## Selenium Concentrations in Largemouth bass in the Sacramento-San Joaquin Delta

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## **Executive Summary**

The Sacramento-San Joaquin Delta is uniquely located between two selenium hotspots, subsurface tile drain water from the San Joaquin Basin and oil refinery waste from the Carquinez Straits. A large number of fish tissue samples were collected from the Sacramento and San Joaquin watersheds and from the Delta between 2000 and 2007 for mercury analysis. Archived largemouth bass samples from this collection were analyzed for selenium to answer two questions. First, what was the primary source of the selenium being bioaccumulated in bass in the Delta? Second, were selenium concentrations in bass in the estuary above recommended criteria for the protection of human and wildlife health?

No difference was observed in selenium concentration (fillet wet weight) in largemouth bass caught over 70-miles of Sacramento River between Veterans Bridge and Rio Vista in 2005. Similarly, there was no difference in selenium concentration on the San Joaquin River between Fremont Ford and Vernalis. Selenium concentrations did increase in the San Joaquin River in 2005 below Mud Slough but the difference was not statistically significant. Paradoxically, no difference was observed in selenium fillet concentrations in bass collected from the Sacramento River at Rio Vista and from the San Joaquin River at Vernalis in 2000, 2005 and 2007. The lack of a difference in bioavailable selenium between the two river systems was unexpected as the San Joaquin is considered a selenium "hotspot" and it was assumed that fish from the San Joaquin watershed would have the higher concentration. Also unexpectedly, inter-annual differences were observed in bass concentrations in both the Sacramento and San Joaquin Rivers. Concentrations were higher in both river systems in 2007 than in earlier years.

The Central Valley appears to be the primary source of bioavailable selenium to bass in the Delta in two of the three years analyzed. In 2005 fillet concentrations were statistically higher in Central Valley Rivers and decreased seaward in the delta consistent with the Central Valley being the primary selenium source. Also, selenium concentrations in bass increased statistically between 2005 and 2007 in both river systems and at all downstream delta locations again implying that the rivers were the primary source. The highest selenium concentrations in bass were observed in a dry water year type consistent with predictions of the Presser and Luoma bioaccumulation model.

Selenium concentrations in largemouth bass were compared against criteria recommended for the protection of human and wildlife health. Average concentrations were always less than the criteria. However, the upper 95 percent confidence limit of concentrations at several sites in the lower San Joaquin River and South Delta exceeded the U.S Fish and Wildlife Service toxicity threshold suggesting a limited threat of impairment to the warm water fish community.

### Introduction

Selenium is an essential micronutrient at low levels but toxic at higher concentrations. The most lethal forms of selenium are selenomethionine and selenocysteine (Chapman *et al.*, 2009). These are produced by microorganisms and biomagnify or increase in concentration in higher trophic levels. Diet is the primary route of selenium exposure in aquatic food chains (Lemly, 1982, 1985).

Death and deformities of waterfowl from selenium was observed in 1983 at the Kesterson National Wildlife Refuge in the San Joaquin Basin. The source of selenium was the discharge of subsurface agricultural tile drain water from the west side of the valley. In 1996 the Central Valley Regional Water Quality Control Board adopted a Basin Plan Amendment to control subsurface agricultural drainage (Central Valley Regional Water Quality Control Board, 1996). The program included a prohibition against the discharge of tile drain water to wetlands, a rerouting of selenium contaminated drainage water around the wetlands to Mud Slough, a schedule to decrease selenium loads in contaminated areas and a set of water quality objectives for both Mud Slough and the San Joaquin River. The control program also prohibited agricultural discharge to Mud Slough after September 2010 unless water quality objectives were met in the San Joaquin River<sup>1</sup>. The agricultural community has recently requested a time extension to comply with the selenium quality objective for the River. The Central Valley Regional Board has not yet considered whether to approve the time extension. Overall, the control program has been successful in eliminating toxicity in the wetlands and reducing selenium loads from the San Joaquin Basin by about 55 percent between 1984-1988 and 1997-2000 (Cutter and Cutter, 2004).

In 1987 the Department of Health Services issued a human health advisory for the consumption of three species of diving ducks in Suisun Bay because of elevated concentrations of selenium (Tetra Tech, 2008). The source of the selenium was determined to be the discharge of oil refinery waste into the Carquinez Straits area of San Francisco Bay. The San Francisco Bay Regional Water Quality Control Board responded by adopting more stringent selenium waste discharge permit limits for the oil refineries. Selenium loads from the refineries declined by about 65 percent between 1984-1988 and 1997-2000 (Cutter and Cutter, 2004). However, in 2004 the State Department of Health Services extended the human health advisory to also include San Pablo and San Francisco Bay. The State of California listed San Francisco Bay on the Clean Water Act 303(d) list as impaired by selenium and the San Francisco Bay Regional Board began development of a selenium Total Maximum Daily Load (TMDL) control program.

The Delta is uniquely located between two selenium hotspots, subsurface tile drain water from the San Joaquin Basin and oil refinery waste from the Carquinez Straits. Selenium is transported into the Delta in water from both sources. The majority of water from the San Joaquin Basin is diverted into the south delta by the State and Federal pumps and re-

<sup>&</sup>lt;sup>1</sup> The selenium objective for the San Joaquin River below the confluence of the Merced River is 5  $\mu$ g/l as a 4-day average after September 2010.

entrained back into the San Joaquin Basin. However, in wet years the River still flows across the Delta to San Francisco Bay. In contrast, water from Suisun Bay is tidally dispersed up estuary into the Delta. The largest amount of water from Suisun Bay is present in the western Delta in the late summer and fall of dry years. The importance of the two selenium sources is hypothesized to vary both temporally and spatially in the Delta. No information has been collected to evaluate whether these hydrologically induced changes are reflected in selenium concentrations in the warm water fish community.

Selenium accumulation in top predators is a biologically mediated process. Selenium loads are important but the processes involved in the conversion of inorganic to organic selenium and its transfer up the food chain are also important and unpredictable between ecosystems (Chapman *et al.*, 2009). This study uses fillet tissue concentrations in largemouth bass, a top pelagic predator, as an indicator of the amount of biovailable selenium present for transfer in the pelagic food web. Changes in tissue concentrations over time and space are assumed to represent differences in the amount of biologically available selenium being moved in the pelagic food web.

Largemouth bass have previously been used to assess the bioavailability of mercury in the Delta (Melawi *et al.*, 2007). Both mercury and selenium are bioaccumulative substances. Bass were selected for mercury analysis because they are a top predator with elevated mercury concentrations. They are also a non migratory species with a small home range (Moyle, 1976). So, their tissue concentrations are assumed to represent local conditions. Strong positive correlations have been observed between mercury concentrations in bass and other pelagic fish species in the delta (Wood *et al.*, 2008). Less information is available on selenium concentrations in California fish communities but Beckon *et al.* (2003) found that selenium levels in bass and other warm water fish species were positively correlated at different locations in the San Joaquin Basin. This suggests that bass might be a used as a surrogate for selenium contamination in the warm water fish community.

