SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 24, No. 1, pp. 224–230, 2005

Printed in the USA
0730-7268/05 $12.00 + .00

Hazard/Risk Assessment

SETTING SITE-SPECIFIC WATER-QUALITY STANDARDS BY USING TISSUE RESIDUE CRITERIA AND BIOACCUMULATION DATA. PART 1. METHODOLOGY

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(*Received* 22 *August* 2003; *Accepted* 2 *June* 2004)

Abstract—We have developed a method for determining site-specific water-quality standards (SSWQSs) for substances regulated based on tissue residues. The method uses a multisite regression model to solve for the conditional prior probability density function (PDF) on water concentration, given that tissue concentration equals a tissue residue threshold. The method then uses site-specific water and tissue concentration data to update the probabilities on a Monte Carlo sample of the prior PDF by using Bayesian Monte Carlo analysis. The resultant posterior PDF identifies the water concentration that, if met at the site, would provide a desired level of confidence of meeting the tissue residue threshold contingent on model assumptions. This allows for derivation of a SSWQS. The method is fully reproducible, statistically rigorous, and easily implemented. A useful property of the method is that the model is sensitive to the amount of site-specific data available, that is, a more conservative or protective number (water concentration) is derived when the data set is small or the variance is large. Likewise, as the site water concentration increases above the water-quality standard, more site-specific information is needed to demonstrate a safe concentration at the site. A companion paper demonstrates the method by using selenium as an example.

Keywords—Site-specific water-quality standards Tissue thresholds Bayesian Monte Carlo Bioaccumulation

INTRODUCTION

Tissue residue concentrations in some cases provide a more reliable predictor of toxic effects than do water concentrations. In these cases, a tissue residue–based water-quality criterion (TRC) may be appropriate. This is the case for two situations, first, when the relationship between accumulation of a substance at the site of toxic action and corresponding effect is understood. This has been well documented for acute metal toxicity, where the site of toxic action appears to be the respiratory organ (e.g., gill) for some metals (e.g., Ag, Cd, Cu, and Zn). By being able to predict metal accumulation at the gill as a function of waterborne metal concentration and ambient water-quality conditions (e.g., pH, dissolved organic carbon, and hardness), acute metal toxicity is much more reliably predicted than from waterborne-metal concentrations alone. This concept has been developed in a regulatory context in the form of the biotic ligand model [1,2].

The other case where use of a TRC appears appropriate is for substances where dietary exposure may be a dominant route of exposure resulting in elevated tissue concentrations. For these substances, the relative contribution of waterborne and dietary exposure may be quite variable as a function of ambient conditions and, therefore, effects may be difficult to predict based on waterborne concentrations only. For example, the U.S. Environmental Protection Agency has adopted a TRC for methylmercury (MeHg), rather than a water column–based water-quality criterion [3]. In this case, the transformation of inorganic Hg to MeHg and the subsequent degree of bioaccumulation in the food chain is highly site specific and cannot be easily predicted from waterborne Hg concentrations. However, the relationship between dietary MeHg (e.g., as accumulated in fish) and toxicity to humans and wildlife is relatively well understood. As a result, basing the ambient water-quality criterion on a TRC is appropriate. The U.S. Environmental Protection Agency has recently proposed a TRC for Se for similar reasons [4].

The primary disadvantage of a TRC is that if it is exceeded, water is still the medium that must be regulated to reduce tissue residues. Thus, a TRC can help determine whether a water body is impaired, but it does not solve the problem of how to determine the water-quality improvement needed to eliminate the impairment. In these situations, site-specific factors again come into play and must be understood to allow proper management of a water body. In the case of acute metal toxicity, as mentioned above, this problem has been solved through use of a mechanistic model (the biotic ligand model) that can predict metal accumulation on the gill, by taking into account site-specific factors such as pH and concentrations of Ca, Mg, and dissolved organic carbon [1].

