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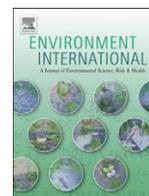
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# Theoretically exploring direct and indirect chemical effects across ecological and exposure scenarios using mechanistic fate and effects modelling



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## ABSTRACT

Predicting ecosystem response to chemicals is a complex problem in ecotoxicology and a challenge for risk assessors. The variables potentially influencing chemical fate and exposure define the exposure scenario while the variables determining effects at the ecosystem level define the ecological scenario. In absence of any empirical data, the objective of this paper is to present simulations by a fugacity-based fate model and a differential equation-based ecosystem model to theoretically explore how direct and indirect effects on invertebrate shallow pond communities vary with changing ecological and exposure scenarios. These simulations suggest that direct and indirect effects are larger in mesotrophic systems than in oligotrophic systems. In both trophic states, interaction strength (quantified using grazing rates) was suggested a more important driver for the size and recovery from direct and indirect effects than immigration rate. In general, weak interactions led to smaller direct and indirect effects. For chemicals targeting mesozooplankton only, indirect effects were common in (simple) food-chains but rare in (complex) food-webs. For chemicals directly affecting microzooplankton, the dominant zooplankton group in the modelled community, indirect effects occurred both in food-chains and food-webs. We conclude that the choice of the ecological and exposure scenarios in ecotoxicological modelling efforts needs to be justified because of its influence on the prevalence and magnitude of the predicted effects. Overall, more work needs to be done to empirically test the theoretical expectations formulated here.

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## 1. Introduction

Ecosystems are inherently complex and understanding how chemicals impact on their structure and functioning is at an incipient phase (Naito et al., 2003; De Laender et al., 2008b; Park et al., 2008; De Laender and Janssen, 2013). The number of variables potentially influencing how ecosystems respond to chemicals represents one dimension of this complexity. Although widely used, the concept of the 'ecological scenario' is, to the best of our knowledge, rarely defined. One approach to characterizing an ecological scenario consists of allocating one value to each variable potentially influencing population- and ecosystem-level responses to an environmental perturbation. Note that this approach does not constrain the number of variables needed to describe a given scenario, as this will depend on the ecosystem considered and the research questions asked.

Examples of variables making up an ecological scenario include trophic state, the degree of isolation of the exposed system, the interaction strength between species in a food-web and the complexity of this food-web. Trophic state may determine the response of individuals, populations, and ecosystems to chemicals through modifying resource availability (Noel et al., 2006; Pieters et al., 2006; Alexander et al., 2013; De Hoop et al., 2013; Gabsi et al., 2014). The degree of isolation will determine if immigration from areas with lower exposure levels can compensate for chemical effects and/or facilitate recovery and recolonization (Liess and Schulz, 1999; Caquet et al., 2007). Based on the ecological literature on disturbances in ecosystems, also interaction strength and food-web complexity can be hypothesised as key variables making up the ecological scenario. For example, the influence of these two variables on various stability measures has been a major topic in community and ecosystem ecology (May, 1972; Neutel et al., 2002; Allesina and Tang, 2012), although existing efforts have focused on random (non-specific) perturbations. To our knowledge, the influence of these two ecosystem descriptors on the response of ecosystems to chemicals has not been tested yet. We expect this response to be different for chemicals than for random perturbations because chemicals often affect specific taxa only. The

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way in which such direct impacts of chemicals travel through an ecological network such as a food-web will most likely depend on the identity of the impacted taxa.

Next to the ecological scenario, the exposure scenario is another dimension to the complexity surrounding ecological effect assessments at higher levels of biological organisation. Again, an approach to defining an exposure scenario consists of attributing values to variables determining chemical exposure. Such exposure is often related to chemical emissions in the environment (application and/or discharge). The timing of application is one potentially important variable making up the exposure scenario, although the influence of the application season is unclear at present (Willis et al., 2004; Van Wijngaarden et al., 2006). Other variables that characterize exposure include those determining chemical fate (e.g. partitioning coefficients) as well as chemical movement across compartments and degradation. In such view, the role of the ecological complexity in defining the exposure is often neglected or overlooked (Di Guardo and Hermens, 2013).

The influence of the exposure scenario on a chemical's effects on ecosystems needs to be examined in concert with that of the ecological scenario, as both scenarios may share common variables. More precisely, certain variables making up the ecological scenario will also define the exposure scenario, and vice versa. For example, trophic state, essentially a characteristic of the challenged ecosystem determining resource availability, will also influence chemical bioavailability in water, and therefore the actual exposure pelagic biota are facing. The timing of application, often considered as a part of the exposure scenario, will likewise determine the ecological scenario in case of strong seasonal fluctuations in community composition.

At present, no information is available on how ecosystem response to chemicals varies across different ecological and exposure scenarios. This may be partly due to the practical difficulty to experimentally test chemical effects on population- and ecosystem-level endpoints for a range of ecological and exposure scenarios and the resources that are required to do so. As opposed to experimental approaches, the use of mechanistic models does not suffer such constraints. Indeed, modelling can play a key role in theoretically exploring how ecological scenarios co-determine the ecological effects triggered by an array of exposure scenarios.

In the field of exposure and fate modelling, efforts are on-going to refine the incorporation of bioavailability into the exposure assessment of organic pollutants (Di Guardo et al., 2006; Infantino et al., 2013). Future efforts will include the evaluation and expression of the spatial and temporal variability of chemical fate in order to define more realistic exposure scenario (Di Guardo and Hermens, 2013). In recent years, advancements have been made in the field of mechanistic effect modelling as well, mostly at the population level (Grimm et al., 2009; Martin et al., 2013), and these efforts have led to strategies to enhance the realism of ecological effect assessments (Forbes et al., 2009). Currently, efforts are on-going to continue the upscaling of effects towards higher levels of biological organisation (De Laender et al., 2011; De Laender and Janssen, 2013).

