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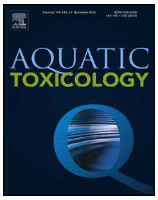

Modeling the direct and indirect effects of copper on phytoplankton–zooplankton interactions

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ABSTRACT

Predicting the effects of pollution at the community level is difficult because of the complex impacts of ecosystem dynamics and properties. To predict the effects of copper on a plant-herbivore interaction in a freshwater ecosystem, we built a model that focuses on the interaction between an alga, *Scenedesmus* sp., and a herbivore, *Daphnia* sp. The model assumes logistic growth for *Scenedesmus* and a type II functional response for *Daphnia*. Internal copper concentrations in *Scenedesmus* and *Daphnia* are calculated using a biodynamic model. We include two types of direct effects of copper on *Scenedesmus* and *Daphnia* that results from hormesis: a deficiency effect at low concentration and a toxic effect at high concentration. We perform a numerical analysis to predict the combined effects of copper and nutrient enrichment on the *Scenedesmus*–*Daphnia* interaction. Results show three types of outcomes depending on copper concentration. First, low ($4\,\mu g\,L^{-1}$) and high ($50\,\mu g\,L^{-1}$) copper concentrations cause deficiency and toxicity, respectively, leading to the extinction of all populations; for less extreme concentrations (between 4 and $5\,\mu g\,L^{-1}$ and between 16.5 and $50\,\mu g\,L^{-1}$), only the consumer population becomes extinct. The two populations survive with intermediate concentrations. Second, when population dynamics present oscillations, copper has a stabilizing effect and reduces or suppresses oscillations. Third, copper, on account of its stabilizing effect, opposes the destabilizing effect of nutrient enrichment. Our model shows that (1) *Daphnia* is affected by copper at lower concentrations when community interactions are taken into account than when analyzed alone, and (2) counterintuitive effects may arise from the interaction between copper pollution and nutrient enrichment. Our model also suggests that single-value parameters such as NOEC and LOEC, which do not take community interactions into account to characterize pollutants effects, are unable to determine pollutant effects in complex ecosystems. More generally, our model underscores the importance of ecosystem-scale studies to predict the effects of pollutants.

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1. Introduction

Laboratory tests used to assess the toxicology of chemicals are mostly based on single species tests. Typically, the effects of chemicals are assessed with a model species, and several parameters describing the toxicological effects for an external concentration are calculated (NOEC, LC_{50}, LD_{50}, etc.). These parameters reflect the toxicological effects of a chemical on a species in the laboratory; such an organism-centered approach (Villeneuve and Garcia-Reyero, 2011) considers only the direct effects (Strauss, 1991). However, estimating toxicological effects on an ecosystem is more challenging because of the complex impacts of ecosystem dynamics and properties (Fleeger et al., 2003). For instance, Lampert et al. (1989) tested the effects of the herbicide atrazine on some aquatic systems. Laboratory tests on *Daphnia* showed an effect with an effective concentration of $2\,mg\,L^{-1}$, while tests on a food chain system with *Daphnia* and algae showed a significant reduction in *Daphnia* population growth at $0.1\,mg\,L^{-1}$. A third test conducted in enclosure experiments with natural communities showed responses to atrazine concentrations between 0.1 and $1\,\mu g\,L^{-1}$. These experiments show that indirect effects can be greater than direct effects (Lampert et al., 1989) and that standard laboratory tests do not reveal the indirect effects of pollution at the community level. In addition to indirect effects, studying the effects of pollutants on ecosystems requires the consideration of the organisms' internal concentration, which varies with trophic level, as well as the pollution from multiple contaminants. As a consequence, predicting the effects of pollution at the community level is a complex issue. Therefore, studying pollutant effects with ecosystem-centered approaches is the focus of the new paradigm

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of the ecological risk assessment (Villeneuve and Garcia-Reyero, 2011).

Mathematical modeling has already proved a useful tool to help predict the effects of a pollutant at the population (Manyin and Rowe, 2008) and ecosystem (Traas et al., 1998; Trudel and Rasmussen, 2001; Van den Brink et al., 2006) levels in a few cases. Although food web models have been applied to the study of persistent organic pollutants such as PCBs, introducing more ecological thinking into the analyses of contaminant effects still represents a major challenge (Campfens and MacKay, 1997; Scharler et al., 2005).

In this article, we build a model designed to predict the effects of copper on an important plant-herbivore interaction in freshwater ecosystems. As a receptor of urban wastewater, industrial and mine effluents, agricultural runoff, and atmospheric pollution, aquatic ecosystems are prone to copper pollution (Jørgensen, 2010; Nriagu, 1979). Copper is an essential element of life (Mertz, 1981) as it enters the composition of numerous enzymes. A low internal concentration may induce deficiency effects (Bossuyt and Janssen, 2003). However, single-species tests in the laboratory showed that copper is highly toxic at high concentrations (Clements et al., 1992). Copper has negative impacts on primary producers, microorganisms, invertebrates, fish, and amphibians (ATSDR, 1990; WHO, 1998).

In this article, we examine the copper effects on the interaction between algae and *Daphnia* sp. for several reasons. First, this interaction plays a key role in the dynamics of many freshwater ecosystems (McCauley and Murdoch, 1987; McCauley et al., 1988) and it is commonly used as a model system in ecology and ecotoxicology. Algae and *Daphnia* are frequently used in toxicology tests on isolated populations (Reynolds, 2011) as well as in standard ecotoxicological tests, for instance, for water quality monitoring. Although our model focuses on a specific prey-predator interaction, it is representative of communities with strong trophic interactions (Berlow et al., 1999, 2004), as is generally the case in freshwater ecosystems (Shurin et al., 2006).

Second, various direct effects of copper on algae and *Daphnia* sp. have been described, which allows us to accurately describe its effects on this particular plant-herbivore interaction.

