February 1, 2017

Paula Wilson
Idaho Department of Environmental Quality
1410 N. Hilton, Boise, ID 83706

Re: Negotiated Rulemaking - Water Quality Standards/Copper Criteria, Docket No. 58-0102-1502

Dear Ms. Wilson,

Thank you for the opportunity to provide comments on the Idaho Department of Environmental Quality's (IDEQ) December 20, 2016 negotiated rulemaking presentation regarding updates to the state's copper aquatic life criteria. GEI Consultants and Windward Environmental, along with our client, the Copper Development Association (CDA), would like to offer several items for your staff to consider in the April 2017 negotiated rulemaking meeting.

We generally support the draft guidance for using the biotic ligand model (BLM) to derive copper water quality criteria presented during the last rulemaking meeting. However, there are several areas that would benefit from further clarification:

- When assessing whether the time period over which BLM sampling is conducted would be temporally representative, consideration should be given to the longer-term hydrograph, in addition to requiring 12 monthly samples be collected over a calendar year. We recommend evaluating any available flow data which may be available concurrent with the BLM sampling, and comparing those results to historical flow data (e.g., 7Q10). An assessment such as this can be used to inform whether the resulting BLM dataset captures a balanced representation of the expected long-term flow conditions. Included as an attachment is an example in which daily average discharge for the BLM sampling period was compared to the 18-year historical flow data. This analysis supported the conclusions that this BLM dataset could be used to derive criteria that would be protective over a range of expected flow conditions.

- In setting permit limits, it is proposed that the 10th percentile of the instantaneous water quality criteria (IWQC) will be used as the basis of the permit. We ask for further clarification on the justification used for the chosen percentile, given that the 15th percentile was presented in a previous version of this guidance.

- We would like clarification on whether there would be flexibility in the percentile of IWQC to be used as the basis of the permit if paired copper and BLM data were collected by a discharger which demonstrates, using some statistical approach (e.g., fixed monitoring benchmark), that a copper concentration different than the 10th percentile of the IWQC would be protective of aquatic life?

- The 2007 acute copper criteria are based on a 24-hour average exposure period (USEPA 2007), while IDEQ plans to use a 1-hour average, per IDAPA 58.01.02.210.03.d.i. We believe that the 24-hour averaging time is more appropriate, as discussed in the attached memorandum.

- We ask for clarification on whether newly adopted site-specific BLM-based standards, which would replace existing hardness-based or regional default BLM-based standards (i.e., based on

IDEQ's BLM monitoring study), would trigger anti-degradation/anti-backsliding review for permit holders if the new BLM-based standards in the receiving waters would result in a "new or increased impact" in the permit. We encourage IDEQ to address this issue within the current implementation guidance and negotiated rulemaking process in order to provide a clear path forward towards incorporating BLM-based criteria into permits. Ultimately, the benefits of the BLM to permit holders cannot be fully realized unless the BLM-based standards adopted for the receiving water can also be used to develop related effluent limitations in discharge permits.

We appreciate the opportunity to provide comments on the proposed implementation guidance and would welcome additional opportunity to participate in the development process. Please let us know if you have any questions and we look forward to discussing this with you further during the April meeting.

