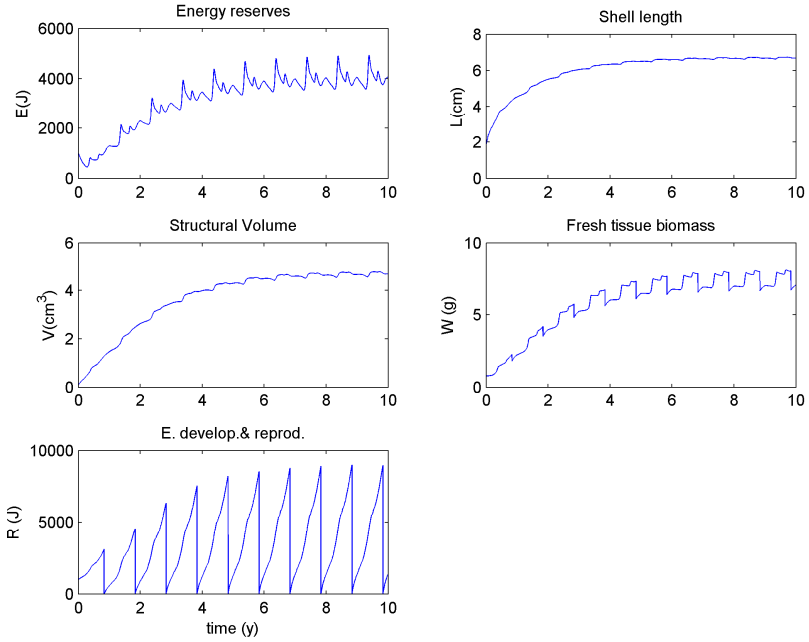

Figure 12. Ten years temporal evolution in Zone C using every year the same forcing from Fig. 7.

3.2. BIOACCUMULATION MODEL

A similar approach as the one followed for the DEB model has been also applied for the bioaccumulation model. As a first step, we have assumed, as before, constant food concentration and a sinusoidal temperature forcing. In addition, we have also considered constant concentration of contaminant in the dissolved phase, C_w= $1.47 \cdot 10^{-14}$ mol l-1 (or 5.3 ng m^{-3}) and in the phytoplankton, C_p= $0.942 \cdot 10^{-2}$ mg kg^{-1}., see Fig. 8. In addition, we have used for r_{da} and r_{ad} the values provided in Van Haren et al (1994) for PCBs:13395.0 (cm d^{-1}) and 2713.0 (cm d^{-1}), respectively. The results of the simulation are depicted in Fig. 13. As it can be seen, there is a sharp decrease in the concentration after each reproduction period where the reserves are set to zero and there is also a transient period during the first year, before the contaminant concentration in the mussels follows a periodic behaviour.