The direct effects of copper on algae include the inhibition of photosynthesis (Havens, 1994), inhibition of growth (Fargasova et al., 1999; Fathi and El-Shahed, 2000; Yan and Pan, 2002), decreased concentrations of glucides, proteins, amino-acids (Fathi and El-Shahed, 2000), and chlorophyll (Fargasova et al., 1999) in algal cells, and decreased alkaline phosphatase activity (Fathi and El-Shahed, 2000). The direct effects of copper on *Daphnia* sp. life-history traits include a decrease in fecundity, survival, body length, weight, and carbon uptake, as well as a delay in maturation (Baird et al., 1991; Ingersoll and Winner, 1982; Knops et al., 2001; Koivisto et al., 1992; Winner and Farrell, 1976). Moreover, some behavioral responses of *Daphnia* to copper are known: their mobility decreases (Clement and Zald, 2004), while their swimming velocity, filtration rate, and ingestion rate are optimal for an intermediate copper range (Ferrando and Andreu, 1993; Untersteiner et al., 2003). These behavioral modifications may indirectly affect ecological interactions. For instance, the effect of copper on *Daphnia*'s mobility (Clement and Zald, 2004; Gutierrez et al., 2012; Sullivan et al., 1983) in turn affects its foraging behavior and ability to escape predators, and, ultimately, its prey and predator populations. Concerning *Scenedesmus*' behavior, copper reduces the colonies that they form in response to *Daphnia*'s predation (Lürling and Van Donk, 2000; Peña-Castro et al., 2004; Van Holthoon et al., 2003; Wu et al., 2013).

The study of copper effects is complicated by copper speciation and environmental factors. The response of each species' life-history trait—for instance, growth rate, predation, and mortality—varies greatly due to copper speciation (Van Veen et al., 2002). For example, the EC_{50} for *Daphnia* sp. can range from simple to twentyfold (Jørgensen, 2010). In addition, many environmental factors such as pH and CO_3^{2-}, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, and SO_4^{2-} concentrations also modify responses to copper concentration (De Schamphelaere and Janssen, 2002). A few toxicity values can be determined for species-pollutant couples with the Biotic Ligand Model. This model allows the LD_{50} and EC_{50} to be determined for some species and pollutants as a function of variable environmental parameters (see Paquin et al., 2002 for an overview and De Schamphelaere and Janssen, 2002 for an example).

In this study, we use our model to analyze the effects of copper pollution on the *Scenedesmus*–*Daphnia* interaction. Nutrient enrichment has major destabilizing effects on prey-predator interactions, known as the paradox of enrichment (Rosenzweig, 1971). As freshwater ecosystems are often subject to nutrient enrichment, which is a major perturbation in aquatic ecosystems (Dudgeon et al., 2006; Sala et al., 2000), we also study the interaction between copper pollution and eutrophication.

2. Methods

2.1. Modeling freshwater ecosystems and copper effects

We consider a simple freshwater ecosystem consisting of two compartments, phytoplankton and zooplankton, with the genera *Scenedesmus* and *Daphnia* chosen as model organisms for these compartments. These genera include many species, but since the associated species have very similar life-history traits (McCauley et al., 1988), we do not distinguish them in our study. Moreover, all *Scenedesmus* species are approximately the same size, which is the main criterion for describing *Daphnia*'s size-based predation (Briand and McCauley, 1978; Burns, 1968; McCauley et al., 1988; Porter, 1973).

In freshwater environments, various phenomena of copper speciation have been described (Nomkoko et al., 2003; Van Veen et al., 2002). Moreover, the amount of bioavailable copper depends on many environmental parameters (Town and Filella, 2000). Among the various chemical forms toxic to freshwater organisms, it is widely acknowledged that copper toxicity is directly related to the concentration of free and bioavailable Cu^{2+} in water (Nomkoko et al., 2003; Van Veen et al., 2002). Therefore, we focus on this form in our study, referring to its concentration as copper concentration in water. Copper impacts on organisms may be either direct or indirect. Direct effects are due to copper bioconcentration in organisms through direct absorption (through skin or gills, or by drinking contaminated water) as well as its progressive accumulation in tissues, as copper excretion is weaker than copper absorption (ATSDR, 1990; WHO, 1998). Indirect effects occur through modifications to the densities and dynamics caused by the pollutant on the life-history traits of the concerned and related species.

2.2. Model

The model development follows several steps. We first model the *Scenedesmus*–*Daphnia* interaction without copper pollution. Next, we calculate the internal concentration of copper and analyze its effects on each species. Finally, we include its effects on model parameters to describe the *Scenedesmus*–*Daphnia* interaction in the presence of copper pollution. Our analysis relies on a classical community model that includes two variables, *Scenedesmus* and *Daphnia* densities.

2.2.1. Scenedesmus–Daphnia *interaction*

In a constant environment, *Scenedesmus* dynamics is assumed to be logistic (McCauley et al., 1988). The functional response of

Table 1
Value of model parameters used for numerical analyses (NS: no source); see text for explanations.

Parameter	Description	Value	Unit	Sources
Populations' dynamics				
r	*Scenedesmus* intrinsic rate of natural increase	1.2	d^{-1}	Rinke and Vijverberg (2005)
K	Range of *Scenedesmus* carrying capacity	0.1–5	$mgC\,L^{-1}$	Murdoch et al. (1998)
I_{max}	Maximum intake rate of the *Daphnia*	1.8	d^{-1}	Rinke and Vijverberg (2005)
h	Half-saturation constant of *Daphnia*	0.164	$mgC\,L^{-1}$	Murdoch et al. (1998)
e	*Daphnia* conversion efficiency	0.6	–	Rinke and Vijverberg (2005)
m	*Daphnia* mortality rate	0.35	d^{-1}	Rinke and Vijverberg (2005)
Copper–internal concentration				
Cu	Range of external copper concentration	0–100	$\mu g\,L^{-1}$	Bossuyt and Janssen (2003)
k_{mS}	*Scenedesmus* maximal intake rate	20	$\mu g\,g^{-1}\,d^{-1}$	NS
k_{mD}	*Daphnia* maximal intake rate	15	$\mu g\,g^{-1}\,d^{-1}$	Lebrun et al. (2012)
k_{cS}	*Scenedesmus* half-saturation constant	6	$\mu g\,L^{-1}$	NS
k_{cD}	*Daphnia* half-saturation constant	7	$\mu g\,L^{-1}$	NS
k_{eS}	*Scenedesmus* constant loss rate	1	$\mu g\,d^{-1}$	NS
k_{eD}	*Daphnia* constant loss rate	1	$\mu g\,d^{-1}$	Lebrun et al. (2012)
Copper–effects				
v_r	*Scenedesmus* growth's deficiency EC_{50}	4	$\mu g\,L^{-1}$	Sandmann and Böger (1980)
u_r	*Scenedesmus* growth's toxicity EC_{50}	50	$\mu g\,L^{-1}$	Yan and Pan (2002)
d_r	Copper effect on *Scenedesmus* growth	5	–	NS
b_r	Copper effect on *Scenedesmus* growth	2	–	NS
v_p	*Daphnia* predation's deficiency EC_{50}	5	$\mu g\,L^{-1}$	Bossuyt and Janssen (2003)
u_p	*Daphnia* predation's toxicity EC_{50}	16.8	$\mu g\,L^{-1}$	Knops et al. (2001)
d_p	Copper effect on *Daphnia* predation	5	–	NS
b_p	Copper effect on *Daphnia* predation	1	–	NS
LD_{50}-*Daphnia*	*Daphnia* LD_{50}	30	$\mu g\,L^{-1}$	Untersteiner et al. (2003)
p_m	Copper response coefficient for Daphnia mortality	0.021	$g\,\mu g^{-1}$	(deduced from LD_{50}-*Daphnia*)

