Environmental Toxicology and Chemistry, Vol. 27, No. 5, pp. 1217–1225, 2008

Printed in the USA
0730-7268/08 $12.00 + .00

Hazard/Risk Assessment

SPATIALLY DISTRIBUTED ECOLOGICAL RISK FOR FISH OF A COASTAL FOOD WEB EXPOSED TO DIOXINS

CHRISTIAN MICHELETTI,† TOMAS LOVATO,‡ ANDREA CRITTO,† ROBERTO PASTRES,‡ and ANTONIO MARCOMINI*†
†University Cà Foscari of Venice, Department of Environmental Sciences, Calle Larga S. Marta 2137, 30123, Venezia, Italy
‡University Cà Foscari of Venice, Department of Physical Chemistry, Calle Larga S. Marta 2137, 30123, Venezia, Italy

(*Received* 27 *February* 2007; *Accepted* 4 *October* 2007)

Abstract—The ecological risk posed by 2,3,7,8-polychlorodibenzo-*p*-dioxins and furans (PCDD/Fs) and dioxin-like polychlorobiphenyl (PCB) congeners to five edible fish species of the aquatic food web of Venice Lagoon, Italy, was estimated by applying a state-of-the-art kinetic bioaccumulation model. Site-specific data were used to define a representative food web. The experimental data set for model validation and application included PCB and PCDD/F congener concentrations in sediments, in water, and in five organisms (both invertebrates and fish). The spatial distribution of risk was evaluated by dividing the lagoon into six homogeneous areas, and for each area, sediment, water, and organism dioxins concentrations were calculated. The bioaccumulation model was calibrated for both nonmetabolizing and metabolizing congeners, the metabolic elimination rates of which were estimated. The model validation showed an acceptable bioaccumulation estimation, evaluated using the model bias parameter. The calibrated model was applied to the six areas of the lagoon to estimate the fish predicted exposure concentration as 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxicity equivalents from sediment concentration. Internal no-effect concentrations were calculated for each fish species from literature data. Risk was estimated by applying the hazard quotient (HQ) approach, obtaining the ecological risk for each fish species on the basis of 90 and 99% protection levels, in each of the six lagoon areas. The sediment dioxins concentration does not pose a significant risk to the selected fish species at the 90% protection target ($HQ < 1$), whereas risk is significant ($HQ > 1$) at the 99% protection target. Risk results were higher near the Porto Marghera industrial district, Italy, and in lagoon zones characterized by a low water-exchange rate and freshwater basin inputs.

Keywords—Ecological risk assessment Polychlorobiphenyls Polychlorodibenzo-*p*-dioxin/furans Bioaccumulation model Internal no-effect concentration

INTRODUCTION

Polychlorodibenzo-*p*-dioxins and furans (PCDD/Fs) and polychlorobiphenyls (PCBs) are anthropogenic, persistent organic pollutants that are amenable to bioaccumulation in the tissues of living organisms. Moreover, PCDD/Fs and PCBs can biomagnify through the food web [1], raising the issue of adverse effects to aquatic organisms at higher levels of the food web [2], such as fish. Ecological risk assessment (ERA) [3] can be applied to predict the potential adverse effects of bioaccumulated pollutants to organisms by comparing the exposure concentration to an effect concentration.

The pollutant concentration in an organism's tissues can be obtained by experimental measurements. Often, however, experimental data are insufficient or not available for economic or technical reasons [4] and, thus, are not suitable to characterize all investigated environmental media as well as all key species composing the food web under consideration. Several authors [5] have demonstrated that bioaccumulation models can be an effective alternative to predict the bioaccumulation of pollutants. To obtain a reliable estimation, however, models need a site-specific calibration [4]. Bioaccumulation of PCBs and PCDD/Fs was extensively investigated and modeled for individual aquatic species, whereas relatively few investigations have been reported concerning the bioaccumulation of PCBs and PCDD/Fs in selected food webs [6–8]. To estimate the effects of mixtures of bioaccumulative pollutants, McCarty and Mackay [9] proposed an approach based on the critical body burden (CBB) concept. The CBB is defined as the highest tissue concentration corresponding to no observed adverse effects. Recently, methods to estimate CBB concentrations were proposed [10], and an open database of residue-effect data (http://el.erdc.usace.army.mil/ered/) [11] was developed. Rarely, however, has the CBB approach been reported as a tool for performing an ERA [12–14].

Within the present work, the CBB approach was applied to Venice Lagoon (i.e., a coastal lagoon), Italy, to estimate the effect concentrations for five species of edible fish exposed to dioxins (i.e., PCDD/F and dioxin-like PCB congeners) stored in sediments. Venice Lagoon is a well-known case study, and a detailed description of environmental characteristics and anthropogenic stressors has been reported elsewhere [13,14]. Previous studies estimating the ecological risk posed by dioxins in Venice Lagoon have been published. In particular, a screening ERA based on 2,3,7,8-PCDD/F experimental tissue concentrations in fish, shellfish, and piscivorous wildlife in Venice Lagoon [12] has been reported. No spatial variability of contaminant concentrations was included, however, and only a few selected organisms were considered. More recently, another study estimating the ecological risk for a limited set of organisms on the basis of PCB and 2,3,7,8-PCDD/F congener experimental tissue concentrations was published [14]. That study, however, took into account only two fish species and was based on a small number of sampling stations (i.e., impeding the spatial representativeness of risk), and the uncertainty associated with effect assessment was not considered.

For the purposes of the present study, it is important to stress the uneven spatial distribution of the contamination

* To whom correspondence may be addressed (marcom@unive.it).
Published on the Web 1/2/2008.

[15,16], which depends on the distance and the typology of point and nonpoint sources, sediment characteristics (e.g., fine fraction), morphology of lagoon habitats, and lagoon hydrodynamics [17–19]. Moreover, mobility and bioavailability of toxic pollutants increased as a result of increased resuspension rate of the fine particle–bound contaminants caused by the fishing activity [20], raising the concern about its potential ecological risk to the aquatic food web. Sediment contamination and pollutant redistribution also can have an economic impact, potentially hampering fish and shellfish farming, with the production of clams being actually at the top in Europe [21].

The objective of the present study was to perform a spatial ERA for fish exposed to dioxin-like PCBs and 2,3,7,8-PCDD/Fs, both directly from the first 15 cm of sediments and through the lagoon food web. The selected food web included five representative lagoon fish species, differentiated by age (i.e., juveniles as well as adults) and by size (i.e., body wt). A state-of-the art, calibrated bioaccumulation model [22] and literature tissue residue-effect concentrations [23] were applied to estimate bioaccumulation and to assess effects for the fish species.

MATERIALS AND METHODS

The risk assessment was performed following the ERA procedure proposed by the U.S. Environmental Protection Agency [3] using the hazard quotient (HQ) approach [24] (i.e., ratio of predicted exposure concentration [PEC] to predicted no-effect concentration [PNEC]). The PEC was obtained by applying a calibrated and validated state-of-the-art bioaccumulation model [22], estimating PCDD/F and PCB congener concentrations in aquatic organism tissues. The PNEC was estimated according to the tissue residue approach from literature benchmarks [23] as the internal effect concentration of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), taking into account the uncertainty in effect estimation. Finally, the ecological risk for five selected fish species was assessed by comparing the PEC expressed as 2,3,7,8-TCDD toxicity equivalents (TEQs) [25] against the corresponding PNEC.

