

UNCERTAINTY OF WATER TYPE–SPECIFIC HAZARDOUS COPPER CONCENTRATIONS DERIVED WITH BIOTIC LIGAND MODELS

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Abstract—One of the aims of the Water Framework Directive is to derive Europe-wide environmental quality standards that are scientifically based and protective of surface waters. Accounting for water type–specific bioavailability corrections presents challenges and opportunities for metals research. In this study, we present generally applicable approaches for tiered risk assessment of chemicals for prospective use. The objective of the present study was to derive water type–specific dissolved copper criteria for Dutch surface waters. The intent was to show the utility of accounting for bioavailability by using biotic ligand models (BLMs) and two different ways of extrapolating these BLMs in order to obtain reliable bioavailability-corrected species sensitivity distributions. Water type–specific criteria estimations were generated for six different water quality conditions. Average hazard concentrations as calculated using the BLMs and the two alternate normalization scenarios varied significantly among the different water types, from 5.6 to 73.6 $\mu\text{g/L}$. Water types defined as large rivers, sandy springs, and acid ponds were most sensitive for Cu. Streams and brooks had the highest hazard concentrations. The two different options examined for toxicity data normalization did impact the calculated hazard concentrations for each water type.

Keywords—Biotic ligand model Copper Uncertainty analysis Water types Environmental quality criteria

INTRODUCTION

The Water Framework Directive (WFD) [1] is one of the most important pieces of European environmental legislation in recent years, requiring all inland and coastal waters to achieve “good status” by 2015. To meet this requirement, European Union countries established a river basin district structure in which environmental objectives will be set, including ecological targets for surface waters and environmental quality criteria for individual pollutants. The biotic ligand model (BLM) is one of the more promising models to derive these environmental quality standards based on true bioavailable fractions and no-effect concentrations. The BLM combines chemical equilibrium modeling for the assessment of metal speciation with a toxicity model that relates metal accumulation at the biotic ligand to a toxic effect. The toxicological principles of BLMs were originally adapted from studies by Pagenkopf [2] that showed that gills of fish are particularly sensitive to metal poisoning. Metal concentrations in the gill were shown to be related to the acute effects in fish, e.g., acute effects on the respiratory system and distortion of osmotic balance. The BLMs were shown to accurately predict metal toxicity in many other organisms if those organisms were in direct contact with the external aqueous environment [3,4]. Differences in effects due to acute and chronic exposure could be captured in the models.

Biotic ligand models are being used in the (voluntary) metal risk assessment reports prepared for the evaluation and control of the risks of existing substances in Europe. “Risk” is defined in these reports as when the predicted effect concentration exceeds the predicted no-effect concentration (PNEC). When

sufficient information on the water characteristics of a specific water body and well-documented toxicity data are available, predicted effect concentration:PNEC ratios may be derived using bioavailability-corrected values for predicted effect concentration or PNEC. Toxicity data are corrected for bioavailability by applying BLMs and then can be used further to construct a water type–specific species sensitivity distribution (SSD). Chronic Cu BLMs have been developed for algae, daphnids, and fish [5–8]. These BLMs are in principle species and effect specific. Within the European Union risk assessment, SSD curves preferably are based on at least eight different species (ecb.jrc.it/tgdoc). Preexisting BLMs are used to extrapolate toxicity predictions for those species with no currently available BLMs. When extrapolating BLMs across species, it is assumed that conditional stability constants for cations (metal of interest and major ions) and the biotic ligand, mechanism of binding, and modes of action are similar across the range of species represented in an SSD. Various (pragmatic) methods have been proposed to use the BLMs across species [9–11] and to calculate PNECs (so-called normalization options). The choice for a certain method depends on the scientific evidence that it is indeed possible to extrapolate the BLMs over different species.

Using bioavailability-corrected PNECs, a water type–specific SSD can be constructed and a corresponding water type–specific hazardous concentration, HC5 (hazardous concentration at which 95% of the species in an ecosystem are assumed to be protected against the adverse effects of the chemical), can be calculated according to the technical guidance documents of the European Union (ecb.jrc.it/tgdoc).

The objective of the present study was to quantify and discuss the uncertainty of estimated HC5 values as a consequence of the variability of the water chemistry in six different

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Table 1. Chemical characteristics (average and SD) of the different water types^{a-c}

Water type description	No.	DOC (mg/L)	pH	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	Cl (mg/L)	Alkalinity (mg/L)
Large rivers	I	3.1 ± 0.9 (12/926)	7.7 ± 0.2 (12/4,024)	70.0 ± 4.8 (11/26)	9.1 ± 1.9 (11/26)	25.5 (2/2)	55.5 (2/2)	120 (2/8)
Canals, large lakes, small lakes	II	8.4 ± 4.4 (16/425)	8.1 ± 0.4 (15/443)	56.6 ± 15.8 (8/13)	19.5 ± 5.5 (6/9)	65.8 (7/7)	120 (7/7)	128 (6/9)
Streams, brooks	III	18.2 ± 4.3 (3/12)	7.4 ± 0.1 (5/401)	75.8 ± 39 (5/58)	8.5 ± 0.4 (3/56)	58.4 (3/8)	102 (3/8)	151 (1/4)
Ditches	IV	27.5 ± 12.2 (4/7)	6.9 ± 0.8 (4/7)	86.7 ± 28 (4/7)	31.9 ± 5.6 (1/4)	60.5 (4/4)	115 (4/4)	265 (1/4)
Sandy springs	V	2.2 ± 1.0 (1/4)	6.7 ± 0.1 (1/4)	20.3 ± 0.4 (1/4)	6.7 ± 0.4 (1/4)	17.0 (1/4)	31 (1/4)	8.6 (1/4)
Small acid ponds	VI	17.3 ± 4.4 (7/22)	5.1 ± 0.8 (7/22)	1.5 ± 0.9 (7/22)	0.8 ± 0.3 (7/22)	3.7 (1/3)	7.0 (1/3)	0.27 (1/4)
Reference conditions	Ref1	2.6	6.6/8.1	11.4/101	2.0/17	5.3	5.6	3.2
Distribution ^d		Normal	Normal	Normal	Normal	Normal	Normal	Normal

^a DOC = dissolved organic carbon; alkalinity = CaCO₃.