Daphnia is well described by a type II functional response (Demott, 1982; Porter et al., 1982). Therefore, the Rosenzweig–MacArthur model (Rosenzweig and MacArthur, 1963) based on logistic growth for *Scenedesmus* and a type II functional response for *Daphnia* realistically describes the *Scenedesmus*–*Daphnia* interaction (McCauley et al., 2008; Murdoch et al., 1998; Nisbet et al., 1991):

$$\begin{cases} \dfrac{\mathrm{d\,S}}{\mathrm{d}t} = r \times \mathrm{S} \times \left(1 - \dfrac{\mathrm{S}}{K}\right) - \dfrac{I_{max} \times \mathrm{S} \times \mathrm{D}}{\mathrm{S} + h} \\ \dfrac{\mathrm{d\,D}}{\mathrm{d}t} = \left(e \times \dfrac{I_{max} \times \mathrm{S}}{\mathrm{S} + h} - m\right) \times \mathrm{D} \end{cases} \tag{1}$$

where S and D are *Scenedesmus* and *Daphnia* densities ($mgC\,L^{-1}$), respectively, r *Scenedesmus* intrinsic rate of natural increase (d^{-1}), K *Scenedesmus* carrying capacity ($mgC\,L^{-1}$), I_{max} the maximum intake rate of the *Daphnia* (d^{-1}), h the half-saturation constant of *Daphnia* (mgC/L), e the *Daphnia* conversion efficiency, and m *Daphnia* mortality rate (d^{-1}). Parameter values derived from the literature are given in Table 1.

2.2.2. Internal copper concentration of organisms

Previous ecotoxicological studies report the toxicity of copper for a given external concentration and a short duration, usually ranging from 24 to 72 h and rarely up to one week. Unfortunately, the trophic position or the effect of biomagnification for the species under examination is rarely specified. We hypothesize here that the variation of the effects can be caused by the copper absorption and exposure durations. As a consequence, taking into account the internal concentration allows us to use these toxicity data for modeling the long-term dynamics of the system. Implicitly, internal concentration reflects the toxicity and neglects the absorption duration. However, this internal concentration should take the species trophic position into account. Consequently, we determine the internal concentration (Cu_{int}) as a function of the external concentration for each population. This can be derived with the following biodynamic model (Luoma and Rainbow, 2005):

$$\mathrm{Cu_{int}} = \frac{(\mathrm{Cu} \times k_u) + (\mathrm{Cu_F} \times \mathrm{AE} \times \mathrm{IR})}{k_e} \tag{2}$$

where Cu is the external concentration ($\mu g\,L^{-1}$), k_u the constant uptake rate ($L\,g^{-1}\,d^{-1}$), Cu_F the copper concentration in food, AE the assimilation efficiency (%), IR the ingestion rate ($g\,g^{-1}\,d^{-1}$), and k_e the constant loss rate (d^{-1}).

Eq. (2) allows us to calculate the internal concentration as a function of the external concentration, direct absorption ($\mathrm{Cu} \times k_u$), and food absorption ($\mathrm{Cu_f} \times \mathrm{AE} \times \mathrm{IR}$). It includes bioconcentration and biomagnification effects, and thus, the species' trophic level.

This equation shows a linear relation between copper external and internal concentrations. However, direct absorption is modified by ionic competition between copper ions (Lebrun et al., 2012). The uptake constant is modified as follows:

$$k_u = \frac{k_m}{k_c + \mathrm{Cu}} \tag{3}$$

where k_m is the maximal intake rate ($\mu g\,g^{-1}\,d^{-1}$) and k_c the half-saturation constant ($\mu g\,d^{-1}$).

The species' internal concentration is thus:

$$\mathrm{Cu_{int(Cu)}} = \frac{\left(\frac{k_m}{k_c + \mathrm{Cu}} \times \mathrm{Cu}\right) + (\mathrm{AE} \times \mathrm{IR} \times \mathrm{Cu_F})}{k_e} \tag{4}$$

This equation is simplified for the algal copper concentration, where only direct absorption occurs.

Consequently, the internal copper concentrations for *Scenedesmus* (C_S) and *Daphnia* (C_D) as a function of external concentration (Cu) are as follows:

$$\mathrm{C_{S(Cu)}} = \left(\frac{\mathrm{Cu} \times k_{mS}}{\mathrm{Cu} + k_{cS}}\right) \times \frac{1}{k_{eS}} \tag{5}$$

$$\mathrm{C_{D(Cu)}} = \left(\frac{\mathrm{Cu} \times k_{mD}}{\mathrm{Cu} + k_{cD}} + e \times \frac{I_{max} \times \mathrm{S}}{\mathrm{S} + h} \times \mathrm{C_S}\right) \times \frac{1}{k_{eD}} \tag{6}$$

where k_{mS} and k_{mD} are the maximal ingestion rates ($\mu g\,g^{-1}\,d^{-1}$) of *Scenedesmus* and *Daphnia*, respectively, k_{cS} and k_{cD} their half-saturation constants ($\mu g\,L^{-1}$), and k_{eS} and k_{eD} their constant loss rates (d^{-1}).