Although a mechanistic approach is certainly desirable, it will not always be feasible. For the biotic ligand model, a relatively limited number of parameters have been shown to control the site-specific accumulation of metals on the gill. In contrast, the environmental chemistry of MeHg, particularly the factors that control transformation of inorganic Hg to MeHg, is considerably more complicated [3]. To date, efforts to mechanistically model these processes have resulted in models far too complex for regulatory application on a routine basis. As another example, Se is even more complex, with multiple oxidation states for inorganic Se, kinetically limited oxidation–reduction reactions, and transformation of inorganic Se to a wide array of methyl-, selenoamino, and selenoprotein

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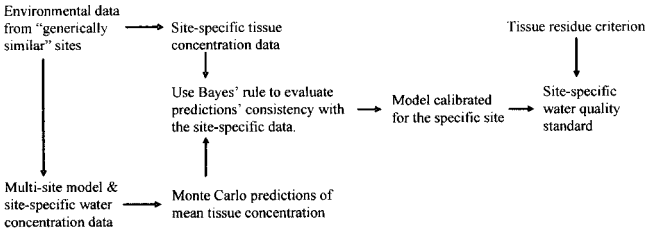

Fig. 1. Framework for calculating site-specific water-quality standards protective of tissue residue criteria.

forms [5–8]. In addition to complex environmental chemistry, for these substances dietary exposure can be quite important, adding an additional layer of complexity in terms of understanding assimilation efficiencies and substance distribution within organisms to toxic sites of action once it is assimilated. Given these factors, the routine use of mechanistic models in regulating substances such as Hg and Se is unlikely.

The infeasibility of mechanistic models for these types of substances, however, does not negate the utility and, perhaps, necessity of using TRCs for their regulation. Alternative approaches are needed for the application of TRCs to these types of substances. The method described in this paper is one such alternative and provides a means to estimate a water concentration that is protective of the TRC based on site-specific data. Our method involves two steps. The first step is to build a probabilistic bioaccumulation model that describes site-to-site variability in bioaccumulation across a range of generically similar sites. The second step in our method uses a statistical updating technique to determine which of the prior predictions from the generic model are consistent with water and tissue residue data from a specific site of interest. This is analogous to generalized sensitivity analysis for water-quality modeling as published by Hornberger and Spear [9]. The exception is that we have added the use of Bayesian Monte Carlo analysis [10,11] for updating the prior model with site-specific information.

METHODS

Given the discussion above, we believe that water-quality standards (WQSs) should be tissue residue–based for substances when the following conditions are met: A reliable, sensitive tissue residue-based endpoint exists; sufficient data are available to model site-to-site variability in the ratio of colocated water and tissue residue concentrations; and a site-specific WQS (SSWQS) can be calculated from the TRC. This paper describes a methodology to translate a TRC into a SSWQS. The basic framework is depicted in Figure 1. If any one of the previous conditions is not met, the TRC cannot be translated into a SSWQS.

When the previous conditions are met, site-specific water and tissue residue concentration data can be used to derive a WQS that is protective of the TRC for that site. The procedure consists of measuring colocated water and tissue residue concentrations at the site for the substance of interest, and comparing the site-specific tissue residue concentration data with a TRC deemed protective of sensitive species. If the TRC is not exceeded, the substance's concentration in water is sufficiently low to protect the organisms at the site. Otherwise, if the TRC is exceeded, the multisite model, the site-specific water and tissue residue concentration data, and Bayes's rule (defined below in the method description) are used to calculate the water concentration that provides a desired level of confidence of meeting the TRC at the site via the SSWQS. The procedure for deriving this SSWQS is described in detail in this paper. This concept is consistent with the tiered framework for deriving water-quality criteria recently described by Reiley et al. [12].

The remainder of this paper describes a method whereby site-specific water and tissue residue concentration data are used to derive a SSWQS that is protective of the TRC. This method is applied to Se in a companion paper [13]. The method uses data from a specific site to calibrate a model developed with data from other similar sites. These are the same types of data used in the MeHg ambient water-quality criterion for the protection of human health [3], although the method we have developed is for the protection of aquatic life and wildlife.

The rationale behind our approach follows. First, when comparing waterborne substance concentrations to a tissue residue concentration, the tissue residue represents integrated exposure, so it should be compared to a temporally and spatially averaged waterborne concentration. The duration and aerial extent of this average may be substance and organism specific. If appropriate averaging is applied, in a typical implementation scenario, one will have a limited range of waterborne concentrations at a site—sometimes only a single concentration—and a limited number of tissue residue samples.

