Derivation of BLM-based Ambient Water Quality Criteria for Lead Following USEPA Guidelines: A Comparison with European Approaches

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Abstract

The U.S. Environmental Protection Agency's (USEPA's) current ambient water quality criteria (AWQC) for lead (Pb) in freshwater were developed in 1984. The criteria are adjusted for hardness, but more recent studies have demonstrated that other parameters, especially dissolved organic carbon (DOC) and pH, have a much stronger influence on Pb bioavailability. These recent studies have been used to support development of a biotic ligand model (BLM) for Pb in freshwater, such that acute and chronic Pb toxicity can be predicted over a wide range of water chemistry conditions. Following USEPA guidelines for AWQC development, and using a methodology consistent with that used by the USEPA in developing its recommended BLM-based criteria for copper in 2007, we propose acute and chronic BLM-based AWQC for Pb in freshwater. In addition to the application of the BLM approach that shows ability to better account for site-specific Pb bioavailability, the toxicity datasets presented here are also much more robust than in 1984 and there are now sufficient chronic Pb toxicity data available that use of an acute-chronic ratio (ACR) is no longer necessary. Over a range of North American surface waters with representative water chemistry conditions, proposed acute BLM-based Pb criteria ranged from approximately 20 to 1000 µg/L and chronic BLM-based Pb criteria ranged from approximately 0.3 to 40 µg/L. Differences exist between US and European approaches used for driving AWQC or aquatic safe thresholds of metals. The key differences include the use of genus means, EC20s, and exclusion of algae and plants from the sensitivity distribution in the US versus the use of species means, NOEC/EC10s, and inclusion of algae and plants in the sensitivity distribution in the EU. Additionally, the approach to distribution fitting is also different. In order to understand the implication of methodological differences, a set of ecological threshold concentrations of Pb derived for selected European freshwater scenarios will be compared with the proposed chronic Pb AWQC.

Introduction

- **USEPA's AWQC for Pb were last updated in 1984.**
  - AWQC account for the influence of hardness on Pb bioavailability.
  - However, it is now well understood that other water chemistry parameters, such as DOC and pH, have a stronger influence on Pb bioavailability.
- **The BLM is now available for Pb.**
  - The BLM accounts for the additional parameters that have a strong influence on Pb bioavailability (e.g., DOC, pH, alkalinity, temperature, and calcium [Ca] [simplified input capability: temperature, DOC, pH, and hardness]).
  - The development of BLM-based AWQC for Pb would ensure a more consistent level of aquatic life protection over a wide range of water chemistry conditions.
- **Proposed BLM-based acute and chronic AWQC for Pb were derived following USEPA guidelines (Stephan et al. 1985).**
  - Proposed AWQC will be compared to BLM-based guidelines following European methodology (Van Sprang et al. 2016).

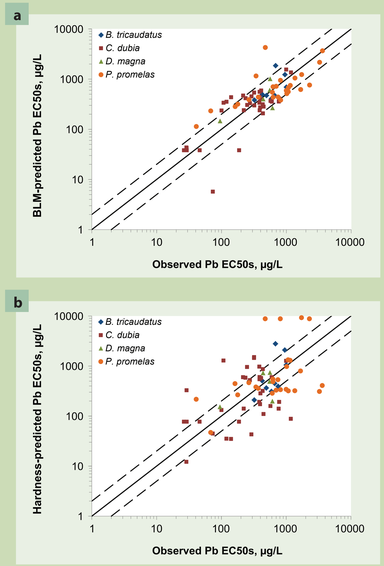
Methods

- **Compiled toxicity data and associated test water chemistry data**
  - Acute: EC50s (50% effect concentrations) for mortality or immobilization
  - Chronic: EC20s (20% effect concentrations) for survival, growth, and reproduction
- **Performed BLM evaluations**
  - For each toxicity test, we ran BLM in "speciation mode" in order to calculate critical accumulations (acute CA50s, chronic CA20s) on the biotic ligand (Version 3.1.2.37; http://www.windwardenv.com/biotic-ligand-model/).
  - We calculated geometric mean CA50s and CA20s for each species.
  - For those species tested over a wide range of water chemistry conditions, we ran BLM in "toxicity mode" using geometric mean CA50s and CA20s for each species and evaluated the ability of the BLM to predict acute and chronic toxicity over a wide range of water chemistry conditions. This step checked the accuracy of the BLM predictions but was not part of the criteria derivation process.
- **Proposed BLM-based Pb criteria derivation**
  - We calculated the 5th percentiles of the acute genus sensitivity distribution (GSD) based on genus mean CA50s and of the chronic GSD based on CA20s.
  - We compared proposed chronic Pb criteria to median 5th percentile hazardous concentration ($HC_{5\text{-}50}$) values following the European Union (EU) approach, as described in Van Sprang et al. (2016).