Exposure characterization

Experimental database. The database used in the present study consisted of selected 2,3,7,8-substituted PCDD/F congeners (Table 1) recorded in sediment, water, and organisms according to up-to-date analytical methods [15,16]. The database contained concentrations of PCDD/Fs and PCBs in 95 sediment samples, in tissue of five typical lagoon organisms (*Mytilus galloprovincialis*, six samples; *Tapes philippinarum*, 23 samples; *Carcinus mediterraneus*, nine samples; *Chelon labrosus*, six samples; and *Zosterisessor ophiocephalus*, eight samples), and in 16 water samples. The experimental data as well as the sampling point location have been reported previously by Micheletti et al. [14].

The sediment sampling sites were homogeneously distributed over the whole lagoon. The water samples were collected in the northern lagoon (three sampling stations); the central lagoon, including the navigable channels (five samples) and the channels within Porto Marghera industrial district (three samples); and in the southern lagoon near the city of Chioggia (four samples). All the homogeneous lagoon areas, including Malamocco and the western lagoon, are identified in Figure 1.

Because of the high spatial variability of environmental contamination in Venice Lagoon, the sediment, water, and organism data were grouped on the basis of both the hydrodynamic features and the contamination level [17] as recorded at each sampling site.

Table 1. Polychlorobiphenyls (PCBs) and polychlorodibenzo-*p*-dioxins and furans as well as log K_{OW} values considered in the present study[a]

Congeners	log K_{OW}
Nonmetabolizing	
PCB 81	6.36[b]
PCB 105	6.65[b]
PCB 114	6.65[b]
PCB 118/123	6.74[b]
PCB 156/157	7.18[b]
PCB 167	7.27[b]
PCB 170	7.37[b]
PCB 180	7.36[b]
PCB 189	7.3[b]
Metabolizing	
PCB 77	6.36[b]
PCB 126	6.89[b]
PCB 169	7.42[b]
2,3,7,8-tetra-CDD	7[c]
1,2,3,7,8-penta-CDD	7.4[c]
1,2,3,4,7,8-hexa-CDD	7.8[c]
1,2,3,6,7,8-hexa-CDD	7.8[c]
1,2,3,7,8,9-hexa-CDD	7.8[c]
1,2,3,4,6,7,8-hepta-CDD	8[c]
1,2,3,4,6,7,8,9-octa-CDD	8.2[c]
2,3,7,8-tetra-CDF	6.4[d]
1,2,3,7,8-penta-CDF	6.7[d]
2,3,4,7,8-penta-CDF	6.7[d]
1,2,3,4,7,8-hexa-CDF	7[c]
1,2,3,6,7,8-hexa-CDF	7[c]
1,2,3,7,8,9-hexa-CDF	7[c]
2,3,4,6,7,8-hexa-CDF	7[c]
1,2,3,4,6,7,8-hepta-CDF	7.4[c]
1,2,3,4,7,8,9-hepta-CDF	7.4[c]
1,2,3,4,6,7,8,9-octa-CDF	8[c]

[a] CDD = chlorodibenzo-*p*-dioxin; CDF = chlorodibenzo-*p*-furan.
[b] Arnot and Gobas [22].
[c] Mackay et al. [42].
[d] Carrer et al. [8].

To estimate the PEC (i.e., pollutant concentration in organism tissues), the 95% upper confidence limit of the mean [26] sediment concentration of PCB and PCDD/F congeners was calculated for each area. The 95% upper confidence limits of sediment contamination estimated using the ProUCL software (Ver 3.0; Lockheed Martin, Las Vegas, NV, USA) [27] (http://www.epa.gov/nerlesd1/tsc/form.htm) are reported in Table S1 of the *Supplemental Information* (http://dx.doi.org/10.1897/07-162.S1).

For an unknown data distribution, the 95% upper confidence limit of the arithmetic mean represents the most reliable estimation of the true average and the limit above which this value is unlikely to occur [26]. This choice allows one to deal with uncertainty and variability of the experimental data set without excessively conservative assumptions that may result in overestimation of risk. The organisms and sediment concentrations were reported for each subarea as 2,3,7,8-TCDD TEQs by applying the toxic equivalency factors proposed by the World Health Organization [25].

Bioaccumulation model for Venice Lagoon. The exposure of the organisms was estimated using the mechanistic food-web bioaccumulation model recently proposed by Arnot and Gobas [22], who presented several improvements compared to the previous version proposed by Gobas [7]. In fact, the

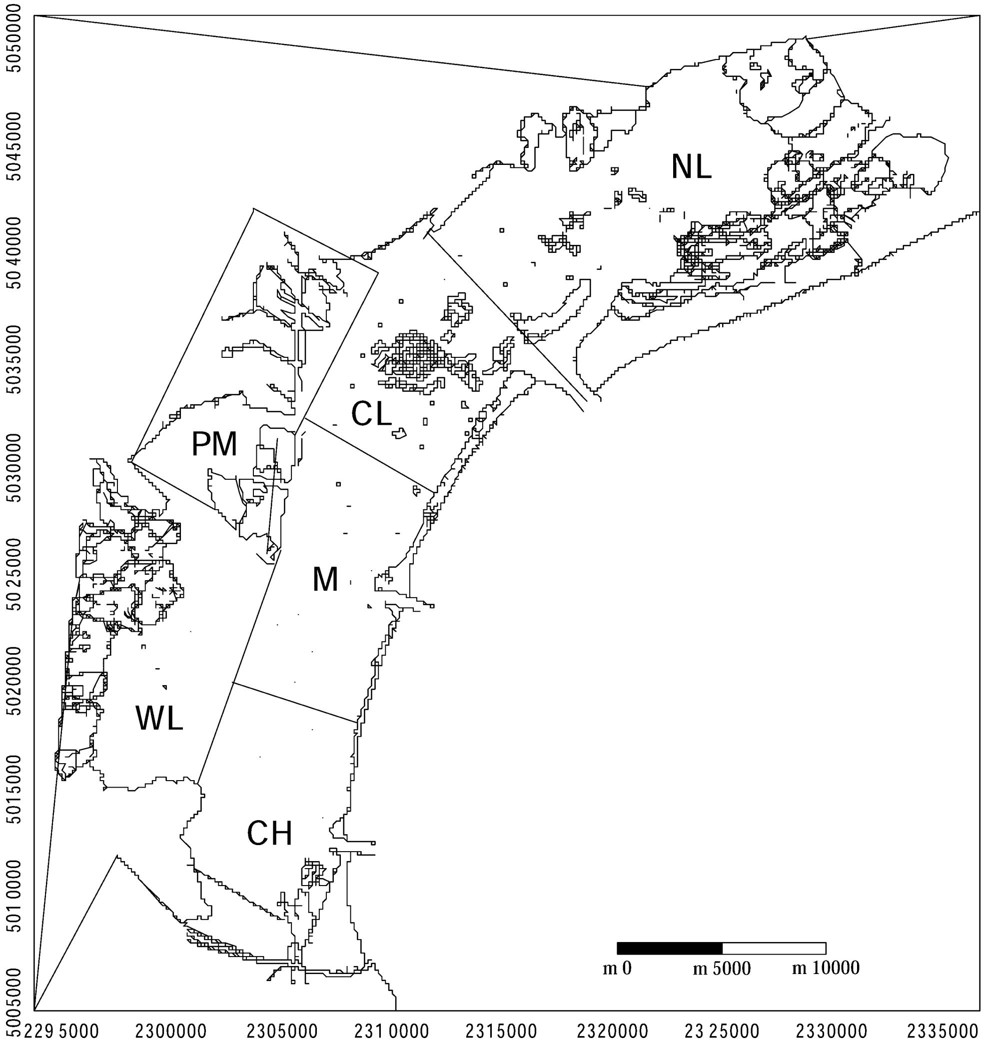

Fig. 1. Selected lagoon areas: Northern lagoon (NL), central lagoon (CL), Porto Marghera industrial district (PM), Malamocco (M), Chioggia (CH), and western lagoon (WL). The model verification was carried out using the data collected in NL, CL and CH areas, whereas the validation was carried out using the data collected in the WL area. Ecological risk was estimated for each lagoon area.

model includes an enhanced estimation of chemical concentrations in algae, phytoplankton, and zooplankton and a set of allometric relationships that allow estimation of species-specific parameters for a wide range of aquatic organisms. Furthermore, mechanistic formulations for prediction of the gastrointestinal magnification of chemical concentrations are included.

