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January 15, 2016

Paula Wilson
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Subject: Comments on Presentations at December 11, 2015 Negotiated Rulemaking Meeting for Update to Copper Criteria for Aquatic Life Use (Water Quality: Docket No. 58-0102-1502)

Dear Ms. Wilson:

Thank you for the opportunity to provide comments to the Idaho Department of Environmental Quality (IDEQ) on the presentations made at the December 11, 2015 negotiated rulemaking meeting for the update to Idaho's copper water quality criteria (WQC) for aquatic life use . These comments are being provided on behalf of our client, the Copper Development Association (CDA), which supported significant technical research in development of the freshwater Biotic Ligand Model (BLM) for copper. Our comments address five primary issues raised in the December 11, 2015 presentations. We would appreciate the opportunity to discuss these comments with you and help answer questions you may have.

1. Sensitivity of the BLM to Dissolved Organic Carbon (DOC)

Background

The presentation by C. Mebane of the U.S. Geological Survey (USGS) included a slide (#7) that lead to the conclusion that the copper BLM response to DOC is too sensitive: at low DOC values, the model over-predicts toxicity (over-protective) and at higher DOC values, the model under-predicts toxicity (under-protective).

Approach

To investigate this potential issue, we evaluated the response of the BLM in predicting copper toxicity over a wide range of DOC concentrations.. We compared the BLM-predicted copper toxicity values to those for the same

organism as measured in five datasets that include measured DOC values ranging from <1-20 mg/L[1]. The differences are calculated as the ratio of predicted-to-measured values. A ratio of 1 corresponds to perfect agreement between predicted and measured values. If the BLM response to DOC were too strong (i.e., it would be under-predicting toxicity), the predicted toxic copper concentrations at high DOC concentrations would need to be greater than observed and the discrepancy between predictions and measured values would increase as DOC concentrations increase. Hence, if the BLM response to DOC is too high, a plot of the ratio of predicted-to-measured copper toxicity versus DOC would exhibit a significant trend with a positive slope (see Figure 1.1). Conversely, if the BLM response to DOC is too low, the same type of plot would exhibit a trend with a negative slope (Figure 1.2). If the BLM response to DOC is appropriate, there should be no trend in this type of plot and the vast majority of data points should lie within ratios of 0.5 to 2.0 (Figure 1.3), a range commonly accepted and shown by the dashed lines on the figures.

Results

Several datasets for acute toxicity to *D. magna* were used in the comparison with DOC concentrations ranging from 0.08 to 20 mg/L (Figures 1.4 -1.7). Over this range of DOC concentrations the plots on the right in each figure show no trend in the ratio of predicted-to-measured copper toxicity where DOC concentrations were greater than 1 mg/L. These results indicate that the BLM response to DOC is not too high, and that the BLM is neither under-protective nor over-protective in waters across typical DOC concentrations. Often, a typical DOC detection level is approximately 1 mg/L. The BLM has been calibrated for up to 29.7 mg/L DOC[2].

Interestingly, in one study our plot might suggest a potential positive bias in BLM-predicted copper toxicity across very low DOC concentrations of 0.08 to 0.15 mg/L (Figure 1.7). In other words, the copper toxicity values predicted by the BLM were lower than observed values at very low DOC, then the ratio increased proportionately with increasing DOC. However, this trend does not exist for DOC concentrations above about 1 mg/L (Figure 1.7).

For samples with very low DOC (<1 mg/L), the DOC concentration is difficult to quantify accurately using typical analytical methods. Uncertainty associated with accurate DOC quantification at these low concentrations may play a role in the evaluation of the BLM in this range such as exhibited in Figure 1.7. However, most natural waters exhibit DOC concentrations well above 1 mg/L. For example, data in EPA (2012) indicate an average 10th percentile DOC concentration of 2.6 mg/L across the continental U.S.

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[1] De Schamphelaere et al. (2002, 2004); Ryan et al. (2009); Villavicencio et al. (2005); Wang et al. (2009)

[2] HydroQual (2007); Santore and Croteau (2015)

(n=69,242 samples across 84 Level III Ecoregions and the Great Lakes). For the nine Level III Ecoregions spanning Idaho, EPA (2012) indicates average 10th and 25th percentile DOC concentrations of 1.4 and 2.0 mg/L, respectively (n=3,822 samples). These data are robust examples to illustrate that typical ambient DOC concentrations are well above 1 mg/L.

An additional dataset for acute copper toxicity to a freshwater mussel also includes some tests conducted with DOC concentrations below 1 mg/L (Figure 1.8). For the samples with very low DOC (~0.3 mg/L), variability in the ratio of predicted-to-measured toxicity ranges from approximately 0.2 to 1.0, which suggests large differences between the model and observed toxicity. However, where DOC concentrations were above 1 mg/L, the ratios were generally well within the 0.5 to 2.0 range shown by the dashed lines and no trend was exhibited (Figure 1.8). Thus, the data from this study support that the BLM is not overly sensitive to DOC (i.e., under-predicting toxicity) in the range of typical ambient DOC concentrations.

The example presented by C. Mebane in the December 11th meeting (his 7th slide) plots acute copper toxicity to rainbow trout across relatively low DOC concentrations (three samples ranged from 0.1 to 0.4 mg/L). We believe that these low DOC concentrations may be playing a similar role in the relatively poor agreement between predicted and measured toxicity. Copper toxicity from the C. Mebane study in samples with DOC concentrations greater than 1 mg/L do match the expected pattern of copper toxicity decreasing as DOC increases (i.e., increasing median lethal concentrations (LC50s)).

Conclusions

Our analysis shows that BLM-predicted copper toxicity in waters with a wide range of DOC concentrations (1 to 20 mg/L) show good agreement between predicted and measured copper toxicity. We found no tendency for the BLM response to be too high (or too low) in waters with typical DOC concentrations.

We appreciate the example provided by C. Mebane in the December 11th meeting. However, we note that it was for a limited dataset and for very low DOC concentrations that may be atypical of many natural waters. In addition, the DOC concentrations are so low that there may be significant uncertainty with the analytical quantification of DOC.

Furthermore, the predicted effect in the BLM of small amounts of DOC is minimal. The BLM is most useful to predict the effects of DOC on metal toxicity (and for WQC derivations) for waters where DOC concentrations are high enough to be relevant and within ranges of typical natural waters. Our analysis suggests that for waters with environmentally meaningful ranges of DOC concentrations the response of the BLM matches observed toxicity quite

well. Therefore, while DOC is an important parameter in the BLM, the model is not overly sensitive to this parameter such that it would under-protective in waters with high DOC.

