



European environmental scenarios of chemical bioavailability in freshwater systems



Antonio Di Guardo ^{a,*}, Melissa Morselli ^a, Giuseppe Morabito ^b, Matteo Semplice ^c, Paul J. Van den Brink ^{d,e}, Frederik De Laender ^f

^a Department of Science and High Technology, University of Insubria, Via Valleggio 11, 22100 Como, CO, Italy

^b National Research Council, Institute for Ecosystem Study, Largo Tonolli 50, 28922 Verbania-Pallanza, Italy

^c Dipartimento di Matematica, Università degli Studi di Torino, Via C. Alberto 10, 10123 Torino, TO, Italy

^d Wageningen Environmental Research (Alterra), P.O. Box 47, 6700 AA Wageningen, The Netherlands

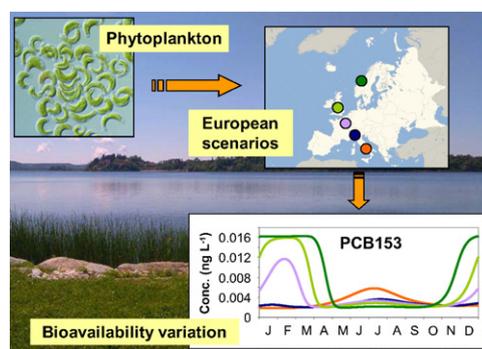
^e Department of Aquatic Ecology and Water Quality Management, Wageningen University, 6700 AA Wageningen, The Netherlands

^f University of Namur, Research Unit in Environmental and Evolutionary Ecology, Rue de Bruxelles 61, 5000 Namur, Belgium

HIGHLIGHTS

- In environmental risk assessment, there is a need for more realistic models and scenarios.
- Phytoplankton and organic carbon dynamics can cause exposure fluctuations.
- A new dynamic spatially-explicit model for aquatic environments was proposed.
- 5 dynamic scenarios representative of different European areas were developed.
- PCB bioavailable concentrations varied seasonally and across scenarios.

GRAPHICAL ABSTRACT



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ABSTRACT

In exposure prediction for environmental risk assessment, the transition to more dynamic and realistic modelling approaches and scenarios has been recently identified as a major challenge, since it would allow a more accurate prediction of bioavailable concentrations and their variations in space and time. In this work, an improved version of the multimedia model ChimERA fate, including a phytoplankton compartment and equations to calculate phytoplankton, detritus and dissolved organic matter variations in time, was developed. The model was parameterized to simulate five dynamic scenarios for shallow meso-eutrophic water bodies based on a latitudinal gradient (in Europe); such scenarios include seasonal profiles of water temperature, phytoplankton biomass, detritus, and dissolved organic matter. Model runs were performed for each scenario for 8 hydrophobic chemicals (PCB congeners), with the aim of investigating the influence of scenario characteristics and compound properties on bioavailable concentrations. The key processes were adsorption/uptake by phytoplankton and deposition to sediment of detritus-bound chemicals. The northern scenarios ("Scandinavia" and "UK") showed the highest bioavailable concentrations, with annual maximum/minimum concentration up to 25; in contrast, for example, maximum concentrations in the "Mediterranean" scenario were lower by a factor of 2 to 9 with respect to the northern ones (depending on chemical hydrophobicity), due to the generally higher biomass and carbon

* Corresponding author.

E-mail address: antonio.diguardo@uninsubria.it (A. Di Guardo).

levels, and showed only limited seasonal variability (up to a factor of 4). These results highlight the importance of including biomass and organic carbon dynamics in both modelling approaches and scenarios for the evaluation of exposure concentrations in aquatic environments.

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1. Introduction

There is a growing need to enhance environmental risk assessment (ERA) by trying to introduce more ecological realism in order to address the uncertainties of the current procedures. More specifically, the lack of ecological realism was underlined in a recent joint scientific opinion document from the three scientific committees of the European Commission (EC (European Commission), 2013; Vighi, 2013) and a number of suggestions were made to incorporate more complexity both in the exposure and in the effect field. Such complexity is needed to account for processes, which are currently not implemented in the existing assessment procedures, and for the spatial and temporal variability of both exposure and ecosystem response. Recently, Di Guardo and Hermens (2013) additionally pointed out research needs to address some of the challenges in the exposure prediction, raised in the scientific opinion mentioned above. While the current approach for studying the environmental fate in ERA in Europe employs steady-state models (such as EUSES; EC (European Commission), 2004) for industrial chemicals and unsteady-state models for pesticides (FOCUS (Forum for Co-ordination of pesticide fate models and their USE), 2001), their current cover of ecosystem dynamics is rather simple and based on a generally static “image” of the environmental compartments. If this on one side reduces complexity, on the other side it confides on a “steady-state attitude”, as defined by Di Guardo and Hermens (2013), in describing environmental processes. This may lead to neglect of specific and peculiar variations which may differentiate the response of ecosystems, such as the aquatic ones, located in different regions of the world. For example, models which are currently used for exposure assessment in aquatic environments generally ignore the role of primary producers (i.e., macrophytes and phytoplankton), detritus and dissolved organic matter (DOM) in influencing bioavailable concentrations (here defined as the truly water-dissolved concentration of a chemical), while evidence indicates the importance of such phases and their dynamics in driving the environmental fate of hydrophobic chemicals (e.g., Taylor et al., 1991; Dachs et al., 1999; Berglund et al., 2001; Schwarzenbach et al., 2003; Nizzetto et al., 2012).

The concept of “ecological scenario” has been used by many authors to describe specific sets of ecosystem complexity patterns. Parysow and Gertner (1997) used the concept of “ecological scenario” and employed conceptual models as tools to perform a “virtual experimentation” and a tool to predict the response of a system under a “wide range of conditions”. Another use of models for the analysis of ecological scenarios can be found in the paper by Kardaetz et al. (2008), who used an ecological model applied to a shallow lake to test 33 different scenarios characterized by a combination of nutrient loadings, climatic conditions, and manipulation events, such as resuspension of sediments. Recent works (De Laender et al., 2015; Franco et al., 2016) proposed definitions for “ecological” and “exposure scenarios” in the context of ERA. While the ecological scenario is defined “allocating one value to each variable (such as trophic state, interaction among species, and the complexity of food web) potentially influencing population- and ecosystem-level responses to an environmental perturbation”, the exposure scenario is related to chemical discharge and fate in the system (De Laender et al., 2015). The authors recognize though that both types of scenarios are influenced by the same variables, such as trophic state. In a more recent work by Rico et al. (2016), the authors describe the strong links between ecological and exposure scenarios in pesticide risk assessment and stressed the need for a comprehensive scenario (called “environmental”) that integrates “biotic and abiotic parameters and their input

values required to provide a realistic worst-case representation of the pesticide exposure, effects and recovery for the ecological entities that are evaluated”. Despite the authors focus on pesticides, the concept of environmental scenario can be expanded also to industrial chemicals.

