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Modelling the fate of dioxins in a trophic network by coupling an ecotoxicological and an Ecopath model

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Abstract

This paper shows the possibility to combine a trophic network model and an ecotoxicological food web model to calculate toxic concentrations of area-specific aquatic species. The trophic network model was derived from an Ecopath application made for a shallow water area (Palude della Rosa), situated in the northern part of the Lagoon of Venice. The organisms-specific output data from the energy model, such as metabolic rates, diet composition and structural characteristics were used as input to the ecotoxicological food chain model. The toxic substance model estimated bioaccumulation (pg/g lipid) of dioxins (e.g. 2378-TCDD, 12378-PeCDD, 123478-HxCDD, 123789-HxCDD, 1234678-HpCDD and 12346789-OCDD) and dibenzofurans (e.g. 2378-TCDF, 12378-PeCDF, 123478-HxCDF, 123678-HxCDF, 123789-HxCDF, 234678-HxCDF, 1234678-HpCDF, 1234789-HpCDF and 12346789-OCDF) for all groups in the trophic network. A sensitivity analysis showed that the toxic concentration in the aquatic species was highly affected by the following parameters: K_{ow}, fraction of organic carbon in the sediment, lipid fraction, and fraction of unassimilated food. The coupling of the two models was validated with data from four sites in the Lagoon (two in the industrial zone, and two in the southern basin). Calibration and comparisons with measured data were conducted for a clam (*Tapes philippinarum*), a mussel (*Mytilus edulis*) and a fish (*Scardinius eritrophtalamus*). Model output showed that the discrepancy between chemical analysis and model estimations were in the range of one order of magnitude for *T. philippinarum* and *M. edulis* (except for tetra- and penta-furans, where the overestimation reached two order of magnitude). It was also shown that more monitoring efforts should be made on fish species, to have a set of data useful for the validation of the model.

Keywords: Trophic network; Food chain model; Dioxins; Dibenzofurans; Aquatic ecotoxicology

1. Introduction

The presence in the aquatic environment of toxic substances, such as many organic micro-pollutants, may not only affect the health of aquatic organisms, but also of humans exploiting these organisms as food sources. The hydrophobicity of such compounds, often quantified as the octanol–

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water partition coefficient, K_{ow}, causes their bioconcentration and subsequent bioaccumulation in the organism.

Several studies focused on the transfer of toxic substances from sediment to organisms (Thomann, 1989; Mackay, 1991; Thomann and Connolly, 1992; Thomann et al., 1992; Gobas, 1993; Thomann et al., 1995; Wang et al., 1996; Campfens and Mackay, 1997). Other studies focused on the transfer of matter and energy occurring between organisms, and on the relationships they establish in a trophic network. The output is a network of flows between components of the trophic web, based on metabolic characteristics and feeding preferences of organisms, and on the particular features of the site considered (Steele, 1970; Odum, 1972; Ulanowicz, 1986; Wulff et al., 1989; Christensen and Pauly, 1993).

Most toxic substance models focus on the dynamics of the chemical, and therefore simplify the problem of assessing the rate of consumption of contaminated food by using empirical equations based on the dimensions of organisms (e.g. Thomann, 1989). However, the complexity of the ecosystem described as a set of pathways of energy usage by organisms should be taken into account in models. The flow rates and metabolic parameters obtained from a trophic network are determined by the interaction of all processes occurring in the ecosystem, comprising direct and indirect effects.

The aim of this paper is to provide a method to use the holistic information contained in the trophic network to assess the transfer of a toxic substance toward higher levels of the trophic web. The idea is thus to couple these two kinds of models: a trophic network model and a toxic substance–food web model.

The trophic network model is derived from an Ecopath application made for a shallow water in the northern part of the Lagoon of Venice (Carrer and Opitz, 1999). Metabolic rates and indices plus information on feeding preferences of organisms were the output of the Ecopath model that were used as input to the ecotoxicological model. The latter is derived from an approach proposed by Thomann (1989) and Thomann et al. (1992). The resulting model was validated with data of polychlorinated dioxins and dibenzofurans, such as: 2378-TCDD, 12378-PeCDD, 123478-HxCDD, 123678-HxCDD, 123789-HxCDD, 1234678-HpCDD, 12346789-OCDD, 2378-TCDF, 12378-PeCDF, 23478-PeCDF, 123478-HxCDF, 123678-HxCDF, 123789-HxCDF, 234678-HxCDF, 1234678-HpCDF, 1234789-HpCDF, 12346789-OCDF, in sediments and biota from the Lagoon of Venice. Fig. 1 shows the area of sampling sites for toxic compounds as well as the site where the data for the trophic network model were collected.

The aim of such an application is to show how information obtained from these models may be used in a coherent framework to assess the toxic level of exposed edible organism. The application was thus carried on with this purpose, notwithstanding a certain lack in site-specific data and a different spatial location between data on sediment's and biota's chemical concentrations and data on organisms' density (trophic network).

2. The two models

2.1. The trophic network model

A trophic network model describes the trophic interactions between components of an ecosystem. Such interactions are determined by feeding relationships as well as by other processes, such as production, growth, respiration, excretion and natural mortality. Each of these processes is associated to a flow of matter, or energy, in the network.

Carrer and Opitz (1999) constructed a steady-state trophic network model for a shallow water (Palude della Rosa) in the Lagoon of Venice. Basic equations of the model are described in detail in that previous paper. In this work, the previously published model was simplified to 12 compartments from the original 16 by lumping phytoplankton and bacterioplankton and by omitting birds, macro-benthos omnivore predators and macro-benthos mixed feeders. Phytoplankton and bacterioplankton were aggregated, since in the toxic substance model they both were considered as suspended micro-organisms only

bioconcentrating the toxic substances dissolved in the water. The other three groups were omitted because the predation on such groups was less than 1% of their total outflow, thus they do not result relevant for the transfer of chemicals towards higher trophic levels. The result is shown in Fig. 2. The unit of measure adopted for biomasses and flows is *energy*, thus biomasses are expressed in kcal m^{-2} and flows in kcal m^{-2} per time.

Metabolic parameters are either input or output of the model, since some of them can be determined by energy balance equations. Among the most important metabolic rates, there are: production/biomass ratio (P/B), consumption/biomass ratio (Q/B), percentage of food that is not assimilated ($\%NA$). Respiration (R) is always an output of the model obtained from the following equation, solved for each compartment i of the model:

$$R_i = (1 - \%NA_i) * Q_i - B_i * (P/B)_i \quad (1)$$

The diet composition of organisms is of fundamental importance to determine the flows associated to grazing and predation. Information on feeding preferences of organisms is contained in the *diet matrix* of the model. The element DC_{ij} of the diet matrix is the percentage of item i in the diet of compartment j.

Metabolic rates calculated in the Ecopath model and useful for the ecotoxicological model are reported in Table 1, whereas Table 2 reports the diet matrix of the trophic network model. The original model was realised on a seasonal basis, so the time unit adopted was *month*. Metabolic rates

Fig. 1. Location of sampling sites for toxic substances (sites 1–4) and for biological data used to construct the trophic network (TN).

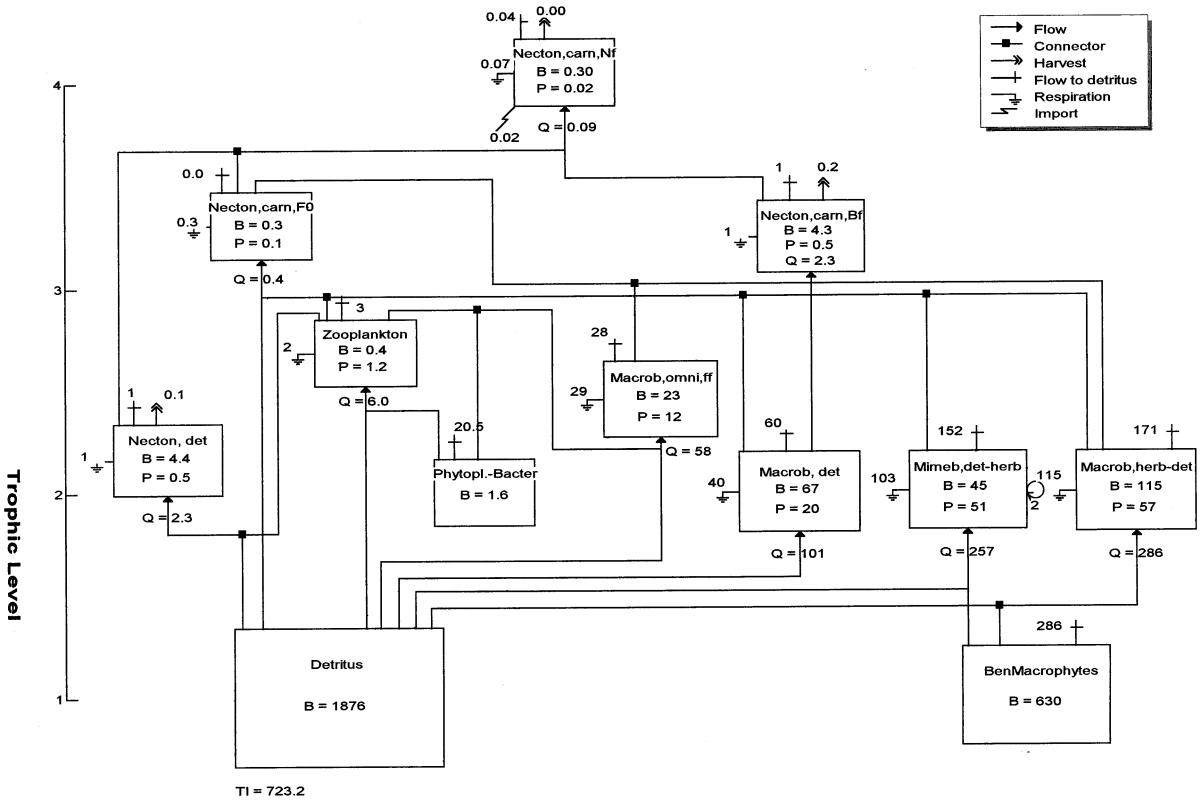

Fig. 2. Ecopath model — summer 1994 — 12 compartments. The area of each box is proportional to the logarithm of the biomass (B, in kcal m^{-2}) of each group. Flows are in kcal m^{-2} per month. Q is the total flow entering a compartment and P is the production of a compartment (carn, carnivorous; det, detritivorous; herb, herbivorous; omni, omnivorous; Bf, benthic feeders; ff, filter feeders; Nf, nekton feeders).

