Direction de l'Environnement et de l'aménagement du Littoral
Ecologie Côtière
DEL / EC

Anne Christine Le Gall
Véronique Loizeau
Alain Abarnou
Bert van Hattum (IVM, Amsterdam)
Louis-Alexandre Romaña

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Rapport Final du projet GEMCO
Generic **E**stuary **M**odelling system to evaluate
Transport, fate and impact of **CO**ntaminants

The food web model

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Auteurs principaux :	**Organisme / Direction / Service, laboratoire**
Anne Christine Le Gall Véronique Loizeau Alain Abarnou	DEL / Ecologie Côtière / Brest
Bert van Hattum	Institut d'Etudes Environnementales, Université Libre d'Amsterdam
Louis-Alexandre Romaña	DEL / Polluants Chimiques / Toulon

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Organisme commanditaire : nom développé, sigle, adresse
European chemical industry council (CEFIC), Avenue E. Van Nieuwenhuyse 6
1160 Bruxelles

Organisme(s) réalisateur(s) : nom(s) développé(s), sigle(s), adresse(s)
IFREMER/ Direction de l'Environnement et de l'aménagement du Littoral
Centre de Brest, BP 70, 29280 Plouzané

Responsable scientifique : Louis-Alexandre Romaña, DEL / Polluants Chimiques / Toulon

Projet GEMCO

Ifremer

Résumé

Ce rapport présente l'étude du transport trophique des contaminants réalisée dans le cadre du Projet GEMCO. Ce projet, financé par l'industrie chimique européenne (CEFIC) dans le cadre du programme LRI (Long range Research Initiative) a impliqué des chercheurs du DELFT Hydraulics, de l'Université d'Amsterdam et d'IFREMER (DEL/PC Toulon et DEL/EC Brest) pour développer un modèle de distribution des contaminants dans les différents compartiments (eau, matières en suspension, sédiment et organismes vivants) et cela dans tout estuaire européen. Après un premier chapitre d'introduction, le deuxième chapitre fait le point des différents aspects de la biologie dans les estuaires en Europe et débouche sur la définition de deux réseaux trophiques simplifiés, celui du poisson rond et celui du poisson plat, représentatifs de chaînes trophiques caractéristiques d'écosystèmes estuariens en Europe. Les contaminants organiques hydrophobes entrent dans le «vivant» par l'intermédiaire du phytoplancton. Le troisième chapitre établit les équations qui expliquent la distribution en estuaire de la production primaire, représentée par la chlorophylle. Les niveaux de concentrations dans le matériel en suspension sont forcés à partir de concentrations dans l'eau calculées par le modèle abiotique. Le quatrième chapitre constitue le cœur du rapport présente le modèle de bioaccumulation basé sur la connaissance des processus biologiques, nutrition, respiration, excretion, croissance, agissant sur la bioaccumulation. Il est suivi par une approche systématique des équations des processus. Le modèle générique proposé est une extension de travaux réalisés par notre équipe, sur la limande en Baie de Seine et sur le bar en estuaire de Seine. Une attention particulière est apportée à la biotransformation ;ce processus ,très différent selon les substances, conduit dans certains cas à une bioaccumulation trophique (PCB et composés persistants) et dans d'autres cas à une biotransformation partielle plus ou moins rapide (HAP et composés partiellement dégradables). Finalement le modèle générique basé sur des résultats antérieurs sur les PCB dans les réseaux trophiques du bar et de la limande, a été validé par des résultats obtenus dans les organismes de l'Escaut et l'Ebre ainsi que pour des substances moins fréquemment étudiées. L'étude de sensibilité des différents paramètres sur les résultats du modèle démontre l'importance des variables forçantes (K_{ow}, chlorophylle a, température de l'eau, concentration en contaminants dans la phase dissoute), et l'importance de fixer ces paramètres au plus près possible de la réalité pour améliorer la prédiction.

Ce travail sert de base à la réalisation du modèle GEMCO, outil en cours de validation, qui permette de suivre la distribution de composés hydrophobes compte tenu des propriétés de la substance et des quantités rejetées en estuaire d'une part et des caractéristiques géomorphologiques et hydrodynamiques de l'estuaire d'autre part

Mots clés : estuaire, contaminants organiques, réseau trophique, bioaccumulation, biotransformation

Abstract:

This report presents the study on the trophic transport of contaminants which has been carried out within the GEMCO project (Generic Estuary Modelling system to evaluate transport, fate and impact of Contaminants). This research project, funded by the Chemical Industry in Europe (CEFIC) within its LRI (Long range Research Initiative) to which took part several scientists from the Delft Hydraulics, from the University of Amsterdam and from IFREMER (Brest and Toulon). The aim of the project was to develop an easy to use model that allows to simulate the distribution of chemical substances in the various compartments (water, suspended particulate matter, sediment, biota) within any estuary in Europe. After a first chapter that presents briefly the objective of the study, the second chapter deals with the main characteristics of the biology in estuaries and ends with a definition of two simple and typical trophic webs, schematically one for round fish and the other for flatfish food chain, which are representative of estuarine trophic webs. In the aquatic environment hydrophobic organic contaminants enter the living compartment via the phytoplankton. The third chapter gives the equations that determine the primary production in estuaries and its distribution with space and time. The contamination in the suspended particulate matter are forced using calculated concentration using the abiotic model. The four chapter appears as the core of the study and gives the basics of the model which depends on biological processes like feeding, respiration, excretion, growth; then the equations describing these processes are given systematically. The proposed generic model is an extension of works carried out by our group on the dab and on the sea bass in the Baie de Seine and in the Seine estuary. A special care is given to biotransformation because it acts differently on the fate of chemicals in foodwebs; according to the nature of the substances, it leads to either bioaccumulation like in the case of PCBs and other persistent compounds or to biotransformation in the case of partially metabolizable substances like PAHs. Last, the generic model based on previous results obtained so far in the seabass and the dab foodwebs in the Seine estuary, has been validated by data from the Ebro and Scheldt estuaries, using PCB measurements or a few other less studied contaminants. The sensitivity analysis has shown the importance of forcing variables (K_{ow}, chlorophyll a, water temperature, dissolved concentration of contaminant) on the results of the model and the need to adjust those parameters very close to real conditions in order to improve the accuracy of the simulations.

This work is the base of the GEMCO model, a simple and « easy to use tool », still being validated, that will be able to simulate and forecast the distribution of hydrophobic substances, taking into account the properties of the substances, the amount released and also the geomorphological and hydrodynamical characteristics of the estuary.

Keywords : estuary, organic contaminants food web, bioaccumulation, biotransformation

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION: AIMS AND SCOPE

Estuaries are the inevitable link between river fresh water and marine waters. All organic and inorganic matter transported by river transits there before reaching the sea. During this transit, this material is diluted by sea water, and the sudden change in ionic strength of the water occasions a change in chemical properties of most substances, whether they are simple elements or complex mixtures of elaborated organic molecules. This chemical change can be enhanced by physical mixing caused by the strength of the river flow, by wind and more importantly along the North West European coast, by tides. These cause the water level to fluctuate daily with amplitude that itself oscillates with a fortnightly period. The fluctuation of the water level implies that some expanses of land are alternatively covered and uncovered with water. The currents that are present in estuaries follow complicated patterns and erode or let particles sediment. To these conditions, a number of living organisms have adapted. They cope well with the changing conditions of the estuaries, and complex assemblage of plants and animals can be observed, varying along the salinity gradients or with the nature of the estuary bottom. The effects of pollutants on these assemblages, or biocenoses, have still to be fully understood.

The present work has been commissioned by the Long range Research Initiative funded by CEFIC (European Chemical Industry Council). The aim is to obtain a modelling tool to assess transport of chemicals through and within a European estuary. This task has been divided in two parts:

- ⇨ Transport through the abiotic compartment (water, suspended particles and sediment) and phytoplankton, which was carried out by WL Delft Hydraulic in The Netherlands in cooperation with IFREMER ;

- ⇨ Transport through the biological compartment, which was carried out by IFREMER, France. This is the first report related to this part of the study.

The final objective is to build and validate an easy-to-use "virtual estuary" computer model called GEMCO (Generic estuary modelling system to evaluate transport, fate and impact of contaminants). Figure I-1 shows the structure of the research programme: the user input data relative to the contaminant and to the estuary of interest. Calculations are performed according to codes developed and validated by the various teams involved in the project. Finally, GEMCO's output will consist in "predicted environmental concentrations" (PEC) in the abiotic and the biotic compartments of an estuary. Fluxes from estuaries to open waters will also be evaluated.

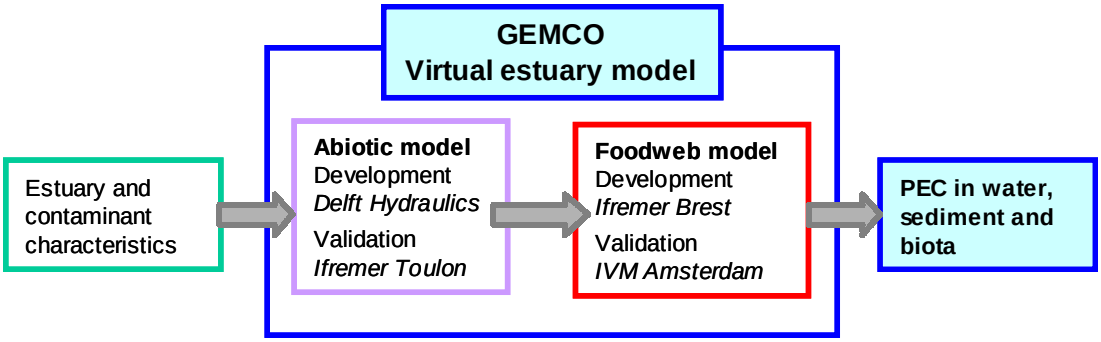

Figure I-1: Schematic structure of the GEMCO project showing its different modules and the organisations responsible for each.

Before modelling the behaviour of compounds in a food web, it is important to understand how the environment may modify this behaviour and to understand the functioning of the food web.

The processes discussed in this report do not exclusively occur in estuaries. Some are relevant whatever the ecosystem considered, some are more specific to aquatic or to marine environments. All are necessary to understand the estuarine environment. A synthesis of relevant information is presented in this report in five parts:

1. *The estuarine environment: the biology's point of view:* The physico-chemical environment of the estuary is presented first, emphasising the most important processes affecting life. The area considered in this study covers the North West of Europe, from the Mediterranean to the Norwegian fjords and to the Baltic. However, fjords and river mouths in the Mediterranean and in the Baltic are very different environments from macrotidal estuaries found along the North East Atlantic coast elsewhere in Europe. The specificities of each and their common points are discussed.

2. *The biology in European estuaries:* A presentation of estuarine life follows. This focuses on the different habitats that are available in the estuaries and how they influence trophic links (who eats who) between organisms.

3. *Pollution and contaminants:* Then the behaviour of some contaminants in biota is described. Emphasis has been put on polychlorobyphenyls (PCBs) because they are some of the most persistent man made compounds and can be used as a model compound and compared to less persistent compounds. Amongst those, polyaromatic hydrocarbons (PAHs) are often quoted in this report because numerous studies have established their ubiquity in the environment and their toxicity for living organisms. PCBs and PAHs may not be of immediate concern for the chemical industry but they are good test compounds for the modelling exercise for two main reasons: first, there are many studies that give their concentrations in the environment and in organisms. Second, contrarily to the generally persistent PCBs, PAHs are generally biotransformed by organisms. The two classes of compounds stand therefore as examples for two different behaviours of contaminants in biota. The knowledge gained from their study will be useful to develop approaches that might be valid for other types of chemicals.

4. *The biological response to contaminants:* The last point to understand before modelling is possible is when persistence occurs or when a compound is transformed

in organisms. The different approaches used to evaluate bioaccumulation are discussed.

5. *Simplified food chains:* Finally, typical European estuarine food webs are presented.

Once defined the main biological features in the estuary, it becomes important to explain how it works, and within the frame of this project it becomes of great importance to identify the key processes acting on the transport, the distribution and the fate of contaminants in the estuarine food chains.

The role of the primary production is discussed firstly as contaminants exchange occurs at the very first levels of the trophic web between the dissolved phase and the phytoplankton cells. The primary production follows by chlorophyll a measurement and the representation of chlorophyll a, its distribution and variation in estuaries are presented; the suspended material appears a key parameter to explain the primary production as an increasing turbidity reduces the available light and thus reduces the phytoplankton biomass.

The core of this work on the generic trophic deals with the trophic transport of contaminants and is presented in the fourth chapter of this report. The work relies on previous studies on the dab from the Baie de Seine and on the seabass from the Seine estuary. From this starting point, two generic food webs are considered leading to two complementary approaches, the round fish and the flat fish model. Both models rely upon the same basic bioaccumulation equation and the similar processes which are closely related to the biological functions: respiration, feeding, metabolisation or biotransformation, excretion, growth, reproduction. The mathematical representations of these processes enable the construction of the bioaccumulation model which has been validated in the case of PCBs. For other compounds which are not so persistent biotransformation has to be taken into account; various possibilities are discussed: the measurement of metabolites of contaminants, the use of BCF and BAF which are often reported in the literature, and also, promising results from experimental study. Therefore it remains very difficult to use bioaccumulation model for non fully persistent compounds which are not bioaccumulated but which therefore are temporarily transported in estuarine food chain and might have deleterious effects on higher organisms. For the time being, bioaccumulation models simulate the worst situation as the predicted concentration are overestimated. In absence of more specific information on the biotransformation of the compounds this situation should be studied first, and as far as possible these such high predicted concentrations are to be compared to the known non-effect concentrations. An important aspect of the work has consisted in the validation of the model using field data from other estuaries or for other compounds. This part of the work was done at the Institute for Environmental Studies of the Free University of Amsterdam and has demonstrated that our model can run and produce results within an acceptable confidence. This validation steps have also confirmed the lack of information on compounds (excepting PCBs) in the estuarine biota and more generally in the estuarine ecosystems. Last, the sensitivity analyses were carried out by estimating the effects on the output data of the model of variation of the forcing variables, biological, chemical or environmental parameters acting separately or together.

II. BIOLOGICAL SYSTEMS IN EUROPEAN ESTUARIES

II-1 THE ESTUARINE ENVIRONMENT/ THE BIOLOGICAL POINT OF VIEW.

II-1-1. PARTICULARITIES COMPARED TO FULLY MARINE OR FRESHWATER ENVIRONMENTS

"An estuary is a semi enclosed coastal body of water which has a free connection with the open sea and within which seawater is measurably diluted with freshwater derived from land drainage" (Pritchard, 1967).

This is the most commonly quoted definition of an estuary. From a biological point of view, this implies that the estuary is the endpoint of both marine and freshwater habitats. The mention of dilution of freshwater by marine water indicates that a number of physico-chemical characteristics of the estuarine environment are variable within an estuary as well as between different estuaries due to geomorphology and variations of both river hydraulic regime and tide characteristics. This variability has a direct implication on the biology: organisms unable to tolerate a wide range of salinity, temperature, currents and particles concentrations cannot survive in estuaries, or have to develop very specific survival behaviours. As a result, there is a sharp decrease in the number of species found in estuaries compared to the number found in either marine or fresh waters (Figure II-1). However, estuaries receive a regular nutrient and particles input from the river and from the sea. This means that primary productivity is generally not limited, except by turbidity, and food is abundant. As a result, the species that are able to cope with the estuarine environment variations develop large populations: there might be up to 1 750 000 worms per square meter in soft substrata. Estuaries are also extensively used as nurseries for some marine and some freshwater species and are a compulsory passage between fresh and marine waters for species that migrate between the two. Estuaries are places where the biomass can be high, although the biodiversity is limited compared to the seas and the rivers (IECS, 2000). The influence of estuaries main characteristics on the biomass and the biodiversity is detailed below.

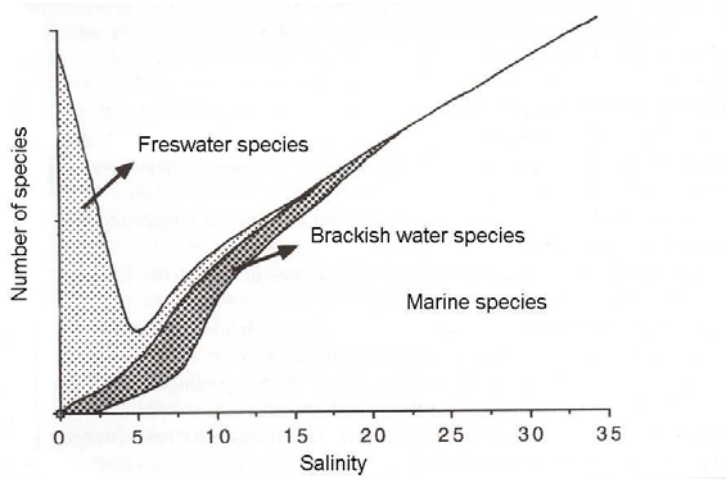

Figure II-1: The variation of number of species along a salinity gradient (from Remane and Schliefer, 1958).

II-1-1-1 Salinity

A strong gradient in salinity is one of the most characteristic features of an estuary. The salt content of the water is a limiting factor for many species due to changes in osmotic pressure: if the salt content of the water is lower than the salt content in an organism tissues, osmotic pressure forces salts out of the organism or forces water into cells. If the reverse is true, it is water that will be forced out of the body or salts might be taken in. In both cases physiological equilibrium can be modified, with potentially lethal consequences for the organism. As a result, many marine or freshwater species cannot survive in brackish water and only those who have physiological mechanisms to regulate ionic concentrations in their body fluids have been able to colonise estuaries (Bachelet et al., 1997).

The minimum in species number is found at salinity around 5, closer to the fresh water end of the estuary than to the marine water (Figure II-1). This suggests that fresh water species are more sensitive to the presence of salt than marine water species are to desalinised water.

The limits of distribution of different species and of species at different stages of development are variable, but it is sometimes convenient to define zones in estuaries based on the salinity S. Remane and Schliefer's (1958) definitions of four main areas are commonly used. They are:

- $0.5 < S < 5$ oligohaline;
- $5 < S < 18$ mesohaline;
- $18 < S < 30$ polyhaline;
- $S > 30$ euhaline.

In tidal estuaries the location of each of these zones moves relatively to the shore as marine water flood into or recedes away from the estuary. Furthermore, depending on the shape of the estuary bottom, on the river hydrology and on the tide amplitude, the water column can stratify, with heavy salty water moving up the estuary along the bottom underneath out flowing freshwater. If the estuary is large enough, the Coriolis effect forces an asymmetrical circulation and a salinity gradient occurs across the estuary width. The limits defined by Remane and Schliefer (1958) are obviously not static in time or in space, but can be useful to indicate in which range of salinity a given organism is likely to be found.

II-1-1-2 Temperature

In tidal estuaries, the temperature at a given geographical point fluctuates as a function of the tide and of the difference between the river and the sea waters. River water is generally warmer than seawater in summer and colder in winter. Moreover, as estuaries are generally shallow environments, their water temperature undergoes rapid changes following atmospheric conditions. In spring and early summer, this may cause the estuary waters to be warmer than coastal water and can favour organisms' growth and early spawning (McLusky, 1981).

The temperature in coastal waters is a parameter likely to control organisms' growth and most biological functions. It is also a parameter that influences the geographic distribution of species within Europe. There is some evidence that fish abundance is

positively correlated to temperature whereas diversity is related to salinity (Gerson Araujo *et al.*, 2000).

II-1-1-3 Suspended particulate matter (SPM)

Tidal estuaries receive suspended particulate matter (SPM) both from the river and from the sea. This material is transported through the estuary by water movements and undergoes a number of physico-chemical modifications. River borne material coagulates and flocculates as the ionic strength of the water changes when sea and river waters mix. The alternance of ebb and flood and the distortion of the tidal wave due to the estuary geomorphology results in transport of particles up the estuary bottom. This "tidal pump" transport stops where the energy of the tidal current becomes insufficient to keep particles in suspension. The particles can originate from resuspended bottom sediments, from the estuary banks, from the sea or may be settling particles brought in the estuary by the river. These processes are schematised on (Figure II-2) and contribute to the occurrence of the turbidity maximum observed in many European estuaries (Bachelet *et al.*, 1997; Le Hir *et al.*, 2001; McLusky, 1981; Tait, 1981). There, SPM concentrations of up to several thousands of mg/l can be observed. Migniot and Le Hir (1997) report concentrations of around 10 000 mg/l in the Loire. These particles are reactive and provide sites where hydrophobic chemicals adsorb easily. As a consequence, the concentrations of most compounds in an estuary are not simply controlled by the dilution of fresh water into seawater, but by processes resulting from the varying physicochemical properties of the water and of its particle load.

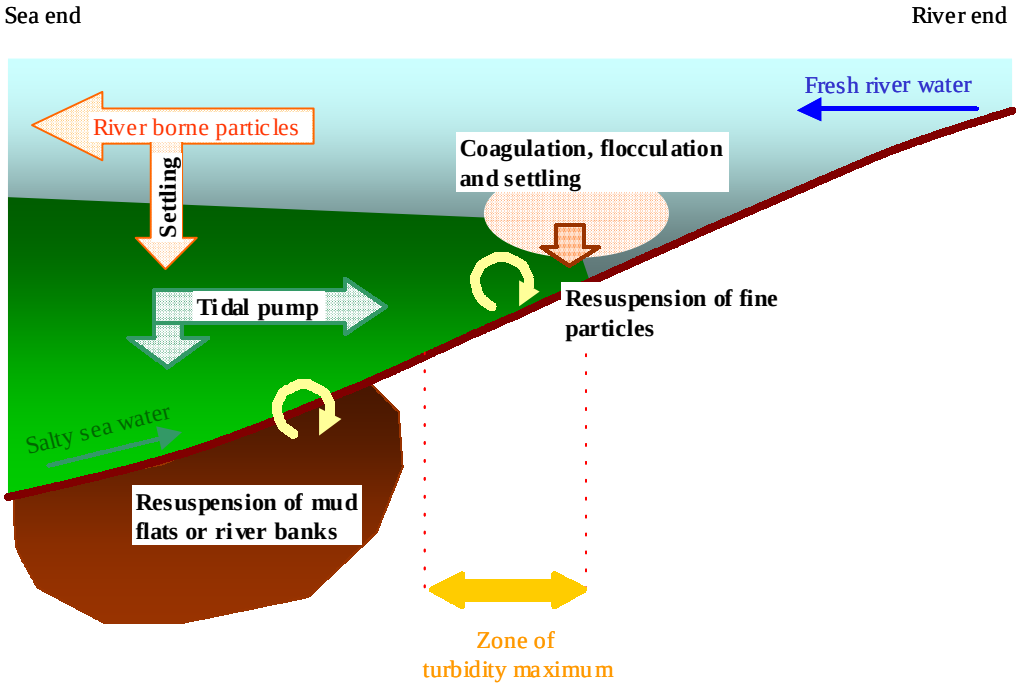

Figure II-2: Schematic representation of the various processes that lead to the formation of a turbidity maximum in a tidal estuary. The yellow round arrows represent the energy that causes the resuspension of sedimented material and that keeps fine marine material in suspension near the estuary bottom. The thick arrows represent the transport of particles. The approximate area where the turbidity maximum can be found in indicated.

In the turbidity maximum zone, light penetration and therefore photosynthesis are restricted to the water surface. Inorganic particles are substrates for bacterial growth and are

associated with a significant amount of organic carbon up to 10% of their weight in Dutch rivers, (van Leeuwen *et al.*, 1991) and are, together with phytoplankton, at the base of estuarine food chain providing energy to filter, suspension and deposit feeders. These animals are usually specific about the size, the quality and the quantity of the particles they ingest. Too fine or too coarse particles will be rejected and SPM concentrations similar to those encountered in a turbidity maximum can be deleterious to the functioning of fish gills or for filtering animals. For instance, at high (greater than 40 mg/l) SPM concentrations, mussels stop filtering, close their shell and stop feeding. On the other hand, some organisms can find refuge against predators in the turbidity maximum (IECS, 2000).

Particles are potential carriers for contaminants as hydrophobic compounds absorb on their surface preferentially to remaining in solution. Hence contaminants concentrations in SPM can be high compared to their concentration in water (truly dissolved). This partitioning between water and particles is of ecological importance since particles constitute the basic diet of a number of organisms that are thus contaminated with toxicants that risk accumulating in their tissues to harmful doses to themselves and to their predators.

II-1-1-4 Dissolved oxygen

At 20°C, seawater in equilibrium with atmosphere contains about 8 mg/l of dissolved oxygen. Concentrations above equilibrium values can be observed when the water temperature decreases rapidly or when primary productivity is intense. These are sursaturation conditions. Water becomes depleted in oxygen when consumption by micro-organisms becomes greater than inputs. This undersaturation may occur when organic load and temperature are high and when mixing of water is minimal and can be aggravated by stratification that limits further input of oxygen from the atmosphere. Such conditions are often observed in summer, after an algal bloom, in periods of calm and warm weather.

When large quantities of anthropogenic organic matter are released in estuarine waters through sewers or via the river, serious lack of oxygen may be observed as it has been demonstrated by the constant anoxia of the Thames that started in the 19th century and that was solved only after important water treatment work were achieved in the 1960s. Anoxic events caused by eutrophication have been reported in some Brittany estuaries (as for instance in 1982 in the Vilaine, Chapelle, 1991) and in the Loire estuary where they occur during neap tide at the end of the summer (Sauriau *et al.*, 1996). These generated spectacular fish mortality, and less spectacular but as important destruction of benthic populations. Partial oxygen depletion can also disturb biological equilibrium. It has been shown that some fish species would not enter waters where the oxygen concentrations were less than 4.5 mg/l at temperatures greater than 15°C (Pomfret *et al.*, 1982).

Oxygen concentrations rapidly fall near 0 in sediments. Benthic animals depend on the overlying water for their respiration, extending their gills above the sediment surface, or pumping water in their burrows. The figure II-3 illustrates the fauna distribution as a function of sediment organic enrichment. Excessive organic content in sediment generates a high bacterial activity that depletes the sediment from its oxygen and therefore creates anoxia.

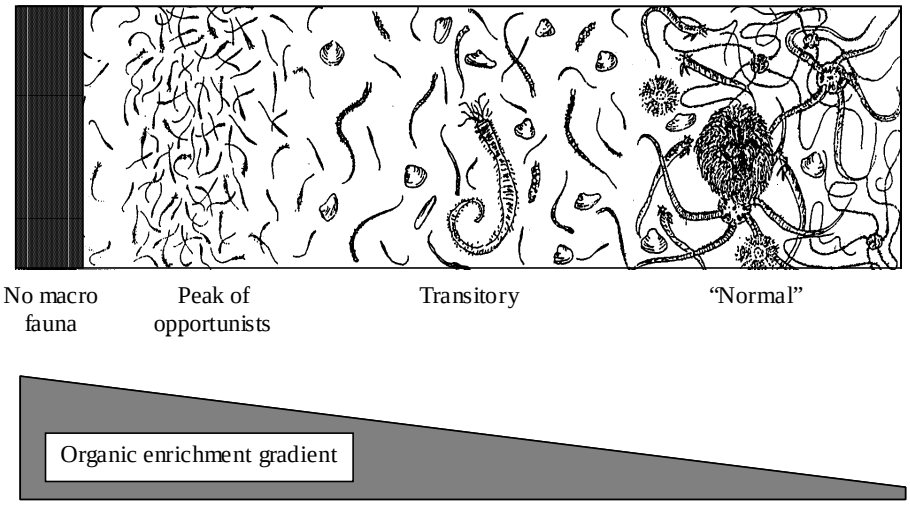

Figure II-3: Illustration of the changes in biodiversity with an increase in the sediment organic load and concomitant oxygen depletion (from Pearson and Rosenberg, 1978).

II-1-1-5 Tide and currents

In North West Europe, most estuaries experience semi-diurnal tides. This has several implications. First, some areas in the estuary are alternatively covered and uncovered by water. This leads to variations in temperature, salinity, and oxygen content and to possibilities of dehydration during emersion. Secondly, the residual currents in estuaries are seaward but at most locations in an estuary the tidal cycle leads to an alternation of upstream and downstream currents to which organisms have to adapt. These currents carry with them particles and therefore bring a constant food supply essential to suspension and filter feeders. On the other hand, in narrow and shallow parts of the estuaries, currents can be strong enough to pull fixed organisms away from their substrates, to erode soft sediments, destroying benthic habitats and flushing out to sea any non-attached and non-swimming organisms. Estuarine animals have used different strategies to cope with these water movements. Some organisms in their planktonic stage are able to take advantage of currents to move up the estuary during the flood tide always remaining within their preferred salinity range, taking refuge at the sediment interface during ebbing. Others have a marine larval phase and come back in the estuary as adults. Species such as the immigrant american crab *Rhithropanopeus harrisi* have developed an exclusively benthic larval stage whereas the planktonic larval stage of the worms *Nereis* and *Arenicola* has completely been suppressed to avoid the risk of being transported out of the estuary (McLusky, 1981).

The average intensity of the currents, either caused by the river flow or the tides, together with the wave action, generates a zonation of the substrates in estuaries. The seaward end and the higher shores tend to be rocky areas. The middle shore is covered by mud and muddy sands on its upper part while its lower part consists in coarse shifting sand banks. The bottom of the estuary is constantly submitted to tide or river flow and will often be gravely or exposed rocks. This schematic distribution of the substrates is represented on Figure II-4.

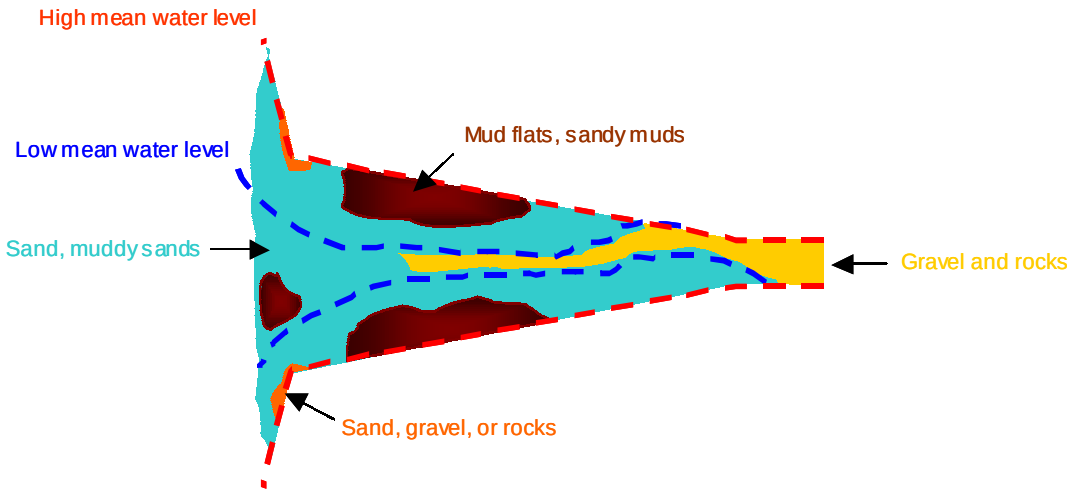

Figure II-4: Schematic zonation of substrates in a simplified estuary. The limits of the high and low waters are also indicated in dashed lines.

The nature of the substrates determines which species settle in an area. On exposed upper shore, only species tolerant to strong turbulence can attach themselves. Muddy tidal flats shelter a large number of burrowing species and are the most productive areas in an estuary. These differences will be detailed later.

II-1-2 FJORDS

Fjords are long narrow and deep valleys shaped by glacier erosion and flooded by the sea. The longest fjord in the world is the 204 km long and 1296 m deep Sognefjorden. Land limits are steep mountains or cliffs whereas underwater sills usually restrict exchanges of water with the sea. The Kvænangen fjord in Northern Norway has three sills, 3, 7 and 160 m deep separating three distinct basins 56, 108 and 200 m deep. Often, fresh water input is done via several streams. Fjord hydrology is such that behind the sills, stratification between fresher surface waters and saline deep water occurs. At the highest European latitudes, the water temperature reaches the freezing point in winter. Deep sediment tends to be sandy or silty. The main specificity of fjords compared to other European estuaries is the common occurrence of hypoxic or even anoxic conditions in bottom water behind the sills. This deep water is periodically renewed, usually during winter, by spills of seawater over the sills. These conditions are less variable than that found in other estuarine environments in Europe, but low oxygen conditions can regularly deplete benthic communities from their macrofauna. Events of complete anoxia may be triggered following eutrophication in surface water or are caused by large inputs of organic matter, such as those frequently resulting from fish farming activities.

II-1-3 THE BALTIC SEA

The Baltic Sea is one of the largest brackish areas in the world with no tides and with salinities ranging from 2 in the North to 10 in the South. A permanent halocline 60 – 80 m deep restricts vertical circulation. The water exchanges with the North Sea are limited by the

narrow and shallow straits in the Kattegat and occur mostly during occasional salt water inflow pulses generated by meteorological conditions. This leads to water residence time of about 25 to 30 years, and more importantly for biology, accumulation of pollutants in water and sediments and to low levels of oxygen at depths: about one third of the central part of the Baltic is devoid of life due to lack of oxygen (Kautsky and Kautsky, 2000).

The Baltic Sea is surrounded by densely populated and industrialised countries whose numerous rivers drain 1.7 million km^2 and are a constant source of nutriments. Although the first signs of a decrease in nutrients inputs have been observed in the last decade, eutrophication contributes to the occurrence of anoxic events in coastal waters (Nausch *et al*., 1999).

Overall, the whole Baltic can be considered as an estuary, somewhat a bit deeper (with a maximum depth at 459 m) and larger (420 000 km^2) than other North West European estuaries. Due to the absence of tide, the mixing between river fresh water and Baltic brackish water occurs in plumes outside river mouths. In these plumes, species are essentially freshwater ones and there is a general tendency for biomass to decrease with increasing distance to the river outlet until the limit of freshwater influence (Postel *et al*., 1995). This corresponds to the pattern described by figure II-1.

There does not seem to be any species endemic to the Baltic Sea. The organisms found there are similar to the ones found in other North European brackish waters. The two factors that mainly control their distribution are the salinity that restricts the distribution of marine and freshwater species and the low oxygen concentrations in deep or eutrophic zones. Sediment recolonisation after a period of anoxia depends on the improved oxygen conditions, is started by opportunistic species and, near the Kattegat, is enhanced by episodic larval input from the North Sea (Prena *et al.*, 1997).

II-1-4 THE MEDITERRANEAN SEA

Like the Baltic, the Mediterranean Sea has little or no tides, so large rivers form deltas and mixing between fresh and sea waters occurs essentially in plumes outside river mouths. These plumes can extend to a long distance at sea (the Rhone plume is more than 50 km long), are often shaped by wind and general hydrographic currents and therefore are highly variable in both time and space (Kourafalou, 1999). Plumes exhibit salinity gradients to which species have adapted in the water column as well as in the sediment below. Like in tidal estuaries, biodiversity decreased but biomass increases with decreasing salinity (Guelorget and Perthuisot, 1994).

Compared to the other areas considered in this report, the Mediterranean is characterised by high salinities and high temperatures. This clearly has an impact on distributions of species, a number of organisms living elsewhere along North Western European coasts being in their most southern range, while others are unknown east of Gibraltar strait.

Most freshwater discharged in the Mediterranean is brought in by rivers (Po, Rhône, Ebro and Nile account for 43% of inland water inflow) but coastal lagoons are economically important zones where fresh and seawater mix. They are highly productive zones where

fisheries and shellfish farming represent a large part of local economy. Because they are enclosed water bodies and often shallow, lagoons are very sensitive to meteorological conditions (particularly variations of heat and fresh water runoff), are zones of sedimentation of the particulate material they receive from rivers and are prone to eutrophication events, leading to anoxic conditions (Castel *et al.*, 1996). They need to be intensively managed so that water quality remains acceptable for aquaculture and other local industries such as tourism. Like other brackish water zones, they are colonised by freshwater and marine species and also support a range of resident species. The distribution of these species depends on the water quality (oxygen levels, salinity, turbidity), the habitats available and the communications with the sea that allow or prevent migration of marine species (Crivelli *et al.*, 1995).

II-1-5 TIME AND SPATIAL VARIABILITIES IN ESTUARIES

Estuaries are variable and varied environments, especially if their definition is widened compared to that generally accepted to include fjords, coastal lagoons and deltas. The time scales of the variability of some processes affecting estuary water quality and biological processes are represented on Figure II-5. Along the Atlantic coast, tides are present and some variations occur daily. The alternation of neap and spring tides adds a fortnightly variation. Along the Atlantic, Mediterranean and Baltic coasts, occurrence of floods and droughts modulates the river flow on a seasonal and on an inter annual basis. These variations cause some populations to be destroyed, because the salinity becomes too low for a too long period during a flooding event for instance, or because a cover of soft sediment is removed during a storm. A direct consequence is that habitats will be regularly lost and recolonised due to natural events. This might be seen as a strength of an estuarine ecosystem, as it can easily adapt to modifications. Yet it is equally its weakness as any added stress, such as anthropogenic pollution, may prevent recolonisation or accelerate habitat loss. Recolonisation will be easy for species with a short life span and rapid reproduction cycles but the destruction of a habitat might be fatal to a community with long life span and slow reproduction cycles.

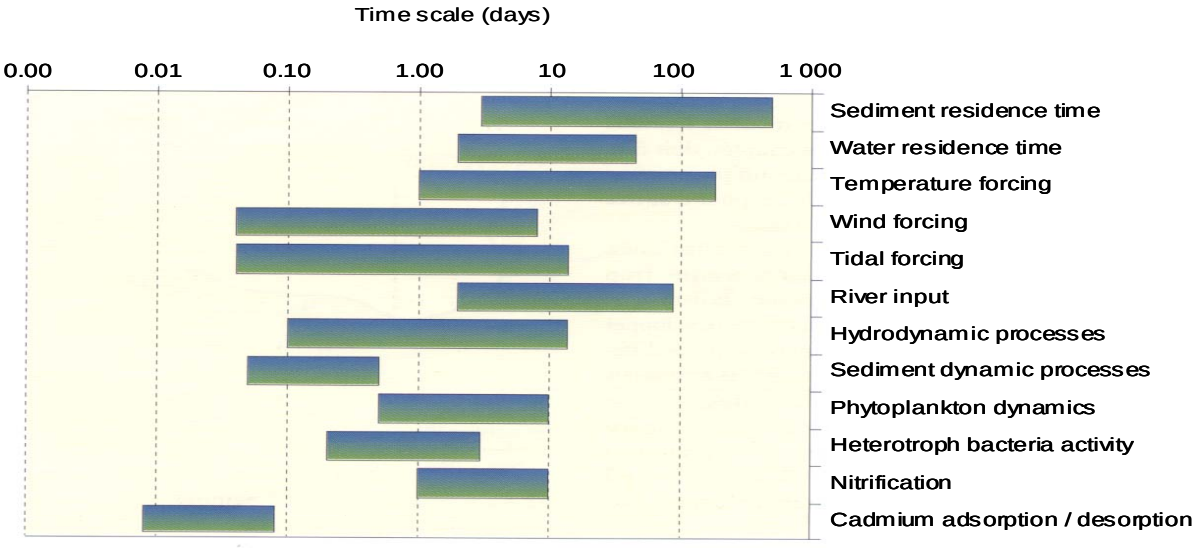

Figure II-5: Time scales for some processes occurring in estuaries and affecting water quality and related to biological activity (from Thouvenin et al., 1999).

The biological responses to natural variations of salinity, temperature, dissolved oxygen or SPM differ: highly mobile marine fish come in the estuary with the tide, and go out on the ebb so that they may remain in their preferred salinity range. Sedentary animals may find some protection by burrowing in the sediment or by closing down their shells. For these organisms, the tide cycle regulates the periods during which they can feed and SPM overloads may shorten these periods even further. The growth of these species will consequently be hindered. Yet, some reports suggest that because of the large quantities of food available and thanks to higher water temperature especially in spring and summer, there are several examples of species, especially herbivorous ones (*Littorina littorea*, *Mytilus edulis*, *Cerastoderma edule*), that grow faster and larger, that mature more rapidly and spawn earlier in the year in the stressful estuarine conditions than in a coastal areas that may *a priori* seem more adequate because they experience less variable conditions (Nelson-Smith, 1977; Tait, 1981).

Within each estuary, these variations of physico-chemical properties create a wide range of habitats. Each is used by different assemblages of organisms according to their tolerance to salinity, temperature or dissolved oxygen and to their needs relative to the substrate.

II-2 THE BIOLOGY IN EUROPEAN ESTUARIES

II-2-1 CLASSIFICATION

For the sake of scientific study, organisms of the animal kingdom have been classified in groups such as phyla, branches, classes, cohort, orders, families, tribes and genus. Such classifications are based on organism likeness and evolution. The complexity and the variety of the animal world are such that not all the above groups are systematically used, although at times extra subdivisions, sub- and super-groups (sub-phyla, sub- or super-classes, sub-orders), have been inserted to rank all animals. This taxonomist approach is useful for the systematic study of organisms, to determine their distribution, their abundance and to compare their physiology. The most common phyla found in the estuarine environment are fish (*chordata*), crustaceans (*arthropoda*), worms (nemathelminthes and *annelida*), molluscs (*mollusca*) and echinoderms (*echinodermata*, urchins, star fish and brittle stars). In the present study, such classification has been useful during the initial phase to identify species present in European estuaries but does give little information on the interactions between species and their environment. Besides taxonomy and physical resemblances, a number of organism behavioural characteristics can be used to classify and study estuarine populations.

Elliott and Dewailly (1995) have defined ecotrophic guilds that allow differentiating fish by their biological characteristics, and more specifically by the use they make of estuaries and by their feeding and reproductive modes. They used data from estuaries in the North West Atlantic (Portugal being the southern limit), the Irish Sea, the North Sea and the Skagerrak. In their study, a majority of fish taxa are either estuarine residents living their entire life in estuaries, marine fish that appear irregularly in estuaries without any apparent requirement for estuaries or marine fish juveniles. Also encountered in estuaries, but with a lesser diversity of taxa, are adults fish that visit the estuaries at set times on the year, or that pass the estuary from fresh to marine water, or reverse, towards their spawning areas. The least number of taxa are of freshwater fish.

Fish are the larger species and are economically the most important inhabitants of the aquatic environment, but invertebrates make up the largest part of the biomass. The latter are essential as they are prey for carnivorous fish and therefore form a link for the transfer of energy between particles (primary producers and detritus) and fish. Some, such are shrimps and mussels, also have an economic value.

Reading through the literature, more than 350 organisms have been recorded in an "ACCESS" database as inhabiting European estuaries at some stage of their life. This list is far from being exhaustive and the selection is obviously biased by the availability of reports: species that are easily observed are studied more often than species that are difficult to see, to catch or to handle. This is particularly true for worms: there are many studies on the 10 cm long polychaete *Nereis diversicolor*, and very few on small oligochaete worms who are nevertheless suspected to play an essential role in the recycling of organic matter in the sediment. The "ACCESS" database has nevertheless been used to gather information on species distribution, on their trophic mode, on the characteristic of their habitat and on the prey-predator interactions between species. The results are presented below.

II-2-2 HABITATS

In the marine environments, habitats are zones characterised by the nature of the sediment (rock, sand, mud…), the water depth, the tidal regime (if relevant), the currents and the species that inhabit it. In order to facilitate their study, habitats, like organisms, have been named and classified. Various classifications have been set up, with various degrees of precision depending on the classificator's needs. The EC "Corine" and "Natura 2000" classifications were designed in order to evaluate and manage the widest possible range of marine habitats. These descriptions are relatively coarse and include just one class to describe the estuarine environment. Other studies that have concentrated on coastal areas, have determine a host of habitats (MarLIN, 2001) differentiated by particularities that only specialists may be able to identify. While this approach would be valuable to understand the details of functioning of estuaries, this is well beyond the scope of the present study. An approach that seemed more suitable was that followed by IECS (2000). This research group has defined 9 estuarine habitats, primarily characterised by their substrates, *i.e.* the type of sea bottom, by their position relative to the seawater level or by their vegetation. They are:

1. *Tidal fresh water*: Salinity in this habitat is inferior to 0.5 and the water movement are influenced by the tide as the down flowing river water is pushed back up stream during flood and flows out during ebb.
2. *Reed beds*: Tidal low salinity zones (S<0.5) where dense herbaceous plants grow.
3. *Salt marsh*: Intertidal vegetated habitats that can form the transition between saline to freshwater areas and between marine to terrestrial areas.
4. *Intertidal soft substratum*: Unvegetated areas situated between the high and the low tide marks consisting of soft sediments (from fine silt to shingles).
5. *Intertidal hard substratum*: Areas in the intertidal zone either unvegetated or with fixed vegetation. Substratum ranges from gravel to hard rock.
6. *Subtidal soft substratum*: Unvegetated areas composed of soft sediments located below the level of the lowest tide.
7. *Subtidal hard substratum*: Areas either unvegetated or with fixed vegetation located below the lowest tide mark. Substratum ranging from gravel to hard bedrock.
8. *Subtidal sea grass beds*: Subtidal areas colonised by permanently submerged macrophytes adapted to brackish to marine waters.
9. *Biogenic reefs*: Elevated structures on seabed, in tidal or subtidal areas, formed by calcareous organisms or surface dwelling bivalves (such as mussels).

Figure II-6: Example of intertidal soft substratum: tidal flat in the Seine estuary (Photo courtesy of "Laboratoire de morphodynamique continentale et côtière", University of Rouen, France).

These habitats are essentially characterised by their substrates or their benthic fauna and flora. In their classification, IECS (2000) have considered the water column as included in the habitats defined above. Yet, in estuaries, it is possible to distinguish benthic organisms from pelagic ones as they have developed different behaviours and, to some extend, feed on different prey. A pelagic habitat needs therefore to be added to the above list: this is the water column that is little influenced by the sediment and that supports an array of organisms independent of the benthic production. This habitat main physico-chemical characteristics are its hydrodynamics, its salinity and its SPM content. Its primary production is provided by phytoplankton and bacteria.