2. BLM-based Copper Toxicity Predictions in Soft Waters

Background

Another point made in the presentation by C. Mebane (Dec 11, 2015 meeting) cautioned that fathead minnows (a common test organism) are more sensitive to copper in soft waters than expected by the BLM (slides 3 and 4). However, the material presented did not specify the range of soft water hardness, nor did it address the question of whether the BLM-based WQC for copper would be protective in soft waters. Compared with other organisms, fathead minnows are relatively insensitive to copper, and thus there is a considerable margin of safety between the BLM-predicted WQC and copper toxicity to fathead minnows. Mr. Mebane further suggested that if one of the invertebrates that are sensitive to copper was similarly as sensitive in soft waters as fathead minnows, the BLM WQC for copper may not be protective. Sensitive invertebrates, such as *Daphnia magna*, *Daphnia pulicaria* and *Ceriodaphnia dubia* tend to be key determinants of copper WQC magnitudes much more so than relatively insensitive organisms such as fathead minnows.

Approach

To address this concern, we evaluated the extent to which acute BLM-based WQC are protective for a sensitive invertebrate over a wide range of hardness concentrations. For purposes of synthetic laboratory waters used in toxicity tests, EPA defines "soft" water hardness as 40-48 mg/L as $CaCO_3$ (EPA 2002). For this evaluation, copper toxicity data for *C. dubia* were used because it is the second most sensitive species in the data used by EPA to derive their nationally recommended copper WQC based on the BLM (EPA 2007). While *D. pulicaria* has the lowest SMAV used in EPA's derivations, there is relatively little copper toxicity data for *D. pulicaria* with which to conduct the evaluations. Data for *C. dubia*, in contrast, are robust—copper toxicity measurements for *C. dubia* are available from 20 studies[3] with a total of 89 samples ranging in hardness from 3 to 1300 mg/L (as $CaCO_3$). The data from these studies were combined to conduct this analysis.

Results and Conclusions

[3] Carlson et al. (1986); Belanger et al. (1989); Belanger and Cherry (1990); Oris et al. (1991); Diamond et al. (1997); Gensemer et al. (2002); Naddy et al. (2002); Banks et al. (2003); Harmon et al. (2003); Naddy et al. (2003); Bossuyt and Janssen (2005); Bossuyt et al. (2005); Hyne et al. (2005); Markich et al. (2005); Jun et al. (2006); Kolts et al. (2006); Nimmo et al. (2006); De Schamphelaere et al. (2007); Van Genderen et al. (2007); Wang et al. (2007); Cooper et al. (2009)

In our analysis, the BLM (version 3.1.2.37) was used to generate an acute water quality criterion for the water chemistry conditions associated with each of the measured *C. dubia* acute copper toxicity values determined in these 20 studies. The ratio of the measured LC50 to the BLM-based criterion was then calculated—ratios less than 1 would indicate the BLM-based acute criteria are higher than the acute toxicity observation, which would suggest that the BLM may not be providing sufficiently protective criteria. Because EPA sets national aquatic life criteria based on the 5th percentile copper toxicity value from a distribution of a wide variety of aquatic species (Stephan et al 1985), some number of these ratios below 1 would be acceptable. However, in our analysis, none of the ratios for *C. dubia* were less than 1. In other words, none of the BLM-based acute copper criteria were less than the measured LC50s. More importantly, there is no suggestion in Figure 2.1 that the ratio trends downward at low hardness. Therefore, we believe the BLM is protective for a sensitive invertebrate such as *C. dubia* over a wide range of hardness concentrations including soft waters. Because this is true for one of the most sensitive species to copper, this would also certainly be true for fathead minnows.

3. BLM Versioning

The IDEQ's current copper criteria rulemaking proposal is to adopt the EPA's 2007 copper criteria by referencing the BLM software version 2.2.3. However, version 2.2.3 is an outdated software version. It is important to note that a number of BLM software versions have been available to generate copper WQC consistent with the EPA's 2007 copper criteria. The EPA website previously included a download link for version 2.2.1, which was released at the time of the 2007 EPA criteria document. Version 2.2.3 was also released in 2007 and, up to November 2015, the EPA website provided a download link version of 2.2.3, which directed the user to www.hydroqual.com/wr_blm.html. However, this link is no longer available via the EPA website. Version 2.2.3 not only generates the EPA's 2007 copper WQC, but also provides multiple metal and multiple organism "Research Mode" capabilities. Version 2.2.4 has also been available, and is capable of calculating a Fixed Monitoring Benchmark (FMB; a capability not available in version 2.2.1 or 2.2.3). Thus, a reference to only version 2.2.3 in the Idaho water quality standards language is inflexible and will be problematic if additional rulemaking will be required to change standards language when BLM software versions change or version 2.2.3 becomes obsolete (for example, as a result of changes to the Microsoft Windows operating system). An update to version 2.2.3 (version 3.1.2.37) that performs exactly the same criteria calculations can be found at http://www.windwardenv.com/biotic-ligand-model/. Updated versions are likely to be available in the future on the US EPA website.

Because of the various BLM software version numbers capable of generating copper WQC consistent with EPA 2007, we recommend revising the rulemaking language to remove the BLM version number. Instead, we recommend the language stipulate that the software version used must generate copper WQC compatible with the EPA's 2007 criteria document.

4. Fixed Monitoring Benchmark (FMB) and Caution with Hypothetical Examples

In the December 11th meeting, slide #25 in IDEQ's presentation had two plots to illustrate FMB scenarios. In this slide, the plot on the left showed BLM-based chronic copper WQC and an FMB value (copper concentration) of approximately 12 µg/L, which was well above the approximately 1-3 µg/L ambient copper concentrations observed for the example water body (Boise River). None of these copper concentrations exceeded the BLM-based WQC shown on the plot. The plot on the right was for a hypothetical scenario with the same BLM-based WQC, but with the ambient copper concentrations raised to values near the FMB from the left plot, and with a new FMB of approximately 4.8 µg/L corresponding to the new copper distribution. In this hypothetical scenario, the new FMB value was much lower than it was for the actual data in the slide on the left; however, unlike the plot on the left, the hypothetical copper concentrations often exceeded respective BLM-based WQC (4 out of 12 data points). It appears that this hypothetical scenario was generated to support the bottom bullet on the following slide (#26), thereby leading to the suggestion that caution was needed in using FMBs to estimate safe metal concentrations for a receiving water body.