The main objective of this work was to develop a dynamic modelling tool and five dynamic environmental scenarios for the evaluation of the temporal and spatial trends of bioavailability of chemicals in aquatic environments in an ERA framework. More specifically, an improved version of the dynamic multimedia model ChimERA fate (Morselli et al., 2015) was implemented by including a phytoplankton compartment (exchanging chemical with water) and ordinary differential equations (ODEs) to calculate autochthonous phytoplankton biomass, detritus and dissolved organic matter variations in time. The model was parameterized to simulate five environmental scenarios for shallow, meso-eutrophic lentic systems located at different latitudes in Europe. Such scenarios were defined as “environmental”, according to the terminology proposed by Rico et al. (2016), since they integrate traditional exposure parameters (pesticide use information, physical-chemical properties, environmental compartment properties, mass transfer coefficients, etc.) with some ecological aspects (e.g., primary producer biomass and detritus abundance and variations in time), also influencing chemical fate. It must be remarked that the modelled profiles do not depict specific water bodies located in the selected European areas, but rather realistic temporal patterns of autochthonous algal and carbon pools which can be encountered at different latitudes. This effort aims at answering the need for (1) more dynamic fate modelling tools to be used for ERA purposes and (2) spatial and temporal patterns of those parameters which are known to drive bioavailable concentrations in aquatic environments, for which complete and time-resolved records deriving from monitoring campaigns are seldom available.

2. Material and methods

2.1. Modelling approach

2.1.1. Multimedia fate model

In the present work, an improved version of the ChimERA fate model (Morselli et al., 2015) was implemented for the simulations (Fig. 1). The

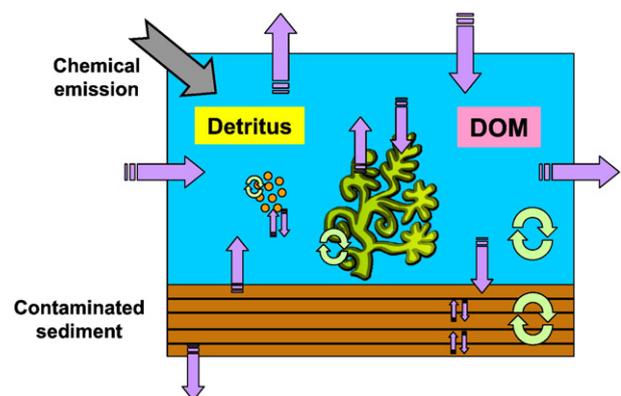


Fig. 1. Schematic representation of the improved ChimERA fate model unit, with the water, sediment, macrophyte and phytoplankton compartments and detritus and DOM sub-compartments. Purple arrows indicate chemical fluxes between compartments or accessing/leaving the system, while circular green arrows indicate degradation processes.

original model, based on the fugacity concept (Mackay, 2001) and on the dynamic water-sediment model DynA (Di Guardo et al., 2006), was developed to investigate the fate of organic chemicals in dynamic macrophyte-dominated shallow-water environments. Key features of the model are as follows: (1) the macrophyte compartment exchanges chemical with the water compartment, and is thereby capable of influencing concentrations in water; (2) particulate and dissolved organic matter are modelled as water sub-compartments (i.e., in equilibrium with water), and are also capable of affecting chemical bioavailable concentrations; (3) the sediment is discretized vertically to allow a more accurate description of the chemical movement with depth and to account for the spatial variability in exposure of benthic populations, and (4) the model domain is flexible, i.e., more model units can be combined to simulate complex environmental systems (e.g., networks of streams and ponds) or different zones of a single water body (e.g., littoral and pelagic in a lake). Details concerning model formulation and applications for macrophyte-dominated environments are reported elsewhere (Morselli et al., 2015), while in Text S1 an overview of model equations is provided.

In this study, the ChimERA fate model was improved by including a phytoplankton compartment. Chemical exchange between water and phytoplankton was modelled accounting for four main processes, two occurring at the phytoplankton cell surface (adsorption and desorption) and the other involving phytoplankton cell matrix (uptake and depuration) (Del Vento and Dachs, 2002). The two types of processes were modelled in parallel (Dachs et al., 1999). In the past two decades, several efforts have been devoted to the experimental determination of rate constants for these processes for a number of chemicals and phytoplankton species (e.g., Swackhamer and Skoglund, 1993; Sijm et al., 1998; Koelmans et al., 1999; Sobek et al., 2004; Ko et al., 2012). In the ChimERA fate model, the predictive relationships based on K_{OW} reported in Del Vento and Dachs (2002) were implemented to derive rate constants, as described in Text S2. Other modelled processes included degradation, settling to sediment, inflow and outflow with water, and biomass loss through mortality and excretion. For details concerning the calculation of D -values for all phytoplankton-related processes see Text S2 and Table S3. The model was coded using Microsoft Visual Basic 6.0 and the ordinary differential equations (ODEs) describing chemical mass balance were solved using a 5th-order accurate, diagonally implicit Runge-Kutta method with adaptive time stepping (Semplice et al., 2012).

2.1.2. ODEs for phytoplankton, detritus and DOM mass balance

While in the original ChimERA fate model, hourly records of macrophyte biomass and particulate and dissolved organic matter volumes were input through external files, in the present work 3 ODEs were included in the model to calculate hourly dynamics of phytoplankton biomass, detritus and DOM concentrations during the simulation period.

Phytoplankton and detritus temporal profiles were modelled using the ODEs reported in De Laender et al. (2015), with a slight modification to obtain results with hourly (instead of daily) resolution:

$$\frac{dPhy}{dt} = Phy \left\{ \left[1 - a \cdot \cos\left(\frac{2 \cdot \pi \cdot t}{24 \cdot 365}\right) \right] \cdot Gpp \cdot (1 - Resp - Excr) \cdot \left(1 - \frac{Phy}{K}\right) - Mort \right\} - Graz \quad (1)$$

where Phy (mg C m^{-2}) is phytoplankton biomass, t (h) is time, $[1 - a \cdot \cos(\frac{2 \cdot \pi \cdot t}{24 \cdot 365})]$ represents a seasonal forcing driven by the amplitude a (unitless), Gpp (h^{-1}) is gross primary production rate, $Resp$ and $Excr$ (both unitless) are the fractions of Gpp spent for respiration and excretion, respectively, K (mg C m^{-2}) is carrying capacity, $Mort$ (h^{-1}) is mortality rate and $Graz$ ($\text{mg C m}^{-2} \text{h}^{-1}$) represents the predation by higher trophic levels.

The ODE for detritus was modified to account for the amount of detritus lost via deposition to sediment and resuspended:

$$\frac{dDet}{dt} = Mort \cdot Phy - Diss \cdot Det - Dep + Res \quad (2)$$

where Det (mg C m^{-2}) is detritus concentration, $Diss$ (h^{-1}) is detritus dissolution rate, Dep ($\text{mg C m}^{-2} \text{h}^{-1}$) is detritus deposition, and Res ($\text{mg C m}^{-2} \text{h}^{-1}$) is detritus resuspension.