Waterborne concentration and tissue residue data provide a site-specific bioaccumulation factor (BAF). If the BAF were constant as a function of waterborne concentration, one could simply use the BAF to calculate the water concentration at which the tissue residue would reach the threshold, and use this information to set a SSWQS. However, this does not work if the BAF is concentration dependent, as has been shown for a number of substances (e.g., metals) [14,15]. The BAF has been shown to vary inversely with waterborne exposure concentration. It also has been shown that this inverse relationship can be species and site specific, further complicating predictions for a site with limited data [14].

Given this, the problem lies in determining the site-specific relationship between waterborne concentration and tissue residue, typically based on a single mean tissue residue for a given site. Because of the limited range of waterborne concentrations, and the uncertainty in the mean tissue residue concentration, it is difficult to extrapolate these data to a water concentration that results in a mean tissue residue concentration less than or equal to the TRC. Data from other similar sites can provide a broader range of waterborne and tissue residue concentrations, but we know there is significant site-to-site variability in the relationship between waterborne concentration and mean tissue residue. However, we can use the pooled data from other similar sites to define a set of possible waterborne concentration–mean tissue residue relationships, then use our site-specific data to determine which relationships, from the set of possibilities, fit our specific site (Fig. 2). Once we have determined which of the set of possible relationships fit our specific site, we can extrapolate from the observed water concentration to a water concentration that results in a tissue residue concentration at or below the TRC. The result is a SSWQS.

A useful property of the methodology is that better site-specific data reduce the range of relationships possibly fitting the specific site, resulting in a smaller margin of safety being placed on the SSWQS. Similarly, the shorter the water concentration extrapolation required to reach the SSWQS, the more able the methodology is to reduce the range of relation-

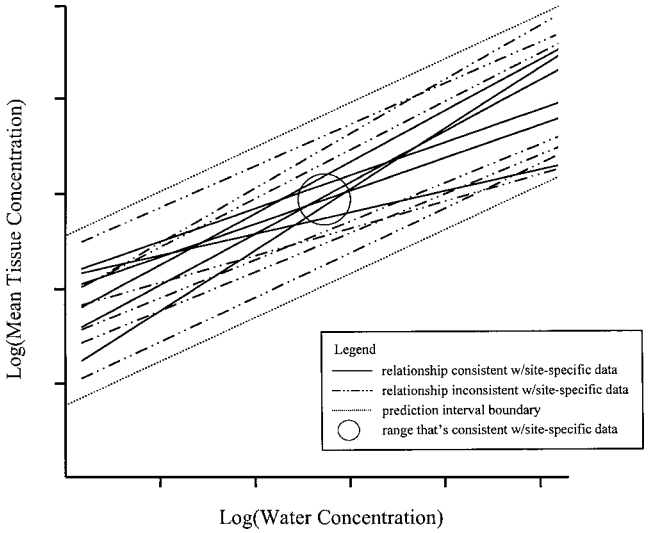

Fig. 2. Conceptual illustration of using site-specific data to determine which relationships from a set of possibilities fit a specific site.

ships possibly fitting the specific site (i.e., the greater the extrapolation, the more site-specific information is needed to achieve the same margin of safety reduction in the SSWQS).

Bayesian Monte Carlo analysis

The statistical technique we use in our methodology is Bayesian Monte Carlo (BMC) analysis [10,11]. Bayesian Monte Carlo analysis evolved from earlier procedures used to ensure that the probability distribution function (PDF) of a model's predictions was consistent with observed data. These earlier acceptance–rejection procedures involved deleting predictions that, based on expert judgment, were inconsistent with observations [9,16,17]. The difference between BMC analysis and earlier procedures is that BMC analysis is more statistically rigorous, in the sense that it defines the acceptance–rejection procedure by using the axioms of probability theory, as expressed in Bayes's rule.