Although we would need to look carefully at the analysis to be sure, it is possible that this hypothetical calculation did not represent a relevant interpretation of how the FMB would correspond to adjusted copper concentrations in a receiving water body.

First, it is important to acknowledge that this is a hypothetical example. The intent of the FMB is to calculate a safe copper benchmark that can be used to evaluate ambient copper concentrations. When the FMB is higher than ambient copper concentrations, proper interpretation would be to conclude that there is no impairment from copper, and not that it would be desirable to increase copper loads to meet the FMB.

If it would be helpful, we can demonstrate how to adjust the in-stream copper concentrations in a similar manner, such that the covariance between copper concentration and WQC distributions is not changed, resulting in no change in FMB between simulations with adjusted or original copper concentrations.

The FMB does depend on the ambient copper concentrations to the extent that they are needed to calculate the frequency of exceedances with the instantaneous water quality criteria. If the adjusted copper concentrations in IDEQ's example calculation changed the covariance between the copper concentration and WQC distributions,

then the adjustment will result in changes to the FMB, and this is the most likely explanation for why the FMB value changes in the hypothetical example given in IDEQ's slide 25. The fact that the FMB does change, indicates that the adjusted copper concentrations in slide 25 are not consistent with a revised copper distribution in compliance with time-variable WQC (an example of a compliant copper distribution calculated as part of the FMB procedure is shown graphically on IDEQ's slide 22 as a red dashed line).

Therefore, the hypothetical scenario may not be an entirely realistic situation suitable for drawing general conclusions. Further evaluations would be helpful to determine the circumstances where FMBs would be appropriate for use as WQC. It is important to note that the FMB approach seeks to solve a general implementation problem common to a number of time variable WQC besides BLM-based copper WQC, and so hardness-based WQC for other metals and ammonia WQC would need the same attention.

5. Confirmation that the BLM-based Copper Criteria Will Rely on Site-specific Data When Available

Appendix C of NOAA's Biological Opinion (BiOp) poses the following question: "Can the BLM-based criteria be safely estimated for different water body types even if measurements of all the BLM inputs are not available?"

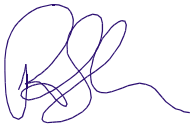
In order to answer this question, NOAA compiled datasets of BLM input parameters in their BiOp for representative waters and examined these for seasonal patterns of "critical conditions," which were defined as annual worst case conditions for that water body (i.e., conditions where copper bioavailability and, hence, toxicity would be expected to be the greatest). Ultimately, the BiOp concluded that regional and seasonal water chemistry patterns were "sufficiently predictable that conservative (realistic but protective) default BLM-criterion table values can be defined" and that "the most critical conditions almost invariably occur in the fall, and over the range of waters with listed anadromous fish in Idaho, data relevant to these conditions were either directly available or could be estimated from watersheds with similar characteristics." Some examples of critical copper benchmarks for sub-basins within the range of anadromous salmonids in the Snake River basin, Idaho were then provided in Table 3 of Appendix C of the BiOp.

We found this evaluation to be interesting and the approach provided does appear to be a technically viable option for deriving BLM-based copper criteria that meet the targeted level of protection in water bodies lacking BLM input parameter data.

However, we recommend that Idaho water quality standards language (or appropriate guidance) allow the option for deriving BLM-based copper criteria based on actual site-specific measurements. This option should be available to stakeholders (local, state and federal agencies/authorities; and NPDES permittees) to prevent use

of potentially over-conservative BLM-based criteria based on default input parameters where more representative measurements are available.

Sincerely,



Carrie Claytor	Robert Santore	Scott Tobiason	David DeForest
CDA	Windward	Windward	Windward

cc: Robert Gensemer, PhD, GEI Consultants
Eric Van Genderen, PhD, International Zinc Association