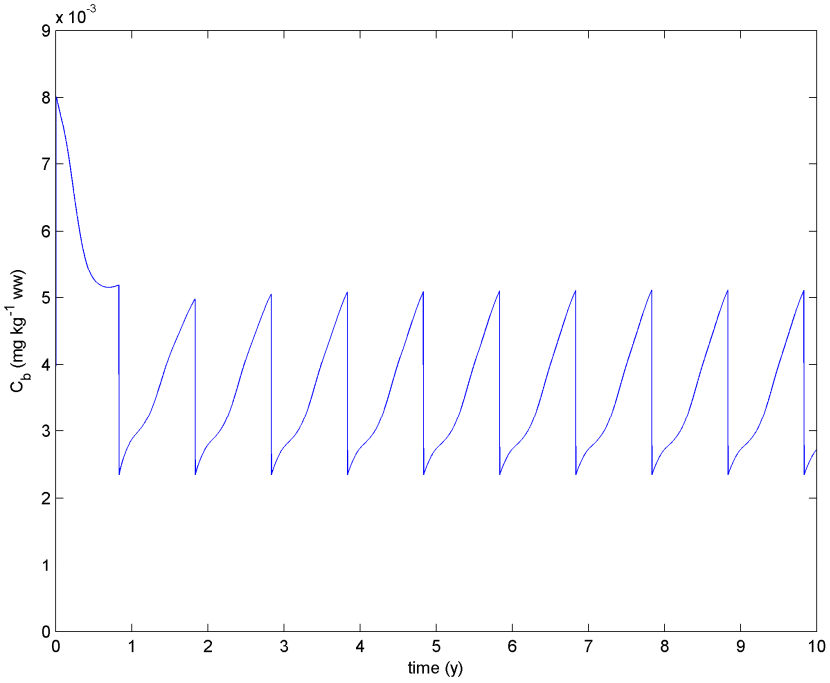

Figure 13. Temporal evolution of the concentration of PCB153 in mussels (mg kg^{-1}dw) during a ten years period.

A more realistic ten year simulation with temperature, [*Chla*], PCB153 water dissolved concentration and PCB153 phytoplankton concentrations provided by the 3D model of Thau lagoon (Marinov et al., 2008c), see Fig.7-8, is depicted in Fig. 14 for two sampling stations in Zones A and C (see, Fig. 1), respectively. As it can be observed in this figure, there are several differences on the evolution of the concentration of PCB153 on mussels in both stations, with Zone A (average ± sd; 0.00385±0.00216 mg kg^{-1} ww) showing higher concentrations than in Zone C (0.00304±0.00156 mg kg^{-1} ww). This is mainly due to the differences in PCB153 concentrations in the water column and in phytoplankton, which, according to the 3D model, are higher in this Zone.

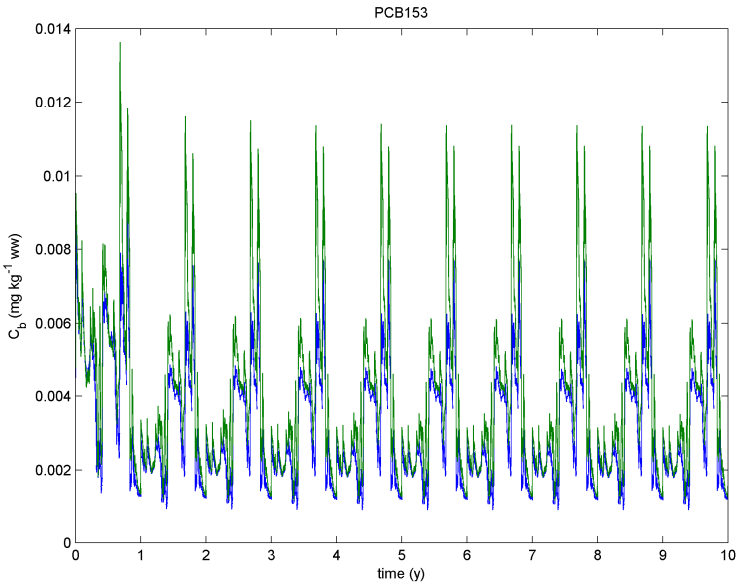

Figure 14. Temporal evolution of the concentration of PCB153 in mussels (mg kg^{-1}dw) in Zone A (green) and C (blue) stations during a ten years period. Temperature, [*Chla*], dissolved concentration and phytoplankton concentration forcing from Figs. 7 and 8.

A similar ten year simulation with temperature, [*Chla*], OCDD water dissolved concentration and OCDD phytoplankton concentrations provided by the 3D model of Thau lagoon (Marinov et al., 2008c), see Fig.7-9, is depicted in Fig. 15 for two sampling stations in Zones A and C, respectively. In this case we have used the same values of r_{da} and r_{ad} than for PCB153. From Fig. 15, it can be observed that OCDD mussel concentrations in Zone C ($9.693 \cdot 10^{-7} \pm 6.935 \cdot 10^{-7}$ mg kg^{-1} ww) are slightly higher than in Zone A ($6.930 \cdot 10^{-7} \pm 4.6533 \cdot 10^{-7}$ mg kg^{-1} ww).