At steady state, the overall uptake and loss rates are equal; therefore, the model mass-balance equation for a given chemical reads is

$$C_{B,l} = \frac{k_1 C_{WD} + k_D C_{D,m}}{k_2 + k_E + k_G + k_M} \quad (1)$$

where $C_{B,l}$ (g/kg wet wt), C_{WD} (g/L), and $C_{D,m}$ (g/kg wet wt) represent, respectively, the estimated concentrations of a chemical in biota (B) l included in the food web, the dissolved concentration in water, and in organism m of the diet. The remaining parameters characterize the uptake and loss routes: k_1 (L/kg·d) and k_D (kg/kg·d) are, respectively, the uptake rates through respiration and through diet, and k_2, k_E, k_G, and k_M (all 1/d) represent the respiration, excretion, growth dilution, and biotransformation rates, respectively. The C_{WD} was estimated using the equation proposed by Gobas [7], based on the partitioning between the suspended organic matter and the total water concentration:

$$C_{WD} = \frac{C_{WT}}{1 + \left(\frac{K_{OW} \cdot MOM}{d_{OM}}\right)} \quad (2)$$

where C_{WD} is measured in g/L, C_{WT} is the total concentration in water (g/L), K_{OW} is the octanol–water partitioning constant, MOM is the organic matter concentration in water (kg/L), and d_{OM} is the organic matter density (kg/L).

The model was calibrated and validated using as input the sediment and water concentration data [15,16]. The MOM was estimated by the product of the suspended solids concentration in water (kg/L; as reported by Micheletti et al. [14]) by the organic carbon fraction in suspended solids, which was assumed to be identical to the organic carbon fraction in sediment. The K_{OW} values of the examined compounds are reported in Table 1, whereas the density of the organic matter was assumed to be 0.9 kg/L [7].

The C_{WT} data, which was used for the model verification and calibration, were reported previously by Micheletti et al. [14]. Unfortunately, the C_{WT} data sets for the sampling stations

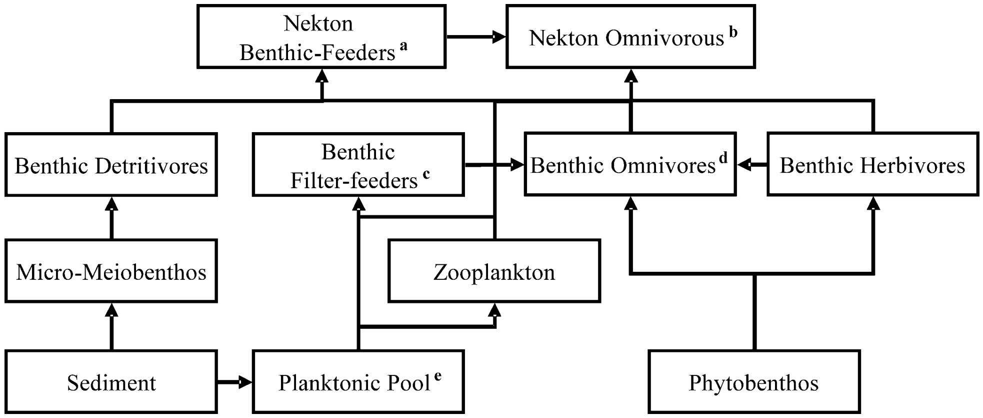

Fig. 2. Diagram of the food-web structure adopted for Venice Lagoon, Italy. **a.** Nekton carnivorous benthic feeder group, *Chelon labrosous* adults and juveniles, *Atherina boyeri*, *Zosterisessor ophiocephalus*, and *Sparus aurata* adults and juveniles. **b**. *Dicentrarcus labrax* adults and juveniles. **c**. Macrobenthos omnivorous filter-feeder group and *Tapes philippinarum* adults and juveniles. **d**. *Carcinus mediterraneus* as well as macrobenthos omnivorous mixed-feeder and omnivorous predator groups. **e.** Bacterioplankton and phytoplankton.

included in the western lagoon and Porto Marghera areas were not available. Therefore, to apply the bioaccumulation model to the whole lagoon for risk assessment, C_{WT} was estimated for each lagoon area by applying the following equations:

$$C_{WT} = C_S K_{BSW}^{-1} \tag{3}$$

where C_S (g/kg dry wt) is the concentration in sediments. The partition coefficient between bottom sediment and water (K_{BSW}) was estimated according to the equation of Seth et al. [28]:

$$K_{BSW} = \phi_{BS} \cdot 0.35 \cdot K_{OW} \cdot d_{BS} \tag{4}$$

where ϕ_{BS} is the organic carbon fraction in bottom sediments and d_{BS} (kg/L) represents the bottom sediment density.

A site-specific food web was selected to apply the model (Eqn. 1) based on the results presented in literature [29–33]. The food web includes three planktonic, nine benthonic, and six nektonic organisms, which are represented in Figure 2.

Organisms belonging to the lower trophic levels (i.e., microzooplankton and macroinvertebrates) were grouped on the basis of common habitat and feeding similarities. In some instances, juveniles and adults were considered as different compartments to account for the differences in their metabolism, internal tissues composition, and feeding habits. The diet matrix (Table S2 [http://dx.doi.org/10.1897/074-1692.S1]) was defined on the basis of the previously cited literature. Organism- or group-specific parameters, such as the gill ventilation rate or the feeding efficiency, were estimated using the allometric equations proposed by Arnot and Gobas [22]. Parameters concerning the environmental conditions and biota are reported in Tables S3 and S4 (http://dx.doi.org/10.1897/074-1692.S1), respectively.

Bioaccumulation model verification, calibration, and validation. The model [22] was verified (i.e., used for predicting the bioaccumulation) for nonmetabolizing PCBs (Table 1) and was calibrated and validated for metabolizing PCBs and PCDD/Fs using available field data for *T. philipinarum*, *C. mediterraneus*, *C. labrosus*, and *Z. ophiocephalus*. Therefore, the data set was divided into a calibration set (i.e., data collected in the northern lagoon, central lagoon, and Chioggia areas in Fig. 1) and a validation set (i.e., data collected in the western lagoon area). Median sediment, water, and biota concentrations were used as input data. The logarithm of the overall model bias (MB_O) [22] was taken as a measure of the performance of the model and of its tendency to over- or underestimate the bioaccumulation factors (BAFs). The logarithm of MB_O can be interpreted as the mean of the difference between the predicted and observed logarithms of the BAFs for all chemicals in all species, with the ideal fit-to-data being the zero value. The criterion for accepting or rejecting the model setup and calibration was assessed by testing whether the log MB_O was significantly different from zero as determined with a Student's t test ($\alpha = 0.05$).

In the evaluation of model performance, the MB_O was expressed on an exponential scale to permit a straightforward evaluation of model behavior with respect to the observed data. In other words, a MB_O of greater than one indicates a general tendency of the model to overestimate the BAFs.

Estimation of PECs through the numerical model. The validated numerical model was applied to estimate the bioaccumulation of dioxin-like PCBs and PCDD/Fs in the aquatic food web for each of the six areas of Venice Lagoon (northern lagoon, Porto Marghera, central lagoon, Malamocco, Chioggia, and western lagoon) (Fig. 1). The input parameters used for the model application were those reported in Tables S1 to S5 (http://dx.doi.org/10.1897/074-1692.S1).

