Solomon River Basin Selenium Assessment Project
Final Report

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by

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Introduction

Selenium (Se) is an essential trace nutrient but it can be toxic to aquatic life at excessive levels. Being a natural nonmetallic element, selenium can be found throughout the environment. Selenium has five oxidation states (-2, 0, 2, 4, 6) and the two major inorganic forms of selenium normally observed in aquatic environment are selenate ion (SeO_4^{2-}) and selenite ion (SeO_3^{2-}). High levels of selenium in waterbodies have mostly been related to irrigation of western soils that are naturally high in selenium, disposal of ash produced by coal-fired power plants, petroleum refinery effluents, and runoff or discharges from certain mining activities. Selenium is a bioaccumulative pollutant. Aquatic life is exposed to selenium primarily through food consumption rather than from direct exposure to selenium in the water column. Although selenium bioaccumulates, it does not significantly biomagnify. Unlike mercury or PCBs, selenium concentrations do not increase significantly in successive levels of a food chain.

The United States Environmental Protection Agency (USEPA) is currently revising the 1987 water-column based aquatic life criterion for selenium (5 μg/L) and has been soliciting scientific information pertaining to the criterion since December 2004. Because fish tissue samples provide a better indicator of the presence of ecologically harmful amounts of selenium in a particular waterbody, due to the bioaccumulative property of selenium, whole-body fish tissue based criterion [7.91 μg/g dry weight (dw)] has been proposed to replace the water column based criterion.

The USEPA has not established a threshold-effects level (TEL) or probable-effects level (PEL) for selenium. Nevertheless, according to Lemly and Smith (1987), concentrations equal to or greater than 4.0 mg/kg in sediment are a concern because there is a potential for bioaccumulation in fish and wildlife. Long-term exposure to high levels of selenium can be

toxic to humans, causing hair and fingernail loss and damage to kidney and liver tissue and the nervous and circulatory systems. The drinking water Maximum Contaminant Level (MCL) for selenium is 50 µg/L. The Section 303(d) of the Clean Water Act requires states to develop Total Maximum Daily Loads (TMDLs) for water-quality impaired waterbodies. The Kansas Department of Health and Environment (KDHE) developed TMDLs for impaired surface waters in each of the 12 major river basins in Kansas to meet the federal requirements. For the Solomon River Basin, the 2002 Section 303(d) list is carried over from the 1998 303(d) list and includes newly identified impairments. Excessive levels of fecal coliform bacteria, selenium, chloride, sulfate, low dissolved oxygen (DO), and biological impairment limit the use of the Solomon River Basin streams. Eutrophication, low DO, and high sulfate level are main causes of impairment for the lakes in the basin (www.kdheks.gov/tmdl/solomon.htm).

The Solomon River drains approximately 6,840 square miles of mainly agricultural land in north-central Kansas. Designated use for the Solomon River include: aquatic life support, primary contact recreation, domestic water supply, food procurement, ground water recharge, industrial water supply, irrigation, and livestock watering (KDHE 2004). North Fork Solomon River and South Fork Solomon River are two major tributaries of the Solomon River. There are three reservoirs in the Solomon River Basin: Kirwin Reservoir on the North Fork Solomon River, Webster Reservoir on the South Fork Solomon River, and Waconda Lake on the Solomon River. The Solomon River Basin is impaired from selenium because its watershed is rich in Cretaceous marine shales that are naturally high in selenium.

In 1998, the United States Geological Survey (USGS) and the Bureau of Reclamation studied chemical constituents in reservoir bottom sediment of the Solomon River Basin. Sediment core samples were collected from all three reservoirs for analyses of selenium and

other constituents. In Kirwin Reservoir, selenium concentrations in bottom-sediment core samples ranged from less than 0.3 to 2.2 mg/kg. In Webster Reservoir, selenium concentrations in bottom-sediment core samples ranged from 0.3 to 4.0 mg/kg. In Waconda Lake, selenium concentrations in samples from bottom-sediment cores ranged from less than 0.4 to 3.4 mg/kg. Overall, there were increasing trends of selenium concentration in bottom reservoir sediment of these three reservoirs (Christensen 1999).

Objectives

As mentioned earlier, although Kirwin Reservoir, Webster Reservoir, and Waconda Lake are currently not listed as selenium-impaired reservoirs, there were increasing trends of selenium concentration in bottom reservoir sediment of these three reservoirs (Christensen 1999). Thus, there is a need to continue monitoring selenium levels in the basin, especially in tributaries above Waconda Lake, most of which are selenium impaired. In addition, there have been limited data on selenium levels in fish tissue and sediment in the basin. Thus, the goal of this project is to supplement KDHE's continuing sampling efforts with additional selenium data necessary to address TMDLs and fish-tissue selenium data for the EPA draft aquatic life chronic criterion for selenium. The objectives are:

1. Assess selenium levels in the stream flow, bed sediment, and fish tissue at multiple stream sites in the Solomon River Basin above Waconda Lake;
2. Correlate selenium levels among the three media to determine the role of water-column selenium concentrations on impacting aquatic life; and
3. Characterize fish-tissue concentration within and among stream sites relative to the proposed EPA draft aquatic life chronic criterion for selenium.

Study Approach

The study area includes Osborne, Smith, Rooks, and Phillips counties in north-central Kansas. The selected six stream sites are the major tributaries to the three reservoirs in the Solomon River Basin and are at or near KDHE monitoring sites (see Table and Figure 1).

Field sampling was carried out in the spring, fall, and winter months of June and September 2007 and January 2008, respectively. During each of the field collections, DO, water temperature, specific conductance, pH, and turbidity were measured *in situ* using a Horiba U-10 Water Quality Checker. Concurrent with the field measurements, two one-liter grab water samples were collected and transported on ice in a cooler to Kansas Biological Survey (KBS) Ecotoxicology Laboratory for analyses of selenium, nutrients (total nitrogen and phosphorus, nitrate, nitrite, ammonia, and orthophosphate), and chlorophyll *a*. Fish tissue samples for selenium analysis were collected by seining, a backpack electroshocker, or boat electroshocker depending on stream flow and water depth. Three sediment samples were collected at each site using a sediment corer for composite sediment selenium analysis. A summary of water-quality parameters, analytical methods, detection limits, and sample holding time per Standard Methods (APHA *et al*. 2005) is listed in Appendix Table 1.

The seasonal and cross-media variability of selenium levels was evaluated and the relationship between selenium levels in aquatic life and the water-column selenium concentrations at the six locations were assessed. Statistical and graphical analyses were preformed using the NCSS statistical analysis software program (NCSS 2007) and Microsoft Excel 2003 edition (MSExcel). Data were examined for normality and possible outliers. Typically correlation matrices were produced, linear and non-linear regression analysis preformed, and *post hoc* relationships examined using Tukey-Kramer pair wise multiple

comparison tests (PWMCT). All tests were conducted with a proposed level of significance of 95 % confidence (P≥.05). Descriptive statistics were generated for general water chemistry parameters and selenium concentrations in sediments, water column, and fish tissue samples. General analysis for mean concentrations of selenium in the three media were performed in MSExcel.

Table 1. Study sites in the Solomon River Basin in north-central Kansas.

Site ID	Stream Name	Latitude	Longitude	Stream Order
14	Lower North Fork Solomon River above Waconda Lake, at Portis, KS	39.55428	-98.69211	6
543	Lower South Fork Solomon River above Waconda Lake, at Osborne, KS	39.42758	-98.65746	5
544	Oak Creek above Waconda Lake, near Cawker City, KS	39.53817	-98.47646	4
545	Bow Creek above Kirwin Reservoir, near Stockton, KS	39.55349	-99.32303	4
546	Upper North Fork Solomon River above Kirwin Reservoir, at Glade, KS	39.67353	-99.30924	5
547	Upper South Fork Solomon River above Webster Reservoir, near Damar, KS	39.37388	-99.58515	5