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FIGURES

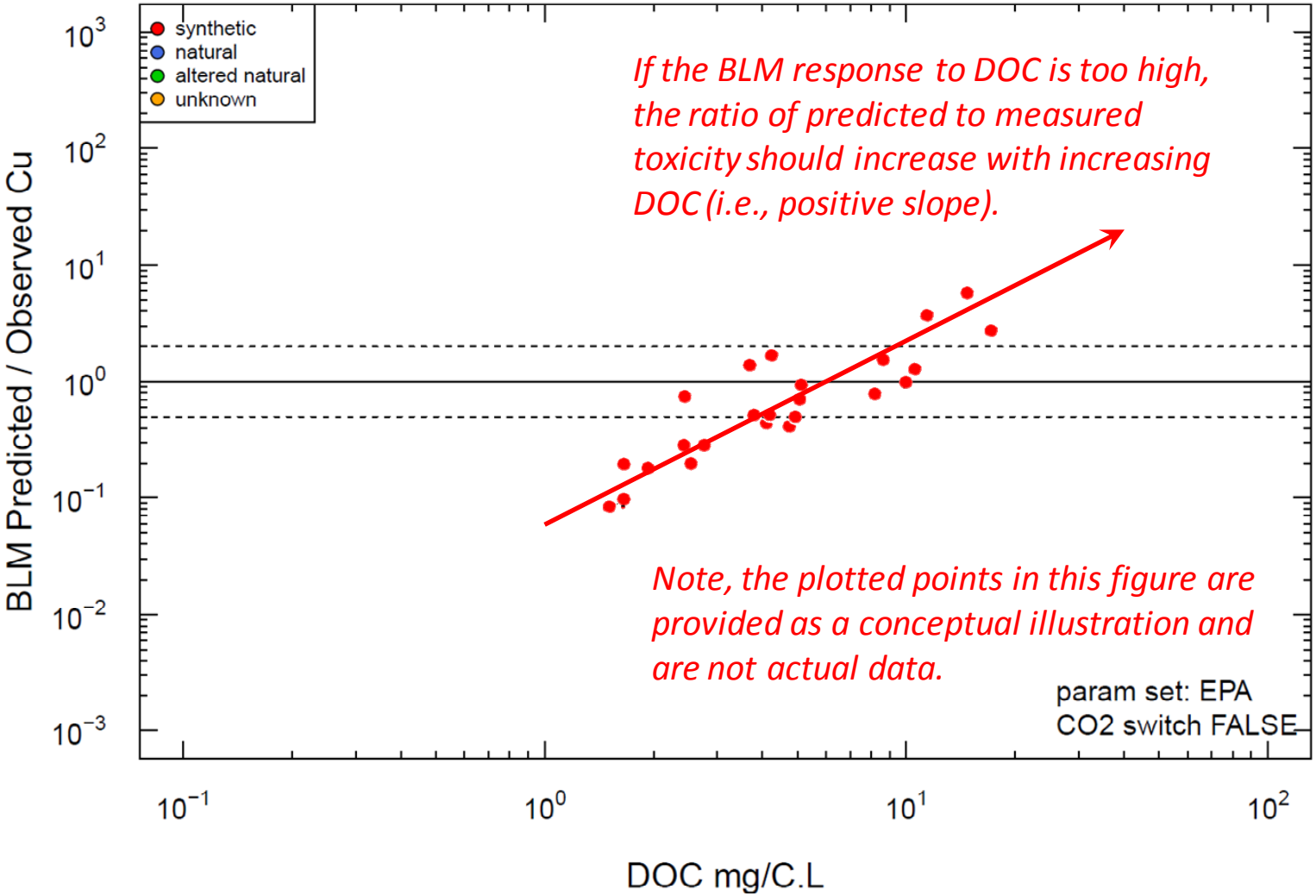

Figure 1.1. BLM-predicted ratio vs DOC: Conceptual example of a BLM response to DOC that is too high.

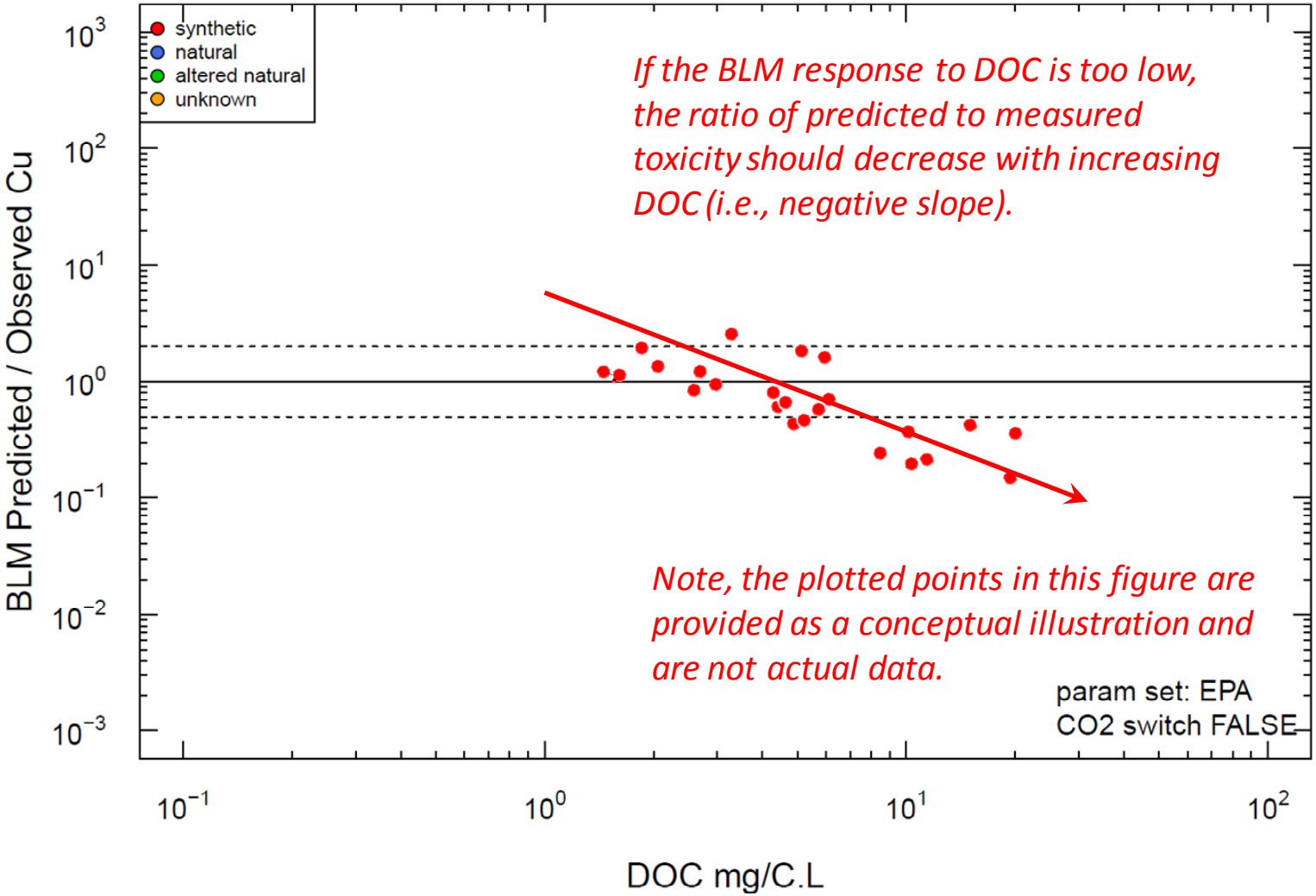

Figure 1.2. BLM-predicted ratio vs DOC: Conceptual example of a BLM response to DOC that is too low.