Bayes's rule states that the probability associated with a prediction given some new data is proportional to the probability of the prediction before the new data were available times the probability of having observed the new data if the prediction were true

$$P(B_k|A) = \frac{P(A|B_k)\cdot P(B_k)}{\sum_{j=1}^{n} P(A|B_j)\cdot P(B_j)} \quad (1)$$

where B_k is the kth prediction of a model, where $k \in J = \{1, 2, \ldots, n\}$; A is new data about the variable(s) that the model predicts; B_j is the jth model prediction, $j = 1, 2, \ldots, n$; $P(B_k|A)$ is the assessed probability that the kth model prediction is true after having observed the new data A, also known as the posterior probability of the kth model prediction; $P(A|B_k)$ is the probability of observing the new data A if the kth model prediction is true, also known as the likelihood of the kth model prediction; and $P(B_k)$ is the assessed probability that the kth model prediction is true before having observed the new data A, also known as the prior probability of the kth model prediction. The two terms in the numerator on the right side of Equation 1 are the likelihood and prior probability of the kth model prediction. The denominator is a proportionality constant, which ensures that the posterior probabilities of the model's n predictions sum to 1 [18,19].

The use of Bayes's rule to define the acceptance–rejection procedure for evaluating a Monte Carlo PDF was first illustrated by Dilks et al. [10,11], who introduced the term BMC analysis. Other applications include those of Patwardhan and Small [20] and Dakins et al. [21]. Several investigators used Bayesian techniques in the late 1980s and early 1990s (e.g., Erdy [22] and Iman and Hora [23]), but the techniques were computationally limited until combined with Monte Carlo analysis.

In BMC analysis, we can simplify Equation 1. Because the predictions B_j ($j = 1, \ldots, n$) are a Monte Carlo sample, the prior probability on each prediction is equal

$$P(B_j) = \frac{1}{n} \qquad (j = 1, 2, \ldots, n) \quad (2)$$

where n is the number of replications in the Monte Carlo analysis. Therefore, Equation 1 becomes

$$P(B_k|A) = \frac{P(A|B_k)\frac{1}{n}}{\sum_{j=1}^{n}\left[P(A|B_j)\frac{1}{n}\right]} = \frac{P(A|B_k)\frac{1}{n}}{\frac{1}{n}\sum_{j=1}^{n} P(A|B_j)} = \frac{P(A|B_k)}{\sum_{j=1}^{n} P(A|B_j)} \quad (3)$$

By Equation 3, the posterior probability on the kth replication of a Monte Carlo analysis equals the probability of observing the data A if the kth prediction is correct, divided by the sum of the probabilities of observing A if the jth prediction is correct ($j = 1, 2, \ldots, n$).

Example. The following is a textbook-style example of the BMC methodology. The problem in this example is dissolved oxygen (DO) deficits downstream of a biochemical oxygen demand (BOD) point discharge to a river. There is a single BOD point source at the upstream end of the study reach. A probabilistic model is used to predict DO concentration as a function of distance downstream from the point source. A probabilistic analysis is being conducted of whether the minimum DO (i.e., the lowest DO observed at any distance downstream of the point source) will fall below a regulatory threshold of 5 mg/L. In an initial Monte Carlo analysis, 6,000 of 10,000 model runs predicted a minimum DO downstream of the point source below 5 mg/L

$$P(\mathrm{DO}_{\min} \geq 5) = 0.4$$
$$P(\mathrm{DO}_{\min} < 5) = 0.6 \quad (4)$$

Next, we get new data on DO concentration 15 km downstream from the point source. These data indicate that the DO concentration at 15 km is between 5.5 and 7.0 mg/L.

Examination of the 4,000 model runs that predicted a minimum DO downstream of the point source ≥5 mg/L found that 2,000 of these runs (50%) predicted DO concentration at 15 km between 5.5 and 7.0 mg/L. Of the 6,000 runs that predicted a minimum DO downstream of the point source <5 mg/L, 1,800 (30%) predicted DO concentration at 15 km between 5.5 and 7.0 mg/L

$$P(5.5 < \mathrm{DO}_{15} < 7.0 | \mathrm{DO}_{\min} \geq 5) = 0.5$$
$$P(5.5 < \mathrm{DO}_{15} < 7.0 | \mathrm{DO}_{\min} < 5) = 0.3 \quad (5)$$

Now, in light of the new data, what is the probability that the water-quality threshold is violated?