The PEC for the organisms included in the food web was estimated from the bioaccumulation of individual congeners in organism tissues. This was estimated by the model, expressed as 2,3,7,8-TCDD TEQs, and then summed to obtain the PEC. Next, the PEC was compared with the effect concentration in fish tissues estimated for the 2,3,7,8-TCDD.

Effects characterization

The PNEC of the dioxin-like PCBs and PCDD/Fs in fish tissues was estimated according to the CBB approach [9] as the internal no-effect concentration for 2,3,7,8-TCDD ($INEC_{TCDD}$). The $INEC_{TCDD}$ was estimated using residue-effect benchmarks for fish recently reported in the open literature by Steevens et al. [23], which proposed tissue effect concentrations in terms of ng 2,3,7,8-TCDD/g lipid in fish, defining two values corresponding to 90 and 99% of fish species. These data were estimated using a species-sensitivity distribution obtained from 26 studies concerning 10 fish species (mainly freshwater salmonids) that are considered to be more sensitive than other species to dioxin-like chemicals [23]. According to this range of tissue effect concentrations, two $INEC_{TCDD}$ values were estimated by multiplying the effect concentration protecting 90% ($INEC_{TCDD}^{90}$) and 99%

($INEC^{99}_{TCDD}$) of the fish community [23] by g lipid/kg fish body weight as calculated from the data reported in Table S4 (http://dx.doi.org/10.1897/074-1692.S1). Therefore, the ecological risk for fish included in the food-web model was estimated using both estimated $INEC_{TCDD}$ values. The application of two $INEC_{TCDD}$ values permitted inclusion in the risk estimation of the uncertainty involved in the extrapolation of effect concentrations for the aquatic community from experimental effect data for few species [23]. Because the considered species are closely related and are more sensitive than other fish to the effects of dioxin, however, there could be a very conservative estimation of PNEC, especially at the 99% protection level. This aspect should be considered when evaluating the risk assessment results.

Risk characterization

Results obtained from exposure and effects characterization were used during the last phase of the ERA procedure to estimate the risk for fish included in the food web. In the present study, ecological risk was estimated using the HQ approach [24]. The HQ was calculated by comparing the exposure concentration (i.e., PEC) in TEQ and the $INEC_{TCDD}$ according to the following equation:

$$HQ = PEC/INEC_{TCDD} \tag{5}$$

where $INEC_{TCDD}$ represents the tissue pollutant concentration correlated with no adverse effects. When PEC is greater than $INEC_{TCDD}$ (i.e., $HQ > 1$), an adverse effect is likely to occur. The HQ allows a relative risk comparison between different areas and for different assessment endpoints.

RESULTS AND DISCUSSION

Ecological risk for five fish species of Venice Lagoon was estimated by comparing modeled tissue concentration of dioxin-like PCBs and PCDD/Fs expressed as 2,3,7,8-TCDD by an internal effect concentration for 2,3,7,8-TCDD estimated on the basis of literature CBB data [9]. The bioaccumulation model was first calibrated and validated using data collected in three lagoon areas and then applied to all six selected lagoon areas to estimate the exposure of fish.

Exposure characterization

To assess the bioaccumulation of PCB and PCDD/F congeners into the aquatic food web of Venice Lagoon, the state-of-the-art bioaccumulation model proposed by Arnot and Gobas [22] was applied to verify the goodness of fit for nonmetabolizing PCB congeners. At the same time, it was calibrated and validated for metabolizing PCB and PCDD/F congeners by estimating the metabolizing rate constant. The bioaccumulation model was then applied to estimate the PEC for fish and, thus, the ecological risk in the six selected lagoon zones.

Verification and validation of the selected bioaccumulation model

The model verification and validation was carried out in two steps using the data available for three areas: The northern lagoon, the central lagoon, and Chioggia (Fig.1). In the first step, the model was verified (i.e., used for predicting bioaccumulation of the nonmetabolized PCBs) (Table 1); in this case, the biotransformation rates (k_M) were set to zero in Equation 1. The results of the first step are shown in Figure 3, which displays the predicted BAFs versus the observed ones for each PCB congener and for *T. philippinarum*, *M. galloprovincialis*, *C. mediterraneus*, *C. labrosus*, and *Z. ophiocephalus* (i.e., *n* in the legend of Fig. 2). The continuous line represents the optimal fit, whereas the dotted lines identify the 95% confidence limit, estimated according to method described by Gobas et al. [34]. The dashed lines indicate the region in which predictions and observations differ by less than one order of magnitude. The model shows a general tendency to underestimate the observations, because $MB_O = 0.84$. Only 1 of 91 predictions (1.1%), however, differs by more than an order of magnitude from observations. Figure 3 shows that the results concerning *T. philipinarum* and *Z. ophiocephalus* are in better agreement with the data; in fact, for these species, the model bias values are 0.98 and 0.90, respectively. Instead, the model underestimates the BAFs for *C. mediterraneus* and *C. labrosus*, but the model bias values of 0.86 and 0.72, respectively, are still acceptable [22]. The logarithm of the predicted BAF ranged between 3.9 and 6.4. According to acceptability criterion, the results were not significantly different from the observations, and the verification step confirmed the suitability of the adopted model parameterization to reproduce bioaccumulation of PCBs in the Venice Lagoon ecosystem.

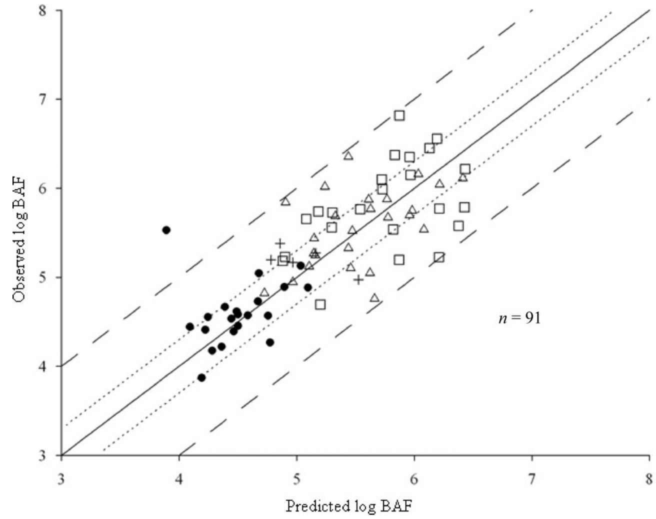

Fig. 3. Observed versus predicted log bioaccumulation factors (BAFs) for the nonmetabolized polychlorobiphenyls for the verification sites: Northern lagoon, central lagoon, and Chioggia (*n* = number of experimental measurements for all polychlorobiphenyl congener and all species). The dotted lines represent the 95% boundary calculated according to the method described by Gobas et al. [34], and the dashed lines represent the boundary of factor 10. ● = *Tapes philipinarum*; □ = *Carcinus mediterraneus*; + = *Chelon labrosus*; △ = *Zosterisessor ophiocephalus*.

