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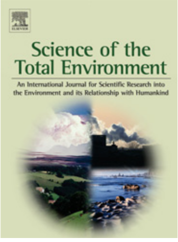

Effects of Mg^{2+} and H^+ on the toxicity of Ni^{2+} to the unicellular green alga *Pseudokirchneriella subcapitata*: Model development and validation with surface waters

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ABSTRACT

In this study, increasing Mg concentrations and decreasing pH were observed to decrease Ni toxicity to the green alga *Pseudokirchneriella subcapitata*. To investigate to what extent the original biotic ligand model (BLM) concept could explain Ni toxicity as a function of water chemistry, the protective effects of Mg^{2+} and H^+ were modeled as BLM-type single-site competition effects. The model parameters representing these effects were log $K_{MgBL}=3.3$ and log $K_{HBL}=6.5$. The BLM was capable of predicting Ni toxicity by an error of less than a factor of 2 in most synthetic and natural waters used in this study. However, since the relationship between 72-h $E_rC50_{Ni^{2+}}$ (i.e. the 72-h E_rC50 expressed as Ni^{2+} activity) and H^+ activity was not linear over the entire tested pH range, only the 'linear part' between pH 6.45 and 7.92 was used for derivation of log K_{HBL}. This nonlinearity indicates that the effect of pH can probably not be attributed to H^+ competition with Ni^{2+} for a single site alone. When modeling the effect of pH as a linear relation between 72-h $E_rC50_{pNi^{2+}}$* (=−log (72-h $E_rC50_{Ni^{2+}}$ corrected for the presence of Mg)) and pH, the applicability of the model was successfully extended to pH levels as low as 6.01. This type of empirical model has also been used in our previous studies on the development of a chronic Ni bioavailability model for *Daphnia magna* and a long-term Ni bioavailability model for rainbow trout. Finally, we could not detect a statistically significant interactive effect of pH and Mg on the toxicity of Ni^{2+} to *P. subcapitata* and this is in line with the formulation of our empirical model.

1. Introduction

As primary producers, planktonic microalgae are a key component of food chains in aquatic systems. Since changes in algal population density and diversity may affect the entire aquatic ecosystem, it is important to understand how algae are affected by aquatic toxicants, such as metals. As for test organisms belonging to higher trophic levels, such as daphnids and fish, metal toxicity to algae has been demonstrated to be dependent on water chemistry. Physicochemical parameters such as water hardness, Ca, Mg, Na, pH and/or dissolved organic carbon (DOC) have been reported to affect the toxicity of several metals to algae (e.g., Al, Parent and Campbell, 1994; Cd, Peterson et al., 1984; Kola and Wilkinson, 2005; Vigneault and Campbell, 2005; Zn, Heijerick et al., 2002; Cu, De Schamphelaere et al., 2003; Heijerick et al., 2005; U, Franklin et al., 2000; Charles et al., 2002; Fortin et al., 2007).

For fish and daphnids, the biotic ligand model (BLM) concept has been demonstrated to be very successful for the development of bioavailability models capable of predicting metal toxicity as a function of water chemistry (reviewed by Niyogi and Wood, 2004). These models are useful tools for regulatory exercises such as aquatic risk assessments and the derivation of water quality criteria. The applicability of the original BLM

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Table 1 – Main physicochemical characteristics of the synthetic test media used in the univariate Ca, Mg and pH test series and in the bivariate pH–Mg test series