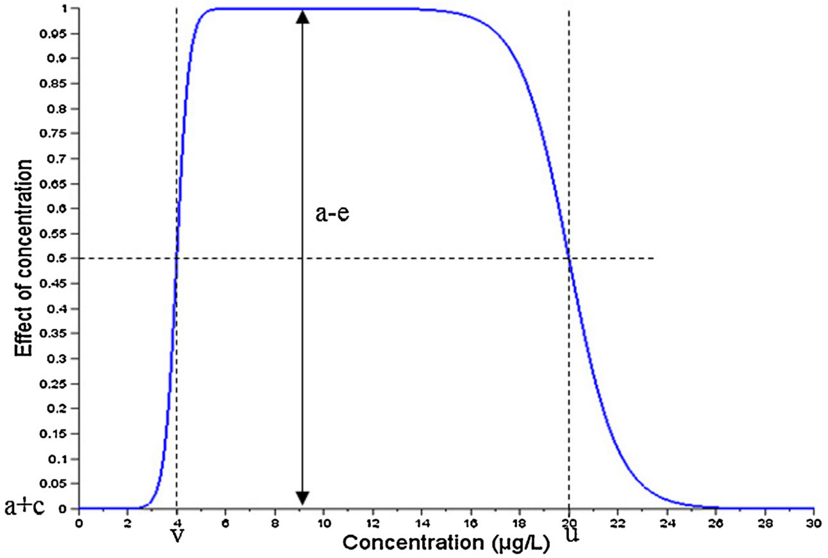

Fig. 1. Effect of copper on a given parameter as a function of its concentration in µg/L. The effect is null when equal to 1. a–e: amplitude of the effect; $a+c$ = minimal value of the effect; v and u: copper concentration for an effect at 0.5.

2.2.3. *Effects of copper on organisms*

It is common to represent copper dose-response relationships by a sigmoid curve that captures only the effect of copper as a pollutant at high concentration. Yet copper is also an essential trace element with a hormetic effect; in other words, a small quantity of copper is vital. Consequently, an asymmetric double sigmoid curve (Fig. 1) with a plateau for the optimal range better captures the various effects of copper on organisms.

The following equation is an asymmetric double sigmoid function with two thresholds, deficiency and toxicity:

$$\mathrm{Cu}_x = (a+c) - \frac{1}{2} \times (a-e) \times \tanh\left(\mathrm{d}\left(C_{x(\mathrm{Cu})} - C_{x(v)}\right)\right) + \frac{1}{2} \times (a-c) \times \tanh\left(\mathrm{b}\left(C_{x(\mathrm{Cu})} - C_{x(\mathrm{Cu})}\right)\right) \tag{7}$$

where Cu_x is the effect of copper on parameter x, $(a+c)$ the minimal value of the effect, $(a-e)$ the amplitude of the effect, v the lower EC_{50} (deficiency) and u the higher EC_{50} (toxicity), and d and b the lower and higher slopes of the curve, respectively (see below for explanations). Effects are captured in Eq. (1) where parameter x is weighted by Cu_x, that is, $x \times \mathrm{Cu}_x$.

The effect of copper on *Scenedesmus* growth rate, r, is first negative at low concentrations, then positive with an optimal growth rate at intermediate concentrations, and finally negative again at high copper concentrations. Therefore, the copper effect, Cu_r, ranges from −1 to 1. Thus, $(a+c) = -1$ and $(a-e) = -2$, so $a = -1.5$ and $c = e = 0.5$.

We obtain from (7):

$$\mathrm{Cu}_r = -1 + \tanh\left(d_r\left(\mathrm{C}_{\mathrm{S(Cu)}} - \mathrm{C}_{\mathrm{S}(v_r)}\right)\right) - \tanh\left(b_r\left(\mathrm{C}_{\mathrm{S(Cu)}} - \mathrm{C}_{\mathrm{S}(u_r)}\right)\right) \tag{8}$$

Modeling the effects of copper on *Daphnia* is more challenging as the pollutant effects on the parameters used in the model are not those tested in laboratory experiments (i.e., functional response and conversion efficiency versus growth and mortality rates). Copper effects on the mortality rate are well documented but, to our knowledge, there are no experiments on the effects of copper on Daphnia's functional response and conversion efficiency. Copper effects on *Daphnia* velocity were previously reported (Gutierrez et al., 2012; Sullivan et al., 1983; Untersteiner et al., 2003). As velocity is an advantage for a mobile predator (Gerritsen and Strickler, 1977) like *Daphnia*, these results show that copper affects predation. To capture the effects of copper on the consumer's population growth as described in Eq. (7), we weight *Daphnia*'s growth rate (i.e., the product of its conversion efficiency and functional response) with a copper parameter.

As a consequence, the effect of copper on predation, $\mathrm{Cu_p}$, ranges between 1 and 0, that is, between no effect on predation at intermediate concentrations and total inhibition of predation at low and high concentrations. Thus, $(a+c) = 0$ and $(a-e) = -1$, so $a = -0.5$ and $c = e = 0.5$.

We thus obtain from (7):

$$\mathrm{Cu_p} = \frac{1}{2}\tanh\left(d_\mathrm{p}\left(\mathrm{C}_{\mathrm{D(Cu)}} - \mathrm{C}_{\mathrm{D}(v_\mathrm{d})}\right)\right) - \frac{1}{2}\tanh\left(b_p\left(\mathrm{C}_{\mathrm{D(Cu)}} - \mathrm{C}_{\mathrm{D}(u_p)}\right)\right) \tag{9}$$

Because there is no hormetic effect of copper on *Daphnia* mortality but only a negative effect, we model a linear effect on this parameter as follows:

$$\mathrm{Cu_m} = 1 + p_\mathrm{m} \times \mathrm{C}_{\mathrm{D(Cu)}} \tag{10}$$

where p_m is a copper response coefficient.