^b Values given in parentheses are number of locations/number of observations.

^c For the reference water, the 10th or 90th percentile (10P/90P) concentrations of pH, Ca, and Mg are given.

^d Distributions are based on the fits of actual data of water types I and II.

water types using two normalization options for the BLMs. Copper was used as an example metal in the present study because much information on monitoring data could be collected and the BLMs were available. The results of the analyses are discussed in the context of risk assessment.

MATERIALS AND METHODS

Water types

The water types studied were classified based on the basis of physicochemical characteristics, especially dissolved organic carbon (DOC), amount of cations, and pH, and broadly corresponding to the water types as defined in the WFD [1]. The types used include large rivers (I), canals and lakes (II), streams and brooks (III), ditches (IV), sandy springs (V), and small acidic ponds (VI).

Water types I to III cover approximately 90% of all freshwater in the Netherlands. Water types IV to VI cover the remaining 10% of freshwater environments, typically representing more extreme freshwater environments.

To be able to apply the BLM models, the following water parameters should be known for all water types: pH, activity of cations (Ca²⁺, Mg²⁺, Na⁺) and anions (Cl⁻, SO₄²⁻), alkalinity, and DOC content. The BLMs are built on the assumption that DOC in freshwater can be composed of 50% fulvic acid and 50% DOC without binding affinity for copper [10]. Sulfide species are assumed to play no significant role in the speciation of copper in fresh surface water. Water temperature of the surface waters was set at a default value of 15°C, being a representative value during the year. Details on the main water characteristics can be found in Table 1.

For a realistic uncertainty analysis, the average value, standard deviation (variability), distribution function, and correlation coefficients among all water parameters should be known. The uncertainty analysis is straightforward if all this information is readily available. However, for water types III to VI in particular data are insufficient. This will often be the case in national monitoring programs. Having little information on the nature of the water characteristics has consequences. A significant effort is needed to make reasonable estimates of missing water characteristics necessary in the uncertainty analysis. The uncertainty analysis needs to be carried out in a two-step procedure: a sensitivity analysis is used to examine which parameters contribute most to the variability of calculated HC5 values. Data gathering for the uncertainty analysis can then be limited to the most important water parameters that contribute to HC5 variability.

Two comprehensive sources of information were used for the water characteristics data set. Water types I and II are regularly monitored by Dutch authorities, and the results of these analyses are available through an online database (www.waterbase.nl). For water types III to VI, data were available from an inventory of metal concentrations in Dutch surface waters collected in the context of the WFD.

In this way, average values and associated variability for most of the water parameters were gathered for all water types. For the water parameters—alkalinity and Na⁺ and Cl⁻ concentrations—only average values were readily available. It must be noted that the information on water types III to VI is based on far fewer measurements than those for water types I and II.

The distribution (e.g., normal, log normal, and triangular) that describes the observations best should be known. Based on actual measurements in water types I and II, the variability

Table 2. Pearson's correlation coefficients among the different water chemistry parameters for water type I^{ab}

	pH	DOC	Ca	Mg	Na	K	Alkalinity	SO ₄ ²⁻	Cl ⁻
pH	<i>1</i>	<i>-0.12</i>	<i>-0.16</i>	<i>-0.37</i>	<i>-0.27</i>	<i>-0.27</i>	<i>0.34</i>	<i>-0.10</i>	NA
DOC	1,302	<i>1</i>	<i>0.23</i>	<i>0.21</i>	<i>0.62</i>	<i>0.58</i>	<i>-0.21</i>	<i>0.07</i>	NA
Ca	291	83	<i>1</i>	<i>0.71</i>	<i>0.69</i>	<i>0.64</i>	<i>0.65</i>	<i>0.72</i>	NA
Mg	287	81	382	<i>1</i>	<i>0.88</i>	<i>0.86</i>	<i>0.22</i>	<i>0.71</i>	NA
Na	1,022	614	387	382	<i>1</i>	<i>0.91</i>	<i>0.05</i>	<i>0.78</i>	NA
K	834	661	287	284	846	<i>1</i>	<i>0.07</i>	<i>0.73</i>	NA
Alkalinity	371	81	194	192	276	268	<i>1</i>	<i>0.42</i>	NA
SO ₄ ²⁻	199	132	238	234	303	193	91	<i>1</i>	NA
Cl ⁻	NA	NA	NA	NA	NA	NA	NA	NA	<i>1</i>

^a DOC = dissolved organic carbon; NA = not available.

^b Top right are the correlation coefficients (italic); bottom left are the number of value pairs upon which the correlation coefficient was calculated.

of pH and DOC could be described best with a normal probability distribution function. For other water parameters and water types, the distribution function could not be assessed due to the lack of data. A normal probability function was used to describe the variability of the water parameters. This assumption has been tested by comparing the use of theoretical distributions for pH and DOC to empirical distributions as input for the uncertainty in calculated HC5 values [10].