In the second step, the model was calibrated for metabolizing non-*ortho*-PCBs congeners, dioxins, and furans: k_M values were estimated using the observations for *T. philipinarum*, *C. mediterraneus*, *C. labrosus*, and *Z. ophiocephalus* in the calibration areas represented by the northern lagoon, the central lagoon, and Chioggia. Because specific values for k_M in fish and invertebrates were not available, biotransformation rates were estimated by minimizing the residual error, which equals $|C_{predicted} - C_{observed}|$ [35], and assuming as the maximum acceptable $k_M = 0.5$/d [36], whereas the rate was set to zero in the remaining compartments for which experimental data were not available. The calibration of the parameters was conducted separately for each of the three areas, adopting as final

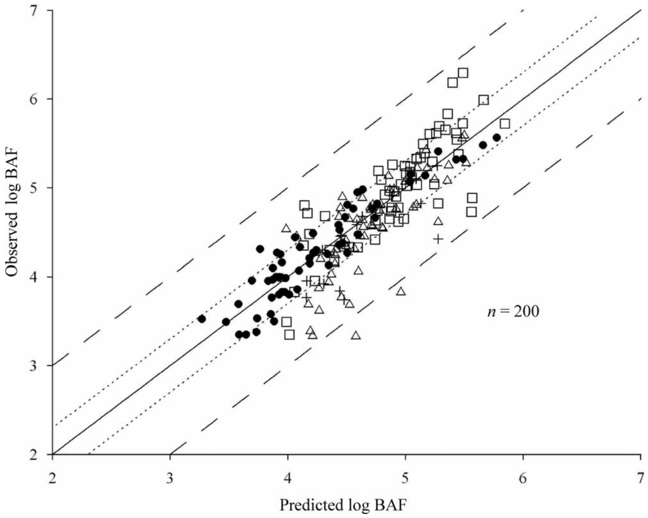

Fig. 4. Observed versus predicted log bioaccumulation factors (BAFs) for the metabolized non-*ortho*-polychlorobiphenyls and polychlorodibenzo-*p*-dioxins and furans for the calibration sites: Chioggia, central lagoon, and northern lagoon (*n* = number of experimental measurements for all polychlorobiphenyl congener and all species). The dotted lines represent the 95% boundary calculate according to the method described by Gobas et al. [34], and the dashed lines represent the boundary of factor 10. ● = *Tapes philippinarum*; △ = *Carcinus mediterraneus*; + = *Chelon labrosus*; △ = *Zosterisessor ophiocephalus*.

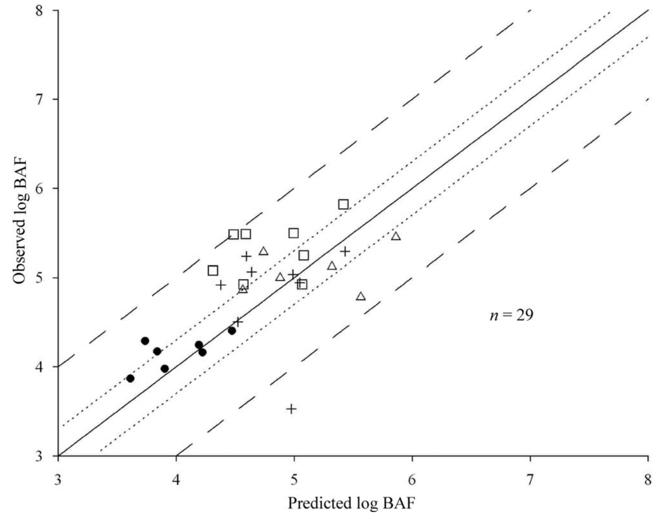

Fig. 5. Observed versus predicted log bioaccumulation factors (BAFs) for the nonmetabolized polychlorobiphenyls for the validation site: Western lagoon (*n* = number of experimental measurements for all polychlorobiphenyl congener and all species). The dotted lines represent the 95% boundary calculated according to the method described by Gobas et al. [34], and the dashed lines represent the boundary of factor 10. ● *Tapes philippinarum*; □ = *Carcinus mediterraneus*; + = *Chelon labrosus*; △ = *Zosterisessor ophiocephalus*.

rates the average of the three estimates (Table S5 [http://dx.doi.org/10.1897/074-1692.S1]).

The results obtained from the calibration are shown in Figure 4. The predicted log BAFs ranged from 3.3 to 5.9, whereas the MB_O was 1.01. The MB_O indicates that the model tends to overestimate the field data, but the statistical difference of the mean was not significant. In particular, this tendency was more pronounced for *C. labrosus* (MB = 1.4) and for *Z. ophiocephalus* (MB = 1.37). Overall, the performance of the model was still good, with 99% of data falling within the factor-10 confidence bounds.

Subsequently, the model was validated by comparing the predicted and observed BAFs of the western lagoon (Fig. 1) area for all congeners. The results for nonmetabolized and metabolized chemicals are shown in Figures 5 and 6 and are not dissimilar to those reported in Figure 4 (i.e., representing a good model performance).

As expected, in both groups, the MB_O was less accurate than that obtained during the verification and calibration steps. The results for nonmetabolized PCBs (MB_O = 0.7) were underestimating the observations, whereas for metabolized chemicals, the MB_O of 1.17 indicated a slight overestimation. Nevertheless, the model still satisfied the acceptability criteria, because differences between observed and predicted BAFs were not statistically significant. For the two sets of compounds, only 4 and 7%, respectively, of log BAFs were beyond the one-order-of-magnitude region. The predicted log BAFs ranged between 3.6 and 5.8 for nonmetabolized PCBs and between 3.5 and 5.6 for metabolized PCBs.

Application of the bioaccumulation model

Application of the calibrated Arnot and Gobas [22] bioaccumulation model permitted estimation of the PEC for the mixture of PCDD/F and dioxin-like PCB congeners in the fish tissues. Because the capability of fish to biotransform PCDD/Fs has been widely recognized [37], it adopted a background value for the metabolizing rate constant (k_M = 0.01; i.e., the minimum obtained from calibration) to include such parameterization for the remaining fish species.

Table 2 reports the results expressed as 2,3,7,8-TCDD TEQs for the bioaccumulation estimated in fish tissues for the sum of dioxin-like PCBs and PCDD/Fs in the six investigated lagoon areas (Fig. 1). The lagoon areas with the highest bioaccumulation were Porto Marghera (located near the chemical industrial district), Malamocco, and the central lagoon. The

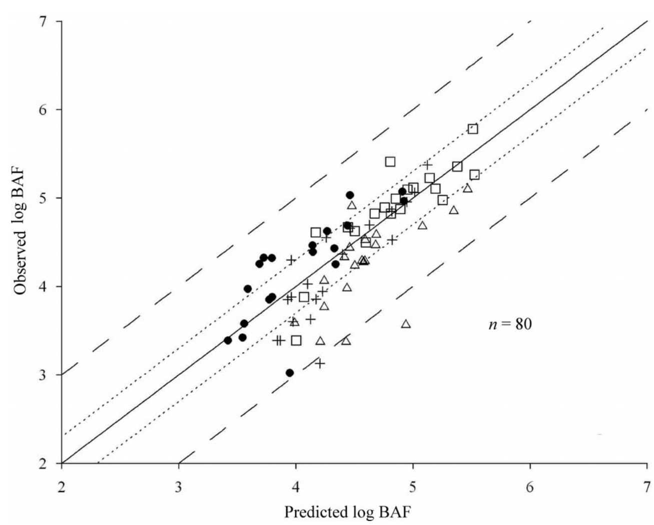

Fig. 6. Observed versus predicted log bioaccumulation factors (BAFs) for the metabolized non-*ortho*-polychlorobiphenyls and polychlorodibenzo-*p*-dioxins and furans for the validation site: Western lagoon (*n* = number of experimental measurements for all polychlorobiphenyl congener and all species). The dotted lines represent the 95% boundary calculated according to the method described by Gobas et al. [34], and the dashed lines represent the boundary of factor 10. ● = *Tapes philippinarum*; □ = *Carcinus mediterraneus*; + = *Chelon labrosus*; △ = *Zosterisessor ophiocephalus*.