The objective of the presented paper is to formulate theoretical expectations for ecological effects and recovery across a range of exposure and ecological scenarios, using a combined chemical fate and ecosystem model. The chemical fate model is based on the fugacity approach. The choice for a fugacity approach was based on the availability of a dynamic fugacity-based aquatic model (Di Guardo et al., 2006; Infantino et al., 2013), which could be easily modified to simulate exposure for this exercise. The ecosystem model is defined as a set of coupled ordinary differential equations, at present the only approach available to model ecosystem dynamics in ecotoxicology. We summarize effects on the biomasses of the included functional groups in two ways: (1) using the maximum difference in time between the exposed and control biomass, and (2) using the time-integrated biomass difference between the exposed and control dynamics. We consider both direct and indirect effects (Fleeger et al., 2003) across sixteen ecological scenarios, differing

in trophic state (oligo- vs. mesotrophic), the interaction strength between producers and consumers (high vs. low), the immigration rate (fast vs. slow), and the complexity of the ecological system (food-web vs. food-chain). The four chemicals considered represent all combinations of two sorption characteristics (hydrophobic vs. hydrophilic), and two toxicological profiles (targeting micro- vs. mesozooplankton). By also varying the season of emission between spring and late summer, a total of eight exposure scenarios were considered. The fate model was used to predict the dynamics of the water dissolved chemical concentrations, taking into account trophic state by using phytoplankton and detritus mass for bioavailability calculations. We stress that our exercise should be interpreted as a model-aided quantification of the theoretical expectations on how ecological effects of chemicals vary across ecological and exposure scenarios. In our discussion, we qualitatively confront our predictions with results from micro- and mesocosm studies but this comparison does not waive the need for a more formal confrontation with data in the future, when these become available.

## 2. Material and methods

### 2.1. Chemical fate model

Chemical fate was calculated using a modified version of the DynA (Di Guardo et al., 2006) and EcoDynA (Infantino et al., 2013) models. These models are fugacity-based (Mackay, 2001) and were developed to investigate the fate of organic chemicals in a dynamic aquatic system. Model dynamics depend on chemical emission (which can be varied on an hourly basis) and on environmental parameters. More specifically, model input includes hourly values of water temperature, water inflow and outflow rates and suspended solid concentration in water. Suspended solids are modelled as a water sub-compartment; equilibrium with water is therefore assumed. The presence of particulate organic carbon (POC) is simulated by defining the organic fraction of the suspended solids. In the implementation of the model used in the present work, also a dissolved organic matter (DOM) sub-compartment was included. More details concerning model formulation and the application in this paper can be found in Text S1.

For all simulations, the model was parameterized to represent a typical shallow pond, characterized by an area of 450 m<sup>2</sup> and a depth of 1 m. A water residence time of six months, sufficiently high to prevent the chemical outflow with POC and DOC to become the dominant fate process, was simulated, as the result of constant input and output water fluxes of 0.1 m<sup>3</sup> h<sup>-1</sup>. A seasonal profile of water temperature similar to those measured in a set of UK temperate ponds, with values ranging from 3 to 15 °C in winter and summer, respectively, was adopted (Martin, 1972; Young, 1975) (Fig. S1, Supporting information). The sediment compartment, in terms of the fraction of solids and fraction of organic carbon in solids, was parameterized elsewhere (Armitage et al., 2008).

### 2.2. Food-web model

A food-web model was implemented in R (R Development Core Team, 2010) as a set of ordinary differential equations. Each equation represented the dynamics of one functional group (mg C/m<sup>2</sup>), based on gain and loss processes quantified as surface-specific carbon exchange rates (mg C/m<sup>2</sup>/d), including functional group-specific immigration (Table 1 lists all parameters). The model included 6 functional groups: phytoplankton, omnivores, microzooplankton, mesozooplankton, detritivores, and invertebrate predators (consuming all heterotrophs) (Fig. 1). Phytoplankton growth was described as:

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

**Table 1**  
Parameters of the food-chain and food-web models.

Parameter	Explanation	Value	Unit	Source
<i>Abiotic</i>				
<i>a</i>	Amplitude of seasonal forcing	1		Scheffer et al. (1997)
<i>d</i>	Detritus dissolution rate	0.01	d <sup>-1</sup>	Donali et al. (1999)
<i>Biotic</i>				
All groups				
<i>I</i>	Immigration rate	10 <sup>-5</sup> (high); 10 <sup>-15</sup> (low)	mg C m <sup>-2</sup> d <sup>-1</sup>	Scenario-specific; similar to and smaller than (Scheffer et al., 1997), respectively
Phytoplankton				
<i>K</i>	Carrying capacity	50 (oligotrophic); 500 (mesotrophic)	mg C m <sup>-2</sup>	Scenario-specific (Carlson, 1977)
<i>Gpp</i>	Gross primary production rate	1.5	d <sup>-1</sup>	Moisan et al. (2002)
<i>Resp</i>	Fraction of Gpp spent to respiration	0.1		Bidwell (1977)
<i>Excr</i>	Fraction of Gpp spent to excretion	0.1		Baines and Pace (1991)
<i>Mort</i>	Mortality rate	0.2	d <sup>-1</sup>	Janse (2005)
Detritivores, omnivores, and predators				
<i>Ing, Het</i>	Ingestion rate	0.5	d <sup>-1</sup>	Hansen et al. (1997)
<i>AE, Het</i>	Assimilation efficiency	0.6		Hendriks (1999)
<i>Resp, Het</i>	Respiration rate	0.1	d <sup>-1</sup>	Park et al. (2008)
<i>Excr, Het</i>	Ratio of excretion to respiration	0.6		Vezina and Platt (1988)
<i>K, Het</i>	Half saturation constant for feeding	50; 500	mg C m <sup>-2</sup>	Scenario-specific; motivated in the text
<i>Mort, Het</i>	Mortality rate	0.01	d <sup>-1</sup>	De Laender et al. (2008c)
Microzooplankton				
<i>Ing, Miz</i>	Ingestion rate	2	d <sup>-1</sup>	Hansen et al. (1997)
<i>AE, Miz</i>	Assimilation efficiency	0.6		Hendriks (1999)
<i>Resp, Miz</i>	Respiration rate	0.1	d <sup>-1</sup>	Park et al. (2008)
<i>Excr, Miz</i>	Excretion	0.6		Vezina and Platt (1988)
<i>K, Miz</i>	Half saturation constant for feeding	50; 500	mg C m <sup>-2</sup>	Scenario-specific; motivated in the text
<i>Mort, Miz</i>	Mortality rate	0.05	d <sup>-1</sup>	De Laender et al. (2008c)
Mesozooplankton				
<i>Ing, Mez</i>	Ingestion rate	1	d <sup>-1</sup>	Hansen et al. (1997)
<i>AE, Mez</i>	Assimilation efficiency	0.6		Hendriks (1999)
<i>Resp, Mez</i>	Respiration rate	0.1	d <sup>-1</sup>	Park et al. (2008)
<i>Excr, Mez</i>	Excretion	0.6		Vezina and Platt (1988)
<i>K, Mez</i>	Half saturation constant for feeding	50; 500	mg C m <sup>-2</sup>	Scenario-specific; motivated in the text
<i>Mort, Mez</i>	Mortality rate	0.01	d <sup>-1</sup>	De Laender et al. (2008c)