For the purposes of answering that question, our river below the BOD point source has two predicted states: either the regulatory threshold is violated (minimum DO is <5 mg/L) or it isn't. Our new datum is the measurement of DO concentration at 15 km below the BOD point source, which indicated that the DO at that location is between 5.5 and 7.0 mg/L. Applying Bayes's rule

$$\begin{aligned} &P(\mathrm{DO}_{\min} < 5 \,|\, 5.5 < \mathrm{DO}_{15} < 7.0) \\ &= [P(5.5 < \mathrm{DO}_{15} < 7.0 \,|\, \mathrm{DO}_{\min} < 5) \cdot P(\mathrm{DO}_{\min} < 5)] \\ &\quad \div [P(5.5 < \mathrm{DO}_{15} < 7.0 \,|\, \mathrm{DO}_{\min} < 5) \cdot P(\mathrm{DO}_{\min} < 5) \\ &\qquad + P(5.5 < \mathrm{DO}_{15} < 7.0 \,|\, \mathrm{DO}_{\min} \geq 5) \cdot P(\mathrm{DO}_{\min} \geq 5)] \\ &= \frac{0.3 \cdot 0.6}{(0.3 \cdot 0.6) + (0.5 \cdot 0.4)} = \frac{0.18}{0.18 + 0.20} = \frac{0.18}{0.38} = 0.47 \end{aligned} \quad (6)$$

So, in light of the new data, the predicted probability of violating the DO water-quality threshold drops from 60 to 47%.

Methodology for deriving SSWQSs for bioaccumulative chemicals

The remainder of the *Methods* section develops the BMC methodology for deriving SSWQSs for bioaccumulative chemicals. The methodology uses a multisite bioaccumulation model to define the prior PDF for mean tissue concentration (MTC) as a function of water concentration. Site-specific tissue residue data are used to define the likelihoods of MTC predictions.

Because of uncertainty and variability in bioaccumulation of a substance, a single water concentration put into a non–site-specific model produces a broad prior distribution of MTC predictions. Observed site-specific MTCs also are uncertain because of sampling and measurement error.

The BMC analysis accounts for both the uncertainty in MTC predictions (from site-to-site variability) and the uncertainty in MTC observations (from sampling and measurement error). The BMC methodology asks, given the uncertainties in the site-specific data, which of the model's predictions could be representative of the site? In other words, it uses the data from multiple sites to define the range of possible water-to-MTC relationships (i.e., BAFs), then uses data from a specific site to narrow down the set of relationships that could apply to that site. Some predictions of MTCs will be more similar than others to the sample average tissue concentration observed at a specific site. The BMC analysis statistically compares the uncertain predictions of the non–site-specific model to the site-specific data, and measures the degree of similarity between the predictions and observations. It updates the model by increasing the probabilities (i.e., putting more weight) on predictions that are more consistent with observations, and reducing the probabilities (putting less weight) on predictions that are less consistent with observations. Therefore, BMC uses observed data to make predictive models more site-specific. The mechanistic details of this conceptual approach follow.

Prior distributions. We start with a set of colocated mean water concentrations (MWCs) and MTC data (i.e., BAFs) from multiple, generically similar sites, and develop a linear regression model from the {MWC, MTC} pairs. For purposes of this example, and in the companion paper, we use a hockey stick regression model [24–26] because it best describes Se bioaccumulation [27]. Hockey stick regression models were fit in S-Plus (V 4.0, Insightful, Seattle, WA, USA) by using the function *nls*, which employs a Gauss–Newton algorithm [28] to minimize the sum of squared residuals between the fitted model and the data.

The model used was

$$\log(\widehat{\mathrm{MTC}}) = \begin{cases} b + s \cdot \mathrm{T}_{n-p} & \log(\mathrm{MWC}) \leq \tau \\ b + m \cdot [\log(\mathrm{MWC}) - \tau] + s \cdot \mathrm{T}_{n-p} & \log(\mathrm{MWC}) > \tau \end{cases} \quad (7)$$

where $\widehat{\mathrm{MTC}}$ is the model prediction of MTC; m, b, and τ are the slope, intercept, and inflection point, respectively; and s is the standard error in the prediction of log(MTC). The parameter T_{n-p} is the T distribution with $n - p$ degrees of freedom, where n is the number of independent {MWC, MTC} pairs in the multisite database and p is the number of coefficients in the multisite model ($p = 3$).

