SETTING SITE-SPECIFIC WATER-QUALITY STANDARDS BY USING TISSUE RESIDUE THRESHOLDS AND BIOACCUMULATION DATA. PART 2. CALCULATING SITE-SPECIFIC SELENIUM WATER-QUALITY STANDARDS FOR PROTECTING FISH AND BIRDS

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Abstract—In a companion paper, a method for deriving tissue residue–based site-specific water-quality standards (SSWQSs) was described. In this paper, the methodology is applied to selenium (Se) as an example. Models were developed to describe Se bioaccumulation in aquatic-dependent bird eggs and whole fish. A simple log-linear model best described Se accumulation in bird eggs ($r^2 = 0.50$). For fish, separate hockey stick regressions were developed for lentic ($r^2 = 0.65$) and lotic environments ($r^2 = 0.37$). The low $r^2$ value for the lotic fish model precludes its reliable use at this time. Corresponding tissue residue criteria (i.e., tissue thresholds) for bird eggs and whole fish also were identified and example model predictions were made. The models were able to predict SSWQSs over a wide range of water–tissue combinations that might be encountered in the environment. The models also were shown to be sensitive to variability in measured tissue residues with relatively small changes in variability (as characterized by the standard error) resulting in relatively large differences in SSWQSs.

Keywords—Selenium  Site-specific water-quality standards  Bioaccumulation

INTRODUCTION

An alternative to the traditional ambient water-quality criterion (AWQC) is to establish a tissue residue criterion (TRC). The U.S. Environmental Protection Agency has already adopted a mercury TRC [1] and has recently proposed one for selenium (Se) [2]. In general, setting a AWQC protective of tissue residue–based endpoints poses problems because bioaccumulation is site dependent. Bioaccumulation is influenced by site-specific water and sediment chemistry; site-to-site variations in trophic relationships; and site-to-site differences in co-occurrence of habitat, stressor, and receptor [3,4]. Metal bioaccumulation also is concentration dependent because of several factors, including essentiality, active regulation of body burdens, and saturable uptake kinetics [5], further complicating use and interpretation of TRCs.

As a result, a significant issue with TRCs is that although they can determine whether water quality is impaired, the degree of water-quality improvement needed to eliminate the impairment is not readily estimated (i.e., the waterborne concentration needed to achieve compliance with the TRC). A way to solve this problem was proposed in a companion paper [6]. We presented a method for deriving site-specific water-quality standards (SSWQSs) that are designed to ensure, with a desired level of confidence, that tissue residue concentrations will not exceed a TRC contingent on model assumptions.

In this paper, the methodology is applied to Se. Selenium provides a good example because considerable research has gone into development of a TRC and site-specific variability in Se bioaccumulation has been extensively demonstrated. For example, Adams et al. [3] examined site-to-site variability in the waterborne Se concentrations that result in an egg Se concentration of 20 mg/kg dry weight in aquatic-dependent birds. The waterborne Se concentration associated with this TRC was 4 µg/L for the 10th percentile site and 29 µg/L for the median site. In an analogous study on fish, Adams et al. [4] found that the waterborne Se concentration associated with whole-body fish tissue concentration spanned an order of magnitude. This paper provides an example of how the methodology described by Toll et al. [6] can be used to address this variability.

The following considers how a tissue-based SSWQS for fish or birds may be implemented from a regulatory perspective. It is predicated on exceedence of a trigger concentration in the water column. Using the current chronic AWQC of 5 µg/L and the draft fish tissue criterion of 7.9 mg/kg dry weight as an example, there are three general scenarios. First, assume the site water Se is less than 5 µg/L. The discharger already meets the AWQC and no site-specific evaluation is necessary. Second, assume the water Se is greater than 5 µg/L and the mean fish Se concentration at the site is less than 7.9 mg/kg. Under this scenario, the discharger did not meet the generic AWQC, but examination of site-specific fish Se data demonstrated compliance with the tissue-based criterion. Finally, under the third scenario, a site exceeds the AWQC of 5 µg/L and site-specific fish Se data exceed the draft criterion of 7.9 mg/kg. Under this scenario, the discharger would be required to reduce Se concentrations in its discharge such that fish Se would decline to <7.9 mg/kg. The following methodology demonstrates an approach for estimating the amount by which water Se must be reduced for fish Se to fall below 7.9 mg/kg.
METHODS

A detailed discussion of the statistical methodology for deriving SSWQSs is described in the companion to this paper [6]. We briefly summarize the approach here followed by the specific methods used for the Se case study.