Table 2. Sum of the estimated tissue concentration of dioxin-like polychlorobiphenyl and polychlorodibenzo-*p*-dioxin and furan congeners (μg/kg wet wt 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxicity equivalents) in fish included in the food-web model for each considered lagoon area

Fish species	Northern lagoon	Central lagoon	Porto Marghera	Malamocco	Chioggia	Western lagoon
Chelon labrosus juveniles	1.95×10^{-2}	1.70×10^{-2}	4.34×10^{-2}	4.56×10^{-2}	1.66×10^{-2}	5.46×10^{-2}
Chelon labrosus	8.77×10^{-4}	9.18×10^{-4}	2.18×10^{-3}	2.46×10^{-3}	8.19×10^{-4}	2.26×10^{-3}
Atherina boyeri	2.30×10^{-2}	1.91×10^{-2}	4.76×10^{-2}	5.20×10^{-2}	1.87×10^{-2}	6.37×10^{-2}
Zosterisessor ophiocephalus	8.60×10^{-4}	7.30×10^{-4}	1.82×10^{-3}	2.46×10^{-3}	8.38×10^{-4}	2.22×10^{-3}
Nekton carnivorous benthic feeders	1.55×10^{-2}	1.23×10^{-2}	2.85×10^{-2}	3.40×10^{-2}	1.22×10^{-2}	4.19×10^{-2}
Sparus aurata juveniles	1.55×10^{-2}	1.36×10^{-2}	3.48×10^{-2}	3.66×10^{-2}	1.33×10^{-2}	4.35×10^{-2}
Sparus aurata	9.28×10^{-3}	7.04×10^{-3}	1.34×10^{-2}	1.91×10^{-2}	8.01×10^{-3}	2.19×10^{-2}
Dicentrarcus labrax juveniles	1.99×10^{-2}	1.71×10^{-2}	4.37×10^{-2}	4.54×10^{-2}	1.67×10^{-2}	5.52×10^{-2}
Dicentrarcus labrax	1.73×10^{-2}	1.45×10^{-2}	3.68×10^{-2}	3.78×10^{-2}	1.44×10^{-2}	4.70×10^{-2}

estimated concentrations were in the range of 7.3×10^{-4} and 4.76×10^{-2} μg TEQ/kg wet weight. In the northern lagoon, Chioggia, and the western lagoon, the estimated TEQ concentrations were between 8.38×10^{-4} and 6.37×10^{-2} μg TEQ/kg wet weight. The highest concentration was estimated for *Atherina boyeri*.

The TEQ tissue concentrations estimated by the Arnot and Gobas model [22] were used as the PEC to be compared with the $INEC_{TCDD}$ according to Equation 6.

Effects characterization

As described in *Materials and Methods*, two $INEC_{TCDD}$ values at two protection targets (i.e., 90 and 99% of the fish community) [23] were estimated. Thus, the ecological risk was estimated by comparing the PEC with both the $INEC^{90}_{TCDD}$ and the $INEC^{99}_{TCDD}$ to estimate the risk with regard to the two levels of fish community protection. Steevens et al. [23] reported 2,3,7,8-TCDD residue-effect concentrations protecting 90 and 99% of the fish community of 6.99×10^{-4} and 5.7×10^{-5} μg TCDD/g lipid, respectively. To estimate the INECs in terms of μg TCDD/kg body weight, the residue-effect concentrations were normalized by the lipid content in fish tissues per kilogram of body weight (on a wet-wt basis) (Table 3). The resulting INECs for fish species included in the food-web model are reported in Table 3. The $INEC^{90}_{TCDD}$ concentration was included between 3.5×10^{-2} μg TCDD/kg body weight for Nekton carnivorous benthic feeders and 9.35×10^{-2} μg TCDD/kg body weight for *Dicentrarchus labrax*. The $INEC^{99}_{TCDD}$ values were between 3.9×10^{-3} and 7.63×10^{-3} μg TCDD/kg body weight for *C. labrosus* and *D. labrax*, respectively, resulting in values one order of magnitude lower than the $INEC^{90}_{TCDD}$. These results reflect the difference between the 90 and 99% 2,3,7,8-TCDD residue-effect concentrations, resulting in a high uncertainty regarding the PNEC estimation.

Risk characterization

The ecological risk from the bioaccumulation of the dioxin-like PCB and PCDD/F congeners mixture was estimated using the HQ approach [24] for fish included in the aquatic food web applied in the bioaccumulation model. Accordingly, the HQ was calculated for each lagoon subarea (i.e,. northern lagoon, central lagoon, Porto Marghera, Malamocco, Chioggia, and western lagoon) by comparing the modeled bioaccumulation (i.e., the PEC) for fish with both the $INEC^{90}_{TCDD}$ and the $INEC^{99}_{TCDD}$ (Eqn. 5).

The HQs obtained for each lagoon zone (Table 4) were calculated according to the following equation:

$$HQ_{ij}(\text{PCDD/Fs + dioxin-like PCBs}) = \frac{TEQ_{ij}(\text{PCDD/Fs + dioxin-like PCBs})}{INEC_{TCDD}} \qquad (6)$$

where i is the lagoon subarea ($1 \le i \le 6$) and j is the trophic group ($1 \le j \le 9$).

The hazard posed by the PCBs and PCDD/Fs mixture generally decreases from the lowest level of the fish of the food web (i.e., *C. labrosus* juveniles and adults) to the highest level (i.e., *D. labrax* juveniles and adults). The ecological risk estimated for fish included in the food-web model using the $INEC^{90}_{TCDD}$ was in the range 0.02 to 1.2, with a negligible risk for fish (i.e., HQ < 1 means the absence of potential adverse effects for the considered species) according to the HQ results obtained by Micheletti et al. [14]. On the contrary, the risk estimation on the basis of the $INEC^{99}_{TCDD}$ resulted in HQs of greater than one in all selected lagoon areas.

In general, the highest values were obtained for small fish (i.e., *A. boyeri*) and for juveniles (i.e., *C. labrosus*, *Sparus aurata*, and *D. labrax*), both of which were characterized by a body weight of less than 4 g. These results can be explained

Table 3. Internal no-effect concentrations for 2,3,7,8 tetrachlorodibenzo-*p*-dioxin ($INEC^{90}_{TCDD}$ and $INEC^{99}_{TCDD}$) estimated for fish included in the food-web model by multiplying the residue-effect concentration protecting 90 and 99% of the fish community [23] by the lipid content per kg of body weight

Fish species	Lipid content (g lipid/kg body wet wt)	Residue-effect concentration, 90% (μg TCDD/g lipid)	Residue-effect concentration, 99% (μg TCDD/g lipid)	$INEC^{90}_{TCDD}$ (μg TCDD/kg body wt)	$INEC^{99}_{TCDD}$ (μg TCDD/kg body wt)
Chelon labrosus juveniles	68	6.99×10^{-4}	5.7×10^{-5}	4.75×10^{-2}	3.88×10^{-3}
Chelon labrosus	68	6.99×10^{-4}	5.7×10^{-5}	4.75×10^{-2}	3.88×10^{-3}
Atherina boyeri	68	6.99×10^{-4}	5.7×10^{-5}	6.71×10^{-2}	5.47×10^{-3}
Zosterisessor ophiocephalus	80	6.99×10^{-4}	5.7×10^{-5}	5.59×10^{-2}	4.56×10^{-3}
Nekton carnivorous benthic feeders	50	6.99×10^{-4}	5.7×10^{-5}	3.50×10^{-2}	2.85×10^{-3}
Sparus aurata juveniles	97	6.99×10^{-4}	5.7×10^{-5}	6.78×10	5.53×10^{-3}
Sparus aurata	97	6.99×10^{-4}	5.7×10^{-5}	6.78×10	5.53×10^{-3}
Dicentrarcus labrax juveniles	133.8	6.99×10^{-4}	5.7×10^{-5}	9.35×10^{-2}	7.63×10^{-3}
Dicentrarcus labrax	133.8	6.99×10^{-4}	5.7×10^{-5}	9.35×10^{-2}	7.63×10