Table 1
Metabolic rates and values obtained from Ecopath (the original model has a *monthly* time scale, here all values have been converted to *day*)

Metabolic rates

Groups/units	Abbreviation	P/B (day^{-1})	Q/B (day^{-1})	%NA (day^{-1})	Respiration R (kcal day^{-1})
Zooplankton	Zoopl	0.100	0.50	0.50	0.060
Micro and Mesobenthos detritivorous-herbivorous	mMdh	0.038	0.19	0.40	3.420
Macrobenthos detritivorous	Md	0.010	0.05	0.40	1.343
Macrobenthos herbivorous-detritivorous	Mhd	0.017	0.08	0.40	3.818
Macrobenthos omnivorous-filter feeders	Moff	0.017	0.08	0.30	0.962
Nekton detritivorous	Nd	0.004	0.02	0.30	0.039
Nekton carnivorous, fish0 (small fish)	NcF0	0.015	0.05	0.10	0.013
Nekton carnivorous benthic feeders	Ncbf	0.004	0.02	0.26	0.042
Nekton carnivorous nekton feeders	Ncnf	0.002	0.01	0.20	0.002

in Table 1 were converted to *day*. Results presented in Tables 1 and 2 were used as input data in the toxic substance model presented below.

2.2. The toxic substance food web model

The following sets of equations were used to model the transfer of toxic compounds from sediment to organisms belonging to different trophic levels.

The mass balances for solids in the water and in the sediment, and the partitioning of the chemical between sediment, interstitial water, overlaying water and suspended solids were stated as suggested in Chapra (1997) for a well-mixed lake. Due to the lack of information on hydrodynamic and on solids budget for the considered site, it was chosen to simulate concentrations in the 'worst case', i.e. a closed basin with no wash-out, no burial, no volatilisation and no decay processes (last ones are actually less important on the whole budget, since the particular compounds considered in this application are among the most persistent).

Let c_{sed} be the concentration of the chemical in the sediment (mg g^{-1}) and c_{dintw} be the dissolved concentration in interstitial water (mg m^{-3}); then:

$$c_{dintw} = c_{sed}/K_{dsed} \quad (2)$$

where the sediment-interstitial water partition coefficient $K_{dsed} = K_{oc} * foc_{sed}$, ($m^3$ g^{-1}), is a function of the organic carbon partition coefficient K_{oc} (m^3 gC^{-1}) and of the fraction of organic carbon in the sediment foc_{sed}.

K_{oc} is obtained by the empirical formula (Karichoff et al., 1979):

$$K_{oc} = 6.17 * 10^{-7} K_{ow} \quad (3)$$

where K_{ow} is the octanol–water partition coefficient (m^3 g^{-1}) of the chemical.

Let Φ be the porosity of the sediment and ρ be the density of the sediment; the dissolved, particulate and total concentrations of the chemical normalised to the volume of the sediment (mg m^{-3}) can be defined as:

$$c_{dsed} = \Phi * c_{dintw} \quad (4)$$

$$c_{psed} = (1 - \Phi) * \rho * c_{sed} \quad (5)$$

$$c_{totsed} = c_{dsed} + c_{psed} \quad (6)$$

The total concentration of the chemical in the water, c_{totw} (mg m^{-3}), is obtained solving the contaminant budget equation (Eq. (7)) at steady state:

Table 2
Ecopath diet matrix[a]

Diet matrix										
Abb.	Group	4	5	6	7	8	9	10	11	12
BM	1				0.80					
Phyt-Bact	2	0.70				0.50				
Zoopl	4						0.10	0.60		
mMdh	5							0.05		
Md	6							0.15	0.25	
Mhd	7							0.10	0.30	
Moff	8								0.40	
Nd	9									0.15
NcF0	10								0.05	0.30
Ncbf	11									0.55
Ncnf	12									
Det	13		1	1	0.2	0.3	0.9	0.1		
Som	14	0.3				0.2				

[a] Det, detritus; Som, suspended organic matter.

$$V*dc_{totw}/dt = -v_s*A*Fp_w*c_{totw} + v_r*A*c_{totsed} + v_d*A*(Fd_{sed}*c_{totsed} - Fd_w*c_{totw}) \quad (7)$$

where:

V	volume of water
A	surface area of the sediment/water interface
v_s	settling velocity (m year^{-1})
v_r	resuspension velocity (m year^{-1})
v_d	diffusion velocity (m year^{-1})
Fp_w, Fd_w	particulate and dissolved fraction of the contaminant in the water
Fd_{sed}	dissolved fraction of the contaminant in the sediment

At steady-state ($dc_{totw}/dt = 0$):

$$c_{totw} = (v_r + v_d*Fd_{sed})*c_{totsed}/(v_s*Fp_w + v_d*Fd_w) \quad (8)$$

Equations for the estimation of velocities and of dissolved fractions in sediment (Fd_{sed}), and water, (Fd_w, correlated to the fraction of organic carbon in suspended matter, foc_w) are reported in the appendix.

The contaminant present in the water may be transferred to biota in two ways: firstly by direct uptake of the dissolved part of the chemical through the gills and the epithelial tissues (*bioconcentration*), secondly by ingestion of contaminated suspended particles (the combination of both processes is termed *bioaccumulation*). Thus, the particulate and dissolved concentrations of the chemical in the water will be used:

$$cd_w = Fd_w*c_{totw} \quad (9)$$

$$cp_w = Fp_w*c_{totw} \quad (10)$$

Primary producers, such as macroalgae and phytoplankton are at the base of each trophic chain. It is then necessary to calculate their bioconcentration factors (BCF), to be able to determine concentrations of chemicals in organism feeding on them, as well as in organisms belonging to higher trophic levels.

The bioconcentration of highly lipophilic compounds for primary producers is very difficult to estimate, and the dynamics of the processes are still not very well known. As for phytoplankton, it has been discovered that with the increase of the compound's lipophilicity, the uptake from the cell becomes more difficult to predict (Chessells et al., 1992). Regression equations proposed by some authors, e.g. Geyer et al. (1981) and Geyer et al. (1984), are not applicable for compounds with a $\log K_{ow} > 6$ (Jørgensen et al., 1998). Swackhamer and Skoglund (1993) and Stange and Swackhamer (1994) show how, for many organic compounds, the logarithm of the bioconcentration factor (on a dry weight basis) versus the logarithm of the octanol–water partition coefficient flattens after a $\log K_{ow} = 6$, reaching a plateau of $\log \mathrm{BCF} = 4.5$ at $\log K_{ow} \approx 6.5$. This value was then used and converted to a $\mathrm{BCF}_{lipid} = 0.25$ m^3 g_{lipid}^{-1}, considering a wet–dry ratio $a_{wd} = 8.3$ (parameter inherited from the trophic network model) and a lipid fraction $f_L = 1.5$ glipid/gww (Campfens and Mackay, 1997). The concentration in the lumped 'phytoplankton–bacterioplankton' compartment, on a lipid basis, is then given by $c_{Lphyto} = BCF_{lipid}*cd_w$ (assuming that bacterioplankton particles behave like phytoplankton ones).

As for macrophytes, a linear regression was adopted from Gobas et al. (1991); the following equation is obtained by fitting bioconcentration data (on a wet weight basis) for compounds with $\log K_{ow}$ up to 8.3:

$$\log BCF = 0.98*\log K_{ow} - 2.24 \quad (11)$$

The value of BCF, obtained by substituting the value of octanol–water partition coefficient for each compound, was then converted to m^3 g_{lipid}^{-1} by using a value of $f_L = 4.5$, average value from experimental data on macroalgae collected in the Lagoon of Venice (Maroli et al., 1993), ri-elaborated applying a conversion factor for wet–dry ratio $a_{wd} = 6.7$ (parameter inherited from the trophic network model).

After the estimation of concentrations in interstitial water, overlying water and in primary producers, the estimation of bioaccumulation factors was conducted, based on the equations proposed by Thomann (1989) and Thomann et al. (1992).

The mass–balance equation for a given compartment i (related to consumer organisms) is

$$\frac{dc_{Li}}{dt} = [k_{ui} * (b_{i\text{sed}} * c_{i\text{ntw}} + b_{iw} * c_{dw})]_{\text{uptake from water}} + \left[a_{ioc} * (d_{i\text{sed}} IL_{ioc} c_{\text{sed\_oc}} + d_{ism} IL_{iocw} c_{sm}) + \sum_j (d_{ji} * a_{ij} * IL_{ij}) * c_{Lj} \right] - [(K_i + G_i) * c_{Li}]_{\text{losses}} \quad (12)$$

where:

c_{Li}	chemical concentration in the ith compartment, on a lipid basis (g kg^{-1} lipid)
k_{ui}	chemical uptake rate from available dissolved chemical (m^3 g^{-1} lipid day)
$b_{i\text{sed}}$ and b_{iw}	fraction of uptake from interstitial and overlying water
$c_{\text{sed\_oc}}$	chemical concentration in the sediment, on an organic carbon basis $= c_{\text{sed}}/foc_{\text{sed}}$ (mg gC^{-1})
c_{sm}	chemical concentration in suspended matter, on an organic carbon basis $= cp_w/foc_w$ (mg gC^{-1})
a_{ij}, a_{ioc}	assimilation efficiency of ingested chemical (in prey j or in dead organic matter)
IL_{ij}	feeding rate on prey j, on a lipid basis (day^{-1})
IL_{ioc}, IL_{iocw}	feeding rate on sediment and suspended matter, on an organic carbon basis (day^{-1})
d_{ji}, $d_{\text{sed}i}$, $d_{sm i}$	diet composition coefficients for prey j, sediment and suspended matter, respectively
K_I	membrane and metabolic losses (day^{-1})
G_I	growth rate (day^{-1}) (can be considered as a growth 'dilution')

The concentration, c_{Li}, in the organism on a lipid basis is then obtained solving this equation for each compartment at steady state ($dc_{Li}/dt = 0$):

$$c_{Li} = \left\{ k_{ui} (b_{i\text{sed}} c_{\text{int}w} + b_{iw} c_{dw}) + \left[a_{ioc} * (d_{\text{sed}i} IL_{ioc} c_{\text{sed\_oc}} + d_{sm i} IL_{iocw} c_{sm}) + \sum_j (d_{ji} a_{ji} IL_{ij}) * c_{Lj} \right] \right\} / (K_i + G_i) \quad (13)$$

The ratio of the concentration in the lipid determined by the uptake from water and the concentration in the water, c_{dw} or $c_{\text{int}w}$, (depends whether the organism is in the sediment, and then in contact with the interstitial water, or in the water column) is the bioconcentration factor, given by Thomann et al. (1992):

$$BCF_i = k_{ui}/(K_i + G_i) \quad (14)$$

The membrane and metabolic losses term K_i is given by two factors (Thomann et al., 1992):

$$K_i = k_{ui}/k_{ow} + K'_i \quad (15)$$

where K'_i is the excretion rate of non-assimilated food by the organism.