Sincerely,
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RWG
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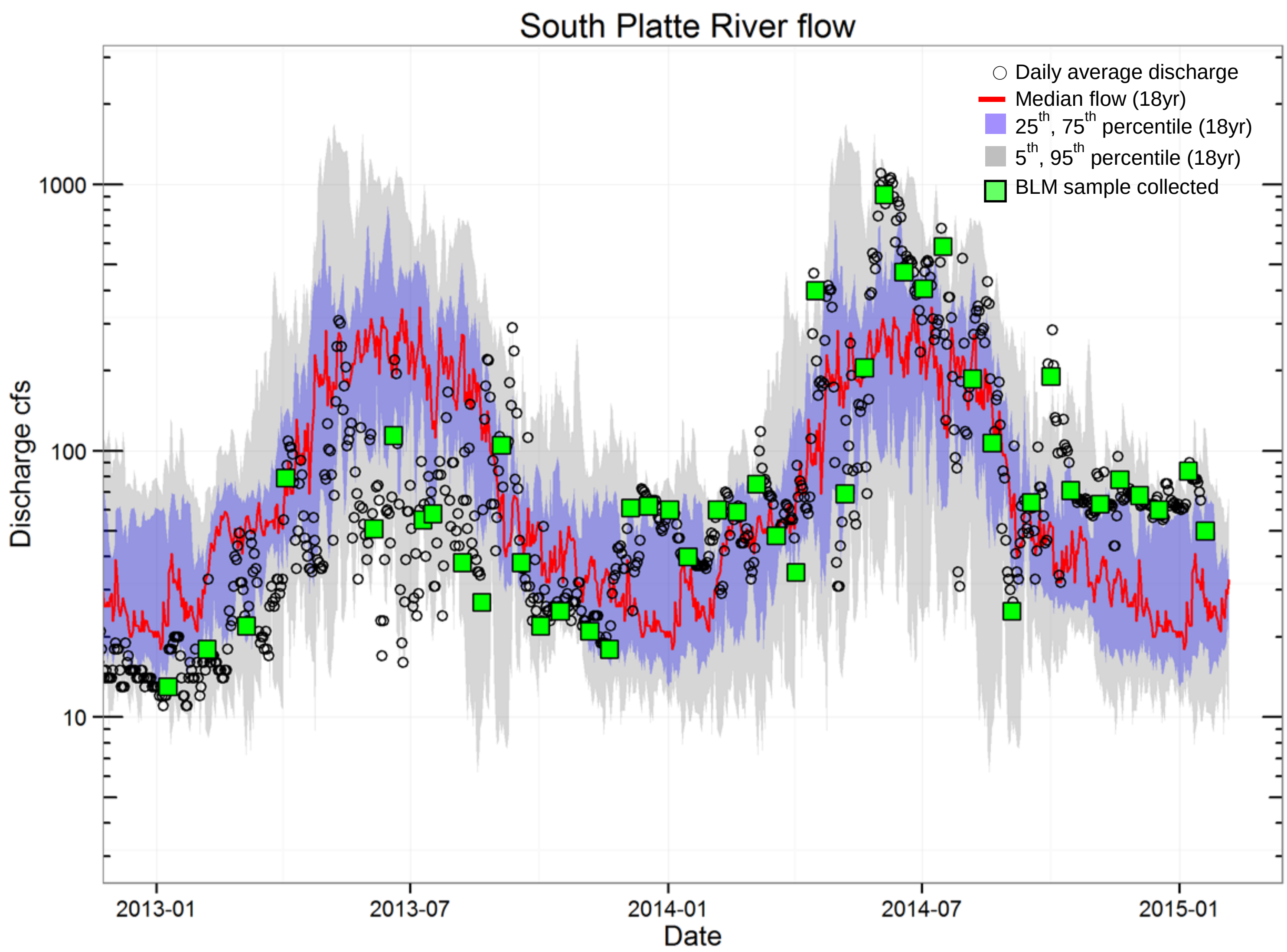
Scott Tobiason, Windward Environmental
Robert Santore, Windward Environmental
Eric Van Genderen, International Zinc Association

References:

[USEPA] United States Environmental Protection Agency. 2007. Aquatic life ambient freshwater quality criteria - copper. Washington, DC. EPA 822-R-07-001.



Comparison of flows measured by the US Geological Survey (USGS) at a gauge station (#06710247) located on the South Platte River, Colorado on the dates sampled for the BLM, against those measured over the last 18 years. Data from USGS National Water Information System (NWIS) (http://maps.waterdata.usgs.gov/mapper/index.html).