The IECS report points out that in the 26 estuaries studied (Table II-1), 50% of the area was of the subtidal soft substratum type. In the Mediterranean and the Baltic where tidal zones are reduced or not significant, this value goes up to 70%. Along the Atlantic and the North Sea coasts, intertidal soft substratum accounted for another 30% of the estuarine habitats. It was also underlined that the subtidal soft sediment habitat is the habitat above which the number of commercial fish is the greatest and where more than 50% of estuarine fish are usually found (IECS, 2000). This is directly related to the fact that soft substrata are important feeding grounds for fishes and birds as they are the home of productive benthic communities such as *Albra alba* or *Macoma baltica* communities (Table II-2). The distribution of these communities depends on environmental parameters such as salinity (the *Abra alba* community is more marine than the *Macoma baltica* one) or the nature of sediment as some species such as the annelid worm *Lanice conchilega* prefer sandy bottom to muddy or silty ones. However, communities are not tightly integrated entities and in every estuary the number of species as well as the type of species present vary continuously from fresh to marine waters, from rocky to soft substrates. The fish that live above the sediment feed as well on a *Macoma baltica* siphon as on *Abra alba*'s.

Estuarine system	Geographic region	Latitude °N			
NW Aland	Baltic/Skaggerak	60	Oosterschelde	NW Atlantic/Boreal	51
Göta River	Baltic/Skaggerak	58	Thames	NW Atlantic/Boreal	51
Gullmarsfjord	Baltic/Skaggerak	58	Somme	NW Atlantic/Boreal	50
Darss-Zingster	Baltic/Skaggerak	54	Seine	NW Atlantic/Boreal	49
Oderhaff/Stettin	Baltic/Skaggerak	54	Loire	NW Atlantic/Boreal	47
			Ria de Aveiro	NW Atlantic/Boreal	41
Loch Etive	NW Atlantic/Boreal	56	Mira	NW Atlantic/Boreal	41
Forth	NW Atlantic/Boreal	56	Óbidos	NW Atlantic/Boreal	39
Humber	NW Atlantic/Boreal	54	Tagus	NW Atlantic/Boreal	39
Mersey	NW Atlantic/Boreal	53	Bay of Cádiz	NW Atlantic/Boreal	36
Weser	NW Atlantic/Boreal	53	Guadalquivir	NW Atlantic/Boreal	36
Elbe	NW Atlantic/Boreal	53			
Ems-Dollard	NW Atlantic/Boreal	53	Ebro	Mediterranean	41
Westerschelde	NW Atlantic/Boreal	51	Messolonghi	Mediterranean	38

Table II-1: The 26 estuarine systems used for the IECS study and their location (IECS, 2000).

	Albra alba community	*Macoma baltica* community
Benthic fauna	Bivalves: *Mya truncata* *Abra alba* *Cultellus pellucidus* *Corbula gibba* *Nucula tenuis* Annelid: *Pectinaria koreni*	Bivalves: Baltic tellin *Macoma baltica* Sand gaper *Mya arenaria* Edible cockle *Cerastoderma edule* Annelids: Lugworm *Arenicola marina* *Pygospio elegans* Snail: *Nassarus reticulatus*
Epifauna	Snail: Common whelk *Buccinum undatum* Brittle star: *Ophiura texturata*	Crustaceans: *Corophium volutator* Common shrimp *Crangon crangon*

Table II-2: The main species of two benthic communities found in soft sediments in coastal European waters (Monbet, 1995).

The species described as belonging to communities are often relatively large, easily identifiable species. Yet, smaller, less charismatic species represent an important proportion of the biomass growing in the sediment. The majority of this meiofauna (animals trapped by a 40µm sieve but go through a 1 mm one) are nematodes (round worms, 50 to 99%) and copepods (small crustaceans, 1 to 50%, Bodin *et al.*, 1997). Often overlooked, these organisms are essential as they reprocess a large quantity of detritus that falls on estuary floor or is trapped in sediment. In the Baltic they contribute to one third of the production within the primary consumer trophic level and in the Lynhe estuary (UK) their biomass is 250 times greater than that of the macrofauna (organisms larger than 1mm, McLusky, 1981). The meiofauna is preyed upon by other benthic, larger organisms and hence is an essential link in food webs.

Habitats other than soft substratum ones cover relatively small percentage of European estuaries bottom. Subtidal hard substratum is essentially found in the Baltic area. Lagoons are often covered with macrophytes. Often reclaimed and drained for agricultural purposes in the past, salt marshes are irregularly distributed between estuaries. Their role as buffer zones protecting the land from the assaults of the sea is now generally acknowledged. They are also known to be important feeding grounds for marine fish. The percentage of surface they

occupy in European estuaries is usually a few percent of the total estuary surface. Tidal freshwater, reed beds, intertidal hard substrata and biogenic reefs contributed less than 5% of the total surface area of the systems selected during the IECS study (IECS, 2000).

In the water column, species distribution is essentially controlled by salinity. For instance, the longitudinal zonation of copepods is as follow (Desprez, 1991):

- Oligo to mesohaline zone: *Eurytemora affinis*;
- Meso to polyhaline zone: *Acartia spp.*;
- Poly to euhaline zone: *Temora longicornis*, *Paracalanus parvus*, *Centropages hamatus*, *Euterpina acutifrons*.

On the other hand, flounders are found in all haline zones independently of the fish maturity, the season or any other identified feature. The pelagic estuarine habitat also shelters a rich community of crustaceans (mysids: *Neomysis integer*, *Mesopodopsis slaberri* and shrimps: *Crangon crangon*, *Palaemon longirostris*). Both species of shrimps are exploited by the fishing industry.

Whether in the pelagic or the benthic areas, a number of organisms and particularly some economically important fish (sea bass, mullets, sprats, eels…) are well adapted to estuarine conditions and use this environment as spawning, nursery or feeding grounds. The varying salinity protects larvae, juveniles and adults from potential predators that are not euryhaline, while the large SPM load present in the estuary and the high primary productivity occurring landward and seaward of the most turbid estuarine waters guaranty a constant food supply.

II-2-3. INTERACTIONS BETWEEN ORGANISMS: THE FOOD WEBS

II-2-3-1 Definitions

Food webs describes the relationships between plants and animals through their feeding behaviour. As consumers eat their prey, energy is transferred from one trophic level to a higher one. It can be convenient to rank organisms according to their trophic level: plants are the primary producers that transform inorganic matter into organic tissues. Secondary producers or primary consumers feed on plants and detritus, secondary consumers prey on primary consumers. Several trophic levels can thus be defined up to top predators, including man, who feed on lower levels. On figure II-7 organisms are positioned according to their trophic level; arrows indicate the prey-predators relationships. This simple food chain suggests an almost linear transfer of matter from the phytoplankton to the top predator. Such linearity does not exist in nature. Organisms may feed on more than one trophic level: shrimps feed on smaller secondary producers crustaceans, on detritus that is classified as belonging to the first trophic levels, and on juvenile plaice, a fish who, adult, can be considered as a top predator. Some species have cannibalistic behaviour. Many species change their diet as they grow older and bigger. Most have an opportunistic feeding behaviour or are omnivorous. The limits that were clear on figure II-7 are blurred in nature. This can be illustrated by the work carried out by Marshall (1995) who has described fish food web in the Humber estuary. His representation of this web is shown on Figure II-8. The complexity of the relationships between estuarine organisms makes it preferable to speak about food webs rather than food chains, an expression that implies simple linear relationships.

A prerequisite to a food web full description is the perfect and complete knowledge of the feeding behaviour of all organisms living in a chosen ecosystem. This is nowadays not achievable in estuarine environments as some organisms, such as those belonging to the meiofauna, are hardly identified, and consequently their feeding behaviour and their predators would hardly be known. The concept is nevertheless often useful so simplified food webs are considered. The degree of simplification is related to the questions that need to be answered. In some cases, the Figure II-7 food web may be sufficient, whereas in others more complex and extensive representations are essential. The Humber food web illustrated on figure II-8 points out to the many prey-predator relationships between identified organisms but is useless at distinguishing different trophic levels, as might be convenient for other studies.

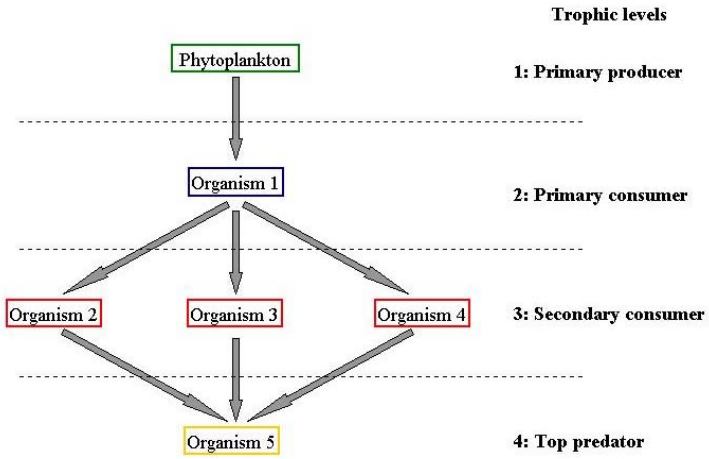

Figure II-7: Schema of a simplified food chain. Grey arrows symbolise the transfer of matter from one trophic level to the next.

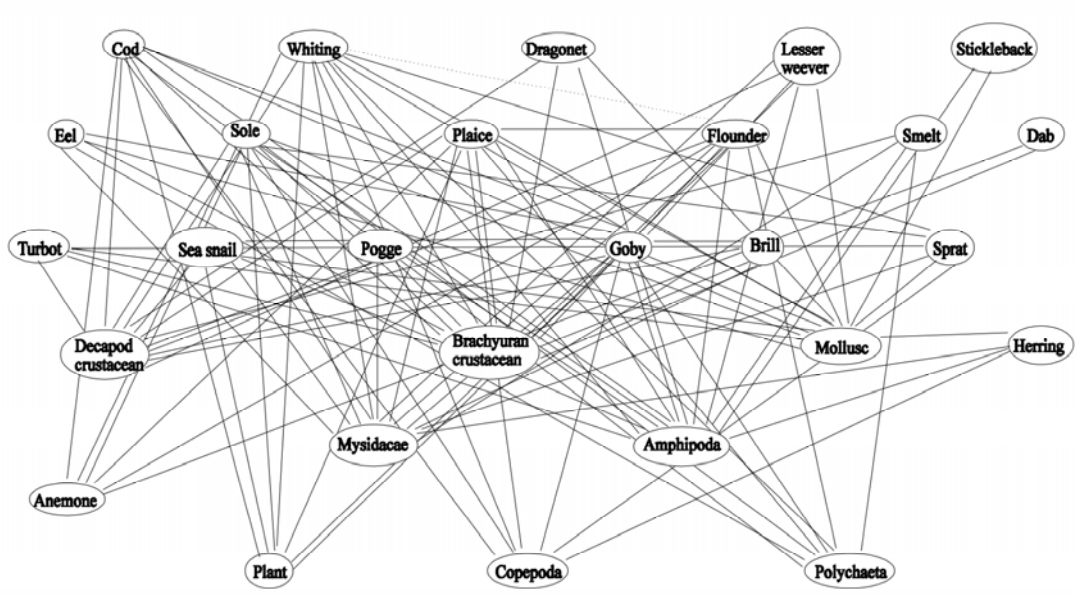

Figure II-8: The simplified food web of the Humber estuary fish assemblage as described by Marshall (1995, quoted in IECS, 2000).

II-2-3-2.Feeding behaviours

The estuarine primary production is based on phytoplankton and microphytobenthos production and on bacteria that grows on detrital material brought in by the river and the tidal currents at a more or less constant rate throughout the year. There are relatively few herbivorous organisms in estuaries, possibly because primary production by phytoplankon, microphytobenthos and macrophytes is greatly limited by turbidity within the estuary. Therefore, many primary consumers are detritivore, at least as part of their diet. Deposit feeders (crustacean amphipod *Corophium volutator*, annelid worm *Arenicola marina*, bivalve *Cultellus pellucidus*…) collect particles sedimented on the sea floor. Suspension feeders (annelid worms *Lanice conchigela*, brittle star *Ophiotrix fragilis*…) collect particles as they are carried by the water. Most benthic organisms adapt their feeding strategies to the environmental conditions and can be both deposit or suspension feeders. Filter feeders (mussels) collect them more actively by pumping large quantities of water through their gills where particles are trapped. These organisms choose particles as a function of their size, and anything suitable would then be trapped. This may include pieces of more or less refractory dead organic matter that support bacteria communities, live phytoplankton cells, or small larvae. The nutritional value of each differ and some species are able to reject directly particles with no or little energetic value, preferring live highly digestible phytoplankton cells to old refractory detrital material. Detritivores are therefore an essential link between non-living organic matter and higher trophic levels. The most ubiquitous detritivores in European estuary are shrimps (*Crangon crangon*), mysids (*Neomysis integer*) and gammarids (*Gammarus* spp., *Bathyporeia*, *Corophium* spp.). These species preferred habitats are intertidal or subtidal soft sediments.

The next trophic level up is occupied by small carnivorous organisms whether they are infauna benthic animals (polychaete worm *Nereis diversicolor*), or live on the sediment surface (brittle star *Ophiura texturata*), or are pelagic organisms (small fish *Pomatoschistus microps*).

In estuaries, amongst aquatic animals, large fishes are usually the top predators. They may be divided into two groups differentiated by their feeding habits (IECS, 2000):

a) A group that forages (mostly subtidal) on fast-moving epi- and suprabenthic prey. These are round fish, such as gadoids (bib: *Trisopterus (Gadus) luscus*, poor cod: *Trisopterus minutus*, whiting: *Merlangius merlangius*), pipefish (*Syngnathus spp.*), sea bass (*Dicentrarchus labrax*) and clupeoids (sprat: *Sprattus sprattus*, herring: *Clupea harengus*);

b) A group that forages on slow (or parts of) sessile benthic organisms (predominantly intertidal), such as flatfish (Sole: *Solea solea*, plaice: *Pleuronectes platessa*, dab: *Limanda limanda*, flounder: *Platichthys flesus*) and common goby (*Pomatoschistus microps*). These fish feed on polychaetes and their tails (*e.g.* of *Arenicola*, *Nephtys* and *Nereis*), bivalve young, siphons and tentacles (*e.g.* of *Macoma* and *Angulus*), tidally active crustaceans such as *Bathyporeia* and *Eurydice* species. Gobies (*Pomatoschistus* spp.) have a significant impact both as predator (particularly on the amphipod *Corophium volutator*) and as prey for larger fish.

Fish that feed on benthic organisms have fuller stomach when they leave intertidal zones as the tide ebbs than when they come to these areas during flood. This highlights, once again, the importance of intertidal zones in the estuarine ecosystem as feeding area (IECS, 2000).

Zooplankton production is seasonal, with highest densities usually found in late spring for phytophage species and in autumn for detritivores. Predation on zooplankton is, as a consequence, seasonal. Fish larvae and juveniles are the main zooplankton predators.

Most estuarine organisms are opportunistic in their choice of prey. This is illustrated by some of the fish behaviours. In the Forth, the Solway (UK) and the Tagus (Portugal), the shrimp *Crangon crangon* is reported to be the dominant prey item for fish, whereas in the Humber (UK), this role is played by mysids and gammarids (all are crustaceans). Zooplankton is preyed upon by young fish. This type of predation is maximum when zooplankton density is at its highest (usually in late spring) and can lead to a crash in zooplankton population. In the Thames the diet of the flounder is mainly based on *Crangon crangon* and *Gammarus zaddachi* but is more varied in the spring and in the autumn, when the number of species visiting the estuary is the greatest. On the contrary, in winter, when crustaceans migrate to warmer waters outside the estuary, the flounder feed on resident species such as bivalves (*Macoma balthica*) and annelid worms (polychaetes). In late summer, flounder prey on marine species as they move out of the estuary to spawn. In July, cases of cannibalism have been observed as juveniles move into their estuarine nursery. This type of behaviour, recorded for most estuarine fish, is assumed to occur to limit competition for food but little quantitative information is available. Overall, it can be concluded that fish have a broad diet varying seasonally and depending on the type of fish (round or flat fish), on its size (small fish eat small prey) and on the food availability and density.

An estuarine food web is therefore mainly fuelled by detrital material and bacteria attached to it. In spring phytoplankton also form an essential part of the primary production. The secondary trophic level consists in zooplankton, benthic and pelagic organisms. These are herbivores, detritivores or primary carnivores. The next trophic level up consists in benthic and pelagic fish (IECS, 2000). These are preyed upon by marine mammals, birds and man.

II-2-4 MARINE MAMMALS AND BIRDS

Many of the European estuaries and deltas are important habitats for avian species and coastal marine mammals. Especially the marine mammals and fish-eating birds are known to be at risk due to biomagnification of persistent compounds (Walker and Livingstone, 1992). The most relevant mammalian species in European waters have been listed in Table II-3

Most of the small cetaceans have nowadays disappeared from the major estuaries in industrialised areas. This is partly attributed to pressure from disturbance and pollution (Evans, 1987) and can also be explained as cetacean feeding areas are not confined to the estuarine zones. The same holds for the pinnipeds, although in recent decades important recoveries have been noted in some areas. In the estuaries considered in this study only the Western Scheldt has a limited population of the common seal, estimated at less than 5 (1987) to more than 20 (1999) individuals (Witte, 2001). Due to exchange with other populations (Wadden Sea, Belgian Coast) and the re-introduction of recovered individuals from animal-care centres, it is not possible to estimate the number of animals that reside permanently in the

Western Scheldt (Witte, 2001); there is no more permanently resident marine mammals in the Seine estuary.

Taxon	Species	Common names	Distribution
Pinnipeds	*Phoca vitulina*	E, common seal, harbour seal F (phoque) veau-marin G Seehond,D zeehond	Coastal with sand/mud plains and low rocks North Sea, North Atlantic, Baltic, North Pacific
	Halichoerus grypus	E, grey seal, F phoque gris G, Kegelrobbe D, grijze zeehond, kegelrob	North Sea, North Atlantic, Channel
	Monachus monachus	E, Mediterranean Monk Seal F, Phoque moine méditerranéen D, monniksrob	Eastern and SW Mediterranean
Small Cetaceans	*Phocoena phocoena*	E, harbour porpoise, F marsouin G, Schweinswal D, bruinvis	Shallow waters in temperate and subarctic Atlantic and Pacific
	Tursiops truncatus	E, bottle-nosed dolphin F, grand dauphin G, grosse Tümmler, D tuimelaar	Shallow waters (sub) tropic and temperate waters Rare in North Sea and Mediterranean sea

Table II-3: Main marine mammals encountered in European coastal waters based on Bonner (1989), Evans (1987) and Lange *et al.* (1994).

Although for the common seal and harbour porpoise the biomagnification of persistent compounds (*e.g.* PCBs, dioxins and other chlorinated pesticides) has been documented (Aguilar and Borrell, 1994; Boon *et al*., 1997; Law *et al*., 1995; Ruus *et al*., 1999; Walker and Livingstone, 1992) and probably sufficient data exist to estimate biomagnification factors (BMFs) for a food-chain model, it was decided not to include marine mammals as a specific category of top-predators in the food chain model, for the following reasons: uncertainties in migratory patterns and feeding behaviour, the limited regional distribution of most species, and absence from most industrialised estuaries. The otter (*Lutra lutra*), for which bioaccumulation data have been published by Leonards *et al*. (1997), was not considered for this study as in most European countries this species is mainly restricted to freshwater habitats and only in some Northern countries (UK, Norway, Denmark) this species may be encountered in coastal environments.

A large variety of fish- and invertebrate-eating birds can be recorded in most European estuaries. Most of the species are migratory and are only present in a specific estuary during the breeding period, the moulting period or in the winter period. Only very few species reside permanently in the same estuarine habitat. A (far from complete) selection of relevant species, for which bioaccumulation studies have been documented (based on which BMFs probably could be deduced) have been listed in Table II-4. Since most species have different breeding

and winter areas, and since they are opportunistic in their feeding behaviour, it was decided not to include predatory birds in the food chain model.

Common name	Species	Ref. bioaccumulation studies
Cormorant	*Phalocrocorax carbo*	van Hattum *et al*. (1993)
Double crested cormorant		Sanderson *et al*. (1994), Yamashita *et al*. (1993)
Shag	*Phalocrocorax aristotelis*	
Common tern	*Sterna hirundo*	Bosveld et al. (1993) Yamashita *et al*. (1993)
Oystercatcher	*Haematopus ostralegus*	Boon et al. (1989) Stronkhorst *et al*. (1993)
Knot	*Calidris canutus*	de Voogt *et al*. (1984) Goede (1993)
Herring gull	*Larus argentatus*	
Black headed gull	*Larus ridibundus*	Stronkhorst *et al*. (1993)
Blue Heron		Renzoni *et al* (1986)
White Pelican		Renzoni *et al* (1986)
Spoonbill		van Hattum *et al.* (1998)
Gannet	*Sula bassana*	
Great crested grebe	*Podiceps criststur*	
Guillemot	*Uria aalge*	Dietz *et al*. (1990), Stewart *et al*. (1994)

Table II-4: Selection of estuarine bird species for which bioaccumulation has been documented to some extent.

II-3 POLLUTION AND CONTAMINANTS

II-3-1 DEFINITION

A contaminant is a substance, natural or man made, present in the environment at concentrations greater than its natural background level. Its presence may not have any effect on biota. If it has, contamination is perceived as pollution. More generally, pollution means by **the introduction in the environment of energy or of substances that have deleterious effects on biota** (GESAMP, 1989). Considering energy first, discharges of cooling water increase river or estuarine water temperature (by about 10°C around power stations) decreasing the dissolved oxygen, displacing temperature sensitive autochthonous species and attracting foreign ones (Nelson-Smith, 1977). Discharges of fresh water can also alter the salinity and therefore the local flora and fauna. The physical form of a chemical can damage habitat: long chain aliphatic hydrocarbons coat surfaces and smother organisms. Detergents reduce aeration at the water surface, inducing a decrease in the dissolved oxygen concentration, facilitate the entry of other pollutants into living organisms and damage cells membrane at the sites where respiratory and ion exchange takes place (Nelson-Smith, 1977). Dredging activities and building of solid structures (dams, flood barriers, effluent pipes…) directly remove habitats or modify them by changing sedimentation patterns. Other types of pollution include radioactivity from military, energy, industrial, medical, or research sources, pathogens and biological pollution from effluents, or the introduction of foreign species. In this report, it is the chemical aspect of pollution by man made contaminants that will be discussed in greater details.

In the 80's, over 100 000 compounds were registered in the European Inventory of Existing Commercial Substances and this number has been growing since. The potential chemical effects of these substances on biota depend on their reactivity and on their bioavailability. Reactivity is the result of the physico-chemical properties of a molecule and will determine the persistence of the compound in the environment. Highly reactive molecules are broken down easily by abiotic (acid-base, oxydo-reduction, photolytic reactions) or by biotic processes. Reactivity is enhanced by the following properties:

- Low molecular weight
- Small size
- Linear chains (minimum steric hindrance)
- No resonating forms (in particular absence of benzene cycles)
- High polarisation
- Presence of reactive substitution groups in the molecule carbon (-OH; -NH_2)

Non-reactive or persistent molecules are stable, remain unchanged in the environment and are available for long periods to biota. Bioavailability refers to the potential that a substance has to be transferred from one compartment, biotic or abiotic, into the tissues of a living organism. Bioavailability, as defined here, depends on the physico-chemical properties of the molecule as well as on the physiological processes of the organism (particularly feeding, respiration, membrane permeability…) through which the substance might be assimilated. For instance, hydrophobic compounds sorbed on particulate organic matter might not be bioavailable to gill breathing organisms, but might be available to particle feeders

(Björk and Gilek, 1997). The following organism and contaminant properties or characteristics are likely to increase bioavailability:

- ⇨ High feeding activity
- ⇨ High membrane permeability

and concerning the chemical compound

- ⇨ High water solubility
- ⇨ Absence of ligands
- ⇨ Association with fine particles
- ⇨ Association with non refractory material
- ⇨ High concentration in environment.

Other parameters such as pH, temperature and salinity affect both reactivity and bioavailability as they may modify for instance the degree of ionisation, the complexation of metals, the redox and acidity status of molecules and the physiological activity of organisms.

Some of these properties are easily quantifiable (molecular weight, size, solubility). Other can be observed (steric hindrance, substitution groups) but it is more difficult to associate numerical values to such properties and to rank them although attempts have been made (Jørgensen *et al*., 1998). This particular field has been investigated by molecular chemists and has been used to predict some biological processes, as for instance biodegradation rates (Parsons *et al*., 1991) or chemical properties of compounds (Chu and Chan, 2000; Govers and Krop, 1998; Govers *et al*., 1991; Makino, 1998). Finally, some properties have been shown to be related to others, which are more easily measured. Hence, a number of environmental properties of organic compounds (sorption on soils, toxicity, bioconcentration factors…) is derived from the octanol-water partition coefficient, K_{ow} (Bintein and Devillers, 1994; di Toro and McGrath, 2000; Hope et al., 1998; Leeuwen et al., 1992; Meylan et al., 1999).

II-3-2 CONTAMINANTS IN ESTUARIES

Contaminants can reach estuaries via several routes: river, atmosphere, direct industrial and urban effluents are the most obvious sources. These releases might be accidental (unexpected leakages during loading or transport), a result of industrial production (leakage, wastes…) or of their use in estuary catchment areas, as for instance pesticides on agricultural lands. They can also be released as they are used within the estuary, as it is the case for antifouling agents used on boats. In some cases, the estuary sediment may also be considered as a source. This might happen when the release of a contaminant is stopped after a period long enough for significant quantities to have been stored in the sediment. Once the contaminant concentration in the water has been reduced, the thermodynamic reactions are reversed and displaced toward the redissolution of the sorbed contaminant into the water phase. Trapped in the sediment, the contaminant desorbs from particles surface, and redissolves in water. Resuspension of sedimented particles, during storms or dredging activities, is also a process through which sediment becomes a source of pollution in estuaries. Sediment bioturbation by infaunal species that ingest particles in their burrows and defecate at the water sediment interface has also been suggested to be a process through which contaminant trapped in the sediment may be released back into the water column (McElroy *et al.*, 1989).

Only a few compounds, such as natural salts, have conservative behaviours in estuaries, that is have concentrations proportional to the dilution of freshwater by marine water. Most contaminants entering estuaries react in the water with suspended matter, other organic and inorganic molecules and can be transformed in the water column and in the sediment by biological processes such as bacterial degradation. Thermodynamic equilibrium favours the partitioning of hydrophobic compounds to non-polar phases, such as organic carbon, dissolved in the water column or associated with particulate matter. Once bound to particles, hydrophobic compounds can be trapped in turbidity maximum zones and in sediment. Some metal ions are complexed by organic or inorganic molecules. Due to the changes in physico-chemical properties of the medium that occur when fresh and marine water mix, some molecules also flocculate and precipitate whereas others become more soluble. It is because this large set of processes occurs that estuaries act as reactors and filters between freshwater inputs and the marine environment. Particles to which organic contaminants are bound tend to settle to sediment and remain in the estuarine environment. Hence their residence time, and therefore the time they might be available to estuarine biota, may be longer than water residence time. Yet particles transport is clearly related on the estuary hydrology. Due to lower river flow rates, water and particle residence times are, in most cases, longer in summer, when biological activity is at its highest, than in winter when high river flow rates and storms flush water and, sometimes, turbidity maximum out of the estuary.

The physico-chemical processes controlling the concentrations of pollutants in estuarine water, suspended matter and sediments are described in more details in Villars and Delvigne, (2001) as part of the GEMCO project.

II-3-3 TRANSPORT TO AND ACROSS THE BIOTIC COMPARTMENTS

II-3-3-1 Uptake

The main routes of uptake are adsorption, respiration, diffusion through integument (skin, scales, shell, etc) and feeding. Uptake depends on many factors, including tissue lipid content, metabolic activity (especially respiration and feeding rates), feeding strategy (suspension or deposit feeders, grazers, carnivores, etc), animal health, exposure to contaminant (limited in time or chronic), its presence as dissolved in the water or bound to particles… Age and reproductive condition may also explain some variability between individuals of the same species sampled in the same environment.

In the case of algae, the main mechanism of uptake is adsorption followed by diffusion into the tissues. This uptake is controlled by partitioning between the water phase and the vegetal tissues, a process dependent on the lipophilicity of the contaminant and on the lipid content of the tissue. This is an important pathway for contaminants between abiotic and biotic compartments because plants are at the lowest level of trophic chains.

Respiration is a process during which dissolved gas involved in metabolism (O_2 and CO_2) are exchanged between water and organism. If present, contaminants also diffuse through the organs that are normally used for respiratory exchanges. This diffusion is a thermodynamic process where the direction of the flux depends on the contaminant

concentrations on both sides of the organism membrane. The magnitude of the exchange is partly regulated by the dissolved contaminant concentration in water and is increased if organisms have active ventilatory movements. Uptake of compounds with low K_{ow} and by organisms with active ventilatory movements (*e.g.* fish, mussels) leads to higher body burdens than passive uptake, especially of compounds characterised by high K_{ow}. Contaminant uptake is affected by variations in temperature because ventilation increases with temperature. In fish, uptake from water appears to be controlled by aqueous diffusion rather than gill membrane permeability and uptake efficiencies from water does not seem to vary substantially between different PAHs or chlorinated aromatic hydrocarbons with log K_{ow} less than about 6.5 (Konneman and van Leeuwen, 1980; McKim *et al*., 1985; Meador *et al*., 1995b; Opperhuizen, 1991).

There are very few conclusive studies on contaminant diffusion through integument. Intuitively, it seems that this route might be more important for infaunal species in permanent contact with sediment than for other species. Yet, it is likely that the contribution of diffusion through the skin to contaminant body burden is generally negligible (Meador *et al*., 1995a).

All species can be contaminated while ingesting contaminated food and feeding has been shown to be a major route of contamination from lower to higher trophic levels (Bierman, 1990; Loizeau *et al*., 2000; Thomann and Connolly, 1984). For organisms that feed on particles, xenobiotic bioavailability has been related to their logK_{ow}. Highly hydrophobic compounds are more tightly bound to particles and have been shown to be less easily transferred through biological membranes: their assimilation during their transit in guts is therefore hampered compared to that of more water soluble compounds but assimilation is increased if the time of the gut transit is increased. Assimilation may also be limited by the molar volume of the compound (Niimi and Dookhran, 1989). Greater assimilation rates of fish and crustaceans cause these organisms to be more exposed to contamination than worms and bivalves. More generally, accumulation rates are often positively correlated with organism size. Feeding strategies also affect the exposure to contaminants: deposit feeders ingest particles to which the most hydrophobic compounds are bound while filter feeders are more exposed to water soluble compounds. Low chlorinated PCBs are slightly more present in filter feeders than in other species, whereas in worms and crustaceans that feed on detritic material highly chlorinated compounds dominate. A number of studies have shown that once in the organism, hydrophobic compounds preferentially accumulate in lipid rich organs, such as the gall bladder and the liver in vertebrates, the hepatopancreas in invertebrates and to lesser extend in brain, blood and female gonads (Hellou *et al*., 1997; Loizeau, 1992; Meador *et al*., 1995a; Schneider, 1982; Seaton and Tjeerdema, 1996).

II-3-3-2 Elimination

Once in an organism, contaminants can be eliminated by different processes: excretion, defecation, diffusive losses, spawning, moulting and biotransformation are the main ones. Somatic growth is also viewed as a loss mechanism (dilution in tissues).

Diffusive loss, like diffusive uptake (through respiration and epithelial exchanges), is controlled by thermodynamic partitioning between the organism and its environment (water, sediment) and therefore is correlated to hydrophobicity. As they tend to remain in tissues with high water content that are more perfused and as they cross membranes more easily, more

water soluble compounds are excreted more readily than more hydrophobic compounds. A function of hydrophobicity, diffusive loss determines a compound minimum elimination rate, which may be increased by any additional biotransformation processes. If biotransformation is substantial, the relation between elimination rate and hydrophobicity may be masked (Meador *et al*., 1995b).

The variation of contaminant with age seems to be similar to that of the growth curve, with an apparent steady state reached at adulthood. In those conditions, growth can be seen as the dilution of a given amount of contaminant in a larger body. Although the organism looses no contaminant, the contaminant concentration is effectively decreased. This is why growth is considered as a loss process. Lipid rich female gonads are organs where hydrophobic compounds are concentrated during maturation and from which they are eliminated from the parent animal during spawning. (Rossi and Anderson, 1977) have shown that if polychaete eggs were contaminated by naphthalene, this contaminant load was lost by the time the worms reach the juvenile stage.

Excretion is the elimination of metabolic waste products whereas defecation is the removal of material ingested by organisms but not absorbed in their tissues. Both are routes of elimination of contaminants. In this report, excretion refers essentially to elimination of metabolised compounds and occurs via urine. As such it is the last step of elimination when biotransformation is observed.

During biotransformation, a compound is generally transformed into a more water soluble chemical. The transformation of the parent compound is usually catalysed by enzymatic reactions and divided in two phases. The first one introduces a functional group on the contaminant while the second phase attaches a polar substrate to the functional group. Both reactions produce metabolites and are designed to increase the solubility of the parent molecule and its elimination through excretion (Livingstone, 1992). Globally, the enzymes responsible for the catalysis of these reactions are present in vertebrates and invertebrates but are usually less active in the latter. Moreover, these detoxifying systems are more diversified in vertebrates than in invertebrates. Hence, fish have a greater capacity to metabolise and to excrete metabolites, via the bile, than crustaceans and polychaetes. Bivalves that were thought to be unable to biotransform organic compounds have been shown to have a limited ability to do so (Meador *et al*., 1995b).

Although biotransformation is an efficient detoxifying mechanism for certain xenobiotics, some metabolites can be more toxic and persistent than their parent compounds. This is the case for BaP and non ortho substituted PCBs. Thus, the effect of a contaminant on an organism can be evaluated properly only if both the metabolisable parent compound and its metabolites concentrations are measured. Due to thermodynamic partitioning, hydrophobic compounds tend to accumulate in lipid rich tissues of organisms (Petersen *et al*., 1995) but the relative proportion of metabolite to parent compound differ according to the capacities for biotransformation of each tissue. This metabolites distribution is in part a function of metabolic rates and therefore of temperature variations (Kennedy *et al*., 1989). In fish, BaP metabolites concentrations seem to be similar in bile and liver, lower in skin, and lowest in muscles whatever the fish and the type of exposure considered (Varanasi and Stein, 1991).

The rates of elimination, by diffusion through membranes, metabolisation or excretion, have been shown to depend on environmental conditions. Their seasonal variations can affect metabolic rates (ventilation, growth…) and consequently contaminants uptake and

elimination rates. Results of experiments tend to show that elimination is slower at lower temperature, but this is not the conclusion of all studies.

Contaminants half-lives in organisms have been evaluated as they give information on elimination rates and on the time necessary to organisms to recover once the source of pollution has been removed. Several studies have shown that organism capacity to eliminate a xenobiotic was dependent on the length of exposure (Livingstone, 1992; Meador *et al*., 1995b). Short term exposure (from a few hours to a few days) lead to faster elimination rates and shorter contaminant half lives (a few hours long) than long term or chronic exposures (days to years long) (Foster *et al*., 1987; Neff *et al*., 1976; Pruell *et al*., 1986). This is especially true for the most hydrophobic compounds. Based on simple diffusion kinetics, high molecular weight PAHs (HPAHs, 4 aromatic rings or more) diffuse more slowly out of an organism compared to more water soluble low molecular weight PAHs (LPAHs, 2 or 3 aromatic rings) and therefore will be more persistent. However the poor ability of diffusion of HPAHs is balanced by their rapid metabolisation by enzymatic systems. Hence in fish, both half lives are generally reported to be relatively short (a few days) (Meador *et al*., 1995a; Varanasi *et al*., 1992).

Some authors have looked for a relationship between PAH concentrations in organisms and $LogK_{ow}$. Such a relationship may not be always observed as elimination of low molecular weight, less hydrophobic PAHs is done by diffusion and is fast, whereas highly hydrophobic high molecular weight PAH are eliminated via biotransformation, a process that can be equally fast (Meador *et al*., 1995b).

II-3-4. ROLE OF THE FAUNA IN THE TRANSPORT AND FATE OF CONTAMINANTS

In the marine environment, fauna influence the distribution and the cycling of contaminants through:

Detrital feeding. Organisms transfer contaminant from the dissolved to the particulate phase: in the Swedish coastal zone of the Baltic, mussels remove annually 850 000 tonnes of carbon from the water column and simultaneously biodeposit, via faeces, 220 000 tonnes of carbon with PCB concentrations at least 50% higher or more than that in settling particles. The polychaete worm *Nereis diversicolor* faeces was shown to be 1.8 times more concentrated than the sediment surrounding its burrows (Gunnarsson *et al*., 2000). Another polychaete has been reported to produce faeces with DDT concentration 3 to 8 times higher than the particles on which it fed (Muslow and Landrum, 1995).

Carnivorous feeding. In this case, contaminants are transferred from one trophic level to an other. Each prey can be seen as preconcentrating persistent contaminants for organisms of higher trophic levels (Gunnarsson *et al*., 2000; Loizeau and Ménesguen, 1993). The mobility of these predators, whether they are crustaceans, fish, birds or mammals, implies that the contaminant might be transported away from the point where it was originally released or trapped in sediment.

Bioturbation. This modifies the sediment in two ways. First, oxygenated water penetrates into the burrows and modifies redox conditions of the burrow walls. This modifies the local chemical conditions and may favour the transfer of contaminant from water to solid phase or the reverse. Second, sediment is ejected as faeces at the water sediment interface, potentially increasing the flux of contaminant from the sediment to the water as mentioned above.

Spawning. The release of eggs in the water column has two immediate effects: first, as mentioned earlier, this represents an elimination from the mature female of contaminants that have accumulated preferentially in the relatively high lipid eggs. Second, as contaminated eggs are released in the water column, the contaminant previously trapped in the parent is effectively dispersed again in the environment (Gunnarsson *et al*., 2000).

Through these processes contaminants are continuously recycled and transported between biotic and abiotic compartments. In some cases, they are trapped in sediments, but in some other they are dispersed becoming more widely available.

II-4. THE BIOLOGICAL RESPONSE TO CONTAMINANTS

The contamination of biota that we observe in "natural" estuarine environments is the result of chemical, physical and biological processes discussed previously. In the case of chronic pollution, **an apparent steady state** may be observed: contaminant concentrations in organisms reach constant levels determined by uptake rates within a time that is set by elimination rates (Meador *et al*., 1995b). Steady state equilibrium is expected to be observed if diffusive exchanges between biota and water control the contaminant concentrations and if environmental conditions do not vary. These conditions are often assumed to be met but they are rarely a field reality in estuarine environments, where tides, river flow, and human activities change on time scales varying from a few hours to a few years. In some instance a steady state representation might be sufficient to explain observations, but often care is to be taken when interpreting measurements, and even more when extrapolating laboratory experiment results to the natural environment.

Whether steady state assumptions apply, it is observed that the concentrations of persistent organic contaminants in biota are often larger than in their surrounding environment and this is explained by bioconcentration and bioaccumulation processes. Regardless of the sources of contamination and the detailed mechanisms, such accumulations occur, for any organism, when the input of a compound exceeds its output.

II-4-1 BIOCONCENTRATION

Bioconcentration is a process by which there is a net accumulation of a chemical directly from water into one aquatic organism resulting from simultaneous uptake and elimination. It is a diffusive process resulting from equilibrium partitioning between water and biological tissues and its experimental determination assumes that water is the only source of contamination and that steady state is reached (Haitzer *et al*., 1998; Hope *et al*., 1998). In order to describe and quantify observations, a bioconcentration factor, BCF, has been defined as the ratio between the concentration measured in the organism tissues and the concentration measured in water, or as the ratio of the organism uptake and elimination rate constants. At steady state, both definitions give similar results (Haitzer *et al*., 1998). As such, BCF can be predicted on the basis of the chemical properties, and numerous authors have described relationships between $LogK_{ow}$ and LogBCF (Chaisuksant *et al*., 1997; de Voogt *et al*., 1991; Hope *et al*., 1998; Meylan *et al.*, 1999). These relationships tends to be linear for values of $LogK_{ow}$ less than 7, or parabolic if values greater than 7 are considered (Bintein and Devillers, 1994; Meylan *et al*., 1999; Thomann *et al*., 1992). Experimentally, bioconcentration factors can be determined but a few requirements must be met: long exposure to contaminant, equilibrium conditions, low concentrations in water, constant concentration of the contaminant in water during the test,...

It must be kept in mind that BCF are meaningful only for accumulation from water. BCF values can only be compared if water is the only source of contamination for the organism and if thermodynamic partitioning is the property controlling uptake and elimination. These conditions can be met for organisms at the lowest levels of the trophic chain, such as phytoplankton, but are generally not true for any carnivorous animals whose sources of contamination include their prey. A BCF determined experimentally for a fish is

representative only of the contamination due to respiration but is not representative of the contamination sustained by the fish in its natural environment as this contamination also emanates from food. The relevance to these experiments to evaluate the impact of a contaminant in the environment has therefore to be questioned, except for phytoplankton.

Similarly to BCF, biota to sediment accumulation factors (BSAF) have been defined as the ratio of contaminant concentration in a benthic organism to the contaminant concentration in the sediment where it has its burrow. As the definition of BSAF is based on the same assumptions of that of BCF, the limitations on these two factors are the same. These limitations are important and a number of studies have concluded to the absence of correlation between BCF or BSAF and K_{ow} (Boon *et al*., 1985; Joiris *et al*., 1997; Rimkus, 1999; Serrano *et al*., 1997).

II-4-2. BIOACCUMULATION

Bioaccumulation is the ability of organisms to accumulate substances from their environment. This accumulation is the result of bioconcentration and biomagnification, the latter being defined as the accumulation of substance in successive trophic levels of a food chain. A consequence of biomagnification is that the longer the food chain the greater the bioaccumulation of persistent chemicals, as each trophic levels act as a "preconcentration step" for its predators. Eventually, concentrations several orders of magnitude higher in top predators than in water or sediment can be measured Figure II-9. As the result of all uptake and elimination processes that affect organisms in their environment, bioaccumulation is a more comprehensive representation of contaminant transfers to biota than bioconcentration.

A number of properties are required for a contaminant to be bioaccumulable (Grimaldi *et al*., 2001):

- it should be chemically stable so that it resists transformation through the biotic compartment.
- it should be easily absorbed through intestinal tissues into the organism flesh.
- it should be stored in tissues for long period of times, displaying long half-lives.
- it should not be so toxic that at the concentrations it accumulates it kills organisms, breaking then the bioaccumulation chain.

Hence a molecule with a low water solubility, a high particle or lipid affinity, and few or no reactive sites is not likely to be eliminated by an organism and is likely to be bioaccumulated as long as it is not biotransformed. For instance, the greater the number of chlorine atoms in a PCB molecule, the more likely it is to be bioaccumulated. However, the structure of molecules has been shown to influence bioaccumulation too: PCBs accumulation differs according to the chlorine substitution pattern (Borlakoglu and Haegele, 1991; Maruya and Lee, 1998).

The largest compounds will have long half-lives, but may not be easily absorbed into biological tissues. Their concentrations in organisms are then lower than expected and this partly explains that LogBCF–LogK_{ow} relationships are not linear for LogK_{ow} values greater than 7: the molecules properties, particularly large molar volume and steric hindrance, prevent them from being assimilated and negative relationships are observed between bioaccumulation factors and LogK_{ow} for the most hydrophobic molecules (Maruya and Lee, 1998). Moreover, for compounds with very high K_{ow}, affinity with organic rich particular

material or sediment reduce their ability to be transferred from solid material to biota (*i.e.* reduce their bioavailability).

Other processes that limit bioaccumulation are elimination and biotransformation. These processes are species and compound dependent, and generally speaking are more developed in vertebrates than in invertebrates. When a compound is biotransformed, its concentration decreases from prey to predator and the concentration pattern along the food chain is inverse compared to that observed for persistent compounds as each animal acts as a "cleaning step". This is illustrated by BaP concentrations in the sea bass and flounder food chains (Figure II-9). This figure points out that differences in biotransformation ability exists between species occupying the same trophic level: like other molluscs, *Abra alba* has a little biotransformation capacity and therefore exhibits greater BaP concentrations than zooplankton and other secondary producers. The BaP measurements in zooplankton reported in have been carried out on the copepod *Eurytemora spp.*, which shows similar biotransformation ability as the shrimp *Crangon crangon*. Differences in bioaccumulation capacities exist also between related species as shown for three types of annelid worms by Kane Driscoll and McElroy (1997), or between gender as suggested by Moese and O'Connor's (1985) results on the blue crab *Callinectes sapidus*.

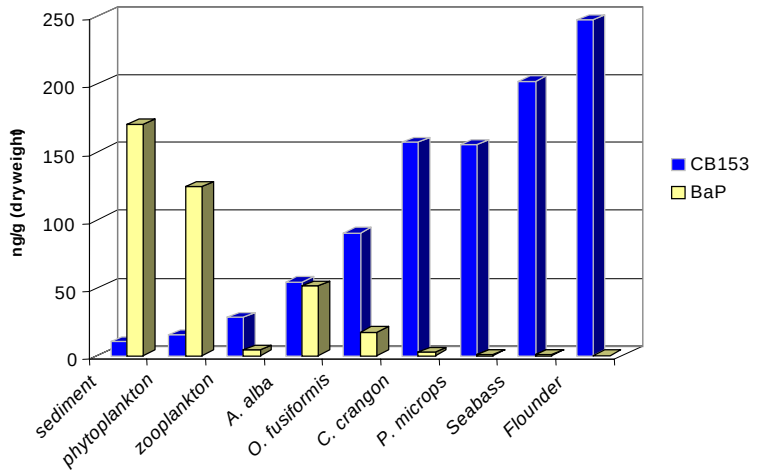

Figure II-9: PCB153 and BaP concentrations in some species of the sea bass and flounder food webs in the Seine estuary in spring 1998 (Jaouen-Madoulet, 2000). Four trophic levels are represented here: sediment and phytoplankton are on the lowest; zooplankton is a primary consumer, *A. alba*, *O. fusiformis*, *C. crangon*, and *P. microps* are secondary consumers. The sea bass and the flounder are two top predators. The increase in PCB153 with the trophic levels illustrates bioaccumulation whereas the pattern shown by the BaP concentrations is typical of a biotransformed compound.