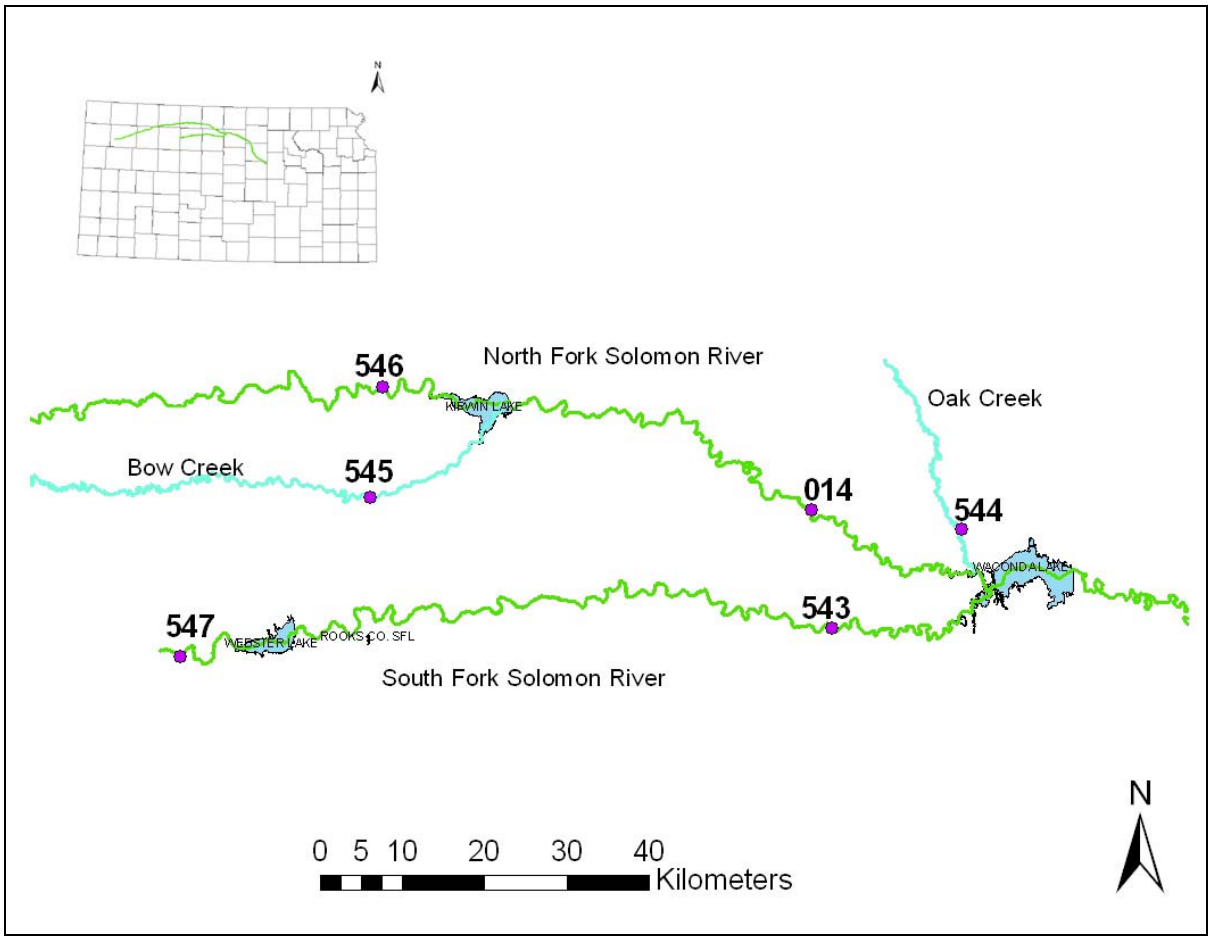

Figure 1. Kansas Department of Health and Environment water quality monitoring sites within the Solomon River Basin.

Results

Water and sediment samples were collected for 15 out of 18 possible sampling events among the six sites surveyed (Table 2). Water column and sediment selenium concentrations were obtained for all sites and most seasons, except those where streambeds were dry. Dissolved selenium concentrations in the aqueous phase from 10 of the 15 sampling events were not detected (MDL = 2 µg/L). Sites having detectable dissolved selenium concentrations in the water column, were North Fork of Solomon River near Glade (site # 546), Old Creek near Cawker City (site # 544), and North Fork of Solomon River at Portis (site # 14); detectable concentrations were 2.5, 2.7,

and 4.7 µg/L, respectively. One-way ANOVA results for both season dissolved concentrations (µg/L) and sediment mass fractions (mg/kg-dw) were not significantly different among seasons or sites. Though fish samples were not collected at Site 544 there were measurable amounts of sediment selenium in the spring and fall seasons (0.05 and 0.24 mg/kg-dw respectively) which were included in statistical analysis.

Table 2. Selenium concentration values for water column, sediment and mean fish tissue concentrations (and standard error) observed by season for KDHE water quality monitoring sites in the Solomon River Basin (dw=dry weight).

KDHE Site Code	Season	Sampling Date	Selenium			Remarks
			Water (µg/L)	Sediment (mg/kg dw)	Fish tissue (µg/g dw)	
14	fall	09/23/2007	<2	0.09	2.91 (±3.38)	
14	winter	01/15/2008	<2	0.04	-	Fish not collected
14	spring	06/04/2008	4.7	0.33	-	Fish not collected
543	fall	09/24/2007	<2	0.19	2.20 (±1.91)	
543	spring	06/05/2008	<2	0.13	1.86 (±1.53)	Water level ~ 1 to 2 ft higher than normal.
543	winter	01/15/2008	<2	0.07	0.91 (±0.32)	
544	winter	01/15/2008	<2	0.05	-	Fish not collected
544	spring	06/05/2008	2.7	0.24	-	Fish not collected
545	fall	09/23/2007	<2	0.11	3.88 (±3.48)	
545	spring	06/04/2008	<2	0.25	2.38 (±2.00)	Water level ~1 to 2 ft higher than normal.
545	winter	01/14/2008	<2	0.16	1.91 (±1.40)	
546	spring	06/04/2008	2.5	0.05	1.65 (±1.00)	This site was dry except on this date, about 2 to 3 ft deep.
547	fall	09/23/2007	<2	0.22	3.49 (±2.80)	
547	spring	06/04/2008	<2	0.2	2.77 (±1.64)	Water level ~ 1 to 2 ft higher than normal.
547	winter	01/14/2008	<2	0.15	7.89 (±4.54)	

When sediment selenium concentrations where evaluated by site alone in a one-way ANOVA, concentrations were found to be significantly different ($p < 0.0001$) between all sites except 543, 545. Site 547 had the highest mean sediment selenium concentration (0.19 mg/kg-dw) among all sites (Figure 2). Selenium sediment concentrations were strongly correlated with pH ($p < 0.0001$, $R^2 = 0.43$) and slightly related to specific conductance ($p < 0.0001$, $R^2 = 0.13$).

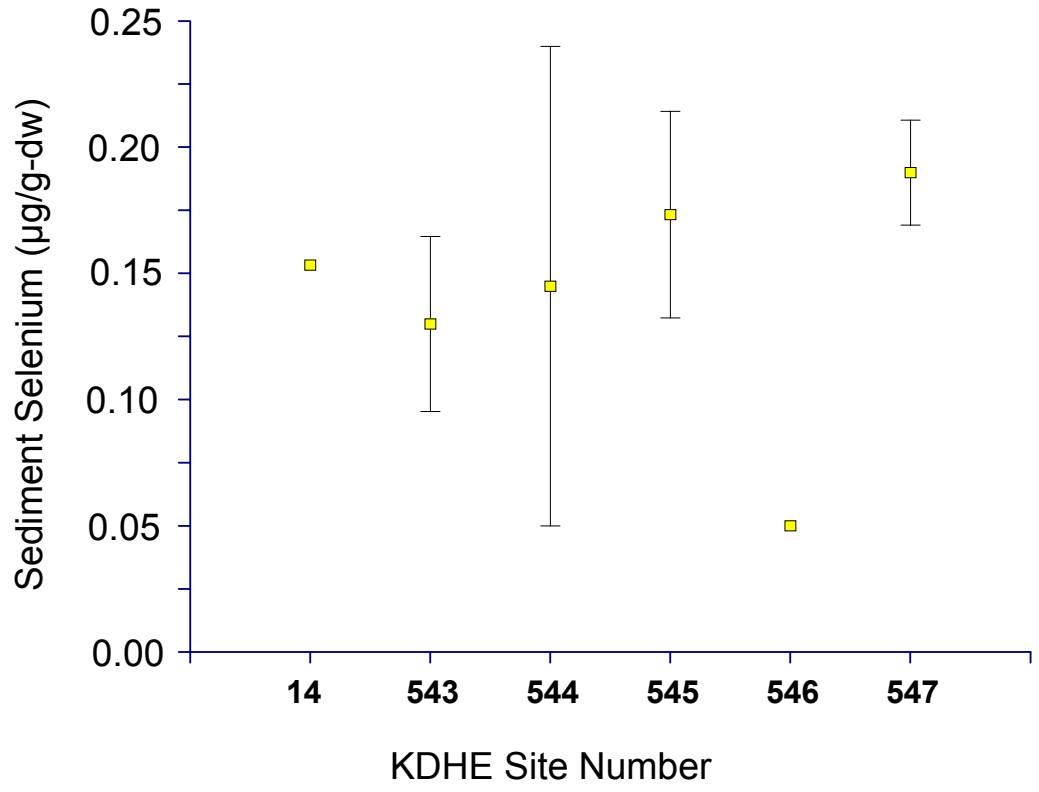

Figure 2. Error bar plots of mean sediment selenium concentrations by site. Sites 14 and 546 are represented by only one value.

Two-way GLM ANOVA analysis of fish tissue samples by site and season found that there remained significant differences in mean tissue concentrations among sites ($P = 0.00$) but not among seasons. A significant interaction was found between site and season ($p = 0.00$)

despite the lack of a seasonal effect. However, the presence of a significant interaction term indicates that some caution must be exercised in interpreting the presence of a site effect. Nevertheless, results from Tukey-Kramer Pair-wise, Multiple Comparison Test (see Table 3)suggests the occurrence of four primary groups: two high body burden groups (Sites 547 and 14 group and Sites 547, 14, 545, 546 group), and two low body burden groups (Site 543 and Sites 545, 546, 543 group).

Table 3. Tukey-Kramer Multiple-Comparison Test: Response: Fish tissue samples Se µg/g, Alpha=0.050 Error Term=S(AB) 2-way ANOVA. Term A: Site, DF=305 MSE=8.547029 Critical Value=3.8808.

Group	Count	Mean	Different from groups
543	72	1.66	14, 547
546	15	2.00	547
545	91	2.72	547
14	43	3.32	543
547	99	4.72	543, 546, 545

One-way ANOVA of mean fish tissue concentration of selenium (µg/g-dw) for the sites by season revealed that site 547 was significantly different (P = 0.00) from both 543 and 545 during the winter season and that 543 and 545 were not statistically different from one another (Table 4). No statistically significant differences in mean fish tissue concentrations were found among sites 543, 545, 546, and 547 for the spring sampling season (P = 0.24) and sites 14, 543, 545, 547 in the fall (P = 0.07).

Table 4. Tukey-Kramer Multiple-Comparison Test Response: Se µg/g-dw, Term A: KDHE Site Code Alpha=0.050 Error Term=S(A) DF=68 MSE=13.11117 Critical Value=3.3886.