It is known that many water parameters are interrelated and that simultaneous change of different water chemistry parameters affects response variables. For a realistic assessment of the uncertainty of the calculated HC5 values, the correlation among the different water characteristics should be known. Therefore, Pearson's correlation coefficients among various water parameters were calculated for the different water types. For water type I, calculated correlations were based on measurements from three locations at the entry of the large rivers Rhine and Meuse in the Netherlands. The correlation coefficients are given in Table 2.

Correlation coefficients between chloride and other parameters could not be calculated due to lack of data, and no correlation could be determined in these cases. The lack of these correlations can be expected to have negligible impact on the derived hazard concentrations, because chloride ions have only a small influence on the calculated Cu speciation and Cl⁻ is assumed not to interact with the biotic ligand in the Cu-BLM.

For water type II, correlation coefficients were derived from observations at seven locations in larger canals and lakes. The correlations are given in Table 3.

For water type II, lack of correlation among SO₄²⁻, Cl⁻, and most other water characteristics was assumed. The lack of these correlations was again expected to have negligible impact on the final results in deriving hazard concentrations.

Correlations among water chemistry parameters for water

types III to VI could not be calculated due to lack of data. For these water types, the correlation coefficients were estimated by first taking the average values for the water characteristics for the six water types. The correlation coefficients were then calculated from these average water characteristic values. The correlations coefficients used within the uncertainty analyses are given in Table 4.

The general observation was that the correlation coefficients of water parameters for each specific water type are different, which is inherent with classifications based on water characteristics.

Calculations

A step-by-step approach to apply water type-specific characteristics toward calculation of water type-specific effect concentrations is represented in Figure 1.

Cu-BLMs

The algae BLM used in the present study is the bioavailability model for different algae species as described in de Schampelaere and Janssen [12]. The chronic Cu model used for waterfleas is described in de Schampelaere and Janssen [7]. This model was proven to accurately predict comparable phyla [9]. Toxicity data for fish were fitted as described in de Schampelaere and Janssen [6], which is a Cu BLM that can be used to predict either fish toxicity or acute daphnids toxicity. Inorganic Cu species considered in the calculations were based on the equilibrium constants as given by Martell, Smith, and Motekaitis [13]. The WHAM V model [14] was used to calculate all copper species. The response variable HC5 of the models gave a nonmonotonic relationship with the water data that were the input of the model.

Calculation of the bioavailability-corrected no-effect concentrations for all species and all endpoints as measured in

Table 3. Pearson's correlation coefficients among the different water chemistry parameters for water type II^{ab}

	pH	DOC	Ca	Mg	Na	K	Alkalinity	SO ₄ ²⁻	Cl ⁻
pH	<i>1</i>	<i>0.11</i>	<i>-0.41</i>	<i>0.02</i>	<i>0.07</i>	<i>-0.17</i>	<i>-0.68</i>	<i>0.09</i>	<i>-0.29</i>
DOC	1,340	<i>1</i>	<i>-0.39</i>	<i>0.33</i>	<i>-0.04</i>	<i>0.13</i>	<i>-0.34</i>	NA	NA
Ca	59	43	<i>1</i>	<i>0.14</i>	<i>0.17</i>	<i>0.24</i>	<i>0.34</i>	NA	NA
Mg	54	40	53	<i>1</i>	<i>0.85</i>	<i>0.86</i>	<i>-0.08</i>	NA	NA
Na	219	148	54	53	<i>1</i>	<i>0.66</i>	<i>-0.04</i>	NA	NA
K	350	309	54	53	205	<i>1</i>	<i>0.20</i>	NA	NA
Alkalinity	329	230	57	53	78	78	<i>1</i>	<i>0.46</i>	<i>-0.38</i>
SO ₄ ²⁻	49	NA	NA	NA	NA	NA	7	<i>1</i>	<i>0.40</i>
Cl ⁻	155	NA	NA	NA	NA	NA	7	48	<i>1</i>

^a DOC = dissolved organic carbon; NA = not available.

^b Top right are the correlation coefficients (italic); bottom left are the number of value pairs upon which the correlation coefficient was calculated.

Table 4. Pearson's correlation coefficients among the different water chemistry parameters for water types III to VI based on average measurement observations of all water types^{a,b}

	pH	DOC	Ca	Mg	Na	K	Alkalinity	SO ₄ ²⁻	Cl ⁻
pH	<i>1</i>	<i>-0.31</i>	<i>0.71</i>	<i>0.44</i>	<i>0.72</i>	<i>0</i>	<i>0.51</i>	<i>0.54</i>	<i>0.75</i>
DOC	6	<i>1</i>	<i>0.36</i>	<i>0.47</i>	<i>0.38</i>	<i>0</i>	<i>0.60</i>	<i>0.54</i>	<i>0.36</i>
Ca	6	6	<i>1</i>	<i>0.70</i>	<i>0.80</i>	<i>0</i>	<i>0.94</i>	<i>0.87</i>	<i>0.85</i>
Mg	6	6	6	<i>1</i>	<i>0.73</i>	<i>0</i>	<i>0.86</i>	<i>0.93</i>	<i>0.76</i>
Na	6	6	6	6	<i>1</i>	<i>0</i>	<i>0.81</i>	<i>0.84</i>	<i>1.00</i>
K	6	6	6	6	6	<i>1</i>	<i>0</i>	<i>0</i>	<i>0</i>
Alkalinity	6	6	6	6	6	6	<i>1</i>	<i>0.97</i>	<i>0.85</i>
SO ₄ ²⁻	6	6	6	6	6	6	6	<i>1</i>	<i>0.88</i>
Cl ⁻	6	6	6	6	6	6	6	6	<i>1</i>

^a DOC = dissolved organic carbon.