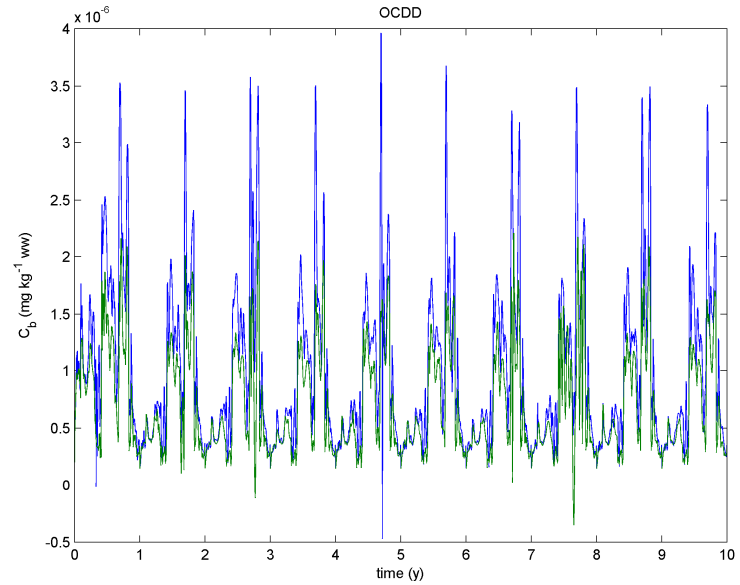

Figure 15. Temporal evolution of the concentration of OCDD in mussels (pg g^{-1}dw) in Zone A and C stations during a ten years period. Temperature, [*Chla*], dissolved concentration and phytoplankton concentration forcing from Figs. 7 and 9.

3.3. COMPARISON WITH EXPERIMENTAL DATA

Experimental data, concerning mussel concentrations on PCDD/Fs and PCBs have recently been summarized for Thau lagoon in Castro-Jiménez et al. (2008) and in Munschy et al. (2008). In this work, we have tried to simulate the experimental conditions to reproduce their results. Even though the 3D model provides with the forcing values, there are some uncertainties on the initial conditions of the state variables of the model, i.e. E, V, R and C_b. According to Munschy et al. (2008) all mussels spent at least six months on site before collection and each composite sample contained at least 50 mussels of homogeneous size: 45-55 shell length. To avoid transients due to errors in the initial conditions, since the data from Castro-Jiménez et al. (2008) for mussels, summarized in Table 4, refer to the month of May; we have run the model for one year and then until May of the second year. By doing that, the simulated shell lengths also correspond to the defined values in Munschy et al. (2008), i.e. 50.5 mm at Zone A and 54 mm at Zone C.

Since our objective was to develop a general approach, we have tried to adjust r_{ad} and r_{da} for each compound we have data on Table 4 for the two Zones simultaneously. We have used an unconstrained optimization algorithm from Matlab®. The objective function was to minimize the distance between experimental and simulated results for both Zones for each compound. Table 5 summarizes the results concerning r_{ad} and r_{da} as well as the experimental and simulated results on the accumulation in mussels. To convert from wet weight to dry weight we have used the conversion factor 0.096 (shell free)sfdw:ww from Palmerini and Bianchi (1994). Missing columns are due to the absence of forcing data to run the 3D fate model.

Table 4. Measured and simulated mussels concentrations (pg g^{-1} dw). Experimental data from Castro-Jiménez et al. (2008) and Munschy et al. (2008).

Compounds	Measured concentrations (pg g^{-1} dw)		Simulated concentrations (pg g^{-1} dw)	
	Zone A	Zone C	Zone A	Zone C
PCB28	173	118	113	146
PCB52	254	92	193	154
PCB101	3543	955	2247	2237
PCB118	3327	802	1273	2073
PCB153	18670	5242	16400	9400
PCB138	12229	2305	4579	7137
PCB180	503	322	260	451
TCDD	-	-	-	-
PeCDD	-	0.24	0.08	0.19
HxCDD	0.4	1.16	-	-
HpCDD	1.6	2.91	-	-
OCDD	6.4	10.44	6.14	11.28
TCDF	4.0	2.7	2.52	3.30
PeCDF	0.9	1.0	0.72	0.97
HxCDF	0.3	0.6	0.29	0.60
HpCDF	0.4	1.3	-	-
OCDF	0.4	1.2	-	-

The correlation coefficient between experimental concentrations and simulated values, see Table 4, is r^2=0.75 with p<0.05.