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TECHNICAL MEMORANDUM

To: Michael Campbell

From: Robert Santore, Adam Ryan, Kelly Croteau, David DeForest

Subject: A review of metal toxicity and exposure duration for determining the suitability of a 24-hour averaging period for comparison with acute water quality criteria

Date: September 15, 2016

SUMMARY

Although EPA's recommended acute water quality criterion (WQC) for copper is based on a 24-hour average concentration (US EPA 2007), EPA recently proposed an acute copper WQC for Oregon based on a 1-hour average. In addition, EPA has recently changed its recommended averaging period for assessing compliance with the acute WQC for cadmium from 24-hours to 1-hour (US EPA, 2016). These changes are a reversal of an earlier move from 1-hour to 24-hours used in both the 2001 cadmium document (US EPA 2001), and the 2007 copper document (US EPA 2007). The justification for moving to the longer 24-hour averaging period in the 2001 and 2007 documents was based on an analysis by US EPA that demonstrated a strong dependence of metal toxicity, including copper toxicity, on exposure duration, such that metals were more toxic (lower EC50 or LC50 values) in acute exposures with longer durations (US EPA 1995). EPA has recently stated in the 2016 cadmium criteria document that the reasons for going back to a 1-hour duration are that it is consistent with the guidelines for deriving aquatic life criteria (US EPA, 1985), and that the analysis of exposure duration (US EPA, 1995) had a "focus on fish" and therefore the 24-hour averaging period may not be protective for invertebrates (US EPA, 2016). No new analysis accompanied the recommendation for returning to a 1-hour averaging period in the 2016 cadmium document, so it was not clear why EPA determined that the 1995 analysis might not be protective. Was there simply a lack of supporting

evidence to suggest a 24-hour averaging period was protective for invertebrates, or was there evidence to suggest 24-hours was not protective?

To address these questions, we reviewed the 1995 analysis by EPA and subsequent toxicity literature to assess:

- Whether invertebrates were included in the 1995 analysis.
- Whether toxicity data for invertebrates that were published since 1995 could be used to provide additional evidence to strengthen the analysis.
- Whether invertebrate data would confirm or refute that a 24-hour averaging period would be protective for invertebrates as well as for fish.

As a result of our review we determined that invertebrates were part of the 1995 analysis, and therefore it was not accurate to characterize the analysis as having a "focus on fish". The invertebrate data included in US EPA 1995 showed a strong relationship between exposure duration and metal toxicity, including copper toxicity, similar to that observed in the toxicity data for fish.

Furthermore, we found additional toxicity studies published after US EPA (1995) that approximately tripled the number of invertebrate studies used to characterize the relationship between exposure duration and copper toxicity. These additional studies further support the conclusion that there is a pronounced reduction in acute copper toxicity with decreasing exposure duration using an approach recommended in US EPA (1991) for deriving a scientifically justifiable averaging period. Both the US EPA (1995) analysis, and the extended analysis presented here, show that the recommended 24-hour averaging period in the 2001 cadmium and 2007 copper criteria documents would be protective for invertebrates.

BACKGROUND ON RECENT CHANGES TO THE AVERAGING PERIOD

The 1985 EPA guidance on deriving water quality criteria recommended a 1-hour averaging period (USEPA 1985). Quoting from the guidance document:

> "*For the CMC the averaging period should again be substantially less than the lengths of the tests it is based on, i.e., substantially less than 48 to 96 hours. One hour is probably an appropriate averaging period because high concentrations of some materials can cause death in one to three hours*."

The language in this document acknowledges that there is uncertainty in the 1-hour recommendation. Consequently, a few relevant questions, as follows, should be addressed. What is the definition of "*substantially less than 48 to 96 hours*"? One hour is "*probably appropriate*" but could a different averaging period be appropriately protective? While "*high concentrations of some materials can cause death in one to three hours*", is a metal such as copper one of the materials for which this concern is relevant?

The 1991 Technical Support Document for Water Quality-based Toxics Control (EPA 1991) provides a further explanation of the acute averaging period as follows:

> *"For acute criteria, EPA recommends an averaging period of 1 hour. That is, to protect against acute effects, the 1-hour average exposure should not exceed the CMC. The 1-hour acute averaging period was derived primarily from data on response time for toxicity to ammonia, a fast-acting toxicant. The 1-hour averaging period is expected to be fully protective for the fastest-acting toxicants, and even more protective for slower-acting toxicants. Scientifically justifiable alternative (site-specific) averaging periods*
>
> *can be derived from (1) data relating toxic response to exposure time, if coupled with considerations of delayed mortality (mortality occurring after exposure has ended), or (2) models of toxicant uptake and action, such as presented by Erickson [5] and Mancini et al. [4]."*