The ODE for DOM was modified from the one reported in De Laender et al. (2008), based on the AQUATOX model (USEPA, 2000; Park et al., 2008). Since the environmental systems described in this work are phytoplankton-dominated small lakes, contributions to DOM from macrophyte excretion were neglected. Moreover, since consumer biomass is generally much lower than primary producer biomass, the contribution of zooplankton to DOM was also neglected. Therefore, excretion from phytoplankton was the only source of DOM considered. DOM (mg C m^{-2}) variation in time was thus calculated as

$$\frac{dDOM}{dt} = ExcrR \cdot Phy - Dec \cdot DOM \quad (3)$$

where $ExcrR$ is the excretion rate (h^{-1}) and Dec is DOM decomposition rate (h^{-1}).

Eqs. (1)–(3) were coded in Microsoft Visual Basic 6.0 and solved simultaneously with chemical mass balance ODEs, thus allowing chemical fate to be affected by phytoplankton biomass, detritus and DOM at each time step.

2.1.3. Evaluation and sensitivity analysis

A preliminary evaluation was performed to investigate model accuracy in predicting hydrophobic chemical uptake in phytoplankton. As case studies, two lakes (L110, oligotrophic, and L227, eutrophic) located in the Experimental Lake Area of north-western Ontario, Canada, were selected (Jeremiason et al., 1999). For model evaluation purposes, the water and sediment-trap concentrations of two PCBs (congeners 52 and 153) measured in the two lakes during 1994 were selected (Jeremiason, 1997; Jeremiason et al., 1999). The adopted physical-chemical properties for the two PCBs are reported in Table S4, while in Table S5 lake characteristics and model parameters for the two case studies are listed. More details on methods can be found in Text S3.

A sensitivity analysis was also performed to identify the most influential parameters on the fate of two chemicals characterized by different hydrophobicity and persistence (pyrene and lambda-cyhalothrin, Table S6). Water-dissolved and phytoplankton concentrations were selected as target, while tested parameters included physical-chemical properties and degradation half-lives, environmental and ecological scenario characteristics. The sensitivity analysis was performed by varying each parameter by 0.1% and calculating the corresponding index S , as reported in MacLeod et al. (2002). More details on methods can be found in Text S4.

2.2. Scenario development

The improved ChimERA fate model was parameterized to simulate five scenarios for shallow lentic water bodies (ponds) characterized by different temperature, phytoplankton, detritus, and DOM seasonal profiles as representative of five different European systems, namely Mediterranean, Northern Italy, Central Europe, UK and Scandinavia. Such scenarios refer to meso-eutrophic, lowland, shallow systems, which are probably the most widespread lake typology across Europe (Moe et al., 2008, 2012). Since primary production and other characteristics of ponds and shallow lakes can exhibit great variations in response to site-specific and instantaneous conditions (e.g., morphology, air temperature, and wind speed) (Reynolds, 2006), no efforts were devoted in this work to simulate specific water bodies located in the mentioned areas and/or specific periods. Instead, realistic annual profiles of the

simulated parameters were built to investigate the potential variability in exposure concentrations in different environmental and ecological conditions, which could be deemed as characteristic of the selected areas. Water temperature for each scenario was derived as described in Section 2.2.2 and input to ChimERA fate through an external file, while temporal patterns for phytoplankton, detritus and DOM were calculated by the model (Eqs. (1)–(3)), parameterized as described in Sections 2.2.3 and 2.2.4. The data collected from a reference water body located in Northern Italy (Lake Candia, see Section 2.2.1) were used to extrapolate temperature and grazing pressure for phytoplankton for all scenarios, and to evaluate model performance in predicting particulate and dissolved organic carbon (POC and DOC) levels.

2.2.1. Reference water body

Lake Candia is a small (1.26 km²), shallow (max depth 7.7 m, mean depth 4.7 m, theoretical water residence time 6.5 years), meso-eutrophic (i.e., yearly mean total phosphorus concentration between 20 and 40 µg L⁻¹) lowland lake located in Northern Italy (Fig. S1). This water body was selected since its limnological characteristics were investigated at least on a monthly basis for several years (1985–2010). The year 2000 was chosen as reference year in this exercise, since data were available for all the parameters of interest (temperature, chlorophyll, POC and DOC concentrations), together with other physical and chemical variables which were useful to get a complete characterization of the ecological status of the lake. Moreover, the year 2000 was representative of a relatively stable trophic condition of the lake, after the restoration intervention carried out since 1986 which aimed at reducing eutrophication (Giussani et al., 1990). In this year, total chlorophyll, POC and DOC were measured from March to December, taking samples at four water depths (integrated sample 0–2 m, 3 m, 4 m, integrated sample 5–6 m), while for temperature measurements were taken at 0.5 m depth intervals (Cozza et al., 1993; Callieri and Bertoni, 1999; Fig. S2).

2.2.2. Water temperature

In Lake Candia, temperature changes seasonally according to a regular pattern, which can be mathematically described by a polynomial regression of the type:

$$y = ax^5 - bx^4 + cx^3 - dx^2 + qx - h \quad (4)$$

where y is the average temperature of the water column, x is the Julian month (January = 1, February = 2 and so on) and a, b, c, d, g and h are constant coefficients. This equation, obtained fitting the temperature data measured in Lake Candia, was then used to estimate monthly values of temperature for the other scenarios. In order to take into account latitude-related differences in temperature, the coefficients of the equation were fine-tuned to reproduce a similar seasonal pattern, although starting from different winter minima and reaching different summer maxima. Yearly cycles of average monthly air temperature in four European cities were used as a reference to choose the most appropriate coefficients for the above equation: Trondheim (Scandinavian scenario), Manchester (UK scenario), Frankfurt (Central Europe scenario), and Naples (Mediterranean scenario). Data were taken from EuroMETEO (2016). The temperature profile for Northern Italy was built with the values measured in Lake Candia, but using Eq. (4) to derive the missing records for January and February (reference city: Milan). In Lake Candia, the water column temperature ranged from 4.5 °C in January to 25 °C in August. The following ranges were chosen for the other scenarios: from 4 °C in April to 20 °C in August for Scandinavia; from 5 °C in February to 24 °C in July for Central Europe; from 4.5 °C in March to 22 °C in August for UK; from 7 °C in January to 26 °C in August for Mediterranean. Since the ChimERA fate model needs hourly records of water temperature, the monthly values obtained for each scenario were linearly interpolated to reach the required hourly resolution.