Table 4. Hazard quotients (HQs) estimated for fish included in the food web model in the six selected lagoon areas by using both the internal no-effect concentration ($INEC^{90}_{TCDD}$ and $INEC^{99}_{TCDD}$) estimated from the tissue effect concentration protecting 90 and 99% of the fish community [23][a]

HQ	Northern lagoon	Central lagoon	Porto Marghera	Malamocco	Chioggia	Western lagoon
$INEC^{90}_{TCDD}$						
Chelon labrosus juveniles	0.4	0.4	0.9	1.0	0.4	*1.2*
Chelon labrosus	0.02	0.02	0.05	0.05	0.02	0.1
Atherina boyeri	0.3	0.3	0.7	0.8	0.3	1.0
Zosterisessor ophiocephalus	0.02	0.01	0.03	0.04	0.01	0.04
Nekton carnivorous benthic feeders	0.4	0.4	0.8	1.0	0.4	*1.2*
Sparus aurata juveniles	0.2	0.2	0.5	0.5	0.2	0.6
Sparus aurata	0.1	0.1	0.2	0.3	0.1	0.3
Dicentrarcus labrax juveniles	0.2	0.2	0.5	0.5	0.2	0.6
Dicentrarcus labrax	0.2	0.2	0.4	0.4	0.2	0.5
$INEC^{99}_{TCDD}$						
Chelon labrosus juveniles	*5*	*4.4*	*11.2*	*11.8*	*4.3*	*14.1*
Chelon labrosus	0.2	0.2	0.6	0.6	0.2	0.6
Atherina boyeri	*4.2*	*3.5*	*8.7*	*9.5*	*3.4*	*11.7*
Zosterisessor ophiocephalus	0.2	0.2	0.4	0.5	0.2	0.5
Nekton carnivorous benthic feeder	*5.4*	*4.3*	*10*	*12.0*	*4.3*	*14.7*
Sparus aurata juveniles	*2.8*	*2.5*	*6.3*	*6.6*	*2.4*	*7.9*
Sparus aurata	*1.7*	*1.3*	*2.4*	*3.5*	*1.5*	*4.0*
Dicentrarcus labrax juveniles	*2.6*	*2.2*	*5.7*	*6.0*	*2.2*	*7.2*
Dicentrarcus labrax	*2.3*	*1.9*	*4.8*	*5.0*	*1.9*	*6.2*

[a] HQ values greater than one are presented in italic.

by the diet of the juvenile fish, which includes mainly zooplankton and small benthic organisms rather than other fish, and by the role of body weight in the bioaccumulation model [22], which is used to estimate the growth elimination rate constant (i.e., k_E), meaning that a lower body weight causes a relative increase of the pollutant tissue concentration.

As far as ranking the lagoon areas according to estimated risk, Porto Marghera, Malamocco, and the western lagoon were the most potentially affected areas, with HQs (based on $INEC^{99}_{TCDD}$) ranging from 0.6 (for *C. labrosus* adults) to 14.1 (for *C. labrosus* juveniles) and 14.7 (for Nekton carnivorous benthic feeders). Porto Marghera and Malamocco are directly affected by past emissions from the Porto Marghera industrial district [16] as well as by the actual pollutants emissions [38], resulting in extended areas of contaminated sediments [16]. The western lagoon is a confined area with a water residence time of between 20 and 40 d [39] that receives freshwater inputs [40] and is characterized by sediments with a high content of organic carbon [16]. All these factors caused localized hot spots with high concentrations of persistent pollutants [16] and, thus, an increased bioaccumulation potential through the food web from the detritivorous and filter-feedings benthic organisms to predator fish species. In Chioggia, the central lagoon, and the northern lagoon, HQs (based on $INEC^{99}_{TCDD}$) in the range of 2.2 to 5 for small fish and juveniles and of 0.2 to 2.3 for adult fish were estimated, ranking these areas as having an intermediate hazard condition. Chioggia was the area with the lowest risk to fish, having the lowest HQ. Chioggia and the central lagoon are characterized by a higher exchange between sea and lagoon (water residence time, 15–20 d [39]), whereas the central lagoon also is characterized by an erosion process started in the year 1990, transferring contaminated sediments from the lagoon to the sea and, thus, reducing the concentration of pollutants [41]. The northern lagoon is a confined area with a water residence time of more than 60 d, but it is less affected by anthropogenic activities and receives a low freshwater input from the drainage basin.

The present study carried out a site-specific analysis, taking into account a representative food web (including a significant number of benthic and fish species), the spatial distribution of sediment contamination in the lagoon, and the age and size differentiation. Comparison of the present results with previous results reported in the literature [12,14] for Venice Lagoon, however, confirmed a negligible risk to the fish community because of exposure to dioxin-like PCBs and PCDD/Fs, especially taking into account the 90% protection level for the fish population.

The use of two protection thresholds (i.e., 90 and 99% of fish population) allowed the present study to take into account the uncertainty of effect estimation into a preliminary risk assessment and to support the risk management process (i.e., identification of risk acceptability) by estimating risk in relation to the level of aquatic life protection. The potential risk to fish that is obtained by applying the $INEC^{99}_{TCDD}$ needs to be evaluated further by means of experimental measurements and lines of evidence (e.g., bioaccumulation measurements and toxicity bioassays) to address the uncertainty related to estimation of the $INEC^{99}_{TCDD}$.

SUPPORTING INFORMATION

Table S1. Estimated 95% upper confidence limits of sediment contamination (ng/kg dry wt) for the six areas of Venice Lagoon, Italy. CDD = chlorodibenzo-*p*-dioxin; CDF = chlorodibenzo-*p*-furan; PCB = polichlorobiphenyls.

Table S2. Diet composition (% volume) for Venice Lagoon, Italy. Note that suspended solids are grouped with sediment. juv = juvenile.

Table S3. Sediment and water parameters for Venice Lagoon, Italy. OC = organic carbon.

Table S4. Biota parameterization for biomass, lipid fraction (LF), nonlipidic organic matter (NLOM) fraction, and water fraction (WF). juv = juvenile.

Table S5. Estimated values for biotransformation parameter, k_M (1/d). CDD = chlorodibenzo-*p*-dioxin; CDF = chlorodibenzo-*p*-furan; PCB = polichlorobiphenyls.

All found at DOI: 10.1897/07-162.S1 (18 KB PDF).

Acknowledgement—We are thankful to the Venice Water Authority–Consorzio Venezia Nuova for providing the experimental data and to the Consortium for the Co-ordination of the Research in the Lagoon of Venice, which partly supported the research. A special thanks to Simone Libralato and Elena Semenzin for their technical support.

