today's consultants for tomorrow's challenges

International Manganese Institute

DEVELOPMENT OF A CHRONIC BIOTIC LIGAND MODEL FOR MANGANESE

Adam Peters[1], Bill Stubblefield[2], Graham Merrington[1], Steve Lofts[3], Keven Harlow[4], Bruce Brown[5] and Lindsey Sturdy[5]

[1]Howbery Park, Wallingford, OXON OX10 8BD, UK [2]Dept of Environmental and Molecular Toxicology, Oregon State University, OR, USA [3]Centre for Ecology & Hydrology, Lancaster Environment Centre, Library Avenue, Bailrigg, Lancaster, UK
[4]The International Manganese Institute, 17 rue Duphot, 75001 Paris, France [5]Environment Agency of England and Wales, Almonsbury, Bristol, UK E-mail contact: graham.merrington@wca-environment.com

Abstract

Biotic Ligand Models (BLMs) which are able to predict metal toxicity to organisms as a function of water chemistry conditions have been developed for several metals in recent years, and have already been adopted for regulatory applications in some cases. These models are typically developed from laboratory tests covering a wide range of water quality conditions, and are validated against ecotoxicity tests performed on natural water samples. Similar approaches have recently been applied to assess manganese toxicity to three aquatic organisms: *Pimephales promelas, Ceriodaphnia dubia,* and *Pseudokirchneriella subcapitata*. The key physicochemical factors influencing the bioavailability of manganese are calcium, magnesium and pH. Manganese bioavailability to fish and invertebrates, when expressed as free manganese ion concentrations, is affected by Calcium concentrations. Manganese bioavailability to algae, when expressed as free manganese ion concentrations, is affected by pH. This poster shows the stages in the development of the MnBLM in addition to outlining levels of performance against validation data. Practical regulatory approaches for implementing bioavailability corrections for manganese are described, and examples based on UK data are shown. We also provide an opportunity for meeting participants to trial the completed BLM.

Methods

In previous freshwater BLM development work (e.g. De Schamphelaere and Janssen 2002), concentrations of potentially competing ions (e.g. H^+, Na^+, Mg^{2+}, K^+, Ca^{2+}) were varied singly and biotic ligand binding constants were derived from the slope of a plot of the toxic endpoint activity of the metal against the activity of each competing ion. Inspection of this dataset showed that the differences in activity of each competing ion in the test solution were not sufficiently univariate to allow this method to be applied. Therefore, an alternative method, that of Thakali and co-workers (Thakali et al. 2006a&b) was used. This method involves the use of all the dose-response data generated, rather than a single endpoint from each water composition. The method makes the assumption that toxicity is directly related to the concentration of toxic metal bound to the biotic ligand, and fits a single dose—response curve to the entire set of data.