Finally, introducing the copper effects captured in Eqs. (8)–(10) into model (1) leads to the following equations:

$$\begin{cases} \dfrac{\mathrm{d\,S}}{\mathrm{d}t} = r \times \mathrm{Cu}_r \times \mathrm{S} \times \left(1 - \dfrac{\mathrm{S}}{K}\right) - \dfrac{I_{\max} \times \mathrm{S} \times \mathrm{D}}{S+h} \times \mathrm{Cu}_p \\ \dfrac{\mathrm{d\,D}}{\mathrm{d}t} = \left(e \times \mathrm{Cu}_p \times \dfrac{I_{\max} \times \mathrm{S}}{\mathrm{S}+h} - m \times \mathrm{Cu}_m\right) \times D \end{cases} \tag{11}$$

2.2.4. *Model dynamics with copper effects and nutrient enrichment*

Nutrient enrichment can destabilize prey-predator interactions by changing the equilibrium point from stable to unstable (Appendix A). This effect is known as the paradox of enrichment (Rosenzweig, 1971). Nutrient enrichment and copper pollution might interact and the effects of their interaction might be unpredictable, that is, antagonistic or synergetic. To address this issue, we conducted computer simulations of the *Scenedesmus*–*Daphnia* system where we varied the algal carrying capacity (K) to simulate nutrient enrichment and copper concentration in water (Cu).

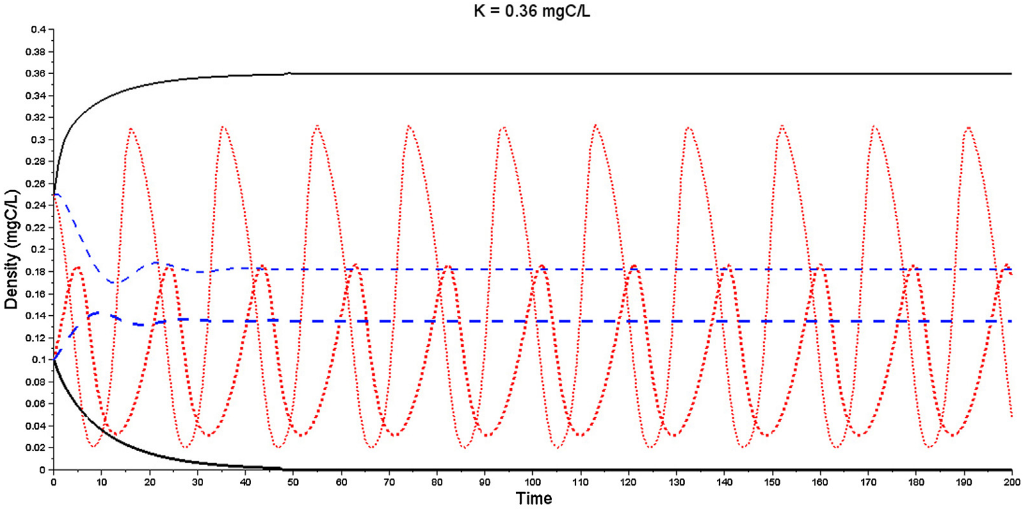

Fig. 2. *Scenedesmus* (thin lines) and *Daphnia* (bold lines) dynamics for three copper concentrations: 6.5 (dotted lines), 13 (dashes), and 16 (solid lines) μg Cu/L. The dynamics where both populations become extinct is not shown (copper concentration >50 μg Cu/L). The carrying capacity is set to 0.36 mgC/L.

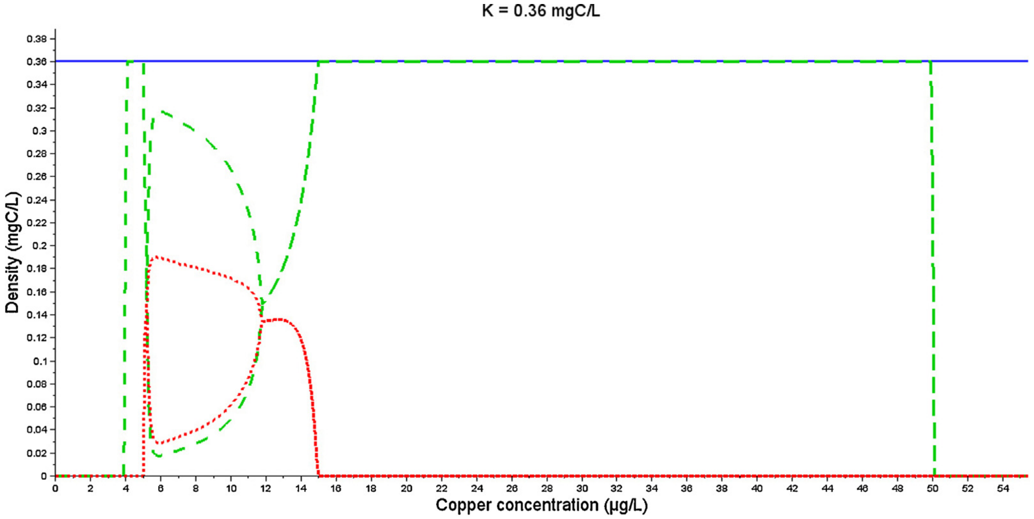

Fig. 3. *Scenedesmus* (dashes) and *Daphnia* (dotted lines) equilibrium values for copper concentrations ranging between 0 and 55 μg Cu/L. Solid line: carrying capacity. The two lines per population between 5.2 and 11.8 μg Cu/L show the oscillations' minima and maxima.

2.3. *Parameter values and sensitivity analysis*

We parameterized our model with the parameter values provided in Table 1. Some of these values may be found in the literature, while others may not; we therefore gave them arbitrary values.

We then performed a sensitivity analysis by running the model with a 10% increase or decrease in the value of each parameter for different copper concentrations and algal carrying capacities.

3. Results

3.1. *Effects of copper on* Scenedesmus *and* Daphnia *populations*

Depending on the copper concentration, the dynamics of *Scenedesmus* and *Daphnia* were stable, cyclic, or showed population extinction (Fig. 2). For low (6.5 μg Cu L^{-1}) and medium (13 μg Cu L^{-1}) copper concentrations, both populations coexist with either oscillations or stable densities. With increasing concentrations of copper (16 μg Cu L^{-1}), the *Daphnia* population becomes extinct and for a copper concentration exceeding 50 μg Cu L^{-1}, the algal population also becomes extinct (Fig. 2).

