

**FINAL REPORT**  
**Trace Metals in Sediments of a Mine Impacted River Basin:**  
**Clear Creek, California Project**

**Dr. Johnnie N. Moore & Danielle Hughes**

**Department of Geology**

**University of Montana**

**Missoula, MT 59812**

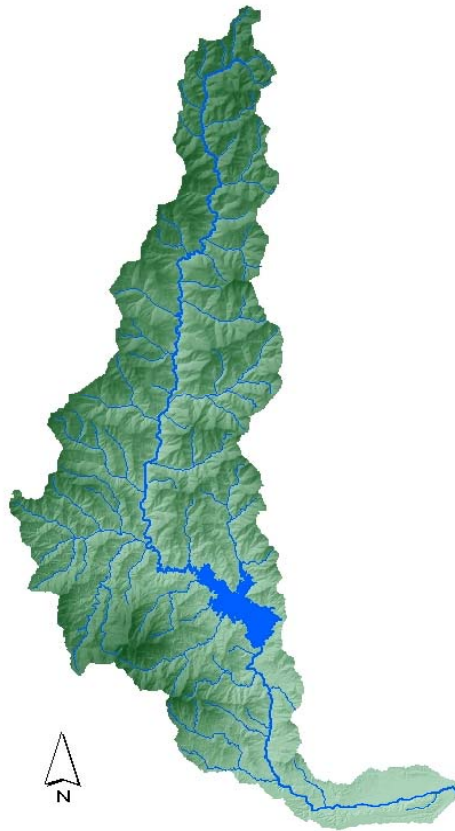
**(406) 243-2341**

**FAX: (406) 243-2048**

**E-mail: [gl\\_inm@selway.umt.edu](mailto:gl_inm@selway.umt.edu)**

**[dhughes@hotmail.com](mailto:dhughes@hotmail.com)**

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## **ABSTRACT**

Chemical composition of fine-grained channel bed sediments (<63 micrometers) collected in 2003 was compared to samples collected in 2001 and 2002 to assess metal contamination of the Clear Creek watershed. Samples collected in 2001 & 2003 followed higher flows while 2002 samples were collected during a continual low flow period. Sediment samples collected throughout Clear Creek and its major tributaries were analyzed for various metals including As, Cd, Cr, Cu, Hg, Pb, and Zn, which signify contamination from mining to the watershed. Background/baseline levels were determined from un-mined tributaries, national sediment averages and NOAA Apparent Effects Thresholds, and it was found that certain elements were elevated compared to these values. To understand the extent of contamination, sampling extended from the uppermost part of the basin beyond where most mining was known to occur, downstream through Whiskeytown National Recreation Area, where several tributaries were sampled, into the Clear Creek “Gorge,” and ended at the confluence with the Sacramento River. The results show that different metals are of concern in different sections of the basin. Potential toxicity from an element may be extremely localized, down to one specific site or may extend up to several miles downstream from the source. In the Upper basin arsenic, copper, lead and mercury are of primary concern. Cadmium, lead, zinc, mercury, and selenium are elevated in the vicinity of Whiskeytown Lake, where Clear Creek and its tributaries are supplying metal-contaminated sediment to Whiskeytown Lake. Clear Creek Gorge had relatively low concentrations of metals. Lower Clear Creek, in general had far less metal contamination than in the upstream sites, however, some localized areas had elevated metal concentrations. While no one metal is of concern throughout Clear Creek watershed, some metals should be monitored in specific areas of the basin. Several “hotspots” within the basin are located downstream of active mines or tailings piles, which are likely sources of contamination.

# INTRODUCTION

## BACKGROUND<sup>1</sup>

The gold rush of 1848 brought miners from all over the world into California to extract gold and other precious metals. Soon after, surficial deposits were exhausted and miners came together to dam and reroute rivers to expose underlying gold. By the mid 1850's the lone miner was replaced by the industrious corporation. With these corporations brought new extraction techniques including hydraulic mining, stamp mills, dredging and amalgamation with mercury. Hydraulic mining destroyed stream banks and hillsides, flooded farmers downstream, and wreaked havoc on fish habitats. By 1884 hydraulic mining was banned in the Sierra Nevada region but continued to leave a devastating trail in the Klamath-Trinity Mountains for another 70 years.