To address a lack of data supporting the 1-hour averaging period, EPA conducted an analysis of the speed of action of metal toxicity to aquatic organisms (US EPA, 1995) using the approach in recommended in US EPA (1991). This analysis evaluated how the toxicity of various metals changed with increasing exposure duration. The analysis involved tabulating the median lethal or median effect concentrations (LC50 or EC50) of metals at various exposure durations. An exponential function was then fit to the data, such that:

$$LC50_t = LC50_\infty * \frac{1}{1-e^{-kt}} \qquad \text{(Equation 1)}$$

Where t is the exposure duration (hours), $LC50_t$ is the measured LC50 at exposure t (µg/L), k is an exponential constant (1/hours), and $LC50_\infty$ is the asymptotic value of the LC50. For each experiment, values of $LC50_t$ and t were tabulated and the value of k and $LC50_\infty$ were determined by non-linear regression. An example of the data and exponential function is shown in Figure 1, where the strong relationship between copper exposure duration and toxicity is evident. The calculated k for this example is 0.0008, and the averaging period (1/k) is 1250 hours, which in the EPA analysis was reported as >120 hours, thereby constrained by the total exposure duration. The strong relationship between toxicity and exposure duration means that copper toxicity at 24 hours occurs at a concentration that is approximately twice that at 48 hours (Figure 1).

To understand the relevance of this information for understanding the selection of averaging period, it is helpful to review again the quote from the EPA guidance on deriving water quality criteria. The reason that "*averaging period should again be substantially less than the lengths of the tests it is based on*" is because shorter averaging periods are inherently more conservative. The new information in the 1995 speed of action analysis provided a quantitative assessment as to the length of exposure duration that would be appropriate and yet still be "*substantially less*" than the 48 hours used to derive toxicity data for invertebrates in the WQC documents.

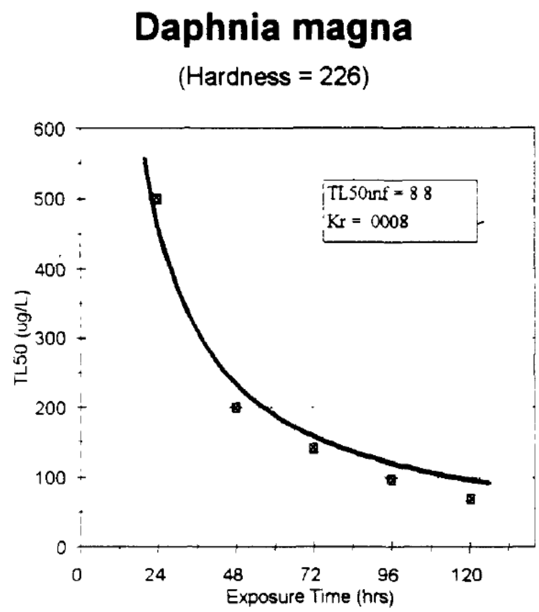

Figure 1. Example data showing copper toxicity to *D. magna*, and the exponential function (equation 1) fit to determine k and $LC50_{\infty}$.

Although the 1995 speed of action analysis was not cited in the 2001 cadmium or 2007 copper WQC documents, both of these documents changed the averaging period for acute WQC to 24-hours. In the 2016 cadmium WQC, this change was reversed back to 1-hour, but this time the 1995 speed of action analysis was referred to, although it was still not explicitly cited. Quoting from the 2016 cadmium document (US EPA, 2016):

> *"For the 2016 acute cadmium criteria, EPA has changed the duration to 1-hour from the 24 hours EPA applied in the 2001 final cadmium criteria document. EPA made this change to the 2016 criteria to reflect the acute criteria duration recommended in the 1985 Guidelines. The draft 2001 cadmium criteria document used a 1-hour duration, which EPA subsequently revised to 24 hours in the final criteria document. The final cadmium criteria document did not detail the rationale for this change, and EPA has further examined this issue as part of the 2016 criteria update.*
>
> *The 24-hour duration used in the 2001 final cadmium criteria document was based on a limited number of fish toxicity studies that were conducted in the mid-1990s and which suggested that cadmium time-to-effect may be longer than reflected by the 1-hour averaging period. These studies were focused on fish and did not address trends in duration for other aquatic species, such as invertebrates. Because of the limited nature of these investigations and absence of additional supporting information, EPA decided to revise the acute duration in this document to be consistent with the more protective 1-*

hour duration, which is generally supported by and consistent with the 1985 Guidelines."