Group	Count	Mean	Different From Groups
543	4	0.91	547
545	25	1.91	547
547	42	7.89	543, 545

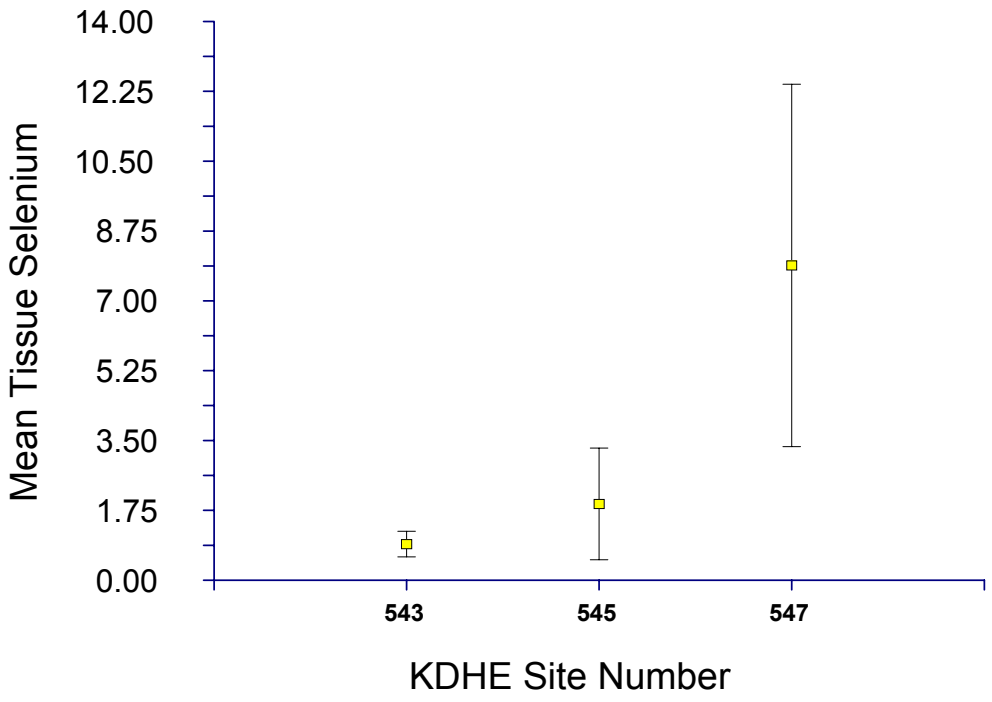

Figure 3. Mean Selenium concentrations (µg/g dw) and standard deviations for the winter season samples.

Significant differences in mean tissue concentrations existed among the 16 fish species collected (P=0.00, DF 315) when analyzed with GLM ANOVA. The bullhead minnow had the highest mean value (9.04 µg/g-dw) for any one fish species based on all bullhead minnows specimens collected in this study. There were 40 specimens that exceeded state recommended fish tissue concentration benchmark value of 7.91 µg/g dw. These occurred at all sites but 546 and in fall and winter seasons only. twenty eight (86 %) of these occurrences were winter samples. Only four occurrences of exceedance were observed at site 14 and one at site 543 also during the fall sampling season. Out of eight species represented, four species commonly associated with high selenium tissue concentrations: *Pimephales vigilax* (bullhead minnow), *Campostoma anomalum* (central stoneroller), *Etheostoma spectabile* (orangethroat darter), and *Gambusia affinis* (western mosquitofish). Most exceedances were at site 547 (28 occurrences, 70

%), with 24 of those occurring in the winter season. Of these 24 exceedances, one of them occurred in the *Motropis stramineus (*sand shiner). Four exceedances occurred at site 547 during the fall in the western mosquitofish (three counts) and the *Semotilus atromaculatus* (creek chub). The bullhead minnow, central stoneroller, and the orangethroat darter were the common species having high tissue concentrations of selenium at site 547. Site 545 had only seven occurrences in the fall season. Of the seven occurrences at Site 545, six occurred in the orangethroat darter samples and one in *Ictalurus punctatus* (channel catfish) tissue sample. 24 of the total 71 winter samples (34 %) exceeded the EPA recommended limit of 7.91 µg/g-dw. Evaluation of mean values for fish tissue selenium (µg/g-dw) among species by site (not accounting for season) revealed that four species exceeded the EPA recommended levels of 7.91 µg/g-dw (Table 5). Analysis of mean tissue concentrations among species by site and season found the central stoneroller to be among this group (Table 6). All exceedances occurred in the winter and fall seasons and comprised only 12 % of the total samples from all seasons.

Table 5. Mean, median, percentile, and geometric mean values for fish tissue selenium (µg/g-dw) by site among fish species whose mean values exceeded EPA recommended limit of 7.91 µg/g-dw.

Site ID	Fish Species	Count	ArithMean	StdDev	StErr	Min	Max	Median	25th Ptile	75th Ptile	Geo Mean
14	western mosquitofish	7	8.40	4.02	1.52	2.81	16.20	7.83	7.00	9.22	7.56
547	sand shiner	2	8.78	2.84	2.01	6.77	10.78	8.78	6.77	10.78	8.55
547	orangethroat darter	4	10.62	4.66	2.33	5.50	16.80	10.08	6.57	15.19	9.84
547	bullhead minnow	11	11.18	2.36	0.71	8.05	14.54	10.22	9.32	13.67	10.96

Table 6. Mean, median, percentile, and geometric mean values for fish tissue selenium (µg/g-dw) by site and season among fish species whose mean values the exceeded EPA recommended limit of 7.91 µg/g-dw.

+Site ID	Season	Fish Species	Count	Arith Mean	Std Dev	StErr	Min	Max	Median	25th Ptile	75th Ptile	Geo Mean
547	winter	orangethroat darter	3	12.32	3.89	2.24	9.78	16.80	10.39	9.78	16.80	11.95
547	winter	bullhead minnow	11	11.18	2.36	0.71	8.05	14.54	10.22	9.32	13.67	10.96
547	winter	sand shiner	2	8.78	2.84	2.00	6.77	10.78	8.78	6.77	10.78	8.55
545	fall	orangethroat darter	9	8.68	3.77	1.26	2.62	13.56	9.91	4.75	11.35	7.72
14	fall	western mosquitofish	7	8.40	4.02	1.52	2.81	16.20	7.83	7.00	9.22	7.56
547	winter	central stoneroller	16	8.01	4.09	1.02	1.11	14.66	8.01	5.37	11.26	6.67

Fish tissue concentration negatively correlated (t-test P= 0.00) to length of fish but was not completely explained by this physical characteristic (R^2 = 0.23). GLM ANOVA analysis of selenium fish tissue concentrations by species using length and site as covariants revealed that significant differences of mean selenium concentrations (P= 0.00) in tissue samples among fish and that length was a significant covariant (P= 0.00). Differences in tissue selenium mean concentration values were not significantly influenced by site (P = 0.45).

Robust linear regression analyses found significant, negative relationships between selenium concentrations in fish tissue and the length of fish for both benthos and water column associated species (except *Cyprinus carpio*, common carp), having significant probability values (P<0.00) and R^2 values of 0.30 and 0.28, respectively. However, the data spread indicates that a nonlinear relationship exists between the two parameters. Evaluation of the two terms in MSExcel identified a nonlinear best fit as $y = 8.875x^{-2.1153}$, R^2 = 0.4836 for the water column associated species. NCSS estimated a best fit model of $y = (11.99)* (LENGTH\_\_IN\_)^{\wedge(-2.17)}$, R^2

= 0.45 at 7 iterations. This model best fit lengths greater than two inches, with considerable amount of scatter in smaller lengths.

MSExcel best fit nonlinear model for bottom dwelling fish was also a powers function with equation $y = 21.84x^{-2.27}$, $R^2 = 0.52$. NCSS estimated linear model for benthos associated fish was y = (31.73)*(LENGTH__IN_)^(-2.52), $R^2 = 0.49$ at 12 iterations. This model indicated a great amount of variance among lengths less than 3.5 inches. Length explained approximately half the variance in the selenium fish tissue concentrations among all fishes, as indicated by the MSExcel powers function ($y = 9.15x^{-2.15}$, $R^2 = 0.50$ in Figure 4. NCSS-estimated powers model was determined to be (12.27)*(LENGTH__IN_)^(-1.85), $R^2 = 0.35$ at seven iterations. Robust linear regression resulted in an $R^2 = 0.24$ (P = 0.00, DF 319).

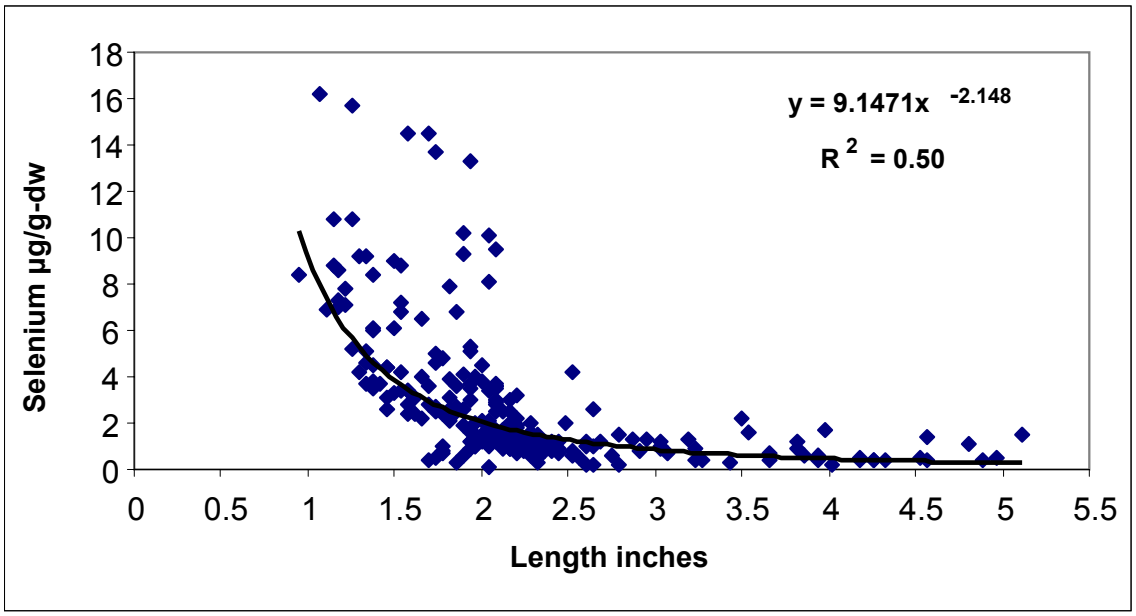

Figure 4. Scatter plot of fish tissue selenium concentration over length with best fit powers model, MSExcel.