Following the discovery of placer gold, prospectors began searching for other riches including silver, copper, lead, zinc, and mercury. Mercury, or quicksilver, was used to separate gold during the milling process, and therefore was a valuable commodity. Over 220,000,000 lbs of mercury was produced in California (Churchill, 1999), the majority obtained from the mercury belt along the California Coast Ranges. Although the greater part of this mercury was exported, over 26,000,000 lbs was used for gold recovery within California. It has been estimated that mercury loss during these processes was at least 10% under the best conditions and up to 30% under normal conditions. This mercury is still transported through the river systems of the Coast Range and Sierra Nevada Foothills. The mining of gold, silver, mercury, copper, and zinc paved the way for California to become the successful and diverse state it is known as today. It drove the economy to levels unheard of, unfortunately, the environment paid the price, with abandoned mines and their contaminated runoff, which degraded landscapes, groundwater, lakes and rivers with mercury, arsenic and other metals.

A current estimate by the California Department of Conservation's Abandoned Mine Lands Unit is that there are approximately 39,000 historic and inactive mines existing in California; 4290 of these are estimated to present environmental hazards including heavy metals from acid rock drainage, mercury, arsenic, and chromium (CAL-DOC, 2000). However, very little data has been evaluated to identify the

distribution of these contaminants at the basinwide scale; even less is known about the changes over time.

Understanding the distribution and variation of widespread contamination is essential to river restoration efforts. The ability to predict changes in transportation and deposition of contaminated sediments, especially where dredging, filling, excavation, and floodplain construction may lead to remobilization of metals can help achieve rehabilitation goals to restore rivers to their natural form and function and limit release of contaminants from abandoned mine lands.

## **OBJECTIVES**

The purpose of the research reported here is to expand on a previous report (Moore, 2002) on the distribution of contaminated fine-grained sediment within the Clear Creek watershed. The results presented here are a combination of efforts in the Whiskeytown National Recreation Area and the Clear Creek watershed both upstream and downstream from Whiskeytown Lake. The objective was to combine the data from two years of sampling of previous work with another year of data to establish the magnitude of potential metal contaminants in the fine-grained bed sediments of the Clear Creek watershed and understand the variability throughout the basin over this time. The goal of this research is to begin to establish a baseline of metals concentrations in the watershed as well as start to understand the processes mobilizing and transporting metals from abandoned mine sites and mining wastes throughout the watershed.

## **SCOPE**

In previous work in 2001 and 2002 Moore and co-workers (Moore, 2002) sampled sediment from sites distributed throughout the basin including major tributaries and the main stem of Clear Creek. Unmined tributaries were sampled to determine potential background values (baseline conditions) for comparison to mined tributaries and the main stem of Clear Creek. Samples were also collected from floodplain ponds in Lower Clear Creek associated with/adjacent to suspected mining

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<sup>1</sup> Much of the information in these sections is from the previous report (Moore, 2002).

debris/tailings (e.g., dredge tailings). Sampling sites extended from the upper part of the basin above the majority of known mines to the confluence with the Sacramento River. Results from 2001 and 2002 show that specific areas were of more concern than others. No one metal was found to be of concern in all areas and some metals were of more concern than others in the different parts of the basin. Arsenic and mercury were elevated mostly in the upper basin and contaminate Upper Clear Creek. In the Whiskeytown Lake area, metals of most concern were cadmium, mercury, zinc and copper. Clear Creek Gorge had relatively low concentrations of contaminants. Lower Clear Creek had less contamination than in the upstream sites. However, some localized areas in the floodplain had highly elevated concentrations of mercury, lead, cadmium and zinc. Mercury was substantially elevated over background concentrations throughout the Clear Creek drainage, however, distribution in Lower Clear Creek was not substantially different than that throughout the basin and there was only one site identified as a potential "mercury hot spot". Results from detailed sampling in the newly constructed Clear Creek channel in the restoration project area suggested there was little concern for mobilization of mercury above the basinwide levels during construction of this type.