Table 5. Estimated r_{da} and r_{ad} (cm d^{-1}) mussels concentrations (pg g^{-1} dw). Experimental data from Castro-Jiménez et al. (2008) and Munschy et al. (2008).

Compounds	Estimated values concentrations (cm d^{-1})	
	r_{da}	r_{ad}
PCB28	3969	4426
PCB52	496.2	5116
PCB101	1376	4967
PCB118	6430	4111
PCB153	16381	2183
PCB138	13392	2848
PCB180	2611	4579
TCDD	-	-
PeCDD	2932	4951
HxCDD	-	-
HpCDD	-	-
OCDD	10465	4341
TCDF	13722	2746
PeCDF	4567	4385
HxCDF	1603	4946
HpCDF	-	-
OCDF	-	-

To provide a general tool to evaluate bioaccumulation potential for a chemical compound, we need to find a general correlation between uptake and depuration rates that depend on the physico-chemical properties of the compound. For this reason, we have estimated those values minimizing the error between experimental and simulated values. The relationships between r_{da} and r_{ad} and the log K_{ow} are depicted in Fig. 16. Unfortunately, there is no significant linear correlation between r_{da} and r_{ad} and the log K_{ow}. There are several possible explanations to the absence of correlation between them: the 3D simulations refer to 2005 whereas mussel concentrations refer to 2004 (Marinov et al., 2008c). There was only one experimental measurement carried in November 2005 to assess the model results. Clearly, this value is not enough to validate the PCBs and PCDD/Fs fate model and therefore the forcing of the mussels model. However, the fact that it is possible to predict concentrations in the mussels from those of the water, clearly indicates that this is a promising route for developing bioaccumulation assessment tools.

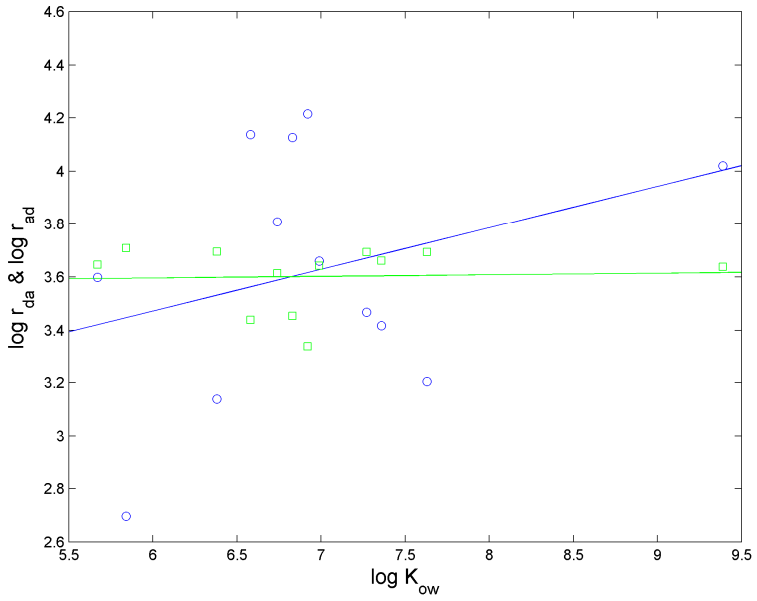

Figure 16. log r_{da} and log r_{ad} (cm d^{-1}) as a function of log K_{ow} for the PCBs and PCDD/Fs considered congeners.

4. CONCLUSIONS

A bioaccumulation model to predict, based on the concentration of contaminants in the water column, the concentration in mussels (*Mytillus galloprovinciales*) has been implemented, and calibrated using experimental data from Thau lagoon (France). The model uses input data from a 3D biogeochemical model that provides biomasses in the different compartments, i.e. phytoplankton, zooplankton and bacteria (Marinov et al., 2009; Dueri et al., 2009); and from a 3D fate model that provides the concentrations in the water column as well as in the sediments (Carafa et al., 2006; Jurado et al., 2007; Marinov et al., 2009). The bioaccumulation model is based on the Dynamic Energy Budget approach (DEB). The model predicts correctly the concentrations of several POPs families: PCBs and PCDD/Fs. However, it is not able to provide a clear correlation between physico-chemical properties and uptake and depuration rates. This is probably due to the experimental data used which are not sufficient for this approach.

