Delta RMP TAC Teleconference

Thursday, September 19⋅9:00 – 10:00am

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Conference ID: 238-626-034#

Agenda

1. Introductions and review agenda
2. Decision on whether to give notice to proceed to Deltares
   - have they adequately addressed our comments on an earlier draft of their tech memo describing their analysis methods?
3. Wrap up and conclusion

Memo

To
Matthew Heberger

Date
September 4, 2019

Number of pages
7

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Subject
Response to additional comments

Dear Matt,

In this memo you will find in italic our response to the additional comments you have posed concerning Deliverable 3.3. “Final memorandum on analytical methods to be used”.

Kind regards

Erwin Roex

Issue #1 Regression analysis, and how you are manipulating the data to create the dependent variable and independent variables.

Based on our teleconference on July 15, I understood that you were going to create 2 different dependent variables based on the results of toxicity test lab results. The first variable is a continuous variable based on percent effect in the toxicity test. We understand this, and think it is appropriate. However, we noted that you would be censoring (removing) some of the data if it was below a toxic threshold and replacing it with a zero. Is this the case? You should explain the rationale for doing this or clarify how you will use 'binning' (i.e., grouping the data as 'toxic' and 'non-toxic') to interpret the results. The general feeling is that it would be inappropriate to remove data or to manipulate it in this way.

The CEDEN Effect Codes are useful for summarizing the data, e.g. making statements like, "X% of samples were found to be toxic to *C. dubia* in lab testing." However, it does not seem appropriate to use these codes to change values in other fields or to modify the percent effect.

Are you also proposing to create a binary or categorical response variable based on the CEDEN Effect Codes? Is this correct? And that you would decide which "bin" to put each observation in based on the effect code, something like this:
0 = Not Significant Less Similarity
1 = Significant Greater Similarity
2 = Significant Less Similarity

We think this approach needs more explanation. By doing this conversion, you are losing a lot of information, and overall your regression would have less power. If this is what you are planning to do, we would like to see an explanation as to why this is appropriate. And if so, what are the statistical techniques that you would use in this regression? (Presumably logistic regression, but it is not described in the memo.)
A categorical analysis could be appropriate. For example, do the sum TUs explain what category each sample fell into, or do the categories have statistically different mean or median sum TUs. What is probably inappropriate is categorizing the data, and then substituting data for one category with zeros, then analyzing with regressions, which is our understanding of your approach. If you wish to categorize the data and run a regression, we recommend that you perform an analysis of covariance or similar, to test the statistical significance of categories and the regression all together.

Answer:
Based on the input we have received during the teleconference on July 15, we have decided that the best way forward is to consider all the bioassay results, regardless of their outcome and not discriminate between toxic and non-toxic results. We will adjust Deliverable 3.3 on this point.

Issue #2 Choice of analysis method *a priori*

Our advisors had fairly serious concerns with this statement on page 7: "Linear regression and log/linear regression were used depending upon which method generates stronger correlations." This appears to be a case of "p-hacking," i.e. trying different statistical methods until you get the result you are looking for. This is poor statistical practice. You should state in advance how you plan to analyze the data. It is appropriate to transform independent variables so that they are well-behaved, i.e. approximately normally distributed. You may wish to consult a statistician about this.

Answer: based on information we have obtained from statisticians and other sources, we have concluded to adjust our analysis method.
In a first step we will plot the data on a scatterplot, as a lot of visual insight can be obtained from plots. In a next step we will check if the data are normally distributed. If not, then we will log-transform the data to see if that will result in normally distributed data sets. If so, we will use the parametric Pearson's r test to measure the linear association between the two variables. If also log-transformation will not result in normally distributed datasets, we will use either Kendall's tau test or Spearman's Rho, which are both non-parametric correlation tests. The choice between these two tests depends on the nature of the data. With Spearman's rho, differences between data values ranked further apart are given more weight, whereas Kendall's tau is more suited for variables which show skewness around the general relationship. Choice of the test will partly depend on the visual insights obtained from the scatter plots. Based on the outcome of the statistical analysis, a conclusion will be drawn regarding the relationship between the observed toxicity (bioassays) and the calculated toxicity, based on the chemical analysis. We will adjust the Deliverable 3.3 accordingly.