When common carp were excluded from the analysis of bottom dwellers the estimated best fit model became y = (31.88)*(LENGTH__IN_)^(-2.53), $R^2 = 0.47$ at nine iterations, while

robust linear regression analysis resulted in $R^2 = 0.39$ ($P<0.0000$). Evaluation of the best fit nonlinear model for common carp alone was found in MSExcel to be $y = 0.0161X^{2.4054}$, $R^2 = 0.75$ (linear fit $y = 0.38X - 1.11$, $R^2 = 0.72$). Due to the small number of points representing this single species an estimated best fit was unattainable in the NCSS statistical software program. However, the slope is positive, indicating that higher concentrations are associated with longer (i.e. larger) fish (Figure 5). The relationship was not found to be significant which may reflect the low number of data points represented.

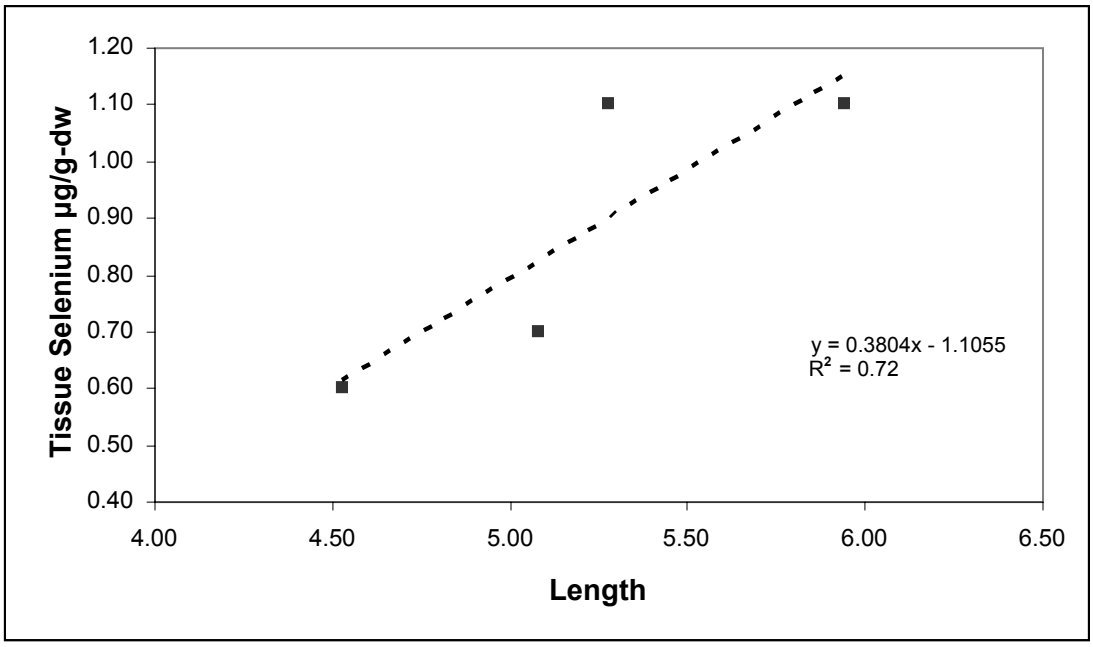

Figure 5. Scatter plot and simple linear regression of fish tissue selenium concentration as a function of length for the common carp, MSExcel.

General Linear ANOVA evaluation of fish tissue selenium concentrations by site, using length as a covariant (excluding all factors with <3 values per site) was conducted to examine for possible site effects. Probability values of $P< 0.00$ were found for both the covariant (length) and site indicating that even after the variance associated with differing fish sizes at sites (i.e. length) there remained a significant difference between sites. The Tukey-Kramer Multiple-comparison test was used to examine possible site groupings (Table 7). Site 547 had the highest mean fish

tissue levels and formed a single site group that was different from all others. Sites 543 and 545 found to be different from one another but not from all other sites.

Statistically significant correlations between selenium fish tissue and water column selenium concentrations could not be derived with only one point observed for dissolved selenium concentrations (Table 2). However, for those few sites that water samples were collected and selenium concentrations were detected, some general relationships were observed. Higher selenium concentrations in the sediments were found at sites with higher water column concentrations (Figure 6).

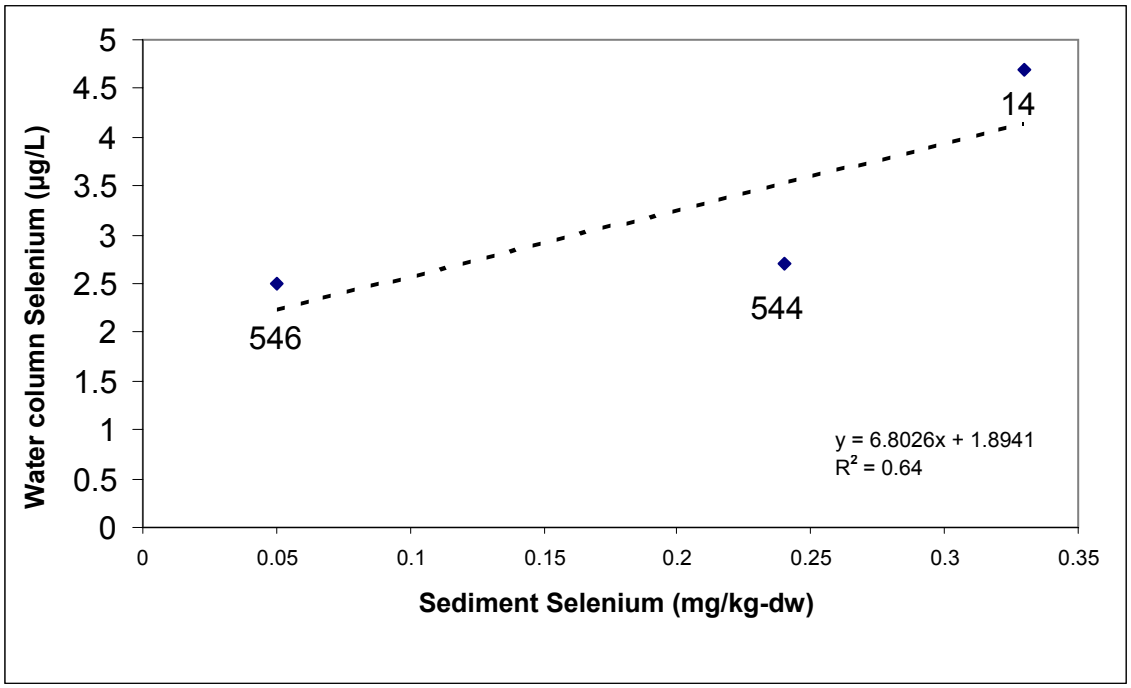

Figure 6. Plot of water column verses sediment selenium concentrations. Only one value for each X and Y value observed.

When Robust linear regression was used to evaluating the relationship between fish tissue concentrations of bottom-dwelling fish and sediment selenium concentrations for all sites , no significant relationship was found ($P>0.05$). The t-test determined a level of significance of $P= 0.09$ and $R^2= 0.03$, therefore the hypothesis that the slope is zero was not rejected. The

relationship between selenium concentration in the sediment and fish tissue concentration was found to be insignificant for those species most associated with water column. The hypothesis that the slope is zero was not rejected since the level of significance was determined to be P = 0.05 with an R^2 value of 0.02. However, in all instances the amount of fish tissue burden explained by selenium levels in the sediment were so limited as to be of little consequence and could be attributed to spurious regression. Because the common carp was the only species having a positive slope as indicated by the scatter plot in Figure 5, a Robust linear regression was performed on this species alone. The t-test level of significance (P =0.49) indicated no significance in the relationship between tissue selenium and sediment concentration; and thought the slope was positive the R^2 value remained low at 0.26. Robust linear regression analysis between selenium fish tissue (all species) and sediment mass fractions of selenium (mg/kg-dw) showed no significant correlation between the two measures (P = 0.84, R^2= 0.07, DF = 10). However, a more general analysis indicated that a positive relation existed between the two parameters (figure 7).