^b Top right are the correlation coefficients (italic); bottom left are the number of value pairs upon which the correlation coefficient was calculated.

the toxicity tests was performed with Ver 0.0.0.17 of the software that has been developed for the European Union's voluntary metal risk assessment reports for Cu [15]. In this way, toxicity data based on total concentrations and information on the water characteristics as given in the toxicity tests can be used to derive ion-specific no-effect concentrations.

Normalization options

In general, BLMs will account for both the interaction of a metal ion with the media, which should be common to each model, and the interaction of the available forms of the metal with the organism, which is species specific. For Cu numerous chronic toxicity data are available, and in some situations it has been demonstrated (through testing) that a BLM for one

taxonomic group is applicable to another taxonomic group. Examples are the justification to use a single algae model for different species of algae [12] and the use of the BLM for daphnids to predict toxicity for similar phyla, such as rotifers [9]. These extrapolations over species have resulted in the acceptance of BLMs developed for algae and daphnids to dissimilar types of organisms that are sporadically represented in the effects databases, such as amphibians, mollusks, and insects. This extrapolation of species-specific BLMs over different species is an established approach; the so-called full normalization [15]. The assumptions underlying this full normalization among organisms are similarity of toxicity mechanism, similarity of biotic ligand, and similarity of binding constants. The advantage of this full normalization approach

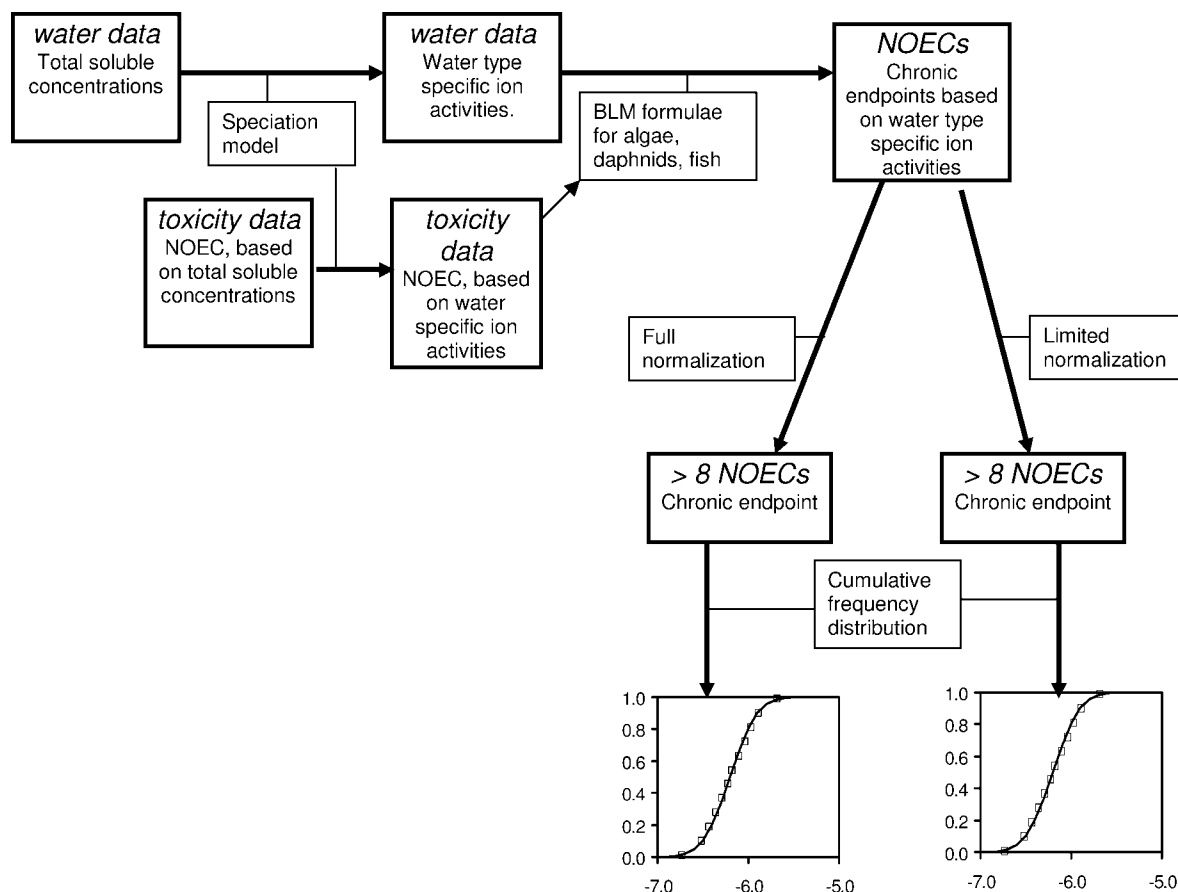


Fig. 1. Schematic representation of each calculation step to apply water type characteristics to water type-specific effect concentrations. For each water type, these steps were made. BLM = biotic ligand model; NOEC = no-observed-effect concentration.