Using these results as a backdrop for our 2003 sampling our goal was to determine any changes from the original data set after the relatively high streams flows of winter 2002 and spring 2003. Potentially, these high flows could have mobilized more contaminants from sources or concentrations could have been diluted by cleaner sediment brought in from non-contaminated areas in the watershed or there could be no measurable response in metal concentrations. Also, other potential sources were located based on discussions with U.S. Geological researchers and WNRA staff. The 2003 sampling was concentrated in the tributaries and the main stem of Clear Creek that would address these two aspects, locating new sources of contamination and identifying response to high runoff. No samples were taken in the floodplain ponds along Lower Clear Creek that were sampled in 2001 and 2002.

## **METHODOLOGY**

The methods used in the three years of the study were the same and are described in Moore (2002) and listed in Appendix II of this report. It is well established that metals concentrations are significantly higher (4 to 5 orders of magnitude) in riverbed sediments than in the water alone (Gibbs 1977; Martin and Meybeck, 1979; Meybeck and Helmer, 1989). Because of these relationships, the majority of contaminant transportation is through the solid phase or sediment fraction. There is also commonly a strong relationship between the percent of mud and metal concentration in sediment. A major concern with contaminants sorbed to aquatic sediments is that fine-grained sediment particles can adhere to gas exchange membranes of aquatic organisms or be ingested along with these sediments, which provides a pathway for chemical consumption and biomagnification further up the food chain (Lemly et al., 1988; Moore et al. 1991; Adams et al. 1992). Therefore, bed sediment surveys using sediments less than 63 micrometers (mud) is an excellent way to assess and locate areas of potential harm to aquatic life. Fine-grained (<63  $\mu\text{m}$ ) bed sediments were collected to determine metal, arsenic, and selenium contamination in Clear Creek (As, Cd, Cr, Cu, Hg, Pb, and Zn; Appendix IV).

## **SAMPLING DESIGN AND SAMPLE PREPARATION**

Sediment sampling sites were distributed throughout the basin including major tributaries and the main stem of Clear Creek (Appendix I). Un-mined tributaries were sampled to determine potential background values (baseline conditions) for comparison to mined tributaries and Clear Creek. However, because nearly all tributaries had some mining, the establishment of baseline concentrations was difficult (discussed below). Sampling sites extended from the upper part of the basin above the majority of known mines to the confluence with the Sacramento River (Figure 3). Some sites were sampled all three years to determine the variability over three years. During 2001, 59 sites were collected throughout the basin (Appendix I & IV). In 2002, 27 of the original sites were re-sampled and 20 sites were added (mostly in tributaries in the vicinity of Whiskeytown Lake). In 2003, 52 sites in total were collected, 35 sites that were previously collected in 2001 & 2002 (to establish yearly variability) and 17 new sites.

The sampling areas are divided into four river reaches (Figures 4-9): upper Clear Creek (above Whiskeytown Reservoir); Whiskeytown (including tributaries flowing into Whiskeytown Lake); Clear Creek Gorge (the canyon area below Whiskeytown Dam to the Clear Creek Road bridge); lower Clear Creek (below Clear Creek Road bridge to the confluence with the Sacramento River). In each of these reaches sampling locations were located as dictated by access and proximity to potential metal sources (abandoned mines, tailings and other mining wastes). Access in many areas was difficult because of terrain and landowner restrictions.