where  $1 - a \cdot \cos\left(\frac{2 \cdot \pi \cdot t}{365}\right)$  and *Predation* represent seasonal forcing and predation by higher trophic levels, respectively. *Predation* was calculated by summing phytoplankton ingestion by omnivores, microzooplankton, and mesozooplankton. These variables are calculated dynamically during model simulation.

Growth of the heterotrophic groups (*Het* = omnivores, microzooplankton, mesozooplankton, detritivores, or invertebrate predators) was described as:

$$\frac{dHet}{dt} = Het \cdot \left[ Ing_{Het} \cdot AE_{Het} \cdot \frac{Food}{Food + K_{Het}} - Resp_{Het} \cdot (1 - Excr_{Het}) \cdot \max \left[ Mort_{Het}, \ln \left[ 1 + \left( \frac{C}{LC_{50Het}} \right)^{slope} \right] \right] \right] - Predation + I$$

where *Food*, *C*, and *Predation* represent the total food concentration, the chemical concentration, and loss by predation (equal to zero for predators), respectively. *Food* was calculated as the biomass summed across all diet items (e.g. for omnivores, *Food* = *Phy* + *Det*, where *Det* represents the state variable for detritus). The dynamics of *Det* were included explicitly to simulate detritivory by detritivores and omnivores:

$$\frac{dDet}{dt} = \sum_{i=1}^5 \left[ Ing_i \cdot (1 - AE_i) \cdot \frac{Food_i}{Food_i + K_i} + Mort_i \right] - d \cdot Det$$

where **Ing**, **AE**, **Food**, **K**, and **Mort** represent arrays (of size 5) containing specific ingestion rates, assimilation efficiencies, food concentrations, half-saturation constants, and mortality rates of all six functional groups. Note that the entries for phytoplankton in **Ing**, **AE**, and **Food** are set to

zero. This equation represents detritus accumulation when egestion and mortality exceed dissolution, and depletion when the opposite is true.

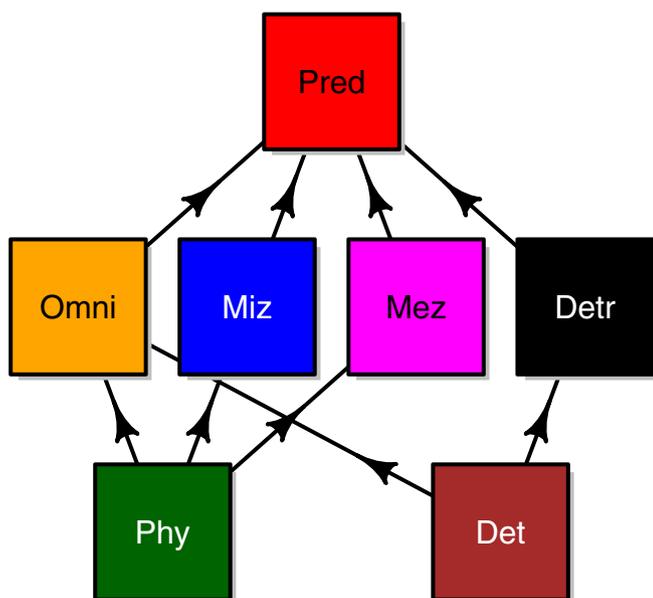
The food-web model was equipped with logistic concentration–response functions to describe the direct toxic effects of an aqueous chemical concentration, *C* (input variable), on the mortality rate of mesozooplankton or microzooplankton (depending on the exposure scenario), as done previously (Traas et al., 2004; De Laender et al., 2008a). Parameters of these functions were the median lethal concentration (*LC*<sub>50</sub>) and *slope* (Table 2). Actual mortality was defined as the maximum of the toxicant-induced mortality and background mortality.

### 2.3. Food-chain model

We constructed two food-chain models as a special parameterisation of the food-web model. A first food-chain model only consisted of phytoplankton and mesozooplankton; a second food-chain model only consisted of phytoplankton and microzooplankton. These food-chain models were constructed by simply setting the initial biomass densities and immigration rates of all functional groups not present in the food-chains to zero.

### 2.4. The scenarios

Sixteen ecological scenarios were obtained by varying trophic state (mesotrophic vs. oligotrophic), immigration rate (high vs. low), grazing rate as a proxy for interaction strength between producers and consumers (strong vs. weak), and the complexity of the system (food-chain vs. food-web). Trophic state was altered by changing the phytoplankton carrying capacity from 1 µg Chlorophyll a/L for



**Fig. 1.** Structure of a food-web including phytoplankton (Phy), detritus (Det), omnivores (Omni); microzooplankton (Miz), mesozooplankton (Mez), detritivores (Detr), and invertebrate predators (Pred). The structure of the food-chain can be obtained by removing all groups except for phytoplankton and mesozooplankton (exposure to chemical 1 or 2) or microzooplankton (exposure to chemical 3 or 4).

oligotrophic scenarios to 10  $\mu\text{g}$  Chlorophyll a/L for mesotrophic scenarios (Carlson, 1977). Average carbon to Chlorophyll a ratios of 50  $\mu\text{g}$  carbon/ $\mu\text{g}$  Chlorophyll a and the pond depth of 1 m were used to convert these numbers to  $\text{mg C m}^{-2}$ , the currency used by the food-web and food-chain models (Riemann et al., 1989). Immigration rates ( $I$ ) were set to values that were either comparable to (high immigration) or smaller than (low immigration) those used elsewhere (Table 1). Grazing rates were changed by setting the half saturation rate constant  $K$  from 50 (fast grazing) to 500 (slow grazing), i.e. corresponding to the carrying capacity of the phytoplankton in the oligotrophic and mesotrophic scenarios, respectively. This choice was made to prevent grazing limitation to be either too high or too low in all scenarios. Lastly, system complexity was altered by using the food-chain model (simple) or the food-web model (complex).