Results

Acute

- **Auto-validation results:**
  - BLM: Predicted acute EC50s within a factor of 2 of observed EC50s in 53 of 70 tests (76%) (Figure 1a).
  - USEPA hardness model: Predicted EC50s within a factor of 2 of observed EC50s in 36 of 75 tests (48%) (Figure 1b).



Solid line represents perfect 1:1 agreement and dashed lines represent a factor of ±2 agreement.

Figure 1. Comparison of (a) BLM-predicted acute EC50s and (b) hardness-predicted acute EC50s to observed acute Pb EC50s for species tested over a wide range of water chemistries

- **Proposed acute criteria:**
  - The four most-sensitive genera represent amphipods and daphnids (Table 1).
  - In moderately hard water, proposed acute criteria are 223, 409, and 782 µg/L at DOC concentrations of 2, 4, and 8 mg/L, respectively (Table 1).
  - Proposed BLM-based acute criteria are generally greater than USEPA's current hardness-based criteria for example field waters (Figure 2).

Chronic

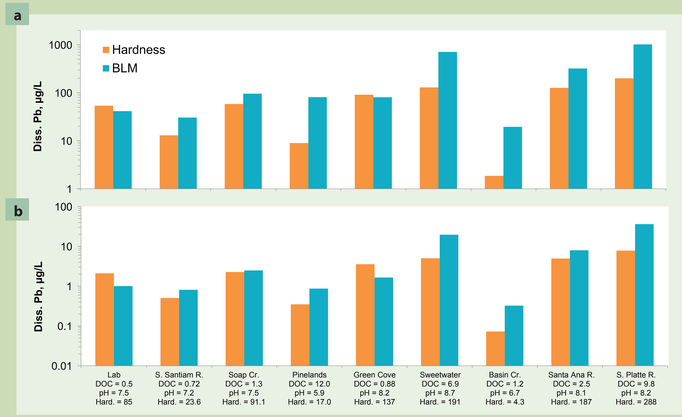
- **Auto-validation results:**
  - BLM: Predicted chronic EC20s within a factor of 2 of observed EC50s in 48 of 79 tests (61%) (Figure 3a).
  - USEPA hardness model: Predicted EC20s within a factor of 2 of observed EC50s in 35 of 79 tests (44%) (Figure 3b).
- **Proposed chronic criteria:**
  - The four most-sensitive genera represent snails, rotifers, amphipods, and daphnids (Table 1).
  - In moderately hard water, proposed chronic criteria are 3.8, 7.3, and 14.5 µg/L at DOC concentrations of 2, 4, and 8 mg/L, respectively (Table 1).
  - Proposed BLM-based chronic criteria are generally greater than USEPA's current hardness-based criteria for example field waters (Figure 2).

Table 1. Ranking of four most-acutely and -chronically sensitive genera and resulting 5th percentile critical accumulation concentrations and genus mean acute and chronic values for a standard water chemistry

	Acute					Chronic				
			Water Chemistry-adjusted Genus Mean Acute Value (µg/L)[1]					Water Chemistry-adjusted Genus Mean Chronic Value (µg/L)[1]		
Rank	Genus	Genus Mean CA50 (nmolg/g ww)	DOC = 2 mg/L[1]	DOC = 4 mg/L[1]	DOC = 8 mg/L[1]	Genus	Genus Mean CA20 (nmolg/g ww)	DOC = 2 mg/L[1]	DOC = 4 mg/L[1]	DOC = 8 mg/L[1]
	n = 32					n = 13				
4	*Daphnia*	0.442	612	963	1,666	*Ceriodaphnia*	0.00381	34.7	67.3	132
3	*Gammarus*	0.162	359	622	1,150	*Hyalella*	0.00234	22.9	44.5	87.7
2	*Ceriodaphnia*	0.0577	213	393	753	*Philodina*	0.00136	14.0	27.3	53.9
1	*Hyalella*	0.0443	186	245	665	*Lymnaea*	0.000446	4.8	9.5	18.8
	5th percentile	0.0628	223	409	782	5th percentile	0.000341	3.8	7.3	14.5

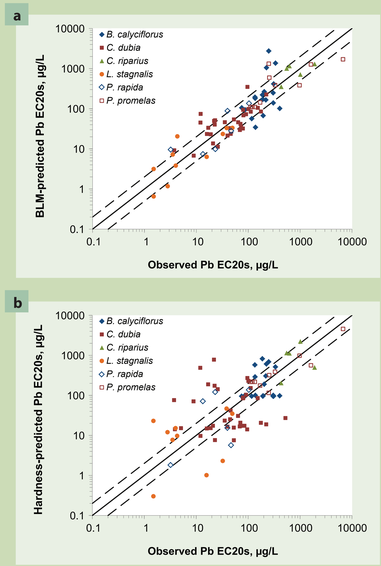
[1] Adjusted to the following water chemistry: temperature = 20°C; pH = 7.5; humic acid = 10%; Ca = 14 mg/L; Mg = 12.1 mg/L; Na = 26.3 mg/L; K = 2.1 mg/L; SO4 = 81.4 mg/L; Cl = 1.9 mg/L; alkalinity = 65 mg/L (as CaCO3); S = 0.0003 mg/L.