2.2.3. Phytoplankton biomass

Gross phytoplankton biomass profiles (i.e., excluding grazing pressure) for the five scenarios were obtained by calibrating amplitude a and gross primary production rate Gpp (Eq. (1)), in order to obtain a realistic “shift” in primary production related to climatic conditions (Fig. S3). The other parameters were taken from the literature and considered as fixed among the five scenarios. More specifically, for phytoplankton, $Resp$ the fractions of gross primary production spent for respiration ($Resp$) and excretion ($Excr$) were both set to 0.1 (De Laender et al., 2015), while the mortality rate $Mort$ was set to 0.0083 h⁻¹ (i.e., 0.2 d⁻¹) (De Laender et al., 2015). A carrying capacity K of 20 mg w.w. L⁻¹ (i.e., 1 mg C L⁻¹ = 212.8 mg C m⁻², assuming a water depth of 4.7 m, as in Lake Candia) was selected for all scenarios, as representative of meso-eutrophic conditions (OECD (Organisation for Economic Co-operation and Development), 1982; Håkanson and Peters, 1995).

The Northern Italy profile was depicted first using, as a guide, the total chlorophyll data measured in Lake Candia during the year 2000 converted into fresh phytoplankton biomass. For this purpose a fixed chlorophyll proportion of 0.00505 (i.e., 0.505% chlorophyll of phytoplankton wet weight) was adopted as an average of literature values (from 21 works) reviewed by Kasprzak et al. (2008). Although the reference approach referred to chlorophyll a , we considered total chlorophyll as equal to chlorophyll a , since the difference between the two values is usually small (Rice et al., 2012). A fixed organic carbon fraction of 0.05 was used to convert fresh biomass values into carbon-normalized phytoplankton concentrations (Reynolds, 2006). An average Gpp for each scenario was calculated by means a growth rate-temperature relationship derived from data reported in Reynolds (2006) for *Aphanizomenon* sp. ($R^2 = 0.9801$, $p = 1.52 \cdot 10^{-4}$, $n = 6$). Although *Aphanizomenon* cannot be considered as the most representative *taxon* for the systems investigated here, its growth rates are within the range of those of the most common freshwater algae (Reynolds, 2006). The calculated Gpp values refer to the yearly average water temperature calculated for the different scenarios. Amplitude a was scaled accordingly, with values ranging from 0.5 to 1 to reproduce latitude-related differences in growing season duration. A summary of the values adopted for Gpp and a is provided in Table 1.

Afterwards, net phytoplankton biomass for all scenarios was calculated applying a variable grazing pressure (mg C m⁻² h⁻¹) to the gross biomass profiles obtained as explained above. The year 2000 chlorophyll in Lake Candia clearly showed four peaks, thus reflecting at least four algal bloom events. However, the analysis of the whole dataset (years 1998–2010) revealed a great variability in total chlorophyll profiles (Fig. S4), with no clear seasonality but at least two biomass peaks in spring and autumn. For this reason, and since simulating specific years or situations was beyond the scope of this work, grazing pressure was applied to simulate, for the Northern Italy scenario, a net phytoplankton biomass profile characterized by a peak occurring in spring (around mid March) and a second one in autumn (early November). In Fig. S5, the result of the application of the grazing pressure to the gross phytoplankton biomass profile for the Northern Italy scenario is reported. Grazing for all other scenarios was derived by means of a 2nd-order polynomial relationship devised for the Northern Italy scenario between gross phytoplankton biomass and grazing (Fig. S6). In cases in which the grazing

Table 1

Summary of the values adopted for a (unitless) and Gpp (d⁻¹) for the different scenarios.

	a (unitless)	Gpp (d ⁻¹)
Mediterranean	0.5	0.74
Northern Italy	0.5	0.6
Central Europe	0.65	0.55
UK	0.75	0.48
Scandinavia	1	0.33

pressure calculated for a given hour exceeded the available phytoplankton biomass, the net phytoplankton value was set to initial value.

2.2.4. Detritus and DOM

Detritus concentrations were simulated for all scenarios using Eq. (2). A dissolution rate $Diss$ of $4.2 \cdot 10^{-4} \text{ h}^{-1}$ (i.e., 0.01 d^{-1}) (De Laender et al., 2015) was selected, and detritus deposition Dep ($\text{mg C m}^{-2} \text{ h}^{-1}$) was calculated as the product of detritus concentration Det during the previous hour, a solid deposition velocity of $4.2 \cdot 10^{-2} \text{ m h}^{-1}$ (i.e., 1 m d^{-1} ; Armitage et al., 2008) and an average water column depth of 4.7 m. Resuspension Res ($\text{mg C m}^{-2} \text{ h}^{-1}$) was modelled as a fraction of Dep ($=0.7 \cdot Dep$; Armitage et al., 2008).

DOM profiles were calculated for all scenarios according to Eq. (3). Excretion rate $ExcrR$ (h^{-1}) was set to $0.1 \cdot Gpp$ (De Laender et al., 2015), while decomposition rate Dec was set to 0.25 times the maximum decomposition rate reported in De Laender et al. (2008) ($1.2 \cdot 10^{-2} \text{ h}^{-1} = 0.29 \text{ d}^{-1}$).

2.3. Model parameterization for scenario analysis

A set of illustrative simulations was performed for a phytoplankton-dominated system to show the potential variability in the bioavailable concentration derived from different phytoplankton biomass, detritus and DOM levels which can be encountered in water bodies located at different latitudes. It must be remarked that efforts were focused on autochthonous biomass and organic carbon, while no attention was devoted to simulate specific environments, in which allochthonous inputs can be dominant (e.g., DOC in some northern European lakes). Two-year simulations were run for eight PCB congeners (15, 33, 52, 101, 153, 195, 207 and 208; Table S7), representative of an array of $\log K_{OW}$. The simulated system consisted of a 450-m^2 , 50-cm deep pond overlaying a 1-cm deep sediment compartment, similar to that described in Morselli et al. (2015) but neglecting the macrophyte compartment and the spatial discretization. A constant water flow of $0.09 \text{ m}^3 \text{ h}^{-1}$ was selected to obtain an average residence time in the pond of about 100 days (Peretyatko et al., 2007, 2009). Water temperature, as well as phytoplankton biomass, detritus and DOM concentrations, were scenario-specific and were calculated as detailed as described in 2.2. Other parameters, such as sediment depth and properties, densities and particle setting velocity, were common to all scenarios. No efforts were made to simulate realistic PCB concentrations in water; instead, for comparison purposes, the same constant discharge ($=1 \cdot 10^{-10} \text{ mol}$) was adopted for all the investigated chemicals. A summary of input parameters is reported in Table S8.

3. Results and discussion

3.1. Model evaluation

The results of the comparisons between predicted and measured concentrations in phytoplankton for the two chemicals and lakes are reported in Table S9 and Fig. S7. It must be remarked that efforts were focused on assessing the overall accuracy of algal uptake predictions rather than on reproducing temporal trends of concentrations in phytoplankton. For PCB52 the agreement was very good, with predictions within a factor of 2 to 2.5 of observations, while for PCB153 the model generally underestimated uptake by an average factor of 4, suggesting the need for refinements in the estimation of rate constants for highly hydrophobic chemicals. However, considering all the uncertainties in model parameterization, mostly due to the low temporal resolution of the input data available, the ChimERA fate model performance can be considered as satisfying. Additional details on these results can be found in Text S5.