We considered four hypothetical model chemicals, characterized by different physical–chemical and toxicological properties. Chemicals 1 and 3 (hydrophilic), and 2 and 4 (hydrophobic) share environmental fate determinants with atrazine and pyrene, respectively (Table 2). The fate of these two types of chemicals (hydrophilic and hydrophobic) was calculated separately for the two trophic states considered in the ecological scenarios. We used the phytoplankton and detritus control densities predicted by the food-chain and food-web models to estimate

**Table 2**

Physical–chemical properties at 25 °C, and toxicity to zooplankton of the chemicals selected for the simulations. Note that other groups than micro- and mesozooplankton are always tolerant to both chemicals (i.e.  $\text{LC}_{50\text{s}} \gg$ ).

Parameter	Chemicals 1, 3	Chemicals 2, 4
Molecular weight (g/mol)	216	202
Melting point (°C)	176	156
Water solubility (g/m <sup>3</sup> )	33	0.13
Vapour pressure (Pa)	$3.85 \cdot 10^{-5}$	$6 \cdot 10^{-4}$
Log $K_{ow}$	2.5	5.2
Half-life in water (h)	1320	1700
Half-life in sediment (h)	4800	55,000
24 h- $\text{LC}_{50}$ for mesozooplankton (chemicals 1, 2) or for microzooplankton (chemicals 3, 4) (ng/L)	1000	1000
Slope of concentration response curve for micro- or mesozooplankton (-)	2	2

POC concentrations in the fate model. In addition, fate calculations for the oligotrophic state were performed using a sediment depth of 5 cm and a constant DOC concentration of 5 mg/L, while in the mesotrophic state sediment depth was set to 7 cm and a constant DOC concentration to 50 mg/L was assumed. No feedback from chemical-induced changes in phytoplankton and detritus stocks to chemical fate was considered in the current exercise. The four chemicals also differed in their toxicological profile. Chemicals 1 and 2 selectively targeted mesozooplankton, while chemicals 3 and 4 selectively targeted micro- or mesozooplankton. We assumed that these chemicals affected micro- or mesozooplankton by reducing survival in a concentration-dependent fashion. By combining these four chemical types with two seasons of emission (spring: April 4th–June 4th; late summer: August 5th–October 6th) we created eight different exposure scenarios.

All simulations were ran using a time-step of 1 h (0.04 days) and initial conditions were always set to 50 (the carrying capacity of the oligotrophic system), 1, and 0  $\text{mg C m}^{-2}$  for autotrophs, heterotrophs, and detritus, respectively.

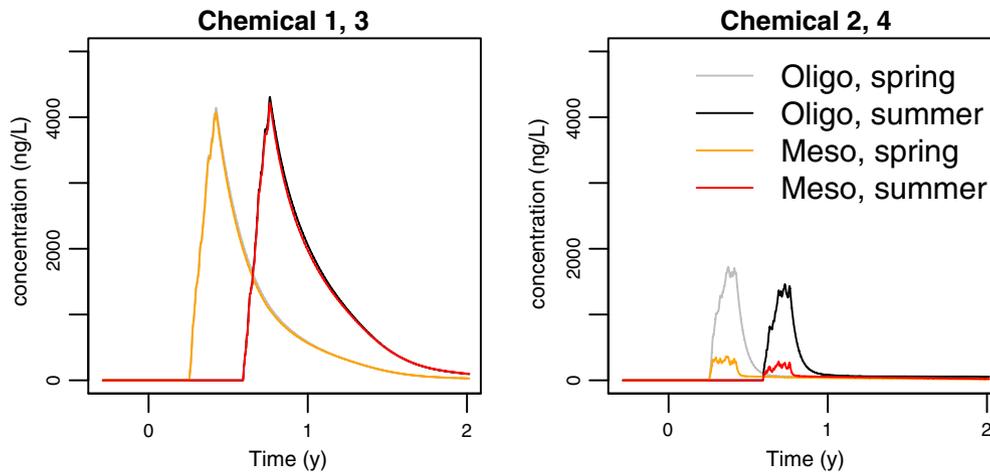
We used the fate and effect models to inspect how direct and indirect effects varied across the ecological and exposure scenarios. We note that calculations for chemicals 1 and 2 (targeting mesozooplankton) were done with the phytoplankton–mesozooplankton food-chain model. Calculations for chemicals 3 and 4 (targeting microzooplankton) were done using the phytoplankton–microzooplankton food-chain model. Direct effects were assessed by comparing meso- (chemicals 1 and 2) or microzooplankton biomass (chemicals 3 and 4) between the exposed and the control dynamics. Recovery was concluded when exposed and control biomasses were identical during the last 31 days of the simulation time. When this was the case, recovery time was calculated as the time between the onset of effects and the start of the 31-day period of permanent recovery. Because both groups only feed on phytoplankton, we evaluated indirect effects by calculating effects and recovery time for phytoplankton. To aid visualization of the modelled direct and indirect effects, we summarized these effects in two ways: (1) using the maximum effect size (unitless quotient of exposed and control dynamics), and (2) using the time-integrated difference between the control and exposed biomass ( $\text{mg C m}^{-2} \text{d}$ ). The maximum effect size was defined as the largest absolute deviation of the quotient of the exposed and control dynamics from 1.

### 3. Results

#### 3.1. Chemical fate

Water-dissolved concentrations of chemicals 1 and 3 were about two times higher than those of chemicals 2 and 4, as expected from the relatively high octanol–water partitioning coefficient ( $K_{ow}$ ) of chemicals 2 and 4, which caused their fast removal from water through partitioning onto POC and DOC and the subsequent deposition of particles (Fig. 2). The influence of trophic state and season of emission on the fate of chemicals 1 and 3 was small, as expected from their relatively low log  $K_{ow}$ . For this reason, very similar exposure levels were predicted for all emission timings and trophic states. Chemical removal processes were quite slow, due to a combination of the high residence time of the water compartment (i.e., 6 months) with the relatively high half-life of chemicals 1 and 3 in water (about 55 days).