At each site a sediment sample was taken using a specific protocol (Appendix II). Fine-grained bed sediment samples ( $<63\mu\text{m}$ ) were collected with sampling sieves and bottles that had been previously cleaned using "ultra-clean methods". Under this method, all sample bottles and sampling devices are cleaned in two different types and strengths of acids and then washed multiple times in ultra-pure, de-ionized water. Once cleaned, they are sealed in plastic bags until sampling in the field. At each site we used a new sampling kit and "Nitrile" gloves to avoid cross-contamination. Samples from the upper 1-3 cm were collected with a large plastic spoon and sieved through a plastic Buchner funnel containing a 63 micrometer mesh screen into a clean 250 ml bottle purged with river water. Samples were then capped and stored on ice until return to the University of Montana Geology Analytical Laboratory. Once in the laboratory the slurries were centrifuged to separate the water from the sediment, then decanted and dried in an oven at  $70^{\circ}\text{C}$ . After dehydration samples were ground, in the collection bottles, using a separate acid-washed glass rod for each sample to avoid contamination. Once ground the sediment was removed from the bottle and stored in clean snap-cap vials until digestion.

## **DIGESTION AND ANALYSIS**

All sediment samples were digested using EPA Method 3050B where 0.25-0.5g dry weight samples including duplicates, method-spikes, method-blanks and external standards were refluxed and oxidized in acid at  $90^{\circ}\text{C}$  (Appendix II) to dissolve the elements which could become "environmentally available." This method is not considered a complete digest but it dissolves all elements commonly of interest in

mining contaminated sediment, including those elements tied to organic compounds, adsorbed to mineral surfaces and those within metal sulfides, oxides and hydroxides. The method will only partially dissolve silicate minerals, so elements tied tightly to those compounds (E.g., Al, Fe, K, Na, etc.) are not representative of the total elemental concentration in the sediment. Digested samples were analyzed for selected elements including As, Cd, Cr, Cu, Hg, Pb, and Zn using Inductively Coupled Argon Plasma – Emission Spectroscopy (ICAP-ES)(USEPA Method 200.7). Mercury was analyzed using Atomic Fluorescence Spectrometry (AFS) (USEPA Method 245.7). Selenium was analyzed by Hydride Generation Atomic Adsorption Spectrometry (AAS) (method details reported in Appendix II). Before analyzing for selenium a second digest had to be performed to get Se into solution (Appendix II). Again, duplicates, spikes, lab-blanks, and external standards were used for quality assurance and quality control (QA/QC). QA/QC data for 2001 and 2002 are presented in Moore (2002) and for 2003 in Appendix III.

## **RESULTS AND DISCUSSION**

### **GENERAL OVERVIEW**

Clear Creek originates in the Trinity Mountains at over 6000 ft in elevation then flows into Whiskeytown Reservoir. From Whiskeytown dam the river flows south through a deep gorge for approximately 8 miles then flows east for another ~8 miles where it meets the Sacramento River just south of Redding. The Clear Creek watershed has hot dry summers with the majority of precipitation occurring from November to April. The average annual precipitation varies from over 60 inches in the upper basin down to 20 inches in the lower basin (McBain and Trush, 2000). Average daily discharge from the Igo gauging station, located in the lower half of the basin, is presented in Figure 1. Streamflows on Clear Creek were highly variable over the time of the study, with summer baseflows less than 100 cfs in 2002 and peak stages reaching over 3500 cfs in June 2003 (Figure 1). The sampling in 2003 was after very high winter-spring flows in the basin. During this time sediment was remobilized from Whiskeytown reservoir and sediment concentrations appeared quite high in Clear Creek and its tributaries (Jennifer Gibson, WNRA, Personal Communication). Sampling in



2001 and 2002 were during relatively low flow years. Sampling during 2001 occurred during the runoff period and 2002 sampling followed that same period during low flow.