Overview of modeling approach

The approach is comprised of three main components. The first component is a prior distribution model based on colocated water and tissue residue concentration data from sites that are generically similar to the site in question. This prior distribution model is analogous to a generic data set that might be used to derive a national AWQC. Prediction intervals on this model provide an estimate of the site-to-site variability in the mean tissue concentrations (MTCs) at a given water concentration, or conversely, of the site-to-site variability in the mean water concentration (MWC) at a given MTC. Predictions based on the prior distribution are termed prior predictions.

The second component of the approach is a likelihood function. The likelihood function used in this approach is the distribution on the average of a representative sample of tissue residue concentrations from the site in question. The likelihood function answers the question, what are the chances of obtaining this sample average if a particular prior prediction of MTC is correct?

The third component of the approach uses Bayesian Monte Carlo analysis to answer the question of how new tissue residue data affect the probabilities on prior predictions of MTC. Bayesian Monte Carlo analysis compares the uncertain prior predictions of the generic model to the site-specific data, and measures the degree of similarity between the prior predictions and the measured values for the site being evaluated. It increases the probabilities on predictions that are more consistent with observations, and reduces the probabilities on predictions that are less consistent with observations. The result is the posterior distribution that can be used to predict SSWQSs [6].

The remainder of this paper discusses a case study for Se where a SSWQS protective of both fish and aquatic-dependent birds is derived. Before describing the site-specific data, we first discuss the generic bioaccumulation models and TRCs derived for Se.

Generic Se bioaccumulation models for fish and birds

The first step in this approach is to develop generic bioaccumulation models (i.e., prior distributions) based on data from sites generically similar to the one being evaluated. Adams et al. [3] previously described the methods used to build a statistical bioaccumulation model describing the relationship between waterborne Se and egg Se for aquatic-dependent birds. The data set was assembled from 15 study sites in the western United States, most of which were evaluated under the National Irrigation Water Quality Program (Denver, CO, USA). These sites were primarily lentic environments into which selenate was the main form of Se released. The same model is used in this study to derive SSWQSs protective of aquatic-dependent birds (Fig. 1).

Because a similar bioaccumulation model has not been developed for fish, monitoring data were assimilated from many of the same sites used to construct the bird model, plus additional data from sites in the western United States that were identified in literature searches (Table 1). Similar to the bird model, selenate was the primary form of Se released to the environment at all the sites evaluated. However, unlike the bird model, the fish monitoring data came from a mix of lentic and lotic environments.

Initially, we considered developing a fish model based on the relationship between waterborne Se and Se accumulated in fish ovary. From a toxicological perspective, this would be ideal because the ovary is the site of toxic action [7–9]. However, a relatively limited amount of data on Se concentrations in fish ovaries is available. Further, from a regulatory implementation perspective, sampling of ovaries is limited to certain times of the year and is impractical for small fish species. The U.S. Environmental Protection Agency chose to develop a
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Given this, we proceeded with developing a model based on whole-body fish Se for similar reasons [2]. Similar to the methods described in Adams et al. [3], paired waterborne Se and whole-body fish Se data were compiled from the various study sites. Data were carefully screened to ensure they were both spatially and temporally colocated. Initial model fitting of log-transformed data indicated a relatively poor relationship between waterborne and whole fish Se ($r^2 = 0.32$). Inspection of the data suggested that Se bioaccumulation might be different in lentic versus lotic systems, consistent with previous studies [10].

Mechanistically, this makes sense, particularly for systems where Se is introduced as selenate and conversion to more bioavailable forms is limited. Selenate is relatively mobile, with low adsorption affinities to suspended solids and sediment [11–13]. Hence, in highly oxic systems (i.e., lotic systems), selenate will not be reduced to forms that more readily partition to sediments where they can be biotransformed to organoselenium compounds that rapidly accumulate up the food chain. Based on this environmental chemistry, oxic systems with selenate contamination would be expected to experience less bioaccumulation than lentic systems and probably lotic systems with selenite contamination.