In contrast to what was observed for chemicals 1 and 3, the higher affinity of chemicals 2 and 4 for the organic sub-compartments in water and sediment caused very different exposure profiles for the four simulation scenarios (Fig. 2). Concentrations following summer emission were about 15–20% lower than concentrations following spring emission, regardless of the trophic state. This behaviour can be mainly ascribed to the higher POC levels in summer than in spring, which caused a more effective chemical removal from the water phase. In the mesotrophic systems, the concentrations of chemicals 2 and 4 were about 5 times lower than in oligotrophic systems. Removal of chemicals 2 and 4 from the



**Fig. 2.** Aqueous concentrations of chemicals 1, 2, 3, and 4 for the two trophic states (considered in the ecological scenarios) and two emission seasons (considered in the exposure scenarios).

water phase was faster than for chemicals 1 and 3, and the main process involved was suspended solid deposition. In mesotrophic systems, for example, the deposition flux was up to 90% of chemical emission.

3.2. Ecosystem dynamics: control

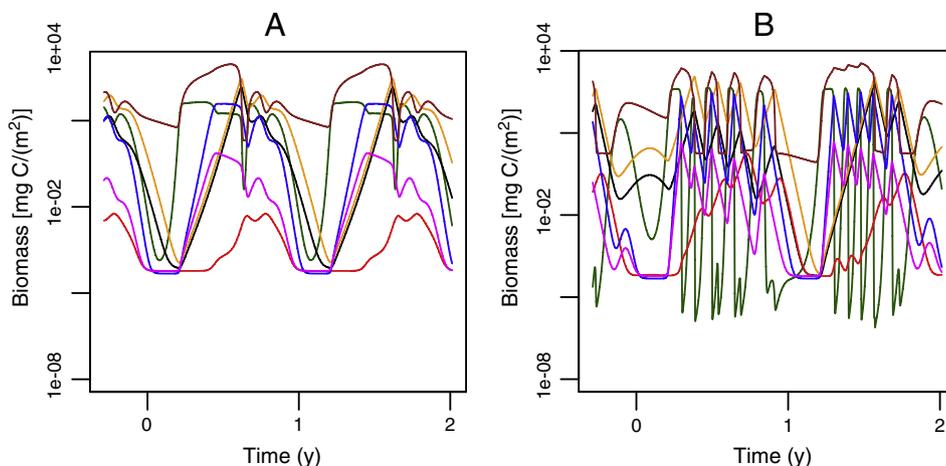
In general, oscillations through time were more pronounced in the mesotrophic systems than in the oligotrophic systems, both for the food-chain as for the food-web (Fig. 3 includes an example for the food-chain as for the food-web). In oligotrophic systems with low immigration rates and occupied by slow grazing heterotrophs, only phytoplankton maintained biomass densities  $> 10^{-8}$  mg C m<sup>-2</sup>, while the other groups virtually disappeared from the system (Fig. S2, Supporting information). Immigration promoted co-existence and limit cycle stability (an example is provided in Fig. S3, Supporting information). Mesozooplankton biomass density was lower in the food-web than in the food-chain (Fig. S4, Supporting information) and was mostly 10 to 100 times lower than that of microzooplankton when both groups were present in the food-web (Fig. 3A).

3.3. Ecosystem dynamics: exposure to chemicals 1 and 2

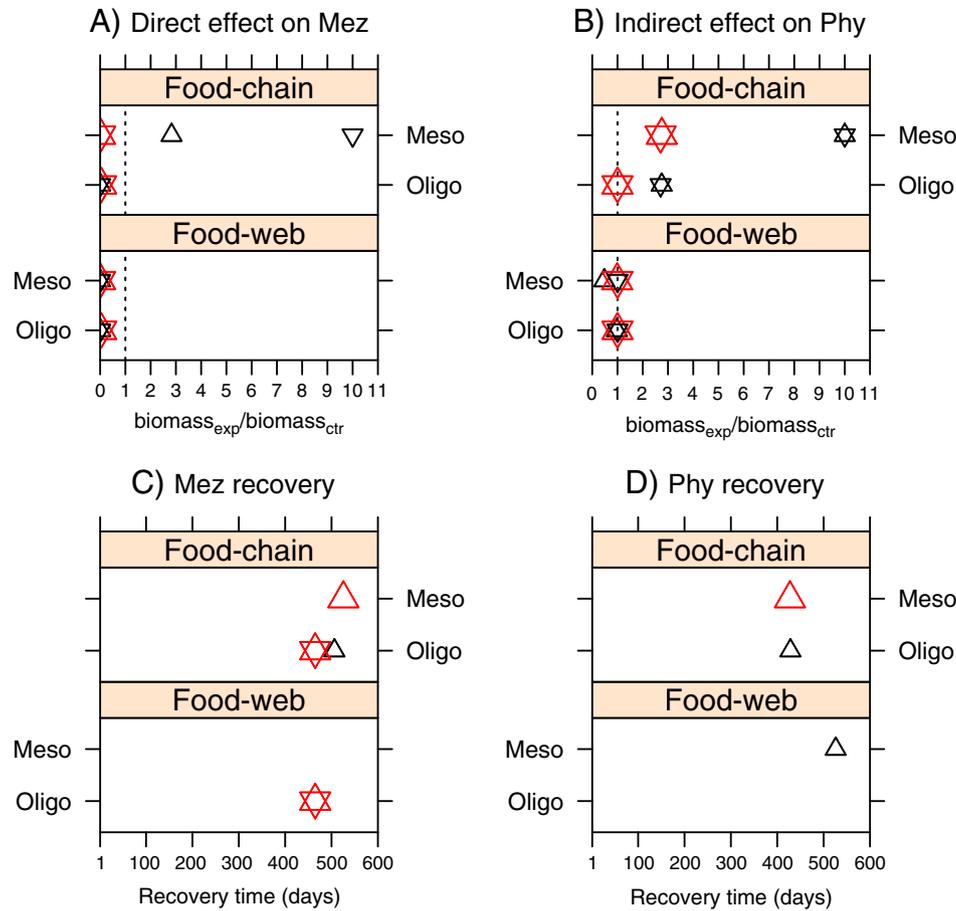
Because effects following spring and late summer emissions were similar, only the former are discussed, after which the differences between both exposure scenarios are briefly highlighted.