This is the first step for developing a general screening tool able to predict the bioaccumulation of new chemicals in mussels based on its physico-chemical properties that will contribute to B (bioaccumulative) and vB assessments. In addition, the model could be use by MS to convert measured concentrations in mussels to water concentrations for the WFD (Water Framework Directive) compliance checking.

5. REFERENCES

Amanieu M., Legendre P., Trousselier P., Frisoni G. F., 1989. Le programme ecoThau: théorie, écologie et base de modélisation. Oceanologica acta 12, 189-199.

Arnot J.A. and Gobas F.A.P.C. 2006. A review of bioconcentration factor (BCF) and bioaccumulation factor (BAF) assessments for organic chemicals in aquatic organisms. Environ. Rev. 14, 257–297.

Bacelar, F. S., Dueri, S., Hernández-García, E. and Zaldívar, J.M. 2008. Joint effects of nutrients and contaminants on the dynamics of a food chain in marine ecosystems. Mathematical Biosciences (accepted).

Bacher C., Millet B. Vaquer A., 1997. Modélisation de l'impact des mollusques cultivés sur la biomasse phytoplanctonique de l'étang de Thau (France). C. R. Acad. Sci. Ser. 3 sci. Vie/life ssc. 320, 73-81.

Booij, K., Smedes, F., Van Weerlee, E.M. and Honkoop, P.J.C. 2006. Environmental monitoring of hydrophobic organic contaminants: The case of mussels versus semipermeable membrane devices. Environ. Sci. Technol. 40, 3893-3900.

Boese B. 1984. Uptake efficiency of the gills of English sole (Parophrys vetulus) for four phthalate esters. Can. J. Fish. Aquat. Sci. 41,1713-1718.

Carafa, R., Marinov, D., Dueri, S., Wollgast, J., Ligthart, J., Canuti, E., Viaroli, P. and Zaldívar, J. M., 2006. A 3D hydrodynamic fate and transport model for herbicides in Sacca di Goro coastal lagoon (Northern Adriatic). Marine Pollution Bulletin 52, 1231-1248.

Carafa, R., Marinov, D., Dueri, S., Wollgast, J., Giordani, G., Viaroli, P. and Zaldívar, J.M. 2009. A bioaccumulation model for herbicides in *Ulva rigida* and *Tapes philippinarum* in Sacca di Goro lagoon (Northern Adriatic). Chemosphere (accepted).

Casas, S. and Bacher, C. 2006. Modelling trace metals (Hg and Pb) bioaccumulation in the Mediterranean mussel, Mytilus galloprovincialis, applied to environmental monitoring. Journal of Sea Research 56, 168-181.

Castro-Jiménez, J., Deviller, G. , Ghiani, M., Loos, R., Mariani, G., Skejo, H., Umlauf, G. , Wollgast, J., Laugier, T., Héas-Moisan, K. , Léauté, F., Munschy, C., Tixier, C. and Tronczyński J. 2008. PCDD/F and PCB multi-media ambient concentrations, congener patterns and occurrence in a Mediterranean coastal lagoon (Etang de Thau, France). Environmental Pollution 156, 123-135.

Chapelle A., 1995. A preliminary model of nutrient cycling in sediments of a mediterranean lagoon. Ecological Modelling 80, 131-147.

Chapelle A., Lazure P., Souchu P., 2001. Modélisation des crises anoxiques (malaïgues) dans la lagune de Thau (France). Oceanologica acta 24, 87-97.

Chapelle A., Menesguen A., Deslous-Paoli J. M., Souchu P., Mazouni N., Vaquer A., Millet B., 2000. Modelling nitrogen, primary production and oxygen in a mediterranean lagoon. Impact of oysters farming and inputs from the watershed. Ecological modelling 127, 161-181.