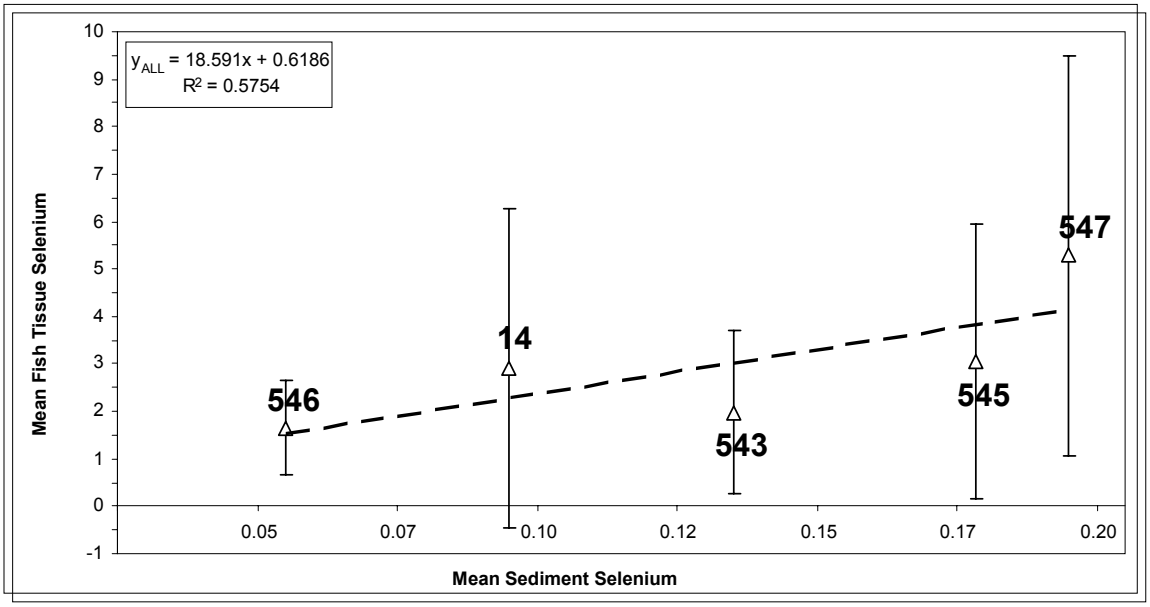

Figure 7. Linear relationship between the mean selenium concentrations in fish tissue (µg/g-dw) and sediment (mg/g-dw) for and all species.

Table 7. Tukey-Kramer Multiple-Comparison Test results shown site relationships and mean fish tissue concentrations of each site (i.e. Group). Response: Selenium µg/g-dw, Term A: KDHE_Site_Code, Alpha=0.05 Error Term=S(A) DF=247 MSE=8.20 Critical Value=3.89.

Group	Count	Mean selenium concentration	Different from groups
543	42	1.83	545, 547
546	12	2.04	547
14	26	2.40	547
545	78	3.71	543, 547
547	95	5.09	543, 546, 14, 545

Discussion

The high degree of scatter found in NCSS best fit models for nonlinear regression analysis may indicate variation in growth rates among the species. Nevertheless the slope was found to be negative indicating that smaller or presumably younger fish have higher selenium concentrations than more mature specimens (Figure 4). These results indicate that bioaccumulation of selenium is not occurring in fish found at these sites except in common carp. This was the only species showing increased selenium concentrations with increasing size (i.e. total length). However, it should be noted that only four carp specimens were collected having lengths from approximately four and a half to six inches, the highest among the benthos associated species. Selenium concentrations in common carp were not associated with selenium concentrations in the sediment (linear regression t-test P value = 0.49).

Rigorous analyses of the data revealed that site 547 maintained consistently high mean selenium tissue concentrations in four of the 10 species found at this site (see Figures 8-11). These four species were the bullhead minnow, central stoneroller, sand shiner, and orangethroat darter, having the highest individual value of 16.80 µg/g-dw. Notably, the orangethroat darter is the only fish known to consume the eggs of other fishes (Cross and Collins 1974). The second highest selenium tissue concentration was found in a mosquitofish specimen (16.20 µg/g-dw) at

site 14, which also had the third highest mean concentration among all sites when evaluated by season (Figure 12). Sixteen percent of the samples collected at site 14 were mosquitofish specimens all but one exhibiting high values (7.00-16.20 µg/g-dw). That one specimen was the largest of the mosquitofish collected at this site having a selenium concentration of 2.08 µg/g-dw. The high values found in this species most likely affected the mean selenium tissue concentration for this site causing this site to have significantly higher tissue concentrations of selenium than other sites except for site 547, which remained the highest overall. Though site 14 had high mean tissue concentrations, mostly due to selenium levels in mosquitofish, selenium sediment concentrations were low relative to other sites during the fall season (0.09 mg/kg-dw). This reinforces the overall statistical findings that showed that fish tissue concentrations of selenium were not related to either water column or sediment concentrations of this element. High selenium concentrations in fish tissue samples appear to be more associated with fish species present at that site. Further investigations of habitat preference, feeding guild, tolerances, and species distribution may help explain the variability in tissue concentrations found among these fishes.

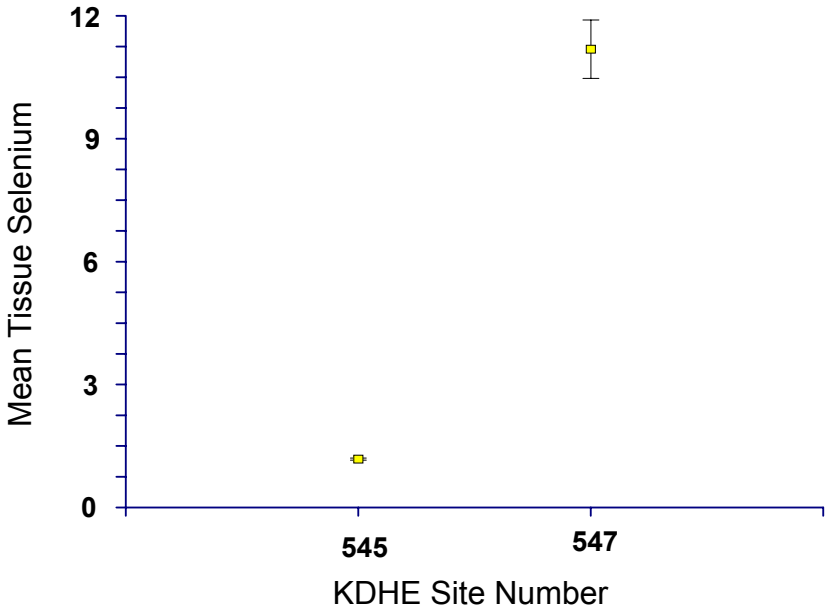

Figure 8. Error bar plot of mean selenium tissue concentration (µg/g-dw) and standard error for the bullhead minnow collected only during the winter season.

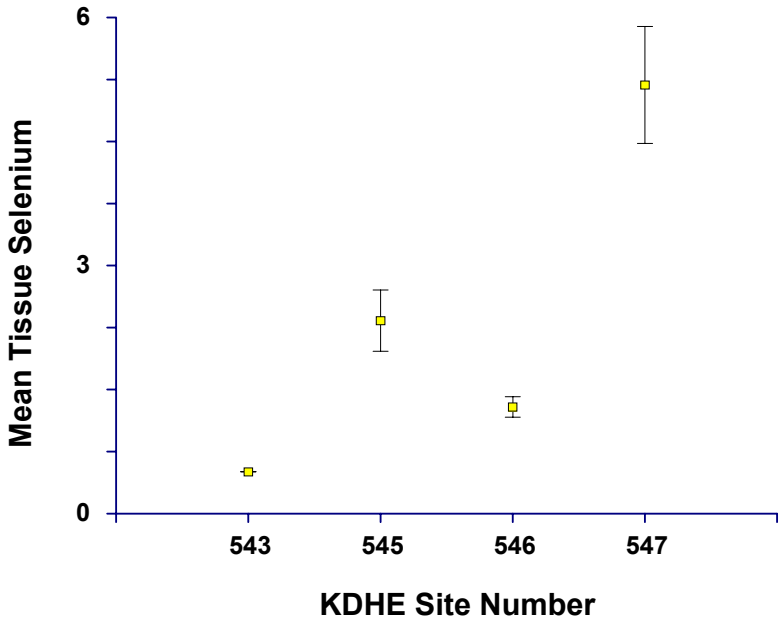

Figure 9. Error bar plot of mean tissue selenium concentrations (µg/g-dw) and standard error for central stoneroller. Note only one specimen collected from site 543 for fall season and site 546 is represented only by spring season.

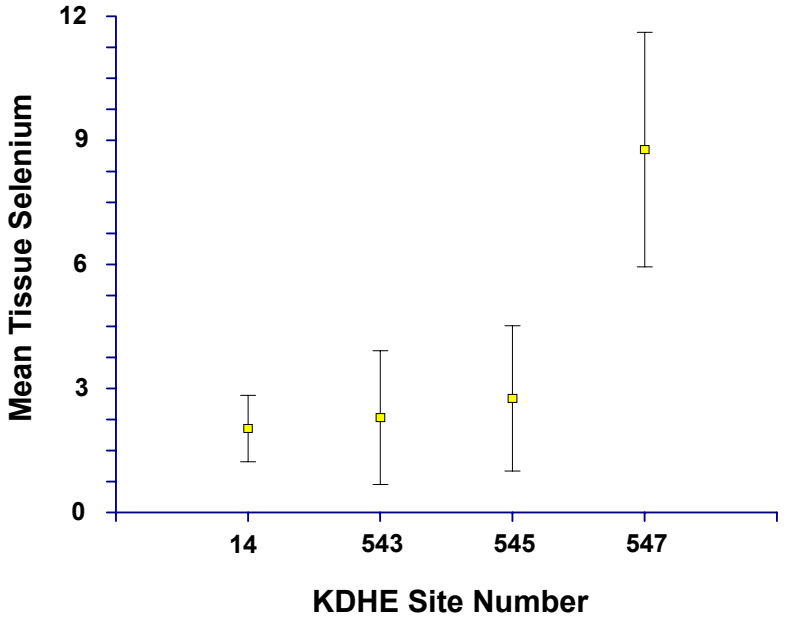

Figure 10. Error bar plot of mean tissue selenium concentrations (µg/g-dw) and standard error for sand shiner. Representative samples for site 547 in winter season only, site 14 in fall season only, site 545 in fall and winter, and site 543 by all seasons.