The quote characterizes the 1995 analysis as "*focused on fish*". The implication is that there is uncertainty in whether the longer averaging period would be protective for other organisms, and especially invertebrates. However, this characterization is inaccurate, because fish and invertebrates were represented in US EPA (1995). For copper, the invertebrate data in US EPA (1995) included 14 observations for nine species (Table 1). The mean effective averaging period for these invertebrate tests with copper was 44 hours, which is well over the 24-hour averaging period recommended in EPA 2001 and 2007. With one of EPAs concerns being the "*absence of additional supporting information*" this review considered whether additional information published since US EPA (1995) could further extend the analysis to include a greater number and types of aquatic invertebrate species.

REVIEW OF ADDITIONAL TOXICITY DATA

A review was conducted to identify additional toxicity data to extend the analysis in US EPA (1995). This review focused on copper toxicity to freshwater invertebrate species to provide a significant number of additional studies to supplement those included in the original analysis.

Datasets were analyzed in Microsoft Excel, using the Solver add-in to fit Equation 1 to the data. The best fit was determined by minimizing the sum of squared residuals (SSR) between the reported and estimated LC50s in Equation 1. The Excel Solver tool was set to use the GRG Nonlinear method for minimizing the SSR, with $LC50_\infty$ and 1/k set as the variables, with the constraint of $1/k \geq 1$. This constraint was used to prevent errors from occurring in the minimization, since a value of $1/k \leq 0$ would result in a divide-by-zero error in some of the equations. Furthermore, $1/k$ was calibrated rather than *k* because the GRG Nonlinear method, being a gradient optimization method, performs better when the variables being optimized are in a similar numerical space to each other.

Before analyzing the new data, the procedure used in the current analysis was applied to some of the datasets from EPA 1995 (Dave 1984; Pickering & Henderson 1966) to ensure that the procedure would yield equivalent results. The calculated $LC50_\infty$ and k_r values were less than a 10% difference from the values reported in EPA 1995, and so we concluded that this numerical approach was equivalent to the approach used in EPA 1995.

The optimization was performed five times for each toxicity test, with five different pairs of starting values for $LC50_\infty$ and *k* so that the minimum SSR found by Solver was more likely to be the global minimum rather than a local minimum. The starting values for the two variables are shown in Table 2, and were selected to cover a wide range of the variable space. The $LC50_{\infty}$ and k values resulting from the calibrations that yielded the lowest SSR are reported in Table 1.

The new datasets provided averaging period information for an additional 32 toxicity tests covering an additional 19 species. These results combined with the copper invertebrate tests included in US EPA (1995) provide information from 46 tests, with 27 invertebrate species. These additional data triple the number of averaging period estimates, and triple the number of invertebrate species used to evaluate the suitability of a 24-hour averaging period. The copper invertebrate data from US EPA (1995) and from this review are summarized in Table 1. Table 1 also includes the calculated averaging periods for the studies in the updated dataset. Averaging periods for these additional data ranged from 18 to 240 hours with a mean of 76 hours.

CONCLUSION

The new data provided in this analysis provide similar results to those presented in EPA 1995. Averaging periods for a wide range of invertebrate species calculating using the approach recommended in US EPA (1991), ranged from 17 to 240 hours with an overall mean averaging period of 66 hours. This range in averaging periods demonstrate that a 1-hour averaging period is overly conservative, and that the 24-hour averaging period recommended in the 2007 copper criteria document would be suitably protective for sensitive invertebrates.

Table 1. Summary of calculated averaging periods from copper toxicity tests for freshwater invertebrate species in US EPA 1995, and in additional literature included in this review.