Finally, it must be emphasised that each factor that affects uptake, elimination and biotransformation affects bioaccumulation. These factors have been mentioned earlier and include: SPM concentration and composition, nature and chemical characteristic of contaminant, chronic and acute exposure, species, gender, animal health, water temperature… This indicates clearly that interpreting bioaccumulation data should be done with caution as many studies are not conducted under similar conditions, and it must be taken into account whether steady state conditions are reached. Within this context modelling appears a very promising tool providing information on the relative contributions of the various factors affecting bioaccumulation.

II-4-3. BIOMARKERS

Pollution, whether physical or chemical, is always a stress on biota additional to natural stresses such as droughts or floods, storms or lack of food. Pollution may increase and exaggerate conditions that are otherwise present. Organisms have developed mechanisms to resist these stresses and to eliminate unwanted substances. These mechanisms induce physiological responses (enzymatic processes of detoxification and neurotransmission or mutagenity) that can be measured analytically and that are called biomarkers. A large research effort is devoted to the measure of these biomarkers and to the interpretation of their occurrence. In controlled laboratory experiments, it is relatively easy to relate biomarker activity to an induced stress, such as the presence of a contaminant in water. In an estuarine ecosystem, stresses are not only caused by a badly identified mixture of pollutants, but also by natural events such as flood, high temperature, high SPM concentrations, salinity changes, tidal currents… That organisms are under some stress in European estuaries and that some pollutants induce enzymatic activity is not contested but, at the moment, the complexity of the natural systems prevents the establishment of relationships between one biomarker and a specific contaminant or its concentration in an estuarine environment from which useful information on the deleterious effects of pollutants at the organism or at its community level could be obtained.

II-4-4. TOXICITY AND CONSEQUENCES

The concern about man-made chemicals is related to their toxicity, whether it is acute and causing death of large proportion of a population, or chronic and causing some health impairment. The aim of any risk assessment is to evaluate the adverse effects caused by a pollutant released in an environment and to indicate whether the exposure levels due to the manufacture or the use of this chemical need to be reduced in order to limit risk to acceptable levels. A chemical that is easily degraded to less toxic compounds can be safely released in large quantities. The release in very small quantities of a bioaccumulable chemical may display toxicity activity even if only at the highest trophic levels of a food chain.

When a compound is biotransformed, its concentrations decrease possibly below detection limits. The products of the biotransformed parent compounds, the metabolites, are usually more soluble and more easily eliminated than the parent chemical, but, unfortunately for organisms, this is not always the case. These metabolites can also be as toxic as, or more toxic than the parent compound. This is why it is important to measure parent compound and metabolites concentrations to evaluate thoroughly the fate and effects of contaminant in an organism and, more generally, in the environment. However the analysis of metabolites of organic contaminants remains a very difficult and even an impossible task because of the various breakdown products from the same parent compound and there polar nature.

The toxicity of a compound is usually thought to be a function of its concentration, and this has lead to the definition of lethal dose (LD_{50}) or lethal concentrations (LC_{50}). Yet, some studies have shown that, rather than body burdens, processes such as rates of uptake, exposure route, or diet during exposure were of importance to evaluate toxicity (Baron *et al.*, 2001). The consequences of the presence of a toxic compound can be multiple. Acute toxicity leads to pathologies and death that can be spectacular but with no more long term effects on an ecosystem than a chronic and less obvious toxicity that leads to a progressive population

diminution. This is observed when fertility is decreased, as with for instance estrogens. It is also observed if pollution in a nursery area causes a high mortality in juveniles. Finally, when living conditions are not suitable, mobile species might “simply pack their bags and move to more pleasant grounds”… If a community is thus displaced by pollution, its role as a predator is removed and its prey (plant or animal) can overdevelop smothering any other form of life unbalancing the local ecosystem.

The species that are present in estuaries are well adapted to the variabilities, in space and time, of their environment. However, they often are at the limit of their tolerance range, and any further disturbance, even small can have serious deleterious effects on a population. Also, the resistance to an accidental pollution is not the same than to a chronic pollution. The former may cause high mortality in a diverse and well established community followed by a rapid recovery, whereas the latter can cause long term damage in a low diversity ecosystem. Weakened by chronic pollution, a community may not be able to cope with any inter annual variations of natural factors such as temperature or salinity.

II-5. SIMPLIFIED FOOD CHAINS

II-5-1. SPECIES DISTRIBUTION: CONTROLLING PARAMETERS

The occurrence of species in an estuary requires that environmental conditions are favourable for the different life stages these organisms may spend in the area. For benthic species, this is conditioned by the nature of the bottom (hard, sand, silt…) and for all species it is conditioned by physico-chemical parameters such as salinity, temperature, SPM concentration and level of dissolved oxygen, as discussed earlier. Outside their range of tolerance for each parameter, species cannot develop. However, large populations of some genus may grow at the lower or upper limits of their tolerance range if this is outside the tolerance range of a predator or of a species competing for the same food source. This is, for instance, how the relative distribution of 3 species of polychaete worms present in European estuaries can be interpreted. *Nereis virens* is larger and more voracious than the other species but intolerant of low salinities. *N. diversicolor* can live in a wide range of salinities but is excluded from high salinities by *N. virens*. *N. succinea* forms an intermediate species but may disappear completely with low temperatures (McLusky, 1981). Another example is given by the small crustaceans of the *Gammarus* genus: *G. salinus* has a mid estuarine range overlapping *G. locusta* at the seaward end of its range and *G. zaddachi* at the river end. These organisms occupy the same trophic level, in different haline zones of the estuary.

Pollution is an additional stress that further limits species distribution. Hence some species will disappear quickly from polluted areas, whereas others (*Arenicola marina*, *Nereis diversicolor*) will be the last living organisms to be observed and the first settlers if conditions improve again after a pollution event that has led to complete removal of life. The recolonisation of polluted areas is generally done by species with short life spans and rapid reproduction cycles.

The availability of food is also a prerequisite for an organism to colonise a habitat. In estuaries a large number of taxa feed on phytoplankton and detritus and are prey to carnivorous animals. These animals are essential in the transfer of energy between plants and detritus to higher trophic levels. Carnivores feed on an array of prey, varying with the seasons and are essentially opportunist. Examples of species where adults feed on their juvenile are frequent, and larvae of big organisms can serve as food to animals they will prey upon as adults. To be an exact description of the existing trophic interactions, a food web would need to be dynamic, varying with seasons and possibly with the tides.

II-5-2. SPECIES DISTRIBUTION: IDENTIFICATION

The study of contaminant behaviour along a food web requires simple examples of suitable and relevant food webs. A selection of representative or important species present in European estuaries seems useful at this point as it would be a bit tedious and not necessarily informative to list all organisms that can be found in European estuaries together with their trophic relationships. Several criteria could be used to define the “representativity” or the importance of a species: biomass, frequency, ecological role, geographical distribution, economic value… Ranking these criteria is necessarily biased by the purpose of the study and the data available. Here, it was decided to base the study on target species and on their prey or predators. The target species has to be a carnivorous fish to allow the observation of

bioaccumulation if it occurred. It seems logic to choose a target species amongst the most common fish found in Europe. The frequency of fish caught in estuaries as reported by IECS (2000) gave an indication on which species visit or inhabit estuaries regularly. Figure II-10 suggests that this is the eel (*Anguilla anguilla*). However, this fish is not suitable for a study of estuarine biota contamination because it is essentially a migratory fish, which uses estuaries just to reach its spawning grounds in freshwaters. The xenobiotic concentration that could be measured in its tissues is more likely to be representative of seawater or freshwater than on estuarine contamination.

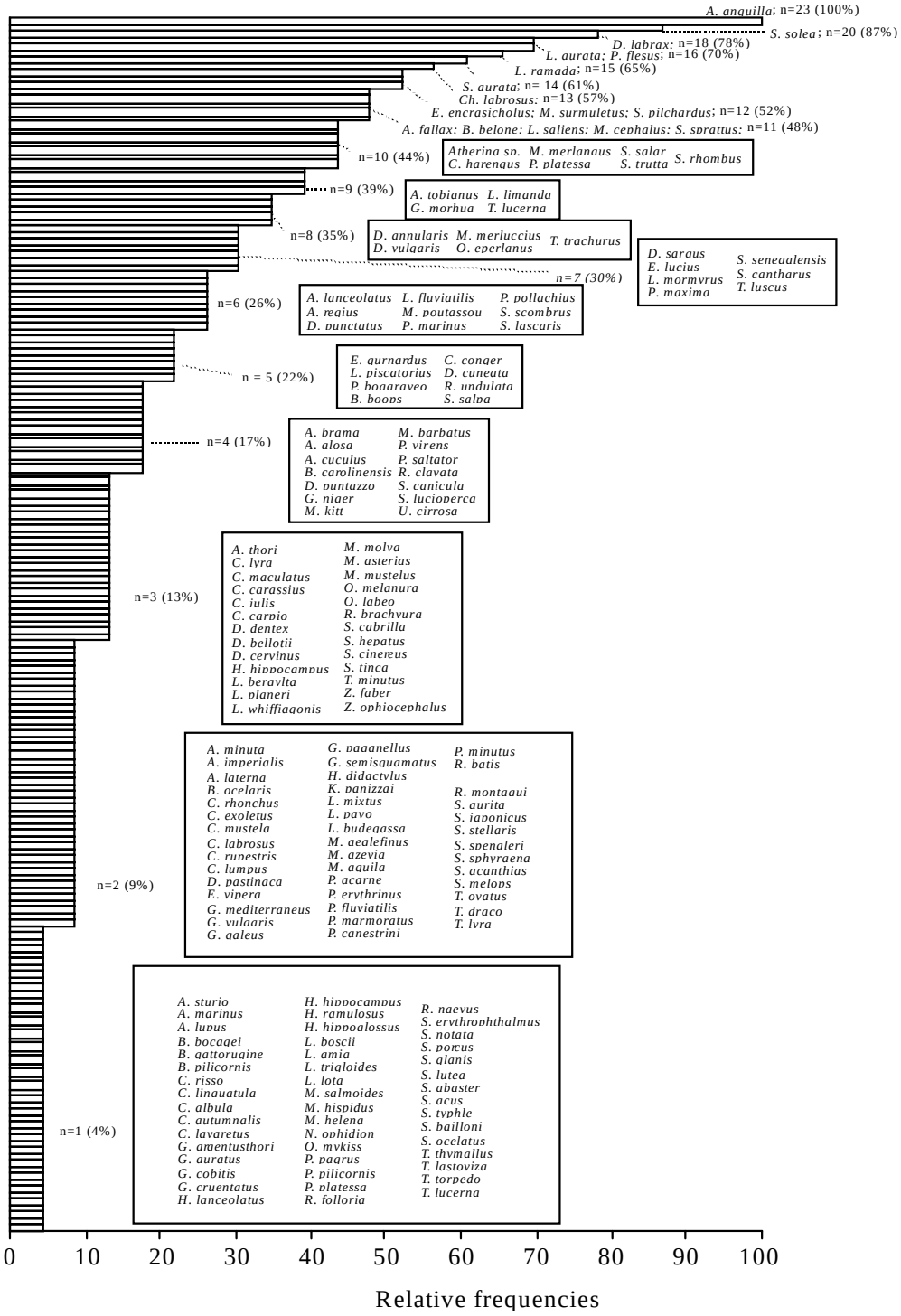

Figure II-10: Frequency of fish catches relative to the number of times eels have been caught in the 29 European estuaries included in IECS (2000) study. This figure is part of the IECS (2000) document.

The next 6 most frequently caught fishes are the sole (*Solea solea*), the sea bass (*Dicentrarchus labrax*), mullets (*Liza auratus*, *Liza ramada*, *Chelon labrosus*), the flounder (*Platichthys flesus*) and the gilthead (*Sparus aurata*). These six fishes can be grouped as round fishes (sea bass, mullets and gilthead) and flat fishes (sole and flounder). Mullets are carnivorous but also vegetarian, a significant part of their diet being benthic diatoms (Mohr, 1986), and are not therefore good examples of top predators. The northern limit of gilthead is the north of the Bay of Biscay. Sea bass is present in most areas in Europe, but does not seem to be present in fjords where its predatorily role may be played by cod (*Gadus morhua*). Both sea bass and cod fish feed on copepod while juveniles. Their diet as they grow bigger is made of small fish, shrimps and other crustaceans such as gammarids. The proportion of fish in their diet increase with age and cannibalistic behaviours are reported. Flat fish occupy a different ecological niche, live closer to the sea bottom, and feed on benthic organisms. This can be seen from the tables below that show some of the prey reported in the literature for flat fish, including dab and plaice . (Tables II-5 to II-8), and for the sea bass (Table II-9).

Abra alba Bivalvia	*Cultellus pellucidus* Bivalvia	*Macoma balthica* Bivalvia	*Mysella bidentata* Bivalvia	*Tellina tenuis* Bivalvia	*Bathyporeia pelagica* Crustacean
Eurydice pulchra Crustacean	*Pagurus berhnardus* Crustacean	*Acrocnida brachiata* Ophiuroidea (brittle stars)	*Amphiura filiformis* Ophiuroidea (brittle stars)	*Ophiotrix fragilis* Ophiuroidea (brittle stars)	*Ophiura texturata* Ophiuroidea (brittle stars)
Arenicola marina Polychaete	*Nephtys hombergii* Polychaete	*Owenia fusiformis* Polychaete			

Table II-5: Some of dab (*Limanda limanda*) preys (Gunnarsson *et al*., 1999; Loizeau and Ménesguen, 1993; MarLIN, 2001).

Abra alba bivalvia	*Macoma balthica* bivalvia	*Mytilus edulis* bivalvia	*Pomatoschistus microps* bony fish	*Bathyporeia spp.* crustacean	*Carcinus maenas* crustacean
Crangon crangon crustacean	*Eurydice pulchra* crustacean	*Eurytemora hirundoide* crustacean	*Palaemon spp.* crustacean	*Arenicola marina* polychaete	*Lanice conchilega* polychaete
Nephtys spp. polychaete	*Nereis diversicolor* polychaete	*Owenia fusiformis* polychaete	*Pectinaria koreni* polychaete	*Copepods* zooplankton	

Table II-6: Some of flounder (*Plathychthys flesus*) preys (Anonymous, 1997; IECS, 2000; MarLIN, 2001).

Boccardia ligerica annelid	*Macoma balthica* bivalvia	*Bathyporeia spp.* crustacean	*Eurydice pulchra* crustacean	*Arenicola marina* polychaete	*Eurydice pulchra* crustacean
Nereis diversicolor polychaete	*Pectinaria koreni* polychaete				

Table II-7: Some of sole (*Solea solea*) preys (Anonymous, 1997; IECS, 2000; MarLIN, 2001)**.**

Boccardia ligerica annelid	*Abra alba* Bivalvia	*Cerastoderma edule* bivalvia	*Macoma balthica* bivalvia	*Mytilus edulis* bivalvia	*Tellina tenuis* bivalvia
Pleuronectes platessa bony fish	*balanus spp.* crustacean	*Bathyporeia spp.* crustacean	*Crangon crangon* crustacean	*Eurydice pulchra* crustacean	*Ampharete* polychaete
Arenicola marina polychaete	*Eteone longa* polychaete	*Lagis koreni* polychaete	*Lanice conchilega* polychaete	*Melinna palmata* polychaete	*Nephtys spp.* polychaete
Nereis diversicolor polychaete	*Owenia spp.* polychaete	*Pectinaria koreni* polychaete	*Pygospio elegans* polychaete		

Table II-8: Some of plaice (*Pleuronectes platessa*) preys (Anonymous, 1997; Bayne, 1976; IECS, 2000; Trevallion *et al.*, 1970)

Prey	Description	Prey	Description
Cerastoderma glaucum	bivalvia	Copepods	crustacean
Abra ovata	bivalvia	*Lekanesphaera hookeri*	crustacean
Liza ramada	bony fish	*Microdeutopus gryllotalpa*	crustacean
Pomatoschistus microps	bony fish	*Diamysis bahirensis*	crustacean
Chelon labrosus	bony fish	*Carcinus maenas*	crustacean
Dicentrarchus labrax	bony fish	*Palaemonetes varians*	crustacean
Pomatoschistus minutus	bony fish	*Crangon crangon*	crustacean
Gobius paganellus	bony fish	*Paragnathia formica*	crustacean
Liza aurata	bony fish	*Mesopodopsis slabberi*	crustacean
Atherina presbyter	bony fish	*Nereis diversicolor*	polychaete
Gobius niger	bony fish	*Pectinaria koreni*	polychaete

Table II-9: Some of sea bass (*Dicentrarchus labrax*) preys (Anonymous, 1997; Costa, 1988; IECS, 2000). This list includes prey of different age sea bass.

The list of preys presented in these tables do not pretend to be exhaustive and they present preys without ranking them by importance in the fish diet. Yet, there are sufficient to show some main trends:

- flat fish feed essentially on
    - polychaete worms (*e.g. Arenicola marina*, *Nereis diversicolor*, *Owenia fusiformis*, *Nephtys hombergii*)
    - bivalves (*e.g. Macoma balthica*, *Abra alba*, *Pectinaria koreni*)
    - small crustaceans (*e.g. Bathyporeia pelagica*, *Eurydice pulchra*)
- round fish feed essentially on:
    - crustaceans (*e.g. Crangon crangon*, *Mesopodopsis slabberi*)
    - small or young fish (*e.g. Pomatochistus microps*)

These preys feed essentially on detritus, phytoplankton and zooplankton, either as suspension feeders (*Lanice*, *Owenia*) or deposit feeders (*Nephtys*, *Bathyporeia*), or are carnivorous (*Pomatochistus*, *Crangon*), although most can adapt their feeding mode if their preferred method is not profitable enough.

The zooplankton species the most often encountered in European estuaries are *Eurytemora spp.* and *Acartia spp.*

The contamination of the target species depends on the levels of contamination of its prey but also on the species ability to eliminate man made chemicals. Round fish such as the sea bass feed on crustaceans and fish that live and feed in the water column or at the sediment

interface and that are able, to some extent, to metabolise chemicals. Flat fish live in contact with the sediment and feed on organisms that live buried in sediment some of which have little ability to metabolise xenobiotics. These differences are expected to lead to different levels of contamination. This needs to be taken into account while modelling the behaviour of contaminants in estuarine food webs and justifies the use of two types of food chains (one for flat, one for round fish) in the evaluation of the transport of chemicals in estuaries biotic compartment. The simple food chain discussed above and schematically represented on Figure II-11 can be used as examples of European estuarine food chains. They are not the "virtual" food chains needed for the development of the GEMCO model but must be seen as their "representatives". They will be used during design, calibration and validation of the GEMCO model. This modelling work will be described in subsequent chapter in this report.

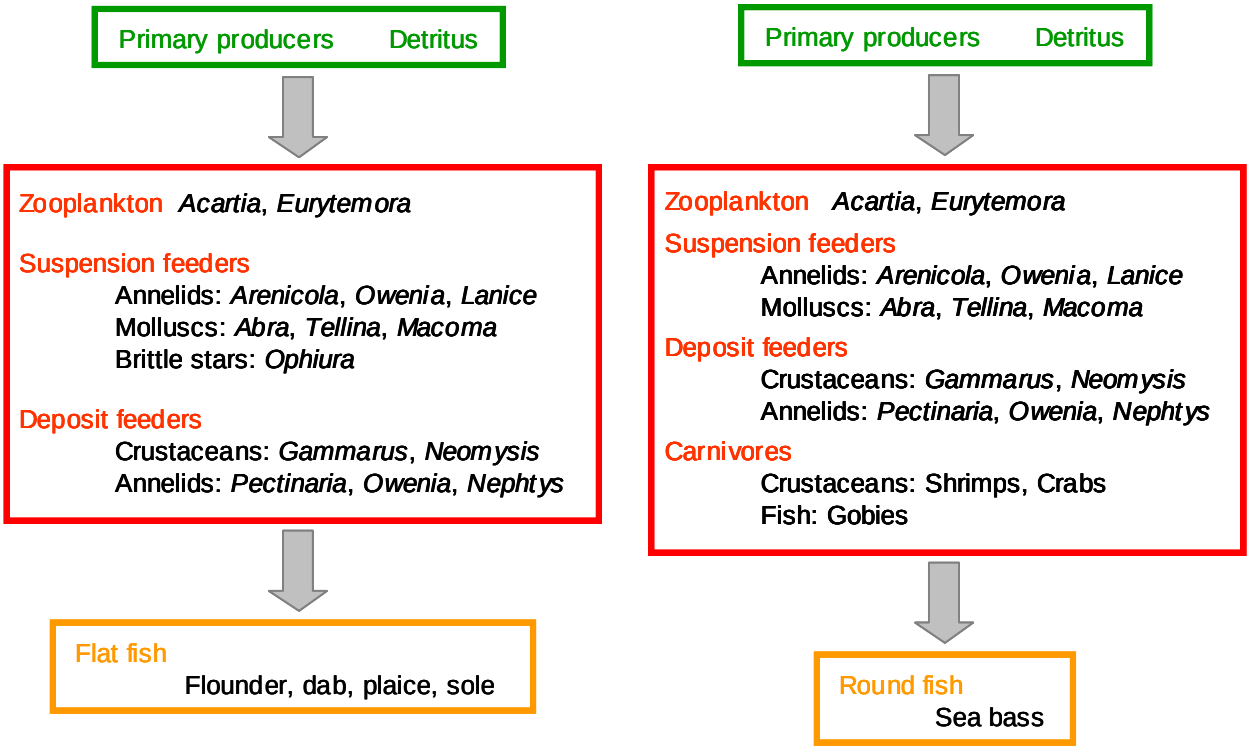

Figure II-11: Suggested simple food chains for flat and round fishes in European estuaries.

II-6. CONCLUSION AND PERSPECTIVES: THE BIOLOGY IN THE GEMCO MODEL

The aim of the work presented here was to review the processes that control organism contamination in order to model the fate of contaminants in European estuarine food chains. For the specific purpose of the GEMCO programme a simple food chain is required that may represent food chains from the Mediterranean, the Eastern Atlantic coast up to the Norwegian fjords and the Baltic Sea.

It is suggested that **two typical food chains are to be considered: one pelagic** one, whose top predator is the sea bass**, and one benthic one** whose top predator is a flat fish, such as the flounder or the dab. These fish prey respectively on suprabenthic and benthic organisms that are feeding on zooplankton, detritus and primary producers. Such food chains are a gross simplification of real food webs, but this is believed to be acceptable here for a number of reasons. First, knowledge of real food webs and of the contamination of all the species they include is insufficient to model them. It is therefore necessary to make some simplifications, bearing them in mind when interpreting the model results. Also previous work (Loizeau and Abarnou, 1994; Loizeau *et al*., 2000) has shown that a simplified food chain was sufficient to model the bioaccumulation of PCB in dab and in the sea bass in the Seine estuary and in the Bay of Seine. In the bioaccumulation process, each link of the food chain acts as a preconcentration step, and initial work done within the GEMCO programme suggests that a chain containing 3 links (two types of primary consumers and one top predator) is sufficient to represent PCB bioaccumulation in sea bass. However, the differences in feeding behaviour and food sources between benthic and suprabenthic organisms require that a pelagic and a benthic food chain are considered. Suprabenthic organisms are more likely to feed on suspended material (zooplankton, phytoplankton and SPM) than benthic organisms, which can also feed on settled particles. The contamination of these two types of particles can be different and may lead to different contamination in the top predator. The food chains chosen here are based on detritivores because in European estuaries these organisms are the main link between the lowest trophic level (primary producers and non living material) and higher ones. Benthic detritivores also live in soft substrate habitats (sand and mud), which are the most extended, and the most productive of benthic habitats in tidal estuaries.

A correct evaluation of top predators contamination has to take food chains into account because food is a major contaminant source for these organisms while uptake from water is relatively more important for organisms of the lowest trophic levels. The approach chosen here is to consider for every link of the food chain all contaminant uptake and elimination processes, an approach that favours the concepts of biomagnification and bioaccumulation over that of bioconcentration as the latter only includes contaminant uptake from water. Amongst the elimination processes, biotransformation can be neglected for persistent compounds such as PCBs but must be taken into account for less persistent contaminants, such as PAHs. The degree of persistence of a compound is a function of its chemical reactivity as well as a function of the organism ability to transform and eliminate it. This ability is often more developed in vertebrates than in invertebrates that lacks the enzymatic systems required to transform compounds into more soluble and therefore more easily eliminated chemicals. The importance of particles as food source at the lowest level of the food chains is one of the reasons why a good understanding of particles dynamics is necessary before it might be possible to evaluate the contamination in top predator fish.

Particles transport is also important because it shapes the habitats: where currents velocities are low, particles settle and create the mud flats inhabited by benthic organisms. In the water column, the combination of processes such as the tidal pump, flocculation, turbulence at the sediment water boundary, particles input from the river and from the sea tend to create a turbidity maximum where the concentration of suspended material is generally so high that it can damage organism respiratory systems and prevents photosynthesis because light cannot penetrate the water column more than a few centimeters. This is a zone where biological activity might be low but where important physico-chemical changes in the water occur and cause compounds to adsorb on or desorb from particles.

These reactions as well as the metabolism rates of living organisms are dependent on environmental factors such as the salinity, the water temperature, the level of dissolved oxygen, and on the suspended particulate matter concentration just discussed. Each of these factors is highly variable in tidal estuaries and contributes in creating a wide variety of habitats, which a relatively small number of species take advantage of at various stage of their life cycle.

The effects of each of these factors will have to be considered for the setting up of the GEMCO food web model. The data required for calibrating will be issued from available studies on the organisms identified for the simple food chains of the sea bass and of the flat fish suggested in this report. An important modification of the already existing sea bass and dab food web models will be to introduce biotransformation. This will require identifying which and how chemical properties can be significantly correlated to biotransformation. This process will also be evaluated as a function of the trophic level of the food chain, so that the differences between the enzymatic systems of mollusc, crustaceans and fish will be accounted for in the model. All this work will be detailed in the following part in this report.

III. THE PRIMARY PRODUCTION IN EUROPEAN ESTUARIES

III-1. THE SEASONAL CYCLES OF THE CHLOROPHYLL IN ESTUARIES

Two different types of measurements are carried out in order to describe phytoplankton occurrence in an aquatic environment. The first one is the primary production, a measure of how much phytoplankton grows within a given area and within a given period of time. This can be expressed as mg $C.m^{-2}.day^{-1}$. The second one, the biomass, is a measure of how much phytoplanktonic material is present at a given time in the water. This is often represented as a mass of chlorophyll a (Chla) per volume of water. The unit of this measure is then µg Chla . l^{-1}. Biomass is the measurement required in GEMCO food web model but both biomass and primary production are reported in the literature and have been used to derive the information described below.

The phytoplankton density present at any point and at any time in an estuary is the result of:

- the hydrodynamic transport of phytoplankton produced in the river and in the sea end of the estuary,
- the phytoplankton that has been produced within the estuary (local production),
- the phytoplankton mortality, whether this is caused by a change of salinity, zooplankton grazing or normal cell senescence.

Phytoplankton production in the estuary, in the river and in the adjacent marine area depends mainly on two environmental parameters: available nutrients and light. Temperature also influences phytoplankton production, but is rarely as limiting as nutrients and light can be, especially in the temperate areas the GEMCO model will be applied to. As only gross approximations of phytoplankton production and biomass are required, the only nitrate is considered because is has limiting effect on the primary production in estuaries. The approach followed for nitrate can be, if required, used for phosphate or silicate, other nutrients known to have limiting effects in coastal areas. An expert knowledge of the estuary will allow to choose which nutrient it is better to use.

In the GEMCO generic model, nutrients, light, zooplankton grazing are not modelled. Temperature is forced. In these conditions, a number of assumptions have to be taken and approximations have to be made in order to represent the chlorophyll concentration in water, a parameter required for the food web model. The variables included in the model have been used as much as possible, but a realistic representation of phytoplankton biomass cannot be obtained without using nutrient concentrations. So it will be necessary to introduce nutrient variables, representing nitrate concentration.

III-2. GENERAL SHAPE OF THE PHYTOPLANKTON DISTRIBUTION

III-2-1. TEMPORAL VARIATIONS

III-2-1-1. Incident light and nutrient limitation

In presence of sufficient concentrations of nutrients, light is the triggering factor for algal blooms. The first algal blooms of the year are usually observed on calm sunny days in spring. In rivers and estuaries, nutrients are usually in sufficient concentrations to allow primary production to persist over the summer and where high load of suspended matter do not block the light, the annual cycle of chlorophyll follows the pattern shown with the plain line on Figure III-1. As the river water carrying its load of nutrients is diluted into relatively nutrient-poor seawater, the pattern of the seasonal cycle of chlorophyll a is progressively modified. Eventually, a pattern common at sea is observed: A sharp spring bloom depletes the water from its nutrients and the combination of low nutrient availability and zooplankton grazing pressure prevents any further growth until the first autumn storms. These lead to a renewal of nutrient in the surface layer of the water column and allow algae to take advantage of the last periods of sufficient light to grow again producing an autumn bloom. Such a cycle is represented by the dashed line on Figure III-1.

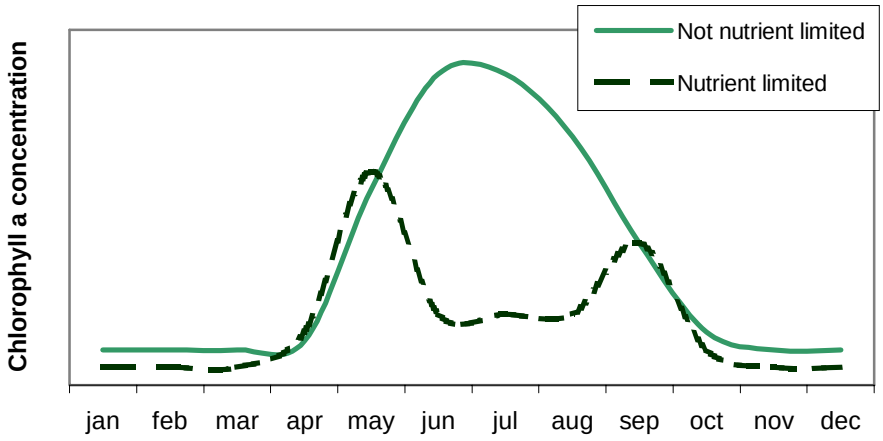

Figure III-1 General pattern of chlorophyll a concentration with and without nutrient limitation *(dashed and plain lines respectively).*

II-2-1-2. Incident light and temperature

The incident light reaching the water surface is a function of the season but is highly influenced by the cloud cover. Its graphic representation appears as a rather noisy signal. The average of this signal can be represented by mathematical functions (Hoch, 1995). Such a function could be used here but it can also be replaced satisfactorily by temperature, a variable required elsewhere in the GEMCO model, as the increase and decrease of temperature are direct consequences of the increase and decrease of the incident radiation. Due to water thermal inertia, maximum water temperatures are reached several weeks after the longest days are gone, but this lag is more or less constant over the years. The substitution of the light by the temperature is particularly interesting as temperature is a parameter much

more commonly and much more easily measured than incident light and can simply be represented by a cos function. Also, temperature is much slower to respond to weather variations, and somehow integrates them. This can be seen as an advantage when building a generic estuary.

The comparison of temperature and chlorophyll data from various estuaries (Seine, Loire (RNO, 2001), Kungsbacka fjord (Olsson and Ölundh, 1974)) suggests that in first approximation, chlorophyll concentrations and primary production start increasing in spring when water temperature is equal to about 60% of its maximum annual value. Maximum chlorophyll concentrations are observed before temperature reaches its maximum. In autumn, chlorophyll concentrations drop to their minimum when temperature falls to values below 60% of the annual maximum Figure III-2.

At sea, the first phytoplankton blooms occur earlier, because the light regime is more favourable (Cugier, 1999). The difference between the timings of the marine and riverine phytoplankton blooms is however less significant when monthly chlorophyll concentrations are considered, as it will be the case for the GEMCO model.

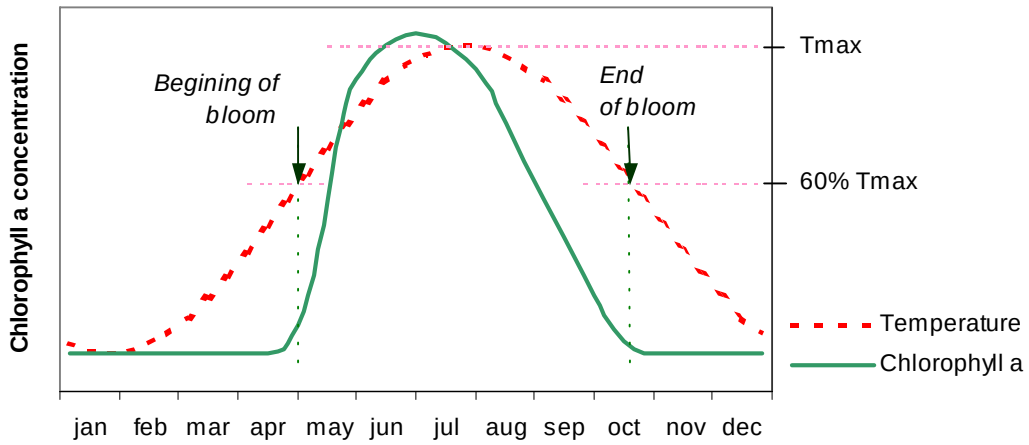

Figure III-2: Chlorophyll and temperature seasonal cycles. The temperature cycle is here simulated by a cos function.

Temperature has also a direct effect on phytoplankton growth rate and therefore production. This can be expressed as:

$$\mu_T = \mu_0 \times e^{0.07T} \qquad \text{(III-1)}$$

Equation III-1: Phytoplankton growth rate

where μ_T is the phytoplankton growth rate at temperature T and μ_0 is the phytoplankton theoritical growth rate at T = 0°C (Cugier, 1999). The direct effect of temperature cannot be observed in the data available for different estuaries, probably because it is much less important than that of light and nutrient availability; so Equation III-1 will not be used here.

III-2-2-1. Effect of suspended material

The light available for phytoplankton growth is directly related to the amount of incident light and decreases rapidly in the water column due to its absorption by suspended particulate matter (SPM), and to a lesser extent to its absorption by the water itself. In an estuary, SPM levels can reach several grams of material per litre of water, and SPM influence on the available light largely dominates over the absorption of the light by water, which will be neglected here. Data on phytoplankton in coastal water suggest that SPM concentration greater than 4 $mg.l^{-1}$ can prevent the development of large blooms (Aminot *et al.*, 1997; Cugier, 1999). Literature however exits that describes primary production in turbid estuaries. It has been shown that production was possible in turbid waters if the water depth, or the upper layer of a stratified water column, was less than the critical depth. Critical depth, Z_m, is a function of the depth of the euphotic zone, Z_{eu} (Fichez *et al.*, 1992; Goosen *et al.*, 1999; Sverdrup, 1953): When the ratio between the two is between 6 and 20, primary production is possible (Fichez et al., 1992). These authors have used a value of 10 in the Great Ouse estuary; this value will be used here too.

The euphotic zone depth is related to the SPM concentration in water because particles absorb a large part of the light that comes through the water. Data from (Fichez *et al.*, (1992) suggest that the following relationship applies in estuarine waters:

$$Zeu = -1.2\log[SPM] + 2.9 \qquad \text{(III-2)}$$

Equation III-2: Relation between SPM concentration and the maximum depth of the euphotic zone.

where Z_{eu} is expressed in m and SPM concentration in $mg.l^{-1}$. Equation III-2 shows that for SPM concentration greater than 200 $mg.l^{-1}$ the euphotic zone is reduced to less than 15 cm and the euphotic zone is negligible for any SPM concentrations greater than 250 $mg.l^{-1}$.

SPM	Z_{eu}	$Z_m = 10\ Z_{eu}$
$mg.l^{-1}$	m	m
10	1.70	17
20	1.34	13
30	1.13	11
50	0.86	8.6
70	0.69	6.9
100	0.50	5.0
125	0.38	3.8
150	0.29	2.9
160	0.26	2.6
175	0.21	2.1
200	0.14	1.4
250	0.02	0.2

Table III-1: Euphotic zone and critical mixing zone evaluated from SPM concentrations using Equation III-2 and a ratio Z_m/Z_{eu} of 10.

The effect of this light limitation will be seen on the distribution of the phytoplankton in the estuary during blooms. Where SPM concentrations are high, particularly in the maximum turbidity zone (MTZ), there will be very little primary production and the phytoplankton biomass will be expected to be minimal. Upstream and downstream of the MTZ, phytoplankton blooms. At the sea end of the estuary, the decrease in phytoplankton density is caused by nutrient limitation. This distribution is schematised on Figure III-3.

In the generic model, Z_m gives the maximum depth above which a net primary production can be observed. If the water column is well mixed, primary production occurs in areas where the total water column height is less than or equal to Z_m. If the water column is stratified, primary production occurs if the upper layer thickness is at less than or equal to Z_m.

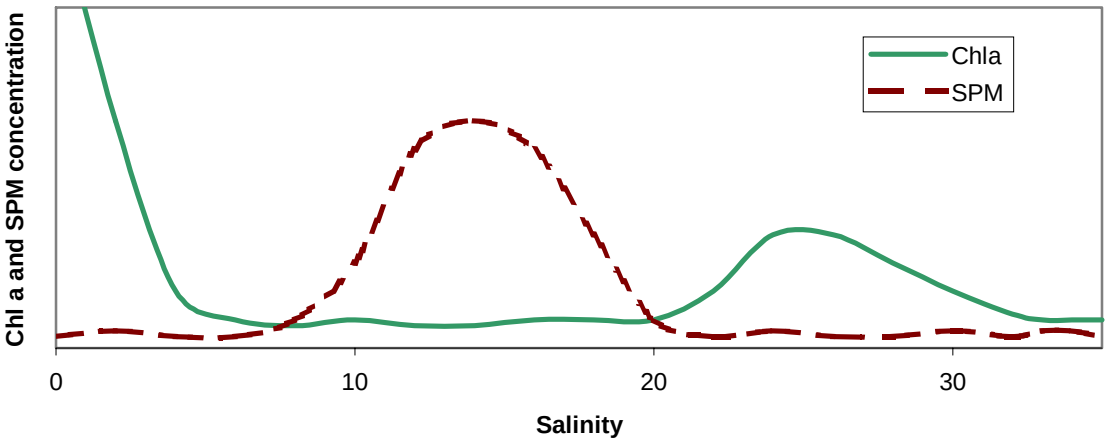

Figure III-3: Typical summer distribution of chlorophyll and SPM along a salinity gradient in a turbid estuary. At low salinity, high levels of chlorophyll are due to the presence of freshwater phytoplankton. Phytoplankton growth is limited at intermediary salinity because of the presence of high SPM concentrations. At the sea end of the estuary, the growth of marine phytoplankton generates an increase in chlorophyll until dilution of freshwater by seawater causes the nutrients to become limiting.

III-2-2-2. Advection

In any point of an estuary, the phytoplankton present might have three possible origins: the river, the sea and local production. Observations show that at a given point in the estuary, chlorophyll biomass can vary with tidal cycles. Fichez *et al.*, (1992) and Goosen *et al.*, (1999) have reported high chlorophyll concentrations at low tides in the Great Ouse and the Westerschelde estuaries, whereas model results in the Seine estuary clearly suggest an input of marine phytoplankton at high tide (Cugier, 1999). However, Cugier's model does not simulate freshwater phytoplankton biomass. It is not therefore surprising that its results show a minimum chlorophyll concentration at low tide. In the Elbe and in the Gironde, no clear relationship appears between salinity and chlorophyll a concentrations (Goosen *et al.*, 1999). All these reports suggest that local production does not always yield the local biomass and that advection is an important process that transports phytoplankton along an estuary. The evaluation of phytoplankton biomass at any point of an estuary must take into account both processes. Here, it is suggested that advection of phytoplanktonic material is represented by considering phytoplankton as a passive tracer in an hydrodynamical model. Within GEMCO, this can be done within Delft Hydrodynamic model.

III-2-3. ESTIMATIONS OF CHLOROPHYLL CONCENTRATIONS

III-2-3-1. Chlorophyll a levels in river water

In rivers, phytoplankton production is not nutrient limited and SPM concentrations are relatively low. Maximum production occurs in the middle of the summer following closely the temperature cycle and production can become limited by phytoplankton self-shading (light limitation caused by the adsorption of light by phytoplankton cells). The maximum chlorophyll a concentration should be generally measured in river. In the present model, freshwater phytoplankton is assumed to be produced in the river and is assumed to survive, but with no local production, in brackish water up to salinity of 8. This is deduced from the rapid decrease of chlorophyll a concentrations in the low salinity parts of estuaries. At S > 8, it can be safely assumed that there are no more living freshwater phytoplankton cells in the estuaries. Therefore the maximum freshwater phytoplankton chlorophyll a that can be found in an estuary is given by the equation:

$$\text{if } S < 8, \qquad [Chla_{fw}] = -\frac{[NO_3^-]}{40}\cdot(S-8) \qquad \textit{(III-3)}$$

$$\text{if } S > 8, \qquad [Chla_{fw}] = 0$$

Equation III-3: Freshwater chlorophyll maximum concentration as a function of salinity. Chlorophyll a concentration is expressed in $\mu g.l^{-1}$.

III-2-3-2. Chlorophyll a concentrations at sea

At sea (S > 35), phytoplankton production becomes nutrient limited. and it has been shown that the maximum chlorophyll a concentration in $\mu g.l^{-1}$ is in the same order as the nitrate concentration in $\mu mol.l^{-1}$ before the bloom (Aminot *et al.*, 1997). Winter nitrate concentration in European coastal waters is about 10 $\mu mol.l^{-1}$. This yields to maximum chlorophyll a concentration of about 10 $\mu g.l^{-1}$ during the spring bloom that lasts for at most one month. Summer concentrations are about 3 $\mu g.l^{-1}$ and the autumn bloom, with concentrations around 7 $\mu g.l^{-1}$ Chla, occurs just before the temperature falls below 60% of its maximum value. Winter concentrations are to be set at 0.5 $\mu g.l^{-1}$.

These chlorophyll a concentrations are to be used as boundary conditions in the model if nutrients are limiting at the model sea boundary and chlorophyll a must be treated like a passive tracer within the estuary. If nutrients are not limiting, the concentrations of chlorophyll will be calculated as described in the next section (III.2.3.3).(Nutrients are limiting if $F_{Nt} < F_{light}$; cf.equations III-6 and III-7).

III-2-3-3-Chlorophyll a concentration in the turbid zone of an estuary

In the turbid part of the estuary the evaluation of chlorophyll a concentration must take into account the limiting effects of the light and of the nutrients. Also, in a system that is

permanently flushed, the residence time of particles has to be considered: if primary production is slow compared to the time during which phytoplankton cells have remained in the estuary, no significant biomass can develop. Hence in any water body of depth Z, the maximum biomass that can be observed is:

$$[C_{phyto}]_{max} = \frac{P_{max} \times T_{res}}{Z} \quad \text{(III-4)}$$

where $[C_{phyto}]_{max}$ is the maximum concentration of phytoplankton carbon that can be produced with a production rate of P_{max} during the residence time T_{res}. Units of all parameters used in the present discussion on chlorophyll concentration are given in Table III-3.

As mentioned above, production can be limited by light and by nutrients. It is usually accepted that it is either one of these parameters that limits production and this is mathematically expressed by:

$$P = P_{max} \cdot \text{Min}\,(F_{light}, F_{Nt}) \quad \text{(III-5)}$$

where Min (F_{light}, F_{Nt}) is the minimum value of either function F_{light} and F_{Nt}. These functions vary from 0 to 1. P_{max} is the maximum production that might be observed in coastal and estuarine waters. This is reported to be about 4 g $C.m^{-2}.day^{-1}$ (Bougis, 1974). This value is higher than values reported for European coastal waters (Loquet *et al*., 2000; Videau *et al*., 1998). Also, since the present approach does not include chlorophyll a loss terms (phytoplankton cells senescence and grazing) a lower default value for maximum production is applied in the generic model of 1 g $C.m^{-2}.day^{-1}$. P is the maximum production rate observed in the conditions of the generic estuary with given SPM and nitrate concentrations when for example nitrate is the limiting nutrient.

F_{NO3} takes the form of a Michaelis - Menten equation:

$$F_{NO_3} = \frac{[NO_3^-]}{[NO_3^-] + K_{NO_3}} \quad \text{(III-6)}$$

where K_{NO3} is the nitrate half saturation constant for phytoplankton, here set to 2 $\mu mol.l^{-1}$, the value reported for diatoms by Cugier (1999). It is otherwise equal to 3 for dinoflagellates. The difference between the two species is not relevant nor is the difference between 2 and 3 for K_{NO3} within the generic model.

The nitrate concentration is to be calculated at any point of the estuary assuming that dissolved nitrate has a conservative behaviour in the estuary. Its distribution along the salinity gradient is as a result controlled by its concentrations in the river and in the sea and the dilution of river water into seawater. The sea winter concentrations can be assumed to be around 10 $\mu mol.l^{-1}$ at salinity of 35 in North European waters and around 5 $\mu mol.l^{-1}$ at salinity of 38 in the Mediterranean. Concentrations in rivers depend on the rivers and it would be better if the user could enter a value. If not available, three levels of river contamination can be offered:

- Pristine rivers: 50 $\mu mol.l^{-1}$ (Which may not exist any longer in Europe).
- Averagely contaminated river: 300 $\mu mol.l^{-1}$
- Highly enriched river (might shows signs of eutrophication): 500 $\mu mol.l^{-1}$.