Given the above, the data set was split into two groups comprising that collected from lentic and lotic systems. Although the model fit was improved for lentic data ($r^2 = 0.64$), it was still poor for lotic data ($r^2 = 0.26$). Visual inspection of the lentic and lotic data sets indicated that Se concentrations in fish remained relatively constant over a range of low waterborne Se concentrations before increasing in an exposure-dependent manner. This was particularly true for lotic systems. Mechanistically, this is attributable to two factors. First, applicable to both lentic and lotic systems, Se is an essential element [14–16]. Hence, it will tend to be actively regulated over a range of exposure concentrations representing background to perhaps slightly contaminated conditions resulting in no net accumulation over this exposure range. This has been extensively demonstrated both in the laboratory and field for other essential metals [17–19], and so it is not surprising that the same is observed for Se. Second, as mentioned above, for selenate discharges to lotic systems, accumulation is expected to be insignificant until relatively high levels of contamination because the sediment–detrital pathway for transformation to organoselenium compounds is significantly less pronounced relative to lentic systems.

To account for these considerations, we used hockey stick regressions to describe the threshold effect observed in the bioaccumulation data [20–22]. This resulted in a lentic model with a similar fit ($r^2 = 0.65$) as previously realized, and a lotic model with a slightly better fit, but still with a low $r^2 = 0.37$. As would be expected, the combined effects of selenate mobility and Se essentiality resulted in the range of waterborne Se over which no significant accumulation in biota occurs to be greater in lotic systems when compared to lentic systems (Figs. 2 and 3). However, the poor fit of the lotic model precludes its use at this time for regulatory purposes. As additional data become available, it may be possible to develop a better

![Fig. 2. Selenium bioaccumulation model for fish in lentic systems.](image_url)
model for characterizing selenate bioaccumulation in lotic systems.

Results from this analysis prompted us to reanalyze the bird bioaccumulation model by using hockey stick regressions as well. Because these data are almost exclusively from lentic environments, the blade of the regression was expected to be relatively small, similar to that observed for the fish bioaccumulation model. However, attempts to develop a hockey stick model with the bird data indicated that tau (τ, the model inflection point) was below the lowest available data point. Upon reflection, this is also consistent with Se toxicology. Unlike the fish models that are based on whole-body Se, the bird model is based on egg Se concentrations and Se is preferentially accumulated in this tissue [23, 24]. Hence, active regulation of Se, which is likely being undertaken on a whole-body basis, does not occur at the egg level and so a hockey stick relationship is not observed for the bird model. As a result, we used the simple linear model for aquatic-dependent birds in the remainder of this paper.

The multisite model (prior distribution)

The models for Se bioaccumulation in fish and aquatic-dependent birds are statistical models describing the relationship between colocated water and whole-body tissue concentrations in lentic and lotic systems. The scatter in the data (Figs. 1 to 3) reflects site-to-site variability in the MWC–MTC relationship. The parameters for each model are presented in Table 2. These generic multisite models provide the prior distributions used in deriving the SSWQSs as described in the companion to this paper [6]. In their general form, the models can be described by

\[
\log(MWC) = \begin{cases} 
    b + s \cdot T_{n-p} & \log(MWC) \leq \tau \\
    b + m \cdot \log(MWC) - \tau + s \cdot T_{n-p} & \log(MWC) > \tau 
\end{cases}
\]

where \( m, b, \) and \( \tau \) 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 (\( p = 3 \)). Setting MTC equal to the TRC, Equation 1 can be rearranged to find the probability density function (PDF) for the mean water concentration that would give a mean tissue residue of TRC

\[
\log(MWC) = \frac{\log(MTC) - b - s \cdot T_{n-p}}{m} + \tau
\]

The regression coefficients \( b, m, \) and \( \tau \) are probabilistic, so the solution of Equation 2 is the probability distribution of MWC. Toll et al. [6] explain in detail how Bayesian Monte Carlo analysis is used to solve Equation 2 for the percentiles of the mean water concentration PDF. The SSWQS is simply the percentile of the MWC PDF corresponding to the desired level of confidence. For example, the 90th percentile gives 90% confidence that the TRC will not be exceeded.