3.2. Sensitivity analysis

Results, depicted in Fig. S8, suggested that (1) phytoplankton-related rate constants, regulating chemical adsorption, desorption, uptake and depuration processes, were among the most influential parameters for phytoplankton concentrations, and (2) for both targets and chemicals, together with chemical emission, K_{OW} and detritus-related parameters (organic carbon fraction, volume and deposition velocity) were the most influential variables, confirming the role of detritus and the organic matter cycle in influencing the fate of hydrophobic chemicals (and in particular of those with $\log K_{OW} > 5.5$) in lentic water bodies (Armitage et al., 2008; Nfon et al., 2011). Results are discussed in detail in Text S6.

3.3. Scenario description

In Fig. 2, the temporal profiles of the four driving parameters (water temperature, phytoplankton biomass, detritus and DOC concentrations) for the five scenarios are reported. It must be remarked that such profiles depict autochthonous contributions only and were developed to isolate their role in influencing bioavailability; for this reason, a full

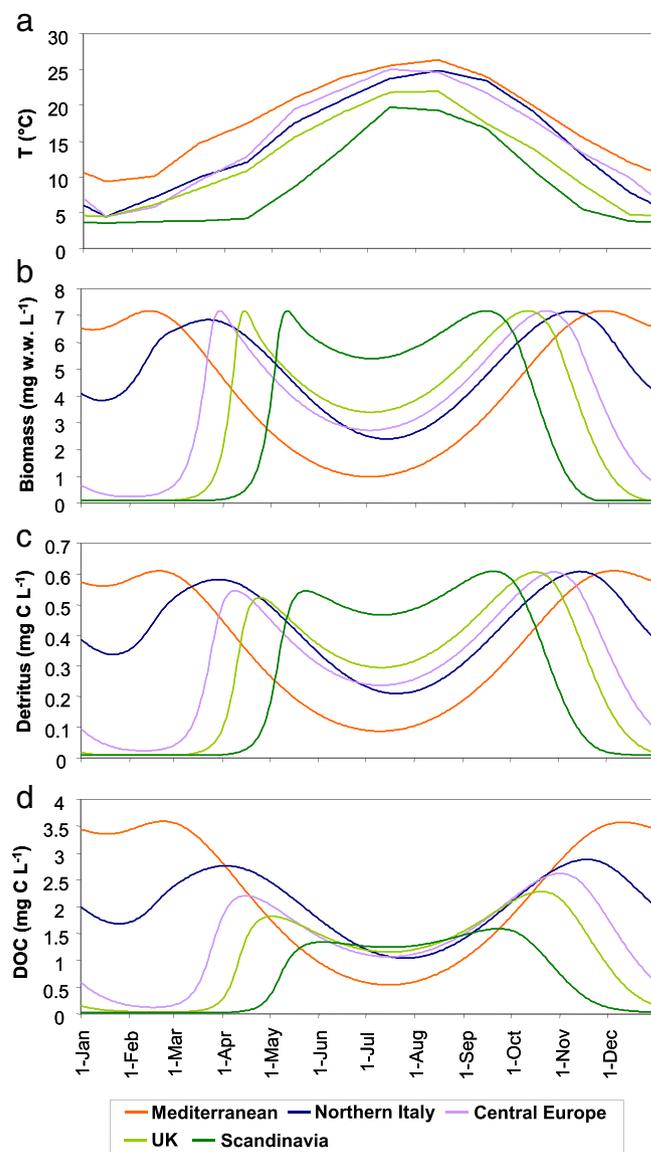


Fig. 2. Temporal profiles of (a) water temperature, (b) net phytoplankton biomass (mg w.w. L^{-1}), (c) detritus (mg C L^{-1}) and (d) DOC concentrations (mg C L^{-1}) for the 5 identified scenarios.

comparison with existing systems, where allochthonous carbon pools can be relevant or even dominant, was not performed. However, in the following discussion, a few examples from the literature are reported to show that the adopted values for the four parameters can be considered as realistic autochthonous values. The annual patterns were simulated as driven by latitude-related conditions (i.e., temperature and light, expressed by the different parameters in the mass-balance ODEs). Moreover, in order to help the comparison between the different scenarios, temperature-related effects such as ice cover of the water bodies during winter months, summer drought or other changes in water regime, were excluded. In the following discussion, acronyms will be used to identify scenarios: MED for Mediterranean, NIT for Northern Italy, CEU for Central Europe, UK for United Kingdom and SCA for Scandinavia.

Water temperature (Fig. 2a) in MED had a 26 °C maximum in August and values always larger than 9 °C; NIT and CEU scenarios showed similar behaviours, with maximum temperatures around 25 °C in July and August and minimum around 5–6 °C; highest temperatures in UK were around 22 °C, while the SCA scenario was characterized by a limited amplitude of the warmer period (from April–May to October–November) and maximum temperatures around 19–20 °C. The profiles devised here were in line with those found in the literature for some European shallow water bodies: the MED pattern, for example, agreed with that recorded in a Portuguese shallow lake (de Figueiredo et al., 2006), where temperature ranged from 10 to 27 °C and was maximum between June and August; similarly, six ponds in Belgium showed a mean temperature (from May to September) ranging from 20 to 23 °C (Peretyatko et al., 2009), in agreement with the CEU profile outlined in this work.

Since all scenarios were meso-eutrophic and assigned the same carrying capacity K (see Section 2.2.3), the highest values reached by phytoplankton biomass were similar in all scenarios; however, due to the selection of scenario-specific amplitudes a and growth rates G_{pp} , biomass maxima occurred in different periods (Fig. 2b). For example, while the NIT scenario was characterized by two well defined biomass peaks in spring and autumn, in MED the first peak occurred already in February, while the second was observed in December. In both NIT and MED scenarios, the lowest values occurred in the summer period, with a minimum in July. In contrast, the CEU, UK and SCA scenarios showed progressively shorter productive periods, with a less pronounced bi-modal behaviour and extremely low values during winter months. While in NIT and MED the biomass range of variability (max/min) was limited (by a factor of 3 and 7, respectively), the range increased with latitude and was around 30 for the CEU scenario and as high as 70 for the UK and SCA scenarios. A similar seasonal variability was observed, for example, in the chlorophyll a values measured in sixteen ponds in Belgium (average max/min ratios around 26; Peretyatko et al., 2007), in agreement with the CEU scenario. Detritus profiles (Fig. 2c) closely followed those of phytoplankton biomass, while a slightly different picture appeared for DOM (reported as DOC in Fig. 2d, assuming $DOC = 0.5 \cdot DOM$), which partially followed the behaviour observed for algal biomass and detritus, but with lower values moving from NIT/MED to higher-latitude scenarios. This can be ascribed to the description of the DOM mass balance (Eq. (3)), in which the source term was proportional to G_{pp} and thus temperature-related, leading to lower DOM (and thus DOC) production at lower temperatures. The inclusion of a temperature dependent DOM degradation term in Eq. (3) may improve the realism of predictions, but more data for model parameterization would be required. In terms of variability range, the same considerations made for algae and detritus can be extended to detritus and DOM. For the Northern Italy scenario, a comparison between the predicted profiles and POC/DOC measurements taken in Lake Candia was performed, indicating a slight underestimation of POC (derived from both phytoplankton and detritus) and a more pronounced underestimation for DOC (by a factor of 1.5 to 4); this