Results from various IFREMER studies (Aminot *et al*., 1997; Cugier, 1999) show that light is not limiting in spring when SPM concentrations are below 4 mg.l^{-1}. According to the regression proposed by Fichez *et al*., (1992) for the euphotic, in the Great Ouse, there is no sufficient light to support production at SPM concentrations greater than 200 mg.l^{-1}. The light decrease between the surface and the bottom of the euphotic zone is known to follow an exponential shape. The light limiting functions reported in the literature do not give satisfactory results compared to these two observations. The above remarks can be rewritten into the following assumptions, from which a new function F_{light} can be derived:

$F_{light}=10^{x}$

- x is a linear function of SPM concentrations: $x=a[SPM]+b$
  - if SPM < 4 mg.l^{-1}, F_{light} = 1, so x = 0.
  - if SPM = 200 mg.l^{-1}, F_{light}= 0.001, so x = -3.

hence,

$$x=\frac{-3}{196}\cdot[SPM]+\frac{12}{196}$$

and the derived light limiting function is defined by

$$\begin{aligned} &\text{if SPM} < 4 \text{ mg.l}^{-1}, && F_{light}=1 \\ &\text{if SPM} > 4 \text{ mg.l}^{-1}, && F_{light}=10^{\left(\frac{-3}{196}\cdot[SPM]+\frac{12}{196}\right)} \end{aligned} \qquad \text{(III-7)}$$

This equation means that for any SPM values less than 4 mg.l^{-1}, there is no light limitation. For greater SPM concentrations, light limitation increase and production is reduced to 0.1% of its maximum value at SPM concentrations of 200 mg.l^{-1}.

The production rate P can be used to evaluate the maximum phytoplankton carbon concentration in the estuary. At any point of the estuary, this is obtained by applying using Equation III-7 the summer residence time for T_{res}. The conversion to Carbon concentration is given by using Equation III-8 established by (Moal, 1980):

$$[C_{phyto}]=40\times[Chla] \qquad \text{(III-8)}$$

Hence the maximum concentration in chlorophyll a at any point is given by the equation:

$$[Chla]=\frac{T_{res}\cdot P\cdot Min(F_{light},F_{NO3})}{40\cdot Z} \qquad \text{(III-9)}$$

The chlorophyll concentration at any time is assumed to be proportional to the chlorophyll maximum concentration following the annual cycle described in section III-2-1-1 and shown on Figure III-1. There are no needs, and probably no possibility to calculate daily values, so monthly values will be evaluated. This is done by multiplying the maximum chlorophyll concentration calculated as indicated above by the coefficients given in Table III-2.

If nutrients are not limiting (Figure III-4) the increase in chlorophyll a in spring occurs within two months and the decrease to winter concentration occurs in three months, maximum values are observed for 2 months.

If nutrients are not limiting	Coefficient	If nutrients are limiting	Coefficient
Winter $T < 0.6\ T_{max}$	0.15	Winter $T < 0.6\ T_{max}$	0.08
Spring $0.6\ T_{max} < T < 0.9\ T_{max}$	Month 1 = 0.2 Month 2 = 0.6	Spring If $T = 0.6\ T_{max}$	1
Summer $T > 0.9\ T_{max}$	1	Summer $T > 0.6\ T_{max}$	0.3
Autumn $0.6\ T_{max} < T < 0.9\ T_{max}$	Month 1 = 0.8 Month 2 = 0.5 Month 3 = 0.3	Autumn $T = 0.6\ T_{max}$	0.6

Table III-2: Coefficients to be applied to the maximum chlorophyll a concentration to obtain annual cycles.

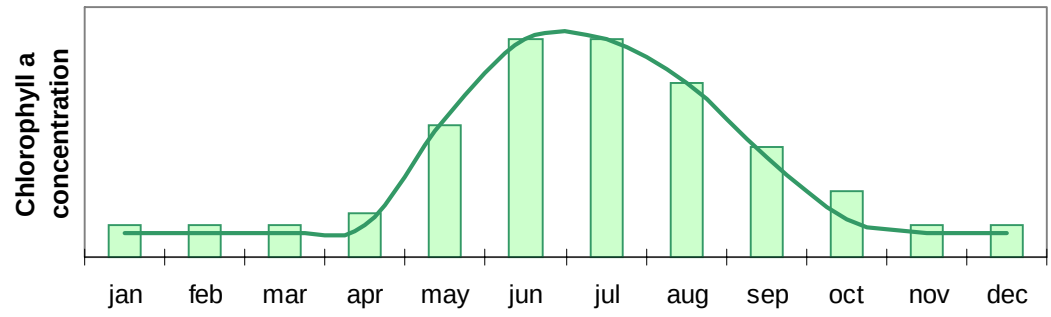

Figure III-4: Annual chlorophyll a concentration cycle <u>when nutrients are not limiting</u> as shown on Figure III-1 (plain line) and approximated monthly values calculated with coefficients given in Table III-3 (bars).

If nutrients are limiting (Figure III-5), the spring bloom is rapid and last only one month as temperature reach 60% of its maximum value, and an autumn bloom is observed as temperature decreases below 60% of its maximum value.Figures III-4 et III-5 show how the chlorophyll a concentrations obtained with these coefficients chosen to fit the cycle depicted in figure III-1.

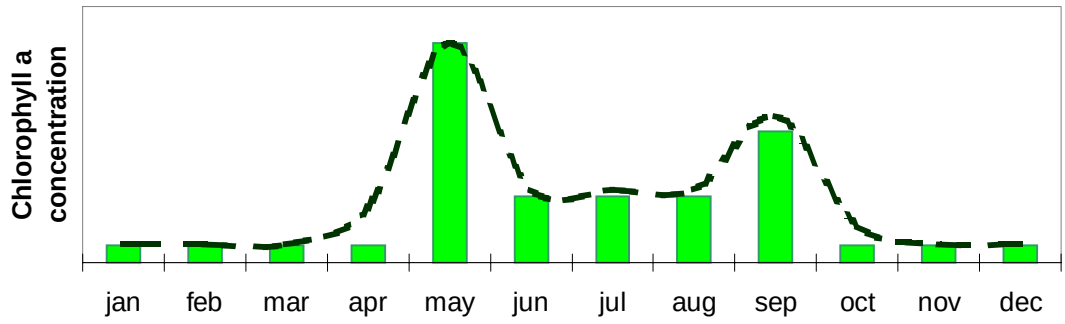

Figure III-5: Annual chlorophyll a concentration cycle <u>when nutrients are limiting</u> as shown on Figure III-1 (dash line) and approximated monthy values (bars) calculated with coefficients given in Table III-3.

III-3. CONCLUSION: THE PRIMARY PRODUCTION IN THE GEMCO MODEL

The *in-situ* primary production in an estuary is rapidly limited by water turbidity. Hence, the evaluation of chlorophyll a concentration in an estuary requires the evaluation of its concentration at the fresh and sea water ends of the estuary as the final concentration at any point of the estuary is likely to be significantly influenced by phytoplankton cells advected from the marine or the freshwater neighbouring areas.

The chlorophyll a concentrations calculated by Equation III-9 are the maximum annual concentrations that are to be used for the warmest months of the year. At any other time of the year, the chlorophyll concentration would have an intermediate value calculated with the coefficients given in Table III-3.

Parameters	Description	Units
[Chla]	Chlorophyll a concentration	$\mu g.l^{-1}$
$[Chla]_{max}$	Maximum chlorophyll a concentration	$\mu g.l^{-1}$
$[Chla_{fw}]$	Freshwater phytoplankton chlorophyll a concentration	$\mu g.l^{-1}$
$[C_{phyto}]_{max}$	Maximum phytoplankton carbon concentration	$mg.l^{-1}$
$[NO_3^-]_{winter}$	Winter nitrate concentration	$\mu mol.l^{-1}$
[SPM]	SPM concentration	$mg.l^{-1}$
μ	Phytoplankton growth rate	day^{-1}
μ_0	Phytoplankton growth rate at 0°C	day^{-1}
F_{light}	Light limiting function for production	-
F_{NO3}	Nitrate limiting function for production	-
P	Primary production	$g\ C.m^{-2}.day^{-1}$
P_{max}	Maximum primary production possible (nor light or nutrient limited)	$g\ C.m^{-2}.day^{-1}$
T	Temperature	°C
T_{max}	Annual maximum temperature	°C
T_{res}	Particles residence time	day
Z	Water column depth	m
Z_{eu}	Depth of the euphotic zone	m
Z_m	Critical depth	m

Table III-3: Table of the parameters used in the calculations of chlorophyll concentration in the turbid part of an estuary and their units

In order to derive Equation III-9 the following assumptions have been made :

- cells senescence; zooplankton grazing and death of marine phytoplankton due to salinity change do not need to be taken into account explicitly,
- there were no significant nutrient recycling or losses, that would otherwise enhance or limit primary production,

The results of Equation III-9 would be greatly improved if the maximum production rate was evaluated for each estuary and not assumed to be constant. The results of this equation are very sensitive to the residence time, T_{res}. This parameter is a function of the river flow and of the tidal current and of the morphology of the estuary. It will need to be evaluated within the hydrodynamic part of the model.

IV. GENERIC MODEL OF CONTAMINANT FATE IN ESTUARINE TROPHIC CHAINS.

IV-1. INTRODUCTION

There are two types of predator fish present in estuaries: round fish that feed essentially on organisms that live in the water column or in the sediment organisms and flat fish that live close to the sediment and mostly feed on benthic and suprabenthic organisms. These two types of fish belong to different food webs and it was anticipated that they might be contaminated through different pathways. Flat fish are more in contact with the sediment and, have shorter food webs than round fish. A greater contact to sediment, which can be a source of contaminant, can facilitate uptake of the most hydrophobic contaminants but a shorter food chain entails less biomagnification. These differences led to the development of two generic models, one for round fish, the other for flat fish..

The generic models have been derived from two bioaccumulation models developed at IFREMER

- A steady state model of PCB accumulation in dab food web (Loizeau and Ménesguen, 1993) was used as the framework for the flat fish model.
-
- The sea-bass model for PCB bioaccumulation (Loizeau *et al*., 2001a; Loizeau *et al*., 2001b) has been used to derive the generic round fish model;

Both models are based on the same concepts and the same processes as described in the following parts of this report.

IV-2. SIMPLIFICATION OF THE FOOD WEBS

Initially, Loizeau *et al.*'s models had been designed for the Seine estuary and therefore with species that live in the Seine estuary. Yet, one of the main requirements for a generic model is that it could be used in different estuaries around Europe. It was therefore necessary to make sure that the food webs included in the models were representative of food webs existing in European estuaries other than the Seine's. The literature search presented in Chapter 2 has suggested that no species had a distribution range spread from the Mediteranean to the Norwegian fjords. However, everywhere along European coasts, there are round and flat predator fish whose food webs have a similar structure to that of the sea bass and the dab, respectively. In every European estuary, top predator fish prey on benthic and suprabenthic organisms who in turn prey on smaller organisms, such as zooplankton, or feed on detritus and phytoplankton. It was therefore decided that the structure of the Seine food web would be preserved in the generic model so that each trophic level present in the original models would be accounted for in the generic models. However, no specific organisms would be designated any longer, only "virtual" species identified by a number (1, 2, or 3) each being representative of one trophic level. Thus the round fish model results are expected for instance to be compared with contamination levels in the sea bass from the Mediterranean Sea or in young cod from Norwegian fjords.

The generic model had to be simple. One way of simplifying existing sea bass and dab model was to simplify the food webs. In Loizeau *et al.*'s models, the top predator fish feeds on four different species. This is already a very small number of preys compared to the real number of sea bass or dab preys but is adequate to reproduce the rate of contamination of persistent PCBs and its variation around the year. It was decided to reduce the number of the top predator preys in each model to a minimum.

The original food webs of the sea bass and the dab models are shown with the simplified food chains of the two generic models on Figure IV-1 and figure IV-2.

At this stage it is necessary to notice one important difference between the round and the flat fish food webs as represented in Loizeau *et al.*'s models. Sea bass preys feed on detritus and phytoplanktonic material but also on zooplankton whereas dab preys feed only on phytoplankton and on detritic material. Zooplankton acts as a biomagnification step in the sea bass food web and has no equivalent in the dab model. In the generic model, as well as in the specific seabass and dab ones, each biomagnification step had to be preserved so that the overall contaminant bioaccumulation was correctly evaluated. This implied that the dab food web could be simplified into a two link food chain (the flat fish and its prey) whereas the sea bass food web had to contain three links: zooplankton, one suprabenthic organism and the top predator. By doing so, the number of trophic links in the generic models was kept equal to the number of trophic links in the original specific models.

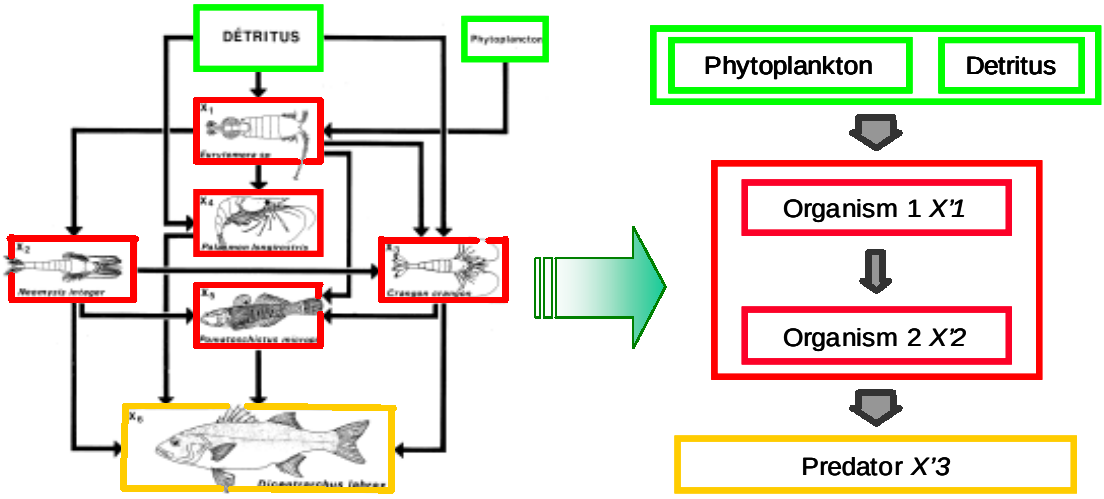

Figure IV-1: The sea bass model food web and its simplified version for the round fish generic model. Colours are used to represent different trophic levels: Green : detritus and primary producers. Red: secondary producers. Orange: predator. X_1= *Eurytemora affinis*, X_2= *Neomysis integer*, X_3= *Crangon crangon*, X_4= *Palaemon longirostris*, X_5= *Pomatochistus microps*, X_6= *Dicentrarchus labrax*.

In the round fish model, the characteristics of the copepod *Eurytemora affinis* and of the mysidacea *Neomysis integer* were respectively assigned to the zooplankton (organism 1) and to the suprabenthic organism (organism 2) on which the round fish was feeding. These organisms are mobile in the water column and they tend to choose their position in estuaries according to their preferred salinity range. The contaminant concentrations they are likely to accumulate should be representative of a water mass in the estuary rather than of a given geographical position. The predator fish (organism 3) has the physiological characteristics of the sea bass described in (Loizeau *et al.*, 2001b). The physiological characteristics of each organism are modelled by the same mathematical expressions used in the original specific models. This guarantees the pertinence of the equations for describing organisms of a given trophic level.

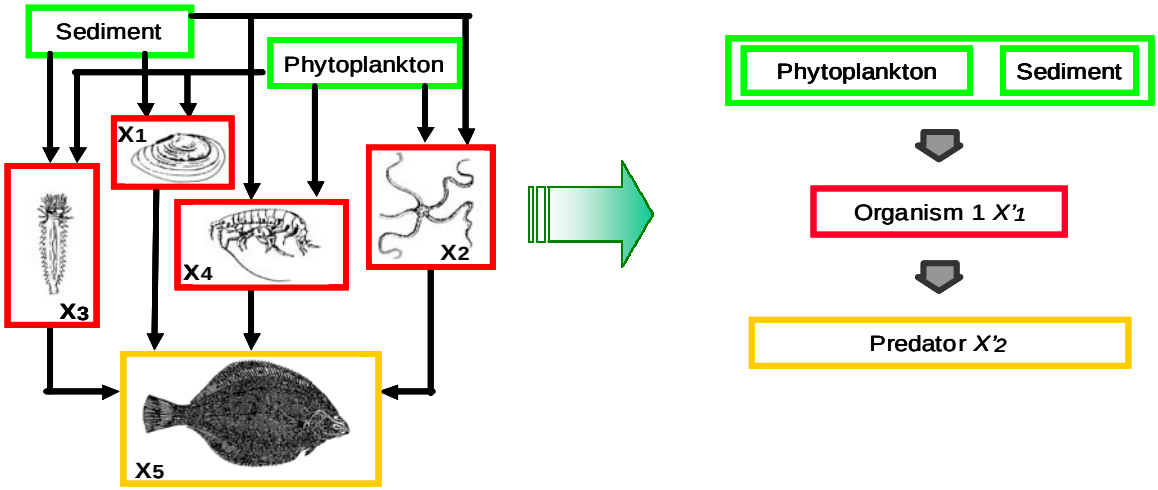

Figure IV-2: The dab model food web and its simplified version for the flat fish generic model. Colours code attention is the same as in Figure IV-1. X_1 = *Tellina fabula*, X_2 = *Acrocnida brachiata*, X_3 = *Pectinaria koreni*, X_4 = *Bathyporeia pelagica*, X_5 = *Limanda limanda*.

For the flat fish model, satisfactory results could be obtained when the predator's single prey had the physiological characteristics of the mollusc *Tellina fabula* described in the dab model. This organism is living in the sediment on which is feeds and is sedentary: the contaminant amounts that this organism can accumulate is therefore expected to be closely linked to the sediment contamination. In the flat model the predator fish has the characteristics of the dab as described in Loizeau and Ménesguen 's model (1993).

IV-3. MODEL CONCEPTUALISATION

IV-3-1. THE STRUCTURE OF THE GENERIC FOOD WEB MODEL

The transfer of contaminants from water to a predator fish follows a number of different pathways schematised on Figure IV-3

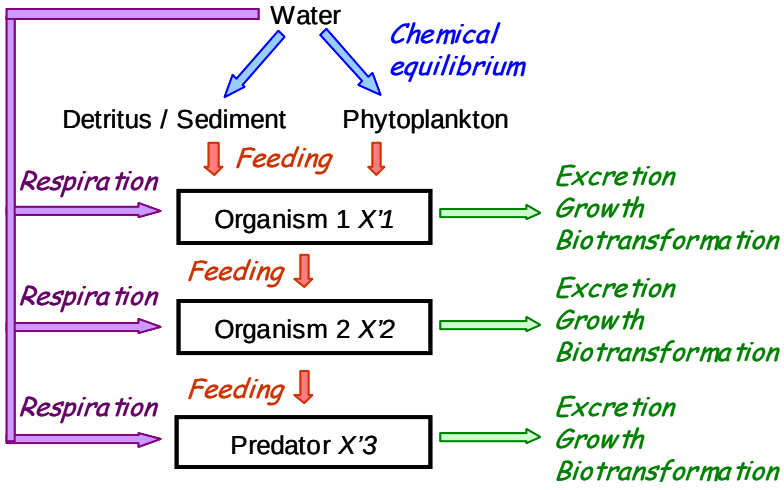

Figure IV-3: Schema of the bioaccumulation model. *Normal characters symbolise the compartments in which the contaminant concentrations are known or calculated. Italics are used to show processes that affect these concentrations. The round fish food chain is represented here. The flat fish food chain contains only one species intermediate between particles and predator.*

The direct uptake of chemical substances from water occurs during respiration. Feeding is the other main pathway through which contaminants adsorbed on particles (living phytoplanktonic cells, bacteria, detritus or sediment) enter the food chain. It is assumed that contaminant adsorption on particles is governed by chemical equilibrium. In the present models, bacteria are assimilated to their substrate (detritus or sediment) and are not modelled as explicit variable. The three loss processes taken into account are excretion, growth (which acts as dilution in enlarging body) and biotransformation. Contaminant is also known to be lost during reproduction by this process is not considered to be relevant for the GEMCO model which is built to represent a steady state situation.

IV-3-2. MODEL GENERAL EQUATION

The GEMCO model bioaccumulation equation is derived from a bioaccumulation model of PCBs in the lake trout food chain described by (Thomann and Connolly, 1984)and has been used in other similar works made at IFREMER (Loizeau *et al*. 1993, 2001a, 2001b). In such models it is assumed that the contaminant concentrations in an organism varied as the result of uptake and loss processes. The relevant biological processes are those shown on Figure IV-3 and the variation of contaminant concentration in organism i with time can be expressed as:

dX_i/dt = (uptake through respiration + uptake through nutrition) –
(loss through excretion + dilution during growth + reproduction + biotransformation)

This balance equation represents the basic equation of bioaccumulation and is valid for each individual species in the trophic web. It shows that bioaccumulation relies upon the supply of food and energy through respiration and feeding and most physiological functions excretion, growth, reproduction metabolisation act on the decrease of the contamination levels. This is a basic characteristic of deterministic bioaccumulation models also called bioenergetic models. It is very important to note that the biological factors that determine the extent of bioaccumulation.

The general equation of bioaccumulation can be written in a more mathematical way when the rates and efficiency of the processes are known:

$$dXi/dt = R_i \alpha_{wi} X_i + N_i \Sigma N_i P_{ij} \alpha_{ij} X_j - (E_i + G_i + S_i + M_i) X_i$$

respiration + feeding on various preys - {excretion, growth, reproduction (spawning) and biotransformation (metabolisation)}

The Gemco project objective is to develop a generic model to be use to estimate the exposure of estuarine species to contaminants, so simplification can and should be done in a generic approach. First, at this stage biotransformation is not represented, as Thomann and Connolly (1984) as well as Loizeau *et al*. (1993, 2001a, 2001b) who have been working on PCBs. PCBs were assumed to be fully persistent and thus to be unaffected by biotransformation. This process is not included in our first approach that we lead to an overestimation on the predicted concentration, in other words the model will predict the worst situation; however biotransformation will be introduced later in the GEMCO model. Secondly, in steady state conditions the reproduction is not considered. Indeed the adult female species usually may loose a significant amount of the accumulated contaminants during the spawning which occur during a short period each year, generally at spring when seawater becomes warmer. Lastly and for simplicity sake, it is assumed that the ecosystems in which trout, flat or round fish food chains are living, have reached equilibrium. This implies that there is no evolution of the contaminant concentration with time:

$dX_i/dt = 0$

and therefore at any time inputs of contaminants are balanced with losses

Xi = (uptake through respiration + uptake through nutrition) / (loss through excretion + dilution during growth)

This has been translated into a mathematical equation Equation IV-1 where the numerator represents the uptake by respiration ($R.\alpha_w.X_w$) and feeding ($\Sigma N.P_j.\alpha_j.X_j$) while the two terms of the denominator represent the loss processes through excretion (E) and growth (G) which are the only relevant biological processes in the case of persistent contaminants in steady state conditions.

$$X_i = \frac{\left(R \cdot \alpha_w \cdot X_w + \sum_j N \cdot P_j \cdot \alpha_j \cdot X_j \right)}{(E+G)} \qquad \text{(IV-1)}$$

Equation IV-1: The general equation of bioaccumulation used in the GEMCO model.

This equation gives the contaminant concentration in organism i and shows the uptake terms (respiration and feeding) on the numerator, and the loss terms (excretion and growth) on the denominator. A brief description of each term is given in Table IV 1

The different terms are of Equation IV-1 are described briefly in Table IV-1 and each process is described in details in the following sections.

Symbol	Description	Units
X_i	Contaminant concentration in organism i	$ng.g^{-1}$
R	Respiration rate of organism i	day^{-1}
α_w	Contaminant assimilation efficiency from water	-
X_w	Contaminant concentration in water	$ng.l^{-1}$
N	Nutrition rate of organism i	day^{-1}
P_j	Percentage of prey j in diet of organism i	-
α_j	Assimilation efficiency of prey j by organism i	-
X_j	Contaminant concentration in organism j	$ng.g^{-1}$
E	Excretion rate of organism i	day^{-1}
G	Growth rate of organism i	day^{-1}

Table IV-1: List of the terms used in the general equation of bioaccumulation.

The equations used in the model to describe the physiological parameters that are represented in Equation IV-1 have been obtained from literature. A more detailed description, including a complete list of literature references, has been given in (Loizeau and Ménesguen, 1993, Loizeau *et al.* , 2001a and 2001b).

IV-3-3. WEIGHT OF ORGANISMS.

Many physiological processes are dependent on animal age and size. In the equations used here, organism weight - which is a parameter easy to measure - is used as a proxi for age or size. The weights of the various organisms used in the GEMCO models are given in Table IV-2. Weights of organisms used for the sea bass and the dab models are given (Loizeau and Ménesguen, 1993; Loizeau *et al*., 2001a).

Organism	Weight	Units	Reference
Round fish model			
Organism 1	$W_1 = 5.323$	µg	Loizeau *et al.,* 2001b
Organism 2	$W_2 = 2.209$	mg	-
Organism 3	$W_3 = 232.5$	g	-
Flat fish model			
Organism 1	$W'_1 = 0.209$	g	Loizeau and Ménesguen, 1993
Organism 2	$W'_2 = 170$	g	

Table IV-2: Weight of organisms as used in the round fish and the flat fish generic models.

IV-3-4. RESPIRATION

During respiration, marine organisms exchange chemicals with the surrounding water. The rate of contaminant exchange has been shown to be related to oxygen uptake rate (Loizeau *et al.*, 2001a; McKim *et al*., 1985). The different equations used in the generic models for respiration rates R are in Table IV-3.

Organism	Equation	Units	Reference
Round fish model			
Organism 1	$R_1=\frac{(0.0453\cdot[Chla]+0.0253\cdot T-0.137)}{[Zoo]\cdot[O_2]}$	$l.g^{-1}.day^{-1}$	Fourqurean *et al*.,(1997),
Organism 2	$R_2=\frac{109.6\cdot W_2^{-0.758}}{[O_2]}$	$l.g^{-1}.day^{-1}$	Vasblom and Elgershuizen (1997)
Organism 3	$R_3=\frac{23.72\cdot W_3^{-1.2209}\cdot T^{1.6867}}{[O_2]}$	$l.g^{-1}.day^{-1}$	Lemaire *et al*. (1992b)
Flat fish model			
Organism 1	$R_1'=\frac{1.219\cdot e^{0.0269T}}{[O_2]}$	$l.g^{-1}.day^{-1}$	Wilkander, (1980)
Organism 2	$R_2'=\frac{10^{10.63}\cdot T^{0.5415}\cdot W_2^{'-5.032}}{[O_2]}$	$l.g^{-1}.day^{-1}$	Paul *et al*., (1990)

Table IV-3: Equations describing respiration rates for the different organisms of the generic food web. T = Temperature in °C; W_i = weight of organism i in mg for organisms 1and 2 of the round fish model and for organism 1 of the flat fish model, in g for organism 3 of the round fish model and for organism 2 of the flat fish model; [Chla] = Chlorophyll a concentration in water in $mg.l^{-1}$; [Zoo] = Zooplankton biomass in $mg.l^{-1}$; [O_2] = Dissolved oxygen concentration in water in $mg.l^{-1}$.

These equations show respiration rate dependency on organism weight, water temperature, oxygen concentration in water and, for zooplankton, on food (chlorophyll) availability. The respiration rate R describes the contribution of respiration to contaminant uptake, is also related to environmental parameters and to the contaminant properties. These contributions depend on the contaminant concentration in water X_w and on the water assimilation coefficient α_w, which is related to the contaminant hydrophobicity Table IV-4.

There is a poor information on the assimilation coefficients used in the bioaccumulation model; they are derived from experimental studies in controlled conditions on specified organisms and for a limited group of compounds. In this model, the α coefficient, or coefficient of assimilation of a contaminant when it is absorbed from the water during respiration, is related to the K_{ow} according to Thomann *et al*. (1992). This relationship was established with a few PCB congeners, in specified conditions and for a few living species; moreover this relationship is biased by a large uncertainty on the estimation of the octanol-water partition coefficient. In the case of predator it should be kept in mind that the contribution of the water remains very low particularly in the case of hydrophobic compounds and that this water contribution decreases when the trophic level increases.

Range of Log Kow	Assimilation efficiency from water, α_w
$4.5 < \text{Log}K_{ow} < 6.25$	$\alpha_w = 0.6$
$6.25 < \text{Log}K_{ow} < 10$	$\text{Log}\ \alpha_w = 2.9\text{-}0.5 \cdot \text{Log}\ K_{ow}$

Table IV-4: Assimilation coefficient from water and its dependency on the contaminant hydrophobicity

IV-3-5 FEEDING

Feeding has been shown to be the main route of contamination for hydrophobic persistent compounds. Contaminants are ingested with the prey and the predator contamination is therefore proportional to its nutrition rate, to its diet composition and of the contamination in preys. It is also a function of the food assimilation efficiency. Assimilation is the process through which food and contaminant pass through the organism guts into its tissues. There is a high degree of uncertainty associated to the evaluation of the food assimilation efficiency. It is likely to be dependent on both the ability of the predator to digest its food and to the quality of the food itself. The lack of information on this process implies that the only differentiation that could be made was between living (phytoplankton and organisms) and non-living preys. As for uptake from water, contaminant assimilation efficiency through feeding has been shown to be related to the contaminant hydrophobicity and this is taken into account in the expression of the assimilation coefficient α. Logically the contamination through feeding is also dependant on the amount and the contamination of the prey. This is expressed by the contaminant concentration in the prey and by the parameter P that gives the percentage of the prey j in the predator i's diet. In the generic model, only organisms 1, of the lowest trophic level, have two food sources (phytoplankton and detritus or sediment). Initially the proportion of each has been set to 50%, but this could be improved to take into account variations in phytoplankton density. Organisms 2 and 3 feed exclusively on the organism from the trophic level below (organism i feeds on organism i-1, so in Equation IV-1, $P_j = 1$).

Organism	Equation	Units	Reference
Round fish model			
Organism 1	$N_1=\frac{0.024\cdot(3.197\cdot[Chla]-1)}{[Zoo]}$	day^{-1}	Hansen *et al*. (1995)
Organism 2	$N_2=0.495\cdot e^{(0.0875\cdot T-0.0434)}$	day^{-1}	Aaser *et al*. (1995)
Organism 3	$N_3=0.187\cdot W_3\cdot e^{(0.004T-2.17)}$	day^{-1}	Ramos *et al*. (1982)
Flat fish model			
Organism 1	$N_1'=0.2736\cdot[Phyto]+0.132[POM]+3.504$	day^{-1}	Hughes and Morgan (1973)
Organism 2	$N_2'=W_2^{'1.536}\cdot 10^{0.0014\cdot T}\cdot 3.048\cdot 10^{-3}$	day^{-1}	Pandian (1970)

Table IV-5: Equations used for the nutrition rates in the generic models.
T = Temperature in °C; W_i = weight of organism i in mg for organisms 1 and 2 of the round fish model and for organism 1 of the flat fish model, in g for organism 3 of the round fish model and for organism 2 of the flat fish model; [Chla] = Chlorophyll a concentration in water in $\mu g.l^{-1}$; [Zoo] = Zooplankton biomass in $mg.l^{-1}$; [POM] = Particulate Organic Matter concentration in water in $mg.l^{-1}$.

As for the assimilation coefficient from water, the assimilation coefficient from food α_i is a parameter derived from previous studies. In their sea bass model Loizeau *et al.* (2001 a) has used various assimilation coefficients between 0.5 and 0.65 depending on the different K_{ow} ranges of the contaminants. In this generic model, and based on the uncertainty of the octanol-water partition coefficient determination it was assumed that a constant assimilation coefficient will correctly describe the assimilation process. Therefore, without any more appropriate and precise definition of this assimilation coefficient from preys, it was kept constant and equal to 0.6 in the generic model. Is also felt that this assimilation coefficient about 0.6 would probably led to an overestimation of the final contaminant concentration in predators.

IV-3-6. EXCRETION

In the context of this model, excretion of this model is considered to be losses of contaminant after it has been assimilated. Contaminant is then evacuated from the organism without chemical modification. The equations describing this process and given in Table IV-6 are issued from literature. Their use implies that the contaminant concentration in faeces is the same as in the body.

Organism	Equation		Reference
Round fish model			
Organism 1	$E_1=\frac{0.199}{([Chla]\cdot[Zoo])}$	day^{-1}	Durbin and Durbin, (1978)
Organism 2	$E_2=0.0985\cdot e^{(0.031\cdot T-0.19)}$	day^{-1}	Aaser *et al*. (1995)
Organism 3	$E_3=0.147\cdot W_3^{0.171}$	day^{-1}	Balestrazzi and Lanari, (1996)
*Flat fish model **			
Organism 1	$Log(E_1')=0.799\cdot Log(W_1')-2.352$	day^{-1}	Salzwedel, (1980)
Organism 2	$E_2'=0.168\cdot N_2'+0.0035\cdot T+0.965$	day^{-1}	Pandian, (1970)

Table IV-6: Equations used for the excretion rates in the generic models. T = Temperature in °C; W_i = weight of organism i in mg for organisms 1and 2 of the round fish model and for organism 1 of the flat fish model, in g for organism 3 of the round fish model and for organism 2 of the flat fish model; [Chla] = Chlorophyll a concentration in water in $\mu g.l^{-1}$; [Zoo] = Zooplankton biomass in $mg.l^{-1}$; N_2': nutrition rate of organism 2 of the flat fish model as defined in table IV-5.

** Caution: in the flat fish model excretion rate for organism 1 is given in natural logarithms (Log or Ln)*

IV-3-7. GROWTH

If there were no contaminant uptake during growth, the amount of contaminant in the body would be diluted as the organism increases its weight and concentration would decrease. So the effect of growth is therefore included as a loss process in the bioaccumulation equation. Contaminant losses here are proportional to growth rates Table IV-7. These are established from length-weight and age-weight relationships reported in literature.

Organism	Equation	Units	Reference
Round fish model			
Organism 1	$G_1=0.278$	day^{-1}	Vidal (1980)
Organism 2	$G_2=0.249$	day^{-1}	Irvine *et al*., (1995); Mees *et al*. (1994)
Organism 3	$G_3=0.992$	day^{-1}	Bertignac, (1987); Masski, (1998)
Flat fish model			
Organism 1	$G_1' = 0.0156$	day^{-1}	Salzwedel, (1980)
Organism 2	$G_2' = 0.028$	day^{-1}	Tassel, (1988)

Table IV-7: Equations used for the growth rates in the generic models

IV-3-8. BIOTRANSFORMATION

Biotransformation is the process through which contaminant assimilated in the organism is transformed via enzymatic reactions into metabolites that are usually less hydrophobic than the parent compounds and that are more easily eliminated

Biotransformation is therefore a process of elimination that is exerted on contaminant incorporated in the organism flesh. In Loizeau *et al.*'s models of PCB bioaccumulation, biotransformation was not included because these compounds are typical persistent compounds and their biotransformation can be neglected compared to their rates of accumulation; this is particularly relevant for PCBs in the case of a contaminated estuarine environnement like the Seine estuary where inputs from the river are continuously elevated. The generic models have to be applied to compounds less persistent ones and therefore biotransformation has to be evaluated. One major limitation of the way biotransformation is introduced in the generic model is that it allows the evaluation of parent compounds losses, but does not consider what happen to its metabolites; that could be a major drawback against their use in chemical risk assessment. In many cases, nature works quite well and biotransformation are detoxification processes and thus, metabolites are less toxic and eliminated faster than the parent compounds. But in some cases, metabolites can be at least as toxic as the parent compound and may not be eliminated from the organism. PAHs are typical examples of such potentially hazardous substances. An other typical example is DDT, biotransformed into DDE, a compound which is more persistent than DDT and thus more bioaccumulated and biomagnified.

IV-3-8-1 Biomarkers

There are several ways used to evaluate the biotransformation capacity of an organism. Some enzymatic activity (EROD, ECOD, GST, BaPMO,) indicates that the organism is under some stress but there are no reliable relationships with level of contamination and the length of the depuration period (den Besten *et al*., 1993). Interested reader might get a very recent and extensive literature review on biomarkers, their use and their interrelation with the bioaccumulation in fish (van der Oost *et al*., 2003).These activity levels vary with time after contamination (Lemaire *et al*., 1992c) and results are therefore highly dependent on when measurements are carried out after contamination has been started and/or stopped. The presence of an enzymatic system in an organism does not warrant the metabolisation of a xenobiotic: the same enzymatic system can induce at different levels the metabolisation of a given contaminant in two different organisms (Lee, 1998). Moreover, these reactions of the organisms defence systems are similar to the effects a change in environmental conditions such as temperature or salinity can induce. It is therefore impossible at the moment to use measurements of enzymatic activities to simulate biotransformation in an organism living in a natural estuary.

Other metabolic activities (growth, respiration, filtration rates…) have been measured to gain information on the effect of a contaminant on marine organisms. Dose-response relationships appear to be dependent on the level of contaminant during exposure and its length (Ching *et al*., 2001; Engelhardt *et al.*, 1985; Lowe and Pipe, 1985). The results of this type of studies do not give information on the concentration of contaminant in organisms but on toxicological effects. This does not correspond to the approach chosen for GEMCO.

IV-3-8-2. Measurements of chemicals in organisms

IV-3-8-2-1. Metabolites

Another approach for the evaluation of biotransformation would consist in measuring in organisms the concentration of parent compounds together with the concentrations of all its metabolites. The analysis of contaminants and more over of the contaminants metabolites is a very difficult task due to the very low concentrations and the number of various metabolites. The difficulty here is to be sure that every metabolites are measured and that they come all from the same parent compounds and that none has a source other than the parent compound of interest. Data set that include concentrations of a given contaminant and its metabolites in the environment (water or sediment) and in organisms have not yet been found in literature. We must keep aware that we are looking for an exposure mode for parent compounds and in a first approach it seems more important to look at the disappearance of the parent compound from the organisms rather than the formation of various metabolites, most of them being polar and should have a rapid body transit through organisms and through the foodchain.

IV-3-8-2-2. Bioconcentration factors

Bioconcentration factor, or BCF, is a measure of the increase in contaminant concentration between the water and organisms that live in it. For persistent compounds, it has been shown that relationships existed between log BCF and log K_{ow}. These are linear as long as log K_{ow} is less than 7 and bell shaped if more hydrophobic compounds are included (Meylan, 1999; Bintein, 1993; Voutsas, 2002). Yet, this approach applies only to non-biotransformable compounds (Goerke and Weber, 2001). Indeed, two compounds may have the same K_{ow} but if one is partially biotransformed, it would display a lower concentration than predicted by the relationship between BCF and K_{ow} that are based on chemical equilibrium of contaminant dissolved and adsorbed on particles or on tissue. For instance, (Shaw and Connell, 1986) has shown that PCB congeners with the same K_{ow} could display different BCF due to their differences in stereochemistry. Amongst PCB, an example can be given by comparing CB149 and CB118. The former has a higher K_{ow} than the later, but is known to be less bioaccumulated. This is supposed to be related to the position of the chlorine atoms on the carbon rings. Finally, if food is a significant source of contaminant compared to water, the K_{ow} - BCF relationships are not observed.

As presented in a review paper, (Abarnou *et al*., 1997) this can be easily seen by considering the general equation of bioaccumulation Equation IV-1 and rewriting it to differentiate the terms according to the contaminant source they represent:

At the steady state,

$$X_i = \frac{R\alpha_w}{E+G} \cdot X_w + \frac{\sum_j N \cdot P_j \cdot \alpha_j \cdot X_j}{E+G} \qquad \text{(IV-2)}$$

(Thomann, 1989) has shown that the first term was equivalent to the BCF, so that if, and only if, the contribution of food was negligible, Equation IV-2 could be simplified to:

$$X_i = BCF \cdot X_w , \qquad \text{(IV-3)}$$

BCF being equivalent to $\frac{R\alpha_w}{E+G}$

This equation gives the contaminant concentration in organism i only if its food is not a significant source of contamination and is likely to be valid for the hydrophobic compounds with $\log K_{ow}$ greater than 3 with $\log K_{ow}$ lower than 5 (Thomann, 1989).

IV-3-8-2-3. Biomagnification factors

The biomagnification factor (BMF) is defined as the ratio of contaminant concentration in a predator to that in its prey. It gives an indication on the ability of an organism to eliminate the contaminant it has ingested with its food. If BMF are smaller than 1, this means that the predator has been able to eliminate more contaminant than it has ingested, and a decrease in contaminant concentration is observed from the prey to its predator. Biomagnification factors greater than 1 imply that the predator is not able to depurate the assimilated contaminant, and that there is bioaccumulation along the food chain.

With the important data set gathered by Jaouen-Madoulet (2000), it has been possible to calculate BMFs for different organisms of the flounder and sea bass food chains in the Seine Estuary for a range of PCBs and a range of PAHs. In order to ease the comparison between the two-contaminant families, log values of BMFs are used on the figures below. Note that:

if log (BMF) > 0 then the contaminant is bioaccumulated; like PCBs (Figure IV-4)

if log (BMF) < 0 then the contaminant is not bioaccumulated; like PAHs (Figure IV-5).

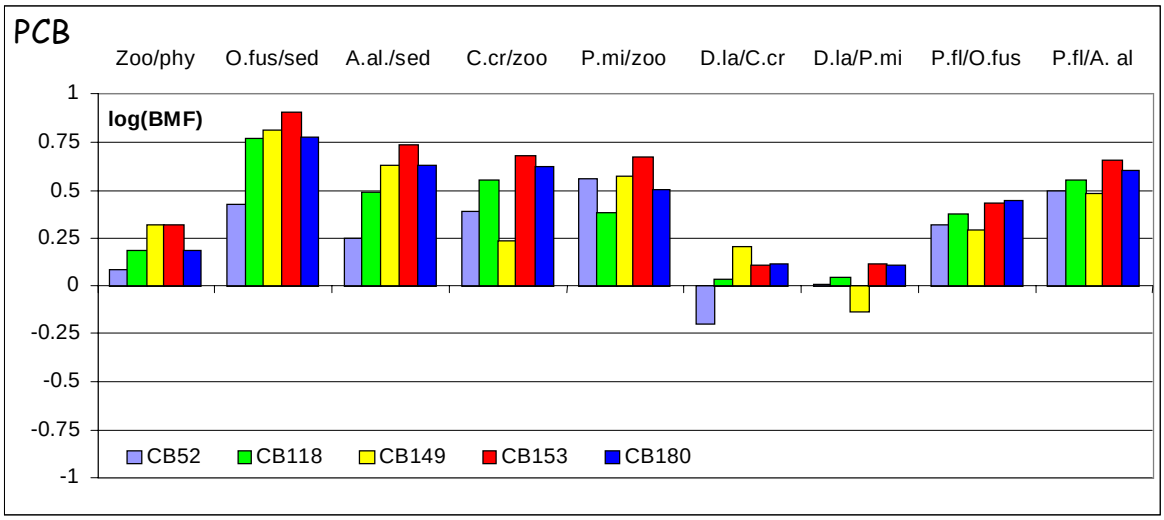

Figure IV-4: PCB biomagnification factors in the sea bass and the flounder food webs in the Seine estuary (data from Jaouen-Madoulet, 2000).
Legend for organisms: ***Zoo***: *Zooplankton.* ***Phy***: *Phytoplankton.* ***Sed***: *Sediment.* ***O. fus***: *Owenia fusiformis.* ***A. al***: *Abra alba.* ***C. cr***: *Crangon crangon.* ***P. mi***: *Pomatochistus microps.* ***D. la***: *Dicentrarchus labrax, sea bass.* ***P. fl***: *Platichthys flesus, flounder.*

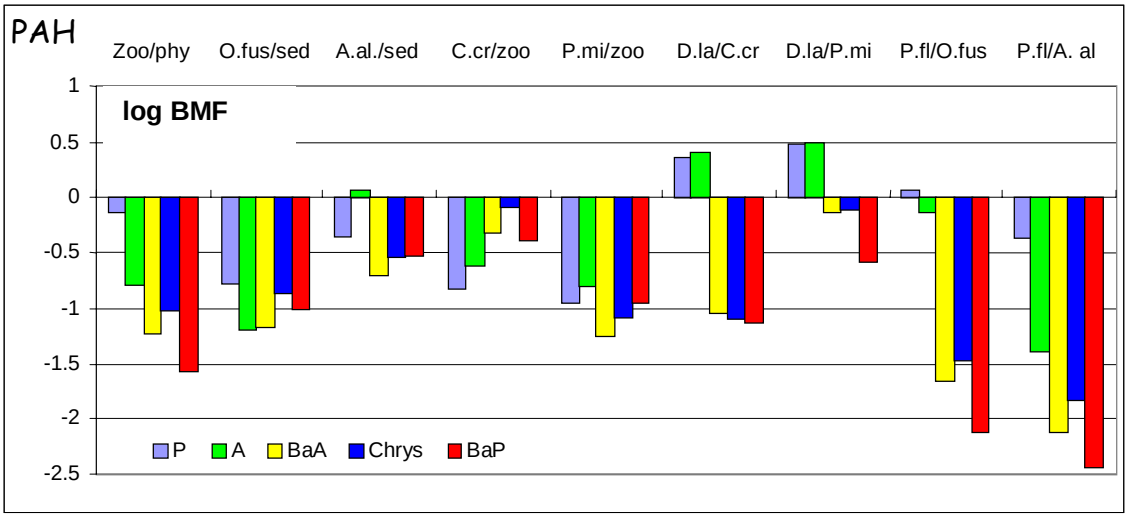

Figure IV-5: PAH "biomagnification factors" in the sea bass and the flounder food webs in the Seine estuary (data from Jaouen-Madoulet, 1992). Legend for organisms as for Figure IV-4.
Legend for PAHs*: **P**: phenanthrene. **A**: anthracene.* ***BaA**: benzo(a)-anthracene.* ***Chrys**: chrysene.* ***BaP**: benzo(a)pyrene.*

The first, and expected, remark that the comparison of the Figure IV-4 and IV-5 allows is that PAH biomagnification factors log values are usually negative, whereas PCB's ones are positive. This reflects the well known bioaccumulation of PCBs and the known biotransformation of PAHs.