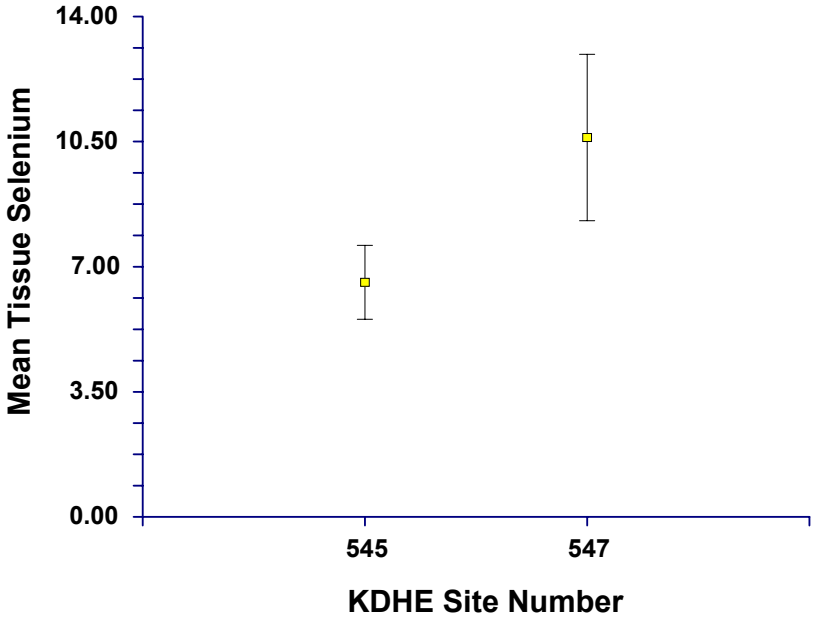

Figure 11. Error bar plots of mean tissue selenium concentrations (µg/g-dw) and standard error found in the orangethroat darter, collected only in the spring and fall season at site 545 and spring and winter season at site 547.

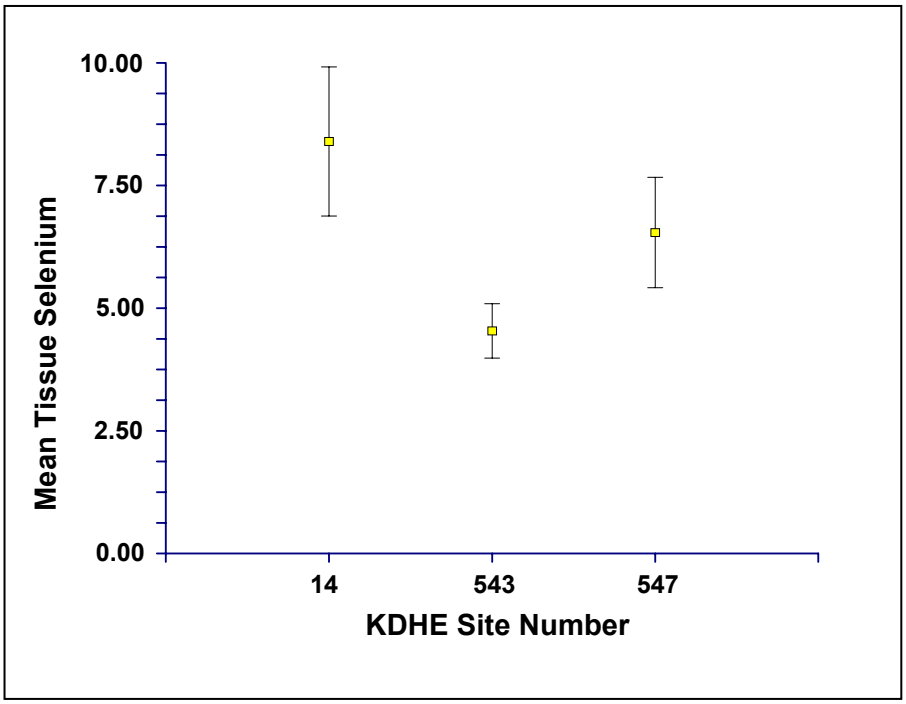

Figure 12. Error bar plot of mean selenium concentration and standard error in Western mosquitofish collected during fall season.

Water quality monitoring sites 546 and 547 were cited as impaired in the 2004 Solomon Basin Total Maximum Daily Load report and recommended for improvement in water quality to achieve full support of chronic aquatic life use (KDHE 2004). Though, this study observed dissolved selenium concentrations below the current standard of 5 µg/L for both water quality monitoring stations, site 546 did not support aquatic life comparatively to other sites. It had the lowest number of species collected of all sites sampled, with notable absences of species having commonly high selenium concentrations (Table 8). Because site 546 has historically been observed as having higher selenium concentrations and now has shown relatively low species richness, it is suspected that species prone to elevated sorption of selenium may have been extirpated from this area. However, it should also be noted that the streambed was dry for two seasons and that absences of adequate habitat may also be a significant factor in these findings.

Table 8. Fish species and count by site.

Fish Species	Common Name	14	543	545	546	547	specimen count
Ictalurus melas	black bullhead*		1				† 1
Lepomis macrochirus	bluegill	8				2	10
Pimephales vigilax	bullhead minnow *			3		11	14
Campstoma anomalum	central stoneroller*		1	9	5	33	48
Ictalurus punctatus	channel catfish*	2		7			9
Cyprinus carpio	common carp*		1	2	1		4
Semotilus atromaculatus	creek chub	3	4	23		14	44
Pimephales promelas	fathead minnow		10	6	7	3	26
Aplodinotus grunniens	freshwater drum	3					† 3
Dorosoma cepedianum	gizzard shad	4	1	1			6
Lepomis cyanellus	green sunfish		7				7
Percina caprodes	log perch*			2			† 2
Lepomis humilis	orangespotted sunfish		19				19
Etheostoma spectabile	orangethroat darter			15		4	19
Fundulus zebrinus	plains killifish			3	2	13	18
Notropis Lutrensis	red shiner	11	12	4		6	33
Motropis stramineus	sand shiner	5	6	15		2	28
Gambusia affinis	western mosquitofish	7	10			11	28
Catostomus commersoni	white sucker*			1			† 1
	number of species	9	11	13	4	10	TOTAL
	Site Count	43	72	91	15	99	320
† excluded from linear regression							
* indicates benthos associated species							

Though water column selenium concentrations do not indicate impairment in this study, sites such as 545 and 547 should be taken into serious consideration when developing improvements for chronic aquatic life. Furthermore, monitoring of impaired sites may be better achieved through combined fish tissue and sediment analysis, given that some general positive correlations were found between the two parameters. Also, higher concentrations of selenium and more exceedances were found in fishes during the winter season (Figure 12). These results were similar to those found in another study, where it was determined that higher body burdens were associated with decreased activity and higher fat tissue adsorption of selenium (Lemly 1993). This observed phenomenon emphasizes the importance of collecting representative

samples from all seasons and that selenium fate is further complicated by ambient water conditions.

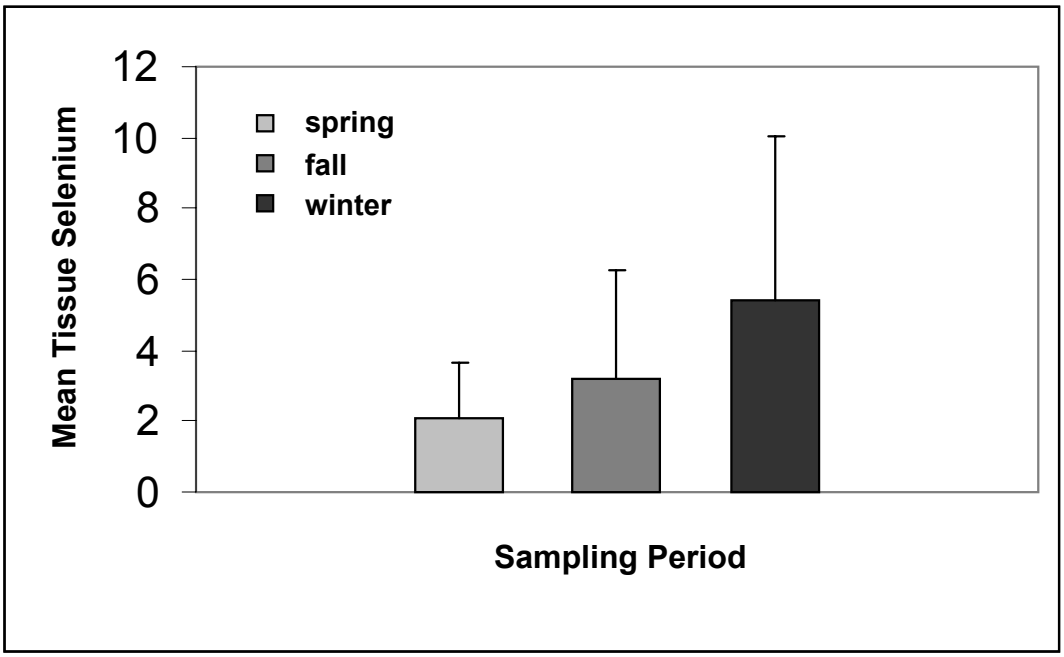

Figure 12. Comparison of seasonal fish tissue concentrations (µg/g-dw) of selenium for all KDHE sites.

Conclusions

Water column selenium concentrations µg/L did not exceed EPA recommended limit (5 ppb) for aquatic life at any sites sampled. Sediment concentrations were not found to be significantly different between sites, though site 547 had the highest mean value with the least amount of deviation about the mean (Figure 2). Mean selenium concentrations in fish tissue (whole body analysis) were found to be significantly higher at site 547 when analyzed by a single term. Inclusion of a second term, season, showed that site 14 and 547 were not statistically different from another, though site 547 maintained the highest mean value followed by site 14. No statistically significant relationships were found between fish tissue selenium (µg/g-dw) and either water column (µg/L) nor sediment selenium concentrations (mg/kg-dw).