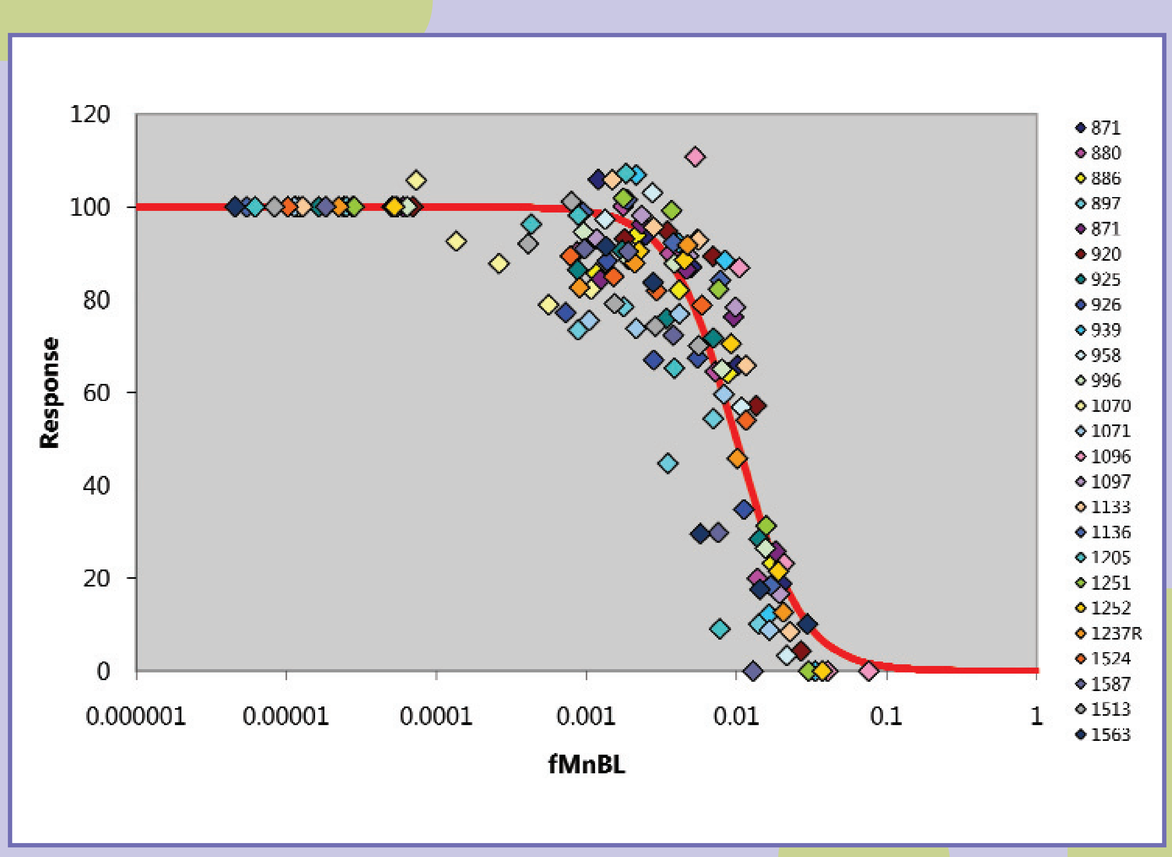

Figure 1. Results of BLM fitting to the fathead minnow dose-response curves. The responses have been scaled to their respective controls on a percentage scale. The legend shows the test number.

Model Development

Algae

The toxicity of manganese to algae is influenced by competition from protons (H^+) at a single receptor site. A single model is used to predict the effects of manganese on both growth and biomass endpoints.

Invertebrates

The toxicity of manganese to invertebrates is influenced by competition from both calcium and magnesium at a single biotic ligand.

Fish

The toxicity of manganese to fish is influenced by calcium. The effects are modelled assuming two biotic ligand sites for manganese, with competition from calcium only being effective at one of these sites. This model reproduces data obtained at high Calcium concentrations better than a single site model.

Model Validation

Ecotoxicity tests were performed for all three test species in five natural waters with different water chemistries. The selected waters cover a range of conditions of pH, water hardness, and dissolved organic carbon (DOC) concentrations that are considered to be broadly representative of the types of conditions under which the models are likely to be applied. The water quality conditions of the validation test waters are shown in Table 1.

Table 1. Water quality of samples used for BLM validation testing.

Water	pH	DOC	Calcium	Hardness	Alkalinity
Peninsula	7.7	7.0	17	60	56
Santiam	7.6	0.7	7	24	36
Texoma	8.1	4.8	77	304	124
Soap Creek	8.0	1.3	21	84	96
Pinelands	6.7	12.0	4	12	8