2.3. Coupling of the models

Fig. 3 shows the information passed to the ecotoxicological model; each input to the ecotoxicological model is derived from an output of one of the other boxes.

Table 3 shows the 'links' between the outputs of the Ecopath model and the inputs of the toxicological model.

Below a more detailed explanation will be given about the connections between each parameter.

2.3.1. Chemical uptake rate k_{ui}

This parameter is obtained from an empirical formula suggested by Thomann (1989)

$$k_{ui} = 10^6 \frac{r_{oc} a_{cd}}{o_w a_{wdi} f_{Li}} \frac{E_c}{E_o} r_i \quad (16)$$

where:

R_i	respiration rate of organisms in compartment i (day^{-1})
a_{wdi}	wet weight–dry weight ratio for organisms in compartment i (derived from the construction of the trophic network)

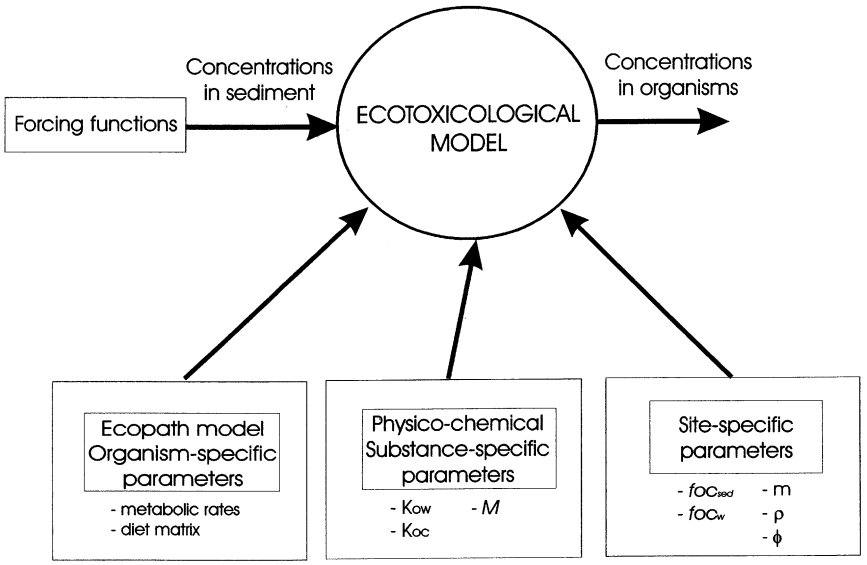

Fig. 3. Flow of information in the coupling of models

f_{Li} lipid fraction of organisms in compartment i (gLipid g^{-1} wet weight)
r_{oc} oxygen–carbon ratio ≈ 2.67 kg O kg C^{-1}
a_{cd} carbon-dry weight ratio ≈ 0.4 kg C kg dw^{-1}
o_w oxygen concentration in the water (8.5 mg l^{-1})

(E_c/E_o) is the ratio between the chemical transfer efficiency and the oxygen transfer efficiency for the organism, obtained from an empirical formula (Thomann and Connolly, 1992) reported in Table 4. The same equation was used to determine assimilation efficiencies of ingested chemicals, a_{ij} in Eq. (12), since some of the factors governing the transport mechanism across the gut wall of organism into the blood stream would be expected to be similar to the factors affecting the efficiency of transport across the gill membrane (Thomann, 1989).

In this case, R_i (kcal $time^{-1}$) and B_i (kcal) are the Ecopath model outputs used as inputs in the toxic substance model for calculating the uptake k_{ui}. In fact, the respiration rate, r_i may be obtained from R_i, dividing by the biomass B_i and by the correct time scale if necessary (in this case, the time unit was already converted to *day*), so

$$r_i = R_i/B_i \tag{17}$$

$$k_{ui} = 10^6 \frac{r_{oc} a_{cd}}{o_w a_{wdi} f_{Li}} \frac{E_c}{E_o} \frac{R_i}{B_i} \tag{18}$$

and then the uptake, k_{ui} becomes a function of the Ecopath outputs R_i and B_i:

2.3.2. Diet composition coefficients d_{ij}

The diet composition coefficients d_{ij} used in the equation determining the concentration of chemical in organism, are exactly the same coefficients DC_{ij} of the Ecopath diet matrix reported in Table 2, so: $d_{ij} = DC_{ij}$.

Table 3
Links between the Ecopath model and the ecotoxicological model[a]

Ecopath output	Toxicological model input
R_i; B_i	Chemical uptake rate k_{ui}
DC_{ij}	Diet composition coefficients d_{ij}
$(Q/B)_i$; R_i; $(\%NA)_i$	Feeding rate IL_{ij}
$(Q/B)_i$; $(\%NA)_i$	Excretion rate of non assim. food K'_i
$(P/B)_i$	Growth rate G_i

[a] Parameters in the first column were used to determine the corresponding (same row) parameter in the second column. Indexes i and j refer to compartments

Table 4
Equation for the estimation of assimilation efficiency

Assimilation efficiency (Thomann and Connolly, 1992)		
$\log(E_c/E_o) =$	$-2.6+0.5\log K_{ow}$	$2 \le \log K_{ow} \le 4$
$E_c/E_o =$	-3.339 $+0.8976\log K_{ow}$	$4 \le \log K_{ow} \le 4.5$
$E_c/E_o =$	0.7	$4.5 \le \log K_{ow} \le 6.5$
$E_c/E_o =$	$3.3-0.4\log K_{ow}$	$6.5 \le \log K_{ow} \le 8$
$\log(E_c/E_o) =$	$7-\log K_{ow}$	$8 \le \log K_{ow} \le 9$

The main interest here is in how to collect and use information given by the Ecopath model in the toxic substance model; we are in fact aware that, owing to spatial discrepancy between the trophic network's data and toxicity data, diets may change, but the purpose of the present work was limited to underline methodological aspects, also due to the limited database available; therefore we assumed that diet coefficients remain the same in the two cases.

2.3.3. Feeding rate IL_{ij}

The organism's energy usage rate P_i can be computed (Connolly, 1991) as $P_i = \lambda_i * (G_i + r_i)$, where λ_i is the caloric density of the organism i. The energy intake rate is obtained dividing P_i by the assimilated part of the food a, and the feeding rate C_{ij} of organism i on prey j is

$$C_{ij} = \frac{\lambda_i^*(G_i + r_i)}{\lambda_j^* a} \quad \left[\frac{g_j}{g_i} d^{-1}\right] \tag{19}$$

where λ_j is the caloric density of the prey (parameter determined in the construction of the trophic network).

Connolly (1991) and Thomann et al. (1992) assume that the differences in caloric density are related to differences in the wet–dry ratio and that the caloric density of dry tissue is the same for all species. They also use caloric density as cal g^{-1} *wet* weight. With these assumptions, they substitute to the caloric density ratio, the wet–dry weight ratio to obtain a lipid-specific consumption rate given by:

$$IL_{ij} = \frac{f_{Lj}}{f_{Li}} \frac{awd_j}{awd_i} \frac{(G_i + r_i)}{a} \quad \left[\frac{g\,\mathrm{Lipid}_j}{g\,\mathrm{Lipid}_i} d^{-1}\right] \tag{20}$$

On the contrary, the present model is derived from a trophic network constructed using *different* conversion factors for caloric content of dry tissue for *different* species. Thus we refer to caloric densities that are species-specific and given as cal g^{-1} *dry* weight.

The lipid-specific consumption rate is then given by:

$$IL_{ij} = \frac{f_{Lj}}{f_{Li}} \frac{awd_j}{awd_i} \frac{\lambda_i}{\lambda_j} \frac{(G_i + r_i)}{a} \tag{21}$$

having the same units i.e. $[g\,\mathrm{Lipid}_j/g\,\mathrm{Lipid}_i d^{-1}]$.