No recent assessment has been conducted to determine selenium concentrations in the delta and compare them against recommended criteria for the protection of human and wildlife health. A 1988-1990 evaluation concluded that selenium concentrations in pelagic fish in the delta did not constitute a health threat (Urquhart and Regalado, 1991). Selenium loads to the delta have since declined and the assumption is that concentrations in pelagic fish will reflect the decreased loads.

The State of California is considering whether to modify the point of diversion of water pumped from the delta to southern California (Delta Vision, 2007). One option being evaluated is to construct a peripheral canal around the delta. The canal would take Sacramento River water near Hood and deliver it to the State and Federal Canals near Tracy for export south. Two consequences of implementing this option are that the San Joaquin River would become a larger fraction of the total water volume entering the Delta and water residence times in the estuary would increase. Both the increased San Joaquin River water volume and longer residence time may result in an increase in the total load of selenium entering the delta and the amount transformed to an organic, more bioavailable selenium form. Baseline selenium bioaccumulation information is needed now so that any redirected effects from changes in hydrology can be evaluated in the future.

The purpose of this study was two fold. First, largemouth bass tissue concentrations were analyzed to determine the primary source of selenium bioaccumulated in the delta in different water year types. Second, tissue concentrations in bass were compared with recommended criteria to determine whether aquatic life impairments might be occurring. The information may help inform the Central Valley and San Francisco Bay selenium TMDLs about the source of bioavailable selenium in the freshwater delta and the extent of the impairment. The information may also be useful in the future to evaluate redirected effects of changing the hydrology of the delta.

## **Methods and Materials**

Sample Collection Eighty-one largemouth bass were analyzed for selenium from 14 sites in the Delta (Figure 1). All bass used in this study had previously been collected for mercury analysis (Melawi et al., 2007) and archived for use in other studies. Analyzing archived fish is cost effective as no funds are needed for collection but bad in that samples may not be available for all the times and places of interest. Lack of key samples can reduce both the kinds of questions that can be answered and the statistical power of the conclusions. Three fish were analyzed whenever possible from each site and time to estimate both the mean and variance of selenium concentrations. However, on several occasions only two fish were available. These were at Whiskey Slough in 2005 and at the San Joaquin River at Vernalis and at Franks Tract in 2007 (Appendix A, Table 1A). Whenever possible, bass were selected with a total body length near 350mm<sup>2</sup>. This size was chosen as it is slightly larger than the California Department of Fish and Game legal size limit of 320-mm and was the most common length available from the archived mercury samples. The length of bass analyzed was constrained as much as possible as it was not known whether selenium concentrations change as a function of fish length as has been documented to occur with mercury (Wood et al., 2008). Analysis of data in the present study demonstrated no change in selenium concentration with increasing fish size but the range of sizes analyzed was not large and the result should not be considered robust.

**Hydrology** The hydrology of the Delta is complicated. There are three main water sources: the Sacramento and San Joaquin Rivers and tidally dispersed water moved up delta from Suisun Bay. At any location the three water sources are mixed and homogenized over time by tidal action. The source and volume of water at each location is important as it is hypothesized that each carries a unique bioavailable concentration of selenium and when mixed together the three sources determine the amount of selenium available for uptake in the pelagic food chain. Bass caught at Vernalis on the San Joaquin River and at Rio Vista on the Sacramento River are assumed to represent the

<sup>&</sup>lt;sup>2</sup> Mean and range were 349 mm and 215-396 mm, respectively

selenium signature of the two different basins. The Sacramento River is the larger of the two sources and provides the majority of freshwater to the delta. The fraction of water from Suisun Bay increases westward in the estuary. No fish tissue samples are available from Suisun Bay to directly ascertain the bioavailability of material originating there as the Bay is too salty to support a resident bass population. Big Break is the most seaward station monitored in this study. Tissue concentrations from Big Break are assumed to most closely represent conditions in Suisun Bay.

The Delta Simulation Model 2 (DSM2) was used to produce volumetric fingerprints<sup>3</sup> of the primary water sources at three locations in the Delta (Figure 2). Point Antioch is the most seaward of these locations and is about a mile west of the fish collection site at Big Break. The Sacramento River was the major source of water in all years except 2006. Water year 2006 was classified as wet in both the Sacramento and San Joaquin Basins (Table 1). The San Joaquin River was the dominant water source for most of the year. About 20 percent of the water mass at Antioch in summer and fall was consistently from Suisun Bay. Bass were collected at Big Break in 2000, 2005 and 2007. Big Break and Point Antioch are assumed to have similar source water.

A volumetric fingerprint was also generated for Franks Tract (Figure 3). Franks Tract is more landward than Point Antioch. The Sacramento River is still the major source of water. However, an increasing portion of water in spring and early summer is from the San Joaquin River while the fraction from Suisun Bay is smaller than at Point Antioch. Large amounts of water in the spring and summer of 2005 and 2006 were from the San Joaquin Basin. Bass were collected at Franks Tract in calendar year 2000, 2005, and 2007.

Finally, volumetric fingerprints are provided for Prisoner's Point (Figure 4). Prisoner's Point is the most easterly of the three sites fingerprinted and had almost undetectable amounts of Suisun Bay water. The fraction of water at Prisoner's Point from the San Joaquin Basin is greater than at Franks Tract in the spring and summer of most years. Almost all the water at Franks Tract in 2005 and 2006 was from the San Joaquin River. Largemouth bass were collected at Potato Slough in 2000, 2005, and 2007. Potato Slough is about a mile north of Prisoner's Point and assumed to have similar water sources as Potato Slough.

In summary, the source of water at specific locations in the delta is a function of both the location and water year type. The Sacramento River is the major source of water in most years. This is particularly true in below normal and critically dry water years. The fraction of water from Suisun Bay increase as one moves seaward in the delta. Saltwater intrusion is common in the summer and fall of most water years. Finally, the San Joaquin River is only an important source of water in wet years. The fraction of the water from the San Joaquin increases in both wet years and at more southeasterly delta sites.

<sup>&</sup>lt;sup>3</sup> The volumetric fingerprints were obtained from Marianne Guerin at Resource Management Associates, 4171 Suisun Valley Rd, #J, Fairfield CA 94534

<u>Analysis</u> Selenium analysis was conducted at Moss Landing Marine Laboratory with USEPA digestion method 30.52 and analytical procedure 200.8 (ICP-MS). The detection limit of the combined procedures was 0.2-ppm selenium (wet weight). Results are reported as part per million (ppm) fillet wet and dry weight. Whole body dry weights were calculated from wet weights using the formula in Saiki *et al.* (1991).