Exposure to chemicals 1 and 2 in spring always resulted in clear effects on mesozooplankton, the only functional group that was sensitive to these hypothetical chemicals. For mesozooplankton, the maximum effect size was comparable between chemicals 1 and 2 (Fig. 4A and Fig. S5A, Supplemental information). Also the time-integrated effects compared well between chemicals 1 and 2 emitted in spring (Figs. S6A and S7A, Supplemental information). The maximum effects of these chemicals on mesozooplankton were always negative (nearly 100% biomass reductions) in the food-web, but positive in the mesotrophic food-chain when grazing was fast. The maximum and time-integrated direct effects were mostly independent of immigration rate. The maximal direct effects of chemicals 1 and 2 were smaller at high immigration rates but only in mesotrophic food-chains with fast grazing heterotrophs. In contrast, the integrated effect of both chemicals emitted in spring in oligotrophic food-chains with fast grazing heterotrophs was larger at high immigration rates than at low immigration rates.

The maximum size of the indirect effects of chemicals 1 and 2 on phytoplankton was common and positive in the food-chain, and largest when grazing was fast (Fig. 4B, and Fig. S5B, Supplemental information). Also the time-integrated indirect effect on phytoplankton was apparent in food chains (Figs. S6B and S7B, Supplemental information). Regardless of the effect summary considered, indirect effects were mostly absent in the food-web. Both effect summaries suggested the indirect effect size to be nonresponsive to immigration rate.



**Fig. 3.** Control simulations for a food-web with fast grazing heterotrophs, fast immigration and oligotrophic (A) or mesotrophic conditions (B). Colour codes are as in Fig. 1.



**Fig. 4.** Maximum effect sizes and recovery times for mesozooplankton and phytoplankton following exposure to chemical 1 in spring, in mesotrophic and oligotrophic food-webs and food-chains, characterized by fast (upward triangles) or slow immigration (downward triangles), and composed of fast (black symbols) or slow (red symbols) grazing heterotrophs. Maximum effects > 10 are displayed as a maximum effect size of 10. Absence of a symbol for recovery time indicates no recovery.

Recovery of mesozooplankton and phytoplankton from chemical 2 was more frequently observed and occurred more rapidly than recovery from chemical 1 (Fig. 4C, D, and Fig. S5C, D, Supplemental information). Recovery from direct and indirect effects was also more frequently predicted (and was faster) when immigration was fast.

Maximal (Fig. S8, Supplemental information) and integrated effects (Fig. S9, Supplemental information) following summer emission of chemical 1 were comparable to those described for spring emission, both for mesozooplankton (direct) as for phytoplankton (indirect). The same was observed for the maximal effects caused by chemical 2 (Fig. S10, Supplemental information). However, time-integrated effects of chemical 2 were larger for spring than for summer emission (Fig. S11, Supplemental information). Recovery occurred more often and more rapidly following spring emission than summer emission of chemical 1. No consistent differences between recovery patterns of spring and summer emissions could be found for chemical 2 (compare Figs. S5 and S10, Supplemental information).

### 3.4. Ecosystem dynamics: exposure to chemicals 3 and 4

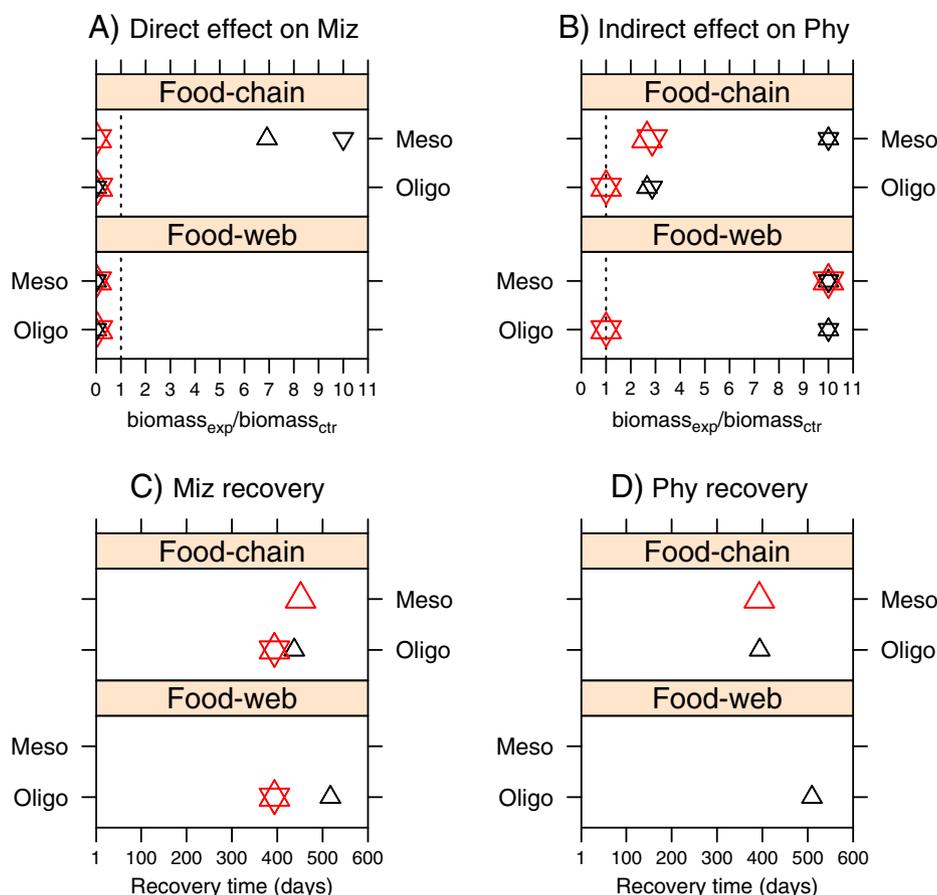
Again, effects following spring and late summer emissions were similar, so that only the former are discussed in detail, after which the differences between both exposure scenarios are briefly highlighted.