The ability to biotransform or may be more accurately the inability to bioaccumulate of the different species at the various trophic levels of the food chain is also illustrated by these figures. It is interesting to note that the PCB log(BMF) of suprabenthic species (*C crangon* and *P. microps*) are similar to that of flounder. This is probably related to the fact that these three species are at the same trophic level (secondary consumers, level 2). Such a comparison does not hold between zooplankton and benthic species (*Abra alba* and *Owenia fusiformis*), although they too are at the same trophic level. This is as if bioaccumulation was different according to the food source. The benthic species sampled here feed essentially on sediment whereas zooplankton feeds in more significant proportions on phytoplankton. Another factor that affects bioaccumulation and induces differences between two groups of species, is the age of the organisms. Benthic species considered here are certainly older than zooplanktonic species whose turnover is considerably faster (a few months against a few years) and have accumulated contaminant for longer. They display higher PAH and PCB concentrations than zooplancton. The BMFs calculated here probably reflect this accumulation over a much longer period for benthic species than for zooplankton. Overall, note that, for PCBs, BMFs are lower for the predator fish than for its preys. For zooplankton the BMFs are intermediate.

Generally speaking, this is also true for the PAHs. The predator fish have slightly lower BMFs than their prey. This is clear for the flounder and the benthic species, but seabass display BMF that are higher than *Pomatochistus microps*, one of its preys. One of the reasons of this apparent inconsistency could be that the representation of BMF Figure IV-5 is only an approximation of the biomagnifying capacity of organisms because predators are compared to only one of their preys, whereas they have several some less contaminated than others. It is because *Pomatochistus microps* is less contaminated than *Crangon crangon* that seabass seems to biomagnify PAHs more if compared to *P. microps* than if compared to *C. crangon*.

Another apparent inconsistency shown of Figure IV-5 is the sea bass BMFs for phenanthrene and anthracene. These two lighter PAHs are the more water soluble among the PAHs measured here. Would their relatively high concentrations in the top predator fish imply that they are bioaccumulated only at the highest levels of the trophic chain? This is unlikely, and is more probably caused by a greater assimilation of these compounds from water (may be through respiration) relatively to assimilation with food. If this is the case, the comparison between these contaminant concentrations in different species is related to their respiration rate, not to their trophic level and it is, for these particular compounds, meaningless to discuss biomagnification. However, the general aspect of the graphs suggests that *Abra alba* biotransforms less than *Owenia fusiformis* and that both benthic organism biotransform the most hydrophobic PAH less than their predator *Plachtythis flesus*. Similarly, the shrimp *Crangon crangon* biotransform hydrophobic PAHs less than the seabass *Dicentrarchus labrax*. This predator BMFs over *Pomatochistus microps* are close to one, which suggests that both fish have a similar capacity to biotransform PAHs.

IV-3-8-2-4. Rates of disappearance

Several authors have reported experiments during which the rates of elimination of contaminants were measured. For persistent compounds such as CB153, this rate of elimination corresponds to the rate of excretion described in IV 3.5. For compounds that are biotransformed this rate of elimination includes both the excretion as defined above and biotransformation.

These experiments simulate situations where the source of contamination is punctual and depuration is made possible at the end of the experiment. Contamination or induction is carried out once or for a relatively short period of time, and then stopped. (Goerke and Weber, 1990, 2001)

These experiments generally show that the rates of elimination are dependent on:

- the species under study, their gender and their age (Ferreira and Vale, 1998),
- the concentration of contaminant in water and in organisms,
- the time when measurement is carried out: decontamination rate can be slow or inexistent on the onset of contamination, increases until a maximum rate is reached and finally decreases exponentially with time (Goerke and Weber, 2001).
- there might be synergetic effects when organisms are contaminated with several chemicals simultaneously (Goerke and Ernst, 1986; Lemaire-Gony *et al.*, 1995).
- the source of contamination (exclusively water, exclusively food, or both) may have an influence on the biotransformation rates and on the effects on organisms (Lemaire *et al*., 1992a). If it is exclusively water, uptake is likely to occur mainly through gills whereas through food the uptake will occur within the digestive track. The level of contamination of the water and of the food will be different and will therefore trigger biotransformation in different parts of the body and at different rates.

These types of experiments have shown that depuration decreased exponentially after contamination was stopped (Goerke and Weber, 2001), these results suggest that for *Nereis diversicolor*, *Palaemon longisrostris* and *Plachthistys flesus* the depuration is described by equations such as:

$$PCB=a+b\cdot e^{-ct}$$

where PCB is the mass of one PCB congener in the organism expressed in µg, t is the time in weeks with t = 0 when contamination is stopped, a, b and c are constants. According to Goerke and Weber, the constant a is about 5% of b. The constants b and c depend on the initial contamination levels, which in their experiments is higher than the contamination level found in the field. This is an interesting approach for accidental contamination and would be useful in a dynamic model. In the case of GEMCO, chronic contamination is to be simulated, assuming that the system has reached steady state equilibrium so this approach is not suitable.

IV-3-8-2-5. PAH transformation by marine invertebrates

Livingstone (1992) has reviewed work carried out on uptake and biotransformation rates of PAH and some other organic compounds in marine invertebrates. His study concludes that:

- Depuration half time $T_{1/2}$ generally increases with increasing hydrophobicity of the chemical following equations such as $T_{1/2}$= a K_{ow} +b where a and b are constants.
- Depuration half time can increase with tissue lipid levels [lip] following equations such as $T_{1/2}$ = c [lip] + d, where c and d are constants.
- Very hydrophobic compounds (K_{ow} > 6) exhibit smaller depuration rates than expected from these types of equations.
- Depuration is normally exponential with time.
- Depuration can be affected by duration of exposure to xenobiotic:
  Long term exposure leads to slow and incomplete elimination
  Short term exposure leads to rapid and complete elimination
- The log of rates of metabolisation linearly increases with log of tissue xenobiotic concentrations over 6 orders of magnitude of the two parameters for the metabolisation of compounds classified as “functional groups” (aromatic amines, nitroaromatics, phenols and others) by crustaceans and molluscs and of hydrocarbons by crustaceans. The equation for metabolisation of hydrocarbons by crustaceans is:

$$\text{Log(Metab)} = - 0.90 + 0.93\ \text{Log[PAH]} \qquad \text{(IV-4)}$$

Equation IV-4: “Metab” are metabolisation rates of HAP by crustaceans according to (Livingstone, 1992). Units are pmol.min^{-1}.g^{-1} ww for Metab and nmol.g^{-1} ww for [HAP].

and for molluscs:

$$\text{Log(Metab)} = - 1.31 + 0.92\ \text{Log[PAH]} \qquad \text{(IV-5)}$$

Equation IV-5: Metabolisation rates of HAP by molluscs according to (Livingstone, 1992).

In these two equations, metabolisation rates [Metab] are in pmol.min^{-1}.g^{-1} wet weight and the PAH concentrations are in nmol.g^{-1} wet weight. The bioaccumulation model suggests that without biotransformation, the BaP concentration in the supra benthic species of the round fish food chain would be 174 ng.g^{-1} dw. According to Equation IV-4, this would generate a metabolisation rate of 35 ng.day^{-1}.g^{-1} dw and the concentration in the suprabenthic organism would be calculated as equal to 139 ng.g^{-1} dw which is much greater than the observed concentrations in the Seine, which are about 0.6 ng.g^{-1} dw in for instance grey shrimps

(*Crangon crangon*). Details of calculations are given in Appendix. Livingstone's equations always produce metabolisation rates that would lead to concentrations much lower than the actual concentrations measured in tissues of experimentally exposed organisms. This would imply that contaminants, particularly PAHs, are never eliminated from tissues. Yet, measurements in the Seine estuary (Jaouen-Madoulet, 2000) clearly show that for most PAHs, concentrations decrease along the food chain, implying that depuration is greater than assimilated contaminant. This suggests that the laboratory experiments used in Livingstone's review do not correspond to a representation of depuration compatible with our model. This might be caused by a difference of organism reaction when they are in laboratory conditions and when they are in the field.

IV-3-8-2-6. Experimental approach on juvenile turbots

Experiments carried out at Le Havre University and in collaboration with IFREMER (DEL/EC Brest) have brought some valuable information on biotransformation rates in fish. Juvenile turbots (*Scophthalmus maximus*) were fed with fish meal pellets contaminated with one PCB congener (CB153, CB118 or CB77) or with Benzo[a]pyrene (Jaouen-Madoulet, 2000) at known levels (Table IV-8).

Contaminant	Low level contamination	High level contamination
CB153	150 $ng.g^{-1}$	1600 $ng.g^{-1}$
CB118	60 $ng.g^{-1}$	600 $ng.g^{-1}$
CB77	0.5 $ng.g^{-1}$	5 $ng.g^{-1}$
BaP	1 $ng.g^{-1}$	10 $ng.g^{-1}$

Table IV-8: Contaminant concentrations in the two sets of pellets used to feed juvenile turbots in experiment. (Jaouen-Madoulet A. 2000) The concentrations in the spiked fish meal corresponds approximately to the contamination levels in gobies from the Seine estuary (low level) and ten fold this level (high contamination level).

Twenty aquaria, each containing 40 juvenile turbots were used. The growth and the contamination of the turbots were monitored for 8 weeks. Data are available to calculate exactly how much contaminant is introduced into the aquaria. Two sets of contaminated pellets were prepared, one being about 10 times more contaminated than the other Table IV-8. Fish in four aquaria were fed with uncontaminated food so that they could be used as controls. Four fish in each aquarium was sacrificed every week and contamination levels were measured. Details of the experimental procedures are in (Jaouen-Madoulet, 2000).

Knowing the fish growth, the amount of contaminant supplied to each aquarium, it is possible to calculate the theoretical amount of contaminant each fish could have ingested and assimilated, assuming there are no losses during feeding and no elimination afterwards. This is shown as "theory" points on figure IV-6. The curve shown by the time series is due to a slowing down of the growth rate. Measurements carried out during the experiments give the actual contaminant concentrations measured in the turbot's tissues (Figure IV-6).

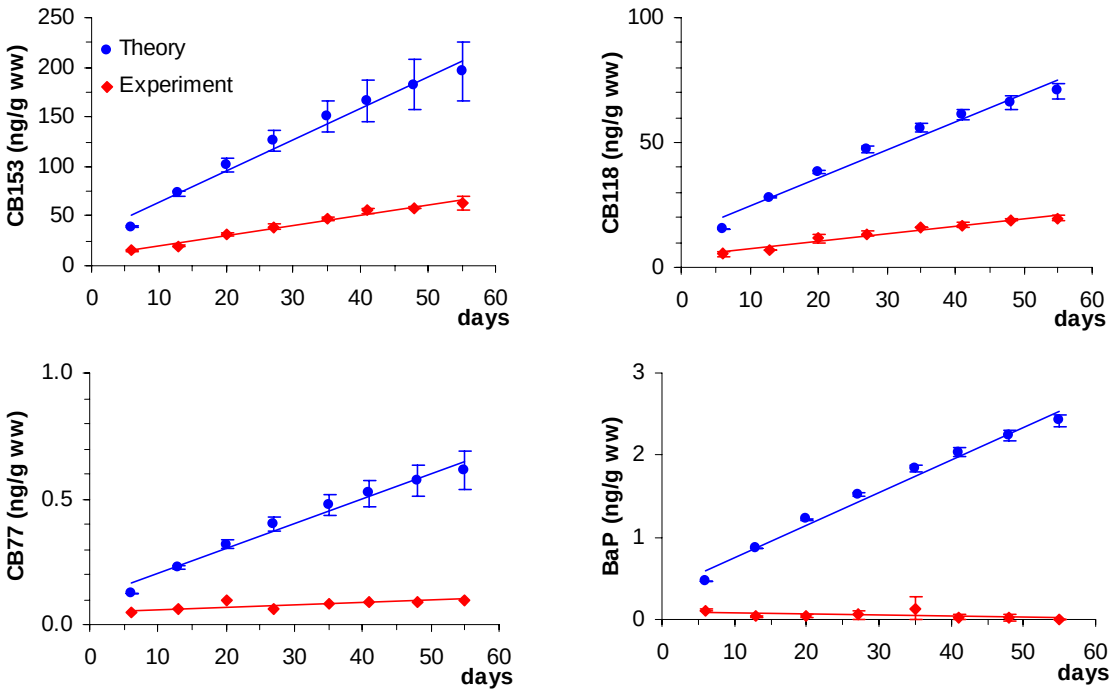

Figure IV-6: Contamination of turbots fed with spiked fish meal (see table IV-8). Theoritical concentrations are calculated from the known supplied quantity of contaminant and the measured fish weights. The error bars on the theoretical data are due to the variation in the weight of the sampled fish (from Jaouen-Madoulet, 2000). Note the different concentration ranges for the various compounds which is due to the level of the spikes in the food distributed to fish.

The absence of curving of these points reflects probably the dependency of metabolic processes (feeding, excretion…) on organism weight and therefore age. The difference between the calculated theoretical and the measured concentrations is due to losses due to non-ingestion of food (messy feeding), to growth and to elimination by excretion and biotransformation.

It is not possible to compare directly these graphs because the levels of contamination in the food differ from one contaminant to the other. It would have otherwise been possible to evaluate the rate of biotransformation of each compound relative to CB153. Indeed, assuming that CB153 is totally persistent and does not undergo biotransformation, the difference between the theoretical concentration and the measured concentration of this contaminant can only be caused by messy feeding and by the physiological processes taken into account in the general equation of bioaccumulation (Equation IV-2). Assuming that all compounds are assimilated with the same efficiency during digestion (which might be a reasonable hypothesis for compounds with similar K_{ow}'s), the difference between the measured CB153 concentrations and other contaminant would be due to the biotransformation of these contaminants. This is illustrated on figure IV-7. A constant growth has been assumed here. Although Figure IV-6 suggests that there had been a slowing down of the growth rate during the 56 days of the experiment, it is not significant and is ignored for the following calculations.

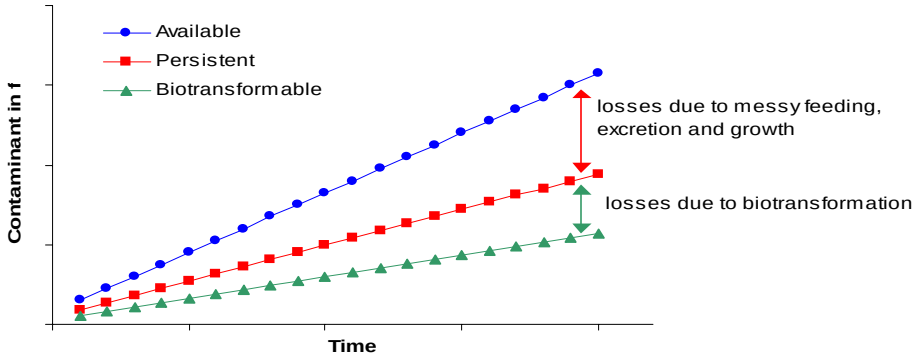

Figure IV-7: Theoretical approach and experimental measurements. Comparison of the maximum contaminant concentration theoretically possible in a fish fed with contaminated food (blue dots denominated "available") and what measurements would give for a persistent compound (CB153 type, red squares) and a biotransformable one (green triangles), assuming that assimilation is similar for all compounds. The difference between the lines denominated available and persistent would give information on losses rates due to messy feeding, excretion and growth. The difference between the lines denominated persistent and biotransformable give information on the biotransformation.

Although it is not possible to obtain biotransformation rates from (Jaouen-Madoulet, 2000) data set in this way, some interesting information can be extracted by calculating the "percentage of bioaccumulation" of each compound under investigation. This percentage is defined as the ratio of the measured concentration (red squares on Figure IV-7) by the theoretical concentration (blue dots on figure IV-6). This gives an idea of the proportion of available contaminant is bioaccumulated in the fish at any time during the experiment.

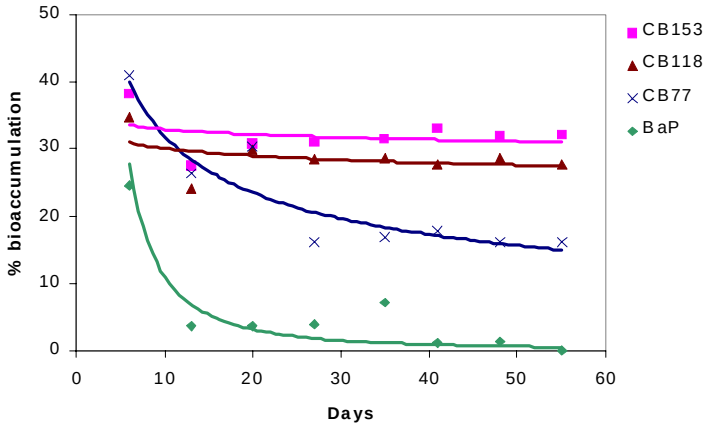

Figure IV-8: Percentage of bioaccumulation for CB153, CB118, CB77 and BaP for juvenile turbots. Each point is the ratio of measured over theoretical concentrations in juvenile turbots. Lines are shown to emphasise the evolution of the percentage of bioaccumulation with time for each contaminant. Data from (Jaouen-Madoulet, 2000).

The interesting point here is that for known persistent compounds such as CB 153, this percentage is roughly constant from the second week of the experiment onward. For a compound known to be biotransformed (BaP), the percentage of bioaccumulation decreases from about 25% in the first week to nearly 0 at the end of the eighth week, suggesting that after a period of acclimatising, the organism eliminates BaP by biotransformation faster than it assimilates it. For both these compounds and for CB 118, equilibrium seemed to have been reached between the uptake of contaminant and its elimination after a few weeks. The percentage of bioaccumulation of CB77 reaches a constant value only after the third week of

experiment. The Figure IV-8 suggests that this congener is less bioaccumulated by the juvenile turbots than the two other PCB congeners and this is in accordance with its known fate and toxicity in food chains.

If it is assumed that CB153 is a fully persistent compound, that on the 8th week of experiment steady state has been reached for all compounds and that the assimilation efficiency and the excretion of all 4 compounds are comparable, it is possible to normalise the percentage of bioaccumulation of all 4 compounds to that of CB153 to obtain a biotransformation coefficient BIOT defined as:

$$BIOT = \frac{\%\ of\ \ bioaccumulation\ of\ \ compound\ \ X}{\%\ of\ \ bioaccumulation\ of\ \ CB153} \qquad \text{(IV-6)}$$

Equation IV-6: Definition of biotransformation coefficient.

This coefficient can vary between 0 for compound totally eliminated by biotransformation (BaP type) to 1 for fully persistent compounds (CB153 type). As biotransformation is a process that affects contaminant that has been incorporated into fish tissues, it is reasonable to apply this coefficient after the calculation of contaminant bioaccumulation with Equation IV-1. Hence, the concentration expected in fish is:

$$X_{f,i} = X_i \cdot BIOT \qquad \text{(IV-7)}$$

Equation IV-7: Biotransformation equation. $X_{f,I}$ is the final contaminant concentration in organism i.

The biotransformation coefficients for the four contaminants used in the turbot feeding experiment are given in Table IV-9. Although experiment data suggested that the turbot eliminated all BaP on the eighth week of the experiment, the BIOT coefficient is set to 0.01. This is justified by several facts:

- Contamination through respiration that will occur continuously in the field is negligible in the experimental tanks whose low contaminated water was changed regularly.

- Despite the apparent full BaP decontamination observed after the 8th week of the experiment, decontamination cannot be expected to occur instantaneously. The residual concentration calculated with a biotransformation factor equal to 0.01 takes this lag between assimilation and elimination into account in the steady state model.

Contaminant	% bioaccumulation	BIOT
CB153	35	1
CB118	30	0.85
CB77	15	0.43
BaP	0	0.01

Table IV-9: Percentages of bioaccumulation and biotranformation coefficients (data from Jaouen-Madoulet).

These coefficients were applied to the round fish generic model; the results (Figure IV-9) show the better agreement between model results and field data when using these biotransformation coefficients.

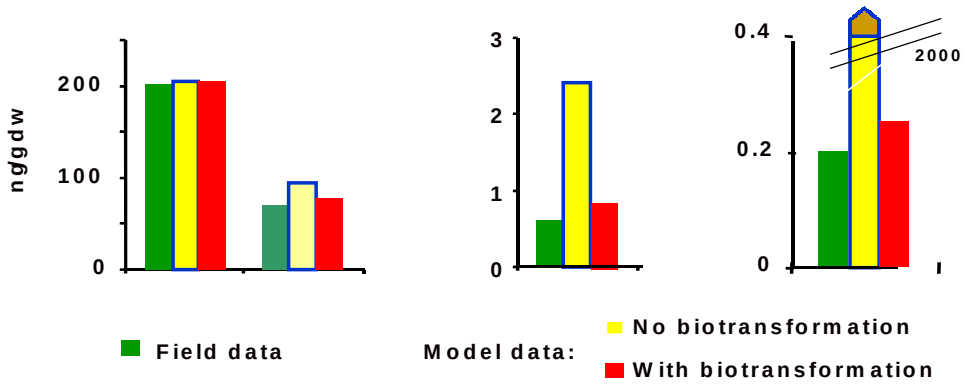

Figure IV-9: Round fish model results for the top predator fish compared to field data with and without taking biotransformation into account.

IV-3-8-3. Biotransformation: practical conclusions.

A lot of studies have been done on the various aspect of biotranformation and the different approaches followed to cope with this important process acting on the fate and distribution of contaminants in biota. From the above discussions, several important points for the GEMCO model can be drawn:

- First, an equation that simulates the effect of biotransformation on chemicals has been established

- Secondly, the biotransformation capacity of organisms varies as a function of the trophic level, and is generally greater in the top predator fish than in their preys. BMFs can give an indication on organisms biotransformation capacity but their interpretation is made difficult by the complexity and the variety of contamination assimilation pathways. In the GEMCO contaminant food web model, biotransformation can therefore be taken into account by introducing biotranformation factor after the general equation of bioaccumulation Equation IV-1.

- Thirdly, in spite of the interest of this approach one should be aware on its limitations. Information obtained so far has been got for a few compounds, in an experiment conducted on one species and in specified controlled conditions. The results of these experiments do not make any difference between the effects of excretion only and that of biotransformation.

In conclusion, taking into account the above limitations on the appraisal of biotransformation, if the final GEMCO model is to be used for chemical risk assessment and for the estimation of concentration exposure, it should be used in two stages.

First the model will be used without using any biotransformation coefficient, so the compound will behave like PCB153 and bioaccumulated as a fully persistent chemical. The PEC (predicted environmental concentration) estimated by the model would be overestimated leading to a “worst situation”. This worst concentration should then be compared with existing data on the PNEC (Predicted non-effect concentration), prescribed concentration or presumed safe concentration. Then, and if the two concentrations are within a close range, a biotranformation coefficient could be entered in the model, with a prudent approach and probably justifying more appropriated studies taking into account the nature, amount and reactivity of the chemicals released in the estuary, its reactivity and the specific local conditions within the estuary.

IV-4. MODEL VARIABLES

As in any model, both the flat fish and the round fish models run with a number of parameters with constant values, state variables, which are the quantities calculated to obtain the model results, and forcing variables, which are not of direct interest as model results but are necessary to calculate the state variables. Forcing variables are given values at the beginning of each calculation and may or may not be recalculated.

Within the GEMCO framework, the foodweb models presented are to be run coupled with a physico-chemical water quality model developed by Delft Hydraulics. During the development phase, the foodweb models had to run independently as "stand alone" versions, from the water quality model that will provide it with all forcing variables. The following sections describe the state variables, whose characteristics remain unchanged whether the models are coupled, and the forcing variables as they are used in the stand alone flat fish and round fish models.

The foodweb models include the calculation of a number of variables, such as phytoplankton contamination, necessary to evaluate the contaminant levels in higher trophic levels. These variables were calculated using empirical equations established in estuarine or marine conditions. This was necessary as some values are difficult to obtain experimentally and some parameters useful to the models were not considered during field sampling. These equations are also described below.

In this present model, the values assigned to forcing variables are part of large data sets gathered during the multidisciplinary research programmes conducted in the Seine estuary (Programme de Recherche Scientifique Seine Aval) and in the bay of Seine (Programme National d'Environnement Côtier, Chantier Baie de Seine). We are fully indebted to several collaborators and colleagues who have provided us with data and empirical equations essential to our work.

IV-4-1. STATE VARIABLES

The state variables of the generic model are the contaminant concentrations X_i in the organisms. There is one for each trophic level so there are 3 of them in the round fish model, 2 in the flat fish one Table IV-10.

State variables	Description
Round fish food chain	
X_1	Contaminant concentration in zooplankton
X_2	Contaminant concentration in suprabenthic organism
X_3	Contaminant concentration in round fish (predator)
Flat fish food chain	
X_1'	Contaminant concentration in benthic organism
X_2'	Contaminant concentration in flat fish (predator)

Table IV-10: List of the state variables of the generic models.

Forcing variables in the model are mainly the variables that depend on and define each estuary as well as the period of the year for which the simulation is carried out. They are the temperature, the chlorophyll a concentrations, the zooplankton density, the SPM concentration in water, the dissolved oxygen concentration and variables that characterise the SPM or sediment organic content.

Forcing variables	Description	Default value in the stand alone model	Unit
[Chla]	Chlorophyll a concentration in water column	18	$\mu g.l^{-1}$
Lip	Phytoplankton lipid concentration	0.045	$g.g^{-1}$
$[O_2]$	Dissolved oxygen concentration in water	5.8	$mg.l^{-1}$
[SPM]	Particles concentration in water column	120	$mg.l^{-1}$
T	Water temperature	14.5	°C
f_{oc}	Organic carbon fraction in SPM (flat fish model)	0.02	-
[Zoo]	Zooplankton density (round fish model)	1.17	$mg.l^{-1}$
[secprod]	Secondary productor density (round fish model)	0.016	$mg.l^{-1}$

Table IV-11: Default values of forcing variables in the food web stand alone model.

There are two other variables of importance, both related to the contaminant: its concentration dissolved in water and its K_{ow}. The values used during model development are given in the two following tables.

Congener	$LogK_{ow}$		Default water conc.
CB 52	5.24	(Hawker and Connell, 1988)	0.315
CB 77	6.36	"	
CB101	6.38	"	0.111
CB118	6.74	"	0.075
CB 138	6.83	"	0.072
CB149	6.67	"	0.120
CB 153	6.92	"	0.075
CB 170	7.27	"	0.025
CB 180	7.36	"	0.040
CB 194	7.80	"	0.001
Benzo(a)pyrene	6.35		

Table IV-12: Octanol-water partition coefficients ($logK_{OW}$) and PCB dissolved concentrations used in the model. Default values of forcing variables in the food web stand alone model. *Data from the Seine estuary (*Munschy *et al., 1996) except compounds marked (**) *which were estimated from* Schulz – Bull *et al. 1991).*

IV-4-3. CALCULATED VARIABLES

IV-4-3-1. Water particle partition coefficient, K_d

A water particle partition coefficient is required to calculate the contaminant concentration on particles when only water concentration was available. An empirical relationship has been established by (Munschy *et al*., 1996) for the Seine estuary:

$$\text{Log } K_d = 0.75 \text{ Log}K_{ow} + 0.46 \qquad \text{(IV-8)}$$

Equation IV-8: Relationship between K_d and K_{ow} for PCBs in SPM (Munschy *et al*., 1996).

This relationship has been validated in the Seine estuary for a series of 7 PCBs with Log K_{ow} varying between 6.65 (CB105) and 7.36 (CB180). It is assumed here to hold for a wider range of PCBs. The water particle coefficient K_d was used to calculate the PCB concentration in SPM and in sediments according to the equation:

$$X_{(Sed,SPM)} = X_w \cdot K_d \qquad \text{(IV-9)}$$

Equation IV-9: PCB concentration in sediment (X_{Sed}, ng.g^{-1}dw) or in SPM (X_{SPM}, ng.g^{-1} dw) calculated from the concentration in water (Xw, ng.ml^{-1}) and the water particle coefficient K_d.

Since similar relationships were not available for PAHs in the Seine, an equation adapted from (Kayal and Connell, 1990) and established with surface sediment data from the Brisbane River estuary (Australia) was used:

$$\text{Log}K_d = 3.584 \text{ Log}K_{ow} - 0.327 (\text{Log}K_{ow})^2 - 3.523 + \text{Log } f_{oc} \qquad \text{(IV-10)}$$

Equation IV-10: Relation between K_{ow} and K_d for PAHs *(adapted from Kayal and Connell, 1990; f_{oc} is the organic carbon fraction of the particulate matter)*

IV-4-3-2. Equations for phytoplankton contamination

Phytoplankton contamination has been shown to be related to contaminant K_{ow} (Brown *et al*., 1982; Harding, 1986). Phytoplankton sampling in the Seine estuary and quantification of its PCB content has allowed to established the following equations (Table IV-13) (Loizeau *et al*., 2001b) used in the stand alone GEMCO bioaccumulation model:

Log Kow range	Equations of phytoplankton contamination
5.5 < Log K_{ow} < 7	Log X_p = Log X_w + 1.0339 LogK_{ow} + Log Lip - 0.6025
7.1 < Log K_{ow} < 8	Log X_p = Log X_w - 0.9743 LogK_{ow} + Log Lip + 13.43

Table IV-13: Equations for the evaluation of phytoplankton PCB contamination. *(X_p) depending on congener Log K_{ow}, on PCB concentration in water X_w and on phytoplankton lipid fraction Lip (Loizeau and Ménesguen, 1993).*

IV-5. DESCRIPTION OF RESULTS

IV-5-1. CONCENTRATIONS IN ORGANISMS

The round fish generic model allows calculating a contaminant concentration in 3 types of organisms: zooplankton, a suprabenthic organism and a predator fish. The concentrations calculated are the contaminant concentration averaged to the whole organism body, shells excepted. Experimental data for large organisms often discriminate between muscles and organs (liver, gonads, bile…). This is not possible with this model whose results are expected to be slightly overestimated compared to concentrations in muscle but would appear largely underestimated compared to concentrations in organs, where lipophilic contaminants are often found at relatively important concentrations.

The model concentrations are expressed per g of dehydrated organism (g dry weight). If the contaminant concentrations in water and sediment or particles are expressed in $nmol.l^{-1}$ or $nmol.g^{-1}$, the results of the generic model will be in $nmol.g^{-1}$ dw in organisms. Alternatively, if the concentrations in the abiotic compartments of the estuary are expressed in $ng.g^{-1}$, the generic model results will be expressed as $ng.g^{-1}$ dw in the organisms.

In many studies on contaminants in biota, the concentrations are reported on a fat basis or ng of contaminants per g of extracted lipids as these compounds are stored in fatty tissues; therefore we don't agree with this mode of expression of the results and that for several reasons:

- The method of determination of the lipid fraction is not well documented, does not satisfy most of Quality Assurance criteria for analytical data and leads to an operationally defined parameter, - the mass of an extracted obtained by solvent of solvent mixture extraction in precised conditions,- and thus the lipids do not constitute a group of chemically related substances.

- The lipid fraction and its composition in biological tissues vary depending on species and moreover, in the same species the lipid content and composition vary in relation with biological and environmental parameters (age, gender, sexual development, starvation, feeding) which means that, without any precision, the contaminant concentrations might vary in a larger range when expressed on a fat basis.

- Last, by expressing the concentration on a fat basis, lean products like most of fish and seafood, are particularly subjected to an over-estimation of the contaminant concentrations and an increasing uncertainty of the results (for example, contaminant concentration will increase two folds when changing the fat content from two to one 2 to 1 %).

For comparing data using various mode of expression of the concentration, practical orders of magnitude might be used that facilitate direct comparison within an acceptable uncertainty, at least comparable with that of the model.

- The water content in tissue from fish and estuarine organisms is approximately 80-85% of the wet weight which means that dry weight based concentrations are multiply by 5 – 7 compared to concentrations on a wet (or fresh) weight basis.

- In liver, commonly used in marine pollution monitoring programmes, the water content is approximately 30-40% the whole wet weight, thus the concentrations on a wet weight basis are to be multiplied by a factor in the range 1.4-1.7 to obtain dry weight concentrations.

- The fat content in fish and marine organisms vary in 5-20 % of the dry weight; 10% represents a good approximation for fish muscle tissue. It means that dry weight concentrations are to be multiplied by a factor of ten for a direct comparison with concentration given on a fat basis.

- The Gemco model is providing calculated contaminant concentrations in the whole generic "virtual" fish without any distinction on its various organs and tissue. Generally, at least for larger species (let say for the target species) measured concentration are given for a specified type of tissue; in many cases either muscle (data obtained in studies related to the quality of food product) or fish liver, very often used in marine pollution programmes. Conversion factors were estimated from measured data in order to facilitate comparison between simulated concentration and real data obtained either in muscle or liver. (see Annex 3).

In the case of the round fish model :

C.fish calc. (fresh weight) = 0.4 conc. measured in liver (fresh weight)

C fish calc. (fresh weight) = 4.4 conc. measured in muscle (fresh weight)

In the case of the flat fish model:

C.fish calc. (fresh weight) = 0.35 conc. measured in liver (fresh weight)

C fish calc. (fresh weight) = 2.4 conc. measured in muscle (fresh weight)

The model has been designed to provide concentrations as accurate as possible in a top predator fish. The information given by the concentrations in organisms from lower trophic levels (organisms 1 and 2 in the round fish model, organism 1 in the flat fish model) should be handled with great caution. In particular, the variables relative to the concentrations in the suprabenthic and the benthic organisms (respectively X_2 in the round fish model and X_1' in the flat fish model) are unlikely to compare well to the concentrations in any specific living organisms from European estuaries. They should at most be assimilated to a rough average concentration of all suprabenthic or benthic preys available to the top predators of the food chains considered. Even in the most comprehensive studies, contaminant concentrations are rarely measured in more than a few organisms of a given food chain. It is therefore not possible, and not intended, to obtain a close relationship between the concentrations in the lower trophic levels represented by organisms 1 and 2 in the round fish model and zooplankton and suprabenthic organisms sampled in the field. Similarly, contaminant concentrations in organism 1 of the flat fish model would only be an indication of concentrations in benthic organisms. The model aims to obtain reasonable contaminant concentrations in the target fish (the round and the flat predator fish) and validation should concentrate on these organisms.

IV-5-2. VALIDATION IN THE SEINE ESTUARY.

Data used to validate the generic models of bioaccumulation are issued from studies carried out in the Seine estuary and reported by Jaouen –Madoulet (2000) and Loizeau *et al.* (2001a, 2001b) in their work on the sea bass and flounder food webs.

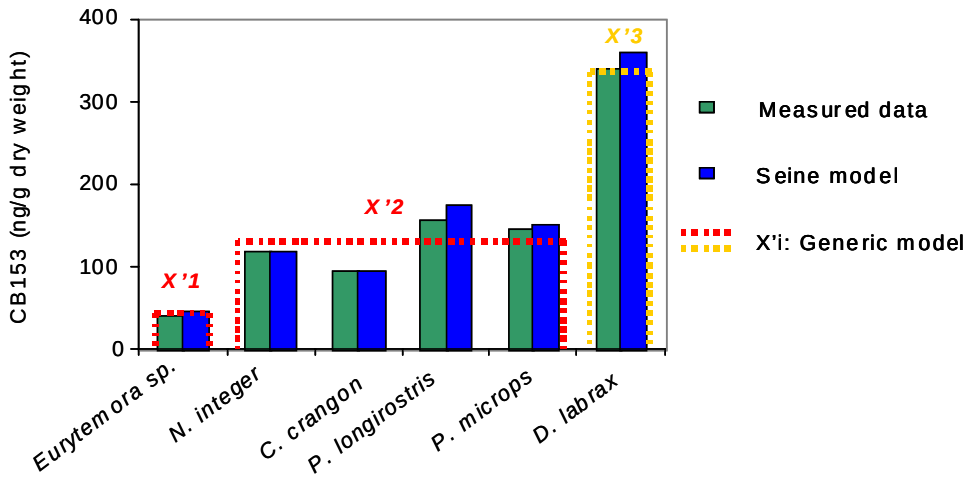

Figure IV-10: Validation of the round fish model with data and model on the sea bass food web from the Seine estuary. Comparison of calculated and measured concentrations of CB153 in the sea bass food chain. The Seine Model refers to the model developed by Loizeau *et al.* (2001a) that includes a detailed food web for he sea bass. The "Generic model" is the round fish model.

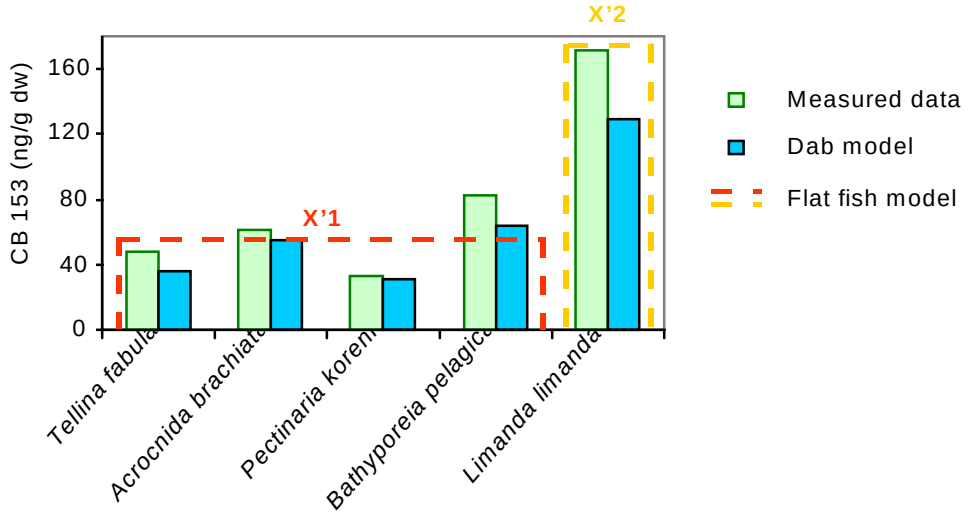

Figure IV-11: Comparison of calculated and measured concentrations of PCB153 in the dab food web. The dab model refers to the model developed by Loizeau and Ménesguen (1993).The flat fish model is the generic version of the previous model in which X'1 represents the suprabenthic organism and X'2 the predator flat fish. Data are from samples taken in the Bay of Seine.

In each case, we can note a fairly good agreement between field measurements and models, either the sea bass model with the generic round fish model or the dab model with the generic flat fish model. This is particularly satisfactory if we take into account the simplification introduced in an simplified, generic and easy to use model.

IV-5-3. VALIDATION FOR THE EBRO ESTUARY

The bioaccumulation generic model has been validated with data gathered from a series of publications on the Ebro estuary (see the references in Table IV-14). The sampling times and locations of each of these studies were not the same, so it has been necessary to assume that the data reported was constant between areas and that seasonal variations in contaminant concentrations were not significant.

In these publications, the PCB concentrations were reported as sum of seven or more congeners or as Aroclor equivalent. The concentrations of CB153 were needed for the model validation. The conversions of these sums of congeners or Aroclor equivalents have been carried out assuming that the proportion of each congener was constant and adequately described by the characterization of commercial mixtures reported by (Schulz *et al.*, 1989). It is however known that some congeners are eliminated faster than other in the environment and such assumption entails an important uncertainty in the data used. This assumption is not valid and cannot be accepted by environmental chemists; the congener specific analyses of PCBs in environmental samples have shown that the PCB pattern may be altered by degradation which is particularly true in biological matrices. However, these "old" PCB data from the Ebro estuary are of great interest in our attempt to validate the model because and in spite of these given limitations they give an acceptable order of magnitude of the concentrations.

	unit	1980s values	Reference	1990s values	Reference
CB 153 dissolved in water	$ng.l^{-1}$	0.120	Cid Montanes *et al.*, 1990	0.0075	(Dachs *et al.*, 1997)
CB 153 in phytoplankton	$ng.g^{-1}$ dw	26.89	Estimated using equation in Table IV-13	1.68	Estimated using equation in Table IV-13
CB153 in SPM	$pg.l^{-1}$	430	Cid Montanes *et al.*, 1990	1.2	Dachs *et al.* 1997
SPM in water	$mg.l^{-1}$	8	Guillèn and Palanques,1992	8	Guillèn and Palanques,1992
CB 153 in SPM	$ng.g^{-1}$ dw	53.8	Estimated	0.2 -3.4	Estimated
Lip	$g.g^{-1}$	0.045	Model Seine	0.045	Model Seine
Temperature	deg C	17.4	Ibanez *et al.*,1997	17.4	Ibanez *et al.*,1997
Chlorophyll	$\mu g.l^{-1}$	12	Estimated	12	Estimated
Dissolved O_2 concentration	$mg.l^{-1}$	4	Casamayor *et al.*,2001	4	Casamayor *et al.*,2001
Zoopk. Biomass	$mg.l^{-1}$	1.2	Model Seine	1.2	Model Seine
CB 153 in sea bass	**$ng.g^{-1}$ dw**	**150-750**	Sanchez Pardo and Rovira, 1985a	**3.2 - 7.3**	Pastor *et al.*, 1996
CB153 calculated	**$ng.g^{-1}$ dw**	450	Round fish model	1.6 – 28	Round fish model

Table IV-14: Data used to validate the round fish model in the Ebro estuary and results of the validation of the model using data from the Ebro estuary.

The publications used have been separated into two sets: the first one report data from the early 1980s and the second data from the 1990s. The legislation between these two periods has lead to a decrease in PCB use and this is clearly reflected in the data with PCB

concentrations in the 90s significantly lower than in the 80s. Two dataset, one for each period, have been gathered, assuming that temporal variations in PCB concentrations within each ot these two periods were negligible.

Data were often reported only on graphs. It has therefore been necessary to calculate values from measurements with a ruler. The error introduced here is probably much less than the error caused by assuming a constant proportion, the same in PCB residues in biota as in PCB technical mixtures.

Seasonal cycles of temperature and of chlorophyll a concentration have been evaluated from a very limited number of data. For temperature, Ibanez *et al*., (1997) provide 14 data points over the years 1998-1990. These points have been pooled so that a sinusoidal function could be fitted to represent the temperature seasonal cycle over a year. The temperature chosen for forcing the model is the one calculated with the sinusoidal function for the 15th May (day 135).

The chlorophyll a cycle has been evaluated from data and information found in various publications (Casamayor *et al*., 2001; Lahet *et al*., 2000, 2001; Sabater and Munoz, 1990; Vives and Planas, 1952)). These references give information either in the Ebro plume or at a specific time in the Ebro delta. As a result, there is a fair amount of personal interpretation in the chlorophyll a cycle chosen.

According to Casamayor *et al*., (2001), the saline wedge of the water in the Ebro is hypoxic or anoxic (range: 0-5 mg.l^{-1}, average: 0.4 mg.l^{-1}). Fish would probably avoid these conditions and live a bit further offshore. Oxygen concentrations in lagoons in the Ebro delta are higher (4 to 8 mg.l^{-1}, Vidal *et al*. 1997). Increasing the oxygen concentration from 0.4 to 8 mg.l^{-1} leads to a decrease of CB153 concentration in the top predator fish of about 6%. A value of 4 mg.l^{-1} was used for this model validation.

The reports of PCB concentrations in SPM were always given as sum of congeners or technical mixtures and may also be in mg.l^{-1} whereas the model requires concentrations in mg.g^{-1}. To convert litterature data into data required by the model, it was therefore necessary to take SPM concentration into account. For this parameter again, data was sparse and with important seasonal and geographical variations. Alternatively, if PCB concentrations in water were known then it was possible to derive PCB concentrations in particles using the partitioning coefficient K_d. This coefficient was calculated with the relationship established for the Seine estuary (Munschy *et al*., 1996) and described above. From the various sources of information gathered, a SPM concentration of 8 mg.l^{-1} has been selected.

The PCB concentrations in biota were also reported as technical mixture equivalent (Aroclor) or in sum of congeners. Conversion into CB 153 is carried out as for SPM and water. Concentrations in biota are either in wet weight or in dry weight. The generic bioaccumulation model gives results in dry weight. It has been assumed that in fish muscle the water content was 70% of total weight. Sea bass is the fish chosen to validate the model. Note also that literature data is for muscle only whereas the generic bioaccumulation model gives results for the whole fish. The organs such as gonads and liver are usually more contaminated than muscle, so the model results should be higher than litterature data for muscle.

The round fish model results shown on the last line agree reasonably well with the concentrations measured in seabass living in the Ebro estuary by (Pastor *et al.*, 1996; Sanchez Pardo and Rovira, 1985a, b). The range of values obtained for the 1990s period is due to the range of value of estimated CB153 in SPM.

The results of the Ebro validation, last lines in bold prints in Table IV–14 show that, in spite of limitations on the quality of the data the orders of magnitude calculated by the generic round fish model fit quite well with field measurements.

IV-5-4. VALIDATION FOR THE SCHELDT AND THE EMS ESTUARY

The validation exercise as described in this chapter, includes the application of the model to two Dutch estuaries, the Western Scheldt and the Ems. For these estuaries sufficient data were available to derive estimated values for input parameters for the model and to compare predicted values in organisms with measured concentrations observed in field studies.

The generic estuarine bioaccumulation model is based on a steady state version of the Seine food web model described in Loizeau *et al*. (2001) and includes two food webs: one for a round fish food web (algae/detritus-zooplankton-secondary producer- roundfish) and one for a flat-fish food web (algae-benthic secondary producer-flatfish). The model was available for the validation exercises in the form of Fortran-codes and in the form of an Excel-file (Flatfish13.xls). The latter format was used for the validation exercise. As described in the previous chapters, the input parameters required by the model include a limited set of environmental parameters (temperature, dissolved oxygen, suspended matter concentration, organic carbon content of suspended matter), biological data (chlorophyll a concentration, zooplankton biomass, lipid content of phytoplankton) and compound specific data ($LogK_{ow}$ and dissolved concentration in the water phase). The model then provides estimations for the compound concentrations in the organisms of the pelagic and the benthic food webs.

In the following sections a short description is given of the approaches used to estimate values for the input variables. As becomes clear from these sections and the previous section on the Ebro estuary, the data used for validation of the model in other estuaries than the Seine cannot easily be derived from literature or databases, because of differences in sampling designs, chemical methods, format of reporting and many other factors. In case of a database with temporal and spatial variability of monitoring data, choices have to be made to select the appropriate monitoring data and aggregation levels to be used for the validation.

In Table IV-15, a summary is provided for the user-defined input variables for PCB 153 in the two estuaries. Data for the Seine and Ebro are provided for comparison. For the Western Scheldt examples are given of different exposure scenarios, varying in position in the estuary (river-end versus sea-end). The resulting predictions using the model are given in Table IV-16 and Fig A.12.