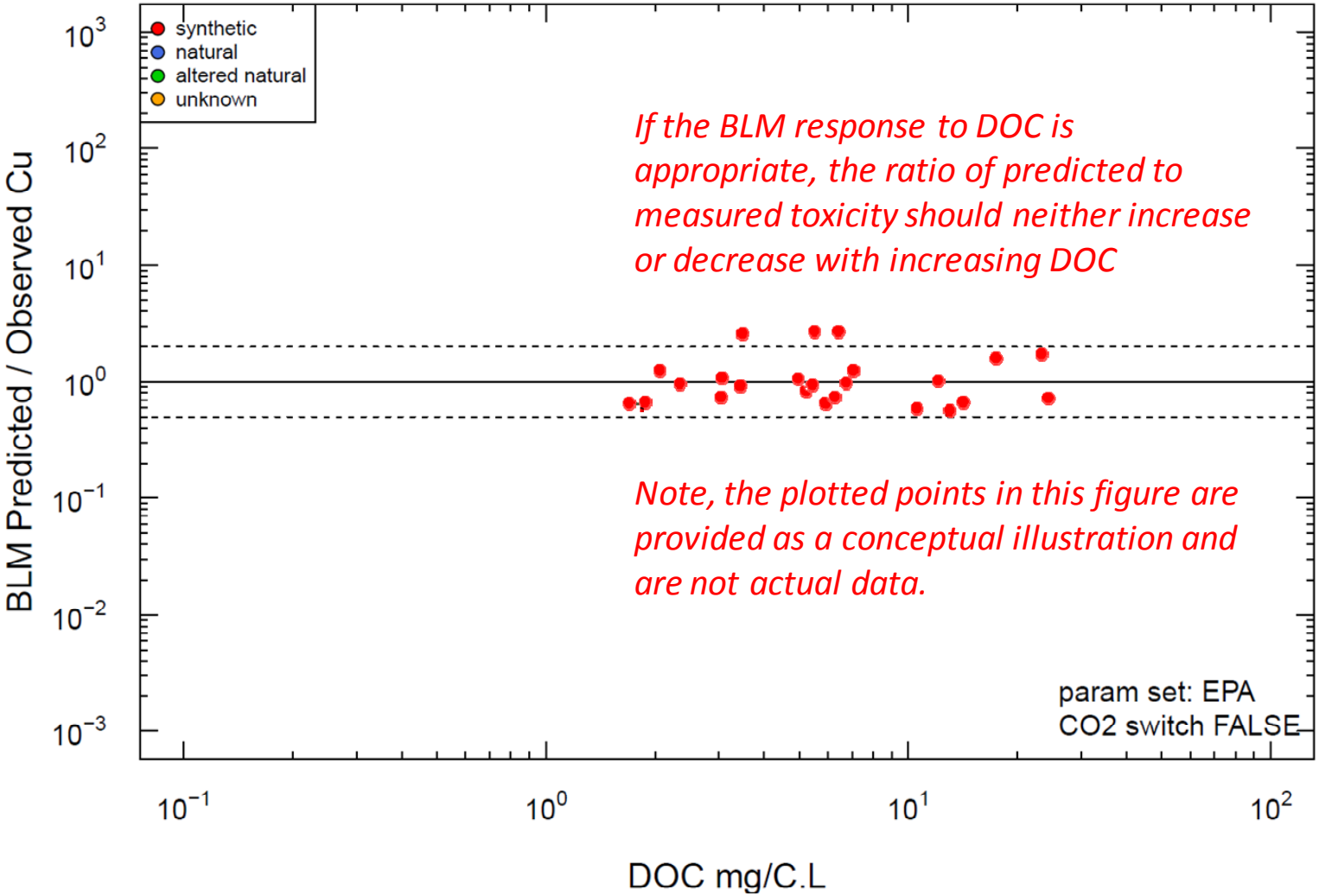

Figure 1.3. BLM-predicted ratio vs DOC: Conceptual example of a BLM response to DOC that is appropriate.

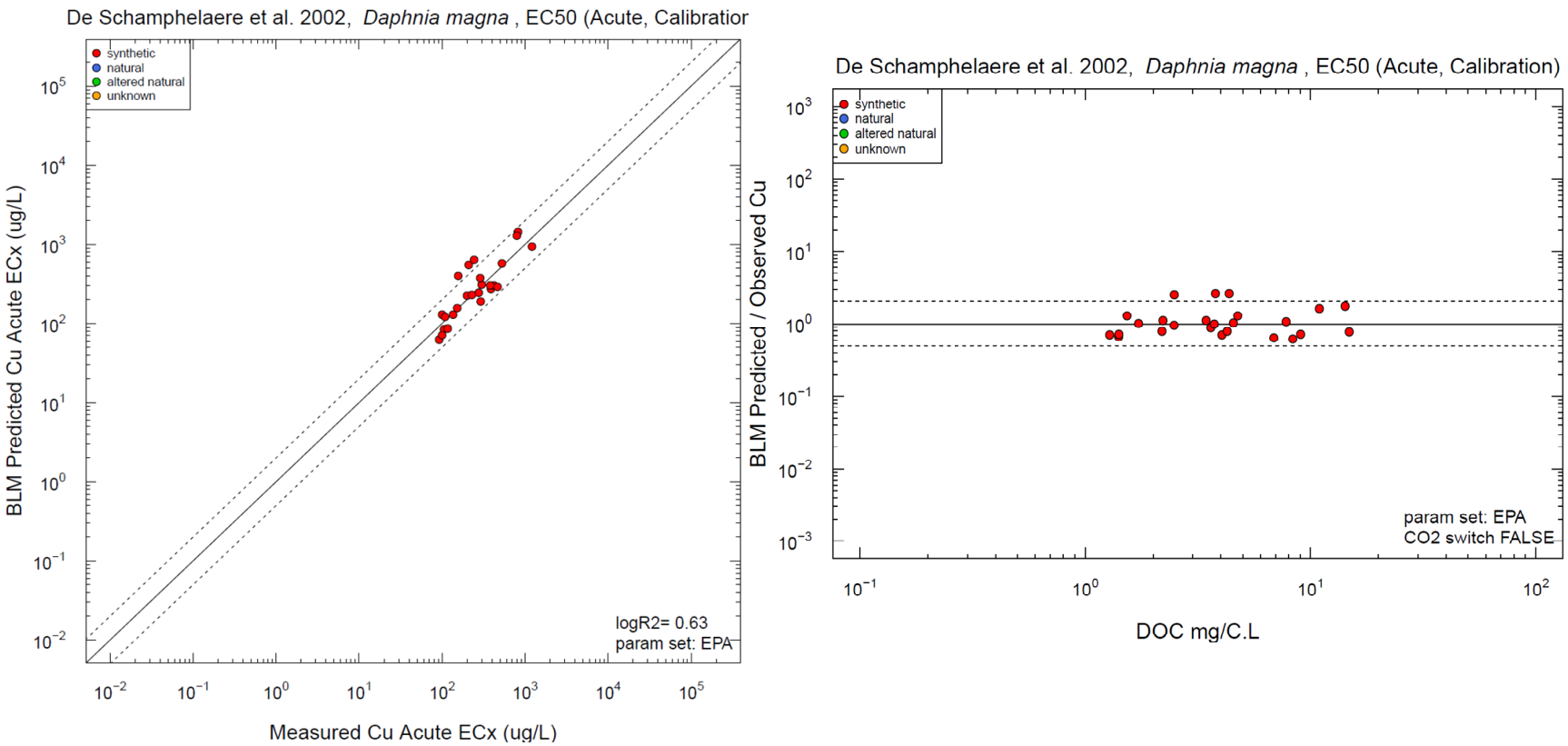

Figure 1.4. BLM-predicted ratio vs DOC: Results (*Daphnia magna,* De Schamphelaere et al. 2002).