Since the total energy intake of compartment i, i.e. $(G_i + r_i)/a$, is exactly the Ecopath parameter $(Q/B)_i$ we can substitute this parameter in the previous formula, so that the lipid specific feeding rate of organism i on prey j is:

$$IL_{ij} = \frac{f_{Lj}}{f_{Li}} \frac{awd_j}{awd_i} \frac{\lambda_i}{\lambda_j} (Q/B)_i (22) IL_{ij} = \frac{f_{Lj}}{f_{Li}} \frac{awd_j}{awd_i} \frac{\lambda_i}{\lambda_j} (Q/B)_i \tag{22}$$

Since *foc* is given as percentage of the dry weight, the feeding rate on sediment and suspended organic matter is given by:

$$IL_{ioc} = \frac{foc_{sed}}{f_{Li}\, awd_i} \frac{\lambda_i}{\lambda_{\mathrm{organicmatter}}} (Q/B)_i \tag{23a}$$

$$IL_{iocw} = \frac{foc_w}{f_{Li}\, awd_i} \frac{\lambda_i}{\lambda_{\mathrm{organicmatter}}} (Q/B)_i \tag{23b}$$

2.3.4. Excretion rate (metabolic losses)

The excretion rate of organisms in compartment i, K_i', refers to the non-assimilated part of the food intake. From Ecopath we obtain the percentage of food that is non-assimilated, $\%NA_i$, and the total intake, $(Q/B)_i$, thus K_i' is simply given by:

$$K_i' = (Q/B)_i^* \%NA_i \tag{24}$$

2.3.5. Growth rate G_i

Growth acts as a 'dilution' coefficient, because the mass of chemical will be normalised to a larger biomass (Chapra, 1997). The growth rate is

obtained considering the ratio between the new biomass produced in the period under consideration and the total biomass. This amount corresponds exactly to the net production–biomass ratio $(P/B)_i$ obtained from the trophic network, i.e.:

$$G_i = (P/B)_i \quad (25)$$

The trophic network model provides organism-specific parameters, such as metabolic rates, diet compositions and structural characteristics, ready to be used in the very ecosystem of the Lagoon of Venice. In the following, recent data on toxic substances measured in the Lagoon are presented. These sets of data allowed us to validate the method of coupling the two models presented above.

Table 5
List of substances considered with their main physico–chemical[a]

Substance-specific parameters			
Chemical	Parameter		
	Log K_{ow}		Mol. weight M
PCDD	Range	Adopted	
2,3,7,8-TetraCDD	5.38–8.48	7.15	322.0
1,2,3,7,8-PentaCDD	6.20–9.69	7.40	356.4
1,2,3,4,7,8-HexaCDD	6.85–9.53	7.80	391.0
1,2,3,6,7,8-HexaCDD	6.85–9.53	7.80	391.0
1,2,3,7,8,9-HexaCDD	6.85–9.53	7.80	391.0
1,2,3,4,6,7,8-HeptaCDD	7.92–10.32	8.20	425.2
1,2,3,4,6,7,8,9-OctaCDD	7.33–10.56	8.30	460.0
PCDF			
2,3,7,8-TetraCDF	5.6–6.73	6.40	306.0
1,2,3,7,8PentaCDF	6.19-6.92	6.70	340.4
2,3,4,7,8-PentaCDF	6.5–7.60	6.70	340.4
1,2,3,4,7,8-HexaCDF	7.2[b]–7.7	7.20	374.9
1,2,3,6,7,8-HexaCDF	7.2[b]	7.20	374.9
1,2,3,7,8,9HexaCDF	7.2[b]	7.20	374.9
2,3,4,6,7,8-HexaCDF	7.2[b]	7.20	374.9
1,2,3,4,6,7,8-HeptaCDF	7.92-8.10	8.00	409.3
1,2,3,4,7,8,9-HeptaCDF	6.90–7.92	8.00	409.3
1,2,3,4,6,7,8,9-OctaCDF	6.94–9.99	8.60	443.8

[a] Sources: Mackay et al. (1992) and Marcomini et al. (1997).
[b] Values estimated using ACD logP software.

2.4. Experimental data and parameters

Recent studies by Bonamin et al. (1997), Marcomini et al. (1997) and by the Magistrato alle Acque of Venice – Consorzio Venezia Nuova (M.A.V.-C.V.N., 1998) analysed the presence of polychlorinated dioxins and dibenzofurans in biota and in sediments of the Lagoon of Venice. Biota and sediment samples were collected at four sites, two in the Industrial Zone (Canale Industriale Nord: site 1 and Canale Industriale Sud: site 2) and two in the southern part of the Lagoon (Canale Poco Pesce: site 3 and Canale Fisolo: site 4). Organisms collected and used for comparison with modelled data were two species of bivalves, *Tapes philippinarum* (sites 1, 2 and 3) and *Mytilus edulis* (site 4), and one fish, *Scardinius eritrophtalamus* (sites 1 and 2).

Even if the model calculates concentrations for all the groups included in the trophic network, the following analysis and discussion of results will focus only on the groups, extracted from the trophic network-ecotoxicological model, that relates to these species. Bivalves such as those studied in this work (especially *T. philippinarum*) occupy a role of primary importance also in the economic, sanitary and social contest of the Lagoon of Venice.

The list of substances analysed, together with physico–chemical parameters such as K_{ow} and molecular weight, M, adopted in the model, is reported in Table 5. Main organism-specific and site-specific input parameters used in the toxic substance model are reported in Table 6.

Table 6
List of main parameters with the value adopted in the model

Organism-specific parameters			
Parameter	Value	Unit	Source
f_L% lipid Nekton det. feed.	2.5	g_lipid/gww	Bonamin et al. (1997)
f_L% lipid Nekton nekt. feed.	8	g_lipid/gww	Bush et al. (1989)
f_L% lipid Mboff.	1.25	g_lipid/gww	Bonamin et al. (1997)
f_L% lipid Zoopl.	2	g_lipid/gww	Wainman et al. (1994)
f_L% lipid Phytopl.	1.5	g_lipid/gww	Campfens and Mackay (1997)
awd% Nekton det. feed.	3.3	gww/gdw	Ecopath model
awd% Nekton nekt. feed.	2.5	gww/gdw	Ecopath model
awd% Mboff.	3.8	gww/gdw	Ecopath model
awd% Zoopl.	5	gww/gdw	Ecopath model
awd% Phytopl.	8.3	gww/gdw	Ecopath model
λ Nekton det. feed.	2.9	kcal/gdw	Ecopath model
λ Nekton nekt. feed.	1.4	kcal/gdw	Ecopath model
λ Mboff.	4.5	kcal/gdw	Ecopath model
λ Zoopl.	5.5	kcal/gdw	Ecopath model
λ Phytopl.	5	kcal/gdw	Ecopath model
(Q/B) Nekton det. feed.	0.018	d^{-1}	Ecopath model
(Q/B) Nekton nekt. feed.	0.012	d^{-1}	Ecopath model
(Q/B) Mboff.	0.083	d^{-1}	Ecopath model
(Q/B) Zoopl.	0.500	d^{-1}	Ecopath model
(P/B) Nekton det. feed.	0.004	d^{-1}	Ecopath model
(P/B) Nekton nekt. feed.	0.003	d^{-1}	Ecopath model
(P/B) Mboff.	0.017	d^{-1}	Ecopath model
(P/B) Zoopl.	0.100	d^{-1}	Ecopath model
(R/B) Nekton det. feed.	0.009	d^{-1}	Ecopath model
(R/B) Nekton nekt. feed.	0.007	d^{-1}	Ecopath model
(R/B) Mboff.	0.042	d^{-1}	Ecopath model
(R/B) Zoopl.	0.150	d^{-1}	Ecopath model
%NA Nekton det. feed.	0.30	%	Ecopath model
%NA Nekton nekt. feed.	0.20	%	Ecopath model
%NA Mboff.	0.30	%	Ecopath model
%NA Zoopl.	0.50	%	Ecopath model

Site specific parameters			
Parameter	Value	Unit	Source
Φ	0.4		Sfriso et al. (1990)
ρ	1.2×10^6	g/m^3	Sfriso et al. (1990)
foc_{sed}	0.01–0.08	gC/g	Consorzio Venezia Nuova (1992),
foc_{wat}	0.05	gC/g	M.A.V.-C.V.N. (1995); Sfriso and Marcomini (1998)
M	40	g/m^3	Sfriso and Marcomini (1997)

3. Results and discussion

3.1. Coupling two models

In a recent study Carrer and Opitz (1999), analysed the exchange of matter and energy between biotic and abiotic components of a shallow water area situated in the Northern part of the Lagoon of Venice. This study showed the possibility to gather a coherent picture of the ecosystem by means of a trophic network model, produced with the help of the software Ecopath 3.0 (Chris-

tensen & Pauly, 1992a,b, 1993). With this model, it was possible to give a first quantification of flows of energy in the ecosystem as well as to gain information on organisms' structural and metabolic characteristics and feeding preferences. The information produced seems consistent with that contained in other studies carried on in the Lagoon (Sorokin et al., 1996).

These results were then used to analyse the transfer of toxic substances stored in the sediments to edible organisms in the same ecosystem.

A slightly simplified version (compared with Carrer and Opitz, 1999) of the energy model (Fig. 2) was produced, cutting out groups not interfering with main processes (e.g. birds) or combining groups to render the application of the toxic substance model more simple (phytoplankton and bacterioplankton were aggregated in one group of planktonic micro-organisms).

The output parameters reported in Tables 1 and 2 were used as input to an existing toxic substance bioaccumulation model, mainly derived by Thomann (1989) and Thomann et al. (1992).

Some of the structure-related parameters inherited from the trophic network model (e.g. a_{wd} and λ for each species) were directly placed in the equations of the toxicological model (e.g. (12) and (21)). Other Ecopath output parameters (e.g. R_i, $(Q/B)_i$, $(P/B)_i$ etc.) were used to derive other species –specific input to the toxicological model, as shown in Table 3.

Solving a bioaccumulation equation (like (12)) for each of the groups considered in the model in Fig. 2, concentration of all chemicals for all species were estimated. A major effort was done on modelling the concentrations of chemicals in the bivalve *T. philippinarum*, not only because the experimental data made it possible to validate the model (40 out of 55 chemical analysis were made on *T. philippinarum*) but also because of the commercial and sanitary importance of this species. In the original Ecopath model, this organism was included in the group of macro-benthos omnivorous filter feeders (Moff, see Table 1 for abbreviations), therefore it inherits the parameters and rates of this group.

M. edulis and *S. eritrophtalamus* were not present in the database used to build the Ecopath model. *S. eritrophtalamus* is a fish most likely found in fresh water and then only in restricted internal areas of the Lagoon, nevertheless measured data on *S. eritrophtalamus* were the only measured data on fish species that could be used for a comparison with modelled concentrations in fish species previously included in the network model.