Fig. 3 summarizes the dynamics observed for copper concentrations ranging from 0 to 60 μg L^{-1}. For a copper concentration below 4 μg L^{-1}, neither *Scenedesmus* nor *Daphnia* population persists because of copper deficiency. For a copper concentration between 4 and 5.2 μg Cu L^{-1}, only the algal population can grow. For a copper concentration between 5.2 and 15 μg L^{-1}, the two populations coexist, first with oscillations and then, beyond 11.8 μg L^{-1}, with stable densities. For a concentration exceeding 15 μg Cu L^{-1}, the *Daphnia* population becomes extinct because of toxicity and for a concentration above 50 μg Cu L^{-1}, the *Scenedesmus* population also becomes extinct for the same reason. In short, with increasing copper concentrations, we observe a gradual change from no population to oscillations, stable coexistence, and finally extinction.

3.2. *Effects of copper and nutrient enrichment on* Scenedesmus–Daphnia *interaction*

The results summarized in Fig. 4 shows that copper pollution and nutrient enrichment have antagonistic effects and that copper pollution partially compensates the destabilizing effect of nutrient enrichment. The range of copper concentration that ensures

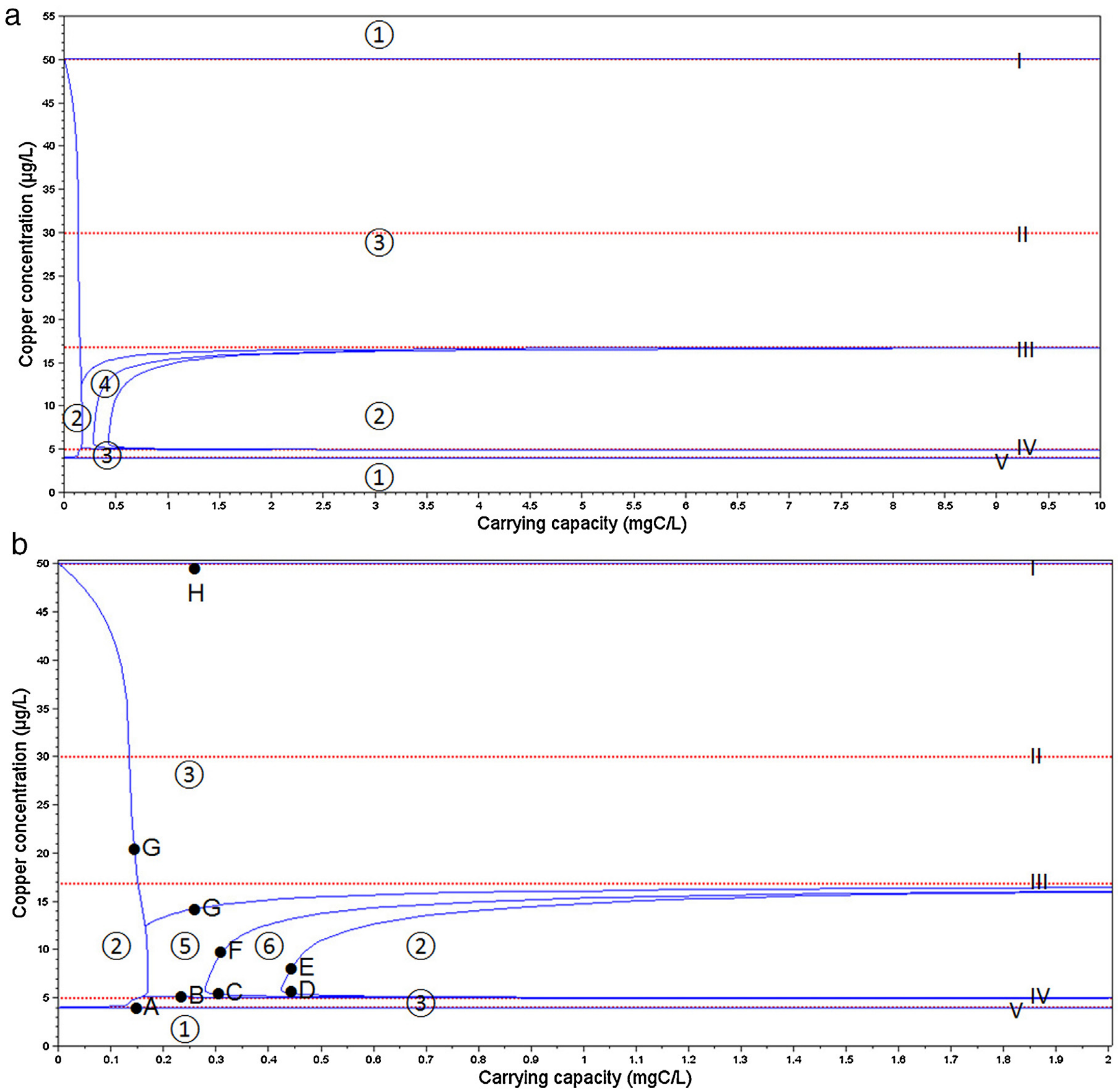

Fig. 4. The different states of the model as a function of copper concentration (µg Cu/L) and carrying capacity (mgC/L). (a) Copper concentrations between 0 and 60 µg Cu/L and carrying capacity between 0 and 10 mgC/L; (b) Copper concentration between 0 and 51 µg Cu/L and carrying capacity between 0 and 2 mgC/L. Horizontal dotted lines show the toxicological values used in the model (from top to bottom, I: toxicity algae-EC_{50}, II: *Daphnia*-LD_{50}, III: toxicity *Daphnia*-EC_{50}, IV: deficiency *Daphnia*-EC_{50}, V: deficiency algae-EC_{50}) For the areas with numbers in circles, see text for explanations. Dots with letters identify the threshold of copper concentrations between states.

the stable coexistence of *Scenedesmus* and *Daphnia* decreases as nutrient enrichment increases.