Therefore, tissue sorption of selenium may be independent of ambient water column or sediment concentrations. Four species of fish were found to have high mean selenium concentrations when values were evaluated by site and fish species (Table 6). The central stoneroller was among those species with high tissue selenium concentrations when seasons were included in the analysis (Table 7). The difference is most likely due to the higher number of low values in the spring season, which brought the annual mean below the EPA recommended selenium tissue concentration value. These species may serve as possible indicator species when evaluating tissue concentrations for regulatory water quality compliance. There was one account of exceedance that occurred in the common sport fish, bluegill. This occurred at site 14 during the fall, having a selenium tissue concentration of 8.36 µg/g-dw. Relatively high concentrations were found in two other bluegill specimens, yet did not exceed recommended limit. Specimen were not considered large enough for consumption (<3 inches).

Limitations imposed by stochastic seasonal variability (i.e. drought and flooding) were undoubtedly a significant factor in the lack of adequate sample collection for this study. Given that dissolved selenium was not detected by standard methods and no definitive relationship between fish tissue and sediment concentrations was found, whole body fish tissue analysis of selenium was found to be a better predictor of selenium fate in this system than either water column or sediment concentration analysis. Comparison of mean selenium concentrations in sediment to fish tissue samples indicated some positive correlation, though it was not shown to be significant with robust linear analysis. Site 547 maintained the highest mean concentration in both sediment and fish tissue concentrations. Site 545 showed a similar relationship between the two measured substrates. High selenium values were observed in fish tissue that cannot be explained by water column or sediment grab samples. The whole body fish tissue samples

indicated potential threats to the aquatic life, not apparent with these other measures. No evidence of bioaccumulation was indicated in this study. In fact the relationship of length to selenium µg/g-dw suggested a negative correlation between the two for all species surveyed except common carp, having some of the lowest tissue concentrations of selenium in this study. Overall, higher mean selenium concentrations were observed during the winter season than either fall or spring.

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Appendix Table 1. Summary of analytical methods, instrument detection limits, and sample holding time of water-quality parameters analyzed in this project.

Parameter	Container	Instrument	Method Citation	Detection Limit	Holding Time	Preservation
Laboratory Analyses						
Total Phosphorus	1L Amber Glass	Digestion @ 250°F Lachat QuikChem 8500	Ebina *et al.* 1983	5 µg/L	28 days	4°C
Orthophosphate-P	1L Amber Glass	Lachat QuikChem 8500	21st Ed. Standard Methods 4500-P	1 µg/L	48 hours	4°C
Total Nitrogen	1L Amber Glass	Digestion @ 250°F Lachat QuikChem 8500	Ebina *et al.* 1983	0.01 mg/L	28 days	4°C
Ammonia-N	1L Amber Glass	Lachat QuikChem 8500	21st Ed. Standard Methods 4500-NH_3	1 µg/L	48 hours	4°C
Nitrate-N	1L Amber Glass	Lachat QuikChem 8500	21st Ed. Standard Methods 4500-NO_3	0.01 mg/L	48 hours	4°C
Nitrite-N	1L Amber Glass	Lachat QuikChem 8500	21st Ed. Standard Methods 4500-NO_2	0.01 mg/L	48 hours	4°C
Chlorophyll *a*	1L Amber Glass	Optical Tech. Devices, Ratio-2 System Filter Fluorometer	21st Ed. Standard Methods 10200-H	1 µg/L	28 days	-20°C
Selenium in Water	1L Amber Glass	Perkin-Elmer Atomic Absorption (AA) Spectrophotometer Model 5100	EPA Method 7740	2 µg/L	180 days	pH < 2 with HNO_3, 4°C
Selenium in Soil	8 oz. Glass Jar	Perkin-Elmer Atomic Absorption (AA) Spectrophotometer Model 5100	EPA Method 3050B	-	180 days	4°C
Selenium in Fish	Aluminum Foil	Perkin-Elmer Atomic Absorption (AA) Spectrophotometer Model 5100	EPA Method 200.3	-	-	≤-20°C
In situ Measurements						
pH	none	Horiba U-10 Water Quality Checker	21st Ed. Standard Methods4500-H^+	0.1	-	-
Specific Conductance	none	Horiba U-10 Water Quality Checker	21st Ed. Standard Methods2510 A-B	0.001 mS/cm	-	-
DO	none	Horiba U-10 Water Quality Checker	21st Ed. Standard Methods 4500-O G	0.1 mg/L	-	-
Turbidity	none	Horiba U-10 Water Quality Checker	21st Ed. Standard Methods 2130-B	1 NTU	-	-
Water Temperature	none	Horiba U-10 Water Quality Checker	21st Ed. Standard Methods2550-B	0.1°C	-	-

Appendix Table 2. Mean water chemistry data for KDHE monitoring sites sampled in this project. ArithMean = arithmetic mean, StdDev = standard deviation, StErr = standard error, Min = minimum value in range, Max = maximum value in range, Ptile = percentile, GeoMean = geometric mean.

Parameter	Site #	Count	ArithMean	StdDev	StErr	Min	Max	Median	25thPtile	75thPtile	GeoMean
Air Temp C	14	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Air Temp C	543	1	21.00	0.00	0.00	21.00	21.00	21.00	21.00	21.00	21.00
Air Temp C	544	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Air Temp C	545	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Air Temp C	546	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AirTemp C	547	3	20.77	8.08	4.66	11.50	26.30	24.50	11.50	26.30	19.50
Water Temp C	14	3	16.67	13.58	7.84	1.00	25.00	24.00	1.00	25.00	8.43
Water Temp C	543	3	15.00	13.08	7.55	0.00	24.00	21.00	0.00	24.00	22.45
Water Temp C	544	2	11.00	15.56	11.00	0.00	22.00	11.00	0.00	22.00	22.00
Water Temp C	545	3	15.67	12.74	7.36	1.00	24.00	22.00	1.00	24.00	8.08
Water Temp C	546	1	25.00	0.00	0.00	25.00	25.00	25.00	25.00	25.00	25.00
Water Temp C	547	3	17.33	13.28	7.67	2.00	25.00	25.00	2.00	25.00	10.77
pH	14	3	8.41	0.41	0.23	7.98	8.79	8.45	7.98	8.79	8.40
pH	543	3	8.22	0.18	0.10	8.03	8.38	8.26	8.03	8.38	8.22
pH	544	2	8.26	0.12	0.09	8.17	8.34	8.26	8.17	8.34	8.25
pH	545	3	8.37	0.37	0.22	7.94	8.59	8.58	7.94	8.59	8.36
pH	546	1	8.12	0.00	0.00	8.12	8.12	8.12	8.12	8.12	8.12
pH	547	2	7.86	0.18	0.13	7.73	7.99	7.86	7.73	7.99	7.86
Specific Conductance mS/cm	14	3	1.41	0.18	0.11	1.20	1.53	1.50	1.20	1.53	1.40
Specific Conductance mS/cm	543	3	1.67	0.38	0.22	1.44	2.11	1.47	1.44	2.11	1.65
Specific Conductance mS/cm	544	2	1.66	0.48	0.34	1.32	2.00	1.66	1.32	2.00	1.62
Specific Conductance mS/cm	545	3	0.74	0.20	0.12	0.61	0.98	0.64	0.61	0.98	0.73
Specific Conductance mS/cm	546	1	1.07	0.00	0.00	1.07	1.07	1.07	1.07	1.07	1.07
Specific Conductance mS/cm	547	3	1.39	0.59	0.34	0.97	2.07	1.14	0.97	2.07	1.32
Salinity %	14	3	0.06	0.01	0.01	0.05	0.07	0.06	0.05	0.07	0.06
Salinity %	543	3	0.07	0.02	0.01	0.06	0.10	0.06	0.06	0.10	0.07
Salinity %	544	2	0.07	0.01	0.01	0.06	0.08	0.07	0.06	0.08	0.07
Salinity %	545	3	0.03	0.01	0.01	0.02	0.04	0.02	0.02	0.04	0.03
Salinity %	546	1	0.04	0.00	0.00	0.04	0.04	0.04	0.04	0.04	0.04
Salinity %	547	3	0.06	0.03	0.02	0.04	0.09	0.05	0.04	0.09	0.06
Turbidity NTU	14	3	196.00	276.43	159.59	27.00	515.00	46.00	27.00	515.00	86.16
Turbidity NTU	543	3	85.00	80.72	46.60	19.00	175.00	61.00	19.00	175.00	58.75
Turbidity NTU	544	2	201.50	280.72	198.50	3.00	400.00	201.50	3.00	400.00	34.64
Turbidity NTU	545	3	220.00	140.99	81.40	58.00	315.00	287.00	58.00	315.00	173.73