Table 2. Regression coefficients for the fish and bird selenium bioaccumulation models presented in Figures 1 to 3. Tissue concentrations are predicted in mg/kg dry wt. Water concentration is in \( \mu g/L \). The terms \( a0w, a1w, a2w, a0t, a1t, \) and \( a2t \) are the coefficients of the standard error models presented in Equations 9 and 10 of the companion paper [6].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bird</th>
<th>Fish, lentic</th>
<th>Fish, lotic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope ( (m) )</td>
<td>0.561</td>
<td>0.761</td>
<td>2.067</td>
</tr>
<tr>
<td>Intercept ( (b) )</td>
<td>0.430</td>
<td>0.330</td>
<td>0.516</td>
</tr>
<tr>
<td>Inflection point ( (\tau) )</td>
<td>NA*</td>
<td>-0.276</td>
<td>1.406</td>
</tr>
<tr>
<td>( a0w )</td>
<td>0.350</td>
<td>0.306</td>
<td>1.261</td>
</tr>
<tr>
<td>( a1w )</td>
<td>0.008</td>
<td>0.008</td>
<td>1.097</td>
</tr>
<tr>
<td>( a2w )</td>
<td>0.004</td>
<td>0.006</td>
<td>0.314</td>
</tr>
<tr>
<td>( a0t )</td>
<td>0.367</td>
<td>0.314</td>
<td>0.413</td>
</tr>
<tr>
<td>( a1t )</td>
<td>0.042</td>
<td>0.021</td>
<td>0.179</td>
</tr>
<tr>
<td>( a2t )</td>
<td>0.021</td>
<td>0.010</td>
<td>0.074</td>
</tr>
<tr>
<td>( n )</td>
<td>70</td>
<td>104</td>
<td>155</td>
</tr>
</tbody>
</table>

*NA = not applicable.
Tissue residue criteria for fish and aquatic-dependent birds

In addition to the prior models, it is also necessary to develop or identify the appropriate TRC. For Se, there is considerable debate in the literature regarding appropriate TRCs for fish and aquatic-dependent birds. For fish, a number of different researchers have proposed whole-body thresholds. Lemly [25] reviewed available literature and recommended a threshold of 4 mg/kg dry weight, whereas DeForest et al. [8], in reviewing the same set of literature, recommended a threshold of 9 mg/kg dry weight for warm-water fish and 6 mg/kg for anadromous salmonids. Recently, the U.S. Environmental Protection Agency released a draft revision to the Se AWQC and derived a TRC of 7.9 mg/kg dry weight based on a study by Lemly [26] that evaluated the combined effects of Se exposure and low temperature on bluegills (Lepomis macrochirus). We selected this threshold as the most appropriate for evaluation of the methodology given the likelihood that it could be implemented in many parts of the country.

As with fish, a number of different TRCs for bird eggs have been published over the past decade. Skorupa [27] derived an egg Se threshold of 6 mg/kg dry weight based on a field data set relating egg Se to clutch viability in the black-necked stilt (Himantopus mexicanus). Fairbrother et al. [28,29] argued that this field data set was unreliable because of potential confounding factors such as other contaminants, weather, and predation. They advocated the use of laboratory data to control for these confounding factors and estimated an egg Se threshold of 16 mg/kg dry weight based on a data set pooled from a number of studies on mallards (Anas platyrhynchos). Ohlendorf [30] subsequently identified several studies not considered by Fairbrother et al. [28,29] and reanalyzed the updated data set to estimate a TRC of 13 mg/kg dry weight. Finally, Adams et al. [22] critically reviewed the field data set used by Skorupa [27] and the laboratory data set used by Ohlendorf [30] by using a variety of statistical models to estimate thresholds. They demonstrated that the field data set used by Skorupa [27] was highly variable and that an effect threshold such as the 10% effective concentration (EC10) could not be differentiated from background as a result of this variability. By using the same techniques to evaluate the laboratory data, they estimated TRCs ranging from 12 to 14 mg/kg dry weight depending on the statistical model used. Given the close agreement between the results of Ohlendorf [30] and Adams et al. [22], we chose a TRC of 13 mg/kg dry weight in bird eggs for use in our model.

