# SITE-SPECIFIC APPROACH FOR SETTING WATER QUALITY CRITERIA FOR SELENIUM: DIFFERENCES BETWEEN LOTIC AND LENTIC SYSTEMS

W.J. Adams, [1]
J.E. Toll, [2]
K.V. Brix, [2]
L.M. Tear, [2]
D.K. DeForest, [2]

[1] Kennecott Utah Copper
P.O. Box 6001
Magna, UT 84044
[2] Parametrix, Inc.
5808 Lake Washington Blvd. NE, Suite 200
Kirkland, WA

## ABSTRACT

Results of an in-depth review of the literature indicates there are significant differences in the bioaccumulation of selenium by fishes and invertebrates from lotic (flowing) and lentic (standing) water bodies and that selenate is much less bioaccumulative than selenite. Bioaccumulation in fish is a factor of 10 or more higher in lentic systems as compared to lotic systems. These differences are a function of selenium's site-specific biogeochemical cycling. Further, we observed considerable variation in bird accumulation of selenium from site to site. To account for differences in bioaccumulation potential of selenium we developed a residue-based Bayesian Monte Carlo model to derive site-specific selenium water quality criteria protective of fish and sensitive avian species.

The approach uses data from a given site of interest to calibrate a model based on data from several other similar sites. When evaluating a specific site, the range of water and tissue concentrations is typically limited. This makes it difficult to use site-specific data to identify a water concentration sufficiently low that tissue concentrations do not exceed the tissue-effect threshold. Data from several similar sites provide a broader range of water and tissue residue concentrations that allow for an appropriate statistical extrapolation of the data to the site of interest. The Bayesian Monte Carlo model accounts for the significant site-to-site variability that exists in the relationship between water selenium and the mean tissue residue. In practice, data from similar sites are pooled to define a set of possible water and mean tissue residue relationships. This set of possible relationships is then used with data from the site of interest to determine which relationships, from the set of possibilities, best fit the specific site. Once we have determined which set of possible relationships fit the specific site, we extrapolate from the observed water concentration to a water concentration that results in a tissue residue concentration less than or equal to a chronic effect threshold. This value becomes the chronic water quality criterion.

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## INTRODUCTION

Selenium contains properties that make it unique relative to other metals and metalloids. It occurs in both organic and inorganic forms which are differentially toxic and is an essential element for most organisms. The selenium forms present in aquatic systems are controlled by the biogeochemical cycling of selenium which is strongly influenced by site-specific environmental factors such as redox, pH, and biological productivity (Lemly and Smith, 1987; Bowie and Grieb, 1991; Porcella *et al.*, 1991).

Reduction of inorganic selenium species tends to immobilize selenium in an aquatic system, while other processes, such as oxidation and biotransformation tend to make selenium bioavailable to aquatic organisms. Biological mechanisms such as uptake of sediment selenium by rooted plants, benthic invertebrates, and detritus-eating invertebrates, can act to re-mobilize selenium into the aquatic food web. Accordingly, lentic systems tend to bioaccumulate selenium much more than lotic systems that have higher flushing rates and lower productivity (Lillebo *et al.*, 1988; Van Derveer and Canton, 1997). For example, Lillebo *et al.* (1988) demonstrated this by plotting bioaccumulation data for impounded and flowing waters; fish selenium residues were approximately six times greater in impounded waters than in flowing waters at a water selenium concentration of 10 µg/L.

Based on increased awareness of the ecotoxicological effects of selenium, a number of water quality monitoring programs have been implemented to evaluate potential selenium contamination at freshwater sites. In order to interpret the significance of the selenium concentrations measured under these programs, several authors have proposed selenium guidelines for various environmental compartments (e.g., Lemly, 1993a; Skorupa *et al.*, 1996). Specifically, guidelines have been proposed for surface water, sediment and various tissues, including ovaries, whole body, diet, liver, eggs and testes based on the authors' reviews of published and unpublished literature.