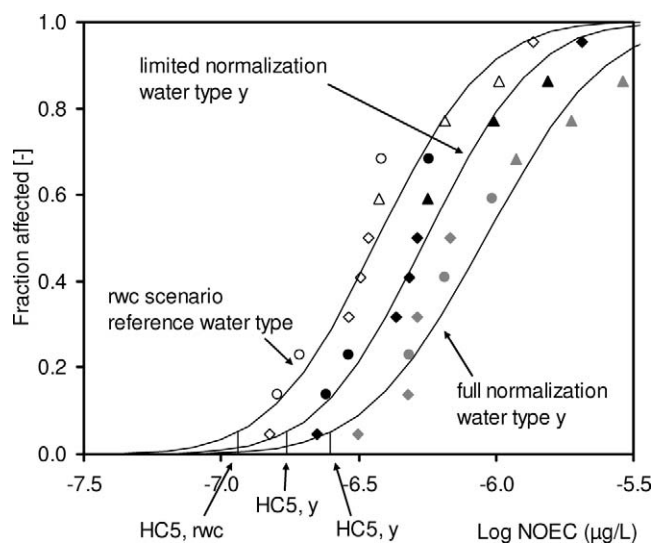


Fig. 2. Hypothetical example of species sensitivity distributions (SSDs) based on the results of either the full or the limited normalization of the observed species mean no-observed-effect concentrations (NOECs). The different symbols (diamonds, squares, circles) represent different taxonomic groups: Algae, daphnids, or fish, respectively. Shown are the species' mean NOEC values normalized to the reasonable worst-case (rwc) scenario, the mean NOEC values for water type *y* according to limited normalization and for water type *y* according to full normalization. HC5 = hazardous concentration at which 95% of the species in an ecosystem are assumed to be protected against the adverse effects of the chemical.

is that it allows for the calculation of water type-specific no-observed-effect concentrations (NOECs) for aquatic species for which no BLM is available.

For normalization, such information is needed as a set of NOECs or observed effect concentrations at which 10% of species are affected (EC10), as measured under different conditions for different species and endpoints. All these NOECs or EC10 values of the different organisms were scaled to the conditions observed at a specific location *y*, which results in an $NOEC_{species,y}$ for every species considered using the appropriate BLM (Fig. 2). Then an SSD was fitted, and from this SSD the HC5 at its lower 50% confidence level was calculated for location *y*.

For comparing the HC5 value to other results using the different normalization options, a description is required of the so-called reference water type. The reference water chemistry conditions were taken from the GEMS-B database as described in the European risk assessment reports [15]. The reference water conditions are aimed to reflect the reasonable worst-case scenarios. The concentrations of the reference water conditions are given in Table 1. Depending on what impact the water parameter has on the effect prediction using the BLMs on how this prediction is affected, these water chemistry conditions are selected. Therefore, water chemistry conditions were selected as follows: 10th percentile concentration of DOC for all organisms and 10th percentile concentration of inorganic parameters for waterfleas and fish. For algae, 90th percentile concentration of inorganic parameters was selected, which gives most reasonable worst conditions.

All NOECs were scaled to these reasonable worst-case scenarios, giving the $NOEC_{species,rwc}$ (Fig. 2). Then an SSD was fitted, and from this SSD the HC5 at its 50% confidence was derived for the rwc scenario.

When there is insufficient information on the toxicity or

when insufficient BLMs are available, bioavailability corrections on toxicity for a range of organisms cannot be made. Consequently, a bioavailability-corrected SSD curve cannot be derived. In cases in which insufficient experimental data are available to support full extrapolation across species, the most conservative bioavailability correction formula available was used. In detail, this means that no-effect concentrations for algae, daphnids, and fish were scaled to the conditions of the six water types as defined in the reasonable worst-case scenario. For this purpose, the reasonable worst-case scenario was again defined as the 10th or 90th percentile concentrations of the parameters affecting metal toxicity (pH, DOC, etc.). Species-specific NOEC values were scaled, resulting in $NOEC_{species,rwc}$ values. All NOEC values were subsequently scaled to the conditions observed at a specific location *y*, which results in an $NOEC_{species,y}$ for every species considered. The highest of the bioavailability factors defined as the ratio of $NOEC_{species,y} : NOEC_{species,rwc}$ of the BLM species was determined and applied across the entire set of toxicity data at all trophic levels. Then an SSD was fitted, and from this SSD the HC5 at its lower 50% confidence was calculated for this water type. This approach is the so-called limited normalization option that provides a pragmatic option for the use of BLMs.

Both normalization options likely result in different SSDs and consequently different HC5 values (Fig. 2). In general, assessing the HC5 using the limited normalization results in HC5 values that are more conservative (thus lower) than the values as calculated using the full normalization. The different outcomes of HC5 calculations as derived using both normalization options were compared using Mann-Whitney statistics.

Uncertainty analyses

The variability associated with the calculated HC5 as a result of variability of water characteristics among different water types and between normalization scenarios was quantified using uncertainty analysis. The uncertainty analyses were based using DOC and pH as predominant parameters for each water type; all other water parameters were used as water type-specific default values. This assumption was proven to be justified from sensitivity analyses on Cu-BLMs. Details on the sensitivity analyses that explicitly account for the nonlinear, nonmonotonic relationship between the input parameters of the correlated water data and the response variable can be found in Vijver and de Koning [10].

For our uncertainty analysis, we defined the ranges and distributions of pH and DOC within the different water types. The normal distribution for DOC in some cases covered negative values; therefore, a cutoff value of zero was used. Generation of samples from the ranges and distributions was obtained by Latin hypercube sampling using Monte Carlo simulation software. Specific HC5 values were calculated using the BLMs based on 100 runs for each water type, which was more than sufficient for a good representation of the distribution.