Because our purpose is to determine a SSWQS, we are primarily interested in the case $\log(\mathrm{MWC}) > \tau$ and we will focus on that in the remainder of this paper. If the site-specific water concentration were below the bioaccumulation threshold, further reductions in water concentration would not be expected to reduce tissue residues. The multisite model gives the prior probability distribution on the predictions of log(MTC).

The standard prediction error is given by the equation

$$s = \sqrt{\sum_{i=1}^{n} [\log(\mathrm{MTC}_i) - \log(\widehat{\mathrm{MTC}}_i)]^2} \cdot \sqrt{(1 + v_o'(V'V)^{-1}v_o)} \quad (8)$$

where v_o is the matrix of derivatives of the model with respect to each parameter evaluated at each water concentration to be evaluated and $(V'V)^{-1}$ is the variance–covariance matrix of the regression parameters computed from derivatives of the model with respect to each parameter evaluated at each measured water concentration. The S-Plus regression model solves for s as a function of MWC. Details about the standard prediction error model can be found in Huet et al. [29], Ratkowsky [30], and Ryan [31].

It is possible to fit a very good quadratic approximation to the standard prediction error values generated by S-Plus, as a function of either MWC or predicted MTC

$$\begin{aligned} s &= \sqrt{\sum_{i=1}^{n} [\log(\mathrm{MTC}_i) - \log(\widehat{\mathrm{MTC}}_i)]^2} \cdot \sqrt{(1 + v_o'(V'V)^{-1}v_o)} \\ &= a_{0w} + a_{1w} \cdot \log(\mathrm{MWC}) + a_{2w} \cdot \log(\mathrm{MWC})^2 \quad \text{or} \end{aligned} \quad (9)$$

$$\begin{aligned} s &= \sqrt{\sum_{i=1}^{n} [\log(\mathrm{MTC}_i) - \log(\widehat{\mathrm{MTC}}_i)]^2} \cdot \sqrt{(1 + v_o'(V'V)^{-1}v_o)} \\ &= a_{0t} + a_{1t} \cdot \log(\widehat{\mathrm{MTC}}) + a_{2t} \cdot \log(\widehat{\mathrm{MTC}})^2 \end{aligned} \quad (10)$$

Equation 9 simplifies computing the prior and posterior probability distributions of log(MTC) predictions. Equation 10 simplifies computing the SSWQS. Substituting Equation 9 into Equation 7, and solving for the water concentration at a specific site for which a WQS is needed gives

$$\log(\widehat{\mathrm{MTC}}) \,|\, \mathrm{MWC_{site}} = b + m[\log(\mathrm{MWC_{site}}) - \tau] + \{a_{0w} + a_{1w}\cdot\log(\mathrm{MWC_{site}}) + a_{2w}[\log(\mathrm{MWC_{site}}]^2\}\mathrm{T}_{n-p} \quad (11)$$

Equation 11 is the prior distribution on MTC predictions for a specific site. If we take a representative sample of n_{pred} values of T_{n-p}, the prior probability for MTC prediction is

$$f'(\widehat{\mathrm{MTC}}_k) = \frac{1}{n_{\mathrm{pred}}} \qquad k \in \{1, 2, \ldots, n_{\mathrm{pred}}\} \quad (12)$$