For the Western Schooled monitoring data were used for the period 1990-2000; the high (pollution load) scenario was based on data from the SPM sampling station for organic contaminants at the river end of the estuary (Scholar van Ogden Dole); the low scenario was based on data for a location at the sea-end of the estuary (WETSDE left bank opposite Vlissingen). Most of the data were derived from a database with results from Dutch water

quality monitoring programmes, available on CD-ROM (RIZA/RIKZ 2000) and with internet access (www.waterstat.nl and www.waterbase.nl) for most of the parameters, locations and time periods. The analytical quality of these data is high and most data are available for different periods and locations in the estuary. These data are also part of the large international database hosted by the Marine Data Centre of the International Council for the Exploitation of the Sea (ICES, www.ices.dk) and part of the Joint Monitoring Framework (JMP) used for the preparation of OSPARCOM and North Sea Quality Status reports. Literature searches in the Science Citation Index (web of science, Institute for Scientific Information) revealed little publications on organic contaminants in biota form the Western Scheldt. Most of the publications in journals on contaminants in the Western Scheldt were related to trace metals in sediments and particulate matter.

User defined input		**Seine a)**	**Ebro '80s a)**	**Ebro '90s a)**	**W. Scheldt sea end b)**	**W. Scheldt river end b)**	**Ems 1990-1999**	**Remarks**
CB 153 conc.in water	ng/l	0.075	0.120	0.008	0.011 c)	0.045 c)	0.007 c)	
Temperature	°C	14.5	17.4	17.4	12	12	11.7	
Chlorophyll a conc.	µg/l	18.1	12	12	13.6	13.6	13.03	
Dissolved O2	mg/l	5.8	4	4	9.0	9.0	11.4	
Log Kow		6.92	6.92	6.92	6.92	6.92	6.92	d)
Zooplankton biomass	mg/l	1.2	1.2	1.2	1.2	1.2	1.2	d)
Phytoplankton biomass	mg/l	2.9	2.2	2.2	2.4	2.4	2.3	e)
Susp.particulate matter	mg/l	120	8	8	48	42	94	
Org-C of SPM	%	0.021	0.02	0.02	0.032	0.032	0.037	

a) see sub-chapters on Seine and Ebro; b) low scenario: at height of Vlissingen; high scenario: Schaar van Ouden Doel; further explained in text section; c) calculated from concentrations in SPM with Kd values from Munschy *et al*. (1996, d) taken similar as in Seine Model; e) calculated from Chlorophyll a concentration (see Chapter-III.)

Table IV-15. Input parameters for PCB 153 for the validation of the generic bioaccumulation model

Species	Seine	Ebro '80s	Ebro '90s	W. Scheldt sea end	W. Scheldt river end	Ems
Pelagic food web						
Phytoplankton	12	19	1	2	7	1
Zooplankton	40	40	3	4	17	2
Secondary producer	115	146	9	10	41	6
Round fish (Seabass)	289	370	23	25	103	14
Benthic food web						
Organism-1 (annelid; *Pectinaria*)	85	28	2	9	33	9
Organism-1 (mollusc, *Tellina)*	57	79	5	8	31	5
Flatfish (Dab) whole body	127	178	11	17	70	11
Flatfish (Dab) liver*						

* extrapolated with factor 4.43; see section IV-5.1

Table IV-16. Summary of model predictions for PCB153 (ng/g dry wt)

For the Western Scheldt aqueous water concentrations of PCBs have been determined at two locations between 1980 and 1990 as total water concentrations, which includes the fractions bound to particulate matter and DOC as well as the freely dissolved fraction of PCBs. Since 1990 the measurement of water concentrations of hydrophobic contaminants was abandoned, because of analytical reasons (representative sampling of SPM; handling of large sample volumes; control of precision, accuracy and blank-control during extractions) and hydrophobic contaminants were measured in suspended matter, which constituted the dominant pool of PCBs and related compounds in the water phase. All data were derived from capillary GC-ECD determinations. In Fig A-1 and A-2 (Annex-4) the temporal fluctuation of SPM concentrations and PCB153 in SPM is indicated for the river-end location and a location close to the sea-end. The border location (Schaar van Ouden Doel) can be considered as an estimate of maximum concentrations in the estuary. For input in the model we used average values for the period 1990-2000 for the two locations. Using the K_d value for PCB153 from the Seine model ($LogK_d$ = 5.65), freely dissolved water concentrations were calculated for PCB153. Another approximation to calculate the dissolved water concentration could be based on organic matter content of SPM in the area, and literature derived K_{oc} values for PCB153.

Most of the other parameters (Temperature, Oxygen, Chlorophyll-a) measured in the Scheldt estuary are indicated in Annex-4 figures. For Chlorophyll-a annual averages for the summer observations (10-13 samples per season) are given. In Soetaert and Herman (1994) the spatial and temporal distribution of Chlorophyll-a is described for the period (1989-1991) with high summer values (bimodal, with peaks in April-May and July-August) in the freshwater part (more than 200 μg/L) and decreasing values at the sea end (less than 20 μg/L). Zooplankton biomass is currently not measured in the national monitoring programme of Rijkswaterstaat. For the zooplankton biomass the average figure from the Seine study was used (1.2 mg/L dry wt), as the zooplankton data of Soetaert and Herman (1994) for the period 1989-1991 (0 – 0.35 mg/L dry wt) might not be representative for the recent period (1990-2000). As seasonal and spatial variation in the estuary can be extremely large (up to order of magnitude differences) for both Chlorophyll-a and zooplankton biomass, as well as the species composition, the selection of this input-parameter values significantly affects the outcome of the model, as is demonstrated in the sensitivity analysis section in chapter IV. As in many river basins nutrient emission reduction programs have become effective during the ‘80s and ‘90s, the selected time-frame also is of great importance. As is demonstrated in figure A-4, chlorophyll levels before 1990 were much higher than current levels, especially at the upstream part of the estuary.

For the Western Scheldt there were no round fish data for the time period considered. For the comparison of predicted flatfish concentrations, measured data were available in the Dutch database for the blue mussel *Mytilus edulis* and flounder *Platichthys flesus* (liver). The time series were available for 2 locations close to the Hansweert Geul area (Figure A-6), between the mid to river-end section of the estuary, although not always complete for the full period (1990-2000). As can be seen in Table A.1 (Annex-4) the biota and suspended matter sampling stations do not coincide in both the Westerschelde and Ems. Furthermore several of the compound classes included in SPM monitoring are not measured in mussels and flounder-liver (e.g. chlorinated pesticides, organotin compounds). The concentrations were available on a wet weight basis and were converted using average measured dry weight fractions for 1998 and 1999 (mussel 12%; flounder liver 31%). The ranges of measured concentrations are indicated in Table 3. It should further be noted that the

target organism in the bioaccumulation model is the dab (*Limanda limanda*), which occupies a lower trophic position than the flounder.

A further comparison of the spatial and temporal variability of PCB-153 in the estuary is made in figure IV-12. Predictions were based on water concentrations derived from measured concentrations of PCB-153 in suspended particulate matter (SPM). Error bars for PCB-153 in SPM, *M. edulis* and flounder-liver in Figure IV-12 represent the standard deviation of annual means in the period 1990-1999. Error bars in calculated parameters (C_{water}, X1 and X3) were derived from the standard deviations of PCB-153 in SPM.

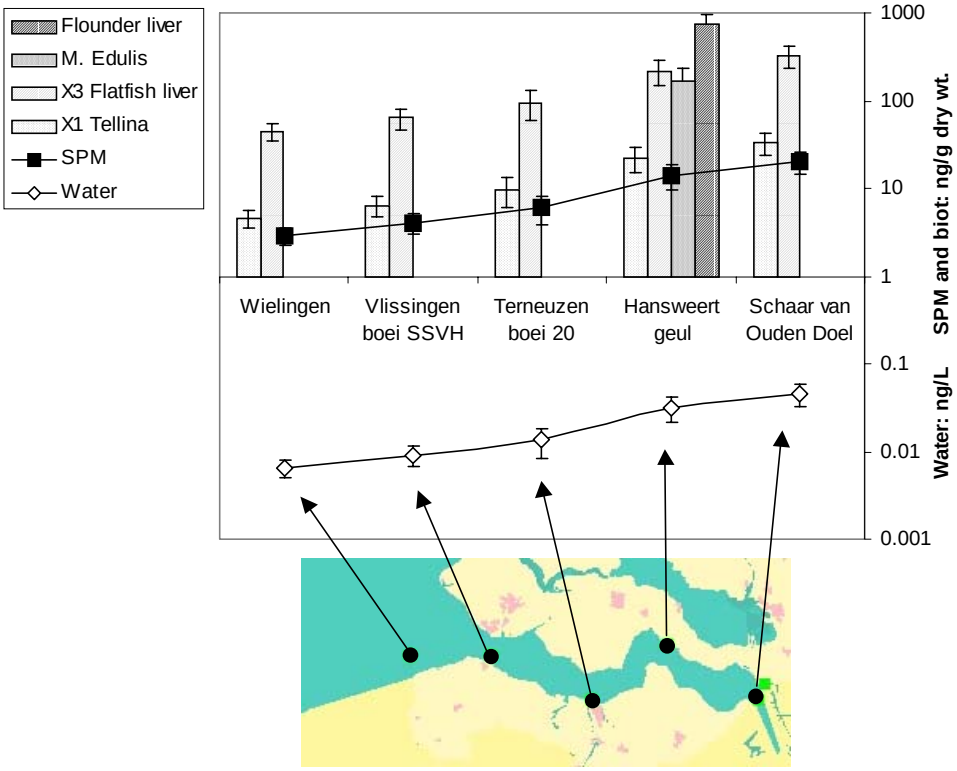

Figure IV-12: Spatial distribution in the Scheldt estuary of predicted PCB-153 concentrations for organisms (X1, X3) in the flat fish model and comparison with measured data for *M. edulis* and flounder-liver. Water concentrations (in ng/L) derived form measured concentrations of PCB-153 in SPM are indicated for the different sampling stations. Further explanation: see text.

Lipid-based biota data for the period 1988-1990 from Stronkhorst *et al*. (1993) have been included in the table to demonstrate the large spatial differences in exposure within the estuary. Lipid weight data to convert the values of Stronkhorst *et al*. (1993) to dry weight based concentrations were not available. Hardly any other data were found in the open literature for organic contaminants in Western Scheldt organisms matching the generic taxa of the round fish model.

From the analysis in figure IV-12 it becomes clear that the spatial differences in the estuary are larger than the temporal variation (annual variation, time trend in period 1990-1999). The measured values in flounder-liver and mussel are from a location between the mid to river-end section of the estuary. The flatfish model predictions for PCB-153 are a factor of

2-8 lower than the measured concentrations in flounder-liver, depending on the estimated water concentrations for the river end or the mid section of the estuary. The measured values in the common mussel are within a factor of 5-18 higher than predicted values for benthic organism-1 at the river end or mid section of the estuary. Taking into account the higher trophic position of the flounder compared to the dab, the lower prediction of the model for the flatfish can be explained at least partly. For the difference between the predicted concentration for the benthic target organism (Org-1, *Tellina*) and the measured concentrations from the mussel transplant studies, we assume that this may also be the result of species differences (see remarks made in section IV-5.1).

	Conc. ng/g d.w.	Locations, remarks	Source
Period 1990 –1999			
Flounder (liver)	510-900	Range of (n=5) annual averages. Locations: Middelgat, Brouwerplaat, Molenplaat	Riza/RIKZ 2000
Mytilus edulis	104-130	Range of (n=10) annual averages. Location: Hoedekenskerke boei 4	
Period 1988-1990			
Small clupeids (6cm)	2070 (lip. wt)	Saeftinge (river end)	Stronkhorst *et al*. (1993)
Small clupeids (6cm)	950 (lip. wt)	Hooge platen (sea end)	
Nereis diversicolor	1780 (lip. wt)	Saeftinge (river end)	
Nereis diversicolor	580 (lip. wt)	Paulina Schor (mid-sea end)	
Cerastoderma edulis	460 (lip. wt)	Neuzenpolder (mid-sea end)	

Table IV-17 : Summary of measured values of PCB153 in the Western Scheldt

Another important factor is the relationship used for the estimation of dissolved water concentrations from PCB-153 concentrations in SPM The relationship between Log-Kd and Log-Kow of Munschy *et al*. (1996) based on Seine data leads to lower water concentrations than procedures based on organic carbon based concentrations and Log-Koc and Log-Kow relationships described in the literature or EU-TGD documents (TGD, 1995). Using the QSARs described by Karickhoff *et al*. (1979,1981) or Sabljic and Gürsten (1995) (one of the benchmark relationships in the TGD document) 1-2 order of magnitude higher water concentrations are calculated from the measured SPM concentrations. Application of the polynomic relationship of Kayal and Connell (1990) based on Brisbane River estuary leads to lower concentrations (1-10 times) for the different PCB congeners. This is demonstrated in Fig. IV-13 for PCB153.

type of study	Authors	QSAR
lab	Sabljic and Gürsten (1995):	LogKoc = 0.81*LogKow + 0.1
field	Munschy *et al*. (1996):	LogKd = 0.75*LogKow + 0.46
field	Kayal and Connel (1990):	$LogKoc = 3.58*LogKow – 0.33*(LogKow)^2 – 3.52$

As it is known from numerous field studies that Koc values derived from experimental studies may underestimate the bioavailability of sediment or SPM-bound contaminants (Kayal and Connell (1990), Readman *et al.* (1984), McGroddy *et al.* (1996); Van Hattum *et al*., 1998) we did not choose to use the TGD recommended relationships of Sabljic and Gürsten, 1995). The polynomial relationship of Kayal and Connell (1990) is to a large extent based on PAHs, for which class of compounds other factors such as ageing or binding to soot particles may be involved (Harkey *et al.*, 1995; Pignatello and Xing., 1996; Belfroid and Sijm, 1996; Gustafsson *et al.*, 1997), which may not all be applicable to compound classes such as e.g. PCBs. For this reason the polynomial relationship was not used.

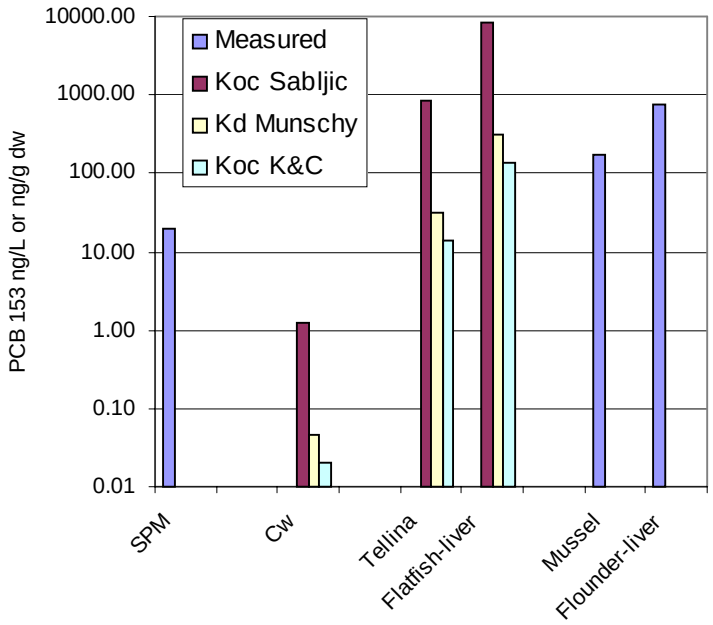

Fig IV-13: Estimation of dissolved water concentrations (C_w in ng/L) from measured concentrations of PCB 153 in suspended matter (SPM in ng/g dry wt) in the Western Scheldt, using 3 different relationships predicting Kd or Koc from Kow (Sabljic and Gürsten, 1995; Munschy *et al*., 1996; Kayal and Connell, 1990. (see text for explanation). The model predictions (Tellina and Flatfish) based on these Cw estimations are indicted and compared with measured concentrations in mussel and Flounder-liver (ng/g dry wt).

In Figure IV-14 a comparison is made of model predictions for the 7 PCB congeners (included in the Dutch monitoring programmes) with measured concentrations in mussels and flounder (DONAR database; RIZA/RIKZ, 2000). Water concentrations were derived from the SPM data at Schaar van Ouden Doel (river end). Organism data were from sampling locations close to Hansweert (mid to river end section of estuary). The mussel may tentatively be compared with the data for Organism-1 (*Tellina fabula*; a small bivalve) in the flat fish food chain.

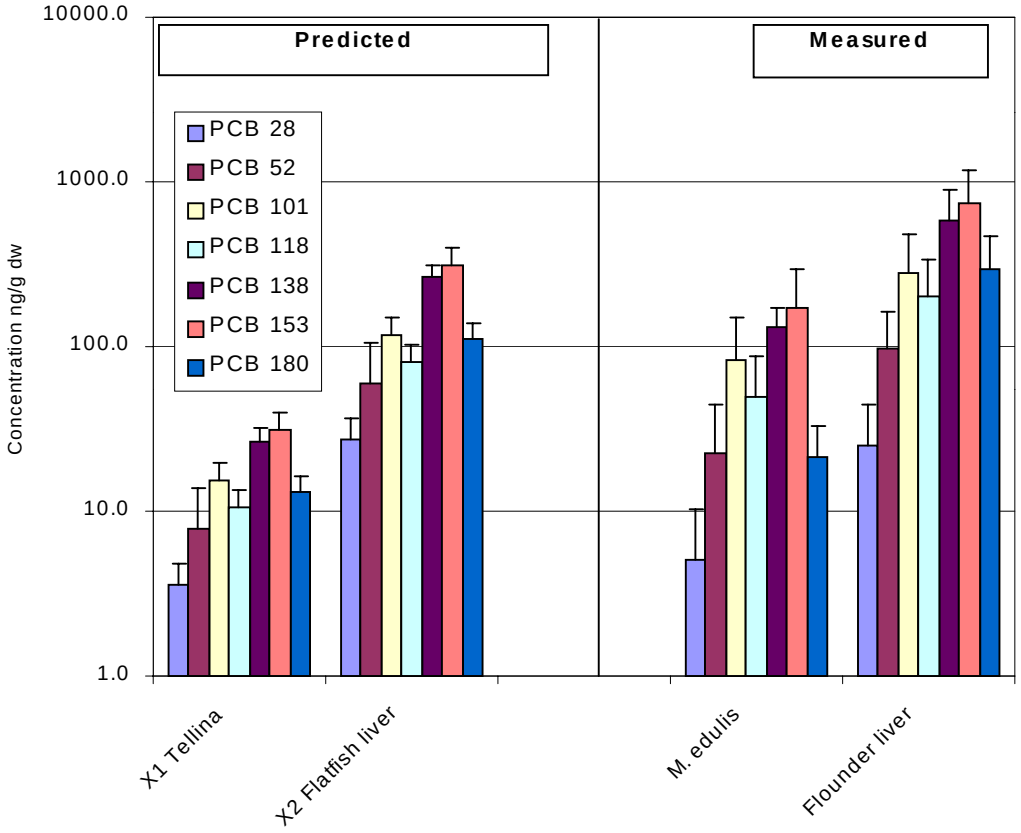

Figure IV-14:.Comparison of model predictions (mean ± 95% CI) and measured concentrations of 7 PCB congeners (mean ± 95 CI ng/g dry wt) in common mussels (*Mytilus edulis*; Hoedekenskerke boei 44) **and in flounder in the Scheldt estuary** (*Platychtus flesus*; Middelgat, Brouwerplaat, Molenplaat). Dissolved water concentrations were derived from PCB concentrations in SPM (Location WESTSDE) using the relationship (Eqn. IV-8) from Munschy *et al*. (1996).

The predicted patterns of the different congeners agree with the congener patterns observed in the measured data.. Similar as for PCB 153 the model predictions are usually lower than measured values, except for PCB-28 in flatfish liver, which is close to the measured value in flounder liver. For the other congeners the measured values for the flatfish are 1-3 times higher than model predictions; for the molluscs model predictions are 18-70% of measured values. This may be due to the previous explained bias in the extrapolation of the water concentrations form measured SPM concentrations, dislocation of SPM and organism sampling stations, differences in trophic position and feeding preferences between both bivalves and both flatfish species, and for the flatfish-liver uncertainties in the extrapolation to liver concentrations. Using different feeding preferences for the flatfish in the model (feeding on annelids and amphipods instead of only on small bivalves, the default-option in the model) slightly higher concentrations (10-20%) are predicted for the flatfish. Considering all the uncertainties, the within order of magnitude match between predicted and measured values for PCBs is not an unreasonable performance for a generic model.

In figure IV-15 the predicted concentrations in the Ems estuary for 7 PCB congeners are compared with measured values. The sampling locations for suspended matter (Bocht van Watum) and biota (mussel: Bocht van Watum; flounder-liver: Paap, Grote Gat, Reider Plaat)

are located near to the Dutch left bank of the estuary, near to the sea end of the Ems estuary. Water concentrations were estimated from measured SPM concentrations with the relationship of Munschy *et al*.. (1996). Comparable as for the Western Scheldt estuary, the measured values for PCB 153 are approximately 2-14 times (for flounder-liver and mussel respectively) higher than model-predicted concentrations for mussels and flounder-liver respectively. The relative contribution of PCB-28 in the Ems predictions is larger that expected. Usually this contribution is smaller than the contribution of PCB-52. For the other congeners, measured values are 2-13 times higher for mussels or 1-5 times higher for flounder-liver, except for PCB-28 where predicted levels in flatfish-liver are 2.5 time higher than measured values.

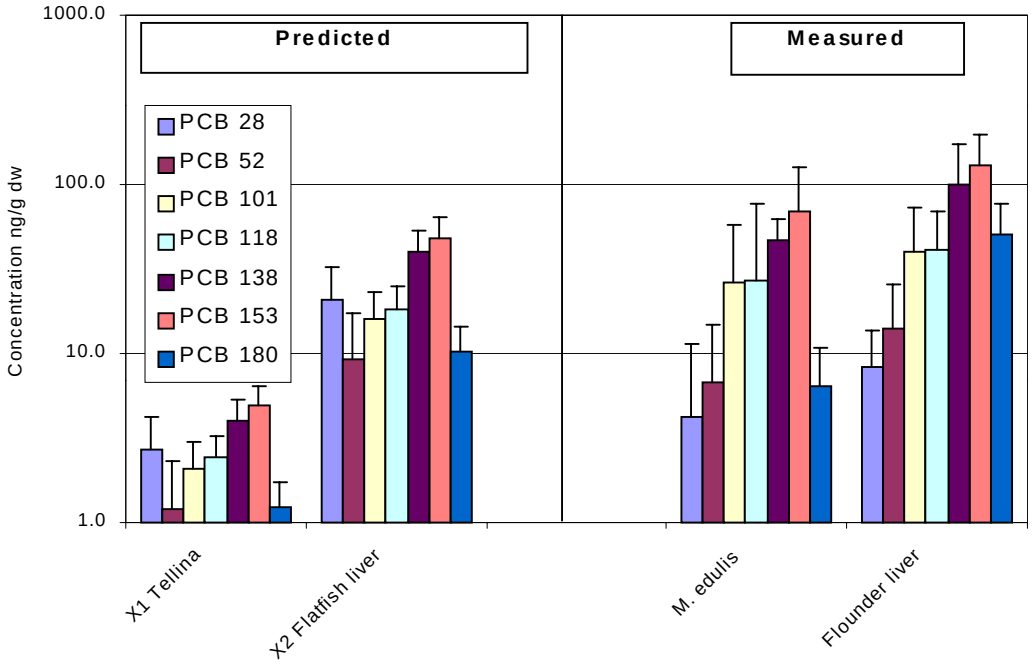

Figure IV-15: Model predicted values and measured concentrations of different PCB congeners in mussels and flounder-liver from the Ems estuary.

A similar comparison was made for hexachlorobenzene (HCB) in the Western Scheldt and the Ems (locations see Table A.1, Annex). A LogKow value of 5.7 was used (Hendriks *et al*., 1995). In figure IV-16 measured values in mussel and flounder-liver are compared with the flatfish model predictions for the small bivalve and dab-liver. The model consistently predicts the differences in exposure conditions between both estuaries and the differences between the trophic levels. The higher values in the Ems are related to known historical emissions of HCB in this estuary, especially in the first half of the 1990s. The predicted values usually are 1-2 times higher than measured concentrations, except for the molluscs in the Scheldt (mussel data approximately 50% higher than predictions for Org-1). No biotransformation factor was applied in the predictions.

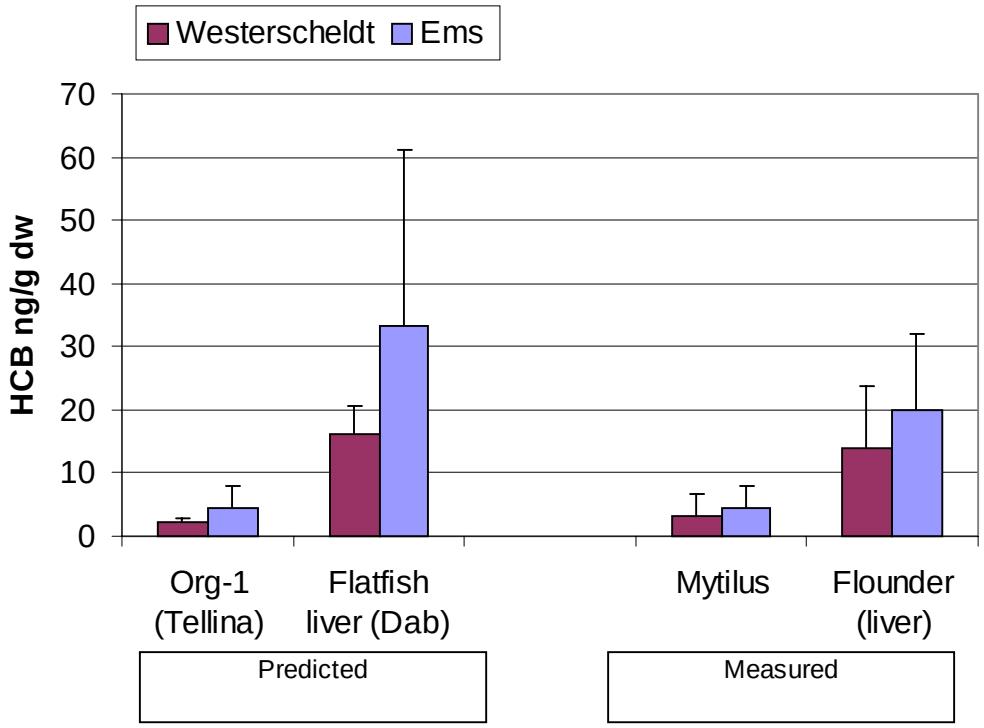

Figure IV-16 : Comparison of model predictions and measured concentrations of hexachlorobenzene (HCB) in common mussels and flounder (mean ± sd in ng/g dry weight; 4-10 yearly averaged values for the period 1990-1999; yearly averages based on 5-23 samples per year). Error bars for predicted values extrapolated from standard deviation in SPM concentrations.

Recent results from a large study on brominated flame retardants in the Western Scheldt, North Sea and UK estuaries (de Boer *et al*., 2001), allowed a comparison of the performance of the model for another class of compound. Average sediment concentrations for BDE47 (2,4,2',4'-tetrabromodiphenylether), BDE99 (2,4,5,2',4'-pentabromo-diphenyl-ether), BDE209 (decabromo-diphenyl-ether), and HBCD (hexabromo-cyclododecane) from 19 locations in the Western Scheldt were used to estimate dissolved water concentrations with the relationship of Munschy *et al*. (1996).

These congeners were chosen because of their occurrence in sediments (BDE209) and biota (BDE47, 99, HBCD). It should be known that the Kow values of these compounds (as derived from Grosharrt *et al*., 2000) are mostly based on QSAR predicted values and show large uncertainty ranges for some congeners. Log Kow ranges applied were 5.8-6.0, 6.6-6.8, 6.3-9.97, and 5.8-7.5 respectively for congeners 47, 99, 209, and HBCD.

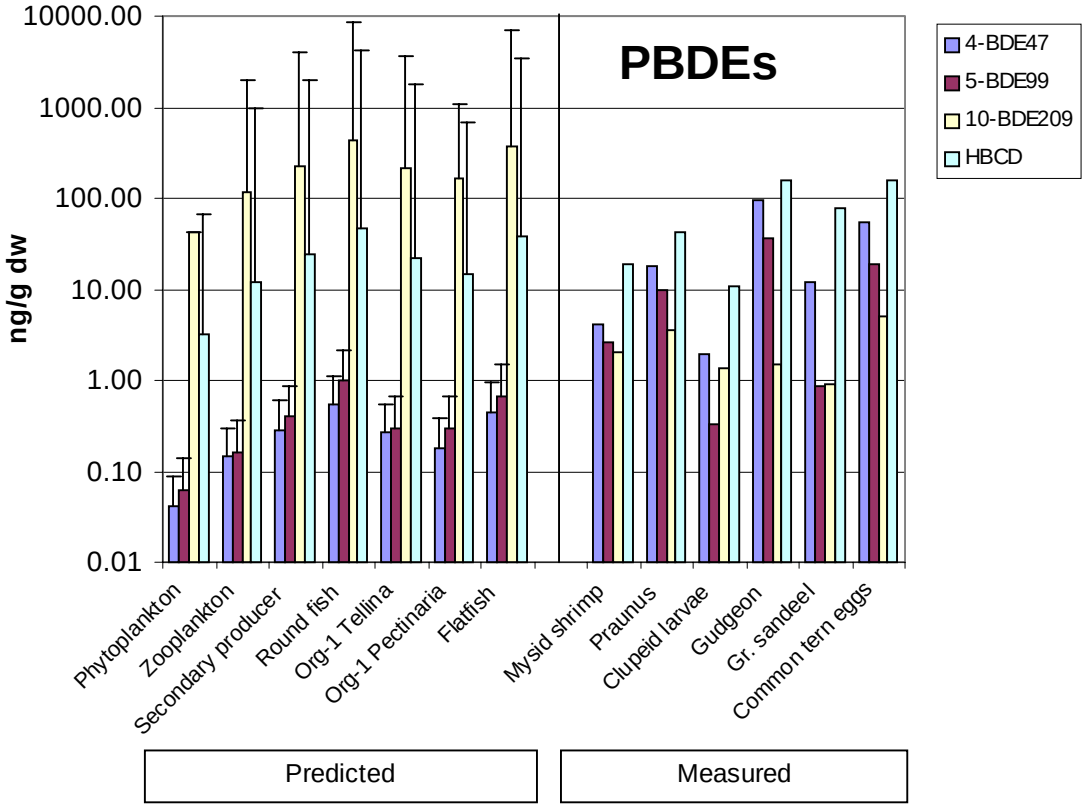

Figure IV-17: Measured concentrations of brominated iphenyl-ethers (PBDEs) in invertebrates and fish from the Western Scheldt (De Boer *et al*., 2001) in comparison to model predicted values based on dissolved water concentrations derived from sediment data. The predicted values were derived using the low (bars) and high (error bars) LogKow estimates discussed in the text .

The measures values in mysids may be tentatively compared with zooplankton in the round fish model. The results for the gudgeon may best be compared with the model predicted values for the secondary producer, taking into account the limitations described in chapter IV-5.1. The measured values for BDE47 and BDE99 are 16-29 times above the model predicted ranges for zooplankton and 90-340 times higher for the secondary producer predictions. For the super-hydrophobic BDE209, which usually is not detected or at very low concentrations in biota, the model overpredicts with approximately 1-3 orders of magnitude for the zooplankton and 2-3 orders of magnitude for the secondary producer. For HBCD model predictions and measurements for zooplankton are matching, using the low Kow estimates; using the high Kow estimate the model seems to overpredict 1-2 orders of magnitude. For HBCD in the secondary producer the model underpredicts (15% of measured value) using the low Kow estimate; using the high Kow estimate model predictions are 1-2 order of magnitude higher compared to measured values.

It should be noted that the Kow values used for BDE209 and HBCD are highly uncertain, and that most currently available food chain models (Thomann *et al*., 1992; Morrison *et al*., 1996; Hendriks, 1995; Mackay and Fraser, 2000; Gobas and Morrison, 2000; Voutsas *et al*., 2002;) are not able to handle the category of super hydrophobic compounds, and would have resulted similarly in orders of magnitude overpredictions. Furthermore it should be acknowledged, that the methods of analysis for these relatively 'new' compounds have not yet been validated as rigidly as for e.g. PCBs of PAHs. Especially the methods for HBCD still have a poor precision.

As stated in Chapter IV.3.7, cytochrome P450-mediated biotransformation of PAHs is known to be well developed in mammals, birds and many fish species (Varanasi *et al*., 1989). Most invertebrates have a less developed MFO-system, but large differences may exist in biotransformation rates among even closely related taxa within aquatic or terrestrial invertebrates (Van Brummelen *et al*., 1998). Although we have no quantitative information on the biotransformation capacity of *Mytilus* in the Western Scheldt or Ems, we tentatively compared predicted concentrations for organism-1 from the benthic food web (*Tellina* with measured concentrations in *Mytilus*. Contrary to the results for PCBs the model predictions are higher than the measured values in Western Scheldt and Ems (pyrene: factor 2-5; benzo(a)pyrene: factor 7-15). This over-prediction of the model is consistent with the fact that no correction for biotransformation was applied for these compounds. In both estuaries the results for pyrene are more close to the model-predicted values in comparison to benzo(a)pyrene, which may be caused by a combination of higher biotransformation and/or lower bioavailability of benzo(a)pyrene.

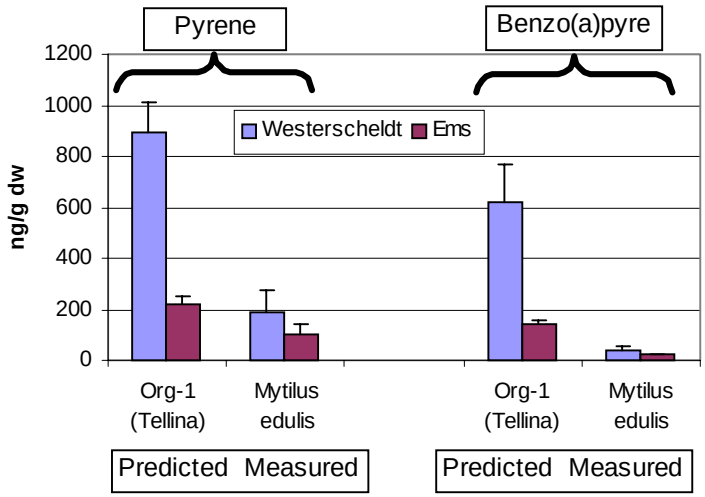

Figure IV-18: PAHs in bivalves from the Scheldt and Ems estuary. Comparison of measured concentrations *(Mytilus edulis*) and model predicted values (flatfish model, Org-1). In the scenario runs executed, biotransformation was assumed to be absent.

A further comparison of model predictions was executed for the class of organotin compounds (TBT, tributyltin; TPT, triphenyltin), which have been measured in SPM from the Scheldt estuary between 1998 and 2002 (at 5 stations, 4-5 measurements per year). Unfortunately these compounds are not included in the routine monitoring programmes for mussels and flounder-liver. Data measured by IVM and reported by Leonards *et al*. (2003 in press) are available for two species (common shrimp and sole) sampled in the Scheldt estuary in April 2000. In figure IV-19 a comparison is made between model predictions and the limited measured concentration data available.

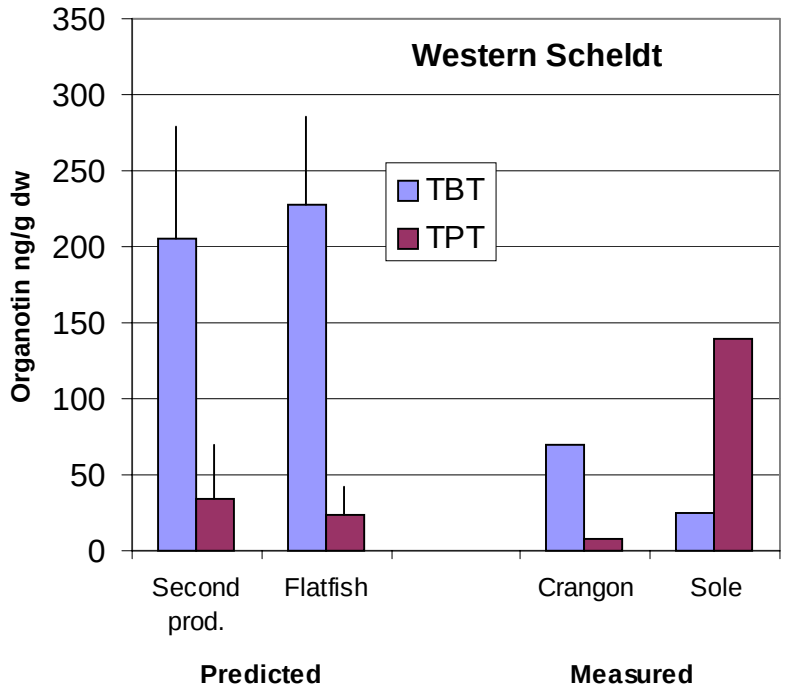

Figure IV-19 Organotin compounds. Model predictions for sea-end (bars) and river-end (error bars) of estuary in comparison to recent measurements of concentration in *C. crangon* and sole (muscle) from the mid section of the estuary.

Water concentrations were derived from SPM concentrations near the sea-end (Vlissingen SSHV) and the river-end (Schaar van Ouden Doel) using the relationship of Munschy *et al.* (1996) and Log Kow values (TBT: 4.76; TPT: 4.17) derived from the Syracuse EFDB database used in the US-EPA EPIWIN programme (Meylan and Howard, 1999). Although it is acknowledged that the partitioning of organotins in water systems is not only determined by organic-carbon water partitioning (Stronkhorst et al., 1999), this was used for this preliminary modelling exercition. TBT predictions exceed measured values for both categories of organisms (2-9 times higher). Model predictions for the TPT in the secondary producer are 5 times higher than measured values in *C. crangon*; predictions for TPT in the flatfish (whole body) are 17% of measured values in sole (muscle). The over-prediction for TBT seems consistent with the reported biotransformation of this compound in various literature sources (e.g. Ten Hallers-Tjabbes *et al.*, 2003). In spite of the limitations involved (limited measurement data, no true matching of sampling locations and time periods, mismatch between target organism of model and species for which measurement data are available, estimation procedure for water concentrations, lack of data on biotransformation) the model predictions seem to be within 1 order of magnitude in comparison to the limited measured concentrations in organisms in the Scheldt.

A summary of the prediction-observation comparisons for the different groups of compounds is presented in figure IV-20. This demonstrates, that although there are large differences between the different groups of compounds, that for most of the classes of compounds the model predictions are within one order of magnitude of measured concentrations in the Scheldt and Ems estuaries. The predictions for the brominated flame retardants (PBDEs and HBCD) deviate much more form measured concentrations, which may partly be attributed to

the large uncertainties in basic input parameters for the model (Kow, SPM-water partitioning). The best match was found for HCB. For PCBs the model seems to under-predict; for PAHs and organotins (OTs) the model usually over-predicts.

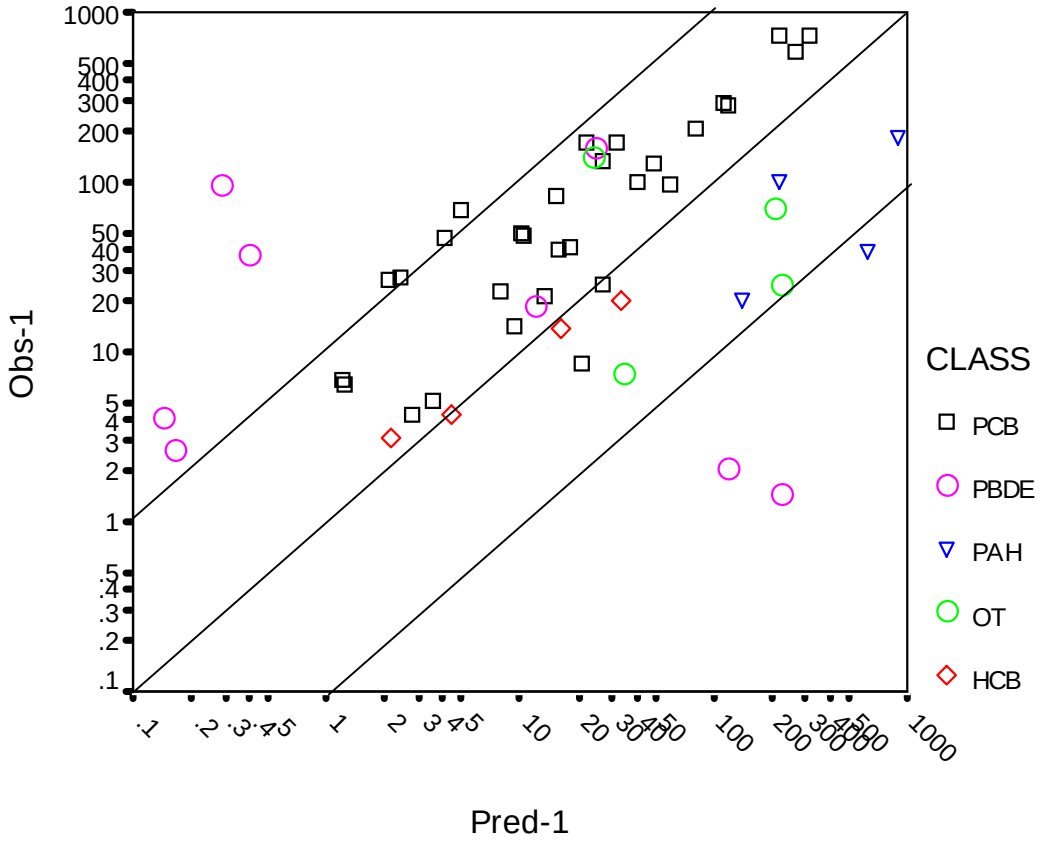

Figure IV-20 Comparison of predicted and observed concentrations in biota from the Scheldt and Ems estuaries for different classes of compounds. Reference lines (Y=0.1*X; Y=X; Y=10X) are indicated for comparison.

A comparison of the predicted apparent bioaccumulation factors (BAF-app dry wt. in L/kg) with Kow of the different compounds is presented in figure IV-21. BAF-app values were calculated as the ratio of the predicted dry weight concentrations and the water concentrations used as model-input. The high Kow scenarios for the brominated flame retardants were not included. As expected the predicted BAF-app showed a consistent trend with Kow, with a strong decline of the phytoplankton BAF-app for Log Kow values above 7 and a slight decline of the BAF-app values predicted for the other species for the Log Kow >7 interval. Similar relationships have been reported from other food-chain or BCF modelling studies (Thomann *et al*., 1992; Morrison *et al*., 1996; Hendriks, 1995; Mackay and Fraser, 2000; Gobas and Morrison, 2000; Voutsas *et al*., 2002;), although in these studies the results usually are expressed on a lipid weight basis.

Although we choose not to use lipid-based values, as these may be biased by limitations in the accuracy and precision of the lipid determination methods, the following ranges of the dry weight lipid content of the model organisms can be used: 5-10% for zooplankton, 8-12% for Org-1 *Tellina*, 6-9% for Org-1 *Pectinaria*, 8% for the round fish, and 6-16% for the flatfish. Expressed on lipid basis, this would have resulted in a upward shift of 0.8-1.3 units on a log scale of the relationships for the different target organisms of the Gemco model.

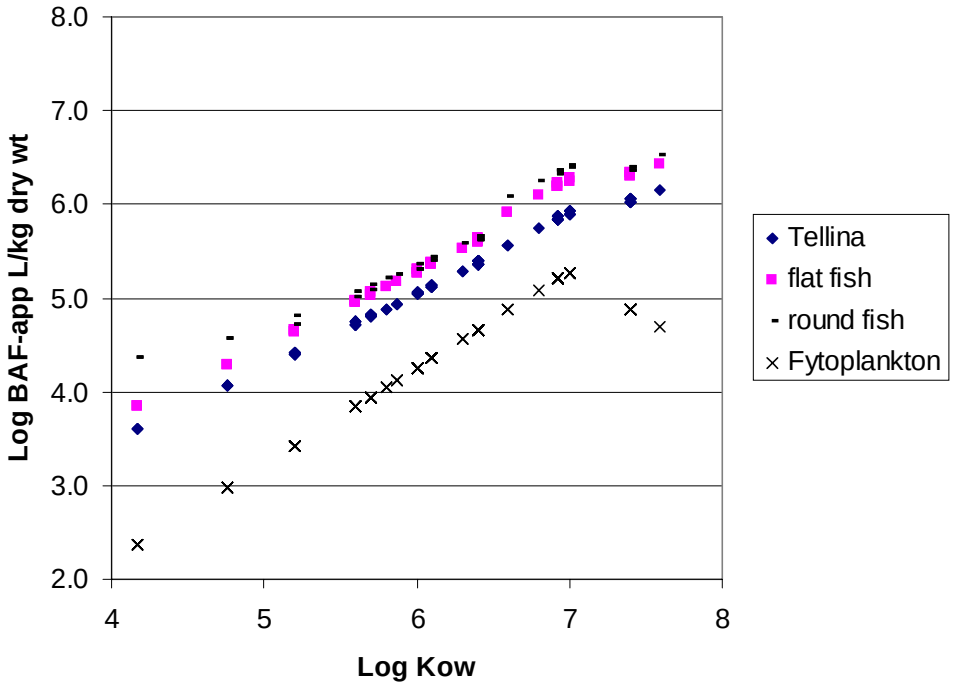

Figure IV-21. Calculated apparent bioaccumulation factors (Log BAF-app) of the modelling trials executed for the Scheldt and Ems estuary in relation to Log Kow.

Conclusions from the application to Western Scheldt and Ems:

- A true validation of the model based on data published in the open literature or from databases is difficult, because of the lack of reliable and recent measurements of freely dissolved water concentrations in European estuaries, and the fact that the few available predictive relationships for Koc and Kd as derived from experimental or field studies may not be generally applicable.

- Additionally, two important input parameters (phytoplankton biomass, zooplankton biomass) are not included in the national Dutch monitoring programmes.

- Furthermore, differences in sampling periods, non-matching locations and other sampling design related factors (selected organisms and tissues), differences in chemical methods, level of aggregation and format of reporting make it difficult to apply data from existing monitoring programmes.