Del Vento, S. and Dachs, J., 2002. Prediction of uptake dynamics of persistent organic pollutants by bacteria and phytoplankton. Environmental Toxicology and Chemistry 21, 2099-2107.

Dueri, S., Hjorth, M., Marinov, D., Dallhof, I. and Zaldívar, J.M., 2009a. Modelling the combined effects of nutrients and pyrene on the plankton population: Validation using mesocosm experimental data and scenario analysis. Ecol. Model. (accepted).

Dueri, S., Marinov, D., Fiandrino, A. Tronczyński, J. and Zaldivar, J.M. 2009b.Implementation of a 3D coupled hydrodynamic and contaminant fate model for the PCDD/Fs in Thau lagoon (France): the importance of air as a source of contamination. (in preparation)

European Commission, 1979. Council Directive of 30 October 1979 on the quality required of shellfish waters (79/923/EEC).

European Commission, 1989. Council Directive of 11 December 1989 concerning veterinary checks in intra-Community trade with a view to the completion of the internal market (89/662/EEC).

European Commission, 1991. Council Directive of 15 July 1991 laying down the health conditions for the production and the placing on the market of live bivalve mollusks (91/492/EEC).

European Commission, 2000. Directive 2000/60/EC of the European Parliament and of the council of 23 October 2000 establishing a framework for Community action in the field of water policy, Off. J. Eur. Commun. L327, 22.12.2000

European Commission, 2006. Commission Regulation (EC) No. 199/2006 of 3 February 2006 amending Regulation (EC) No. 466/2001 setting maximum levels for certain contaminants in foodstuffs as regards dioxins and dioxin-like PCBs. Official Journal of the European Communities L32, 34-38.

European Commission, 2006. Proposal for a Directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directive 2000/60/EC. COM(2006) 398 final. Pp77. 17/7/2006.

Fisk, A.T., Norstrom, R.J., Cymbalisty, C.D. and Muir, D.C.G., 1998. Dietary accumulation and depuration of hydrophobic organochlorines: bioaccumulation parameters and their relationship with the octanol/water partition coefficient. Environ. Toxicol. Chem. 17, 951-961.

Gangery, A., Bacher, C. and Buestel, D. 2004a. Application of a population dynamics model to the Mediterranean mussel, Mytilus galloprovincialis, reared in Thau Lagoon (France). Aquaculture 229, 289-313.

Gangery, A., Bacher, C. and Buestel, D. 2004b. Modelling oyster population dynamics in a Mediterranean coastal lagoon (Thau, France): sensitivity of marketable production to environmental conditions. Aquaculture 230, 323-347.

Geyer, H., Sheehan, D., Kotziasm, D., Freitag, D. and Korte, F. 1982. Prediction of ecotoxicological behaviour of chemicals: relationship between physico-chemical properties and bioaccumulation of organic chemicals in the mussel *Mytilus edulis*. Chemosphere 11, 1121-1134.

Goldberg E.D. 1986. The mussel watch concept. Environmental Monitoring Assessment 7, 91-103.

HELCOM Part D. Programme for monitoring of contaminants and their effects (http://www.helcom.fi/groups/monas/CombineManual/PartD/en_GB/main/).

Jurado, E., Zaldívar, J.M., Marinov, D. and Dachs, J. 2007. Fate of persistent organic pollutants in the water column: Does turbulent mixing matter? Marine Pollution Bulletin 54, 441-451.

Kimbrough K.L., Johnson W.E., Lauenstein GG., Christensen J. D. and Apeti D.A. 2008. As assessment of two decades of contaminant monitoring in the nation's coastal zone. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 74, 105 pp.

Kooijman, S.A.L.M. 2000. Dynamic Energy and Mass Budgets in Biological Systems. 2nd Ed. Cambridge University Press, Cambridge, UK.

Kooijman, S.A.L.M. and van Haren R.J.F. 1990. Animal energy budgets affect the kinetics of xenobiotics. Chemosphere 21, 681-693.