Comparisons between measured data and modelled values for *M. edulis* and *S. eritrophtalamus* were possible only introducing some assumptions: since *M. edulis* was not included in the trophic network, metabolic rates and diet composition where not immediately available for this application. An estimation of the possible concentration in *M. edulis* was thus obtained by changing some characteristics of filter feeding group. It was assumed that metabolic rates were the same for *T. philippinarum* and *M. edulis*, such that it was possible to use the information stored in the trophic network. Since the mussel is not laying in the sediment but is more likely found in the water column, it will be in contact with the chemical concentration in the water column ($b_{sed} = 0$ and $b_w = 1$ in Eq. (13)) whereas the clam is bioconcentrating chemical at the concentration in interstitial water ($b_{sed} = 1$ and $b_w = 0$). In addition to that, a shift in diet composition was also considered, since *M. edulis* is feeding more (the percentage was raised to 40%) on suspended organic matter (concentration $= cp_w$) than on sediment (resuspended) organic matter (concentration $= c_{sed\_oc}$, the percentage of feeding on this item was reduced to 10%)

Estimations of toxic concentrations in fish species are more difficult to compare with measured data for *S. eritrophtalamus*, since it is not sufficient to adjust some parameters of fish species in the trophic network and adapt them to *S. eritrophtalamus*. In this case differences in the typical environment of the species could be too important to be not taken into account. Nevertheless, since *S. eritrophtalamus* is mainly a detritivorous fish, a comparison between modelled values for Nekton detritivorous group (Nd, see Table 1) and measured data for *S. eritrophtalamus* was conducted, with the purpose of having a first glance of toxic levels that could be expected in fish species.

With the limits imposed by a restricted information on many site specific parameters and dynamic transport processes, an attempt to validate the model with existing data on toxic substances in sediment and organisms was made; the performance of the model are described in the following.

3.2. Sensitivity analysis

The sensitivity analysis was conducted emphasising the difference between the type of parameters (chemical-, organism- or site-specific) not only for the groups already mentioned (Moff, characterised as either clams or mussels, and Nd) but also for groups that could be interesting to study in the near future, such as the apex nektonic predators (Ncnf), which includes many valuable species possibly found in the Lagoon of Venice, such as *Morone labrax*. The sensitivity of parameters of species at the base of trophic chains, such as phytoplankton and zooplankton was also tested. Sensitivity of parameter p is determined with the formula $(\Delta x/x)/(\Delta p/p)$, where x is the state variable under consideration (Jørgensen, 1994).

Results of sensitivity analysis indicate that the logarithm of the octanol–water partition coefficient K_{ow} is the most sensitive parameter. In Fig. 4 the 10% sensitivity analysis for $\log K_{ow}$ of five dioxins is plotted. Due to the non-linearity inherent in this parameter the sensitivity is very asymmetric, being much larger when the perturbation is a decrement of the parameter. Sensitivity in-

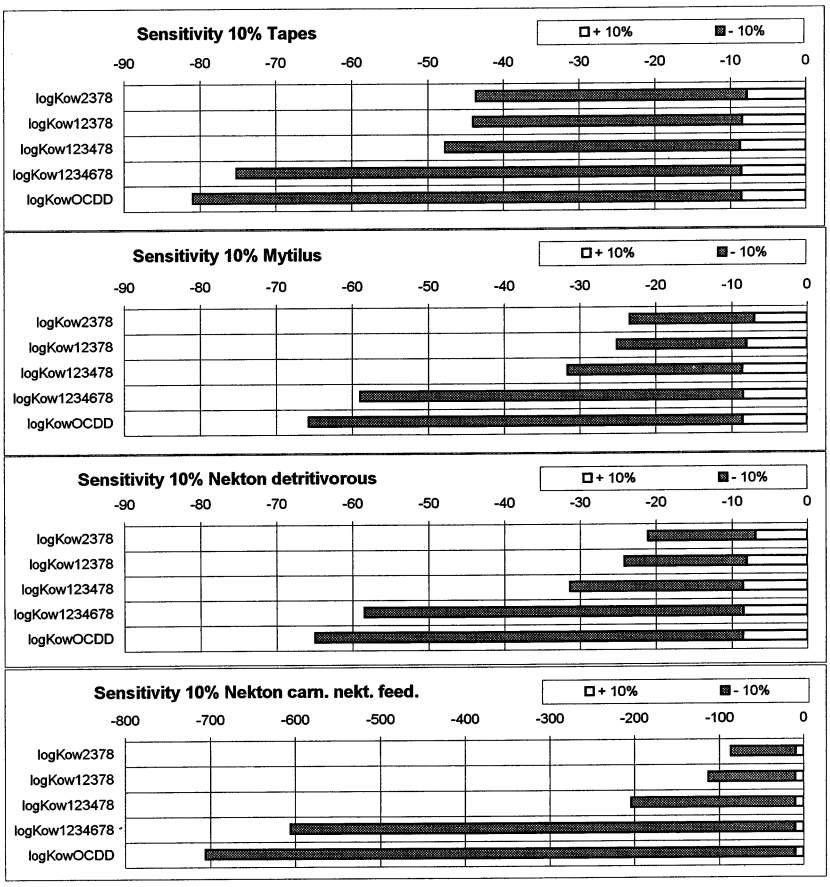

Fig. 4. Sensitivity analysis for $\log K_{ow}$ of five dioxins in different compartments.

Table 7
Sensitivity analysis for Mboff characterised as clams or mussels

T. philippinarum

Parameters	+10%	Parameters	−10%	Parameters	+30%	Parameters	−30%
fL Mboff	−0.942	awd Mboff	−1.111	fL Mboff	−0.777	awd Mboff	−1.429
awd Mboff	−0.909	fL Mboff	−1.062	awd Mboff	−0.769	fL Mboff	−1.402
%NA Mboff	−0.566	%NA Mboff	−0.638	λ Mboff	0.564	%NA Mboff	−0.732
λ Mboff	0.564	λ Mboff	0.564	%NA Mboff	−0.508	Koc-2378	−0.651
(P/B) Mboff	−0.465	Koc−2378	−0.508	BCF Mboff	0.437	focsed-site 1	−0.623
(R/B) Mboff	0.455	(R/B) Mboff	0.488	(R/B) Mboff	0.431	λ Mboff	0.564
BCF Mboff	0.437	focsed-site 1	−0.485	(P/B) Mboff	−0.385	focwat-site 4	−0.545
Koc-2378	−0.415	BCF Mboff	0.436	Koc-2378	−0.350	(R/B) Mboff	0.442
focsed-site 1	−0.397	focwat-site 4	−0.424	focsed-site 1	−0.336	BCF Mboff	0.436
focwat-site 4	−0.347	(P/B) Mboff	−0.339	focwat-site 4	−0.294	(P/B) Mboff	−0.431
focsed-site 3	−0.186	focsed-site 3	−0.228	focsed-site 3	−0.158	focsed-site 3	−0.293
focsed-site 4	−0.080	focsed-site 4	−0.098	focsed-site 4	−0.068	focsed-site 4	−0.126
(Q/B) Mboff	−0.035	(Q/B) Mboff	−0.039	(Q/B) Mboff	−0.030	(Q/B) Mboff	−0.045
BCF Phytopl	0.019	λ Phytopl	−0.022	BCF Phytopl	0.020	λ Phytopl	−0.028
λ Phytopl	−0.018	focwat-site 1	−0.021	λ Phytopl	−0.015	focwat-site 1	−0.027
focwat-site 1	−0.017	BCF Phytopl	0.019	focwat-site 1	−0.015	BCF Phytopl	0.020
mwat-site 4	0.001	mwat-site 4	0.001	mwat-site 4	0.001	mwat-site 4	0.002
mwat-site 1	0.001	mwat-site 1	0.001	v settl.	0.001	v settl.	0.001
v settl.	0.001	v settl.	0.001	mwat-site 1	0.001	mwat-site 1	0.001
M. edulis							
Parameters	+10	Parameters	−10	Parameters	+30	Parameters	−30
fL Mboff	−0.942	awd Mboff	−1.111	λ Mboff	0.866	awd Mboff	−1.429
awd Mboff	−0.909	fL Mboff	−1.062	fL Mboff	−0.777	fL Mboff	−1.402
λ Mboff	0.866	focwat-site 4	−0.922	awd Mboff	−0.769	focwat-site 4	−1.184
focwat-site 4	−0.755	λ Mboff	0.866	focwat−site 4	−0.639	λ Mboff	0.866
%NA Mboff	−0.566	%NA Mboff	−0.638	%NA Mboff	−0.508	%NA Mboff	−0.732
(P/B) Mboff	−0.465	(P/B) Mboff	−0.339	(P/B) Mboff	−0.385	(P/B) Mboff	−0.431
(Q/B) Mboff	0.261	(Q/B) Mboff	0.283	(Q/B) Mboff	0.223	(Q/B) Mboff	0.330
Koc-2378	−0.147	Koc-2378	−0.180	(R/B) Mboff	0.132	Koc-2378	−0.231
focwat-site 1	−0.147	focwat-site 1	−0.179	Koc-2378	−0.124	focwat-site 1	−0.230
(R/B) Mboff	0.139	(R/B) Mboff	0.150	focwat-site 1	−0.124	(R/B) Mboff	0.136
BCF Phytopl	0.030	λ Phytopl	-0.034	BCF Phytopl	0.030	λ Phytopl	−0.043
λ Phytopl	−0.028	BCF Phytopl	0.030	λ Phytopl	−0.023	BCF Phytopl	0.030
mwat-site 4	0.002	mwat-site 4	0.003	mwat-site 4	0.002	mwat-site 4	0.004
mwat-site 1	0.002	mwat-site 1	0.003	v settl.	0.002	v settl.	0.004
v settl.	0.002	v settl.	0.003	mwat-site 1	0.002	mwat-site 1	0.004
v diff. (TCDF)	0.001	v diff. (TCDF)	0.001	v diff. (TCDF)	0.001	v diff. (TCDF)	0.001

creases for more lipophilic compounds and reaches very high levels for organisms in higher trophic levels such as the organism belonging to the nektonic carnivorous nekton feeders group (Ncnf).