Example model application

We performed several example applications of the model to provide characteristic outputs and highlight some key components of the model that strongly influence predicted SSWQSs. The model outputs simply describe the predicted SSWQSs for various water Se and tissue Se combinations by using the bird (Fig. 4) and lentic fish models (Fig. 5). For representative purposes, these model runs assumed tissue concentrations ranging from the tissue threshold (13 mg/kg dry wt for birds and 7.9 mg/kg dry wt for fish) to 60 mg/kg dry weight (a standard error of 1 mg/kg dry wt assumed for each tissue concentration) and water Se concentrations ranging from 1 to 64 μg/L. If the variability in the tissue concentrations were to increase, the predicted SSWQSs would all be lowered. The greater the variability in the individual tissue concentrations, the wider the confidence interval and the lower the site-specific water Se concentration must be to ensure adequate confidence in not exceeding the TRC.

When using the lentic fish model as an example, SSWQS predictions were made over a range of water Se concentrations resulting in a fish tissue concentration of 10 mg/kg dry weight with standard errors for the mean fish tissue concentration ranging from 2.5 to 20 mg/kg dry weight (Fig. 6). Over the same relative range of standard errors, increasing variability in MTC has a larger effect on the SSWQS with increasing water Se concentrations. From a compliance perspective, however, even relatively small reductions in the standard error on the MTC, which could be achieved through collection of additional samples, may be important to a discharger. For example, if a site has an MTC of 10 mg/kg dry weight and the water Se concentration is 16 μg/L, the SSWQS with a standard error of 2.5 mg/kg dry weight is 8.3 μg/L versus 2.8 μg/L with a standard error of 15 mg/kg dry weight.

DISCUSSION

The methodology developed in the companion to this paper [6] and demonstrated in this paper with Se provides a con-
ceptually and statistically rigorous way to derive SSWQSs protective of tissue residue-based endpoints. The model can be run with readily available spreadsheet software. Example calculations using the model demonstrate that it is capable of calculating SSWQSs under a wide variety of scenarios with appropriate levels of conservatism built in for uncertain data.

We believe this type of approach for setting SSWQSs is very promising for substances where regulation is based on a TRC and the environmental fate and chemistry of the substance is too complex to readily model on a case-by-case basis. In this particular example, we were able to use the extensive bioaccumulation data already available for Se in aquatic environments to circumvent the need for a complete understanding of site-specific chemistry.

The major limitation of this type of approach is the reliability of the generic bioaccumulation models used in the calculations. Although we were able to develop reasonably reliable models for Se bioaccumulation in bird eggs and whole-body fish from lentic environments, we could not develop a reliable model for fish in lotic environments. We hypothesize this is largely due to data limitations and this highlights the need for considerable bioaccumulation data to be available across a range of exposure concentrations in order for generic bioaccumulation models (i.e., prior distribution models) to be developed. However, given that this approach will be used for substances that are being regulated on a TRC, relatively large amounts of bioaccumulation data will tend to be available. Additionally, with each SSWQS study conducted with this approach, more data will become available for use in the generic model for future assessments.

CONCLUSION

We have described a simple method for setting scientifically defensible, tissue residue-based SSWQSs. When compared to previous methods for setting SSWQSs, the method is somewhat computationally intensive. However, with modern spreadsheet programs and personal computers, computational intensity does not affect the methods ease of use.

If adopted for a particular situation such as Se in lentic systems, the model can be translated into user-friendly lookup tables or figures (such as Figs. 4 and 5) that make it very easy to calculate a SSWQS. Figures such as Figure 6 also can be produced to help users decide whether collecting more site-specific data is worthwhile, in the sense of reducing the margin of safety needed to ensure the protectiveness of the SSWQS. The Se case study demonstrates that the method works with the types of data sets one should expect to have available for substances that are regulated on a TRC and that it provides useful results. For example, we demonstrated how collecting more field data can significantly increase the SSWQS at a site by reducing the standard error in the mean tissue residue concentration. Reducing the standard error reduced the margin of safety needed to ensure the SSWQS was protective. If used with proper consideration of the caveats presented in this paper and the companion paper [6], the method is fully reproducible, statistically rigorous, easily implemented, and a cost-effective tool for setting protective SSWQSs for chemicals regulated by a TRC.

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