RESULTS

HC5 among different water types

The uncertainty analyses were performed using the distributions and standard deviations for pH and DOC (Table 1) and correlations among water chemistry parameters (Tables 2 and 3). All other parameters were fixed at their average values. Figure 3 shows the variability of the calculated HC5 values

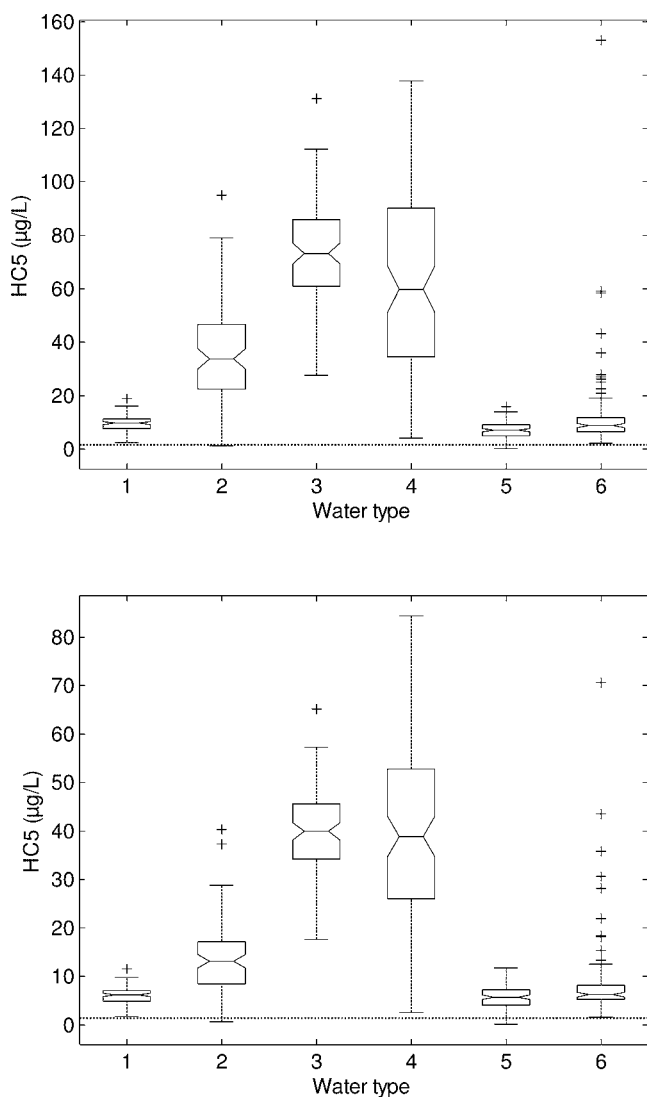


Fig. 3. Box and whisker plots showing the estimated variability of the calculated hazardous concentration (HC5) values in the different water types using both normalization scenarios (**top**, full normalization; **bottom**, limited normalization). The line at $y = 1.5 \mu\text{g/L}$ depicts the current generic Dutch standard for total dissolved Cu in surface waters.

for the different water types using the two normalization scenarios.

Water types I, V, and VI had the lowest estimated median HC5 values. Water types I and V were characterized by a low DOC content and water type VI by a low pH (and intermediate DOC content). Results for water type IV covered a large range, both in terms of lower and upper extremes but also in terms of the interquartile range. Water type VI had a large number of data points not covered in the interquartile range. This was explained by the relative large variation of pH in water type VI and the highly nonlinear relationship between pH and HC5 compared to the other water types.

The calculated HC5 values were compared over the different water types using both normalization scenarios focusing on the 5th percentile (5P) values. Lower 5P values mean that the bioavailability of copper in these waters is higher and hence a similar concentration of total copper in these waters represents a higher risk. Calculated HC5 values for the different water types ordered by normalization scenario are depicted in Figure 3 and given in Table 5.

Based on 5P values, it is obvious that for streams and brooks (water type III) the highest average and median HC5 value was calculated, no matter which normalization scenario was used. In general, rivers (water type I), sandy springs (water type V), and small acid ponds (water type VI) had the lowest HC5 values, and therefore were the most sensitive water types. The calculated median HC5 values all differed significantly from one another according to the Mann-Whitney test except for those of water types III and IV, which did not differ significantly when full normalization was applied.

The Mann-Whitney test also showed that the HC5 values derived using full normalization for all water types differed significantly from HC5 values obtained using limited normalization. Results obtained according to the limited normalization gave, as expected, the lowest HC5 values.

All calculated HC5 values that were corrected for bioavailability based on the 5P are higher than the current generic (based on total soluble Cu concentrations) risk limit in the Netherlands of $1.5 \mu\text{g/L}$ (Fig. 3). The lower extremes of water types II, V, and VI calculated with the full normalization option did not significantly differ from the generic risk limit. For the limited normalization option, water types I, II, V, and VI had lower extreme values that were similar to or below the generic risk limit and were therefore not significantly different.