The calibration process was then conducted mainly through this parameter. Most often a slight overestimation was maintained with the aim of keeping more safe margins. Adopted values (see Table 5) are very close to those proposed by Mackay et al. (1992).

Tables 7 and 8 report results of sensitivity analysis, with 10 and 30% perturbations for all other parameters. For each species considered in the calibration process, parameters were ordered with a decreasing sensitivity; only values ≥ 0.001 are displayed. Where not explicitly stated, values refer to the case of 2378-TCDD.

Table 8
Sensitivity analysis for Nd and Ncnf

Nekton detritivorous

Parameters	+10%	Parameters	−10%	Parameters	+30%	Parameters	−30%
fL Nd	−0.909	fL Nd	−1.111	λ Nd	0.880	fL Nd	−1.429
awd Nd	−0.909	awd Nd	−1.111	fL Nd	−0.769	awd Nd	−1.429
λ Nd	0.880	λ Nd	0.880	awd Nd	−0.769	λ Nd	0.880
%NA Nd	−0.566	%NA Nd	−0.638	%NA Nd	−0.508	%NA Nd	−0.732
(P/B) Nd	−0.426	(P/B) Nd	−0.465	(P/B) Nd	−0.363	(P/B) Nd	−0.464
(Q/B) Nd	0.291	(Q/B) Nd	0.333	(Q/B) Nd	0.222	(Q/B) Nd	0.311
(R/B) Nd	0.134	Koc-2378	−0.138	(R/B) Nd	0.134	Koc-2378	−0.177
BCF Nd	0.121	focwat-site 1	−0.138	BCF Nd	0.121	focwat-site 1	−0.177
Koc-2378	−0.113	focwat-site 4	−0.138	Koc-2378	−0.095	focwat-site 4	−0.177
focwat-site 1	−0.113	(R/B) Nd	0.133	focwat-site 1	−0.095	(R/B) Nd	0.134
focwat-site 4	−0.113	BCF Nd	0.120	focwat-site 4	−0.095	BCF Nd	0.120
%NA zoopl.	−0.003	%NA zoopl.	−0.003	(R/B) zoopl	0.002	%NA zoopl.	−0.004
BCF zoopl	0.002	λ Zoopl	−0.003	BCF zoopl	0.002	λ Zoopl	−0.003
(R/B) zoopl	0.002	BCF zoopl	0.002	%NA zoopl.	−0.002	(R/B) zoopl	0.002
λ Zoopl	−0.002	(R/B) zoopl	0.002	λ Zoopl	−0.002	BCF zoopl	0.002
BCF Phytopl	0.002	λ Phytopl	−0.002	BCF Phytopl	0.002	λ Phytopl	−0.002
λ Phytopl	−0.001	BCF Phytopl	0.002	λ Phytopl	−0.001	(Q/B) Zoopl.	−0.002
(Q/B) Zoopl.	−0.001	(Q/B) Zoopl.	−0.001	(Q/B) Zoopl.	−0.001	BCF Phytopl	0.002
(P/B) zoopl	−0.001	(P/B) zoopl	−0.001	(P/B) zoopl	−0.001	(P/B) zoopl	−0.001
Nekton ncnf							
Parameters	+10	Parameters	−10	Parameters	+30	Parameters	−30
fL Ncnf	−0.909	awd Ncnf	−1.111	fL Ncnf	−0.769	fL Ncnf	−1.429
awd Ncnf	−0.909	fL Ncnf	−1.111	awd Ncnf	−0.769	awd Ncnf	−1.429
λ Ncnf	0.699	λ Ncnf	0.699	λ Ncnf	0.699	Koc-2378	−0.837
(P/B) Ncnf	−0.633	Koc-2378	−0.655	(P/B) Ncnf	−0.482	focwat-site 4	−0.795
Koc-2378	−0.535	focwat-site 4	−0.619	Koc-2378	−0.451	λ Ncnf	0.699
focwat-site 4	−0.507	%NA Ncnf	−0.526	%NA Ncnf	−0.435	focwat-site 1	−0.661
%NA Ncnf	−0.476	focwat-site 1	−0.514	focwat-site 4	−0.429	%NA Ncnf	−0.588
focwat-site 1	−0.421	(P/B) Ncnf	−0.350	focwat-site 1	−0.357	(P/B) Ncnf	−0.521
(R/B) Ncnf	0.305	BCF Ncnf	0.304	(R/B) Ncnf	0.304	(R/B) Ncnf	0.302
BCF Ncnf	0.302	(R/B) Ncnf	0.301	BCF Ncnf	0.300	BCF Ncnf	0.301
(Q/B) Ncnf	0.252	(Q/B) Ncnf	0.228	(Q/B) Ncnf	0.172	(Q/B) Ncnf	0.208
focsed-site 1	−0.112	focsed-site 1	−0.137	focsed-site 1	-0.095	focsed-site 1	−0.176
%NA Mboff	−0.093	%NA Mboff	−0.105	%NA Mboff	−0.084	%NA Mboff	−0.121
(P/B) Mboff	−0.077	%NA Nd	−0.084	BCF Mboff	0.072	λ Mboff	−0.103
(R/B) Mboff	0.075	(R/B) Mboff	0.080	(R/B) Mboff	0.071	%NA Nd	−0.096
%NA Nd	−0.075	λ Mboff	−0.080	%NA Nd	−0.067	(R/B) Mboff	0.073
BCF Mboff	0.072	BCF Mboff	0.072	(P/B) Mboff	−0.063	BCF Mboff	0.072
λ Mboff	−0.065	(P/B) Nd	−0.061	λ Mboff	−0.055	(P/B) Mboff	−0.071
(P/B) Nd	−0.056	(P/B) Mboff	−0.056	(P/B) Nd	−0.048	focsed-site 3	−0.064
focsed-site 3	−0.041	focsed-site 3	−0.050	focsed-site 3	−0.035	(P/B) Nd	−0.061
(Q/B) Nd	0.038	(Q/B) Nd	0.044	(Q/B) Nd	0.029	(Q/B) Nd	0.041
(R/B) Nd	0.018	focsed-site 4	−0.019	(R/B) Nd	0.018	focsed-site 4	−0.025
BCF Nd	0.016	λ Nd	−0.018	BCF Nd	0.016	λ Nd	−0.023
focsed-site 4	-0.016	(R/B) Nd	0.018	focsed-site 4	-0.013	(R/B) Nd	0.018
λ Nd	−0.014	BCF Nd	0.016	λ Nd	−0.012	BCF Nd	0.016
BCF Phytopl	0.007	λ Phytopl	−0.008	BCF Phytopl	0.007	λ Phytopl	−0.010
λ Phytopl	−0.006	%NA zoopl.	−0.007	(R/B) zoopl	0.005	%NA zoopl.	−0.008
%NA zoopl.	−0.006	BCF Phytopl	0.007	BCF zoopl	0.005	λ Zoopl	−0.008
(Q/B) Mboff	−0.006	(Q/B) Mboff	−0.006	%NA zoopl.	−0.005	(Q/B) Mboff	−0.007
BCF zoopl	0.006	λ Zoopl	−0.006	λ Phytopl	−0.005	BCF Phytopl	0.007
(R/B) zoopl	0.005	BCF zoopl	0.006	(Q/B) Mboff	−0.005	(R/B) zoopl	0.005
λ Zoopl	−0.005	(R/B) zoopl	0.005	λ Zoopl	−0.004	BCF zoopl	0.005
(Q/B) Zoopl.	−0.003	(Q/B) Zoopl.	−0.003	(Q/B) Zoopl.	−0.002	(Q/B) Zoopl.	−0.004
(P/B) zoopl	−0.002	(P/B) zoopl	−0.003	(P/B) zoopl	−0.002	(P/B) zoopl	−0.003
mwat − site 4	0.002	mwat-site 4	0.002			mwat-site 4	0.003

Among the other chemical-specific parameters, K_{oc} is the most important (being strictly correlated with K_{ow}) with sensitivity responses that reaches 0.65 and 0.84 for 10 and 30% variations, respectively.

Lipid fraction f_L, wet–dry ratio a_{wd} and caloric content λ are the most important organism-specific parameters, sensitivity values reach 1.11 and 1.43 with a 10 and 30% perturbation, respectively. Of course the sensitivity is relevant when the variation in the concentration and the perturbation of the parameter refer to the same organism (or group); in this application the sensitivity of a predator to a variation in the lipid fraction of its prey never reaches 0.001.

In the database used in this study, measures of f_L taken concomitantly with measures of toxicant concentrations in organism are available, the uncertainty on this important parameter is therefore quite small. Wet–dry ratio and caloric content are parameters inherited as knowledge-base from the construction of the trophic network model.

The other organism-specific parameters such as metabolic rates are less sensitive, reaching 0.64 and 0.73 for 10 and 30% perturbations, respectively; in almost all cases, the most sensitive of the metabolic parameter is the percentage of food that is not assimilated ($\%NA$), followed by P/B and R/B. This limited sensitivity is important because it widens the applicability of the trophic network model as a knowledge-base for the construction of ecotoxicological models.

Site-specific parameters such as foc_{sed} (max values: 0.49 and 0.62 for $\Delta 10$ and $\Delta 30\%$) and foc_{wat} (0.92 and 1.18) show an intermediate level of sensibility, emphasising the importance of a global monitoring of the environment. The sensitivity of the model on foc_{sed} increases with the decrease of the absolute value of the parameter; suggesting that particular attention should be devoted to this parameter in sites poor of organic matter. Highest values of sensitivity on foc_{sed} are reached for *T. philippinarum*, whereas foc_{wat} is particularly important for *M. edulis* and fish species.