CA50 = 50th percentile critical accumulation concentrations on the BL [Σ(BL-Pb, BL-PbOH)]
CA20 = 20th percentile critical accumulation concentrations on the BL [Σ(BL-Pb, BL-PbOH)]
DOC – dissolved organic carbon
BL = biotic ligand
ww – wet weight



The BLM-based acute 5th percentile is divided by two for direct comparison to USEPA's acute criterion.

Figure 2. Comparison of BLM-derived (a) acute and (b) chronic 5th percentile Pb concentrations to USEPA's current hardness-based Pb criteria for a representative set of water chemistries



Solid line represents perfect 1:1 agreement and dashed lines represent a factor of ±2 agreement.

Figure 3. Comparison of (a) BLM-predicted chronic EC20s and (b) hardness-predicted chronic EC20s to observed chronic Pb EC20s for species tested over a wide range of water chemistries

Comparison of USEPA and EU Approaches

- **Methodological comparison:**
  - USEPA approach: EC20s, use of GSDs, exclusion of algae and macrophytes from species sensitivity distribution (SSD), single BLM applied to invertebrates and fish, triangular distribution for determining 5th percentile of GSD
  - EU approach: EC10s, use of SSDs; inclusion of algae and macrophytes in the SSD; separate BLMs applied to algae and macrophytes, invertebrates, and fish; log-normal distribution for determining 5th percentile of SSD
- **Despite methodological differences, proposed chronic criteria that result from following USEPA's approach and $HC_{5\text{-}50}$ values that result from following Van Sprang et al. (2016) are similar across most water chemistries evaluated (Table 2).**
  - Greater differences are observed when hardness is low (Lake Monate, Italy, and neutral acidic lake, Sweden) (Table 2).
  - BLM Version 3.1.2.37 used to derive proposed Pb criteria includes a modest hardness (Ca) effect; the Pb BLM used by Van Sprang et al. (2016) does not.
  - Proposed criteria produced using BLM Version 3.1.2.27 are comparatively conservative in low-hardness waters.

Conclusions

- The BLM allows for improved predictions of both acute and chronic Pb toxicity for a diverse set of water chemistry conditions and for a diverse set of species comprised of arthropods, gastropods, and fish.
- USEPA's current hardness-based Pb criteria are not appropriate, especially for sensitive species that "drive" the acute and chronic criteria.
- BLM-based Pb criteria, such as those proposed herein, would more consistently and accurately achieve USEPA's target level of aquatic protection over a much broader range of water chemistry conditions.

Table 2. Comparison of proposed chronic Pb criteria from the current evaluation to chronic $HC_{5\text{-}50}$ values from Van Sprang et al. (2016)

Scenario	DOC (mg/L)	pH	Ca (mg/L)	Chronic $HC_{5\text{-}50}$ (µg/L) from Van Sprang et al. (2016)[1]	Proposed Chronic Criterion (µg/L) from Current Evaluation
Ditches (The Netherlands)	12	6.9	60.1	31.1 (16.4-66.1)	29.6
River otter (UK)	3.2	8.1	46.9	9.1 (2.9-23.3)	7.9
River Teme (UK)	8.0	7.6	50.1	17.3 (5.8-43.9)	22.3
River Rhine (The Netherlands)	2.8	7.8	68.9	6.3 (2.1-16.0)	9.8
River Ebro (Spain)	3.7	8.2	72.9	7.0 (1.9-22.4)	9.4
Lake Monate (Italy)	2.5	7.7	13.6	8.1 (3.3-18.4)	3.8
Neutral acidic lake (Sweden)	3.8	6.7	8.8	11.4 (5.7-21.1)	3.3

[1] Best-fitting distribution; 5th to 95th confidence limits in parentheses.

DOC – dissolved organic carbon
$HC_{5\text{-}50}$ – median 5th percentile hazardous concentration

References

Stephan CE, Mount DI, Hansen DJ, Gentile JH, Chapman GA, Brungs WA. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. PB85-227049. Office of Research and Development, US Environmental Protection Agency, Washington, DC.

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