- Literature searches, revealed only a limited number of recent European estuarine food chain surveys. Most food chain studies identified were confined to freshwater systems.

- The application of the bioaccumulation model to parameter-estimates for the Ems and Western Scheldt yields predictions for PCBs (7 congeners), HCB which are around (HCB) or within (PCB) an order of magnitude lower than recently measured concentrations in mussels and flounder-liver.

- Predictions of pyrene and benzo(a)pyrene for molluscs were a factor of 2-15 higher than measures values in both estuaries in *Mytilus edulis.* In relation to the results for PCB 153 the over-prediction of the model for PAHs seems in line with the known biotransformation of PAHs in many aquatic organisms.

- Although limited measurement data were available for organotin compounds, the results obtained indicated that the model tended to over-predict within an order of magnitude for TBT. For TPT the model over-predicted for shrimp and underpredicted for sole.

- When applied to a relatively new class of compounds (brominated diphenyl ethers), the model underpredicts 1-2 order of magnitude for tetra- and penta substituted compounds. The model is not capable to account properly for the poor bioavailability of decabromo-diphenylether. For HBCD the results are variable. It should be noted that for this class of compounds reliable experimental estimates of Kow are not available and that methods of analysis have not yet been validated as rigidly as for traditional compounds such as PCBs or PAHs.

- Given the generic nature of the food web model, the lack of some important estuary-specific input parameters (dissolved water concentration; zooplankton biomass), the uncertainties in some of the parameters (biotransformation, Kow, Kow, Kd of some compounds), and the lack of time series measurement data for matching whole species data at representative locations, the around or within

order of magnitude matching between predicted and measured concentrations of PCBs, HCB (mussel, flounder-liver) and to lesser extent PAHs (mussel) and organotins (shrimp, sole) is remarkable. The performance of the model for compounds tested in the LogKow range 5-8 seems acceptable and can be considered as probably sufficient for a low tier risk assessment model.

IV-5-6. VALIDATION OF THE GENERIC MODELS WITH OTHER PCB CONGENERS

The models can also evaluate the concentrations of other PCB congeners that had been measured in both dab and sea bass in the Seine Estuary and Bay. This can be seen on Figure IV-22 for the round fish model and Figure IV-23 for the flat fish model.

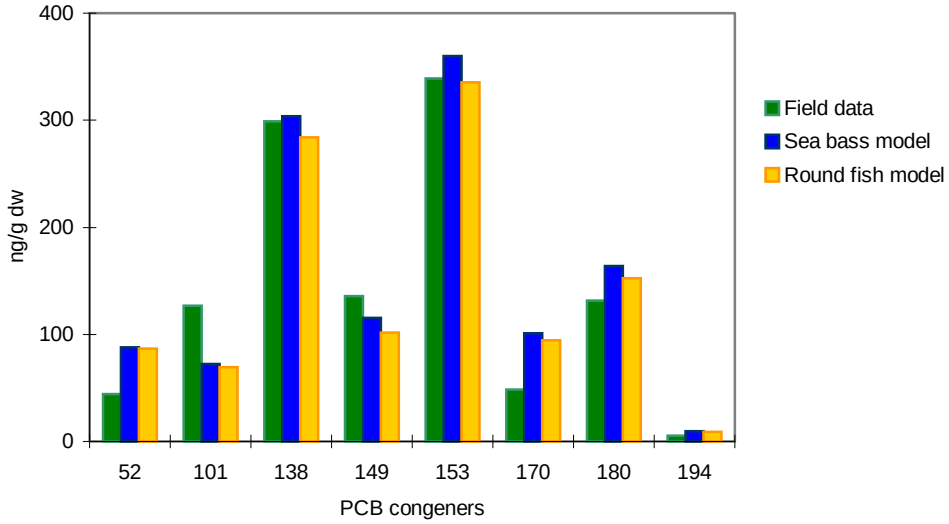

Figure IV-22: Validation of the round fish model for various PCB congeners. Comparison between field measurements and calculated concentrations by models either the seabass model (Loizeau *et al*., 2001b) or the round fish model compared to data from the Seine estuary.

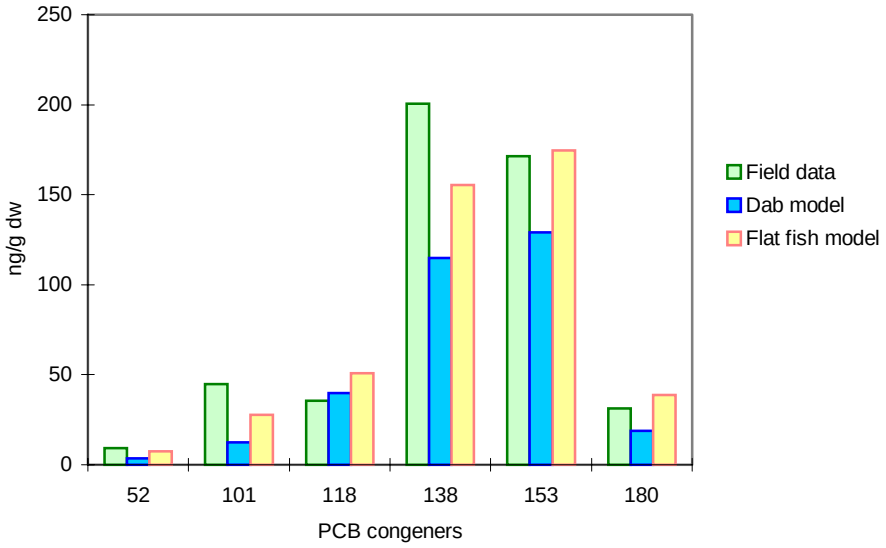

Figure IV-23: Validation of the flat fish model for various PCB congeners. Comparison between field measurements and calculated concentrations by models either the dab model (Loizeau and Ménesguen, 1993) or the flat fish model compared to data from the Seine estuary.

There are some variations between model and field data and particularly for the flat fish model. This can be partly explained by the contamination calculated by the model which is primarily dependent on water contamination. Water contamination is bound to be very variable, depending, of the freshwater flow rates, of the tide, of the position in the estuary or, in the Bay, of distance and position relative to the river mouth. Moreover, organisms were sampled in different part of the bay and of the estuary, and their contamination is expected to be highly variable according to their own individual history, where they have fed and what they fed on.

This inter-organism variability is particularly important for species that indifferently live up or down the estuary, such as the flounder. The concentration measured in this fish cannot be related to its age, its weight, its size or its gender, because its contaminant concentration is primarily a function of its food contamination, which itself is a function of the prey trophic level and of the prey living area. The flounder being an opportunistic feeder, it may consume mollusc or small fish, respectively primary and secondary producers. These two organisms are at different levels of the trophic chains: the contamination of the secondary producer is expected to be higher for bioaccumulable compounds, whereas it is expected to be lower for biotransformable compounds. The amount of contaminant they transfer to their predator is therefore different. Moreover, the flounder is a fish that may swim up and down the estuary feeding in areas with different contamination level. This cannot be taken into account by simple models like the dab model or the generic model.

IV-6. LIMITS OF APPLICATION THE MODEL

Models are designed to represent natural processes. Their quality is usually limited by an imperfect knowledge of nature. We deeply regret to admit that the GEMCO model is no exception and that its application is therefore limited by a number of imperfectly defined processes. These limits are described below.

First of all, the flat fish and the round fish models have been derived from models designed for PCB contamination. The equations used for evaluating the phytoplankton and the particles or sediment contamination have only been validated for PCBs. This should not be an issue once these models are coupled with the water quality model that will calculate particles and phytoplankton contamination independently.

The parameters alpha that evaluate the assimilation efficiency of contaminant by organisms have also been established for PCB. They are function of *Log* K_{ow} value which reflects the fact that contaminant physico-chemical properties exert the main controls on its assimilation by living organisms and are probably more important than inter-organisms differences in metabolism. It can be expected that for most contaminant families, equations similar to that used here (Tables IV-4 and IV-6) but it cannot be expected that these equations would hold for every groups of chemical substances.

The use of these equations and their preponderant role in the evaluation of organisms contamination probably explain the sensibility of the model of *Log* K_{ow} values. In this work, the results from (Hawker and Connell, 1988) have been used. If new investigations were to invalidate these authors results, it may be necessary to evaluate the impact of using different *Log* K_{ow} values on the model results. The Kow values are currently a matter of discussion and information on Kow from literature surveys presents a large variability (Renner, 2002), some times around or more than one order of magnitude even for compounds having similar chemical structures.

This model is a steady state model, which means that it is assumed that there are no variations of contaminant concentrations with time. It cannot be used to evaluate how fish contamination might evolve with time if the contamination in their environment varies. It also means that it is assumed that there are no variations in fish metabolic processes with time. Particularly, the effect of spawning, through which female loose a significant proportion of their contaminant load, is not taken into account. Also, processes such as seasonal migration out of the estuary cannot be considered within a simple steady state model.

This model is designed to evaluate contamination in fish that evolve in an environment in which they can live reasonably normally. This means that the models would not be suitable to use if the estuary was in strong anoxic or eutrophic conditions. This would probably modify both the trophic chains and organism metabolic processes (particularly rate of respiration and feeding) to such extent that the equations used here may not be representative any longer. Also, this model does not take into account any toxic effect of the contaminant. Toxicity can also affect metabolic rates used here to evaluate contamination levels. This implies that the models would not be suitable to apply in a very contaminated estuary, where concentrations above which toxicological effects can be observed.

These models evaluate the transfer of contaminant through a trophic chain, but not the transfer of its metabolites, some of which may be as or more toxic that the parent substance and might accumulate in food chain in case of persistent metabolites. It may therefore be important to take metabolites concentrations into account in risk assessments.

For these models to be fully generic they should be able to represent the transfer of any contaminant from one trophic level to the next. The first remarks in this section underlined that this may not be the case because of the dependency of assimilation coefficient to the contaminant properties. At the beginning of the project it was hoped that a simple relationship could be found that evaluates another important process, the biotransformation of contaminant by organisms. Unfortunately, the state of our present knowledge has not allowed us to reach this goal. Biotransformation is dependant on many factors: the organisms species, but also its age, its trophic level, the length of exposure to the pollutant, are all of importance as well as the contaminant properties, its concentration in water and on particles, whether the pollution is chronic or accidental, repeated or continuous, whether there is one or several contaminant in the environment…(the presence of some contaminants may promote the detoxification systems and the appropriate enzymatic systems that will activate the biotransformation of other related chemical substances. No experimental settings, no field measurements have been able to untangle the complexity made up of so many factors. We have proposed an approach, the turbot feeding experiment, that seems to lead to a reasonable answer, when using the biotransformation equations proposed.

IV-7. SENSITIVITY ANALYSIS

IV-7-1. AIM

The model sensitivity to all parameters has been performed only for CB153 (2,2',4,4',5,5' hexachlorobiphenyl), the PCB congener usually found in largest concentrations in a "natural" environment unexposed to important local pollution sources. The purpose of the sensitivity analysis is to evaluate and describe variations of output state variables induced by perturbations of the model parameters.

IV-7-2. METHOD

Only one model was used to carry out this sensitivity analysis: the "round fish model". This model simulates the bioaccumulation of congener CB153 in a semi-pelagic trophic chain, the target species was a round fish. Calculations assume all model parameters are at steady state. Values corresponding to measurements made in May in the Seine Estuary were assigned to all parameters and forcing variables as standard values.

All results presented below in figures and tables have been obtained for CB153. This model requires different kinds of parameters that were grouped in three classes for the purpose of this sensitivity analysis:

- the chemical parameters:
  - X_w (contaminant concentration in water – forcing variable)
  - $LogK_{ow}$ (octanol/water partition coefficient)
  - $\alpha_{w,i}$ (assimilation efficiency from water).
- the environmental parameters:
  - T°C (water temperature – forcing variables)
  - $[O_2]$ (the dissolved oxygen concentration – forcing variable)
  - [Chla] (the chlorophyll concentration in water – forcing variable)
  - [lip] (the lipid fraction in phytoplankton – parameter).
- the biological processes:
  - R (Respiration – rate)
  - N (Nutrition – rate)
  - E (Excretion – rate)
  - G (Growth – rate)

The environmental parameters (temperature, dissolved oxygen, phytoplankton biomass as represented by the chlorophyll concentration in water and lipid fraction in phytoplankton) describe the «natural» environment and are parameters that control partially the extent of contamination. On the other hand, PCB concentrations in water, the octanol/water partition coefficient (K_{ow}) and the chemical assimilation efficiency, which depends directly from K_{ow}, described the « contaminated » environment and have no

influence on the three other parameters. The biological parameters are the main controls of the contamination level in organism.

The contaminant concentration in phytoplankton and in detritus can be calculated from the contaminant concentration in water.

Standard values for the above variables correspond to averages measured in May in the Seine estuary. Results obtained with these standard values have been validated with field data. These standard results were used in the sensitivity analysis as reference. Each parameter was alternatively increased and decreased by 20 or 25 % relative to its standard value and the model results were recorded and compared to the standard results. This comparison gives the sensitivity of the model to the parameter tested.

During these tests, the calculation that relates the contaminant concentrations in phytoplankton and in detritus to the contaminant concentration in water was disabled. This allowed treating the PCB concentrations in both phytoplankton and detritus as independent parameters. These concentrations standard values were made equal to the concentrations calculated with all other parameters set to their standard values.

The sensitivity of the model to one parameter might be increased by a variation imposed on another parameter: there might be a "synergy" between the sensitivities to different parameters. In order to check how severe could be the effect of such a synergy, several parameters were modified at the same time each one being increased or decreased by 20 or 25 %. The various scenarios tested are described as the results are presented and discussed.

IV-7-3. RESULTS

A variation in a result is considered to be large, and increasing the model uncertainty to an unacceptable level, if it is greater than 20%. This limit of 20% corresponds to an acceptable error on experimental results.

Three trophic levels are represented in the « GEMCO model ». X_1 (zooplankton) is considered to belong to a lower level than X_2 (the supra benthic animals), which is big enough to eat some zooplankton whereas the opposite is impossible. Last comes X_3 (the round fish) that feed on X_2. These three groups of organisms can be differentiated in the interpretation of the sensitivity analysis. Bioaccumulation of contaminants depends on physiological rate of organisms, so in this sensitivity analysis, physiological processes like respiration, nutrition, excretion and growth were also tested. Parameters describing the "natural environment" (the environmental parameters) can influence these processes.

IV-7-1 Chemical parameters

Chemical parameters were tested first. A basic interpretation of the results suggests that the variables that induced the largest changes in the results are the contaminant concentration in water and the octanol/water partition coefficient (K_{ow}). Interestingly, a 10% variation in $LogK_{ow}$ induced a large variation in all compartments. It is interesting to note that an increase of 10% on the value of $LogK_{ow}$ led to up to 180% increase in X_3 standard value

Figure IV-20. The effects caused by a reduction of $LogK_{ow}$ are less important than those caused by its increase. This is because the source of the round fish contamination is mainly its food but there is a "background" contamination level supplied by the water. A variation of K_{ow} value significantly modifies the resulting contamination levels in the top predator, but decreasing K_{ow} has less effect than increasing it because at low K_{ow} values the water contribution becomes more important relatively to the food contribution. The range of variation imposed on $LogK_{ow}$ (from 6.228 to 7.612) corresponds in fact to modeling different compounds. Indeed, it is more than probable, that the compound presenting a $LogK_{ow}$ equal to 6.228 or 7.612 is not the congener CB153. This is why it is important to characterise well the compound with which one wishes to work. Conversely, the model does not seem sensitive to the coefficient of assimilation efficiency from water, since a variation of 20% on this parameter does not induce any significant differences on the state variables. This result must however be taken with care. Indeed, congener CB153 is not a water-soluble compound and this can explain the apparent low sensitivity of the model to the contaminant assimilation from water. If the model was tested with more soluble compounds, it is likely that variations on the water contamination could generate fluctuations on the state variables of the same order of magnitude as what is has been discussed above for $LogK_{ow;}$

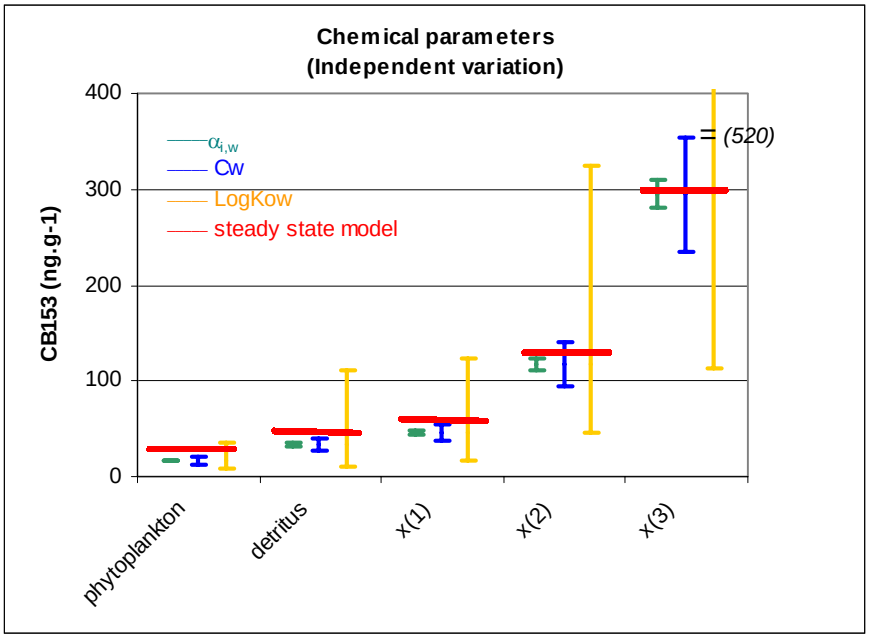

Figure IV-24. Sensitivity analysis of the chemical parameters: effect of independent variations of the chemical parameters on PCB153 in organisms. The vertical bars show the variations in results when chemical parameters were increased or decreased by 20%.

The second step of the sensitivity analysis consisted in varying chemical parameters simultaneously. Only the two parameters to which the model is most sensitive (contamination of water and K_{ow}) were considered. Two scenarios were carried out: variation in the same direction (increase or decrease of the two parameters at the same time) and opposite variation (when one parameter increases, the other decreases). The results obtained are represented on Figure IV-21.

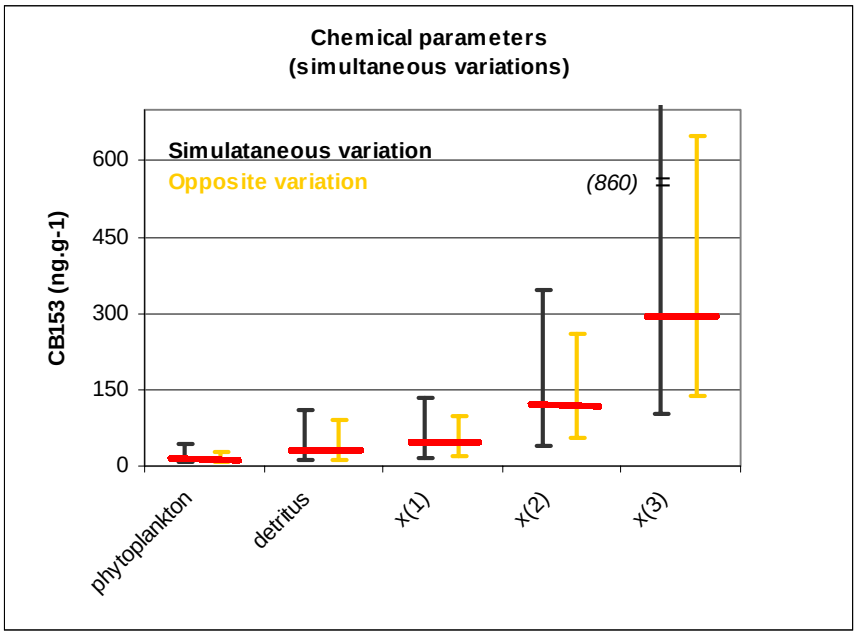

Figure IV-25: Sensitivity analysis of the chemical parameters: Effect of combined variations of the chemical parameters on PCB153 concentrations in the different food web compartments as calculated by the GEMCOmodel. The vertical bars show the variations in results when water contamination and octanol/water partition coefficient are simultaneous increased or decreased by 20%.

These results lead to the same remarks as the ones above. However, amongst these scenarios, the only plausible one is the opposite variation of these two parameters: when K_{ow} increases, solubility in water necessarily decreases and thus the concentration in water also decreases. The combined effects of these two parameters decrease their sensitivity to the model (maximum 120 % of variations, which remains however significant).

IV-7-3-2. Environmental parameters

The results shown on Figure IV-22 suggest that the environmental variables that induced the largest changes in the results are the chlorophyll concentration in water and the temperature. Interestingly, a 20% variation in the temperature induces a large variation in X_2 and in X_3 results, but not in the zooplankton model compartments. However a similar variation in the chlorophyll concentration in water causes the results for all the compartments to vary by just under 20%.

A more detailed study of the results shows that the contaminant concentration in zooplankton tends, as expected, to vary independently from the concentration in the supra benthic organisms X_2. This is because zooplankton physiological processes are relatively simpler, depending only on temperature, dissolved oxygen and phytoplankton biomass, whereas the supra benthic organisms biology also depends on zooplankton. The contaminant concentrations in fish (X_3) generally vary within a wider range than in the other organisms and this reflects the bioaccumulation in the top predator at the end of the food chain.

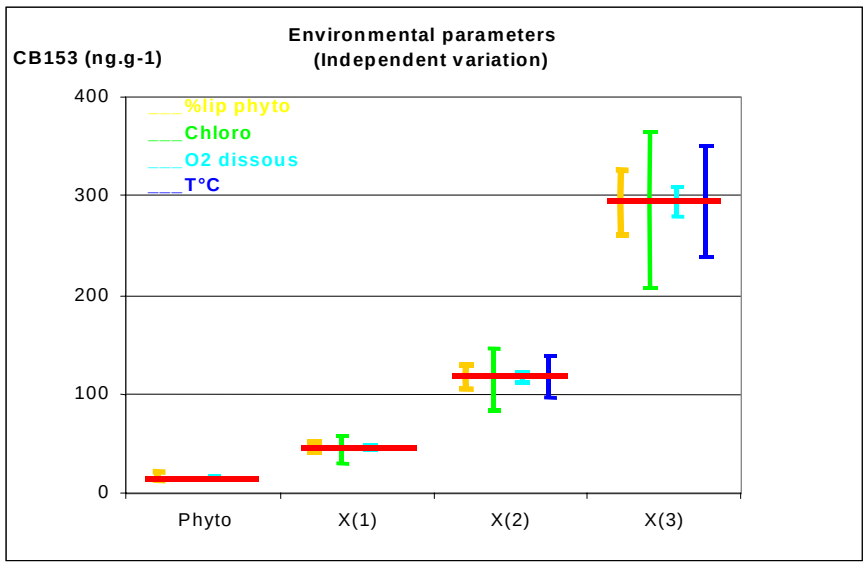

Figure IV-26: Sensitivity analysis of the environmental parameters. Effect of independent variations of the environmental parameters on PCB153 concentrations in the different food web compartments as calculated by the GEMCO model. The vertical bars show the variations in results when environmental parameters were increased or decreased by 25%.

The results obtained for the simultaneous variation of the temperature and the chlorophyll biomass are presented on Figure IV-27. When the temperature increases and the phytoplankton biomass decreases the model becomes much less sensitive to these environmental parameters. The increase in temperature generally will accelerate the physiological processes (the rates of nutrition and breathing will increase). However, as the phytoplanktonic biomass decreases food becomes a limiting factor (and thus its contribution to contamination is less significant). This scenario is however not very likely, since in general, the phytoplanktonic biomass is positively correlated with temperature.

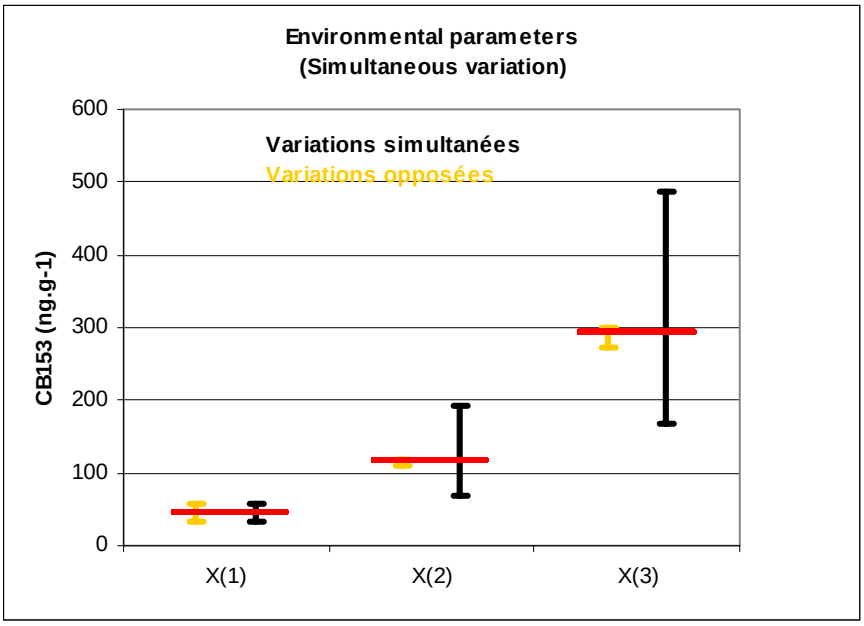

Figure IV-27: Sensitivity analysis of the environmental parameters. Effect of combined variations of the environmental parameters on CB153 concentrations in the different food web compartments as calculated by the GEMCO model. The vertical bars show the variations in results when chlorophyll concentration and temperature are simultaneous increased or decreased by 20%.

The analyses of sensitivity carried out on the chemical and environmental parameters identified four parameters to which the model was sensitive (X_w, K_{ow}, T and Chla). The simultaneous variations of these four parameters were tested on two realistic scenarios where the four parameters were varied according to realistic scenarios (if the temperature and the chlorophyll concentration vary in the same direction whereas K_{ow} and X_w must vary in opposite directions). The results obtained are presented on Figure IV-24. We can thus observe the cumulative effects of each one of these parameters. The fluctuations generated on X_3 when temperature, chlorophyll a concentration and $LogK_{ow}$ increase by 20% and contaminant concentration decreased can reach 400%). When the chemical and environmental parameters vary in the opposite direction (temperature and chlorophyll a concentrations decreased and $LogK_{ow}$ increased and reverse), the fluctuation on X_3 is 100%. These results suggest that the model is more sensitive to the chemical parameters than to environmental parameters since an increase of 20% on $LogK_{ow}$ did not compensate the reduction of 20% of the environmental parameters.

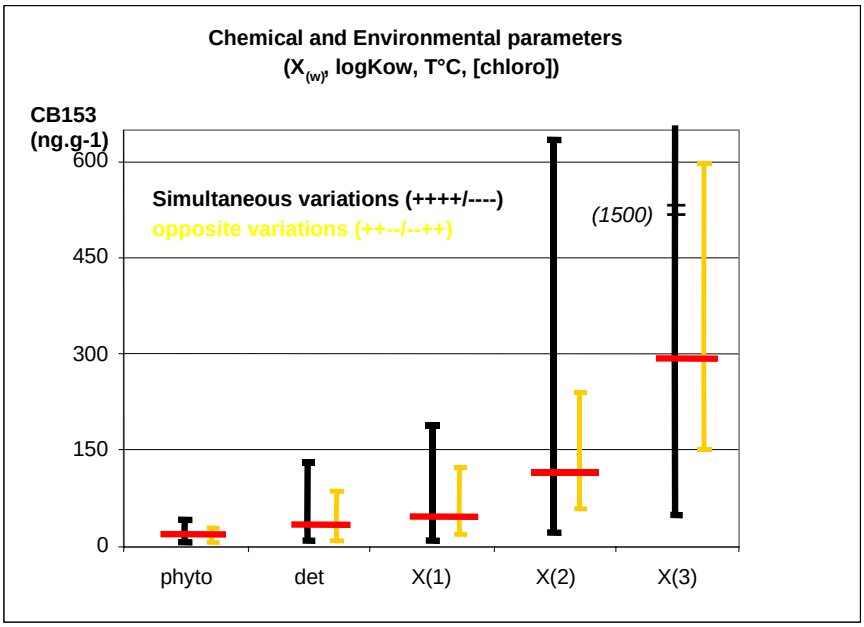

Figure IV-28: Sensitivity analysis of the environmental and chemical parameters. Effect of combined variations of chemical and environmental parameters on PCB153 concentrations in the different food web compartments as calculated by the GEMCO model. The vertical bars show the variations in results when chemical parameters (LogKow) and environmental parameters (Chlorophyll concentration in water and temperature) are simultaneous increased or decreased by 20%.

IV-7-4. Biological parameters

The transfer of the contaminants through a food web is directly dependent on organisms metabolic functions such as respiration, nutrition, excretion and growth. In the GEMCO model, the mathematical expressions describing these functions have been obtained from the literature. In order to test the sensitivity of the model to these functions, a standard value was calculated for each physiological process for the Seine conditions measured in May and then variations of 25% were applied to these values. The concentrations of CB153 were

compared for each set of values tested. The results obtained when the parameters vary in an independent way are presented on Figure IV-25.

This figure shows that the model is not sensitive to the respiration and excretion functions. The maximum fluctuations generated by the variations of these two functions are respectively 0.2 and 9 %. This result confirms the small contribution of water in the direct contamination of organisms. However this result is valid only for the CB153 (a compound far from qualifying as water soluble) and it would be probably different in the case from a more water-soluble compound. Conversely, the model seems particularly sensitive to the variations applied to the nutrition, especially for the highest trophic level. Thus an increase of 25% of the nutrition generates fluctuations of about 40 % on X_3 and of 35% on X_1. The model is also sensitive to growth but contrary to the nutrition, it is for the lowest trophic levels that the fluctuations are most significant: 27 % for X_1 and 22% per X_3. This could be expected as zooplankton turnover is faster than that of fish (at least the one considered in this model) and therefore it is logic that zooplankton growth rate is of greater significance than fish growth rate.

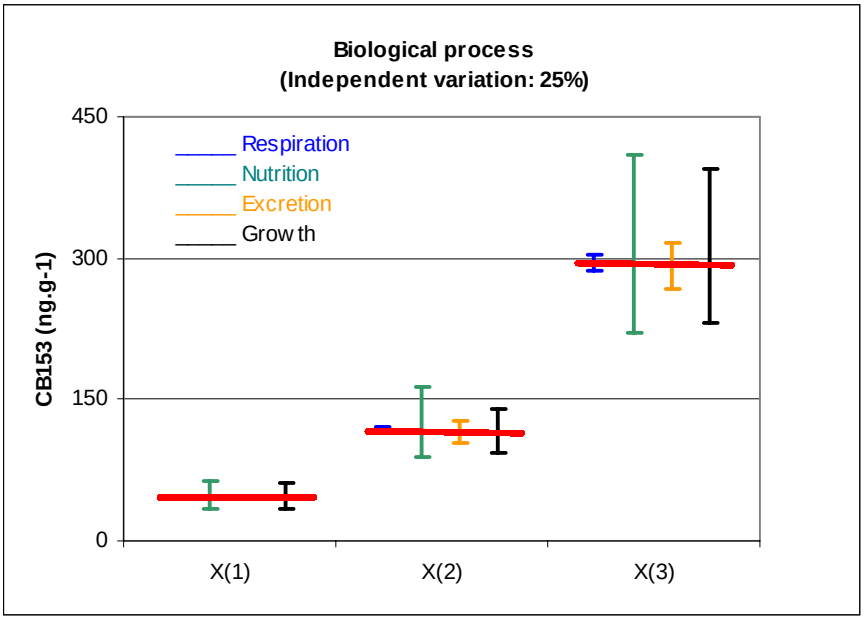

Figure IV-29: Sensitivity analysis of the biological processes. Effect of independent variations of the biological parameters on PCB153 concentrations in the different food web compartments as calculated by the GEMCO model. The vertical bars show the variations in results when biological parameters increased or decreased by 25%.

The results obtained during the increase in these two parameters (Figure IV-26) show the strong correlation between these two processes: when the rate of nutrition increases, the rate of excretion also increases. The model does not appear to be sensitive to this scenario. The opposite scenario is not realistic.

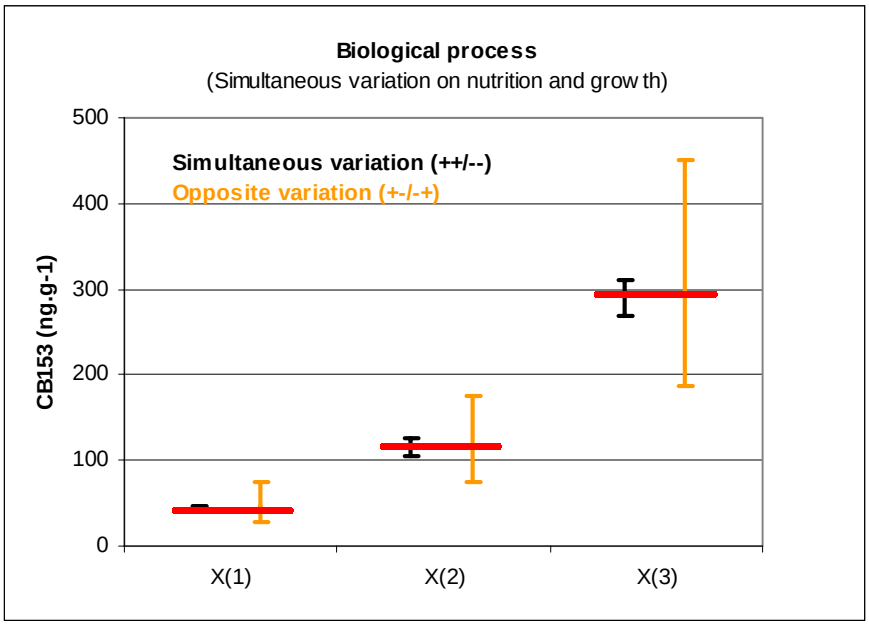

Figure IV-30: Sensitivity analysis of the biological processes. Effect of combined variations of the biological processes on PCB153 concentrations in the different food web compartments as calculated by the GEMCO model. The vertical bars show the variations in results when nutrition and growth are simultaneous increased or decreased by 25%.

IV-7-4. CONCLUSIONS ON THE SENSITIVITY ANALYSIS

This sensitivity analysis highlights the effects of forcing variables on model results. The largest variations in the results are observed when several forcing variables are modified at the same time. It is obvious that if all values of input data are fundamentally wrong, no model will be able to produce correct results. This emphasises the fact that it is important to use a set of forcing variables that represents the real world as precisely as possible. It was however shown that the GEMCO model results for congener CB153 would be particularly sensitive to the octanol/water partition coefficient (K_{ow}), contaminant concentration in water, temperature, and the chlorophyll concentration in water. The variations imposed on forcing variables were in the worst cases amplified by the model generating errors up to 25%. It is therefore important to constrain the uncertainties on some variables as temperature, chlorophyll a concentration, water contamination and octanol/water partition coefficient.

V. CONCLUSIONS AND LIMITATIONS

1. A generic estuarine model of contaminants in trophic web has been built to describe the fate of organic chemical contaminants in estuarine foodwebs.

2. The model allows to estimate the propensity for a compound to bioaccumulate or, on the contrary, to be biotransformed in the estuarine food webs.

3. The model work for neutral organic substances and thus it cannot be used neither for metals nor for ionised organic substances.

4. The model has been validated by PCBs, that is to say for compounds with $LogK_{ow}$ in the range 5-7 and very few other persistent compounds. The results of the validation fits, within an order of magnitude, with measurements done on real fish and species. Is reasonably good if we consider the complexity and variability of the various biological processes. It is probably not feasible to obtain more accurate information using such a simple and generic model.

5. This model relies upon biological processes and is an extension of previous PCB bioaccumulation models validated in the case of the dab food web in the Baie de Seine and that of the seabass in the Seine estuary.

6. Two simplified foodwebs have been considered, one typical of round fish the other one of the flat fish, both are representative of main food chains in estuarine ecosystems.

7. At lower trophic levels contaminants enter the living compartment by adsorption onto phytoplanktonic cells and detritic material. The concentration in the particulate material are given by an abiotic model running separately and forced using empirical equations.

8. The generic flat fish and round fish model have been validated by PCB existing data from studies or monitoring programmes in estuaries. The models work quite well within an order of magnitude and give results in agreement with those obtained by previously validated PCB bioaccumulation models.

9. The trophic model is linked to an abiotic model and results obtained in biota are strongly dependent on the abiotic conditions (dissolved oxygen and water temperature which act on the efficiency of most biological processes).

10. The biological processes are not dependent on salinity : in the generic estuarine models, the considered species are species that live in a salinity range from 15 to 30, and salinity or salinity variation don’t affect their physiology.

11. The model has been validated within a water temperature range currently observed in most European estuaries, commonly between 5 - 25 °C.

12. At the starting point, the model assumes that species are not contaminated by the studied substance, which means there is no background concentration in the organisms.

13. The model does not consider any effects of contamination on the individual specimen, species and populations within an estuary. In clear, bioaccumulation is not affected by any toxic effects due to the exposure to the chemical substance which is considered.

14. The uptake of contaminants from water are only due to respiration across the gills, there is no contaminant uptake by transport through the skin.

15. The model does not take into account loss of contaminants through various processes like spawning. Broadly speaking without more information, in a first global approach, the processes that contribute to an increase of contaminant in biota should be over-estimated whereas other processes that decrease contamination could be neglected. The final result should preferably predict the worst situation.

16. Some conversion factors should be used to compare calculated concentrations to existing data: contaminant concentrations are measured in different type of organs (tissues) or expressed in different manner, either dry weight, fresh weight or lipid basis. The models calculate concentrations in a whole target fish species which are to be compared with actual measurements in organs or tissues.

17. The models provide concentration in a generic target fish. There are no real fish which perfectly match with the virtual fish and to which they could be directly compared. For instance, dab could be compared with the flat fish, seabass is a good representative for the round fish. In the case of lower organisms, there are no real intermediary species which could be compared with intermediary species simulated by the generic models. Mussels have been extensively used as sentinelle species in pollution monitoring programmes so that large information exists on contaminants in these organisms, however mussels do not exactly coorespond to the intermediary species of the models because : they are not eaten by fish, they are filter feeders and thus their contamination levels are more highly dependent on the filtration rates and contaminant concentration in the suspended material.

18. The model produces data for PCBs or for compounds which are persistent and behave like PCBs. In the case of less persistent compounds, the model will over-estimate concentration in biota so that biotransformation should be considered.

19. There is no clear and straighforward definition of persistence of substances, it depends on their chemical reactivity and thus on their structural characteristics. In our attempt, the case of release chemical waste or substance into an estuary, we feel there is still a matter of discussion taking into account the amount of substance to be discharged into the estuary, their reactivity of the substance, the kinetics of the processes from one side the chemical reactivity and from the other the rate of biological processses. The various processes should take place within a same time scale.

20. An attempt to take into account biotransformation is proposed, based on experimental results that show a rapid biotransformation of BaP. These experiments enable to define an empirical biotransformation factor. The concentration of a less persistent compound or partially metabolisable compound can be calculated by the PCB bioaccumulation model and corrected by a biotransformation factor.

21. Therefore, a two step approach is proposed to calculated concentration in biota using the generic foodweb model. First the model run without considering biotransformation,- the substance is persistent and behaves like PCBs- , the calculated concentration is considered as the worst case and this calculated concentration should be estimated considering data on biological effects or existing reglementations. In a second step, this calculated concentration will be corrected to account for biotransformation.

22. At this sage it is very important to note that bioaccumulation models gives information on the exposure but never on the effects on the substance. If necessary, it is recalled that bioaccumulation acts on the exposure of top predator to a contaminant whereas toxicological effects depend on the property of the substance (presence of specific functionnal groups on the molecule which produce biological effects). The combinaison of exposure and toxicity makes a substance harzardous to life.

23. The biotransformation of a compound does not mean there is no more hazards to estuarine life. Firstly, the biotranformation of a less persistent chemical substances might lead to a persistent metabolite that could then be biomagnified and reach unsafe concentration in higher predators. In this case, the fate of a persistent metabolite should be considered like any other persistent compound using a similar approach.

24. Basically the models we are discussing, (distribution model, fate model, trophic model) consider chronical chemical pollution problem. They assume that chemical substances are extremely diluted in the aquatic environment and that they behave like pure compounds which means they have unique and definite physico-chemical properties (definition of a pure compound). Consequently, models are not able to predict the fate of technical mixture (for instance an oil slick or any other complex technical mixture) or what happen if a large amount of a substance is to be released during a short period of time into a closed part of an estuary (dilution).

25. The results of the model represent an instantaneous representation of concentrations, there is no time integrated response. Such information would require a more sophisticated dynamic model which is probably unrealistic within the context of a generic approach. Such a model should consider more detailed information on the real estuary, its biology and the chemical waste.

26 This type of tool is an attempt to built an easy to use model that could help non specialist to assess the distribution of chemical substance in an estuary including its biota. This first version will be necessarily improved taking into account some feed back from users which are gratefully acknowledged in advance.

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VII. APPENDICES

VII-1 ANNEX 1:

CALCULATION OF BAP METABOLISATION RATES IN CRUSTACEANS

According to Livingstone (1992), the metabolisation rates of HAP in crustaceans is given by:
Log[Metab] = 0.90 + 0.93 Log[PAH] equation IV-4 paragraph.

(Equation IV-4, see above part IV-3-8-2-5)

As the model results are in ng/g and Equation IV-4 conversions in ngmol/g are necessary.
Benzo[a]Pyrene : MW = 252 g/mol

In the GEMCO model, the result for organism 1 in round fish model is :
[BaP] = 174 ng/g dw without metabolisation

Assuming a water content of 70% in crustaceans, this is equivalent to:
[BaP] = 52.2 ng/g ww

as BaP molecular weight is 252 g/mol, this is equivalent to:
[BaP] = 0.21 nmol/g ww

Equation IV-4 becomes:
Log Metab = - 0.90 +0.93 Log 0.21

Hence, Log Metab = -1.54 and Metab = 0.029 pmol/min/g ww. Conversion into daily rates gives:
Metab = 42 pmol/day/g ww

And the conversion of wet weight into dry weight yields: Metab = 139 pmol/day/g dw.

Finally, this is equivalent to: Metab = 35 ng/day/g dw

VII-2 ANNEX 2: CALCULATION OF THE BIOTRANSFORMATION RATES FOR CB118, CB77 AND BAP FROM FEEDING EXPERIMENTS.

The biotransformation rates are calculated from results shown on Figure IV-8 in section IV-3-8-2-6, using data from experimental study feeding on turbot fed with spiked fishmeal (Jaouen-Madoulet, 2000). CB153 is taken as the reference of fully persistent contaminant. Its percentage of bioaccumulation is $Pc_{153} = 35$. Since CB153 is assumed to be fully persistent, PC_{153} represents the maximum rate of bioaccumulation that is possible. The calculated percentage of bioaccumulation of CB118 is $Pc_{118} = 30$. The difference between the two is due to the biotransformation of CB118. So the rate of biotransformation is the difference between the bioaccumulated CB153 and the bioaccumulated CB118 over the maximum contaminant bioaccumulation (*i.e.*Pc_{153}):

$$Biot_{118} = \frac{(Pc_{153} - Pc_{118})}{Pc_{153}} \cdot 100$$

Hence

$$Biot_{118} = \frac{(35 - 30)}{35} \cdot 100$$

so

$$Biot_{118} = 14$$

Likewise, $Biot_{77} = 50$ and $Biot_{BaP} = 0.01$.

VII-3 **ANNEX-3: CONVERSION FACTORS TO COMPARE CONTAMINANT CONCENTRATION CALCULATED IN THE FISH WITH MEASUREMENTS.**

Such conversion factors are necessary in the validation of the model in order to facilitate a more direct comparison between calculated concentration obtained by the model with data from measurements carried out either in fish muscle tissue or in fish liver; both type of samples are currently studied.

LSI= hepato-somatic index (liver weight/whole fish weight) is obtained from results on dab and seabass

LSI varies between 2-4 % based on fresh weight in 3 years old male seabass; in the case of dab (also 3 years old male) it varies between 1 and 3 %.

Let X, Y concentrations in liver and muscle ($ng.g^{-1}$ fresh weight)

We assume that the amount of contaminant in the whole fish is equal to the amount in liver plus the amount in muscle

$$Q_{fish} = q_{liver} + q_{muscle,}$$

$$M_{fish}\, C_{fish} = m_{liver}\, c_{liver} + m_{muscle}\, c_{muscle} ,$$

m mass and c concentration

$$(M_{fish}\, C_{fish})/M_{fish} = m_{liver}/M_{fish}\, c_{liver} + ((M_{fish}-m_{liver})/M_{fish})\, c_{muscle}$$

$$C_{fish} = LSI\, c_{liver} + (1-LSI)\, c_{muscle}$$

Let X, Y concentrations in liver and muscle ($ng.g^{-1}$ fresh weight)

$$C\ fish = LSI.\ X + (1-LSI)\ Y$$

For comparison with measurement in liver X

$$C\ fish = LSI.\ X + (1-LSI)\ X/R$$

For sea bass, according to measurement, R mean value is 10.5 (varying between 7 and 16), for dab mean is 7 (the range is 5-11).

Seabass LSI 3% $C_{fish} = 0.3\ X + 0.97\ X/10.5$ $C_{fish} = 0.3924\ x$

$$C_{fish} = 0.3\ RY + 0.97\ Y$$
$$C_{fish} = 4.42\ y_{muscle}$$

For dab, according to measurement, R mean value is 7.2 (varying between 4.9 and 11),

Dab	LSI 2%	C_{fish} = 0.2 X +0.98 X/7.2	C_{fish} = 0.336 X
		C_{fish} = 0.2 R Y +0.98 Y	C $_{fish}$ = 2.42 C muscle

Thus, to conclude here are the conversion factors enabling the comparison of concentrations calculated by the model with measurements either in liver or in muscle when masses of organ (tissue) and concentrations are expressed on a fresh weigh basis. It is important to note the large variation range of these conversion factors.