Citation	**Species**	**Comments**	**Averaging period (hours)**
Rehwoldt 1973	*Amnicola sp.*	Included in US EPA 1995	28
Gutierrez 2012	*Argyrodiaptomus falcifer*		>48
Strode & Balode 2013	*Bathyporeia pilosa (Lindstrom, 1855)*		>96
Bellavere & Gorbi 1981	*Biomphlaria glabrata*		19
Rehwoldt 1973	*Caddisfly*	Included in US EPA 1995	37
Gutierrez 2012	*Ceriodaphnia duba*		>48
Taylor et al. 1991	*Chironomus riparius*		>240
Rehwoldt 1973	*Chironomus sp.*	Included in US EPA 1995	>48
Martin & Holdich 1986	*Crangonyx pseudogracilis*	Included in US EPA 1995	>96
Rehwoldt 1973	*Damselfly*	Included in US EPA 1995	50
Gutierrez 2012	*Daphnia magna*		<24
Adema & Degroot 1972	*Daphnia magna*	Included in US EPA 1995	22
Adema & Degroot 1972	*Daphnia magna*	Included in US EPA 1995	31
Dave 1984	*Daphnia magna*	Included in US EPA 1995	>48
Cabejszek & Stasiak 1960	*Daphnia magna*	Included in US EPA 1995	>48
Dave 1984	*Daphnia magna*	Included in US EPA 1995	>48
Cairns et al. 1978	*Daphnia magna*	Included in US EPA 1995	<24
Cairns et al. 1978	*Daphnia pulex*	Included in US EPA 1995	>48
Charles et al. 2013	*Gammarus pulex*		<24
Güven et al. 1999	*Gammarus pulex*		33
Taylor et al. 1991	*Gammarus pulex*		<48

Citation	Species	Comments	Averaging period (hours)
Vincent et al. 1986 (via Charles et al. 2013)	*Gammarus pulex*		73
Strode & Balode 2013	*Gammarus pulex*		>96
Strode & Balode 2013	*Gammarus pulex (Linnaeus, 1758)*		75
Rehwoldt 1973	*Gammarus sp.*		17
Moon & Wozniewski	*Gammarus sp. (female)*		>96
Moon & Wozniewski	*Gammarus sp. (male)*		>96
Strode & Balode 2013	*Gammarus tigrinus (Sexton, 1939)*		>96
Stephenson 1983	*Gammerus pulex*	Included in US EPA 1995	>48
Stephenson 1983	*Gammerus pulex*	Included in US EPA 1995	>48
Strode & Balode 2013	*Hyalella azteca*		<48
Karntanut & Pasco 2002	*Hydra oligactis*		41
Karntanut & Pasco 2002	*Hydra viridissima*		>96
Karntanut & Pasco 2002	*Hydra vulgaris*	there are two stains of Hydra vulgaris	85
Beach & Pascoe 1998	*Hydra vulgaris*		>96
Karntanut & Pasco 2002	*Hydra vulgaris (Zurich)*	there are two stains of Hydra vulgaris	>96
Khangarot & Ray 1988	*Lymnaea luteola*		>96
Strode & Balode 2013	*Monoporeia affinis*		>96
Strode & Balode 2013	*Monoporeia affinis (Lindstrom, 1855)*		>96
Rehwoldt 1973	*Nais sp.*	Included in US EPA 1995	>48
Gutierrez 2012	*Notodiaptomus conifer*		>48
Strode & Balode 2013	*Pontogammarus robustoides*		>96

Citation	Species	Comments	Averaging period (hours)
Strode & Balode 2013	*Pontogammarus robustoides (Sars, 1894)*		<48
Gutierrez 2012	*Pseudosida variabilis*		>48
Rathore & Khangarot 2003	*Tubifex tubifex (Hard)*		>96
Rathore & Khangarot 2003	*Tubifex tubifex (Soft)*		>96
Rathore & Khangarot 2003	*Tubifex tubifex (Very hard)*		>96
Rathore & Khangarot 2003	*Tubifex tubifex (Very soft)*		57

Table 2. Values for five different initial conditions used for the optimization of $LC50_\infty$ and 1/k.

Calibration	Starting $LC50_\infty$ (µg/L)	Starting 1/k (hours)
1	= min(reported LC50s) / 2	= 1 / 24
2	= min(reported LC50s) * 5	= 2
3	= min(reported LC50s) * 5	= 1000
4	= min(reported LC50s) / 200	= 2
5	= min(reported LC50s) / 200	= 1000

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