Parameter	Site #	Count	ArithMean	StdDev	StErr	Min	Max	Median	25thPtile	75thPtile	GeoMean
Turbidity NTU	546	1	183.00	0.00	0.00	183.00	183.00	183.00	183.00	183.00	183.00
Turbidity NTU	547	3	41.00	37.59	21.70	5.00	80.00	38.00	5.00	80.00	24.77
DO mg/L	14	3	9.93	3.57	2.06	6.60	13.70	9.50	6.60	13.70	9.51
DO mg/L	543	3	8.40	4.37	2.52	5.30	13.40	6.50	5.30	13.40	7.73
DO mg/L	544	2	9.75	3.75	2.65	7.10	12.40	9.75	7.10	12.40	9.38
DO mg/L	545	3	9.63	4.83	2.79	6.60	15.20	7.10	6.60	15.20	8.93
DO mg/L	546	1	6.60	0.00	0.00	6.60	6.60	6.60	6.60	6.60	6.60
DO mg/L	547	3	10.77	4.79	2.77	6.60	16.00	9.70	6.60	16.00	10.08
NO3+NO2 mg N/L	14	3	1.50	1.05	0.61	0.30	2.27	1.92	0.30	2.27	1.09
NO3+NO2 mg N/L	543	3	0.93	0.30	0.17	0.69	1.27	0.84	0.69	1.27	0.90
NO3+NO2 mg N/L	544	2	0.93	0.63	0.45	0.48	1.37	0.93	0.48	1.37	0.81
NO3+NO2 mg N/L	545	3	0.66	0.37	0.21	0.24	0.92	0.82	0.24	0.92	0.57
NO3+NO2 mg N/L	546	1	0.91	0.00	0.00	0.91	0.91	0.91	0.91	0.91	0.91
NO3+NO2 mg N/L	547	3	0.53	0.50	0.29	0.14	1.10	0.35	0.14	1.10	0.38
NO2 mg N/L	14	3	0.04	0.04	0.02	0.01	0.08	0.03	0.01	0.08	0.03
NO2 mg N/L	543	3	0.04	0.02	0.01	0.03	0.06	0.04	0.03	0.06	0.04
NO2 mg N/L	544	2	0.03	0.04	0.03	0.01	0.06	0.03	0.01	0.06	0.02
NO2 mg N/L	545	3	0.02	0.02	0.01	0.01	0.04	0.01	0.01	0.04	0.01
NO2 mg N/L	546	1	0.04	0.00	0.00	0.04	0.04	0.04	0.04	0.04	0.04
NO2 mg N/L	547	3	0.03	0.02	0.01	0.01	0.05	0.02	0.01	0.05	0.02
NH3 µg N/L	14	3	78.17	82.53	47.65	7.80	169.00	57.70	7.80	169.00	42.37
NH3 µg N/L	543	3	116.33	80.05	46.22	38.00	198.00	113.00	38.00	198.00	94.73
NH3 µg N/L	544	2	98.30	95.74	67.70	30.60	166.00	98.30	30.60	166.00	71.27
NH3 µg N/L	545	3	39.20	27.68	15.98	17.60	70.40	29.60	17.60	70.40	33.22
NH3 µg N/L	546	1	94.80	0.00	0.00	94.80	94.80	94.80	94.80	94.80	94.80
NH3 µg N/L	547	3	61.97	20.64	11.91	38.30	76.20	71.40	38.30	76.20	59.29
TOTAL N mg N/L	14	3	2.28	1.24	0.71	1.06	3.53	2.25	1.06	3.53	2.03
TOTAL N mg N/L	543	3	1.66	0.12	0.07	1.53	1.74	1.72	1.53	1.74	1.66
TOTAL N mg N/L	544	2	1.89	1.39	0.99	0.90	2.87	1.89	0.90	2.87	1.61
TOTAL N mg N/L	545	3	1.51	0.81	0.47	0.62	2.19	1.73	0.62	2.19	1.33
TOTAL N mg N/L	546	1	1.84	0.00	0.00	1.84	1.84	1.84	1.84	1.84	1.84
TOTAL N mg N/L	547	3	0.97	0.57	0.33	0.43	1.56	0.92	0.43	1.56	0.85
PO4 µg P/L	14	3	161.27	61.38	35.44	96.80	219.00	168.00	96.80	219.00	152.71
PO4 µg P/L	543	3	104.37	63.95	36.92	56.50	177.00	79.60	56.50	177.00	92.68
PO4 µg P/L	544	2	131.60	146.23	103.40	28.20	235.00	131.60	28.20	235.00	81.41
PO4 µg P/L	545	3	170.83	99.74	57.58	56.50	240.00	216.00	56.50	240.00	143.08
PO4 µg P/L	546	1	263.00	0.00	0.00	263.00	263.00	263.00	263.00	263.00	263.00

Parameter	Site #	Count	ArithMean	StdDev	StErr	Min	Max	Median	25thPtile	75thPtile	GeoMean
PO4 µg P/L	547	3	61.40	74.22	42.85	14.90	147.00	22.30	14.90	147.00	36.55
TOTAL P µg P/L	14	3	362.67	277.35	160.13	139.00	673.00	276.00	139.00	673.00	295.56
TOTAL P µg P/L	543	3	210.67	159.68	92.19	115.00	395.00	122.00	115.00	395.00	176.96
TOTAL P µg P/L	544	2	323.05	405.81	286.95	36.10	610.00	323.05	36.10	610.00	148.39
TOTAL P µg P/L	545	3	410.33	332.33	191.87	103.00	763.00	365.00	103.00	763.00	306.12
TOTAL P µg P/L	546	1	545.00	0.00	0.00	545.00	545.00	545.00	545.00	545.00	545.00
TOTAL P µg P/L	547	3	120.40	152.42	88.00	22.30	296.00	42.90	22.30	296.00	65.67
CHLa µg/L	14	3	12.14	14.14	8.16	2.68	28.39	5.35	2.68	28.39	7.41
CHLa µg/L	543	3	20.65	25.51	14.73	2.43	49.81	9.71	2.43	49.81	10.55
CHLa µg/L	544	2	2.49	2.82	1.99	0.50	4.48	2.49	0.50	4.48	1.50
CHLa µg/L	545	3	4.54	2.63	1.52	2.12	7.35	4.17	2.12	7.35	4.02
CHLa µg/L	546	1	1.99	0.00	0.00	1.99	1.99	1.99	1.99	1.99	1.99
CHLa µg/L	547	3	4.69	3.50	2.02	2.37	8.72	2.99	2.37	8.72	3.95
PHEOa µg/L	14	3	3.78	1.71	0.99	2.00	5.42	3.92	2.00	5.42	3.49
PHEOa µg/L	543	3	4.89	3.80	2.19	2.57	9.28	2.83	2.57	9.28	4.07
PHEOa µg/L	544	2	1.96	2.07	1.46	0.50	3.43	1.96	0.50	3.43	1.31
PHEOa µg/L	545	3	4.94	2.05	1.18	3.55	7.29	3.97	3.55	7.29	4.69
PHEOa µg/L	546	1	1.64	0.00	0.00	1.64	1.64	1.64	1.64	1.64	1.64
PHEOa µg/L	547	3	2.57	1.73	1.00	1.42	4.55	1.72	1.42	4.55	2.23
Sulfate mg/L	14	2	281.00	55.15	39.00	242.00	320.00	281.00	242.00	320.00	278.28
Sulfate mg/L	543	2	293.00	15.56	11.00	282.00	304.00	293.00	282.00	304.00	292.79
Sulfate mg/L	544	1	500.00	0.00	0.00	500.00	500.00	500.00	500.00	500.00	500.00
Sulfate mg/L	545	2	90.70	15.98	11.30	79.40	102.00	90.70	79.40	102.00	89.99
Sulfate mg/L	546	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sulfate mg/L	547	2	380.50	140.71	99.50	281.00	480.00	380.50	281.00	480.00	367.26
Selenium ug/L	14	3	2.23	2.14	1.23	1.00	4.70	1.00	1.00	4.70	1.68
Selenium ug/L	543	3	1.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00
Selenium ug/L	544	2	1.85	1.20	0.85	1.00	2.70	1.85	1.00	2.70	1.64
Selenium ug/L	545	3	1.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00
Selenium ug/L	546	1	2.50	0.00	0.00	2.50	2.50	2.50	2.50	2.50	2.50
Selenium ug/L	547	3	1.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00
Sediment Selenium mg/kg-dw	14	3	0.15	0.16	0.09	0.04	0.33	0.09	0.04	0.33	0.11
Sediment Selenium mg/kg-dw	543	3	0.13	0.06	0.03	0.07	0.19	0.13	0.07	0.19	0.12
Sediment Selenium mg/kg-dw	544	2	0.15	0.13	0.10	0.05	0.24	0.15	0.05	0.24	0.11
Sediment Selenium mg/kg-dw	545	3	0.17	0.07	0.04	0.11	0.25	0.16	0.11	0.25	0.16
Sediment Selenium mg/kg-dw	546	1	0.05	0.00	0.00	0.05	0.05	0.05	0.05	0.05	0.05
Sediment Selenium mg/kg-dw	547	3	0.19	0.04	0.02	0.15	0.22	0.20	0.15	0.22	0.19

Parameter	Site #	Count	ArithMean	StdDev	StErr	Min	Max	Median	25thPtile	75thPtile	GeoMean
Mean Periphyton CHLa µg/m^2	14	1	47141.67	0.00	0.00	47141.67	47141.67	47141.67	47141.67	47141.67	47141.67
Mean Periphyton CHLa µg/m^2	543	1	31968.44	0.00	0.00	31968.44	31968.44	31968.44	31968.44	31968.44	31968.44
Mean Periphyton CHLa µg/m^2	544	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mean Periphyton CHLa µg/m^2	545	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mean Periphyton CHLa µg/m^2	546	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mean Periphyton CHLa µg/m^2	547	1	29616.69	0.00	0.00	29616.69	29616.69	29616.69	29616.69	29616.69	29616.69
Mean Periphyton PHEOa µg/m^2	14	1	10252.91	0.00	0.00	10252.91	10252.91	10252.91	10252.91	10252.91	10252.91
Mean Periphyton PHEOa µg/m^2	543	1	9794.28	0.00	0.00	9794.28	9794.28	9794.28	9794.28	9794.28	9794.28
Mean Periphyton PHEOa µg/m^2	544	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mean Periphyton PHEOa µg/m^2	545	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mean Periphyton PHEOa µg/m^2	546	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mean Periphyton PHEOa µg/m^2	547	1	3494.08	0.00	0.00	3494.08	3494.08	3494.08	3494.08	3494.08	3494.08