Sediment mobilization and redeposition is an important aspect of a healthy river system and understanding the effects of high and low flows on metal concentrations is an important tool for rehabilitation projects. Therefore samples were collected over variable flows including mid to late winter sampling in 2001 and early 2002, late spring sampling in 2002 and 2003, along with late summer sampling of 2003. Composite data collected over three years is presented in Appendix IV. For comparative reasons we have chosen several different types of plots for each element, presented at the end of this report. River miles on all plots start with zero at the confluence with the Sacramento River and increase upstream. All tributaries are plotted at the river mile where they intersect with the main stem. When more than one site is located on a tributary, those data are plotted at the same river mile. Plot A of each series gives an average concentration of the element for all the data collected over the three years at each site over the entire basin. Figures B and C divide the basin into two parts, Figure B begins at the confluence with the Sacramento River and ends at the Whiskeytown dam and C continues upstream from Whiskeytown Dam to the uppermost site in the basin. Figure D gives concentrations as a multiple of the background concentration (discussed below), shown on a semi-logarithmic plot to take a closer look at areas that may be of the most concern. Finally, Figures E and F compare concentrations over time, in the lower and upper halves of the basin, to see if they have changed within the three years of the study.

Potentially toxic elements discussed include As, Cd, Cr, Cu, Hg, Pb, Se and Zn (Appendix IV). These elements have shown distinct changes within the basin and are of concern in specific areas, therefore will be discussed in detail. Data below the practical quantification limit (PQL) are plotted on the graphs as 0.75 times the PQL and where appropriate the PQL is denoted by a horizontal line on the graph.

## **BASELINE CONCENTRATIONS**

In assessing metal contamination of Clear Creek several critical values had to be considered. “Background” or “baseline” values were obtained from unmined or at least

minimally mined tributaries. These values represent concentrations believed to be indicative of the concentrations before mining. In the Clear Creek drainage nearly all the tributaries have some indication of mining (Figure 3) and finding sites on unmined tributaries with enough water and fine-grained sediment proved to be difficult. We chose to use Brandy Creek (site WT09/BRAN) and Paige Boulder Creek (site CC28) as background tributaries (Figure 3 and Table 1), because these two streams have no recorded mining sites above the sample site locations. Other sites throughout the basin are compared to these tributaries by using an enrichment factor normalized to the unmined tributary concentration (i.e., multiples of background concentrations). An enrichment factor of 1 represents values at the same concentration as the background value, and enrichment factor of 2 is two times background, etc. The enrichment factor plots allow comparison among different elements that have very different concentrations.

Other established baseline values (Table 1) were also considered for comparison including NOAA “affects” values, United States average sediment concentrations (Bowen, 1979) and several western Montana rivers (Essig and Moore, 1999). Although there is a large amount of variability in average values throughout the United States and even within specific regions, these concentrations put the Clear Creek background values in a broader perspective. In some cases, the values determined from Clear Creek tributaries are higher or lower than these published values. Cadmium is substantially higher, probably due to the relatively high detection limit for Cd (1 mg/kg) with EPA analytical methods 3050B and 200.7. It is likely that the baseline concentration for Cd is as low as 0.2 mg/kg, however, to remain consistent the higher value of 0.75 mg/kg was used in all comparisons, thus probably underestimating cadmium enrichment. Baseline mercury concentrations at Clear Creek are similar to those determined in core samples from Lake Tahoe (Heyvaert, et al., 2002) and San Francisco Bay, which likely represent regional background levels. Chromium concentrations are fairly high in the background tributaries (sites WT09 & CC28, Appendix IV), perhaps due to geological differences (Figure 1), therefore background chromium concentrations within the basin may be considerably lower than that used, but for consistency we use Clear Creek values for comparison. Background lead and copper concentrations were similar to all

other values obtained and probably represent reasonable background values. Se, a naturally occurring element rarely exceeds 2mg/kg in soils, except those produced by weathering seleniferous marine sedimentary rocks (Lemly and Smith, 1988). In small concentrations selenium is an important micronutrient but at concentrations exceeding nutritional value it can be extremely toxic to biota. Clear Creek background Se values are somewhat higher than NOAA values but are consistent with San Francisco Bay sediments.