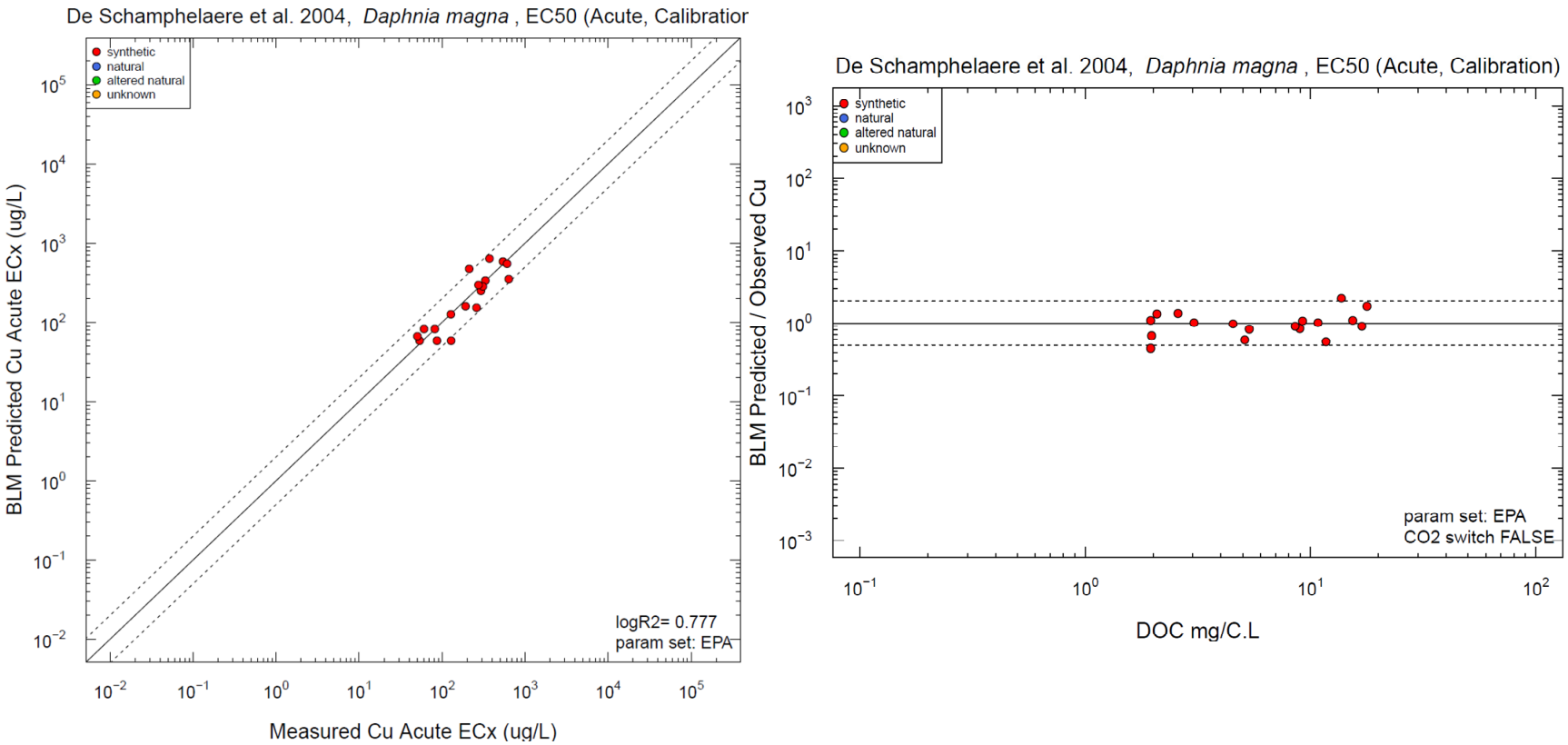

Figure 1.5. BLM-predicted ratio vs DOC: Results (*Daphnia magna,* De Schamphelaere et al. 2004).