These guidelines include recommended toxicity thresholds for abiotic (water, sediment) and biotic (various fish tissues and diet) compartments. Given the site-specific factors that influence selenium bioavailability, bioaccumulation, and toxicity in aquatic systems, we believe that the use of a single guideline value for selenium in surface waters is inappropriate. Different sites will require different selenium water concentrations to ensure that concentrations in tissues such as fish and bird ovaries do not exceed a toxic threshold. Site-to-site variability has been demonstrated for fish by Van Derveer and Canton (1997) and for birds by Adams *et al.* (1998). Van Derveer and Canton (1997) used a sediment-based bioaccumulation model to demonstrate that fish in a lotic system in Colorado were not at risk at water selenium concentrations of approximately 30 µg/L, three times higher than concentrations at which effects were observed in Belews Lake.

Adams *et al.* (1998) evaluated the differences in bioaccumulation in shorebirds (Figure 1). They used probabilistic regression models to assess water, food chain and bird egg residues from fifteen lentic sites in the western United States. Uncertainty analysis of the regression models provided a probability distribution of waterborne selenium concentrations associated with bird egg tissue residues. The 90th and 10th percentile water selenium concentrations associated with a selenium concentration of 20 mg/kg dw in bird eggs ranged from 6.8 to 318 µg/L. These studies support the concept of the need for site-specific water quality guidelines for selenium based on a bioaccumulation model and measurement of selenium concentrations in critical tissues. The Adams *et al.* model is represented in this paper (Figure 2) using a revised selenium concentration of 16 mg/kg dw in mallard duck eggs as a threshold for chronic effects, i.e., EC10 for duckling hatchability and survival (Fairbrother *et al.* 1999). The 90th and 10th percentile water selenium concentrations associated with a selenium concentration of 16 mg/kg dw in bird eggs ranges from 4.6 and 213 µg/L, respectively. These data indicate a large degree of variability in selenium concentrations that are potentially protective for sensitive bird species at different sites depending upon site-specific biogeochemistry, bioaccumulation and bird feeding behavior.

## SITE-SPECIFIC BIOACCUMULATION EVALUATION

The concept that site-specific differences in the biogeochemistry of selenium can significantly alter the potential for toxicological effects is best demonstrated by site-specific differences in bioaccumulation of selenium in sensitive species. We have previously examined this for birds (Adams *et al.*, 1998). To evaluate differences in selenium bioaccumulation in fish we evaluated published fish residue data for essentially the same sites evaluated for birds by Adams *et al.* (1998). We separated the data into lotic sites (flowing water; short hydraulic retention times, i.e., minutes to days) and lentic sites (standing water; long hydraulic retention times, i.e., weeks to years). The concept of lotic versus lentic is one that is used to typify extremes in biogeochemistry (oxygen content, redox, hydraulic retention time, carbon content) that is important in terms of controlling the formation of reduced selenium forms including organo-selenium compounds. In lotic environments, selenium in the water column is most often found in the form of selenate and migration to sediments is limited. In lentic environments, selenate is less prevalent, selenite is more common, and both forms are biologically and chemically reduced to elemental and organo-selenium forms. These reduced forms are prevalent in lentic sediments and form the basis for uptake by benthic invertebrates and subsequent food chain bioaccumulation.

The results of our bioaccumulation data analysis indicates that a clear and distinct difference between the patterns of bioaccumulation by fish in lotic and lentic environments (Figure 3). The data presented here are predominately for warm water fish species (e.g., centrarchids, cyprinids, and ictalurids). Selenium bioaccumulation factors for fish from lentic environments are typically a factor of 10 or more higher than those from comparable water concentrations in lotic environments. Additionally, these data indicate that bioaccumulation factors for fish and selenium are inversely related to exposure concentration. This is consistent with data reported for several other metals (Brix and Deforest, 2000). Recognition of this relationship provides insight into the variability that exists in reported bioaccumulation factors (BAFs) for selenium, i.e., highest BAFs occur at the lowest exposure levels.