<u>**Quality Assurance/Quality Control Program**</u> About 25 percent of the selenium analyses were for quality assurance and quality control (QA/QC) purposes. Accuracy was assessed by digesting and analyzing certified standard reference material<sup>4</sup> with a known selenium content with each batch of samples. The reference material was dogfish tissue (Dorm-2) distributed by the Canadian National Research Council. Precision was assessed with each batch of samples by randomly selecting one tissue sample and conducting a replicate analysis. Finally, potential matrix interference was evaluated by amending a known amount of selenium into a previously analyzed sample and determining the percent recovery.

**Statistics** Statistical analysis was conducted with Statistica<sup>5</sup>. An analysis of variance test (ANOVA) was used when the data met assumptions for normality and homogeneity of variances. If these assumptions where violated, then a non parametric Kruskall-Wallis multiple comparison test was employed. A P-value of 0.05 was used to establish statistical significance although the actual P-values are provided in the text to help the reader evaluate the probability of achieving the results by chance alone.

### **Results and Discussion**

**Quality Assurance/Quality Control Program** The QA/QC program demonstrated that the analytical results were acceptable. The program consisted of an assessment of both laboratory accuracy and precision. On five occasions standard reference material (SRM) with a known selenium concentration was analyzed to establish the accuracy of the analytical procedure. The mean  $\pm$  95 percent confidence limit of the percent recovery of selenium in the SRM was 124 $\pm$ 35 percent (Appendix B, Table 1). The consistently higher recovery than expected in the certified material suggested that the largemouth bass selenium results reported in this study might also be biased high by up to about 25 percent. No adjustment has been made in the reported largemouth bass results to account for this potential bias. Precision was assessed by randomly selecting and reanalyzing one sample with each of the five sets of digestions. The average relative percent difference<sup>6</sup> of the paired analyses was 7 percent (Appendix B, Table 2). Finally, a known amount of selenium was amended into five randomly selected largemouth bass samples and the percent recovery of the added material measured. The mean  $\pm$  95 confidence limit of the percent recovery was 97 $\pm$ 6 percent (Appendix B, Table 3).

### Largemouth bass selenium tissue concentrations

<sup>&</sup>lt;sup>4</sup> http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm\_files\_e/DORM-2\_e.pdf

<sup>&</sup>lt;sup>5</sup> Statistica StatSoft, http:// www.statsoft.com

<sup>&</sup>lt;sup>6</sup> (high value-low value)/((high value+low value)/2)

<u>Central Valley</u> The Sacramento and San Joaquin Rivers are the two largest sources of fresh water to the Delta and may be large contributors of bioavailable selenium. Selenium fillet concentrations were measured in resident largemouth bass from each river system above their confluence with the Delta to establish local instream bioavailability (Table 2 and Appendix A, Table 1A). Bass were caught in the Sacramento River at Veterans Bridge, River mile 44 (RM 44), and Rio Vista in 2005. This is a 70-mile stretch of river. Selenium fillet wet weight concentrations were similar at the three locations in 2005 (P=0.11, ANOVA). The average fillet concentration ranged between 0.32 and 0.58-ppm wet-weight (Table 2). Selenium was also measured in 2000, 2005, and 2007 at RM 44 and at Rio Vista. Again, no site-specific differences were found in any of the three years (P=0.68, Kruskal-Wallis Test). However, an inter-annual difference was observed. The average selenium concentration in bass was about 35 percent lower in 2005 than in 2000 and 2007 (Figure 5). The difference between 2005 and 2007 was significant (P<0.03, Kruskal-Wallis Test).

Selenium fillet concentrations were also measured in largemouth bass in the San Joaquin River (Table 2). Fish were caught at Fremont Ford, Crows Landing, and Vernalis in 2005. Wet weight fillet concentrations were about 30 percent higher at Crows Landing than at either Fremont Ford or Vernalis. However, the increase at Crows Landing was not significant (P>0.3, Kruskal-Wallis test). Mud Slough is the primary source of selenium to the River and enters between Fremont Ford and Crows Landing. Bass were also caught at Vernalis in 2000, 2005, and 2007. Tissue concentrations increased each year but only the difference between 2000 and 2007 was significant (P<0.04, Kruskal-Wallis Test, Figure 6).

Selenium fillet concentrations in largemouth bass from the Sacramento and San Joaquin Rivers were compared to determine whether differences existed between the two river basins. First, concentrations were compared for just the Sacramento River at Rio Vista and the San Joaquin River at Vernalis. No difference in wet weight fillet concentration was observed between the two locations on any of the three years (P=0.89, two-way ANOVA, Table 2). Next, the analysis was repeated after combining the data for RM 44 and for Rio Vista as previous analysis had detected no difference between the two sites and increasing the number of Sacramento River replicates increased the statistical power of the test. Again, no difference was observed between the two rivers on any of the three years (P=0.43). In contrast, inter-annual differences were observed in both statistical comparisons. The combined average tissue concentration for the two river systems doubled between 2000 and 2007 (Figure 7). Concentrations were higher in 2007 than in either 2000 or 2005 (P<0.003, Kruskal Wallis Test). Mean concentrations in Figure 7 are the best estimate of annual bioavailable selenium exports from the Central Valley to the Delta.

In summary, no difference was observed in wet weight fillet selenium concentration in largemouth bass caught over 70-miles of Sacramento River between Veterans Bridge and Rio Vista. Similarly, there was no difference in selenium concentration on the San Joaquin River between Fremont Ford and Vernalis. Concentrations did increase by about 30 percent below Mud Slough but the increase was not statistically significant. Unexpectedly, inter-annual differences were observed in bass concentrations in both the Sacramento and San Joaquin Rivers. Concentrations were higher in both river systems in 2007. Paradoxically, no difference was observed in wet weight tissue concentration in bass on the Sacramento River at Rio Vista and on the San Joaquin River at Vernalis. The lack of a difference in bioavailable selenium between the two river systems was unexpected as the San Joaquin is considered a selenium "hotspot" and it was assumed that the San Joaquin would have the higher concentration.

**Delta** A key objective of this study was to determine whether bioavailable selenium concentrations in bass in the Delta were primarily determined by tributary inputs from the Central Valley or by tidal dispersion up estuary from refinery inputs in the Carquinez Straits. The paradigm employed was that fish tissue concentrations would be highest near important source(s) and decrease further away. Selenium fillet concentrations were determined at nine locations in the Delta in 2005. The sites were the Sacramento River at Rio Vista, San Joaquin River at Vernalis and Potato Slough, Old River at Tracy, Whiskey Slough, Middle River at Bullfrog, Discovery Bay, Franks Tract and Big Break. The Sacramento River at Rio Vista and the San Joaquin River at Vernalis were included to represent bioavailable exports from the Central Valley while Big Break and Franks Tract are furthest west in the Delta and closest to the refineries in the Carquinez Straits and are assumed to most resemble inputs from Suisun Bay.

Wet weight selenium fillet concentrations in largemouth bass at Vernalis and at the Old River at Tracy were about double those at Big Break and Franks Tract in 2005 (Table 2, Figure 8). The differences were significant (P<0.04, Kruskal Wallis). Concentrations at Rio Vista were also larger than at either Big Break or Franks Tract but the difference was not significant (P=0.09 and 0.40, respectively). These results are consistent with the Central Valley, particularly the San Joaquin River basin, being the major source of selenium in 2005 to the Delta.