According to the two effect summaries, chemicals 3 and 4 emitted in spring always affected microzooplankton, the only functional group that was sensitive to these two hypothetical chemicals. The maximum effect size for microzooplankton was comparable between chemicals 3 and 4 (Fig. 5A, Fig. S12A, Supplemental information) and mostly negative.

The maximum effect of these chemicals on microzooplankton was mostly negative but positive in mesotrophic food-chains and food-webs when grazing was fast. Also the time-integrated effect on microzooplankton compared well between chemicals 3 and 4 and differences between both chemicals were most pronounced in mesotrophic systems (Figs. S13A, S14A, Supplemental information). Maximum indirect effects of chemicals 3 and 4 on phytoplankton were common and always positive, both in the food-chain as in the food-web, regardless of the settings for grazing and immigration rate (Fig. 5B, Fig. S12B, Supplemental information). The maximum direct effect size was mostly independent of the immigration rate. The maximal direct effect of chemicals 3 and 4 was smaller at low immigration rates but only in mesotrophic food-chains with fast grazing heterotrophs. In mesotrophic food-webs, fast immigration lowered the maximum indirect effect size in case of slow grazing heterotrophs. The integrated direct and indirect effects were sensitive to the immigration rate but in an inconsistent manner (Figs. S13 and S14, Supplemental information).

Recovery of microzooplankton and phytoplankton from chemical 4 (Fig. S12C, D, Supplemental information) was more frequently observed and occurred more rapidly than recovery from chemical 3 (Fig. 5C, D). Recovery from these direct and indirect effects was also more frequently predicted and faster when immigration was fast, except in oligotrophic food-webs containing fast grazing heterotrophs and exposed to chemical 4.

The maximal direct and indirect effects of spring emission of chemical 3 (Fig. 5) were comparable to those following late summer emission (Fig. S15, Supplemental information). The same was found for the time-integrated effects (Fig. S16, Supplemental information). For chemical 4,



**Fig. 5.** Maximum effect sizes and recovery times for microzooplankton and phytoplankton following exposure to chemical 3 in spring, in mesotrophic and oligotrophic food-webs and food-chains, characterized by fast (upward triangles) or slow immigration (downward triangles), and composed of fast (black symbols) or slow (red symbols) grazing heterotrophs. Maximum effects >10 are displayed as a maximum effect size of 10. Absence of a symbol for recovery time indicates no recovery.

maximal effects following spring emission (Fig. S12, Supplemental information) were larger than those following summer emission (Fig. S17, Supplemental information). The same was found for the time-integrated effects (Fig. S18, Supplemental information).

Recovery occurred more often and more rapidly following spring emission than following summer emission of chemical 3 (Fig. S15C, D, Supplemental information). No consistent differences between recovery patterns of spring and summer emissions could be found for chemical 4 (Fig. S17C, D, Supplemental information).

## 4. Discussion

### 4.1. Ecological and exposure scenarios

Our control simulations illustrated how immigration stabilized population dynamics and facilitated coexistence of trophically similar species, which is in line with findings from earlier theoretical exercises (McCallum, 1992). However, the expected positive effect of immigration on the recovery of the targeted functional group (Caquet et al., 2007) was only predicted for certain ecological scenarios. For other scenarios, the immigration rate did not affect recovery. In both oligo- and mesotrophic systems, interaction strength (using grazing rate as a proxy) was suggested as a more important driver for direct effects than immigration rate, and this result was robust to the effect summary considered (maximum effect vs. time-integrated). In general, weak consumer–producer interactions led to weaker direct (and indirect) effects, i.e. the biomasses of the targeted groups (micro- or mesozooplankton) and of phytoplankton in food-chains and food-webs were less affected

by the chemicals. This finding corroborates with several reports on the importance of strong interactions as determinants of population dynamics and extinction (May, 1972; McCann et al., 1998), although this view has been challenged (Allesina and Tang, 2012). It also suggests that the ‘weak interaction effect’, as defined in basic ecology, plays a role in the occurrence of ecological effects of chemicals as well (McCann, 2000). If half-saturation constants for grazing scale with the competition strength between grazers, our findings also correspond to those recently presented by Kattwinkel and Liess (Kattwinkel and Liess, 2014). It should be noted though that interaction strength can be modified by chemical-induced behavioural changes, e.g. as shown by Brooks et al. for the case of predator–prey interactions in Cd-exposed freshwater ecosystems (Brooks et al., 2009b). Such modifications in behaviour are typically not included in the type of models presented in the present paper. The findings presented by Brooks et al. (Brooks et al., 2009b), indicating that sublethal exposure of prey may modify its vulnerability to predators with specific hunting strategies, make it clear that such extensions are both scientifically challenging and relevant for risk assessment.

The mesotrophic systems we modelled were less dynamically stable, were less resistant to the chemical-induced perturbations, and recovered more slowly from such perturbations. Again, this finding is insensitive to the effect metric considered (maximum or time-integrated effects). Although the combined effects of nutrient enrichment and chemical exposure have been examined (Halstead et al., 2014), we do not know of experiments where the responses to chemicals of food-webs similar to those examined here were compared between different trophic states, so it is not possible at the moment to confirm or reject

this theoretical expectation. We only found reports of experiments where plankton communities were exposed to fish predation as a stressor, showing that effects of predation and recovery rates after fish removal were less severe and faster, respectively, in oligotrophic than in mesotrophic systems (Perez-Fuentetaja et al., 1996).

For some ecological scenarios, our models predicted direct effects that were positive. This result is at first counterintuitive but indicates that care should be taken when classifying a deviation of the most sensitive functional group from its control biomass as a direct effect. Indeed, such positive effects indicate feedbacks caused by large indirect effects on phytoplankton (mostly in mesotrophic systems with fast grazing heterotrophs, e.g. Fig. 5). Meso- (chemicals 1 and 2) or microzooplankton decimation (chemicals 3 and 4) causes phytoplankton blooms, which subsequently stimulate zooplankton density during the recovery phase, when chemical concentrations have dropped to zero. This result demonstrates that changes in the size of a functional group that is targeted by a given chemical cannot be always simply categorized as direct effects but may classify as indirect effects because they originate from a combination of chemical toxicity and a trophic cascade caused by interspecific interactions.