Further analysis of the selenium fish residue data from lotic systems indicates that tissue selenium concentrations remain fairly constant across a range of water concentrations up to about 13 µg/L. In contrast, in lentic systems, selenium tissue levels begin to increase as selenium water concentrations increase above 1.0 µg/L. The hockey-stick regressions presented in Figures 4 and 5 demonstrate distinct differences in bioaccumulation between lotic and lentic systems. While the slopes of the upper parts of the regressions are similar, the inflection points are more than a factor of ten different. Recognizing that selenium is an essential element for fish, the lower part of each regression is thought to represent a range of concentrations across which fish can actively regulate selenium uptake. Recognition of these differences in bioaccumulation provides the basis for developing tools to assess site-specific bioaccumulation.

**SITE-SPECIFIC WATER QUALITY CRITERIA METHODOLOGY**

Bioaccumulation data leave little doubt that water selenium concentrations protective of aquatic life and wildlife differ from site to site as a function of selenium's site-specific biogeochemical cycling. Consequently, from a regulatory perspective to avoid over-regulation with associated costs, there is a need for developing a site-specific water quality criteria methodology for selenium. Existing methodologies for deriving site-specific water quality criteria such as water effect ratios are not applicable to selenium because unlike most contaminants, for selenium, the diet is the critical exposure pathway. Therefore, approaches for deriving site-specific water quality criteria must be based on the dietary exposure pathway to be appropriately protective for both birds and aquatic life. Given this need, identification and agreement on tissue toxicity thresholds for use in site-specific bioaccumulation models are essential. To that end, thresholds for birds and aquatic organisms was recently reviewed and summarized by DeForest *et al.* (1999) and Fairbrother *et al.* (1999).

Overall, Adams *et al.* (1998) found a high correlation between water and mean egg selenium concentrations that is strongly influenced by site-specific factors. In light of the observed site variability, the following was concluded: first, the numerical water quality criterion for selenium is best used as a screening tool. Second, when waterborne selenium approaches or exceeds the criterion, a site-specific assessment should be used to determine whether existing water concentrations pose risk, and if so, identify a safe selenium water concentration for the site.

The conclusions of Adams *et al.* (1998) led us to develop a methodology for developing site-specific water quality criteria using tissue residue concentration and effects threshold data. We have applied the methodology to selenium, but it is applicable to any constituent for which tissue residue-based endpoints are of concern. In general, setting water quality criteria protective of tissue residue-based endpoints for metals including selenium poses problems because the bioaccumulation factor (BAF) is not constant and is inversely related to the exposure concentration (Brix and DeForest, 2000). This must be taken into account in the model. Factors influencing BAF include: site-specific water and sediment chemistry, trophic relationships, and the degree of spatial and temporal co-occurrence of habitat, stressor and the endpoint of concern.

The statistical technique we use in our methodology is Bayesian Monte Carlo analysis (BMC). Monte Carlo methods are numerical techniques for generating a representative sample from a probability distribution function (PDF). BMC evolved from earlier procedures used to ensure that the PDF of a model's predictions was consistent with observed data. These earlier acceptance/rejection procedures involved deleting predictions that were inconsistent with observations (Hornberger and Spear 1980, Beck 1987, Woodruff *et al.* 1992). The difference between BMC and earlier procedures is that BMC is more statistically rigorous. BMC defines the acceptance/ rejection procedure using the axioms of probability theory, as expressed in Bayes' theorem (Bayes, 1763). Additional details on the site-specific methodology is reported by Toll *et al.* (1999). Only a brief synopsis of the method is presented here.