Lazure P., 1992. Etude de la dynamique de l'étang de Thau par modèle numérique tridimensionnel. Vie milieu 42, 137-145.

Luyten, P.J., J.E. Jones, R. Proctor, A. Tabor, P. Tett and K. Wild-Allen, 1999. COHERENS – A coupled Hydrodynamical-Ecological Model for Regional and Shelf Seas: User Documentation. MUMM Report, Management Unit of the Mathematical Models of the North Sea, 911 pp.

Marinov D., Zaldívar J.M., Norro A., Giordani G. and Viaroli P. 2008b. Integrated modelling in coastal lagoons: Sacca di Goro case study. Hydrobiologia 611, 147-165.

Marinov, D. Dueri, S., Puillat, I., Carafa, R., Jurado, E., Berrojalbiz, N. Dachs, J. and Zaldívar, J.M., 2008a. Integrated modeling of Polycyclic Aromatic Hydrocarbons (PAHs) in the marine ecosystem: Coupling of hydrodynamic, fate and transport, bioaccumulation and planktonic food web models. J. of Marine Systems (submitted).

Marinov, D., Dueri, S., Zaldivar, J.M., Fiandrino, A. and Tronczyński, J. (2008c). Thau lagoon case study: Model and Scenario Analysis. Deliverable 4.2.6 Thresholds of Environmental Sustainability Integrated Project, pp. 63.

Moriarty F. and Walker C.H. 1987. Bioaccumulation in Food Chains-A Rational Approach. Ecotoxicology and Environmental Safety 13:208-215.

Munschy C., Guiot, N., Héas-Moisan, K., Tixier, C., Tronczyński J. 2008. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in marine mussels from French coasts: Levels, patterns and temporal trends from 1981 to 2005. Chemosphere 73, 945-953.

OSPAR Commission. 1999. JAMP Guidelines for Monitoring Contaminants in Biota. 49 pp.

Palmerini, P. and Bianchi, C.N., 1994. Biomass measurements and weight-to-weight conversion factors: a comparison of methods applied to the mussel *Mytilus galloprovincialis*. Marine Biology 120, 273-277.

Pavan M., Netzeva T.I. and Worth A. 2008. Review of literature-based Quantitative Structure-Activity Relationship models for bioconcentration. QSAR Comb. Sci. 27, 21-31.

Pereira W.E., Domagalski J.L., Hostettler F.D., Brown L.R. and Rapp J.B. 1996. Occurrence and accumulation of pesticides and organic contaminants in river sediment, water and clam tissues from the San Joaquin River and tributaries, California. Environmental Toxicology and Chemistry15, 172-180.

Picot B., Péna G. Casellas C. Bondon D. Bontoux J., 1990. Interpretation of the seasonal variations of nutrients in a mediterranean: étang de Thau. Hydrobiologia 207, 105-114.

Plus, M., Chapelle, A., Lazure, P., Auby, I., Levavasseur, G., Verlaque, M., Belsher, T., Deslous-Paoli, J.M., Zaldívar, J.M. and Murray, C.N. 2003a. Modelling of oxygen and nitrogen cycling as a function of macrophyte community in the Thau lagoon. Continental Shelf Research 23, 1877-1898.

Plus, M., Chapelle, A., Ménesguen, A., Deslous-Paoli, J.-M., Auby, I., 2003b. Modelling seasonal dynamics of biomasses and nitrogen contents in a seagrass meadow (*Zostera noltii* Hornem.): application to the Thau lagoon (French Mediterranean coast). Ecological Modelling 161, 149-252.

Plus, M., La Jeunesse, I., Bouraoui, F., Zaldívar, J. M., Chapelle, A., and Lazure, P., 2006. Modelling water discharges and nutrient inputs into a Mediterranean lagoon. Impact on the primary production. Ecological Modelling 193, 69-89.

Pouvreau, S., Bourles, Y., Lefebvre, S., Gangnery, A., Alunno-Bruscia, M. 2006. Application of a dynamic energy budget model to the Pacific oyster *Crassostrea gigas*, reared under various environmental conditions. Journal of Sea Research 56, 156-167.