Table 5. Statistical measures describing the variability of the hazardous concentration (HC5) values caused by the variability in the water chemistry for the different water types and normalization scenarios

Water type	Normalization scenario	Average ($\mu\text{g/L}$)	Median ($\mu\text{g/L}$)	SD ^a ($\mu\text{g/L}$)	5th percentile ($\mu\text{g/L}$)	95th percentile ($\mu\text{g/L}$)
I	Full	9.6	9.7	2.9	4.9	14.1
	Limited	6.1	6.2	1.8	3.2	9.0
II	Full	35.0	33.8	17.9	8.4	64.0
	Limited	13.6	13.1	7.3	3.0	26.4
III	Full	73.6	73.3	18.9	43.7	104.6
	Limited	39.8	39.9	8.7	25.6	53.7
IV	Full	64.1	59.9	34.5	11.2	127.9
	Limited	39.9	38.9	19.9	8.4	78.6
V	Full	7.2	7.1	3.1	2.4	12.1
	Limited	5.6	5.7	2.3	1.9	9.1
VI	Full	12.7	8.8	17.0	4.5	28.4
	Limited	8.9	6.3	8.9	4.2	22.3

^a SD = standard deviation.

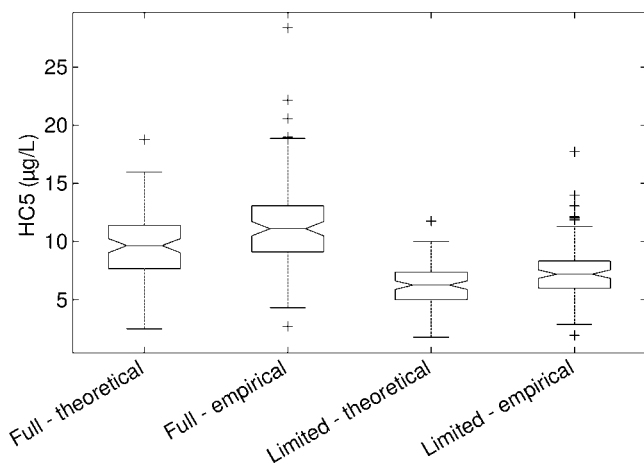


Fig. 4. Comparison of the uncertainty in calculated hazardous concentration (HC5) values using theoretical and empirical (= actual data) distributions for pH and dissolved organic carbon as input data. + = represent data above the upper extremes and below the lower extremes.

Measured parameters versus theoretical distribution functions

For the calculations, we selected a theoretical normal distribution for pH and DOC. The accuracy of this assumption was tested by comparing the use of the theoretical distributions to actual measurements as input for the uncertainty in calculated HC5 values. To make this comparison, pH and DOC have to be measured simultaneously (at the same location and the same time). For water type I, approximately 1,300 combined pH and DOC observations were available from 1982 to 2006. Samples were drawn from this large data set, using it as input for a Monte Carlo analysis and to calculate the variation in the HC5 value according to the full and limited normalization scenarios. These results were compared to the HC5 values as determined using the normal distribution function. This allows for determining the impact of the assumed distribution function on the HC5 values. The result of this analysis is shown in Figure 4.

The estimated average HC5 values were not significantly different when calculated based on either the theoretical distribution functions or the empirical distributions. Between the upper and the lower quartiles, calculated HC5 values did not differ significantly among the different methodologies to describe the distribution of water parameters.

DISCUSSION

Different HC5 values for different water types

The uncertainty analysis shows that HC5 values for Cu among the water types differ significantly. Lowest HC5 values were found for sandy springs (water type V) and large rivers (water type I), and acid ponds (water type VI) were calculated to be sensitive types of water bodies. These results can be explained by the competition processes on which the BLMs are based. For the acid ponds with a pH of approximately 5.1, the sensitivity can be ascribed to the very low concentrations of cations in the water. Thus, competition for binding of copper at the biological target is low, and only inorganic copper species are relevant at this pH. Validation studies on the Cu-BLMs [15] ascertained that the normal range of pH in which the BLMs are valid is from 5.5 to 8.5. The lower limit of the pH in the present study (value of ~5.1) overlaps with the pH of

the most extreme water type: Small acidic ponds. Recently, Balistreri et al. [16] reported on research on the use of BLMs in acidic mine drainage waters (pH < 4). Their results show that even beyond the validated range of BLMs, the BLMs accurately predict the effects. We therefore conclude that the use of BLMs on the water data of water type VI is relevant to our situation and does give reliable results.

For large rivers and acid ponds, the low HC5 values can be ascribed to the low DOC concentrations that are characteristic for these water types. At similar total copper loadings, a lower concentration of DOC implies that the Cu activity in the water phase will be higher; hence, a higher loading of the biotic ligands with Cu ions will be attained.

Streams and brooks (water type III) can have rather high total copper concentrations without any adverse effects, which can be attributed to the protective effect of relatively high DOC concentrations and the neutral to basic pH. Average HC5 values derived for streams and brooks (water type III) and for ditches (water type IV) were not significantly different, but the calculated variability of the HC5 value is somewhat larger in water type IV, reflecting the more diverse nature of ditches. This similarity in average HC5 values can be ascribed to most ditches in the Netherlands being located in the peaty soils or clayish fluvial deposits and therefore having relatively high DOC content, just like the streams and brooks. Based on our results, these water types (III and IV) can therefore be combined when deriving water quality standards for copper. This result also means that the selection of different water types generally leads to a distinct different risk characterization in these water types for Cu.