Selenium fillet concentrations were also compared across the Delta in 2000 and 2007. Sites with data for both years were the Sacramento River at Rio Vista, San Joaquin River at Vernalis, Potato Slough, Franks Tract and Big Break (Table 2). No difference was observed between any of the five locations in either year (P>0.1, ANOVA). Therefore, it is impossible to determine from a spatial-type analysis what the primary selenium source to the Delta was in these years.

Inter-annual wet weight selenium fillet concentrations were compared at five locations in the Delta to determine whether differences existed. The locations were Rio Vista, Vernalis, Potato Slough, Franks Tract and Big Break for 2000, 2005, and 2007. Largemouth bass tissue concentrations were greater at all locations in 2007 (Table 2). The average concentration in the Delta doubled between 2000/2005 and 2007 (Figure 9). The increase was significant (P<0.001, two-way ANOVA). The results for the delta are similar to those observed for the combination of the two Central Valley Rivers in 2007 (Figure 7) and suggest that the increase in bioavailable selenium from the Central Valley was responsible for the observed increase downstream in the Delta. This implies that

selenium from the Central Valley was primarily responsible for determining selenium in bass in the Delta in 2007.

Presser and Luoma (2006) have developed a selenium bioaccumulation model for the Bay-Delta Estuary that predicts concentrations in top predators. The top predators used in their model were white sturgeon, surf scoter, and greater and lesser scaup. The model predicts that the highest concentration of selenium will occur in predators in dry and critically dry years. Largemouth bass were not available to test the model from all water year types. However, fish were caught in 2007. Water year 2007 was a dry year in the Sacramento and a critically dry one in the San Joaquin basin (Table 1). The sum of unimpaired flow in 2007 in the San Joaquin basin was the lowest of the ten years reported in Table 1. Selenium concentrations in bass in the delta in 2007 were the highest measured in the study (Figure 9). Concentrations almost doubled between 2005 and 2007. The fish tissue results for 2007 are consistent with predictions from the Presser and Luoma bioaccumulation model.

In summary, the evidence suggests that the Central Valley is often the major bioavailable source of selenium to bass in the Delta. The evidence for 2005 rests on the observation that tissue concentrations were highest on tributary inputs from the Central Valley and decreased seaward in the delta. In 2007 selenium increased simultaneously in bass collected in both rivers and at all downstream locations in the delta again suggesting that the rivers were the primary source. The highest selenium concentrations in bass were observed in a dry water year type consistent with predictions of the Presser and Luoma bioaccumulation model.

<u>Selenium Risk Assessment</u> A second objective of this study was to compare selenium concentrations in largemouth bass against recommended criterion for the protection of human and wildlife health to ascertain whether present concentrations were a health hazard. Several selenium criteria have been proposed (Table 3). Some are expressed as wet weight in fish fillets while others are as whole body dry weight. Therefore, selenium results are presented as both fillet wet and whole body dry weight values in Table 2.

The U.S. EPA (2004) expresses their draft chronic freshwater criterion as whole body selenium dry weight and recommends that if fish tissue exceed 5.85-ppm in summer or fall then concentrations should be monitored during winter to determine if levels exceed 7.91-ppm (Table 3). All fish analyzed in this study were collected in summer. The upper 95 percent confidence limit for each location was compared against the 5.85-ppm U.S. EPA chronic criterion to determine whether any site specific concentration exceeded the recommended value. The highest upper 95 percent selenium confidence limit was 4.69-ppm whole body dry weight. This value was measured in bass from the San Joaquin River at Potato Slough in 2007. The concentration is about 80 percent of the recommended U.S. EPA chronic criterion suggesting that selenium levels in bass in the delta did not exceed the draft chronic value during our study.

The California Office of Health Hazard Assessment (OEHHA, 2006) has developed a selenium screening value of 2.0-ppm wet weight to protect human health. The highest

upper 95 percent selenium confidence limit measured in this study was 1.38-ppm or about 70 percent of the recommended OEHHA screening value. This value was measured in fish caught on the San Joaquin River at Crows Landing in 2005 (Table 2). The results suggest that selenium concentrations in resident largemouth bass in the Delta did not exceed the recommended OEHHA screening value during our study.

The U.S. Fish and Wildlife Service have developed a set of selenium ecological risk guidelines for application in fresh water (see Beckon *et al.*, 2003). The guidelines include a tiered set of recommendations to protect warm water fish populations (Table 3). The U.S. Fish and Wildlife Service consider it unlikely that adverse effects are occurring to warm water fish populations if tissue concentrations are less than 4.0-ppm whole body dry weight. Tissue levels between 4 and 9-ppm are considered of "concern" while concentrations above 9-ppm are at a potential "toxicity threshold". The Service recommends that if selenium concentrations fall in the "concern" range, then selenium in water, sediment and biota should be monitored on a regular basis as populations of some sensitive species may be at risk. Tetra Tech (2008) summarized the selenium risk assessment recommendations of other researchers. These researchers agree that warm water fish tissue concentrations in the 4 to 9-ppm range are "of concern" while concentrations above that are likely toxic, but Presser and Luoma (2006) argue that lower selenium concentrations may also be problematic.

The mean whole body dry weight selenium concentration of largemouth bass did not exceed 4-ppm dry weight at any site in this study (Table 2). In contrast, fourteen percent of the upper 95 percent confidence interval values were greater than the 4-ppm threshold. These exceedances occurred on the Old River at Tracy in 1999 (4.1-ppm), the San Joaquin River at Crows Landing in 2005 (4.2-ppm), Whiskey Slough in 2005 (4.1-ppm), and the San Joaquin Rive at Potato Slough in 2007 (4.7-ppm). Overall, average selenium levels in bass are less than the "threshold of concern" but some of the upper 95 percent confidence limit concentrations are marginally in the "of concern" range suggesting a limited potential selenium threat to the warm water fish community.

The San Francisco Regional Water Quality Control Board has proposed a selenium TMDL target for white sturgeon of 6-ppm whole body dry weight (personal communication, Barbara Baginska). White sturgeon inhabiting San Francisco Bay predominately feed in a benthic food chain that includes the introduced clam *Corbula amurensis* while bass are piscivorous (Moyle 1976). Therefore, selenium tissue concentrations in the two species reflect biomagnification up different food chains and concentrations in one may have limited value in predicting values in the other.

Juvenile salmonids may be more sensitive to selenium than warm water fish species (Beckon, 2007). Several races of salmon and steelhead spawn and rear in Central Valley streams and use the delta as a migration corridor to the ocean. Terrestrial insects and crustaceans are reported to be their primary prey while in the Central Valley and delta (Moyle, 1976). So, selenium concentrations in resident piscivorous adult bass may not be representative of values in juvenile salmonids rearing in Central Valley Rivers and using the Delta as a migration corridor to the ocean.