Suspended solids, m, sediment density, ρ, and porosity, ϕ, velocities of processes, such as settling, v_s, resuspension, v_r and diffusion, v_d, seem to be not sensitive parameters (all values below 0.01). This result may be affected by the simplifying hypothesis on the mass balance for solids, therefore reliable conclusions on this set of parameters could be drawn when some more information on solids budget and distribution will be available.

Settling velocity, sediment density and porosity and suspended solids data used in this work, were sampled concomitantly only in one site and these values were then extended to all sites. A map of organic carbon fractions in the sediment (foc_{sed}) was obtained from a qualitative map furnished by Consorzio Venezia Nuova (1992).

To test sensibility of parameters determined in the ecotoxicological model, the bioconcentration factor, *BCF*, was chosen. For consumers groups, it is obtained from the ratio $k_u/(K+G)$, which incorporates many other parameters. Results indicate that the sensibility of this parameter is similar to that of metabolic parameters obtained from the trophic network.

A sensitivity analysis on diet composition was not conducted systematically, but by comparing results obtained for *T. philippinarum* and *M. edulis* a stronger influence of dissolved concentration (and then of BCF) in respect to concentration in the particulate matter (and then of diet) was noticed. The percentage of chemical coming from water sums up to about 40% for *T. philippinarum*, compared with a 15% for *M. edulis*.

3.3. Comparison output of the model with experimental data

Comparison between modelled concentrations and measured data for *T. philippinarum* is shown in Figs. 5 and 6 for almost all compounds (not all congeners have been shown for furans). In most cases the modelled values were around the same order of magnitude as the measured ones (e.g. Fig. 5: 2378-TCDD, the most toxic among the investigated compounds, is estimated as 22.6 and 0.6 pg g^{-1} lipid, compared with measured data analysed to 9.5 and 0.3 pg g^{-1} lipid, in site 1 and 3, respectively).

The figures also show (white part of the bars) the relative contribution of uptake from water

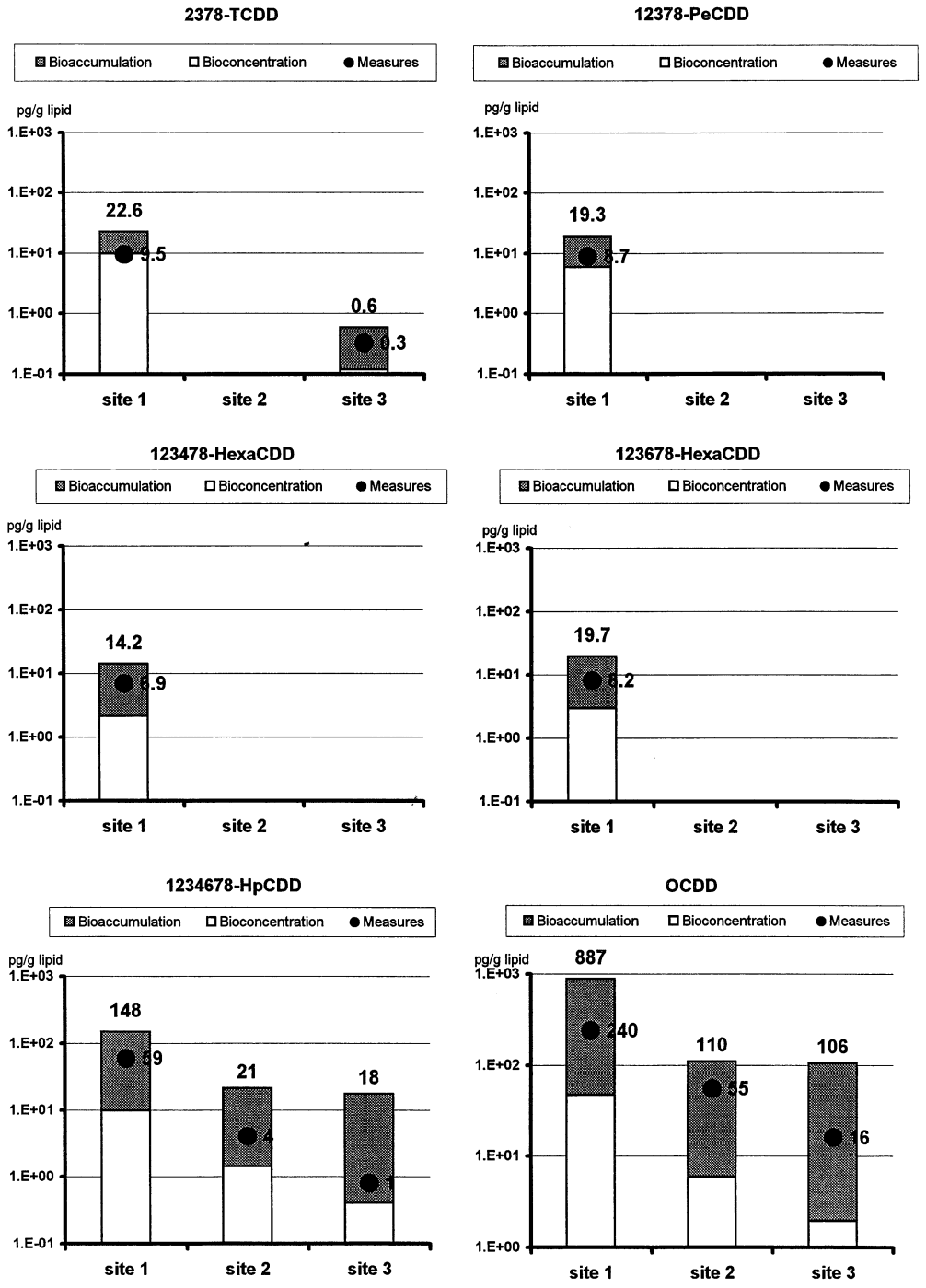

Fig. 5. Comparison between modelled (bars) and measured (points) data on dioxins concentrations in *T. philippinarum*. The white part of the bars indicates the estimate of the uptake from water (bioconcentration).

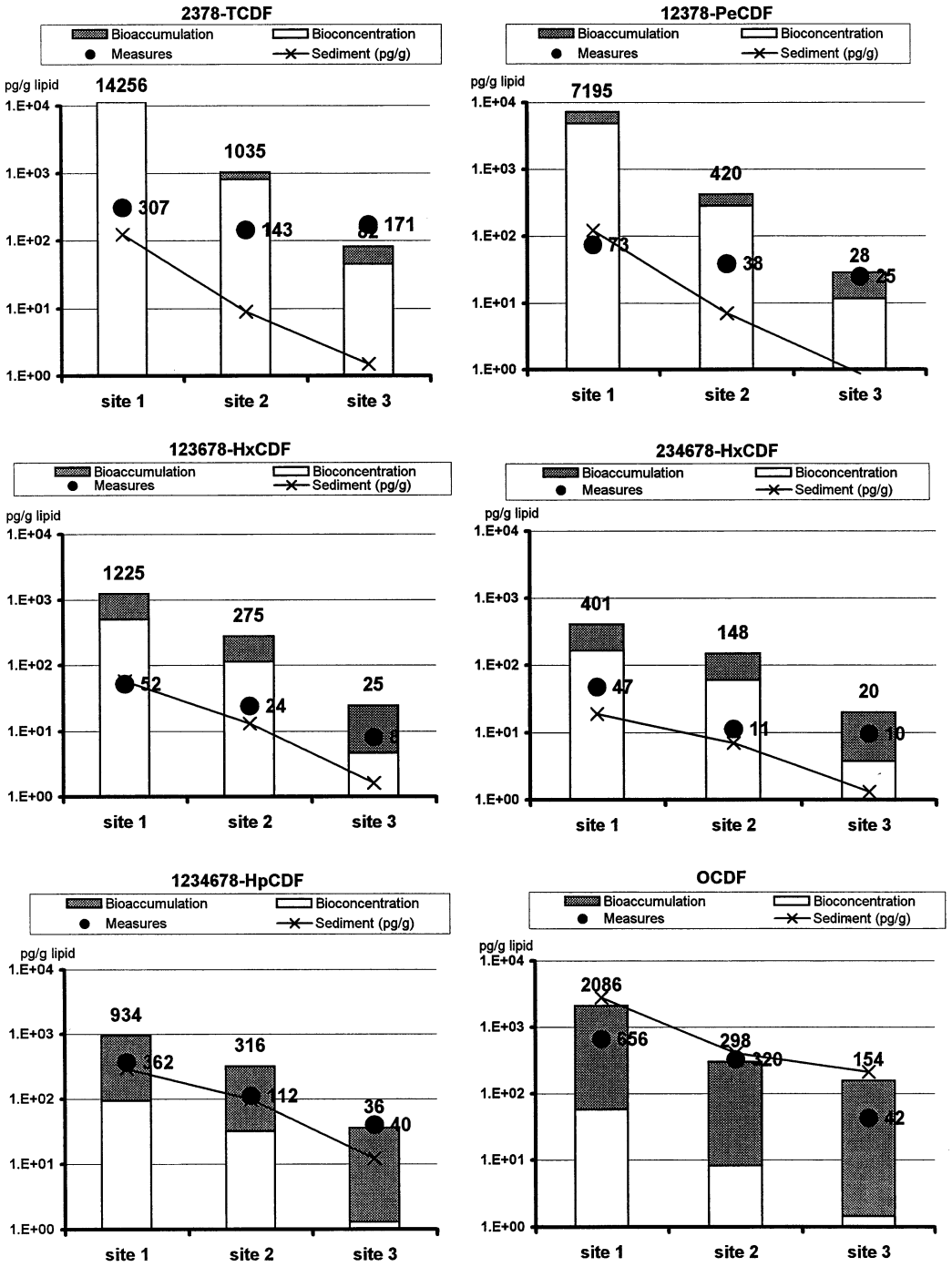

Fig. 6. Comparison between modelled (bars) and measured (points) data on furans concentrations in *T. philippinarum*. Here, the concentrations of toxic substances in the sediment are also shown (cross symbols).