The likelihood function. The likelihood function is the distribution on the average of a representative sample of log-transformed tissue residue concentrations from the site. Because the methodology is based on site-averaged concentrations, and because we are working with log-transformed concentrations, the likelihood function is assumed to be normal, with standard deviation equal to the standard deviation of the log-transformed concentrations divided by the square root of the sample size. The mean of the likelihood function is determined from the prior distribution. Specifically, the likelihood function is based on the assumption that a given MTC prediction is the true site-specific mean. It answers the question, what is the probability of having obtained the observed site-specific sample average, if the given MTC prediction is the true site-specific mean. Thus, the mathematical form of the likelihood function is

$$L[\log(\widehat{\mathrm{MTC}}_k)] = f\left\{\left[\frac{1}{n_{\mathrm{obs}}}\sum_{j=1}^{n_{\mathrm{obs}}}\log(\mathrm{TC_{obs}})\right]\middle|\,(\mathrm{MTC} = \widehat{\mathrm{MTC}}_k)\right\} = \frac{1}{\sqrt{2\pi s_{\mathrm{obs}}^2/n_{\mathrm{obs}}}} \times \exp\left\{-\frac{1}{2}\left[\frac{\frac{1}{n_{\mathrm{obs}}}\sum_{j=1}^{n_{\mathrm{obs}}}\log(\mathrm{TC_{obs}}) - \log(\widehat{\mathrm{MTC}}_k)}{\sqrt{s_{\mathrm{obs}}^2/n_{\mathrm{obs}}}}\right]\right\} \quad (13)$$

which is the mathematical form of the normal distribution, where $\mathrm{TC_{obs}}$ is the measured site-specific tissue residue concentration, s_{obs}^2 is the sample variance of the log-transformed tissue concentration data, n_{obs} is the number of site-specific tissue residue samples, j is the index variable for site-specific tissue residue samples, and k is the index variable for MTC predictions.

The posterior distribution. By Bayes's rule, the posterior probability on prediction k is equal to the product of the prior probability and likelihood of prediction k, divided by the sum of the products of the prior probabilities and likelihoods

$$f''(\widehat{\mathrm{MTC}}_k) = \frac{f'(\widehat{\mathrm{MTC}}_k)\mathrm{L}[\log(\widehat{\mathrm{MTC}}_k)]}{\sum_{k=1}^{n_{\mathrm{pred}}} f'(\widehat{\mathrm{MTC}}_k)\mathrm{L}[\log(\widehat{\mathrm{MTC}}_k)]} \quad (14)$$

where $f''(\widehat{\mathrm{MTC}}_k)$ is the posterior probability of the kth prediction of MTC, $f'(\widehat{\mathrm{MTC}}_k)$ is the prior probability of the kth prediction, and $\mathrm{L}[\log(\widehat{\mathrm{MTC}}_k)]$ is the prior probability of the kth prediction. The prior probability and likelihood function are given by Equations 12 and 13. The steps in solving for the posterior probability are

1. Sample T_{n-p} at one-tenth percentile intervals from $t_{0.001}$ to $t_{0.999}$.
2. Solve Equation 11 for each of the $n_{\mathrm{pred}} = 999$ sampled t values.
3. By Equation 12, each of the MTC predictions has a prior probability of 1/999, so the prior probability cancels out of the numerator and denominator of Equation 14 leaving

$$f''(\widehat{\mathrm{MTC}}_k) = \frac{L[\log(\widehat{\mathrm{MTC}}_k)]}{\sum_{k=1}^{n_{\mathrm{pred}}} L[\log(\widehat{\mathrm{MTC}}_k)]} \quad (15)$$

4. Solve Equation 13 for each $\log(\widehat{\mathrm{MTC}}_k)$.
5. Substitute the results from step 4 into Equation 15 to solve for $f''(\widehat{\mathrm{MTC}}_k)$, $k = 1, \ldots, 999$.
6. The result is the posterior PDF of MTC, it is also the posterior PDF of the sampled t values

$$f''_k = f''(t_{n-p_k}) = f''(\widehat{\mathrm{MTC}}_k), \qquad k = 1, \ldots, 999 \quad (16)$$

The SSWQS. Once we have calculated the posterior probabilities, we can solve for the posterior probability distribution on MWC at any given MTC. In particular we are interested in the solution at the tissue residue criterion (TRC).