Test medium	pH	Major ions (mg/L)				Hardness [b]	Alkalinity [c]
		Ca	Mg	K [a]	Cl [a]	(mg $CaCO_3$/L)	(mg $CaCO_3$/L)
Ca 0.12 mM	7.40	3.36	2.79	136	22.9	19.9	27.3
Ca 0.5 mM	7.38	14.0	2.81	132	49.7	46.4	27.2
Ca 1.0 mM	7.40	27.9	2.82	129	85.1	81.4	27.3
Ca 2.0 mM	7.39	58.0	2.77	125	156	156	27.3
Ca 3.0 mM	7.39	87.2	2.76	123	227	229	27.3
Ca 4.0 mM	7.41	115	2.76	123	298	299	27.4
Ca 5.0 mM	7.44	144	2.79	123	369	370	27.5
Mg 0.12 mM	7.48	3.11	2.99	140	25.0	20.1	27.7
Mg 0.5 mM	7.51	3.02	11.4	133	52.3	54.5	27.9
Mg 1.0 mM	7.50	3.14	20.5	129	86.2	92.2	27.8
Mg 1.5 mM	7.52	3.05	44.6	128	121	191	27.9
Mg 2.0 mM	7.53	3.08	46.3	128	159	198	28.0
Mg 2.5 mM	7.54	3.05	57.1	124	193	243	28.0
Mg 3.0 mM	7.53	2.99	71.2	120	228	300	28.0
Mg 4.0 mM	7.54	3.03	93.5	126	300	392	28.0
Mg 5.0 mM	7.52	2.97	115	124	371	481	27.9
pH 6.0	6.01	3.43	3.06	157	169	21.2	9.30
pH 6.4	6.45	3.49	3.10	157	141	21.5	16.6
pH 7.2	7.29	3.45	2.97	157	72.5	20.8	26.7
pH 7.6	7.65	3.58	2.85	157	46.6	20.7	28.4
pH 8.0	7.92	3.46	3.08	157	34.5	21.3	29.1
pH 6.0							
Mg 0.12 mM	6.23	4.61	3.15	144	141	24.5	12.8
Mg 1.5 mM	6.13	4.57	35.8	144	239	159	11.2
Mg 3.0 mM	6.08	4.18	73.2	144	346	312	10.4
pH 7.0							
Mg 0.12 mM	7.20	4.46	4.33	144	82.4	28.9	26.1
Mg 1.5 mM	7.16	4.42	33.4	144	181	149	25.8
Mg 3.0 mM	7.15	4.47	73.8	144	287	315	25.7
pH 7.8							
Mg 0.12 mM	7.95	4.34	2.96	144	22.9	23.0	29.2
Mg 1.5 mM	7.88	4.37	35.5	144	121	157	29.0
Mg 3.0 mM	7.85	4.28	73.3	144	227	312	28.9

[a] No measurements were conducted for Na, K, SO_4 and Cl, hence nominal values are reported. In all tests, nominal Na and SO_4 concentrations were 13.7 and 5.86 mg/L, respectively.

[b] Water hardness was calculated from measured Ca and Mg concentrations.

[c] Alkalinity was calculated from nominal added inorganic carbon (IC) and measured pH, using thermodynamic stability constants taken from Stumm and Morgan (1996).

concept to algae has been discussed by several authors (e.g., Campbell et al., 2002; Heijerick et al., 2002, 2005; De Schamphelaere et al., 2003, 2005a,b; Hassler and Wilkinson, 2003; Kola and Wilkinson, 2005; De Schamphelaere and Janssen, 2006; Fortin et al., 2007). Although all of these authors encountered difficulties that questioned the applicability of the original BLM concept, some of them have proposed solutions that allow the development of bioavailability models using modified procedures (Heijerick et al., 2002; De Schamphelaere et al., 2003, 2005a,b; De Schamphelaere and Janssen, 2006).

To date, almost all of the studies in which algae were exposed to Ni have focused on the mechanism by which Ni affects photosynthesis and respiration. To our knowledge, only a few studies have investigated the influence of water chemistry (e.g., cations and/or pH) on adsorption, uptake and/or toxicity of Ni (e.g., Macfie et al., 1994; Issa et al., 1995; Mehta et al., 2000; Worms and Wilkinson, 2007). No attempts have been made to develop a Ni bioavailability model for algae. Therefore, the objectives of this study were (i) to investigate how water chemistry affects the toxicity of Ni to a unicellular green alga, and (ii) to develop a bioavailability model capable of predicting Ni toxicity as a function of water chemistry. *Pseudokirchneriella subcapitata* was chosen as the test species (i.e. one of the standard test species listed by OECD test guideline 201, OECD, 1996).

Using an approach similar to that applied in our previous studies on chronic Ni toxicity to *Daphnia magna* (Deleebeeck et al., 2008a) and long-term Ni toxicity to rainbow trout (Deleebeeck et al., 2007), the individual effects of Ca, Mg and pH on Ni-induced growth inhibition of *P. subcapitata* were examined. Additionally, it was investigated whether or not pH affects the effect of Mg and/or the effect of pH is affected by Mg. Based on the results of these experiments it was investigated to what extent the original BLM concept can be used to explain the observed effects. The predictive capacity of the developed model was evaluated using results from toxicity tests in both synthetic and natural waters. The latter also allowed evaluating the importance of DOC in reducing Ni toxicity.