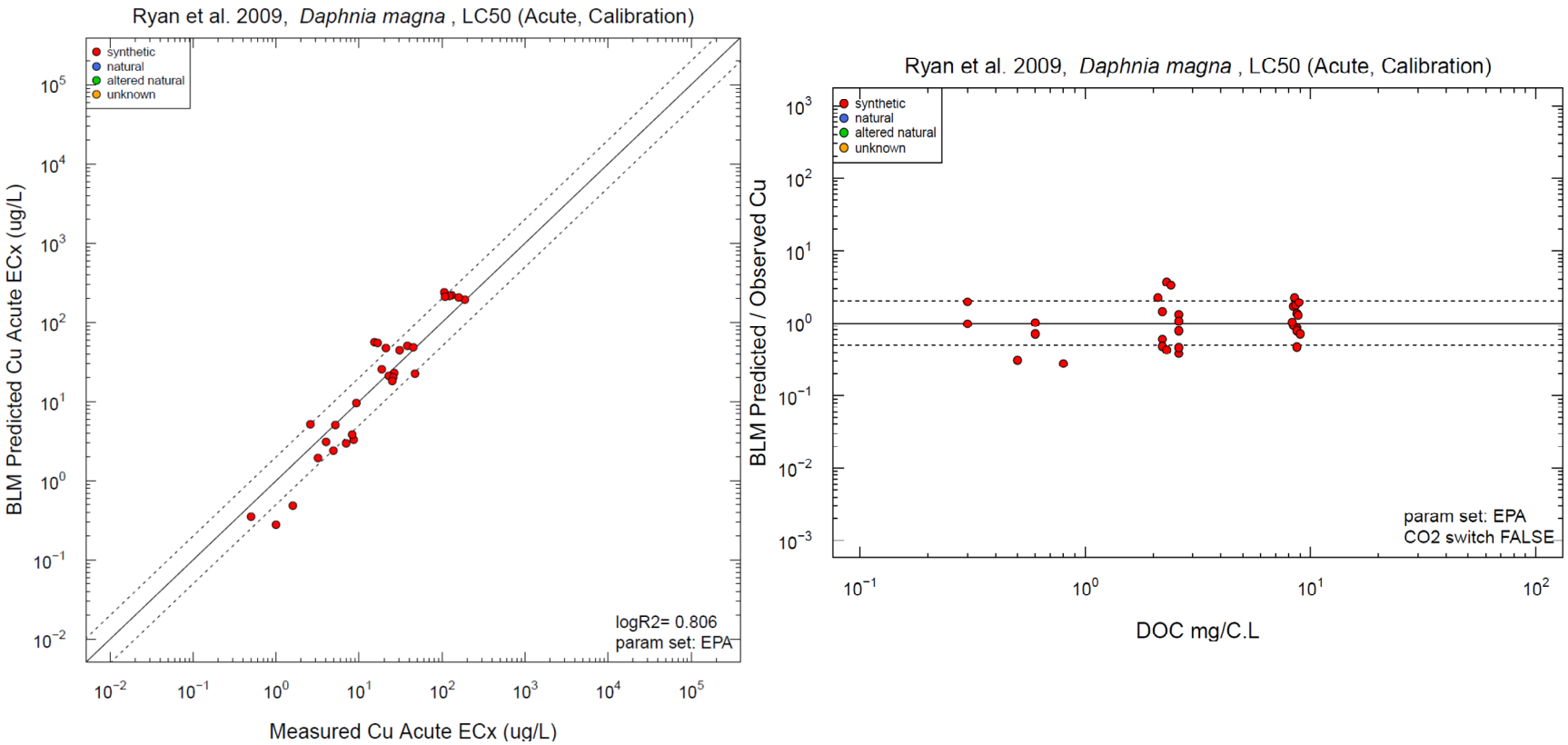

Figure 1.6. BLM-predicted ratio vs DOC: Results (*Daphnia magna,* Ryan et al. 2009).

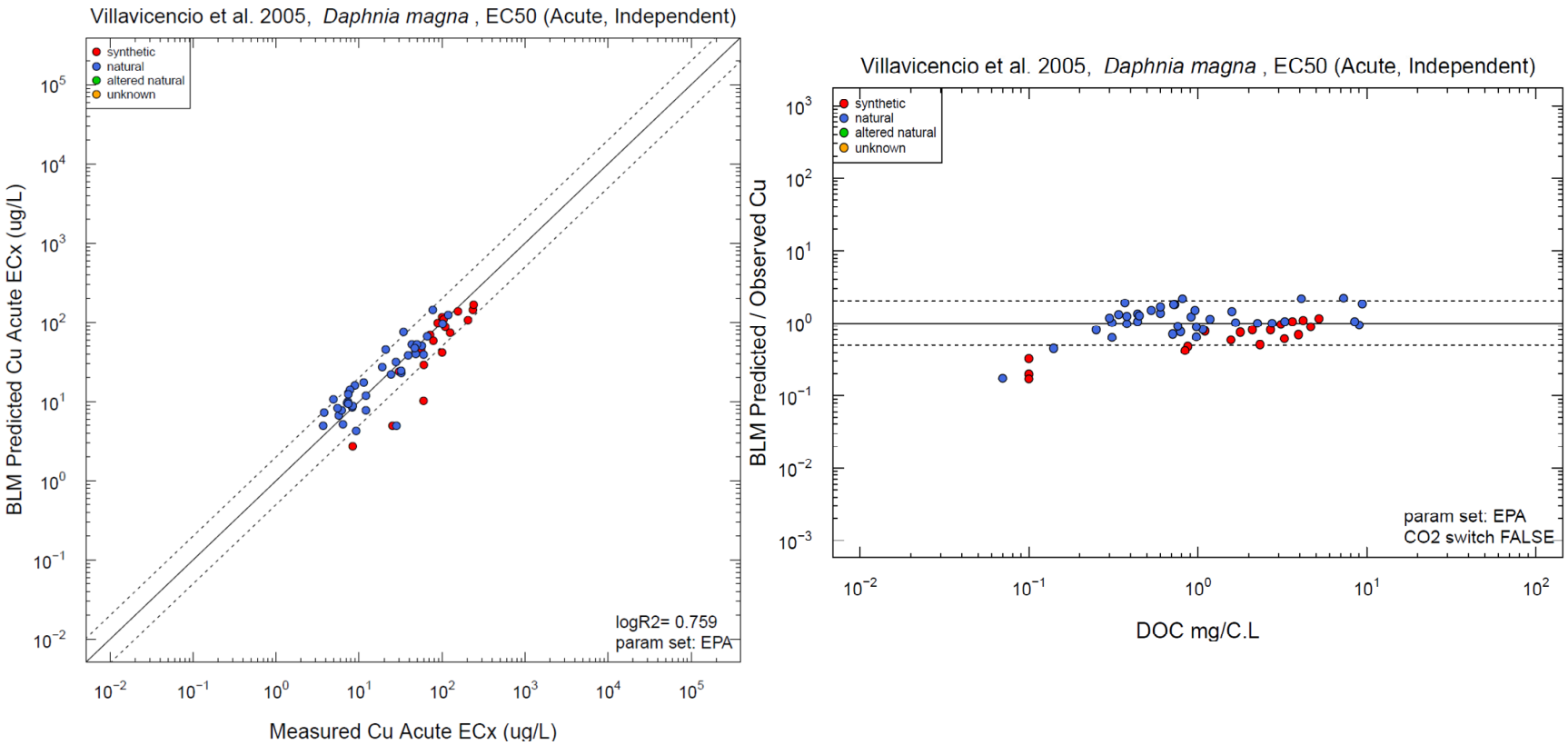

Figure 1.7. BLM-predicted ratio vs DOC: Results (*Daphnia magna,* Villavicencio et al. 2005).