REFERENCES

1. U.S. Environmental Protection Agency. 2000. Bioaccumulation testing and interpretation for the purpose of sediment quality assessment: Status and needs. EPA-823-R-00-001. Final Report. Office of Water, Washington, DC.
2. European Commission. 2001. Community strategy for dioxins, furans, and polychlorobiphenyls. COM (2001) 593 final. Brussels, Belgium.
3. U.S. Environmental Protection Agency. 1998. Guidelines for ecological risk assessment. EPA/630/R-95/002F. Final Report. Washington, DC.
4. Suter GW II, Efroymson RA, Sample BE, Jones DS. 2000. *Ecological Risk Assessment for Contaminated Sites.* CRC, Boca Raton, FL, USA.
5. Mackay D, Fraser A. 2000. Bioaccumulation of persistent organic chemicals: mechanisms and models. *Environ Pollut* 110:375–391.
6. Swackhamer DL, Skoglund RS. 1993. Bioaccumulation of PCBs by algae: Kinetics versus equilibrium. *Environ Toxicol Chem* 12: 831–838.
7. Gobas FAPC. 1993. A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food webs: Application to Lake Ontario. *Ecol Model* 69:1–17.
8. Carrer S, Halling-Sørensen B, Bendoricchio G. 2000. Modeling the fate of dioxins in a trophic network by coupling an ecotoxicological and an Ecopath model. *Ecol Model* 126:201–223.
9. McCarty LS, Mackay D. 1993. Enhancing ecotoxicological modeling and assessment. *Environ Sci Technol* 27:1719–1728.
10. Hendriks AJ, Traas TP, Huijbregts MAJ. 2005. Critical body residues linked to octanol–water partitioning, organism composition, and LC50 QSARs: Meta-analysis and model. *Environ Sci Technol* 39:3226–3236.
11. U.S. Army Corps of Engineers. 2007. The environmental residue-effect database (ERED). Vicksburg, MS.
12. Wenning R, Dodge D, Peck B, Shearer K, Luksemburg W, Della Sala S, Scazzola R. 2000. Screening-level ecological risk assessment of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediments and aquatic biota from the Venice Lagoon, Italy. *Chemosphere* 40:1179–1187.
13. Micheletti C, Critto A, Carlon C, Marcomini A. 2004. Ecological risk assessment of persistent toxic substances for the clam *Tapes philipinarum* in the Lagoon of Venice, Italy. *Environ Toxicol Chem* 23:1575–1582.
14. Micheletti C, Critto A, Marcomini A. 2007. Assessment of ecological risk from bioaccumulation of PCDD/Fs and dioxin-like PCBs in a coastal lagoon, *Environ Int* 33:45–55
15. Venice Water Authority. 2002. Monitoraggio delle acque della laguna di Venezia. Final Report. SAMA, Venice, Italy.
16. Venice Water Authority. 1999. Mappatura dell'inquinamento dei fondali lagunari. Final Report. Consorzio Venezia Nuova, Venice, Italy.
17. Dalla Valle M, Marcomini A, Sfriso A, Sweetman AJ, Jones KC. 2002. Estimation of PCDD/F distribution and fluxes in the Venice Lagoon, Italy: Combining measurement and modeling approaches. *Chemosphere* 51:603–616.
18. Carrer S, Coffaro G, Bocci M, Barbanti A. 2005. Modeling partitioning and distribution of micropollutants in the Lagoon of Venice: a first step toward a comprehensive ecotoxicological model. *Ecol Model* 184:83–101.
19. Critto A, Carlon C, Marcomini A. 2005. Screening ecological risk assessment for the benthic community in the Venice Lagoon (Italy). *Environ Int* 31:1094–1100.
20. Facca C, Sfriso A, Socal G. 2002. Changes in abundance and composition of phytoplankton and macrophytobenthos due to increased sediment fluxes in the Venice Lagoon, Italy. *Estuar Coast Shelf Sci* 54:773–792.
21. Provincia di Venezia. 1998. Piano per la gestione delle risorse alieutiche delle lagune della. Provincia di Venezia. Final Report. Venice, Italy.
22. Arnot JA, Gobas FAPC. 2004. A food-web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environ Toxicol Chem* 23:2343–2355.
23. Steevens JA, Reiss M, Pawlisz AV. 2005. A methodology for deriving tissue residue benchmarks for aquatic biota: A case study for fish exposed to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and equivalents. *Integr Environ Assess Manag* 1:142–151.
24. Jones DS, Barnthouse LW, Suter GW, Efroymson RA, Field JM, Beauchamp JJ. 1999. Ecological risk assessment in a large river–reservoir: 3. Benthic invertebrates. *Environ Toxicol Chem* 18: 599–609.
25. Van den Berg M, Birnbaum L, Bosveld ATC, Brunstorom B, Cook P, Freely M, Giesy JP, Handberg A, Hasewaga R, Kennedy SW, Kubiak T, Larsen JC, van Leeuwen FXR, Liem AKD, Nolt C, Peterson RE, Poellinger L, Safe S, Schrenk D, Tillitt D, Tysklind M, Younes M, Waern F, Zacharewski T, 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ Health Perspect* 106:775–792.
26. U.S. Environmental Protection Agency. 2002. Calculating upper confidence limits for exposure point concentrations at hazardous waste sites. OSWER 9285.6-10. Technical guidance. Office of Emergency and Remedial Response, Washington, DC.
27. U.S. Environmental Protection Agency. 2004. ProUCL version 3.0 user guide. EPA/600/R04/079. Office of Research and Development, Washington, DC.
28. Seth R, Mackay D, Muncke J. 1999. Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. *Environ Sci Technol* 33:2390–2394.
29. Carrer S, Opitz S. 1999. Trophic network model of a shallow water area in the northern part of the Lagoon of Venice. *Ecol Model* 124:193–219.
30. Libralato S, Pastres R, Pranovi F, Raicevich S, Granzotto A, Giovanardi O, Torricelli P. 2002. Comparison between the energy flow networks of two habitats in the Venice Lagoon. *Mar Ecol* 23:228–236.
31. Pranovi F, Libralato S, Raicevich S, Granzotto S, Pastres R, Giovanardi O. 2003. Mechanical clam dredging in Venice Lagoon: Ecosystem effects evaluated with a trophic mass-balance model. *Mar Biol* 143:393–403.
32. Sorokin PY, Sorokin IY, Zakuskina OY, Ravagnan GP. 2002. On the changing ecology of the Venice Lagoon. *Hydrobiologia* 487: 1–18.
33. Sorokin PY, Sorokin IY, Boscolo R, Giovanardi O. 2004. Bloom of picocyanobacteria in the Venice Lagoon during summer–autumn 2001: Ecological sequences. *Hydrobiologia* 523:71–85.
34. Gobas FAPC, Pasternak JP, Lien K, Duncan RK. 1998. Development and field validation of a multimedia exposure assessment model for waste load allocation in aquatic ecosystems: application to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 2,3,7,8-tetrachlorodibenzofuran in the Fraser River watershed. *Environ Sci Technol* 32:2442–2449.
35. Morrison HA, Whittle DM, Niimi AJ, Metcalfe CD. 1999. Application of a food-web bioaccumulation model for the prediction of polychlorinated biphenyl, dioxin, and furan congener concentrations in Lake Ontario aquatic biota. *Can J Fish Aquat Sci* 56: 1389–1400.
36. Van der Linde A, Hendricks AJ, Sijm DTHM. 2001. Estimating biotransformation rate constants of organic chemicals from modeled and measured elimination rates. *Chemosphere* 44:423–435.
37. Niimi AJ. 1996. Evaluation of PCBs and PCDD/Fs retention by aquatic organisms. *Sci Total Environ* 192:123–150.
38. Guerzoni S, Rossigni P, Molinaroli E, Rampazzo G, Raccanelli S. 2004. Measurement of atmospheric deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the Lagoon of Venice, Italy. *Chemosphere* 54:1309–1317.
39. Cucco A, Umgiesser G. 2006. Modeling the Venice Lagoon residence time. *Ecol Model* 193:34–51.
40. Zuliani A, Zaggia L, Collarini F, Zonta R. 2005. Freshwater discharge from the drainage basin to the Venice Lagoon (Italy). *Environ Int* 31:929–938.
41. Sfriso A, Facca C, Marcomini A. 2004. Sedimentation rates and erosion processes in the Lagoon of Venice. *Environ Int* 31:983–992.
42. Mackay D, Shiu WY, Ma KC. 1992. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Compounds.* Lewis, Boca Raton, FL, USA.