We distinguish eight outcomes of the model depending on copper concentration and algal carrying capacity (Fig. 4). In four of them, the two populations become extinct. For $Cu < 4\,\mu g\,L^{-1}$ and $Cu > 50\,\mu g\,L^{-1}$, *Scenedesmus* and *Daphnia* populations become extinct because of copper deficiency and toxicity, respectively (Fig. 4, areas 1). In the optimal range of copper concentration for *Scenedesmus* and *Daphnia*, both populations become extinct because of either a low carrying capacity (below $0.169\,mgC\,L^{-1}$) that is not a rich enough medium to support the populations or a high carrying capacity (above $0.428\,mgC\,L^{-1}$) that is rich medium inducing a strong destabilization and the collapse of the system (Fig. 4, areas 2). For low and high copper concentrations (Fig. 4, areas 3), there are two regions where *Daphnia* is either deficient or poisoned by copper; *Scenedesmus* alone persists and reaches its carrying capacity. Finally, for a copper concentration between 5 and $15\,\mu g Cu\,L^{-1}$ and a carrying capacity between 0.166 and $0.43–0.5\,mgC\,L^{-1}$ (expanding over a narrow range of carrying capacity up to $8\,mgC\,L^{-1}$), the two populations coexist (Fig. 4a, area 4). When $K < 0.28\,mgC\,L^{-1}$ the system is stable (Fig. 4b, area 5). However, beyond this value, there are oscillatory dynamics (Fig. 4b, area 6).

Fig. 4 shows the toxicological values used for model parametrization, i.e., the *Scenedesmus* and *Daphnia* LD_{50}. These values are critical as they define the boundaries of the areas previously described.

Note that copper and nutrient enrichment interact and may promote the stable coexistence of *Scenedesmus* and *Daphnia*. For instance, for $K = 0.4\,mgC\,L^{-1}$, with an increasing copper concentration from 4 to $16\,\mu g\,Cu\,L^{-1}$, the model outputs are *Scenedesmus* alone, population oscillations, stable coexistence, and again *Scenedesmus* alone (Fig. 4b, areas 3, 6, 5 and 3). Population oscillations are due to a high productivity, while increasing copper concentration stabilizes the system before the extinction of the consumer. The interaction between copper pollution and nutrient enrichment also promotes the persistence of *Daphnia* for a limited range of copper concentration and carrying capacity. For instance, for $K = 0.7\,mgC\,L^{-1}$, with an increasing copper concentration from 4 to $16\,\mu g\,Cu\,L^{-1}$, the model predicts the persistence of *Scenedesmus* alone first because of a *Daphnia* copper deficiency (area 3) and then a *Daphnia* exclusion driven by medium richness (area 2), followed by population oscillations (area 6), stable coexistence (area 5), and again *Scenedesmus* alone because of *Daphnia* copper toxicity (area 3).

3.3. Sensitivity analysis

Our model predicts different equilibrium states of the community. The boundaries of these states change with the copper concentration and carrying capacity (Fig. 4), but also depend on other model parameters. Therefore, we conducted a sensitivity analysis to determine how these boundaries or threshold values between states depend on small changes in parameter values. To conduct this analysis, we changed parameter values by −10% or +10% and compared the threshold values of copper concentration between states to the initial threshold values. As the states' boundaries change with the medium richness, we assessed the threshold values for different carrying capacities. We identify the following eight threshold values (circles in Fig. 4b): (A) between no populations and *Scenedesmus* alone (areas 1 and 3); (B) between *Scenedesmus* alone and stable coexistence (areas 3 and 5), or alternatively, for low carrying capacities, between *Scenedesmus* alone and no populations (areas 3 and 2); (C) between stable and unstable coexistence (areas 5 and 6); (D) between unstable coexistence and population extinction (areas 6 and 2); (E) between population extinction and unstable coexistence (areas 2 and 6); (F) between unstable and stable coexistence (areas 6 and 5); (G) between stable coexistence and *Scenedesmus* alone (areas 5 and 3), or alternatively, for low carrying capacities, between no populations and *Scenedesmus* alone (areas 2 and 3); finally, (H) between *Scenedesmus* alone and no populations (areas 3 and 1). The results are summarized in Fig. S3.

The most influential parameters are the growth rate r (maximal variation of 42.15%), maximum intake rate $I_{\max}$ (maximal variation of 42.58%) for a low carrying capacity ($K = 0.14$ mgC/L), and half-saturation constant h (maximal variation of 19.18%) and mortality rate m (maximal variation of 14.61%) of *Daphnia* for high carrying capacity ($K = 0.5$ mgC/L).

The other parameters rarely have an impact above than their own variation (10%). Interestingly, the parameters characterizing the shape of the *Daphnia* response to copper while taking into account the hormetic effects (parameters d_p, b_p, v_p, s_p, and p_m in Fig. S3p–t) affect mostly the threshold values A–D and H (variation superior to 5%). This effect is not found in the *Scenedesmus* response to copper: the parameters d_r, b_r, v_r, and u_r do not have a strong effect on threshold values (Fig. S3i–l) and generally have less effect than *Daphnia*'s parameters.

4. Discussion

4.1. Effects of copper on Scenedesmus *and* Daphnia

Our model shows that the *Scenedesmus–Daphnia* system obeys highly non-intuitive dynamics, with strong threshold effects and sudden population extinctions as the copper concentration increases or decreases in relation to the species' optimal range. Three types of outcomes are observed regarding population extinction and persistence. First, copper deficiency (less than 4 μg L^{-1}) precludes the growth of both species, while an increased copper concentration prevents *Daphnia* growth. Second, for an optimal range of copper concentration (between 5 and 16 μg L^{-1}), the model results show unstable and stable coexistence. Third, as copper concentration increases, toxic effects become apparent with the extinction of *Daphnia* (16 μg L^{-1}) followed by *Scenedesmus* (50 μg L^{-1}). The different equilibriums reached by the *Scenedesmus–Daphnia* dynamics reveal the various noxious effects of copper. Low concentrations induce deficiency for either both species or *Daphnia* alone. High concentrations induce toxicity first on *Daphnia* and then on *Scenedesmus*. The threshold values are more sensitive to the parameters characterizing *Daphnia*'s response to copper than *Scenedesmus*'. These threshold values of copper concentration also depend on the environment fertility. Nutrient enrichment is known to destabilize the *Scenedesmus–Daphnia* dynamics. Our results show that copper tends to counteract the negative effect of nutrient enrichment on the stability of the prey-predator system and even promotes *Daphnia* persistence for a limited range of copper concentration and carrying capacity.