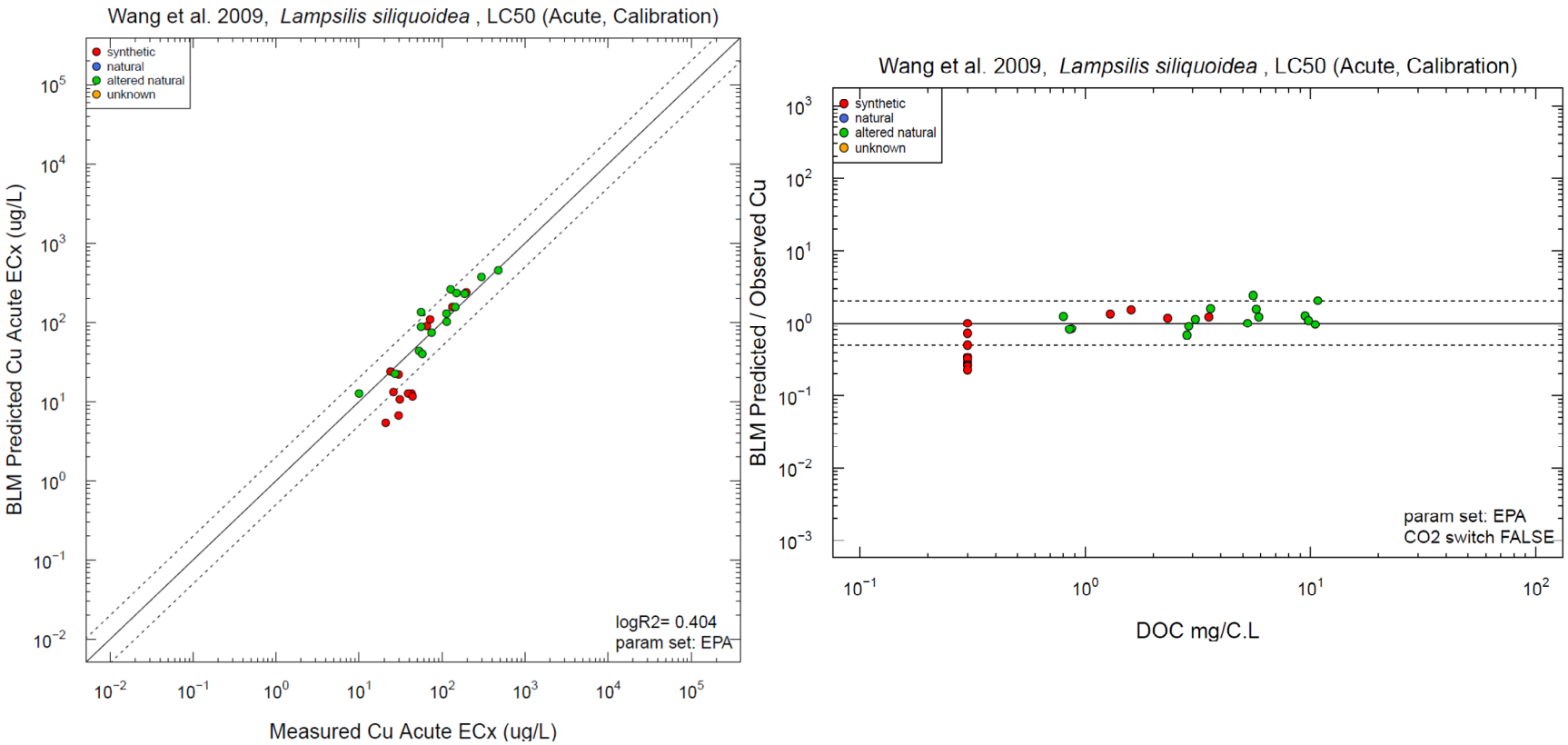

Figure 1.8. BLM-predicted ratio vs DOC: Results (*Lampsilis siliquoidea,* Wang et al. 2009).

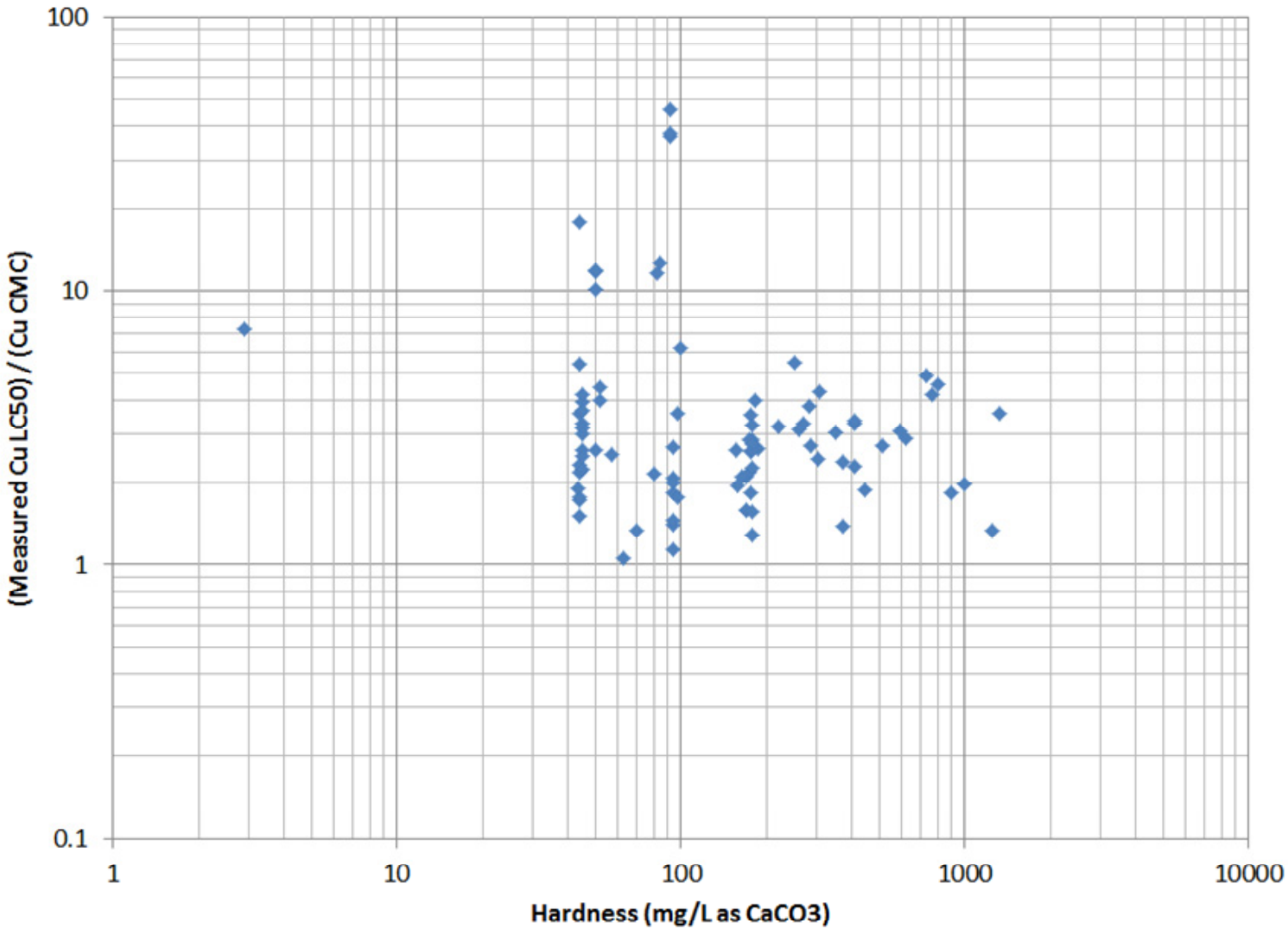

Figure 2.1. *C. dubia* LC50 / BLM-predicted criterion maximum concentration (CMC).