In summary, selenium concentrations in largemouth bass were compared against criteria recommended to be protective of human and wildlife health. Average concentrations were always less than criteria. However, the upper 95 percent confidence limit of concentrations at several sites in the lower San Joaquin River and South Delta exceeded the U.S Fish and Wildlife Service "no effect threshold" suggesting a limited threat of impairment to warm water fish populations in these areas. The finding of a limited selenium threat to the warm water fish community should not be construed to indicate that selenium concentrations do not pose a threat to other fish species, such as sturgeon feeding in a benthic food chain or cold water species such as juvenile salmon rearing in Central Valley Rivers and using the delta as a migration corridor.

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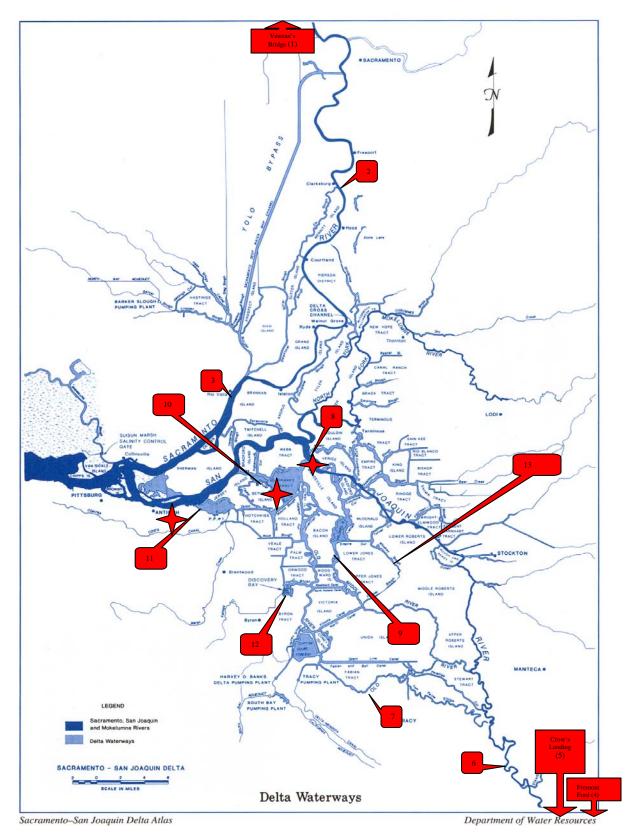


Figure 1. Selenium fish tissue sampling sites. Stars indicate the location of the three sites where the DSM2 computer model was used to generate a volumetric fingerprint of the water source.

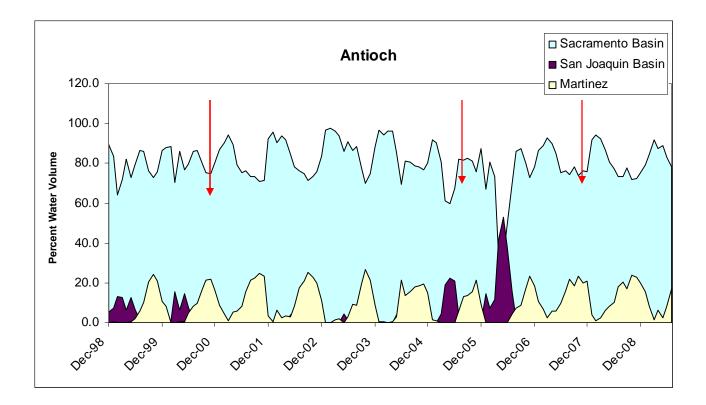


Figure 2.Volumetric fingerprint of the source of water at Point Antioch for the ten year time period between 1998 and 2008. Point Antioch is about 2 miles west of the Big Break fish collection site. Largemouth bass were collected at Big Break in fall of 2000, 2005, and 2007 (vertical arrows).

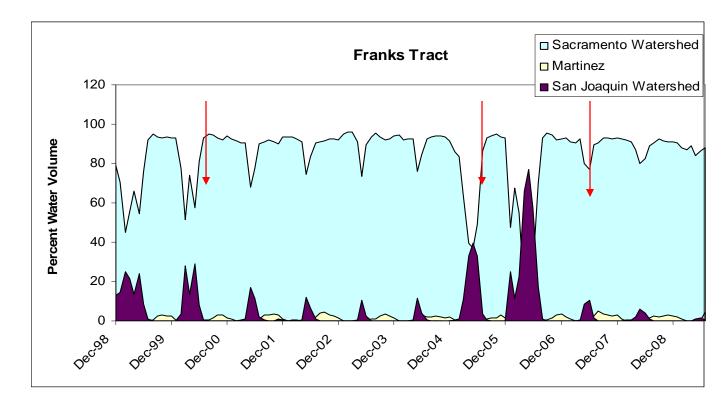


Figure 3. Volumetric fingerprint of the source of water at Franks Tract for the ten year time period between 1998 and 2008. Largemouth bass were collected in Franks Tract in 2000, 2005 and 2007 (vertical arrows).

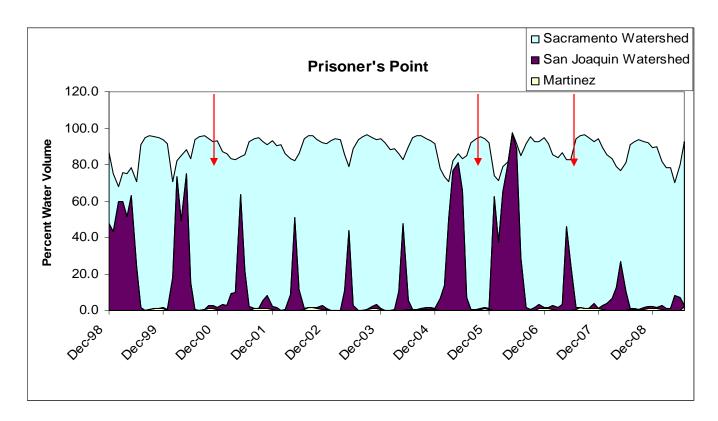


Figure 4. Volumetric fingerprint of the source of water at Prisoner's Point for the ten year period between 1998 and 2008. Potato Slough is about a mile north of Prisoner's Point. Largemouth bass were collected at Potato Slough in 2000, 2005 and 2007 (vertical arrows).

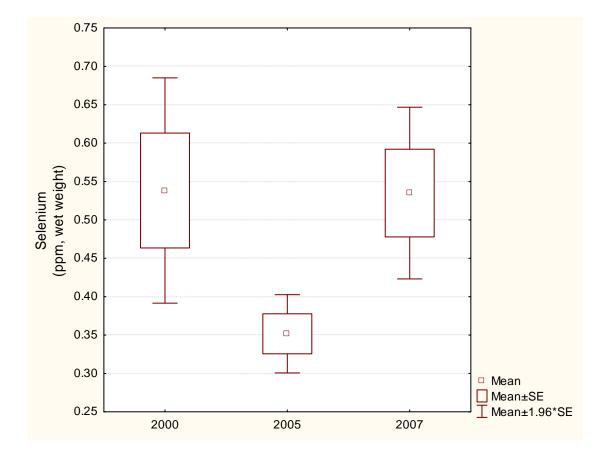


Figure 5. Inter annual mean selenium concentration (ppm, fillet wet weight) in largemouth bass caught in the Sacramento River at Rio Vista. Concentrations in 2007 were higher than in 2005 (P<0.04, Kruskal Wallis Test).