Issue #3 Bioavailability calculations

We are pleased that you have described how you will adjust the bioavailable concentration of copper to account for hardness and other ancillary water quality parameters. However, there are some concerns with the way you are proposing to do these calculations.

1. I encourage you to add a short introduction explaining the overall approach and why it is important to adjust these measurements. Talking to my colleagues, I found that only a few of us understood the rationale for performing these calculations to estimate the aquatic toxicity of metals. It would be good to add a brief explanation of why the raw result from the lab (total copper, in µg/L) is not a reliable indicator of potential toxicity, and that it is important to calculate the dissolved fraction, and to estimate free copper ions. E.g.: "Copper [is] a metal that forms reduced-toxicity complexes with dissolved organic matter" (USEPA 2000). "There is a consensus that free cupric ions are more toxic if compared with other chemical forms such as organically complexed copper" (Nor 1987).

   Answer: We have added the following text as introduction in the paragraph:
   The bioavailable fraction represents the amount of an element or compound that is accessible to an organism for uptake. Therefore, the toxicity of a compound is highly related to bioavailable fraction of this compound, and less to the total concentration. The bioavailability of compounds, and hence the toxic pressure depends on local conditions in the aquatic system on one hand and the physical-chemical properties of the compound on the other hand. For example, the metal copper forms reduced-toxicity complexes with dissolved organic matter.

2. Question
   Please state the source of these equations, and why you chose to use this particular version. There are equations and methods that were developed for use in California or the United States that may be more valid and more acceptable to CA regulators. For example, the EPA Biotic Ligand Model. Or, the water quality standard that is part of national law referred to as the California Toxics Rule (see the table under paragraph b(2) in this section of the federal law).

   Answer:
   We had a look at the two approaches addressed above. Input data for the EPA BLM include: temperature, pH, dissolved organic carbon (DOC), major cations (Ca, Mg, Na, & K), major anions (SO_4 & Cl), alkalinity, and sulphide, information which is not available for most of the events included in our database. The water quality standard for copper that is part of the California Toxics Rule is only dependent on the hardness of the water, which in our opinion is too straight forward.
   The BLM we have used for copper is the result of long-term research, partly at our institute, and has resulted in a PhD thesis (Verschoor, A., 2013, The power of biotic ligand models: Site-specific impact of metals on aquatic communities). We are convinced that this BLM approach, which describes the bioavailability of copper on a limited number of parameters, explains the bioavailability for the most essential part. Other approaches will only result in slight deviations.

3. Question:
   The equations in the memo should not have footnotes. Please reformat these. It looks like the footnote number is part of the equation, like one of the terms raised to a power, and this is confusing.

   Answer: we will adjust the formulas accordingly

4. Global default values for hardness should not be used when a hardness measurement is available for the same sample or at the same location and time. The Delta RMP measured hardness for all water samples that were analysed for pesticides and toxicity. For the lab work sponsored by the Delta RMP, the Aquatic Health Program Laboratory at UC Davis measured hardness. As a result, the hardness data are bundled with the toxicity data, and not "water chemistry", which is confusing. All of these data are available in CEDEN, and can be readily downloaded ("Hardness as CaCO3, Total", in mg/L). Please contact me if you have trouble finding these data using the CEDEN download tool.

   Answer: I think we have used local values where possible, but we will have an extra check on them.

5. Where hardness data are not available, the default for Dutch waterways may not be appropriate for California. It would be better to do a little exploratory data analysis to see what the typical values are in the Delta. One of our TAC members suggested using a value of 40 mg/L hardness as CaCO3 as a typical value. Please see more information below, from Debra Denton, USEPA.