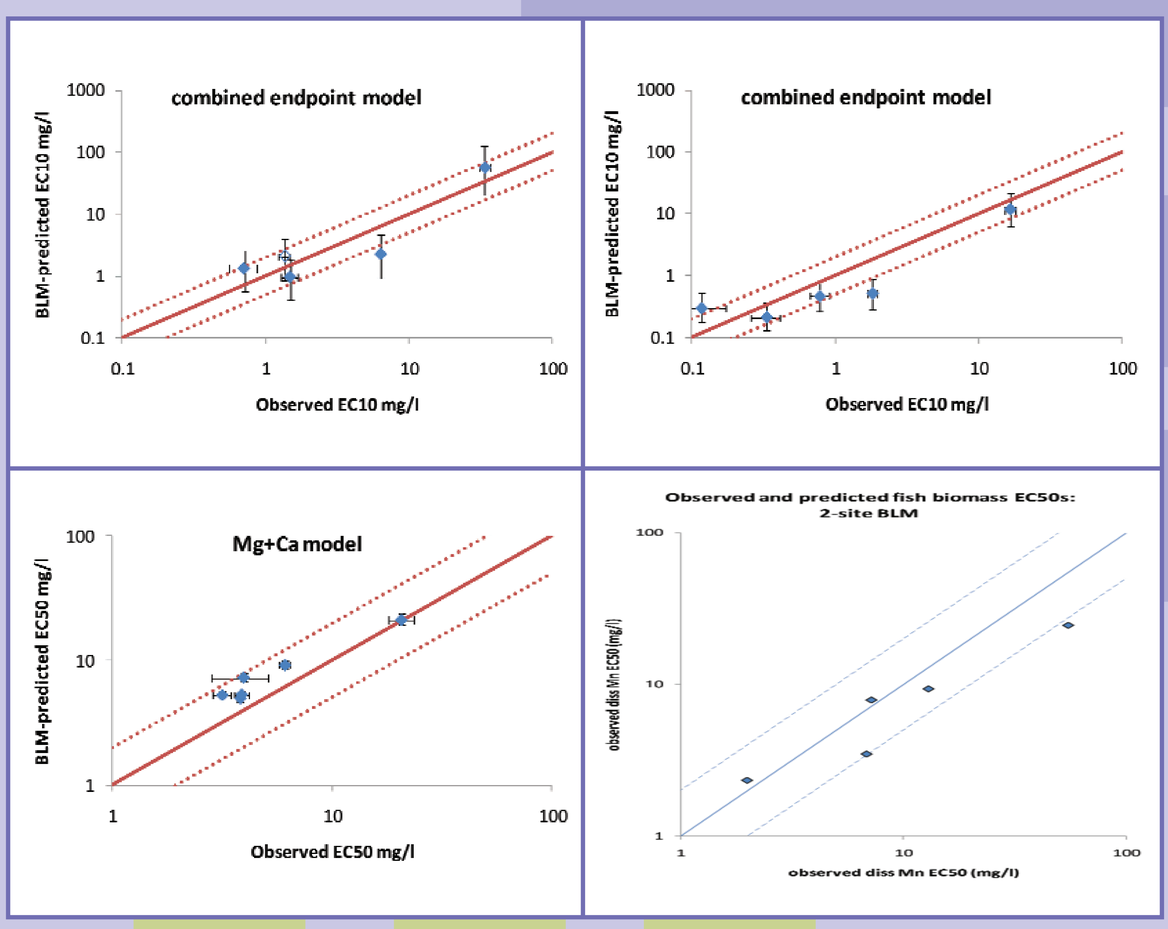

Figure 2. Validation of model performance for algal growth (top left), algal biomass (top right), *C. dubia* reproduction (bottom left), and fish growth (bottom right).

Conclusions

Biotic Ligand Models for manganese have been developed for three species: an alga, an invertebrate, and a fish. Each test species shows a different manganese bioavailability response.

Calcium concentrations affect manganese toxicity to fish and invertebrates, with high sensitivity under soft water conditions, although the responses are not modelled in the same manner.

Manganese toxicity to algae is affected by pH, with high sensitivity at high pH.

The models developed are able to predict the observed manganese toxicity in five natural water samples to within a factor of 2, in the majority of cases.

References

De Schamphelaere KAC, Janssen CR. 2002. A biotic ligand model predicting acute copper toxicity for Daphnia magna: The effects of calcium, magnesium, sodium, potassium, and pH. Environ Sci Technol 36: 48—54.

Thakali S, Allen HE, Di Toro DM, Ponizovsky AA, Rooney CP, Zhao FJ, McGrath SP. 2000. A Terrestrial Biotic Ligand Model. 1. Development and application to Cu and Ni toxicities to barley root elongation in soils. Environ Sci Technol 40: 7085—7093.

Thakali S, Allen HE, Di Toro DM, Ponizovsky AA, Rooney CP, Zhao FJ, McGrath SP, Criel P, Van Eeckhout H, Janssen CR, Oorts K, Smolders, E. 2006. Terrestrial biotic ligand model. 2. Application to Ni and Cu toxicities to plants, invertebrates, and microbes in soil. Environ Sci Technol 40: 7094—7100.

wca environment ltd.
Brunel House, Volunteer Way, Faringdon, Oxfordshire, SN7 7YR
Tel: 01367 246022 Fax: 01367 246041
www.wca-environment.com solutions@wca-environment.com