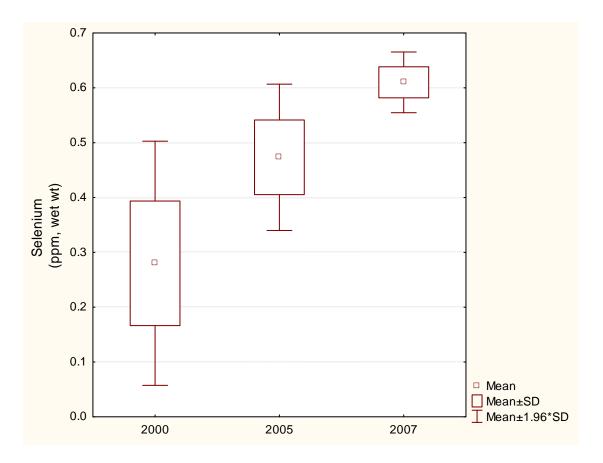


Figure 6. Inter annual mean selenium concentration (ppm fillet wet weight) in largemouth bass caught in the San Joaquin River at Vernalis. Concentrations were higher in 2007 than in 2000 (P<0.04, Kruskal-Wallis test).

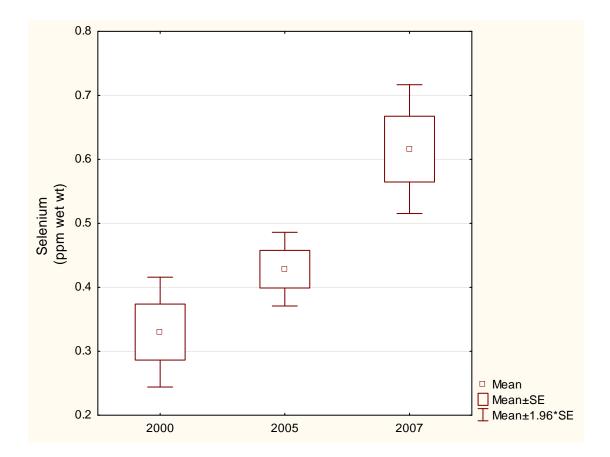


Figure 7. Combined inter annual mean selenium concentration (ppm-fillet wet weight) in largemouth bass caught on both the Sacramento River at Rio Vista and on the San Joaquin River at Vernalis. The combined mean concentration for the two sites in 2007 was greater than in either 2000 or 2005 (P<0.003, Kruskal Wallis test).

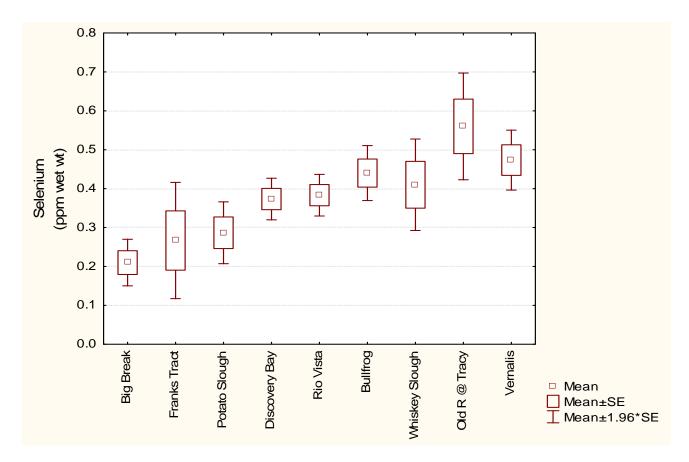


Figure 8. Selenium concentration (ppm-fillet wet weight) in largemouth bass caught in the Delta in 2005. Tissue concentrations on the San Joaquin River at Vernalis and at Old River @ Tracy were greater than at Big Break and Franks Tract (P<0.04, Kruskal Wallis test) while concentrations at Rio Vista were not different than either location.

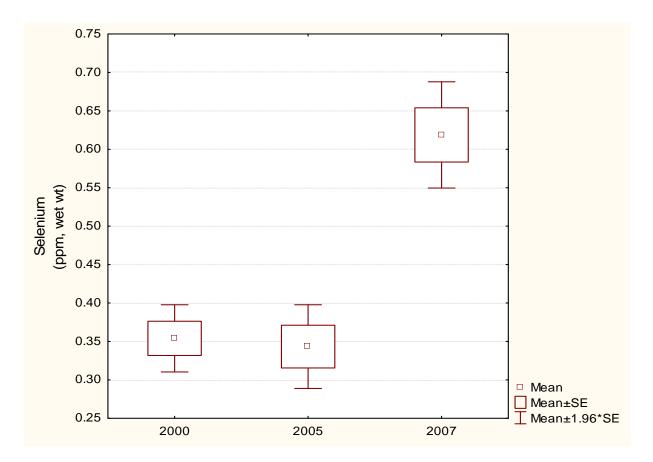


Figure 9 Inter annual mean selenium concentration (ppm-fillet wet weight) in largemouth bass caught at all locations in the Delta. The average concentration in 2007 was greater than in 2000 or 2005 (P<0.001, ANOVA).

	Sacramei	nto Valley	San Joaqu	uin Valley	
Water Year	Water Year Sum	Water Year Type	Water Year Sum	Water Year Type	<b>Fish Collection</b>
	(maf)		(maf)		
1998	31.40	Wet	10.43	Wet	
1999	21.19	Wet	5.91	Above Normal	
2000	18.90	Above Normal	5.90	Above Normal	Yes
2001	9.81	Dry	3.18	Dry	
2002	14.60	Dry	4.06	Dry	
2003	19.31	Above Normal	4.87	Below Normal	
2004	16.04	Below Normal	3.81	Dry	
2005	18.55	Above Normal	9.21	Wet	Yes
2006	32.09	Wet	10.44	Wet	
2007	10.09	Dry	2.51	Critically Dry	Yes
2008	10.28	Critically Dry	3.49	Critically Dry	

Table 1 Unimpaired annual runoff (million acre-feet) and annual water year types for both the Sacramento and San Joaquin River watersheds. Data is from the Department of Water Resources California Data Center.

Table 2 Selenium concentration (ppm) in largemouth bass caught in the Sacramento and San Joaquin River Watersheds and in the downstream Delta.