Roose P., and Brinkman U. A. Th. 2005. Monitoring organic microcontaminants in the marine environment: principles, programmes and progress. Trends in Analytical Chemistry 24, 897-926.

Sijm D.T.H.M., Seinen W., Opperhuizen A., 1992. Life-cycle biomagnification study in fish. Environ. Sci. Technol. 26, 2162-2174.

Stange, K. and Swackhamer, D. L. 1994. Factors affecting phytoplankton species-specific differences in accumulation of 40 polychlorinated biphenyls (PCBs). Environ. Toxicol. Chem. 11, 1849-1860.

Swackhamer, D.L. and R.S. Skoglund. 1993. Bioaccumulation of PCBs by phytoplankton: kinetics vs. equilibrium. Environ Toxicol Chem 12, 831-838.

Tebble, N. 1976. British bivalve seashells, Alden Press Osney Mead, Oxford

Thomann R.V., 1989. Bioaccumulation model of organic chemical distribution in aquatic food chains. Environ. Sci.Technol. 23, 699–707.

Thomann, R.V., Conolly, J.P., Parkerton, T.F., 1992. An equilibrium model of organic chemical accumulation in aquatic food webs with sediment interaction. Environ. Toxicol. Chem. 11, 615-629.

Tronczyński, J. 2006. Dynamics of persistent organic contaminants in the Thau lagoon (Mediterranean): present-day and historical records. Thresholds of environmental sustainability. General Scientific Meeting, CSIC, Madrid 14-15 February 2006

Van der Oost R., Beyer J. and Vermeulen N. P.E. 2003. Fish bioaccumulation and biomarkers in environmental risk assessment: a review. Environmental Toxicology and Pharmacology 13, 57-149.

Van der Veer, H. W., Cardoso, J. F.M.F., van der Meer, J. 2006. The estimation of DEB parameters for various Northeast Atlantic bivalve species. Journal of Sea Research 56, 107-124.

Van Haren, R.J.F., Schepers, H.E. and Kooijman, S.A.L.M. 1994. Dynamic Energy Budgets affect kinetics of xenobiotics in the marine mussel *Mytilus edulis*. Chemosphere 29, 163-189.

Vigano L., Galassi S. and Arillo A. 1994. Bioconcentration of polychlorinated biphenyls (PCBs) in rainbow trout caged in the river Po. Ecotoxicol. Environ. Safe. 28, 287-297.

European Commission

EUR 23626 EN – Joint Research Centre – Institute for Health and Consumer Protection
Title: A general DEB bioaccumulation model for mussels
Author(s): José-Manuel Zaldívar
Luxembourg: Office for Official Publications of the European Communities
2008 – 35 pp. – 21 x 29,7 cm
EUR – Scientific and Technical Research series – ISSN 1018-5593
ISBN 978-92-79-10943-0
DOI 10.2788/36003

Abstract

A bioaccumulation model to predict, based on the concentration of contaminants in the water column, the concentration in mussels (*Mytillus galloprovinciales*) has been implemented and calibrated using experimental data from Thau lagoon (France). The model uses input data from a 3D biogeochemical model that provides biomasses in the different compartments, i.e. phytoplankton, zooplankton and bacteria; and from a 3D fate model that provides the concentrations in the water column as well as in the sediments. The bioaccumulation model is based on the Dynamic Energy Budget approach (DEB). The model predicts correctly the concentrations of several POPs families: PCDD/Fs and PCBs. This is the first step for developing a general screening tool able to predict the bioaccumulation of new chemicals in mussels based on its physico-chemical properties that will contribute to the B(bioaccumulative) and vB assessment. In addition, the model could be use by MS to convert measured concentrations in mussels to water concentrations for WFD (Water Framework Directive) compliance checking.

How to obtain EU publications

Our priced publications are available from EU Bookshop (http://bookshop.europa.eu), where you can place an order with the sales agent of your choice.

The Publications Office has a worldwide network of sales agents. You can obtain their contact details by sending a fax to (352) 29 29-42758.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

LB-NA-23626- EN- C