The toxicological profile of the chemical (i.e. what functional group was targeted by the chemical) was the most influential parameter of the exposure scenario. In contrast, the season of emission appeared far less important. However, it should be noted that the concentrations considered in this paper (500 to 4000 ng/L, depending on the chemical; Fig. 2) were relatively high because they approached or surpassed lethal values for 50% of the organisms tested in a single-species toxicity test (1000 ng/L; Table 2). As a result, effects were inherently large and recovery inherently slow so that differences in these descriptors of ecological effect between exposure scenarios may have been less detectable. Future efforts may perform similar exercises across a gradient of chemical exposure, but no such efforts were pursued in the present paper.

#### 4.2. Indirect effects

The modelling exercise we present in this paper suggests that indirect effects on phytoplankton following direct effects on mesozooplankton (chemicals 1 and 2) occur in simple food-chains but are highly exceptional in food-webs. In contrast, direct effects on microzooplankton (chemicals 3 and 4) more often resulted in indirect effects in food-webs. This difference in the occurrence of indirect effects between both chemical pairs makes both intuitive and mathematical sense. In food-webs, where both zooplankton groups were present, the biomass density of mesozooplankton was mostly 10 to 100 times lower than that of microzooplankton. Correcting for differences in maximum grazing rates between both groups (two times higher for micro- than for mesozooplankton), the maximum grazing pressure on phytoplankton exerted by mesozooplankton was 5 to 50 times lower than by microzooplankton. Thus, a given direct effect on mesozooplankton is likely to result in a smaller indirect effect on phytoplankton than a direct effect of the same size on microzooplankton. This result demonstrates the need to account for dominance patterns when predicting the potential for indirect effects. Our results suggest that, when dominance combines with sensitivity, indirect effects will be larger than when less abundant functional groups are most sensitive.

Are the indirect effects following direct effects of chemicals 1 and 2 on mesozooplankton indeed more likely in simple food-chains than in food-webs? Since we only considered one (simple) food-chain and one (more complex) food-web, it would be incautious to draw conclusions regarding the relationship between the probability of indirect effects and the number of functional groups in a food-web. Based on data from micro- and mesocosm studies, representing systems with varying food-web complexity but exposed to the same insecticide, some empirical support exists for such a relationship. Briefly, Daam and Van den Brink (2007) found positive indirect effects on phytoplankton following 0.1 µg/L chlorpyrifos exposure in indoor microcosms only

containing phyto- and zooplankton and snails. Brock et al. (Brock et al., 1992), using microcosms stocked with plankton and several macroinvertebrates, reported such indirect effects from 5 µg/L chlorpyrifos onwards. Studies with the same chemical in large outdoor experimental ditches by Van den Brink et al. (1996) and Kersting and Van den Brink (1997) only reported these indirect effects at concentrations from 44 µg/L chlorpyrifos onwards. Note that, in these experimental systems, mesozooplankton is more sensitive to the tested insecticides than microzooplankton, i.e. reasonably representative for our hypothetical chemicals 1 and 2. In these experimental studies, indirect effects would have been less likely to occur in complex systems than in simple systems when both would have been exposed to the same concentration. Taking together the predictions made by our models, which only reflect two samples from the full spectrum of system complexity, and these empirical cosm data, covering a broader range of system complexity, we argue that the relationship between food-web complexity and indirect chemical effects at least deserves further empirical testing and theoretical exploration. In addition to the number of functional groups or species, such empirical studies may also want to consider link density as a measure of food-web complexity, because food-web topology and the distribution of the number of links connecting a node in a food-web have been shown to affect the resistance of ecosystems to species removal (Dunne et al., 2002; Jonsson et al., 2006; Dunne and Williams, 2009; Montoya et al., 2009).

As stated in the **Material and methods** section, no feedback from chemical-induced changes in phytoplankton and detritus stocks to chemical fate was considered in the current exercise, because fate calculations were performed using the control biomass dynamics. Because of the indirect effects on phytoplankton observed here, i.e. algal blooms, we hypothesise that taking into account such feedbacks would probably moderate the effects on zooplankton by reducing chemical availability.

#### 4.3. The influence of chemical type

The direct and indirect effects of chemicals 1 and 3 were more pronounced than those of chemicals 2 and 4. This difference is purely driven by chemical fate, as the partitioning of chemicals 1 and 3 to the water phase (i.e. the bioavailability) was higher than for chemicals 2 and 4. Our simulations focused on pelagic systems and we acknowledge that including sediment consuming benthic species or top carnivores may yield contrasting results. Indeed, the models we present here ignore potential dietary uptake and biomagnification, which would increase (internal) exposure. However, our focus on planktonic systems, with organisms smaller than 5 mm, probably limits the contribution of the dietary uptake route to accumulation and toxicity (De Laender et al., 2010a). Experimental evidence indicates that for species with a larger body size, the hunting and feeding strategy, as well as the type of prey consumed, can influence the accumulation and toxicity of chemicals (Brooks et al., 2009a).

#### 4.4. Conclusions and recommendations

The inclusion of sensitivity and uncertainty analyses in ecotoxicological food-web and ecosystem models is common (Park et al., 2008; De Laender et al., 2010b) but the influence of the ecological and exposure scenario on the prevalence of direct and indirect chemical effects in multi-species systems has remained understudied. We show that combining a dynamic fate model and a food-web/food-chain model allows evaluating chemical availability together with the resulting population-level effects in an ecosystem context. The most notable conclusions include that (1) indirect effects are most likely when dominance patterns correlate with sensitivity patterns; (2) direct and indirect effects are most pronounced in eutrophic systems; and (3) interaction strength is a stronger determinant for effect size than the immigration rate. As an overarching conclusion drawn from our simulations, which represent theoretical expectations for a vast

array of ecological and exposure scenarios, we postulate that ecotoxicological research at the ecosystem level and risk assessments based on such research need to sufficiently justify the ecological scenario considered if direct and indirect effects of chemicals are to be assessed in a robust and transparent way.

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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.envint.2014.10.012>.

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