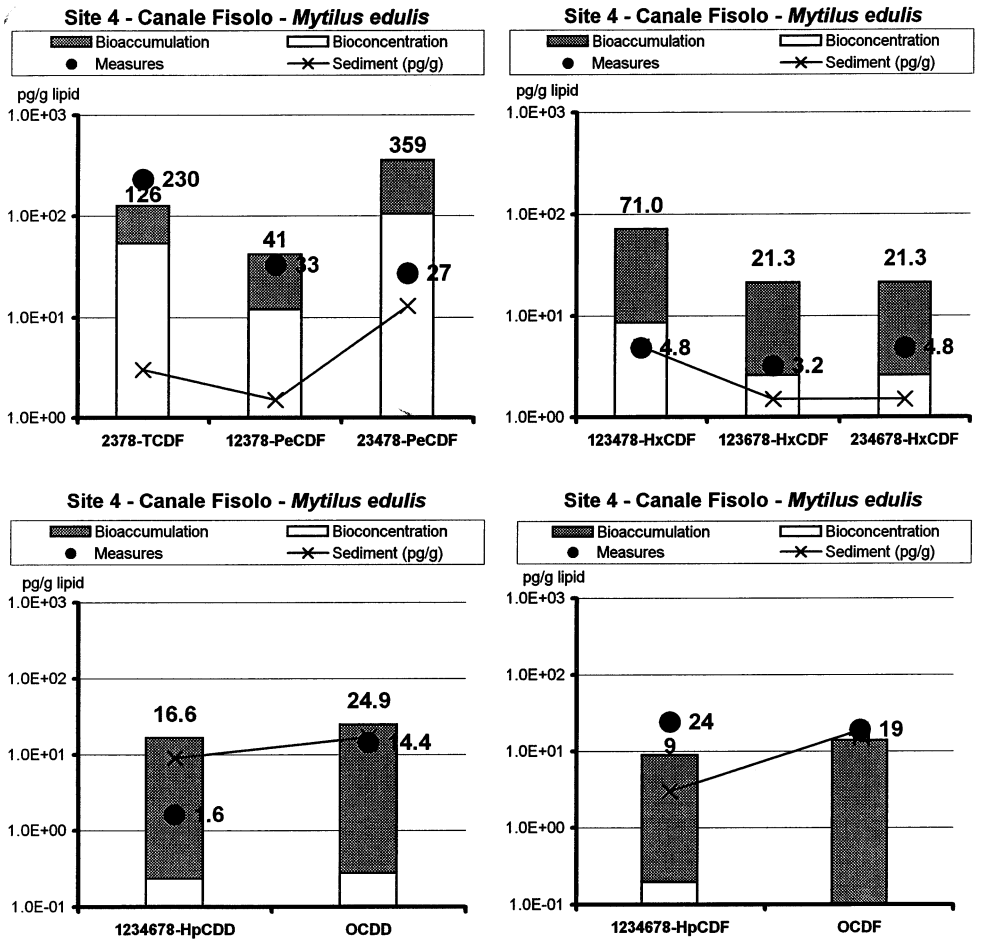

Fig. 7. Comparison between modelled (bars) and measured (points) data for *M. edulis*.

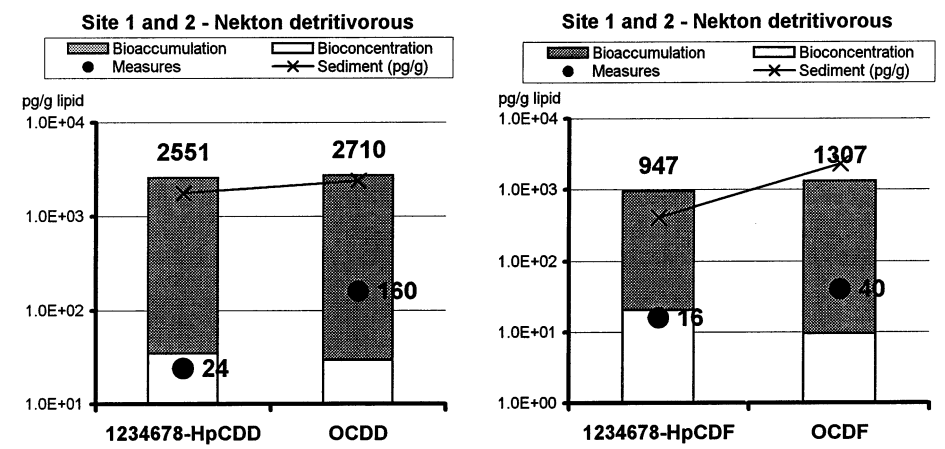

Fig. 8. Comparison between modelled (bars) values for Nekton detritivorous fish species and measured (points) data for *S. eritrophtalamus*.

(bioconcentration) to the total bioaccumulation in organisms (that comprehends the accumulation via food chain). Apart from organism-specific characteristics, two main factors affects the percentage of uptake from water by an organism: the lipophilicity of the compound and the fraction of organic carbon in the sediment.

For superlipophilic compounds, the contribution of bioconcentration to total bioaccumulation is lower, since such compounds tend to remain bounded to the sediment and are hardly dissolved in the water phase. Similarly, an increase of organic carbon fraction in the sediment diminishes the dissolved quantity of all compounds.

Following the bioconcentration contribution (height of white bars) in all graphics in Figs. 5 and 6, it may be noticed that it diminishes for more lipophilic compounds and in sites more rich in organic carbon (site 3: $foc_{sed} = 0.3$, compared with sites 1 and 2: $foc_{sed} = 0.1$), confirming that the model is able to mimic expected behaviours.

Main differences between modelled and measured values occur for tetra- and penta-furans in sites (1 and 2) that are characterised by low values of foc_{sed}. (Fig. 6 2378-TCDF estimated to 14256 and 1035 pg g^{-1} lipid, respectively; measured to 307 and 143 pg g^{-1} lipid, respectively; Fig. 6 Fig. 12378-PeCDF estimated to 7195 and 420 pg g^{-1} lipid; measured to 73 and 28 pg g^{-1} lipid). In such sites and for these two chemicals the patterns of concentrations in organisms are not following the patterns of concentrations in the sediment, whereas this happens for all other chemicals. This may be seen, for example, with 2378-TCDF, where concentrations in the sediments vary between two order of magnitude (1.5–124 pg g^{-1}), whereas concentrations in organism varies between 143 and 307 pg g^{-1} lipid. The reason of the discrepancies of the model could than be due to the fact that for less lipophilic compounds (these two compounds are those with lowest adopted values of K_{ow}), present with higher concentrations in the water body, a removal or wash-out term should be taken into account.

The results of the model simulating concentrations in *M. edulis* (Fig. 7) are still in good accordance with measured values, notwithstanding their small number (12 values). Samples refer to site 4, where $foc_{sed} = 0.8$ was estimated, and this justify the low contribution of bioconcentration to total bioaccumulation, underlining at the same time the importance of the accumulation via food and then of the trophic network. Again, for less lipophilic compounds such as tetra- and penta-furans, it is noticed a smaller influence of sediment concentrations on organisms' ones, if compared with other substances.

The results of simulation of concentrations for fish species are plotted in Fig. 8. The comparison with measured data for the fish *S. eritrophtalamus* denotes that a general overestimation of the toxic concentration (also of almost two order of magnitude) is found for all compounds. These may be due to the impossibility to extend to this fish species the parameters found for the other species included in the trophic network, but until a more extended database for the calibration and validation of the model of fish species will not be available, it is difficult to reach a conclusion about the quality of model results.

4. Conclusions

Main result of this study was the construction of a bridge between two types of model, that could be hopefully used to combine existing biological studies on ecosystems with future or other existing toxicological studies. The process of bioaccumulation of a toxic substance in animal tissues is strongly influenced by the ingestion of contaminated food, i.e. by processes of consumption and recycling of matter occurring in the ecosystem. For this reason, empirical equations for the determination of consumption exclusively based on organisms' dimensions are not useful to estimate 'true' contamination levels. The metabolic rates of consumption, respiration, growth and decay utilised to estimate the transfer of chemicals in a food web must take

into account the effects of the interactions between different organisms in the system, as well as the recycling of matter and the associated indirect effects. A trophic network model implicitly includes all these features, and the metabolic parameters contained in the model resume their effect. This is the value added provided by the use of the tropic network model and incorporated in the new 'coupled model' described in this paper.

Results of sensitivity analysis and calibration with data on dioxins and dibenzofurans in the Lagoon of Venice gave hints for future experimental campaigns on the Lagoon, and showed the possibility to assess the toxic levels of edible organisms such as *T. philippinarum* and *M. edulis*. Model results are in good agreement with measured data for bivalves, whereas more monitoring efforts are needed to validate the model for fish species.

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Appendix A. Equations for the calculation of velocities and dissolved fractions

v_d is given by the empirically derived formula (Di Toro et al., 1981 as quoted in Chapra, 1997):

$$v_d = 69.35 * \Phi * M^{-2/3} \quad \text{(A1)}$$

where M = molecular weight of the compound

v_s was given a value of 1222 m year^{-1}, experimentally obtained for a site in the Lagoon of Venice (ri-elaborated from Sfriso and Marcomini, 1997). This value is higher than the typical value of 912.5 m year^{-1} suggested for organic and clay particles (O'Connor, 1988).

The resuspension velocity v_r is obtained from a mass balance equation for the solids (Chapra, 1997) that, at steady state, gives:

$$v_r = v_s * m/(1 - \Phi) * \rho - v_b \quad \text{(A2)}$$

where m, suspended solids concentration (g m^{-3}) and v_b, burial velocity (considered to be zero in this application).

The dissolved fraction in the sediment is given by the formula

$$F_{dsed} = 1/(\Phi + K_{dsed} * (1 - \Phi) * \rho) \quad \text{(A3)}$$

The dissolved fraction in the water is simply given by

$$F_{dw} = 1/(1 + K_{dw} * m) \quad \text{(A4)}$$

where $K_{dw} = K_{oc} * foc_w$, (m^3 g^{-1}), is the partition coefficient between water and suspended matter, function of foc_w, the fraction of organic carbon present in the suspended matter.

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