was related to the fact that the model excludes allochthonous contributions (for more details see Text S7 and Figs. S9 and S10). For example, in northern European shallow water bodies, DOC concentrations can be higher by an order of magnitude or more with respect to the values devised in this work (Fig. 2d) due to the presence of high concentrations of allochthonous humic substances reaching water bodies via runoff (e.g., Sobek et al., 2006; Dyson et al., 2011). However, the predicted POC/DOC ratios (around 0.25 for all scenarios) were consistent with those reported by Parszuto and Kaliszewska (2007), whom investigated four lakes in Poland; moreover, the predicted DOC concentrations were in agreement with the most frequently measured values in the 7500 lakes investigated by Sobek et al. (2007).

The different amplitude of the variability of phytoplankton biomass, detritus and DOM in the five scenarios is expected to strongly influence bioavailable concentration patterns of hydrophobic chemicals. This will be discussed in the Scenario analysis (see 3.4).

3.4. Scenario analysis

3.4.1. Exposure temporal patterns in the five scenarios

In Fig. 3, the predicted temporal profiles of water-dissolved (i.e., bioavailable) concentrations for three selected PCBs (52, 153 and 208) are reported, while results for all the other modelled chemicals (PCB15, 33, 101, 195, and 207) can be found in Fig. S11. The highest concentrations were predicted from January to March/April and in the last two months of the year (Nov–Dec) for the CE, UK and SCA scenarios, while a reverse situation (with highest concentrations from May to September) characterized the NIT and MED scenarios. This behaviour can be associated with phytoplankton biomass, detritus and DOC concentration profiles (Fig. 2b–d), which regulated exposure concentrations in the five scenarios. As a general rule, exposure concentrations were highest when phytoplankton biomass, detritus and DOC were lowest, and this is also the reason why, in absolute terms, the highest concentrations of each chemical were observed in winter and early spring in the UK and SKA

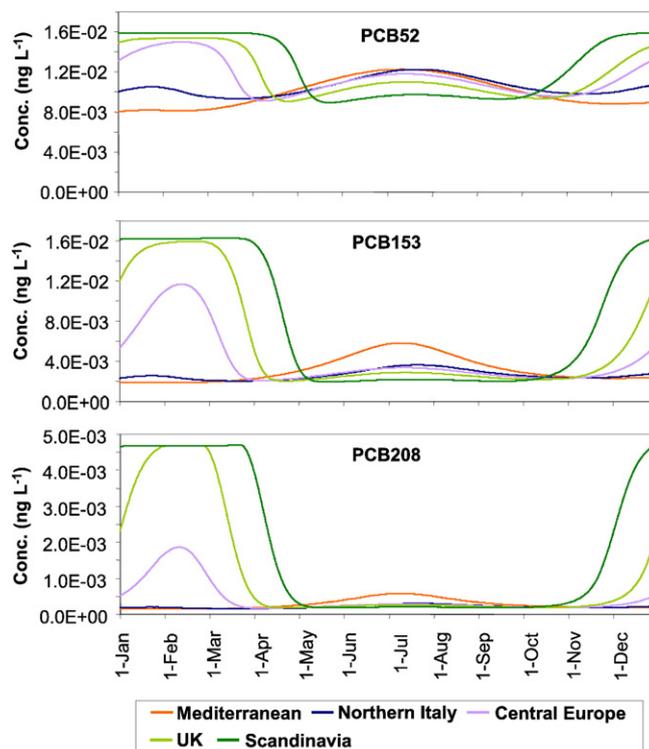


Fig. 3. Modelled profiles of water-dissolved concentrations (ng L^{-1}) in the five scenarios for PCB52, 153, and 208.

scenarios, characterized by similar winter biomass and OC levels. Temporal variations in PCB water-dissolved concentrations and air-water fluxes have been highlighted in a number of lakes and shallow-water bodies (e.g., Jeremiason et al., 1999; Nizzetto et al., 2012) and have sometimes been related to the biological pump operated by phytoplankton (Dachs et al., 1999; Nizzetto et al., 2012). In this work, the processes affecting water-dissolved concentrations differed according to compound properties and in particular $\log K_{OW}$. In order to clarify this concept, in Fig. S12, the processes responsible for chemical depletion from water were plotted as fluxes (mol) for the three selected chemicals and two scenarios (MED and SCA); for simplicity, two days of the year (February 15th, when phytoplankton biomass, detritus and DOC were around their maximum in MED and minimum in SCA, and July 1st, with opposite characteristics) were selected. It can be noticed that (1) for each chemical, the most influential processes were the same in the two compared scenarios, despite, in terms of flux entity, the February plot for MED was more similar to the July one for SCA and the July plot for MED was closer to the February one for SCA. This behaviour was in line with the “opposite” behaviour of phytoplankton biomass, detritus and DOC in the two scenarios (Fig. 2b–d). (2) For chemicals with $\log K_{OW} < 6.4$ (such as PCB15, PCB 33 - results not shown - and PCB52), chemical adsorption by algae dominated depletion from water, followed by deposition onto sediment surface of detritus-bound chemical, volatilization from water and uptake by algae. Adsorption by algae exceeded detritus deposition by a factor of 7.5 for PCB52 (for both scenarios and periods; see Fig. S12) and by more than an order of magnitude for PCB15 (results not shown). (3) In contrast, for highly hydrophobic chemicals ($\log K_{OW} \geq 6.4$), the dominant process was deposition of detritus-bound chemical, followed by adsorption and uptake by algae; an exception was PCB153 during biomass and OC minimum, when volatilization dominated depletion from water. The dominance of detritus-bound chemical deposition with respect to the other processes increased with $\log K_{OW}$: for example, for PCB153, this process exceeded adsorption to algae by a factor of 2, while for PCB208 the difference almost reached 2 orders of magnitude (Fig. S12). These results confirmed the importance of particle deposition in driving the fate of hydrophobic chemicals in shallow water bodies, which was also demonstrated in recent mesocosm experiments and modelling exercises (e.g., Armitage et al., 2008; Nfon et al., 2011; Morselli et al., 2015; Padilla et al., 2015); in addition, the strong need for an accurate description and parameterization of detritus mass balance when predicting bioavailability of such chemicals was stressed. For the set of illustrative simulations presented here, DOC only had a limited influence on bioavailable concentrations: chemical outflow from the system mediated by DOC was among the less influential processes for PCB15 (results not shown) and 52, while for PCB153 and 208 this flux increased becoming comparable to volatilization.