4.2. Copper and the stability of the prey-predator interaction

In the area where the two species coexist (Fig. 4), there are two zones: a stable zone where densities do not vary over time and an oscillating zone where densities present cyclic variations (Fig. 4b, areas 5 and 6, respectively). When carrying capacity increases, the system is destabilized and shifts from the stable to oscillating zone. This is the well-known paradox of enrichment (Rosenzweig, 1971; Appendix A). Conversely, for an algal carrying capacity exceeding 0.3 mgC L^{-1}, when copper concentration increases, the system shifts from the oscillating to stable zone: thus, there is stabilization by copper. In addition, copper favors the persistence of *Daphnia*, which would otherwise become extinct because of a strong destabilization of the prey-predator dynamics, thus leading to the collapse of the predator population. Oscillations are caused by a high algal growth rate and a delay in the consumer numerical response caused by saturation of the predator captured by the type II functional response. The noxious effects of copper on both the prey and predator retard both algal growth and predation and stabilize the interaction. The stabilization of the *Scenedesmus–Daphnia* interaction is also due to the improvement of algal growth conditions following the decline of predator efficiency induced by copper pollution. This stabilization counteracts the destabilization effect of nutrient enrichment described as the paradox of enrichment.

Although surprising, these results have already been described in other contexts. For instance, Abrams and Walters (1996) analyzed a prey-predator model in which the prey can switch between vulnerable and invulnerable states in different locations. Several mechanisms can generate such a situation. For instance, as a prey grows, it may become protected from predation by its large body size. Otherwise, a prey may move back and forth from locations with predators to locations without predators, or it may reduce its activity in the presence of predators, and hence, decrease its vulnerability to predation. Abrams and Walters' model showed a stabilization of the prey-predator interaction and an increase in prey equilibrium density. Copper bioconcentrated by *Scenedesmus* cells makes it toxic to *Daphnia*, which can be viewed as a form of invulnerability. Roy and Chattopadhyay (2007) studied the interaction between a toxic prey and its predator. Their model showed the same results (stabilization of the prey-predator interaction and increase in prey equilibrium density) in addition to an increase in the predator equilibrium density. Our model shows the same results, but differs from these models as copper toxicity affects the predator directly through bioconcentration and indirectly through biomagnification.

Consequently, an antagonistic effect exists between nutrient enrichment and copper, which explains the expansion of the coexistence zone along the carrying capacity axis (Fig. 4). However, the beneficial effects revealed by our model may not apply to other systems. Garay-Narváez et al. (2013) showed that pollutants have a destabilizing effect on more complex ecosystems.

These counterintuitive results reveal that antagonistic effects between pollutants can mask the noxious effects of these very pollutants in natural systems, which is a disturbing observation.

4.3. Copper pollution and threshold values

Our model shows a succession of different threshold values, depending on copper toxicity values (Table 1) for copper concentrations and carrying capacities. As copper concentration increases and moves away from species' optimal value, in a medium of intermediate fertility (0.36 mgC L^{-1}), the system first switches from unstable to stable dynamics, then *Daphnia* becomes extinct, and finally *Scenedesmus* also becomes extinct. The corresponding threshold values are 11.8, 15, and 50 $\mu g L^{-1}$, respectively. If copper concentration decreases, the system switches from unstable dynamics to *Daphnia* extinction and then *Scenedesmus* extinction, with the corresponding threshold values of 5.6 and 4 $\mu g L^{-1}$. However, these threshold values are highly dependent on LD_{50} and EC_{50} values (see horizontal dotted lines in Fig. 4), for which *Daphnia* is more sensitive to copper than is *Scenedesmus*, as confirmed by the sensitivity analysis. Our model predicts a reduction in the optimal range defined by these values and obtained for isolated individuals, especially for the predator. For instance, *Daphnia* becomes extinct for a concentration below EC_{50} (16.8 $\mu g L^{-1}$), with this threshold decreasing with the carrying capacity. As in Lampert et al. (1989) experiments, these results highlight that the toxic effects of contaminants may be strikingly different when assessed on individuals in isolation or in an entire community.

Furthermore, our results challenge the use of the no-observed-effect concentration (NOEC) and lowest-observed-effect concentration (LOEC) that define pollutant concentrations with no or low effects on individuals.

At the community or ecosystem scale, NOEC and LOEC consequently encounter two issues: (1) effects on populations' density (Fig. 3) – our model shows no single NOEC or LOEC since population densities vary with copper concentration and environmental conditions – and (2) effects on equilibrium states (Fig. 4) – in our model, we can define a NOEC for each equilibrium state. For instance, the model shows stable and unstable coexistence with and without copper, and we can define a NOEC for stable and unstable coexistence.

Muyssen and Janssen (2007) estimated the copper NOEC and LOEC for *Daphnia* juveniles to be 75 $\mu g L^{-1}$ and 90 $\mu g L^{-1}$, respectively. The NOEC and LOEC for *Daphnia* adults exceed 130 $\mu g L^{-1}$. As the EC_{50}, NOEC, and LOEC of *Daphnia* individuals alone are higher than the predicted copper concentration of *Daphnia* extinction in our model in which individuals interact with their prey, community interactions may have synergistic effects with pollutants. The interaction between ecological interactions and pollution could thus be assessed by estimating NOECs or LOECs at the community level. For instance, Roussel et al. (2007) estimated the NOEC and LOEC of primary producers in a lotic ecosystem submitted to copper pollution to be 5 or 4 $\mu g L^{-1}$ and 25 or 20 $\mu g L^{-1}$, respectively, while individual organisms were only affected significantly at copper concentrations of 25 and 75 $\mu g L^{-1}$. Our results, however, show that the community dynamics switches from unstable to stable before the extinction of herbivores. This qualitative change in community dynamics is not accounted for in the endpoint tests, whereas it could be seen as a warning signal.

5. Conclusion

The need for more realistic ecotoxicological approaches has been highlighted previously (Kramer et al., 2011). Our model of a simple freshwater prey-predator ecosystem shows that predators may be more affected by copper pollution when community interactions are taken into account than when analyzed alone. At the community level, our analyses show that depending on the nutrient status of the system, copper pollution may stabilize the prey-predator interaction, although this stabilization leads to predator extinction if copper concentration increases further. Copper pollution and nutrient enrichment may have antagonistic effects for a limited range of variation of these two perturbations, which may result in misleading information on ecosystem health.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.aquatox.2015.03.003.

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