The model approach is one that uses a generic bioaccumulation model for fish or birds, such as that developed by Adams *et al.* (1998). The purpose of the generic model is to describe bioaccumulation as reported in the literature for a wide variety of sites. This model provides an a priori estimate of bioaccumulation potential for a given site in the absence of any site-specific data. The generic model's prediction interval (Figure 6) is based on data from all sites in the data set. It describes the range of possible site-specific relationships. The data set for the generic model can be updated as additional site data are obtained. Tissue residue data from a given site can then be compared to the model's estimated value. A determination is then made as to whether or not the site-specific bioaccumulation is greater or less than what would be predicted by the generic model. If the site specific-tissue residue, at a given water concentration is less than predicted by the generic model, then the model calculates a water quality criterion that is higher for the site. This becomes the site-specific concentration in water that is protective of a given tissue threshold concentration. Likewise, if the tissue residue at the site is greater than the generic model would predict, the site-specific water quality criterion would be revised downward to insure that the tissue threshold is not exceeded.

## CONCLUSIONS

(1) Literature data indicate that selenium bioaccumulation varies from site to site for both birds and aquatic organisms.

(2) There is considerable evidence supporting that the conclusion that bioaccumulation of selenium is less at lotic sites than at lentic site.

(3) There is a need for a methodology to derive site-specific water quality criteria for selenium.

(4) Using a residue-based Bayesian Monte Carlo model, site-specific selenium water quality criteria can be calculated for sensitive avian and aquatic species.

## REFERENCES

Adams, W.J., K.V. Brix, K.A. Cothern, L.M. Tear, R.D. Cardwell, A. Fairbrother, and J.E. Toll. 1998. Assessment of selenium food chain transfer and critical exposure factors for avian wildlife species: Need for site-specific data. Environmental Toxicology and Risk Assessment: Seventh Volume. ASTM STP 1333, E.E. Little, A.J. DeLonay, and B.M. Greenberg (Eds.). American Society of Testing and Materials, Philadelphia, PA.

Bayes, Rev. T. 1763. An essay toward solving a problem in the doctrine of chances. Philos. Trans. R. Soc. London 53: 370-418. Reprinted in Biometrika 45: 293-315 (1958).

Beck, M.B. 1987. Water Quality Modeling: A Review of the Analysis of Uncertainty. Water Res. Res. 23: 1393-1442.

Brix, K.V. and D. K. DeForest. 2000. Critical review of the use of bioconcentration factors for hazard classification of metals and metal compounds. Parametrix, Inc., 5808 Lake Washington Blvd. NE, Suite 200, Kirkland WA 98033.

Bowie, G. L. and T. M. Grieb, 1991. A model framework for assessing the effects of selenium in aquatic ecosystems. Water Air Soil Pollution 57-58, 13-22.

DeForest, D.K., K.V. Brix, and W.J. Adams. 1999. Critical review of proposed residue-based selenium toxicity thresholds for freshwater fish. Hum. Ecol. Risk Assess. 5(6): 1187-1228.

Fairbrother, A., K.V. Brix, J.E. Toll, S. McKay, and W.J. Adams. 1999. Egg selenium concentrations as predictors of avian toxicity. Hum. Ecol. Risk Assess. 5(6): 1229-1253.

Hornberger, G.M and R.C. Spear. 1980. Eutrophication in Peel Inlet II: Identification of Critical Uncertainties via Generalized Sensitivity Analysis. Water Resources 14: 43-49.

Lemly, A. D. 1993a. Guidelines for evaluating selenium data from aquatic monitoring and assessment studies. Environmental Monitoring Assessment 28, 83-100.

Lemly, A. D. and G. J. Smith, 1987. Aquatic cycling of selenium: implications for fish and wildlife. U.S. Dept. of the Interior, Fish and Wildlife Service. Leaflet 12. Washington, D.C. 10 pp.

Lillebo, H. P., S. Shaner, D. Carlson, N. Richard, and P. DuBowy. 1988. Regulation of agricultural drainage to the San Joaquin River. State Water Resources Control Board. SWRCB Order No. W.Q. 85-1.

Porcella, D. B., G. L. Bowie, J. G. Sanders, and G. A. Cutter. 1991. Assessing Se cycling and toxicity in aquatic ecosystems. Water Air Soil Pollution 57-58, 3-11.