	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Hg</b>	<b>Pb</b>	<b>Se</b>	<b>Zn</b>
<b>PQL</b>	10	1	10	6	0.03	8	0.02	1.6
<b>WT09</b>	7.5	0.75	89.4	28.3	0.04	19.0	0.34	65.1
<b>CC28</b>	7.5	0.75	110.6	53.2	0.03	11.5	0.48	68.7
<b>Mean Clear Creek</b>	<b>7.5</b>	<b>0.75</b>	<b>100.0</b>	<b>40.8</b>	<b>0.04</b>	<b>15.3</b>	<b>0.41</b>	<b>66.9</b>
<b>NOAA "background"<sup>1</sup></b>	<b>1.1</b>	<b>0.1- 0.3</b>	<b>7-13</b>	<b>10-25</b>	<b>0.004-0.051</b>	<b>4-17</b>	<b>0.29</b>	<b>7-38</b>
<b>Average Sediment<sup>2</sup></b>	<b>7.7</b>	<b>0.17</b>		<b>33</b>		<b>19</b>		<b>95</b>
<b>W. Montana Rivers<sup>3</sup></b>	<b>7.0</b>	<b>0.22</b>		<b>20</b>		<b>15.4</b>		<b>56.5</b>
<b>Lake Tahoe Sediment<sup>4</sup></b>					<b>0.033</b>	<b>11.7</b>		
<b>San Francisco Bay<sup>5</sup></b>				<b>30-50</b>	<b>0.06</b>	<b>3-7</b>	<b>0.3-0.8</b>	<b>75-100</b>

**Table 1:** Background concentrations (mg/kg or ppm) in the Clear Creek drainage taken from Moore (2002) with updated Clear Creek data to include 2003 sampling determined from Brandy Creek (WT09) and Paige Boulder Creek (CC28). If a value was below the PQL, 3/4 of the PQL was used for the background determination. Values that are in *italics are <PQL* which is listed below each element. If more than one sample was collected at a site (field duplicate) the average of those two values is used. <sup>1</sup> Values from NOAA (1999) primarily from Int. Joint Comm. Sediment Subcommittee (1988). <sup>2</sup> Values from Bowen (1979) after Wedepol (1968). <sup>3</sup> Values from Essig and Moore (1999). <sup>4</sup> From pre-industrial core samples, Heyvaert et al. (2002), <sup>5</sup> Hornberger, et al. (1999).

Measuring the toxicity of chemicals to aquatic life is dependant on several factors including the types of organisms, the effects considered and a range of sediment characteristics. Although there are no universally accepted sediment quality guidelines, NOAA has established values for which to prioritize contaminated sites throughout North America. The NOAA apparent effects thresholds (AET's) are guidelines for biotic effects of metals in marine sediments. Although there are guidelines for freshwater sediments (see <http://response.restoration.noaa.gov/cpr/sediment/squirt/squirt.pdf>) the marine criteria were used because the data is more robust and the values higher, giving a more conservative measure of affects. Concentrations above

these levels are known to have adverse effects on biota. The Effects Range-Low (ERL's) represent the value at which toxicity may begin to be observed in sensitive species and Effects Range-Median (ERM's) represents the concentration at which adverse effects commonly occur (NOAA, 1999 and Table 2). The NOAA guidelines (Table 2 and on plots) are used as indicators of potential toxicological effects and are not an absolute measure of sediment toxicity. Examining the "percent incidence" values in Table 2 gives a general idea of the probability for these effects. To determine how accurate these guidelines are at predicting biologic effects, detailed studies would need to be conducted in the Clear Creek system using species of concern, however, the NOAA Threshold values are a reasonable guide to potential effects.

	Guidelines		Percent Incidence of Effects		
	ERL	ERM	<ERL	ERL - ERM	>ERM
<b>As</b>	8.2	70	5.0	11.1	63.0
<b>Cd</b>	1.2	9.6	6.6	36.6	65.7
<b>Cr</b>	81	370	2.9	21.1	95.0
<b>Cu</b>	34	270	9.4	29.1	83.7
<b>Hg</b>	0.15	0.71	8.3	23.5	42.3
<b>Pb</b>	46.7	218	8.0	35.8	90.2
<b>Se<sup>1</sup></b>		1*			
<b>Zn</b>	150	410	6.1	47.0	69.8