	Fillet wet weight <sup>8</sup>			Whole body dry weight <sup>4</sup>				
Location <sup>7</sup>	1999 <sup>9</sup>	2000	2005	2007	1999	2000	2005	2007
Sacramento R @ Veterans Bridge (1)			0.58±0.52				2.27±1.57	
Sacramento R. @ RM 44 (2)		0.70±0.05	0.32±0.17	0.45±0.09		2.64±0.38	1.47±0.65	1.85±0.35
Sacramento R. near Rio Vista (3)		0.38±0.23	0.38±0.11	0.62±0.40		1.50±0.54	$1.74\pm0.43$	2.58±1.39
San Joaquin R. @ Fremont Ford (4)			0.48±0.31				$1.94{\pm}1.12$	
San Joaquin R. @ Crows Landing (5)	0.66	0.75±0.10	0.72±0.66		2.54	2.69±0.40	$2.86 \pm 1.37$	
San Joaquin R. @ Vernalis (6)	0.61	0.28±0.28	0.47±0.17	0.61±0.25	2.37	1.29±1.15	$1.95 \pm 0.47$	2.44±0.13
Old R. near Tracy (7)	$0.58\pm0.47$		0.56±0.30		2.31±1.83		2.41±1.11	
San Joaquin R. @ Potato Sl (8)	0.38	0.34±0.14	0.29±0.17	0.61±0.62	1.59	1.36±0.38	1.32±0.53	2.57±2.12
Middle R @ Bullfrog (9)	0.49		0.44±0.16	0.51±0.16	1.76		1.93±0.77	2.14±0.37
Franks Tract (10)		0.38±0.21	0.27±0.33	0.68±0.25		1.66±0.70	$1.20\pm1.11$	2.37±0.29
Big Break (11)		0.39±0.22	0.21±0.13	0.71±0.37		1.57±0.67	1.03±0.48	2.86±1.02
Discovery Bay (12)			0.37±0.12				1.63±0.35	
Whiskey SI (13)			0.41±0.76				1.74±2.39	

<sup>&</sup>lt;sup>7</sup> Number in parenthesis is the station identification number in Figure 1.
<sup>8</sup> Mean ± 95 percent confidence limits
<sup>9</sup> Values without a confidence limit are the average of a composite of 5 largemouth bass analyzed by the State Toxic Monitoring Program in 1999.
<sup>4</sup> Whole body dry weights were calculated from wet weights using the formula in Saiki *et al.*, (1991)

Matrix	Concentration	Agency
Tissue	7.91-ppm whole body dry wt	Draft US EPA criteria
Tissue	2.0-ppm wet wt	OEHHA human health screening level
Tissue	>9-ppm, whole fish dry wt <sup>1/</sup>	USFWS "toxicity threshold"
Tissue	4 to 9-ppm, whole fish dry $wt^{2/2}$	USFWS "concern threshold"
Tissue	<4-ppm, whole fish dry wt	USFWS "no effect threshold"
Tissue	6-ppm, whole fish dry wt	Proposed San Francisco Regional Board TMDL target for white sturgeon

Table 3 Recommended selenium fish tissue criteria and guidelines to protect human and wildlife heath.

<sup>1/</sup>The toxicity threshold is the tissue concentration at which 10% of juvenile sunfish died. <sup>2/</sup>The concern threshold is the geometric mean of the no and low observed survival level of juvenile sunfish experimentally fed a selenium enriched diet for 90 days.

## Appendix A Largemouth bass selenium tissue data

Station	Station number	Date Collected	Se (ppm wet wt)	Se (ppm dry wt)	Se (ppm whole body dry wt)	Moisture content (%)	Wet wt (g)	Total length (mm)	Age (yr)
Sac R @ Veterans Bridge	1	28-Sep-05	0.4	1.83	1.69	78.2	590	325	2
Sac R @ Veterans Bridge	1	28-Sep-05	0.81	3.49	2.94	76.8	816	369	4
Sac R @ Veterans Bridge	1	28-Sep-05	0.53	2.50	2.19	78.8	998	382	2
Sac R @ River Mile 44	2	1-Aug-00	0.69	3.19	2.72	78.4	000	343	_
Sac R @ River Mile 44	2	1-Aug-00	0.72	3.21	2.73	77.6		392	
Sac R @ River Mile 44	2	1-Aug-00	0.68	2.86	2.46	76.2		386	
Sac R @ River Mile 44	2	6-Sep-05	0.4	1.93	1.76	79.3	318	284	2
Sac R @ River Mile 44	2	18-Oct-05	0.27	1.26	1.25	78.6	380	296	1
Sac R @ River Mile 44	2	18-Oct-05	0.29	1.46	1.40	80.1	325	293	2
Sac R @ River Mile 44	2	6-Aug-07	0.46	2.04	1.84	77.5	150	225	
Sac R @ River Mile 44	2	6-Aug-07	0.41	1.87	1.71	78.1	350	386	
Sac R @ River Mile 44	2	6-Aug-07	0.48	2.24	1.99	78.6	130	215	
Sac R near Rio Vista	3	4-Oct-00	0.3	1.31	1.29	77.1			
Sac R near Rio Vista	3	4-Oct-00	0.36	1.59	1.50	77.3			
Sac R near Rio Vista	3	4-Oct-00	0.48	1.88	1.72	74.5			
Sac R near Rio Vista	3	1-Aug-05	0.33	1.64	1.54	79.9	566	340	3
Sac R near Rio Vista	3	1-Aug-05	0.42	2.07	1.86	79.7	595	340	3
Sac R near Rio Vista	3	1-Aug-05	0.4	1.99	1.80	79.9	562	340	3
Sac R near Rio Vista	3	7-Aug-07	0.8	3.86	3.22	79.3	499	310	
Sac R near Rio Vista	3	7-Aug-07	0.57	2.70	2.34	78.9	850	379	
Sac R near Rio Vista	3	7-Aug-07	0.49	2.50	2.19	80.4	950	396	
SJR at Fremont Ford	4	3-Oct-05	0.5	2.13	1.91	76.5	1089	396	4
SJR at Fremont Ford	4	3-Oct-05	0.6	2.83	2.44	78.8	544	354	4
SJR at Fremont Ford	4	3-Oct-05	0.35	1.54	1.46	77.3	454	324	2
SJR @ Crows Landing	5	19-Oct-00	0.78	3.38	2.85	76.9		393	
SJR @ Crows Landing	5	19-Oct-00	0.76	3.14	2.67	75.8		345	
SJR @ Crows Landing	5	19-Oct-00	0.7	2.95	2.53	76.3		380	

Table 1A. Selenium concentration in largemouth bass by station and date.