   Answer: we have adjusted the "Dutch" default value of 100 mg/L to the "Delta" value of 40 mg/L, where needed.

6. What you have labelled as "fraction Cu ions" should be "Metal activity (M2+) in µg/L) according to the paper by Bootsma and Vink.

   Answer: We will adjust the text accordingly

7. For organics, it needs to be made clear when you are referring to suspended sediment and when you are referring to bed sediment. For the Delta RMP data, the concentration in sediment indicates the concentration sorbed to suspended sediment, NOT the concentration in bulk sediment (the Delta RMP does not collect or analyze bed sediment). It therefore does not make sense to convert these to concentrations in pore water, as the pore water is the same as the bulk water for which we have measured concentrations. If you still want to calculate sorption to organic carbon for the RMP's data, you need to justify that choice (for example, concern that the fraction of bioavailable pesticides will be less than the concentration measured in the water due to sorption to dissolved organic matter that was not filtered out during chemical analysis… in which case, the apparent $C_{dissolved}$ could be corrected using the concentration of DOM and Koc). The equation for organics "$C_{dissolved} = C_{total} / (1 + TSS * 10^{-6} \times POC*10^{-6} \times Koc)$" is inappropriate because the suspended solids are filtered out prior to analysis.

Furthermore, that equation is cited as from the Deltares report “Simple equations for the calculation of free metal ion activities in natural surface waters”, which is not about organics and does not contain this equation.

Answer:
*In order to be able to explain the observed toxicity in the sediment tests performed in different projects, we used the chemical analyses data in bed sediments to explain this observed toxicity. Therefore, we only made conversion from **bed** sediment to porewater, in all other cases we have used bulk water concentrations directly. The equation we used is only to correct bed sediment concentrations to pore water concentrations to be able to compare with toxicity data. This equation originates from reference 4 and applies to organic contaminants, unfortunately only available in Dutch. The report numbers of both Deltares reports start with the same number, as they originate from the same overall project, but two different reports are involved here.*

8. Question

Additionally, Koc values from EPIsuite are calculated values, and should only be used when measured values are not available or not appropriate due to experimental conditions. Koc values can vary substantially, depending on the temperature, ionic strength, sediment mineralogy, type of organic matter, and for polar/ionizable compounds, the pH and acid-base properties of the compound.

Answer: we had an extended closer look at the Koc values we have used. The msPAF tool uses EPIsuite values as a default when no other data are available. Eventually we only used Koc values for 34 compounds in our database, see below. For none of these compounds EPI suite values were used but originated from different sources. Some of these values were experimental, some were calculated because of lack of data. We will adjust the text in the Deliverable and include the table for which bioavailability corrections were used.

Table: Source of used K_{oc} for compounds for which K_{OC} values were used to correct for bioavailability, including source.

Delta_pesticide	Source
Copper	BLM
Diazinon	RIVM calculated
Chlorpyrifos	RIVM calculated
DDT(p,p')	experimental
Cypermethrin, Total	US EPA
Deltamethrin/Tralomethrin	US EPA
Simazine	RIVM calculated
Metolachlor	RIVM calculated
Malathion	RIVM calculated
Atrazine	experimental
Carbaryl	experimental
Diuron	RIVM calculated
Trifluralin	RIVM calculated
Carbendazim	RIVM calculated
Bentazon	RIVM calculated
Imidacloprid	RIVM calculated
Cyhalothrin, Total lambda-Esfenvalerate/Fenvalerate, Total	US EPA US EPA
Linuron	RIVM calculated
Propoxur	RIVM calculated
terbuthylazine	QSAR
DDD(p,p')	experimental
DDE(p,p')	experimental
Dimethoate	RIVM calculated
Quinoxyfen	experimental
Aldrin	experimental
Dieldrin	experimental
HCH, alpha-	experimental
Carbofuran	experimental
MCPA	RIVM calculated
Dichlorvos	RIVM calculated
Trichlorfon	RIVM calculated
Mevinphos	RIVM calculated
s-cypermethrin	US EPA