Skorupa, J. P., S. P. Morman, and J. S. Sefchick-Edwards. 1996. Guidelines for interpreting selenium exposure of biota associated with nonmarine aquatic habitats. U.S. Fish and Wildlife Service National Irrigation Water Quality Program, Sacramento Field Office, March 1996. 74 pp.

Toll, J. E., L. M. Tear, K. V. Brix, D. K. DeForest, and W. J. Adams. 1999. A method for determining site-specific water quality criteria protective of tissue residue-based endpoints, Society of Toxicology and Chemistry presentation (manuscript in preparation).

Van Derveer, W. D. and S. P. Canton. 1997. Selenium sediment toxicity thresholds and derivation of water quality criteria for freshwater biota of western streams. Environmental Toxicology and Chemistry 16(6), 1260-1268.

Woodruff, T.J., F.Y. Bois, D. Auslander and R.C. Spear. 1992. Structure and Parameterization of Pharmacokinetic Models: Their Impact on Model Prediction. Risk Analysis 12: 189-210.

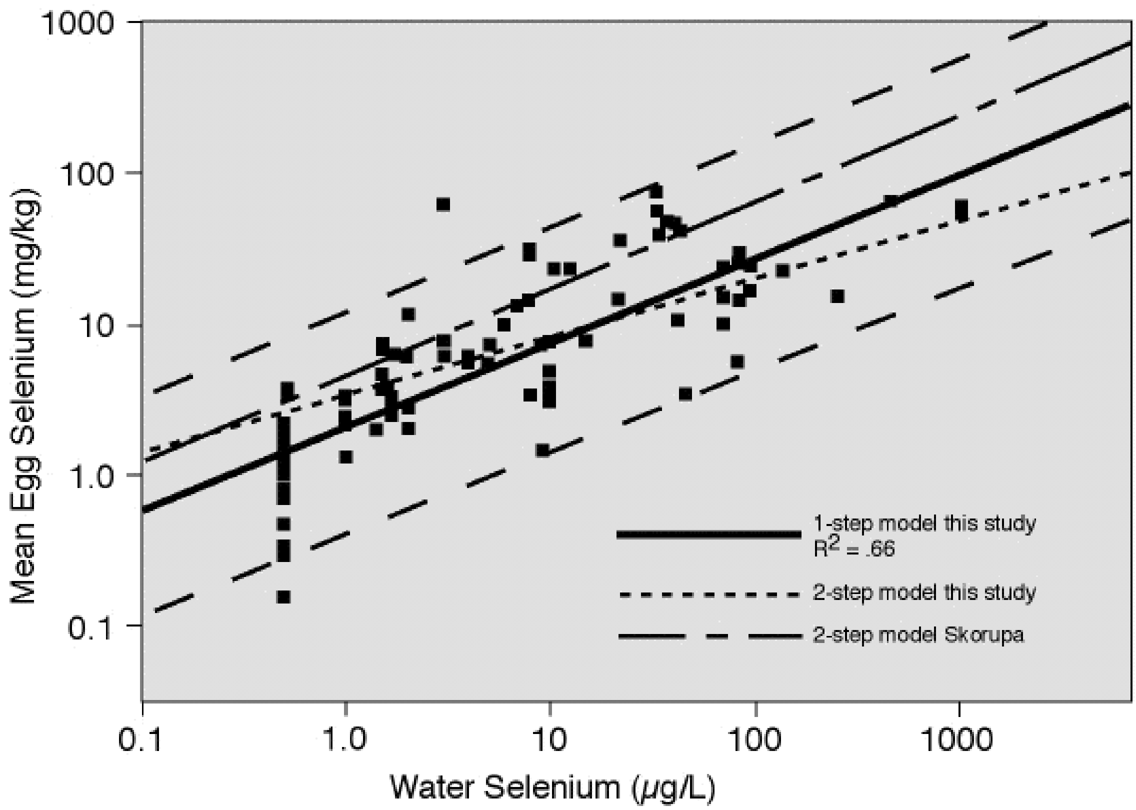


**Figure 1. Relationship between water-selenium and mean bird-egg-selenium.**

**Figure 2. Percentiles of Log water selenium distribution that would produce a mean avian egg selenium value of 16 mg/kg dw.**