Different normalization options

Chronic BLMs are available only for a limited number of aquatic species. Given the data requirements set forward in the technical guidance document (ecb.jrc.it/tgdoc) on tested species, this limitation hinders the derivation of BLM-based PNECs for specific water types. To optimize the use of toxicity data for biota with no available BLM, it is desirable to apply BLMs across taxonomic groups. Therefore, two different normalization options were used in the present study: full normalization and limited normalization. Full normalization is only justified when, first, similarity in the underlying mechanism of toxicity is known. In the case of copper, the dominant mechanism of toxicity is related to the disturbance of sodium homeostasis. The key target tissue for copper toxicity is the water-organism interface with the cell wall and gill-like surfaces acting as target biotic ligands in all species investigated [15]. Second, thorough validation must be carried out showing that the toxicity of species for which no BLM was developed can indeed be accurately predicted. Third, the water conditions of the toxicity test medium need to be within the distribution of the water characteristics of the BLM.

The specific sensitivity of all different species and endpoints among different water types is explicitly considered using the full normalization option. For the limited normalization option, a worst-case approach is applied, accounting for the most conservative bioavailability correction for the species. Hence, differences among those extrapolation options inherently provide information about model accurateness and assist in explaining the differences in HC5 values. The more that is known about the mechanisms underlying toxicity and sensitivity of species, and the more that is known on similarities of these modes of actions among species, the more the

extrapolation of the deduced BLM models over different species is justified. The limited normalization option includes a certain lack of underlying knowledge and is a pragmatic option. Epistemic uncertainties in the models (and the accompanying extrapolation method) are not further accounted for in the present study.

Variability of HC5 values and environmental quality criteria

The current Dutch generic quality target for surface waters is 1.5 µg/L total dissolved copper. The bioavailability-corrected HC5 values for the different water types, in most cases, were greater than this generic quality target (Fig. 3). Only for sandy springs (water type V) was the 5P value of the hazard concentration at the same magnitude as the current Dutch quality target.

This means that, in practice, for water types I to IV and VI, which are in higher-tiered risk approaches, the environmental quality targets for Cu can potentially increase while still providing sufficient protection to the ecosystem. For risk managers, this means that those water types can have lower priority in cleanup activities than other water types that have similar Cu concentrations in the water. The data on which the water type-specific hazard concentrations were derived were based on distributions that reflect concentrations of the water parameters over different seasons. The calculations were repeated using actual measured data of the combinations of water parameters that predominantly describe the bioavailability correction (DOC, pH, and Cu concentration). Those values too reflected all seasons from 1980 to 2006. Therefore, the data used provides an overview of the distributions over a long period. It remains possible that, for extreme environmental situations (e.g., extreme droughts and low water discharges or extreme rain fall and high runoff), combinations of the parameters may result in calculated HC5 values that are even lower than the calculated average values. It is possible that in those cases the risk limits (protecting 95% of the species) are exceeded. Extreme drought conditions lasting short periods were found twice to occur in the Netherlands during the time span we studied [17]. For calculating the risk limits derived in the present study, BLMs based on chronic toxicity are used because the extreme conditions in nature will last a short time. In general, the risk limits will most likely be sufficiently protective. Anticipation toward more extreme conditions within the higher-tiered, water-specific, risk-limit setting can, for example, be performed by considering the calculated HC5 value on the median value or the 25th percentile value (see also Figs. 2 and 3). The level at which the calculated HC5 value should be used as an environmental target, giving the protection to Cu toxicity as desired, is an environmental policy question to be addressed by water managers.

Implementation of BLMs in environmental risk assessment

Ecological risk assessment is primarily performed generically. Depending on the extent of substance-specific information available, assessment factors are applied to quantify the uncertainties in either the exposure or the effects assessment. Within this generic risk assessment, features such as water type-specific characteristics that affect actually occurring adverse effects are not taken into account. This often results in high assessment factors that do no justice to observable adverse effects in the field or in a lack of effects often encountered in aquatic ecosystems considered to be at risk.

This mismatch between generically derived expressions of risks (often based on total concentrations) and observable effects results in inappropriate regulations on chemicals.

Applying a higher-tiered risk assessment approach gives the opportunity to look into the severity of water type-specific effects [18]. Calculating water type-specific HC5 values requires accurate understanding of the variability of pH, DOC, and dissolved Cu concentrations to explain the predominant variability in calculated HC5 for Cu in all water types. These parameters are measured frequently by different regional water authorities. Guidance on how samples of pH and DOC should properly be collected, stored, and analyzed is presented within the supplementary information of the European WFD [1] (EN ISO 5667-3 preservation and handling of samples [metals]). Accounting for the specific variability of environmental parameters that impact the predicted effects provides more realistic water type-specific risk limits. This approach is in line with the water policy described in the WFD that considers good ecological and chemical status at the level of water basin districts. The water basin district structures comprise different water types. The generic risk limits and the water type-specific risk limits of metals will be derived mostly on data originating from surveillance and operational monitoring programs. Within these monitoring programs, the parameters pH and DOC are often determined, together with the concentrations of metals in the surface waters. For higher-tiered approaches considering site-specific variation, data from the monitoring programs can be used to prioritize waters that should be investigated for ecological risks.

Similar studies can be carried out for other metals, but researchers should be aware that the results obtained for Cu are not directly transferable to other metals because different BLMs are underlying the principles for bioavailability correction.

CONCLUSION

In conclusion, HC5 values were calculated as a consequence of the variability of water chemistry in different Dutch water types using two different normalization options. In general, large rivers (water type I), sandy springs (water type V), and acid ponds (water type VI) had the lowest HC5 values. Streams and brooks (water type III) had the highest estimated hazardous concentrations. Results obtained with the full normalization scenario differed significantly from results obtained with the limited normalization scenario for all water types. The differentiation in water type-specific risk limits assists in the deduction of more realistic assessment factors for Cu availability and potential biological effects.

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