3.4.2. Exposure variability and relationship with chemical $\log K_{OW}$

As previously stated, bioavailable concentration profiles in the different scenarios showed minima and maxima mostly related to phytoplankton biomass and detritus abundance as well as to compound properties. In order to investigate the potential variability of bioavailable concentrations in each scenario during the annual cycle, the ratios between maximum and minimum water-dissolved concentrations were calculated for all chemicals. In Fig. 4, all ratios were reported as a function of $\log K_{OW}$. The lowest variations were observed for the NIT and the MED scenarios (with ratios from 1.2 to 1.9 for NIT and from 1.3 to 3.9 for MED), as the result of the limited annual changes in the driving parameters (phytoplankton biomass and detritus) (Fig. 2b–d). Ratios linearly increased with $\log K_{OW}$ ($R^2 = 0.89$ for MED and 0.93 for NIT). The tendency of ratios to increase with $\log K_{OW}$ was progressively more evident for the Central Europe (CEU) scenario (ratios up to 10.8) and for the UK and SCA scenarios (ratios up to 25). Again, this was the response to the highest variations in the adopted phytoplankton biomass and detritus profiles, which reached very low levels during the winter and values close to the NIT and MED maxima during the summer (Fig. 2b–d). For the CEU, UK and SCA scenarios, data were best fit by linear regression if PCB15 and PCB33 data points ($\log K_{OW} = 5.3$ and 5.8, respectively) were excluded ($R^2 = 0.94$ for CEU, 0.90 for UK, and 0.91 for SCA), indicating that for chemicals with $\log K_{OW} > 6$ the amplitude of seasonal changes increased more sharply with chemical hydrophobicity. Moreover, $\log K_{OW}$ around 6 represented a kind of “threshold” after which the effect of changes in scenario conditions became much more effective on bioavailable concentrations. These results suggest that the highest variability in bioavailable concentrations during the annual cycle (and under the assumption of a constant direct discharge to the water body) must be expected in scenarios where changes in primary producer biomass and, more generally, in OC abundance, are highest; moreover, the entity of such variations can exceed one order of magnitude, if biomass and OC oscillations such as those depicted in Fig. 2b–d are encountered.

3.4.3. Concentration depleting capacity of the different scenarios

In order to further investigate bioavailable concentration variability in each scenario and its relationship with compound properties and OC abundance, the predicted concentration depletion (%) with respect to maximum concentrations in each scenario was calculated as a function of $\log K_{OW}$ and POC (mg L^{-1}). Since, as stated before, phytoplankton and detritus were the driving parameters in affecting water-dissolved chemical levels, POC was meant here as deriving from both contributions (i.e., phytoplankton-associated + detritus-associated organic carbon). For each scenario and chemical, the maximum concentrations reached during the simulation period were first determined; afterwards, depletion was calculated for different POC levels (i.e., from

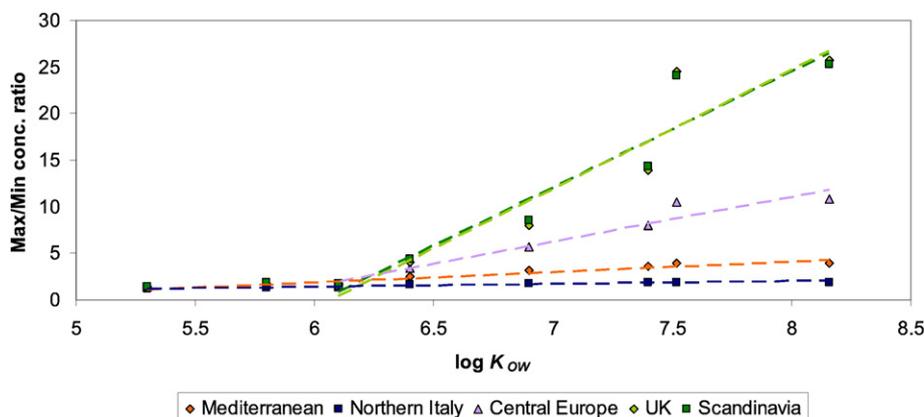


Fig. 4. Plot of $\log K_{OW}$ vs. ratios between the maximum and minimum concentrations during the simulation period, expressing the amplitude of seasonal changes in bioavailability in each scenario.

0.05 to 0.95 mg L⁻¹ with a step of 0.1 mg L⁻¹) by assessing the variation of the predicted bioavailable concentration (at a given time in which the desired POC value was observed) with respect to the maximum one. Results are reported in Fig. 5, with different depletion intensities depicted by means of a colour scale and PCB congeners 15, 33, 101, 153, 195, 207, and 208 selected as representative of the different log *K*_{OW} intervals (see Table S4 for physical-chemical properties).

The lowest depletion intensities were observed for the NIT scenario, with values ranging from 1 to 39%. In MED, depletion was up to 74%, and in the CEU scenario, for chemicals with log *K*_{OW} > 7, depletion was higher than 80% already at POC levels around 0.3–0.4 mg L⁻¹. Finally,

the UK and SCA scenarios showed the highest depletion levels, and, for chemicals with log *K*_{OW} > 7.5, a depletion around 90% was observed for POC concentrations ≥ 0.2 mg L⁻¹. The differences among the five scenarios and the fact that the scenario depletion capacity apparently increases with latitude can be mostly ascribed to the fact that the calculated maximum concentrations refer to different POC levels: for example, the maximum concentrations observed in the NIT scenario refer to POC levels around 0.35 mg L⁻¹, while for SCA to definitely lower POC concentrations (<0.05 mg L⁻¹); consequently, the depletion in the SCA scenario is much more evident when POC levels go up to 1 mg L⁻¹. These results emphasized again that the highest bioavailable