The steps in calculating the SSWQS are

7. Rearrange Equation 7 to solve for log(MWC)

$$\log(\widehat{\mathrm{MWC}}) = \frac{\log(\mathrm{MTC}) - b - s\cdot\mathrm{T}_{n-p}}{m} + \tau \quad (17)$$

8. Substitute Equation 10 into Equation 17 and solve at MTC = TRC for each sampled t value

$$\log(\widehat{\mathrm{MWC}}_k) = \frac{\{\log(\mathrm{TRC}) - b - [a_{0t} + a_{1t}\cdot\log(\mathrm{TRC}) + a_{2t}\cdot\log(\mathrm{TRC})^2]t_{n-p_k}\}}{m} + \tau \quad (18)$$

9. Sort the input–output vector by $\log(\widehat{\mathrm{MTC}}_k)$ in ascending order

$$[t_{n-p_k}, \log(\widehat{\mathrm{MWC}}_k), f''_k]_1$$
$$[t_{n-p_k}, \log(\widehat{\mathrm{MWC}}_k), f''_k]_2$$
$$\vdots$$
$$[t_{n-p_k}, \log(\widehat{\mathrm{MWC}}_k), f''_k]_l$$
$$\vdots$$
$$[t_{n-p_k}, \log(\widehat{\mathrm{MWC}}_k), f''_k]_{999} \quad (19)$$

where l is the rank statistic for the elements of the series given above.

10. Compute the cumulative distribution function (f''_k) for the water concentration at MTC = TRC

$$(\mathrm{F}''_k)_l = \sum_{\lambda=1}^{l} (f''_k)_\lambda \quad (20)$$

11. Identify the maximum value of l such with cumulative probability less than or equal to the prescribed confidence level (CL), where CL is the desired level of confidence that the TRC will not be exceeded at the site, once the SSWQS is achieved

$$l^* = \max(l) \,|\, [(\mathrm{F}''_k)_l \le \mathrm{CL}] \quad (21)$$

12. The SSWQS is the water concentration corresponding to l^*

$$\text{SSWQS} = 10^{\log(\widehat{\text{MWC}}_i)_*} \quad (22)$$

This is the water concentration that, given the existing information about bioaccumulation at the specific site and at other, generically similar sites would provide the desired level of confidence of not exceeding the TRC.

DISCUSSION

The methodology just described provides a means to derive a SSWQS protective of tissue residue-based endpoints. The application of the method to Se is provided in a companion paper [13]. The ability to calculate a SSWQS is essential if TRCs are to be useful, because water, not tissue, is the medium that can be controlled to reduce exposure to a bioaccumulative substance. In principle, the methodology could also be used to establish site-specific sediment-quality standards, although we have not yet explored this possibility.

Our methodology is subject to the same general caveats as would apply to any other modeling technique. Even with a sound technique, the results are only as good as the model and data it uses. Several issues must be considered when adopting this type of approach. First, the methodology currently allows the user discretion in developing an appropriate multisite probabilistic regression model. We would expect that if the technique were adopted for setting tissue residue–based WQSs, the regression modeling procedure would be defined as part of the methodology. Until then, the regression modeling requires case-by-case peer review.

Second, we have not provided data quality objectives for the multisite model, instead leaving it to the user and scientific peer review to determine whether the available data are sufficient to develop a multisite model that captures the range of possible MWC–MTC relationships at all or some defined subset of sites characteristic of the one being evaluated. If the technique were adopted for setting tissue residue–based SSWQS, these too should be defined as part of the methodology.

Third, we have not developed formal data quality objectives for the site-specific water and tissue sampling, stating only that the sampling design must be sufficient to justify specific distributional assumptions about the sample MWC and MTC. Again, if the technique were adopted for setting tissue residue–based SSWQSs, these should be defined as part of the methodology.

Finally, the methodology is somewhat computationally intensive, but with modern spreadsheet programs and personal computers, computational intensity is not a limiting factor. If used with proper consideration of the three caveats provided above, the method is reproducible and statistically rigorous, as well as easily implemented. In our companion paper [13], we show how the results of the analysis can be summarized in a simple lookup figure, obviating the need to rerun the model each time one wants to determine a SSWQS for a particular chemical. The ease of use of lookup figures is a strong practical advantage of the methodology as a regulatory tool.

Acknowledgement—We gratefully acknowledge Kennecott Utah Copper and Rio Tinto for funding this study and Debbie Fetherston for assistance in manuscript preparation.

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