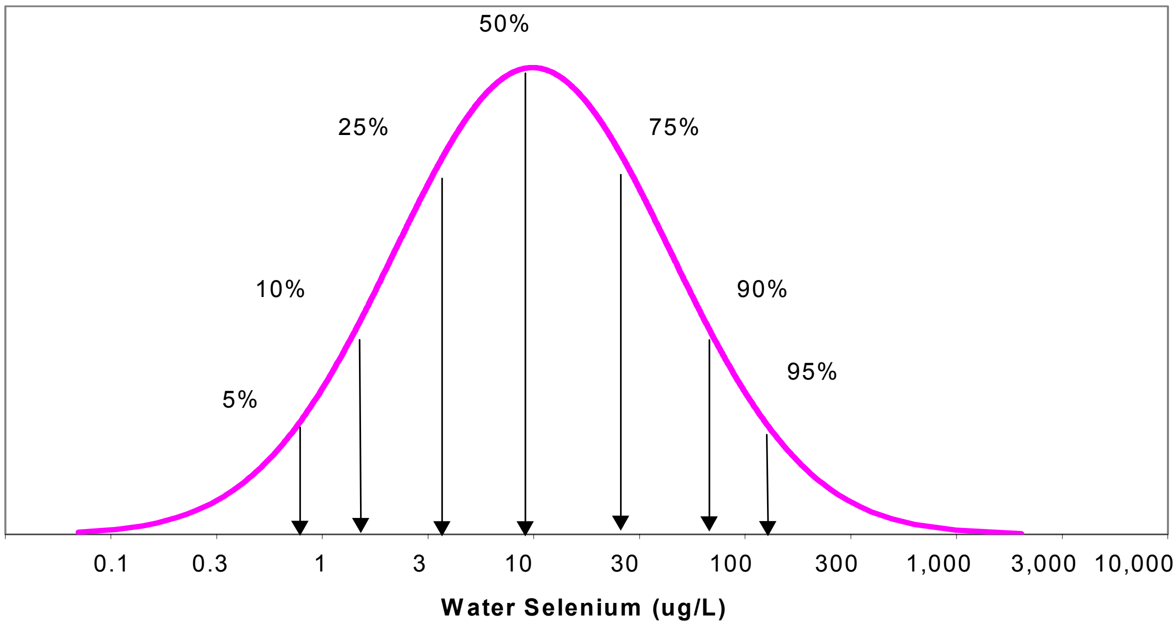


**Figure 3. Log bioaccumualtion factor (BAF) vs. water selenium (WS) for lotic and lentic aquatic systems**

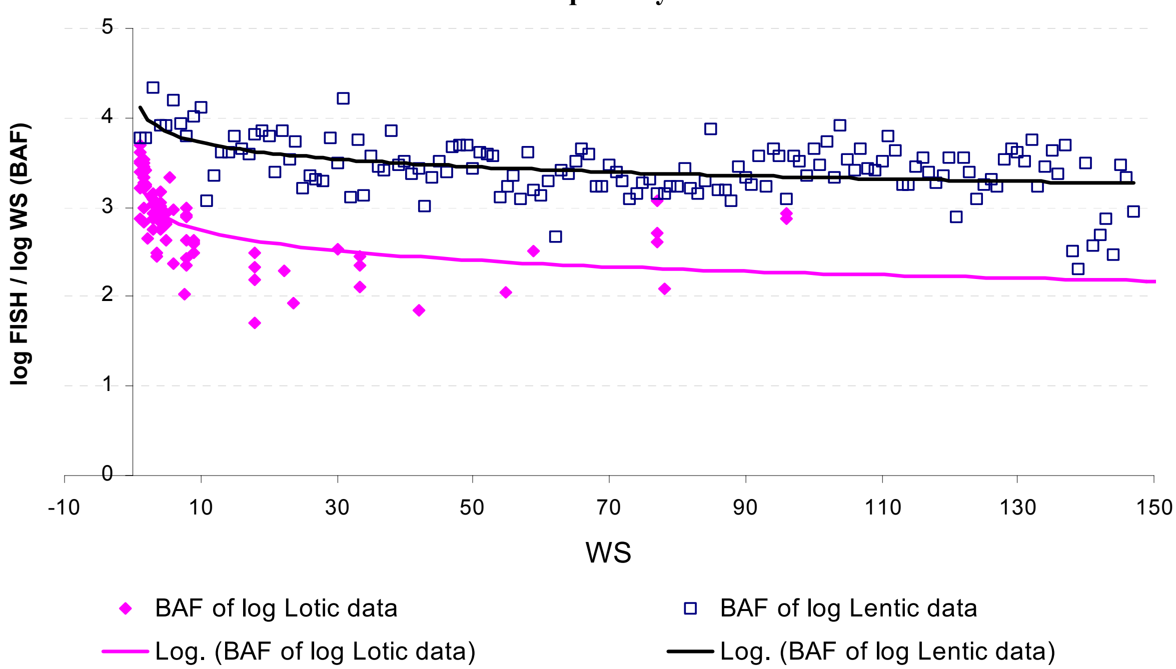