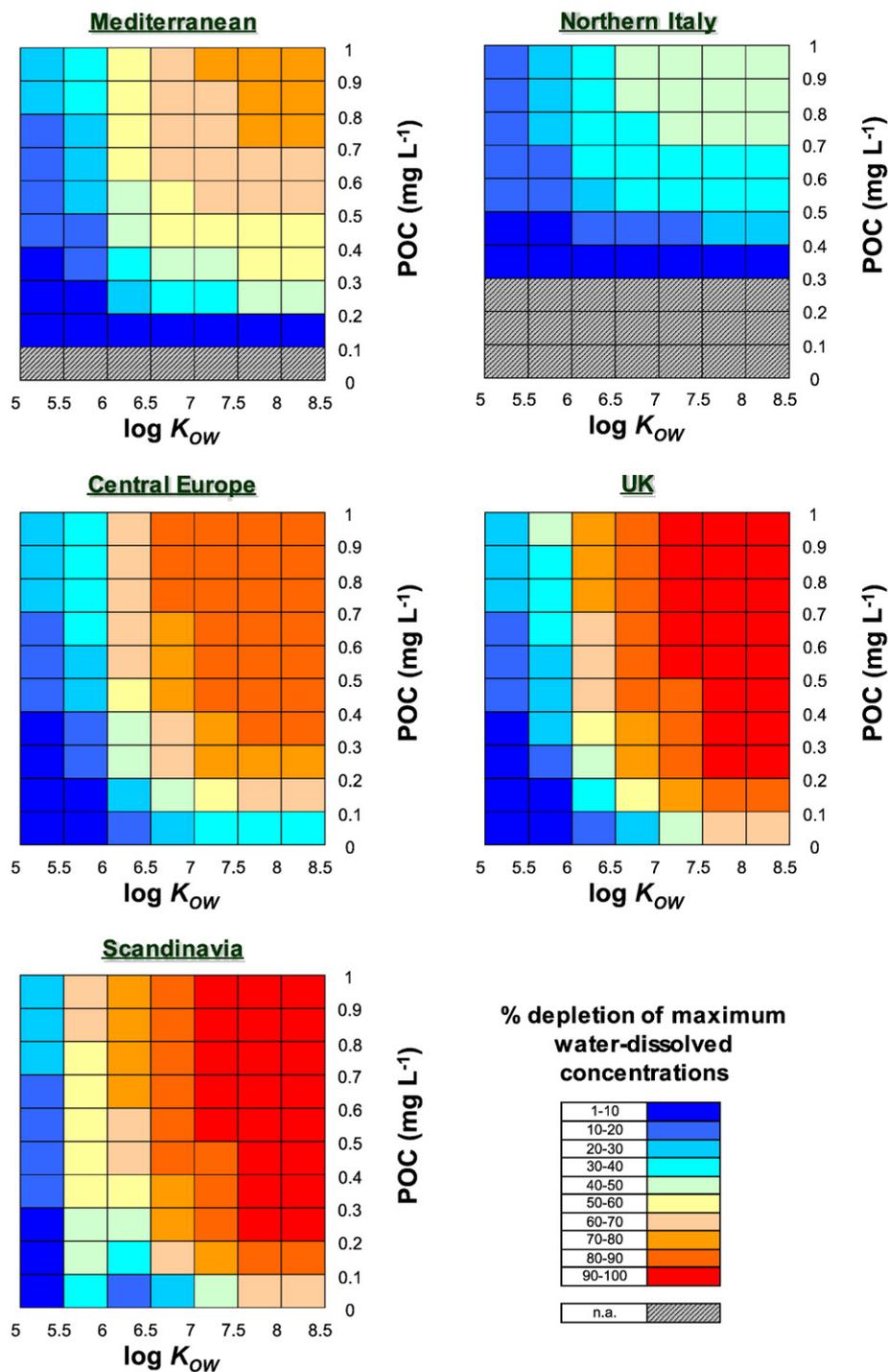


Fig. 5. Predicted depletion (%) with respect to maximum concentrations in the five scenarios as a function of log *K*_{OW} and POC concentration (mg L⁻¹), with POC calculated considering both phytoplankton and detritus contributions. "n.a." = not available (in Mediterranean and Northern Italy scenarios POC concentrations are always higher than 0.1 and 0.3 mg L⁻¹, respectively).

concentration variability is to be expected in water bodies in which high seasonal changes in primary producer biomass and, more generally, in organic carbon pools, occur. Moreover, despite the profiles depicted here may not be representative of specific real systems (e.g., since allochthonous contributions to POC can be important or even dominant), the charts reported in Fig. 5 allow deducing the potential depletion capacity of a given system independently from the POC source (autochthonous or allochthonous).

3.5. Implications for risk assessment

Risk characterization in ERA is currently performed by comparing a single predicted environmental concentration (PEC), deriving from worst-case exposure scenarios, with a single predicted no effect concentration (PNEC), generally extrapolated from individual-level laboratory toxicity data for a few standard test species (van Leeuwen and Vermeire, 2007). This approach is aimed to provide only some evidence of ecological risk, and protectiveness is favoured with respect to accuracy in predictions (van Leeuwen and Vermeire, 2007; Di Guardo and Hermens, 2013; EC (European Commission), 2013; Franco et al., 2016). The results of the illustrative simulations presented in this work highlighted that a large variability in exposure concentrations can be expected, especially for medium to high hydrophobic chemicals and in those environmental systems in which primary producer and OC temporal patterns show a pronounced seasonality. The selection of a single PEC implies a loss of information concerning exposure patterns and potential variability; moreover, the use of worst-case inputs for running the model does not necessarily lead to worst-case predictions and, as highlighted by Rico et al. (2016), such PECs may not correspond with realistic worst-case conditions from an ecological perspective. The development of comprehensive, dynamic environmental scenarios (Franco et al., 2016; Rico et al., 2016) and the application of dynamic fate models such as ChimERA fate in conjunction with selected effect models (De Laender et al., 2014, 2015) could thus provide insights on worst-case combinations which are currently not identified with traditional approaches.

4. Conclusions

In this work, an improved dynamic modelling tool for the evaluation of bioavailability of chemicals in aquatic environments in the ERA framework (ChimERA fate) and five dynamic environmental scenarios based on a latitudinal gradient for meso-eutrophic shallow-water lentic environments, were presented. The five scenarios account for both exposure and ecological aspects, including seasonal profiles of water temperature, and autochthonous phytoplankton biomass, detritus, and DOC. Despite the fact that such scenarios are not referred to specific water bodies (e.g. allochthonous contributions were not modelled), they allowed the investigation of the role of phytoplankton, detritus and DOC abundance and dynamics in influencing bioavailable concentrations of organic hydrophobic chemicals in different environmental conditions. Such comparison on a continental scale can also be used in other geographical contexts (other than Europe) to investigate the relevance of latitudinal driven gradients.

In this work the increasing need of realism and dynamics identified among the major challenges for ERA (EC (European Commission), 2013; Di Guardo and Hermens, 2013) was addressed. More specifically, both the ChimERA fate model and the application scenarios presented here accounted for the influence of primary producer biomass, detritus and DOC and their dynamics on bioavailability; these aspects are generally ignored in currently used approaches for ERA (e.g., FOCUS (FORum for Co-ordination of pesticide fate models and their USE), 2001; EC (European Commission), 2004). Results indicated the dominance of adsorption/uptake by phytoplankton and detritus-mediated chemical deposition onto sediment in determining chemical bioavailability; the latter process was also identified among the most influent in previous

works on macrophyte-dominated systems (Armitage et al., 2008; Nfon et al., 2011; Morselli et al., 2015). Future efforts will be thus focused on (1) refining the relationships used for estimating adsorption/desorption and uptake/depuration rate constants for phytoplankton, also by means of dedicated experiments and (2) enhancing detritus and DOC mass balances and their parameterization in the modelling approach, (3) implementing a more thorough model evaluation (with a focus on water-phytoplankton exchange and temporal patterns of concentrations in phytoplankton), and (4) performing a global sensitivity and uncertainty analyses. Moreover, the ChimERA fate model will be integrated with selected effect models and tested to explore the improved level of realism and the benefits deriving from such an approach (De Laender et al., 2014, 2015), which could represent a valuable tool to assess and regulate the behaviour of chemicals in shallow-water systems.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.12.084>.

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