In the case of the round fish model

C.fish calc. (fresh weight) = 0.4 conc. measured in liver (fresh weight)
C fish calc. (fresh weight) = 4.4 conc. measured in muscle (fresh weight)

In the case of the flat fish model

C.fish calc. (fresh weight) = 0.35 conc. measured in liver (fresh weight)
C fish calc. (fresh weight) = 2.4 conc. measured in muscle (fresh weight)

It should be kept in mind that these conversion factors give an order of magnitude and that they vary in a large range due to variability of biological parameters (water content, LSI, …).

VII-4 ANNEX-4: ADDITIONAL INFORMATION ON THE SCHELDT ESTUARY

This annex refers to the section IV-5-4 and contains additional information related to the application of the generic model to the Scheldt estuary. This figures were prepared by B Van Hattum from the IVM-FU of Amsterdam

Time series data for the Western Scheldt, derived from the Rijkswaterstaat database (RIZA/RIKZ, 2000).

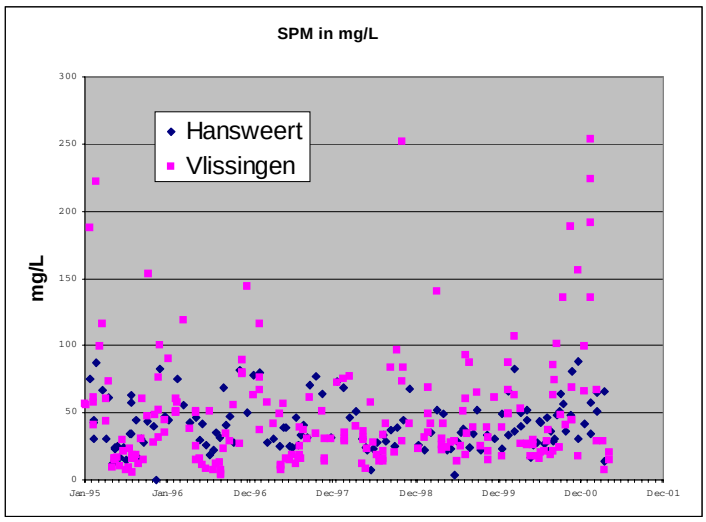

Fig. A-1. **Suspended matter (mg/L; dry wt) concentrations for two locations in the Western Scheldt.**

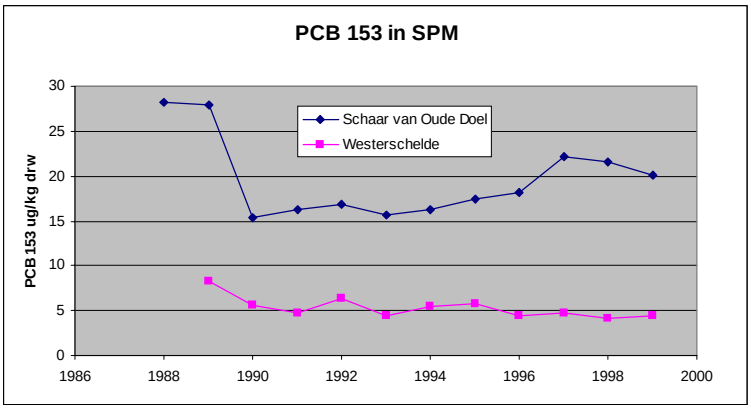

Fig A-2. **PCB 153 in suspended matter (µg/kg dry wt; annual average values) at Schaar van Oude Doel (borderlocation, 9-26 samples per annum) and Westerschelde (midstream; in front of Vlissingen; n=6-8 samples per annum).**

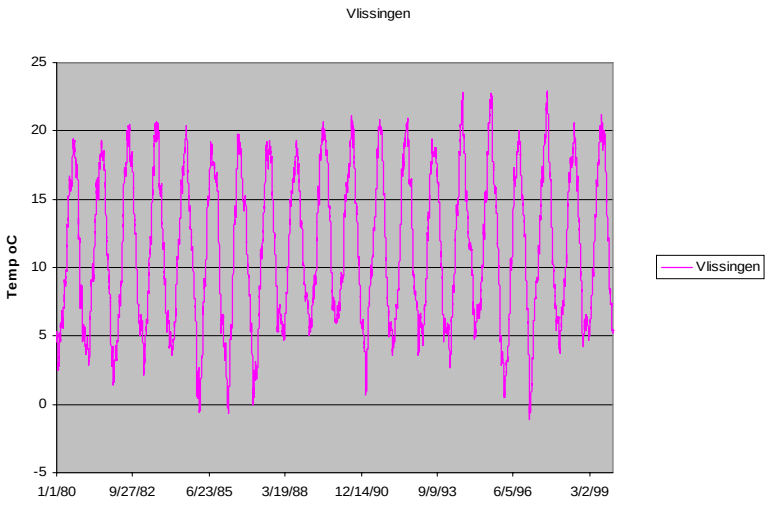

Fig. A-3. Western Scheldt, temperature

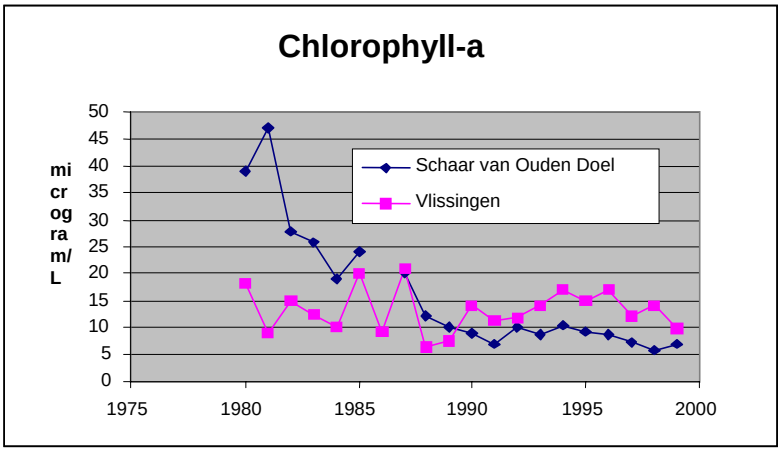

Fig. A-4. Chlorophyll-a in µg/L at two locations in the Western Scheldt

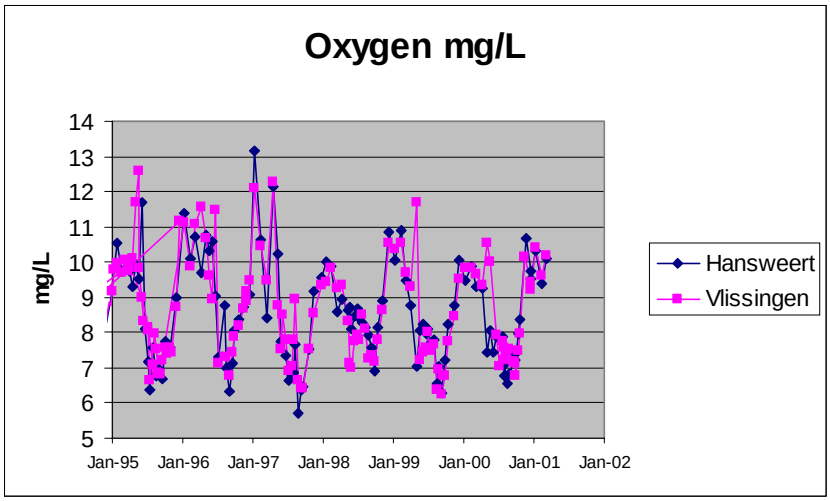

Fig. A-5. Oxygen regime at two locations in the Westeren Scheldt.

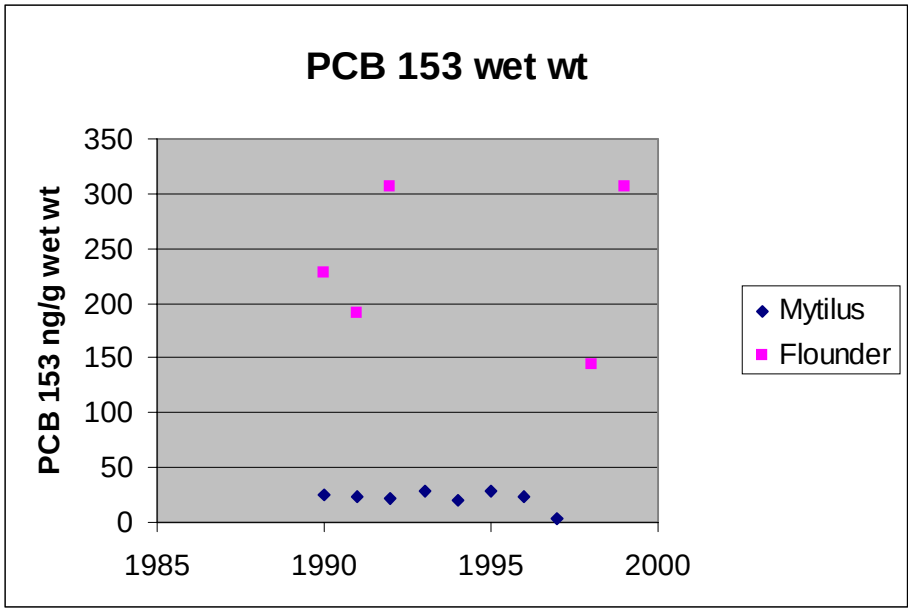

Fig. A-6. **Measured PCB 153 (µg/kg wet wt) concentrations in *Mytilus edulis* (Hoedekenskerke boei 4; results from active monitoring study with transplanted organisms) and liver of flounder from locations (Middelgat, Brouwerplaat, Molenplaat) close to Hansweert.**

Table A-1 **Overview of compounds included for sampling stations in Scheldt and Ems estuary for contaminants in SPM, sediment and biota.**

Western Scheldt

Sampling station	***Suspended matter***	***Mussels***	***Flounder***
Schaar van Oude Doel code: SCHAARVODDL close to river end border location	trace metals PCBs HCB/QCB Chlor. pesticides PAHs	-	-
Westerschelde code: WESTSDE close to sea end, opposite Vlissingen	trace metals PCBs HCB PAHs TBT, TPT	-	-
Middelgat, Brouwerplaat, Molenplaat code: MIDDGBWPMLPT close to Hansweert	-	-	Cd, Hg PCBs HCB
Hoedekenskerke Boei 4 code: HOEDKKKBI4 mid-estuary close to Hansweert		trace metals PCBs HCB/QCB Chlor. pesticides PAHs	

Ems

Sampling station	***Suspended matter***	***Mussels***	***Flounder***
Ems Dollard code: EEMSDLD close to sea end	trace metals PCBs HCB, QCB Chlor. pesticides PAHs TBT, TPT	-	-
Paap, Grote Gat, Reider Plaat code: 'PAAPGTGRDPT near sea end	-	-	Cd, Hg PCBs HCB
Bocht van Watum code: BOCHTVWTM near sea end		trace metals PCBs HCB/QCB Chlor. pesticides PAHs	

VII 4 SYMBOL DESCRIPTION, VALUES AND UNITS

Default values are values used for PCB153 in the Seine model.

Symbol in text	Symbol in code	Description	Default Values	Units
α_{det}	BETADET	Contaminant assimilation efficiency coefficient from non living food	0.35	unitless
α_j	BETAPREY	Contaminant assimilation efficiency coefficient from living prey	Calc.	unitless
α_w	ALPHAWATEI	Contaminant assimilation efficiency coefficient from water	Calc.	unitless
$[O_2]$	O2DISSMG	Dissolved oxygen concentration in water	5.8	$mg.l^{-1}$
[Phy]	BIOMPHY	Phytoplankton biomass	2.86	$mg.l^{-1}$
[Zoo]	BIOMZOO	Zooplankton biomass	1.17	$mg.l^{-1}$
$BIOT'_1$	BIOTMOLL	Biotransformation factor for benthic species	1	unitless
$BIOT'_2$	BIOTLIM	Biotransformation factor for flat fish	1	unitless
$BIOT_1$	BIOTZOO	Biotransformation factor for zooplankton (1= persitent ; 0.001 very rapidly biotransformed)	1	unitless
$BIOT_2$	BIOT2PRO	Biotransformation factor for supra benthic species	1	unitless
$BIOT_3$	BIOTROUND	Biotransformation factor for roud fish	1	unitless
[Chla]	CHLORO	Chlorophyll a concentration	18.1	$\mu g.l^{-1}$
E'_1	EMOLL	Excretion rate of benthic species	Calc.	d^{-1}
E'_2	ELIM	Excretion rate of flat fish species	Calc.	d^{-1}
E_1	EZOO	Excretion rate of zooplankton	Calc.	d^{-1}
E_2	E2PRO	Excretion rate of suprabenthic species	Calc.	d^{-1}
E_3	EROUND	Excretion rate of round fish	Calc.	d^{-1}
F_{oc}	FOC	Organic fraction in sediment	0.021	
G'_1	GMOLL	Growth rate of benthic species	0.0156	d^{-1}
G'_2	GLIM	Growth rate of flat fish species	0.028	d^{-1}
G_1	GZOO	Growth rate of zooplankton	0.278.	d^{-1}
G_2	G2PRO	Growth rate of suprabenthic species	0.249	d^{-1}
G_3	GROUND	Growth rate of round fish	0.992	d^{-1}
Lip	LIP	Lipid concentration in phytoplankton	0.045	$g.g^{-1}$
$LogK_d$	LOGKD	Log. of the sediment water partition coefficient	Calc.	unitless
$LogK_{ow}$	LOGKOW	Log. of the octanol-water partition coefficient	6.92	unitless
N'_1	NMOLL	Nutrition rate of benthic species	Calc.	d^{-1}
N'_2	NLIM	Nutrition rate of flat fish species	Calc.	d^{-1}

N_1	NZOO	Nutrition rate of zooplankton	Calc.	d^{-1}
N_2	N2PRO	Nutrition rate of suprabenthic species	Calc.	d^{-1}
N_3	NROUND	Nutrition rate of round fish	Calc.	d^{-1}
$[O_2]$	O2DISSMG	Dissolved oxygen concentration in water	5.8	$mg.l^{-1}$
$P_{1,det}$	PZOODET	Contribution of detritic material to zooplankton diet	0.5	unitless
$P_{1,phyto}$	PZOOPHYTO	Contribution of phytoplnkton to zooplankton diet	0.5	unitless
[Phy]	BIOMPHY	Phytoplankton biomass	2.86	$mg.l^{-1}$
R'_1	RMOLL	Respiration rate of benthic organisms	Calc.	d^{-1}
R'_2	RLIM	Respiration rate of flat fish	Calc.	d^{-1}
R_1	RZOO	Respiration rate of zooplankton	Calc.	d^{-1}
R_2	R2PRO	Respiration rate of suprabenthic species	Calc.	d^{-1}
R_3	RROUND	Respiration rate of round fish	Calc.	d^{-1}
T	TEMP	Temperature	14.5	°C
W'_1	WMOLL	Weight of benthic organisms	0.209	
W'_2	WLIM	Weight of flat fish	170	
W_1	WZOO	Weight of zooplankton in round fish model		g
W_2	W2PRO	Weight of the suprabenthic organism in the round fish model	2.2	mg
W_3	WROUND	Weight of the predator in the round fish model	230	g
X'_1	CMOLL	Contaminant concentration in benthic species	Calc.	$ng.g^{-1}$ dw
X'_2	CLIM	Contaminant concentration in flat fish	Calc.	$ng.g^{-1}$ dw
X_1	CZOO	Contaminant concentration in zooplankton	Calc.	$ng.g^{-1}$ dw
X_2	C2PRO	Contaminant concentration in supra benthic species	Calc.	$ng.g^{-1}$ dw
X_3	CROUND	Contaminant concentration in rounf fish	Calc.	$ng.g^{-1}$ dw
X_{phyto}	CPHYTO	Contaminant concentration in phytoplankton	Calc.	$ng.g^{-1}$ dw
X_{sed}	CSED	Contaminant concentration in sediment	Calc.	
X_{SPM}	CDET	Contaminant concentration in particles	Calc.	$ng.g^{-1}$ dw
X_w	CWATER	Dissolved contaminant concentration in water	0.075	$ng.l^{-1}$
[Zoo]	BIOMZOO	Zooplankton biomass	1.17	$mg.l^{-1}$

VII-5 ACRONYMS AND ABREVIATIONS

Acronyms	Full text
BaP	Benzo(a)pyrene
BCF	Bioconcentration factor
BMF	Biomagnification factor
BSAF	Biota sediment accumulation factor
CB	One PCB congener (symbol usually followed by a number identifying the congener)
CEFIC	European chemical industry council
Chla	Chlorophyll a
CORINE	Co-ordination of information on the environment
DDE	1,1-dichloro-2,2-bis(chlorophenyl)ethylene
DDT	1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane
dw	Dry weight (weight of dehydrated organisms)
E	Excretion
G	Growth
GEMCO	Generic estuary modelling system to evaluate transport, fate and impact of contaminants
IECS	Institute of estuarine and coastal studies, University of Hull, UK
K_d	Sediment water equilibrium partitioning coefficient = C_{part}/C_w ($mol.kg^{-1}$ / $mol.l^{-1}$)
K_{ow}	Octanol water equilibrium partitioning coefficient
HPAH	High molecular weight polyaromatic hydrocarbons. Contain 4 aromatic rings or more.
LC 50	Lethal concentration (causing 50% mortality in experimental population)
LD 50	Lethal dose (causing 50% mortality in experimental population)
LPAH	Low molecular weight polyaromatic hydrocarbons. Contain 2 or 3 aromatic rings.
MTZ	Maximum turbidity zone
N	Nutrition
NATURA 2000	Protected area under EC habitat directive
PAH	Polyaromatic hydrocarbon
PCB	Polychlorobiphenyl
PEC	Predicted environmental concentration
PNEC	Predicted non effect concentration
POM	Particulate organic matter
R	Respiration
RNO	Réseau national d'observation (includes the French "mussel watch" programme)
SPM	Suspended particulate matter
T	Temperature
W	Weight
ww	Wet weight or fresh weight (weight of organism including its water content)

VII-6. GLOSSARY

Sources for the following definitions include Baretta-Bekker *et al*. (1998), Lincoln *et al*. (1998) and MarLIN (2001)

Anoxia: Situation when the environment (water or sediment) are devoid of oxygen.

Anoxic: Devoid of oxygen.

Benthic: Referring to the sea bottom.

Benthos: Those organisms attached to, or living on, in or near, the seabed, including that part which is exposed by tides as the littoral zone.

Bioaccumulation: General term describing processes by which chemicals are taken up by organisms directly from their environment (air, water, soil) and through the consumption of food containing the chemicals.

Bioavailability: The potential of a substance to be transferred from one compartment, biotic or abiotic, into the tissues of a living organism.The extent and rate at which a substance is absorbed into living system or is made available at the site of physiological actvity.

Bioconcentration: A process by which there is a net accumulation of a chemical into organisms directly from their environment (water, air, soil) resulting from simultaneous uptake (by gill or epithelial tissues) and elimination.

Biomagnification: The increase of contaminant concentration from one species to its predator.

Biomarker: Observable or mesurable modification at the molecular, biochemical, cellular, physiological or behavioural level that has been induced by the exposition, past or present to at least one polluant.

Biomass: The amount of living material present at a certain moment in a certain area expressed in weight unit per unit of area or volume (*e.g.* $g.m^{-2}$ or $g.m^{-3}$).

Biotransformation: Process through which an organism transforms a chemical compound, usually, but not necessarily, making it less toxic and more easily excretable.

Demersal: Bottom dwelling aquatic organism.

Deposit feeders: Animals that are feeding on bottom material with the food value being determined by its organic contents. Particles may be swallowed indiscriminately or sorted for size prior to ingestion.

Ecosystem: A community of organisms and their physical environment interacting as an ecological unit. Examples: the North Sea ecosystem, an estuarine benthic ecosystem, a pond.

Euhaline: Refers to salinity greater than 30.

Euryhaline: Able to tolerate a wide range of salinities and thus a wide variation in osmotic pressure of the environment.Opposite: Stenohaline.

Eutrophication: The over-enrichment of an aquatic environment with inorganic nutrients, especially nitrates and phosphates, often anthropogenic (*e.g.* sewage, fertiliser run-off), which may result in stimulation of growth of algae and bacteria, and can reduce the oxygen content of the water.

Excretion: Elimination of metabolic waste. Excreted substances have taken part in cellular metabolism and have no further use. Their release involve an expenditure of energy in contrast to defecation.

Family: A taxonomic category based on the grouping of related genera.

Filter feeders: Animals that collect their food by pumping water and filtering it to collect suspended particles (phyto and zooplankton, bacteria, detritus).

Food webs or **food chain:** description of what eats what, and therefore of the transfer of matter and energy through different trophic levels. In practice, this transfer is not done along a linear chain, so food web is a more appropriate name.

Forcing variable: A variable in a model whose value is imposed and used for the calculation of other variables, particularly state variables.

Genus: A taxonomic category that includes groups of related families; the principal subdivision of a family.

Habitat: The location where a plant or animal lives. It is defined for the marine environment according to geographical location, physiographic features and the physical and chemical environment (including salinity, wave exposure, strength of tidal streams, geology, biological zone, substratum, 'features' (*e.g.* crevices, overhangs, rockpools) and 'modifiers' (*e.g.* sand-scour, wave-surge, substratum mobility).

Halocline: Layer in which the salinity changes rapidly with depth.

Macrofauna: Organisms greater than 1mm.

Macrotidal: With a tidal range greater than 4m.

Meiobenthos or **meiofauna:** Small animals (50µm – 1mm) living in the spaces between sediment grains.

Mesohaline: Refers to salinities between 5 and 18.

Mesotidal: With a tidal range between 2 and 4m.

Metabolisation: The chemical changes in living cells by which energy is provided for vital processes and activities and new material is assimilated.

Microphytobenthos: Small (usually unicellular) algae living on the (shallow) sea floor. Particularly abundant on tidal flats.

Microtidal: With a tidal range less than 2m.

Oligohaline: Refers to salinities less than 5.

Pelagic: Refers to the water column.

Pelagos: Organisms that live in the water column.

Phytoplankton: The whole group of (usually microscopic) floating algae. The term refers to a functional group (floating algae) not a systematic entity.

Polyhaline: Refers to salinities between 18 and 30.

Species: A taxonomic category rankinf immediately below a genus and including closely related, morphologically similar individuals which actually or potentially interbred.

State variable: A variable which value is calculated by a model and is usually one of the model output. Each model has a minimum number of state variable under which calculations cannot be performed

Suprabenthic: Relative to the layer just above the sea floor.

Suprabenthos: Organisms dwelling in the layer just above the sea floor.

Suspension feeders: Animals that collect their food by passively filtering suspended particles from the water using organic particles (phyto and zooplankton, bacteria, detritus) as food. Many different types of screening apparatus are developed in a wide range of pelagic and benthic organisms. The particles are collected from the suspension by hairy appendages, long tentacles, mucus, etc. Each species usually feeds on a specific size range of particles enabling many species to use the same food source.

Taxa: In taxonomy, level of determination of living organisms: species, genus, families,…

Trophic level: Level in a food web at which an organism takes its food.

VII 7. CODE OF ROUND FISH MODEL

```
      PROGRAMME GETMO3
C     This is programme evaluate the fate of organic contaminants in an
c     European estuarine trophic chain. The top predator is a demersal fish
C     (type sea bass, Dicentrarchus labrax)
C     In this programme, the food chain is simplified and include only the
C     zooplankton (identifier: ZOO), a secondary producer suprabenthic species
C     (identifier: 2PRO) and the top predator (identifier: ROUND).

C     The suffixes DET, PHYTO and WATER refer to detritus, phytoplankton and
C     water respectively.

C     All results in ng/g dw.

C     This version includes the first evaluation of biotransformation based
C     on the idea that biotransformation removes some contamination once this
C     has been assimilated in the organism. The calculation is simple:
C     BIOF is the biotransformation factor, the contaminant concentration
C     in the organism ORG is after biotransformation:
C                              Corg = corg * BIOT
C


C     Forcing variables or constants
      REAL LOGKOW, LOGKD, CWATER, CPHYTO, CDET, ALPHAWATER, BETAPREY,
     &   BETADET, TEMP, O2DISSMG, CHLORO, LIP, BIOMZOO
      INTEGER NCB                    !PCB congener number

C     LOGKOW: Log of the octanol water partition coefficient
C     LOGKD : Log of the ratio sediment water partition coefficient
C     CWATER: Contaminant concentration in water, in ng/l
C     CPHYTO: Contaminant concentration in phytoplankton, in ng/g dry weight
C     CDET  : Contaminant concentration in particles, in ng/g dry weight
C     ALPHAWATER: Contaminant assimilation efficiency from water
C     BETAPREY  : Contaminant assimilation efficiency from living prey
C     BETADET   : Contaminant assimilation efficiency from nonliving food
C                 item (sediment or particle)
C     TEMP  : Temperature in deg C
C     O2DISSMG: Dissolved oxygen concentration in mg/l
C     CHLORO: Chlorophyll concentration in ug/l
C     LIP   : Lipid concentration in phytoplankton in g/g
C     BIOMZOO : Zooplankton biomass


C     Variables for the 3 modelled organisms. The prefixes W, R, N, E,
C     G, BIOT and C refer respectively to organism weight, respiration,
C     nutrition, excretion, growth, biotransformation factor
C     and contaminant concentration.

      REAL BIOMZOO, BIOMPHY, RZOO, NZOO, EZOO, GZOO, PZOOPHYTO, PZOODET,
BIOTZOO, CZOO
      REAL W2PRO, R2PRO, N2PRO, E2PRO, G2PRO, BIOT2PRO, C2PRO
```

```
      REAL WROUND, RROUND, NROUND, EROUND, GROUND, BIOTROUND, CROUND,
DICENTR

10    FORMAT(15X,A4,I4)
C     Opening files where results are stored
      NF1 = 1
      OPEN(NF1, FILE='GETMO3.DAT')

C     Opening file where values for physiological processes are stored
      NFI2 = 2
      OPEN(NFI2, FILE='ROUND_PHYSIO.DAT')


30    FORMAT(A7,G12.3,A16)
31    FORMAT(7X,A7,I3)

20    FORMAT(A7,F12.3,A16)
21    FORMAT(A7,F12.1,A16)
22    FORMAT(A7,F12.2)

C     Assign values to forcing variables:
C     Environmental
      TEMP     = 14.5                    ! deg C
      O2DISSMG = 4.1                     ! mg/l
      CHLORO   = 18.1                    ! ug/l
      LIP      = 0.045          ! g/g

C     Chemical     !The following data refer to CB153
      NCB = 153
      LOGKOW = 6.92
      CWATER = 0.075                     !ng/l

C     Biological
      BETADET   = 0.35           ! assimilation efficiency from sediment
      DICENTR   = 339                  ! ng/g CB153 in 3 yr old seabass from the Seine
estuary
C     This value is given as an example of measured concentration in a flat fish
      BIOMZOO   = 1.171          ! mg/l Zooplankton biomass
      BIOMPHY   = 2.86           ! mg/l Phytoplankton biomass
      W2PRO     = 2.209          ! mg dw  Weight of the suprabenthic organism
      WROUND    = 232.5          ! g dw  Weight of the round fish
      BIOTZOO   = 1.                   ! Biotransformation factor for zooplankton
      BIOT2PRO  = 1.                   ! Biotransformation factor for secondary producer
      BIOTROUND = 1.                   ! Biotransformation factor for the round fish
      PZOODET   = 0.5                  ! Proportion of particles in zooplankton diet
      PZOOPHYTO = 0.5                  ! Proportion of phytoplankton in zooplankton diet


C     Calculation of variables that depend on the above parameters
C     ------------------------------------------------------------

C     Water - particle partitioning coefficient. Equation validated for PCBs.
      LOGKD  = 0.75 * LOGKOW + 0.46

C     PCB concentration in suspended particles
```

```
      CDET = CWATER * 10**LOGKD / 1000        ! ng/g dw

C     Equations for the calculation of phytoplankton contamination.
C     Validated for PCBs.

      IF (LOGKOW.GE.5.5.AND.LOGKOW.LE.7) THEN
       LOG10(CPHYTO )= LOG10(CWATER) + 1.0339 * LOGKOW + LOG10(LIP) – 0.6025
       CPHYTO = 10**LOG10(CPHYTO)              !ng/g dw
      ELSEIF (LOGKOW.GT.7.AND.LOGKOW LT 8.) THEN
       LOG10(CPHYTO) = LOG10(CWATER) - 0.9743 * LOGKOW + LOG10(LIP) + 13.43
       CPHYTO = 10**CPHYTO                !ng/g dw
      ENDIF


C     Equations for the calculation of assimilation coefficients
C     Validated for PCBs.

      IF (LOGKOW.GT.6.25.AND.LOGKOW.LT.10) THEN
         ALPHAWATER =  2.9 - 0.5 * LOGKOW
         ALPHAWATER = 10**ALPHAWATER
       ELSEIF (LOGKOW.GT.4.5.AND.LOGKOW.LT.6.25) THEN
         ALPHAWATER = 0.6
       ELSE
         WRITE(6,*)'Model out of logkow range for ALPHAWATER'
         WRITE(NF1,*)'Model out of logkow range for ALPHAWATER'
         ALPHAWATER = 0.6
      ENDIF

      IF (LOGKOW.GE.6.AND.LOGKOW.LT.7) THEN
         BETAPREY = 0.65
       ELSEIF (LOGKOW.GT.4.5.AND.LOGKOW.LT.6.) THEN
         BETAPREY = 0.5
       ELSEIF (LOGKOW.GT.7.)THEN
          BETAPREY = 0.55
       ELSE
         WRITE(6,*)'Model out of logkow range for BETAPREY'
         WRITE(NF1,*)'Model out of logkow range for BETAPREY'
         BETAPREY = 0.5
      ENDIF


C     Print chemical, environmental and biological variables in result file
      WRITE(NFI1,10) 'CB',NCB
      WRITE(NFI1,*)
      WRITE(NFI1,22) 'LOGKOW', LOGKOW
      WRITE(NFI1,22) 'LOGKD', LOGKD
      WRITE(NFI1,21) 'TEMP', TEMP,'deg C'
      WRITE(NFI1,21) 'O2DISSMG', O2DISSMG,'mg/l'
      WRITE(NFI1,21) 'CHLORO', CHLORO,'ug/l'
      WRITE(NFI1,20) 'LIP ', LIP ,'g/g'
      WRITE(NFI1,20) 'BIOMZOO', BIOMZOO, ' mg/l'
      WRITE(NFI1,20) 'BIOMPHY', BIOMPHY, ' mg/l'

      WRITE(NFI1,*)
```

```
      WRITE(NFI1,20) 'CWATER', CWATER,'ng/l'
      WRITE(NFI1,20) 'CDET', CDET,'ng/g dw'
      WRITE(NFI1,20) 'CPHYTO', CPHYTO,'ng/g dw'
      WRITE(NFI1,20) 'ALPHAWATER', ALPHAWATER
      WRITE(NFI1,20) 'BETAPREY', BETAPREY
      WRITE(NFI1,20) 'BETADET', BETADET
      WRITE(NFI1,20) 'BIOTMOLL', BIOTMOLL
      WRITE(NFI1,20) 'BIOTLIM', BIOTLIM
      WRITE(NFI1,20) 'PZOODET', PZOODET
      WRITE(NFI1,20) 'PZOOPHYTO', PZOOPHYTO
      WRITE(NFI1,*)


C+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
C
C     Calculation of ZOOPLANKTON contamination
C
C+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

C     Respiration
C     -----------
      RZOO = 0.059 * CHLORO + 0.033 * TEMP - 0.178          !umol O2/l/h
C     unit conversion
      RZOO = (RZOO * 0.768) / (BIOMZOO * O2DISSMG)          !l/g/d


C     Nutrition
C     ---------
      NZOO = 0.024*(3.197 * CHLORO - 1.)/BIOMZOO            !/d


C     Excretion
C     ---------
      EZOO = 0.199 / (CHLORO * BIOMZOO)                     !/d


C     Growth
C     ---------
      GZOO = 0.278                                          !/d

C     Contamination
C     -------------
      CZOO = (RZOO*ALPHAWATER*CWATER                        ! input from respiration
     &        + NZOO * BETAPREY * PZOOPHYTO * CPHYTO        ! input from phytoplankton

     &        + NZOO * BETADET * PZOODET * CDET)            ! input from detritus
     &        / (EZOO + GZOO)                               ! losses through excretion and growth


C     Biotransformation
C     -----------------
      CZOO = CZOO * BIOTZOO

      WRITE(NF1,30) 'CZOO', CZOO,' ng/g'
```

```
C+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
C
C       Calculations of SECONDARY PRODUCER contamination
C
C+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

C       Respiration
C       -----------
        R2PRO = 109.6 * W2PRO**(-0.758) / O2DISSMG      !/d


C       Nutrition
C       ---------
        N2PRO = 0.495 * EXP(0.0875 * TEMP - 0.0434)       !/d


C       Excretion
C       ---------
        E2PRO = 0.0985 * EXP(0.031 * TEMP - 0.19)  !/d


C       Growth
C       ------
        G2PRO = 0.249                                     !/d


C       Contamination
C       -------------
        C2PRO = ((R2PRO * ALPHAWATER * CWATER)              ! input from respiration
     &          + (N2PRO * BETAPREY * CZOO))    ! input from zooplankton
     &          / (E2PRO + G2PRO)                         ! losses through excretion and growth


C       Biotransformation
C       -----------------
        C2PRO = C2PRO * BIOT2PRO


        WRITE(NF1,30) 'C2PRO', C2PRO,' ng/g'


C+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
C
C       Calculations of ROUND FISH contamination
C
C+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
C       Respiration
C       -----------
        RROUND = 23.72 * WROUND**(-1.2209) * TEMP**1.6867 / O2DISSMG    !l/g/d


C       Nutrition
C       ---------
        NROUND = 0.187 * WROUND * EXP(0.004*TEMP - 2.17)            !/d
```

```
C       Excretion
C       ---------
        EROUND = 0.147 * WROUND**0.171                                  !/d


C       Growth
C       ------
        GROUND = 0.992                                                  !/d


C       Contamination
C       -------------
        CROUND = (RROUND*ALPHAWATER*CWATER              ! input from respiration
     &          + NROUND * BETAPREY * C2PRO)           ! input from 2ary prod
     &          / (EROUND + GROUND)                    ! losses through excretion and growth

C       Biotransformation
C       -----------------
        CROUND = CROUND * BIOTROUND

        WRITE(NF1,30) 'CROUND', CROUND,' ng/g'
        WRITE(NFI1,21) 'SEABASS', DICENTR,' ng/g dw'


C       Print physiological processes values in file
        WRITE(NFI2,30) 'RZOO', RZOO,' /day'
        WRITE(NFI2,30) 'NZOO', NZOO,' /day'
        WRITE(NFI2,30) 'EZOO', EZOO,' /day'
        WRITE(NFI2,30) 'GZOO', GZOO,' /day'
        WRITE(NFI2,20) 'BIOTZOO', BIOTZOO
        WRITE(NFI2,30)

        WRITE(NFI2,30) 'R2PRO', R2PRO,' /day'
        WRITE(NFI2,30) 'N2PRO', N2PRO,' /day'
        WRITE(NFI2,30) 'E2PRO', E2PRO,' /day'
        WRITE(NFI2,30) 'G2PRO', G2PRO,' /day'
        WRITE(NFI2,20) 'BIOT2PRO', BIOT2PRO

        WRITE(NFI2,30)
        WRITE(NFI2,30) 'RROUND', RROUND,' /day'
        WRITE(NFI2,30) 'NROUND', NROUND,' /day'
        WRITE(NFI2,30) 'EROUND', EROUND,' /day'
        WRITE(NFI2,30) 'GROUND', GROUND,' /day'
        WRITE(NFI2,20) 'BIOTROUND', BIOTROUND


        END
```

VI-8. CODE OF FLAT FISH MODEL

```
      PROGRAMME PLAT4
C     This programme is a simplified model that evaluates the fate of organic
C     contaminants in an European estuarine trophic chain. The top predator
c     is a flat fish (type dab, Limanda limanda).
C
C     In this model only two organisms make up the food chain
C     - a benthic organism (a mollusc), MOLL
C     - a predator flat fish, LIM

C     The suffixes SED, PHYTO and WATER refer to sediment, phytoplankton and
C     water respectively.

C     Forcing variables or constants
      REAL LOGKOW, CSED, LIMANDA, LOGKD, CWATER, CPHYTO,
     & ALPHAWATER, BETAPREY
      REAL FOC, BETADET, LIP, TEMP, CHLORO, O2DISSMG, BIOMPHY
      INTEGER NCB                                   ! PCB congener number


C     LOGKOW: Log of the octanol water partition coefficient
C     LOGKD : Log of the ratio sediment water partition coefficient
C     CWATER: Contaminant concentration in water, in ng/l
C     CPHYTO: Contaminant concentration in phytoplankton, in ng/g dry weight
C     CSED  : Contaminant concentration in sediment, in ng/g dry weight
C     ALPHAWATER: Contaminant assimilation efficiency from water
C     BETAPREY  : Contaminant assimilation efficiency from living prey
C     BETADET   : Contaminant assimilation efficiency from nonliving food
C                 item (sediment or particle)
C     TEMP  : Temperature in deg C
C     O2DISSMG: Dissolved oxygen concentration in mg/l
C     CHLORO: Chlorophyll concentration in ug/l
C     BIOMPHY : Phytoplankton biomass in mg/l
C     LIP   : Lipid concentration in phytoplankton in g/g
C     FOC   : Fraction of organic carbon in sediment


C     Variables for the 2 modelled organisms. The prefixes W, R, N, E,
C     G, BIOT and C refer respectively to organism weight, respiration,
C     nutrition, excretion, growth, biotransformation factor
C     and contaminant concentration.

      REAL WMOLL, RMOLL, NMOLL, EMOLL, GMOLL, BIOTMOLL, CMOLL
      REAL WLIM, RLIM, NLIM, ELIM, GLIM , BIOTLIM, CLIM

C     Opening file where results are stored
      NFI1 = 1
      OPEN(NFI1, FILE='PLAT.DAT')
C     Opening file where values for physiological processes are stored
      NFI2 = 2
```

```
      OPEN(NFI2, FILE='PLAT_PHYSIO.DAT')

10    FORMAT(15X,A4,I4)
20    FORMAT(A7,F12.3,A16)
21    FORMAT(A7,F12.1,A16)
22    FORMAT(A7,F12.2)
30    FORMAT(A7,G12.3,A16)

C     Assign values to forcing variables:
c     ---------------------------------

C     Environmental
      FOC     = 0.021
      TEMP    = 14.5                    ! deg C
      O2DISSMG = 4.1              ! mg/l
      CHLORO  = 18.1                    ! ug/l
      BIOMPHY  = 2.86             ! mg/l
      LIP     = 0.045         ! g/g

C     Chemical    !The following data refer to CB153
      NCB = 153
      LOGKOW = 6.92
      CWATER = 0.075                    !ng/l

C     Biological
      BETADET   = 0.35          !assimilation efficiency from sediment
      LIMANDA = 171.2                   !ng/g CB153 in 3 yr old dab from the bay of Seine
C     This value is given as an example of measured concentration in a flat fish
      WMOLL = 0.209                     !g dw  Weight of the benthic organism
      WLIM  = 170.0             !g dw  Weight of the flat fish
      BIOTMOLL = 1.                     ! Biotransformation factor for the benthic organism

      BIOTLIM = 1.              ! Biotransformation factor for the flat fish


C     Calculation of variables that depend on the above parameters
C     ------------------------------------------------------------

C     Water - particle partitioning coefficient. Equation validated for PCBs.
      LOGKD  = 0.75 * LOGKOW + 0.46

C     PCB concentration in sediment
      CSED = CWATER * 10**LOGKD / 1000        ! ng/g dw

C     Equations for the calculation of phytoplankton contamination.
C     Validated for PCBs.

      IF (LOGKOW.GE.5.5.AND.LOGKOW.LE.7) THEN
       LOG10(CPHYTO )= LOG10(CWATER) + 1.0339 * LOGKOW + LOG10(LIP) – 0.6025
       CPHYTO = 10**LOG10(CPHYTO)           !ng/g dw
      ELSEIF (LOGKOW.GT.7.AND.LOGKOW LT 8.) THEN
       LOG10(CPHYTO) = LOG10(CWATER) - 0.9743 * LOGKOW + LOG10(LIP) + 13.43
       CPHYTO = 10**CPHYTO              !ng/g dw
      ENDIF
```

```
C       Equations for the calculation of assimilation coefficients
C       Validated for PCBs.

        IF (LOGKOW.GT.6.25.AND.LOGKOW.LT.10) THEN
           ALPHAWATER =  2.9 - 0.5 * LOGKOW
           ALPHAWATER = 10**ALPHAWATER
         ELSEIF (LOGKOW.GT.4.5.AND.LOGKOW.LT.6.25) THEN
           ALPHAWATER = 0.6
         ELSE
           WRITE(6,*)'Model out of logkow range for ALPHAWATER'
           WRITE(NF1,*)'Model out of logkow range for ALPHAWATER'
           ALPHAWATER = 0.6
        ENDIF

        IF (LOGKOW.GE.6.AND.LOGKOW.LT.7) THEN
           BETAPREY = 0.65
         ELSEIF (LOGKOW.GT.4.5.AND.LOGKOW.LT.6.) THEN
           BETAPREY = 0.5
         ELSEIF (LOGKOW.GT.7.)THEN
            BETAPREY = 0.55
         ELSE
           WRITE(6,*)'Model out of logkow range for BETAPREY'
           WRITE(NF1,*)'Model out of logkow range for BETAPREY'
           BETAPREY = 0.5
        ENDIF



C       Print chemical, environmental and biological variables in result file
        WRITE(NFI1,10) 'CB',NCB
        WRITE(NFI1,*)
        WRITE(NFI1,22) 'LOGKOW', LOGKOW
        WRITE(NFI1,22) 'LOGKD', LOGKD
        WRITE(NFI1,21) 'TEMP', TEMP,'deg C'
        WRITE(NFI1,21) 'O2DISSMG', O2DISSMG,'mg/l'
        WRITE(NFI1,21) 'CHLORO', CHLORO,'ug/l'
        WRITE(NFI1,21) 'BIOMPHY', BIOMPHY,'mg/l'
        WRITE(NFI1,20) 'LIP ', LIP ,'g/g'
        WRITE(NFI1,20) 'FOC', FOC

        WRITE(NFI1,20) 'CWATER', CWATER,'ng/l'
        WRITE(NFI1,20) 'CSED', CSED,'ng/g dw'
        WRITE(NFI1,20) 'CPHYTO', CPHYTO,'ng/g dw'
        WRITE(NFI1,20) 'ALPHAWATER', ALPHAWATER
        WRITE(NFI1,20) 'BETAPREY', BETAPREY
        WRITE(NFI1,20) 'BETADET', BETADET
        WRITE(NFI1,20) 'BIOTMOLL', BIOTMOLL
        WRITE(NFI1,20) 'BIOTLIM', BIOTLIM
        WRITE(NFI1,*)



C***************************************************************
```

```
C
C       Calculations of BENTHIC ORGANISM contamination
C
C*****************************************************************

C       Respiration
C       -----------
        RMOLL = 1.219 * EXP(0.0269*TEMP) / O2DISSMG          !l/g/d

C       Nutrition
C       ---------
        NMOLL = 0.2736 * BIOMPHY + 0.132 * FOC + 3.504       !d

C       Excretion
C       ---------
        Log(EMOLL) = 0.799 * Log(WMOLL) -2.352               !/d

C       Growth
C       ------
        GMOLL = 0.0156                                       !/d

C       Contamination
C       -------------
        CMOLL = (RMOLL * ALPHAWATER * CWATER                 ! input from respiration
     &             + NMOLL * BETADET * CSED)                 ! input from sediment via feeding
     &           / (EMOLL + GMOLL)                           ! losses through excretion and growth

C       Biotransformation
C       -----------------
        CMOLL = CMOLL * BIOTMOLL                             ! ng/g dw

        WRITE(NFI1,30) 'CMOLL', CMOLL,' ng/g dw'             ! print in result file



C*****************************************************************
C
C       Calculations of flat fish contamination
C
C*****************************************************************

C       Respiration
C       -----------
        RLIM = 10**10.63 * TEMP**0.5415 * WLIM**(-5.032)/O2DISSMG  !l/g/d


C       Nutrition
C       ---------
        NLIM = 3.048*10**(-3) * WLIM**1.536 * 10**(0.0014 * TEMP)          !/d

C       Excretion
C       ---------
        ELIM = 0.168 * NLIM  + 0.0035 * TEMP + 0.965         !/d

C       Growth
```

```
C       ------
        GLIM = 0.028                                    !/d


C       Contamination
C       -------------
        CLIM = (RLIM * ALPHAWATER * CWATER              !input from respiration
     &          + NLIM * BETAPREY * CMOLL)             !input from benthic organism via
feeding
     &          / (ELIM + GLIM)                        !losses through excretion and growth

C       Biotransformation
C       -----------------
        CLIM = CLIM * BIOTLIM                   ! ng/g dw

C       Print in result file
        WRITE(NFI1,30) 'CLIM', CLIM,' ng/g dw'
        WRITE(NFI1,21) 'DAB', LIMANDA,' ng/g dw'

C       Print physiological processes values in file
        WRITE(NFI2,30) 'RMOLL', RMOLL,' /day'
        WRITE(NFI2,30) 'NMOLL', NMOLL,' /day'
        WRITE(NFI2,30) 'EMOLL', EMOLL,' /day'
        WRITE(NFI2,30) 'GMOLL', GMOLL,' /day'
        WRITE(NFI2,20) 'BIOTMOLL', BIOTMOLL

        WRITE(NFI2,30)
        WRITE(NFI2,30) 'RLIM', RLIM,' /day'
        WRITE(NFI2,30) 'NLIM', NLIM,' /day'
        WRITE(NFI2,30) 'ELIM', ELIM,' /day'
        WRITE(NFI2,30) 'GLIM', GLIM,' /day'
        WRITE(NFI2,20) 'BIOTLIM', BIOTLIM


        END
```