**Figure 4. Regression of water selenium versus whole fish selenium in lentic environments**

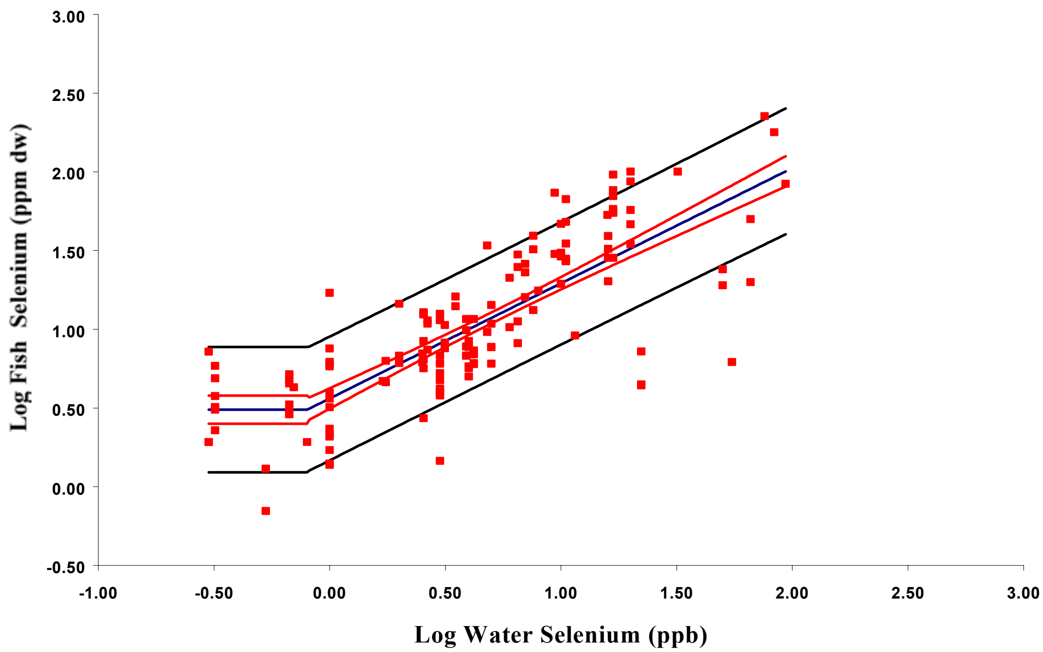


**Figure 5. Water selenium versus whole body fish selenium in lotic environments**