Table 1A.	(Continued)
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Station	Station number	Date Collected	Se (ppm wet wt)	Se (ppm dry wt)	Se (ppm whole body dry wt)	Moisture content (%)	Wet wt (g)	Total length (mm)	Age (yr)
SJR @ Crows Landing	5	28-Sep-05	0.46	2.25	2.00	79.6	454	<b>`</b> 316	3
SJR @ Crows Landing	5	28-Sep-05	0.99	4.74	3.88	79.1	318	305	2
SJR @ Crows Landing	5	28-Sep-05	0.7	3.15	2.68	77.8	680	364	4
SJR @ Vernalis	6	18-Oct-00	0.15	0.63	0.77	76.2		303	
SJR @ Vernalis	6	18-Oct-00	0.36	1.79	1.65	79.9			
SJR @ Vernalis	6	18-Oct-00	0.33	1.53	1.46	78.5			
SJR @ Vernalis	6	8-Sep-05	0.55	2.43	2.14	77.4	544	360	3
SJR @ Vernalis	6	8-Sep-05	0.42	2.20	1.96	80.9	544	346	4
SJR @ Vernalis	6	8-Sep-05	0.45	1.93	1.76	76.7	635	370	4
SJR @ Vernalis	6	7-Aug-07	0.63	2.85	2.46	77.9	520	361	
SJR @ Vernalis	6	7-Aug-07	0.59	2.82	2.43	79.1	615	332	
Old River near Tracy Blvd	7	26-Sep-05	0.45	2.24	1.99	79.9	816	381	4
Old River near Tracy Blvd	7	26-Sep-05	0.69	3.42	2.88	79.8	499	349	3
Old River near Tracy Blvd	7	26-Sep-05	0.54	2.71	2.35	80.1	408	336	2
SJR @ Potato Slough	8	18-Oct-00	0.4	1.64	1.54	75.6			
SJR @ Potato Slough	8	18-Oct-00	0.29	1.26	1.25	77			
SJR @ Potato Slough	8	18-Oct-00	0.32	1.32	1.30	75.8			
SJR @ Potato Slough	8	31-Aug-05	0.36	1.64	1.54	78.1	499	387	
SJR @ Potato Slough	8	31-Aug-05	0.28	1.34	1.31	79.1	181	321	
SJR @ Potato Slough	8	31-Aug-05	0.22	1.08	1.11	79.6	272	360	
SJR @ Potato Slough	8	8-Aug-07	0.89	4.24	3.51	79	740	562	
SJR @ Potato Slough	8	8-Aug-07	0.51	2.76	2.38	81.5	635	356	
SJR @ Potato Slough	8	8-Aug-07	0.42	2.02	1.83	79.2	700	359	

Station	Station number	Date Collected	Se (ppm wet wt)	Se (ppm dry wt)	Se (ppm whole body dry wt)	Moisture content (%)	Wet wt (g)	Total length (mm)	Age (yr)
Middle River @ Bullfrog	9	27-Jul-05	0.49	2.43	2.13	79.8	1270	370	4
Middle River @ Bullfrog	9	27-Jul-05	0.37	1.68	1.57	78	1406	385	4
Middle River @ Bullfrog	9	27-Jul-05	0.46	2.36	2.08	80.5	1134	340	3
Middle River @ Bullfrog	9	6-Aug-07	0.58	2.64	2.29	78	1015	394	
Middle River @ Bullfrog	9	6-Aug-07	0.48	2.24	1.99	78.6	1024	389	
Middle River @ Bullfrog	9	6-Aug-07	0.46	2.41	2.12	80.9	604	341	
Franks Tract	10	5-Oct-00	0.3	1.39	1.35	78.4		397	
Franks Tract	10	5-Oct-00	0.38	1.92	1.75	80.2			
Franks Tract	10	5-Oct-00	0.47	2.11	1.89	77.7			
Franks Tract	10	12-Sep-05	0.15	0.66	0.79	77.1	726	368	
Franks Tract	10	12-Sep-05	0.41	1.82	1.68	77.5	813	373	
Franks Tract	10	12-Sep-05	0.24	1.11	1.13	78.3	680	329	
Franks Tract	10	7-Aug-07	0.66	3.53	2.97	81.3		205	
Franks Tract	10	7-Aug-07	0.7	3.59	3.01	80.5		264	
Big Break	11	17-Oct-00	0.29	1.27	1.26	77.2		349	
Big Break	11	17-Oct-00	0.45	1.83	1.68	75.4		358	
Big Break	11	17-Oct-00	0.43	1.94	1.76	77.8		335	
Big Break	11	30-Aug-05	0.25	1.15	1.17	78.3	408	310	3
Big Break	11	30-Aug-05	0.23	1.09	1.12	78.9	499	329	2
Big Break	11	30-Aug-05	0.15	0.68	0.81	77.9	408	311	6
Big Break	11	6-Aug-07	0.82	3.66	3.07	77.6	1035	389	
Big Break	11	6-Aug-07	0.54	2.76	2.38	80.4	765	382	
Big Break	11	6-Aug-07	0.76	3.73	3.12	79.6	800	364	

Station	Station number	Date Collected	Se (ppm wet wt)	Se (ppm dry wt)	Se (ppm whole body dry wt)	Moisture content (%)	Wet wt (g)	Total length (mm)	Age (yr)
Dicovery Bay	12	12-Sep-05	0.41	1.90	1.73	78.4	680	345	3
Dicovery Bay	12	12-Sep-05	0.39	1.85	1.70	78.9	726	338	2
Dicovery Bay	12	12-Sep-05	0.32	1.55	1.47	79.4	862	370	5
Whisky Slough	13	7-Sep-05	0.35	1.66	1.55	78.9	907	377	3
Whisky Slough	13	7-Sep-05	0.47	2.16	1.93	78.2	544	327	3

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# Appendix B

## **Quality Assurance and Quality Control Tables**

Table 1B. Standard reference material (SRM) with a certified selenium concentration (ppm) was digested and analyzed with each batch of largemouth bass to determine the accuracy of both the digestion and analytical procedures. The mean  $\pm$  95 percent confidence limit of the percent recovery of the certified selenium value was 124 $\pm$ 35 percent.

SRM	SRM	Percent Recovery (%)
(true value)	(measured value)	
3.30	3.42	104
3.30	4.10	124
3.30	3.42	104
3.30	3.91	118
3.30	5.69	172
Mean ±95 percent confide	124±35	

Table 2B. A tissue sample was randomly selected from each analytical batch and reanalyzed to determine the precision of the analytical method. The mean relative percent difference  $(\text{RPD})^1$  of the paired laboratory analyses was 7 percent.

Duplicate #1	Duplicate #2	<b>RPD</b> (%)
0.40	0.42	5.0
0.80	0.78	3.0
0.38	0.31	23.0
0.47	0.46	2.0
1.04	1.02	2.0
	Mean	7.0

<sup>1/</sup>((High value-low value)/(High value+ Low value)/2)

Table 3B. Percent recovery of known amounts of selenium amended into randomly		
selected fish tissue samples. Mean $\pm$ 95 percent confidence limit of the selenium		
recovery was $97 \pm 6$ percent.		

		Recovery in Paired Analysis	
Background	Amendment	(%)	
0.40	1.43	91	111
0.80	4.95	90	88
0.38	1.95	102	104
0.47	2.45	106	95
1.04	2.52	85	99
Mean ± 95 % confidence limits of		97±6	
recovery			