**Table 2:** Sediment guidelines for trace metals (mg/Kg or ppm) and the percent incidence of biological effects. ERL = the effects range-low; ERM = effects range median. The ERL is the value below which effects are not expected. The ERM is the value above which effects are expected at least half the time. Data is from Long et al. (1995). <sup>1</sup>Se value is the AET=Apparent Effects Threshold, a value known to have toxic effects on amphipods, \*this value is not an ERM. This table and discussion of the methods can be found online at: <http://response.restoration.noaa.gov/cpr/sediment/SPQ.pdf>

## BASIN WIDE TRENDS IN CONCENTRATIONS

**Arsenic:** Figure 10A shows average concentrations of arsenic collected over the last three years against river miles of the Clear Creek drainage. The solid black line represents the approximate value of the PQL (10 mg/kg), background (7.5 mg/kg) and ERL (8.2 mg/kg) due to their close vicinity to each other and can be considered a general measure of those parameters. The dashed line indicates the position of the NOAA AET ERM of 70 mg/kg. It is apparent from Figure 10A that the majority of

sites throughout the basin are above background arsenic values but below ERM. There are two areas of potential concern that have concentrations above the ERM of 70 mg/kg, one in Lower Clear Creek at river mile ~7 and the other mostly in tributaries at approximately river miles 28-33. Figure 10B shows the lower portion of the creek, where at site CC14 (Appendix IV) arsenic concentrations are ~130 mg/kg. This site is located just above the old Saeltzer Dam and downstream from Reading Bar (Appendix I). To examine the source of arsenic we should take into consideration that the sample sites surrounding CC14 are almost 10 times less than this site, and that the 2003 value is exceptionally higher than the sample taken in 2001 (Figure 10B and 10E). While sampling at this location there were obvious signs of recreational use including sunbathers, ATV's and large amounts of trash. This suggests that there may be extremely localized arsenic contamination at this site, with a questionable source. It is highly possible that the arsenic came from something other than the mining because an elevated concentration was only found in the 2003 sample (Appendix IV). Because of the transient and localized nature of this value it is likely not indicative of arsenic contamination in Lower Clear Creek and should be considered an outlier unless subsequent sampling shows a persistence.

The highest arsenic concentrations are located in samples from the upper portion of the basin, where eight sites exceed ERM. Figure 10C shows that seven of these upper basin sites are located in tributaries of Clear Creek. The two highest values are samples collected from Scorpion Gulch (715 mg/kg) and America Gulch (564 mg/kg). Scorpion Gulch converges with French Gulch, which has the fourth highest value (Appendix IV). Similarly, America Gulch flows into Cline Gulch, which also exceeds ERM. Both of these areas have small active mines and abandoned mine wastes from historical mines upstream from the sampling sites, which are likely the source of contaminated sediments to the stream. It appears that dilution is occurring down stream as seen by the lower concentrations of sample sites CLN1/CC44, CLN2, and FRGL (Figure 10C and Appendix IV) downstream from the mines. The one value above the ERM in the main stem of Clear Creek (CC40, Appendix IV) is downstream from Cline Gulch and French Gulch but because sites with lower concentrations are between the

confluence and this site the source is likely from tailings deposits located immediately upstream from this site (Appendix I).

As seen in Figure 10D, the majority of the sites in the basin are between 1 and 10 times the background value. However, the 9 sites previously mentioned are more than 10 times background, with Scorpion Gulch at 100 times background. These areas that have high enrichment factors and lie above the ERM have high potential for negative effects on biota. Maps of the concentrations (Figure 11), enrichment factors (Figure 12) and threshold levels (Figure 13), show the spatial distribution of arsenic contamination in the basin.

Figure 10E & 10F represent Clear Creek sediment arsenic data through time. Figure 10E, shows that arsenic concentrations have changed very little during the time of this study in the lower half of Clear Creek, excluding CC14, which was discussed in the previous paragraph and CC31 (Appendix IV). CC31 is located in an area downstream of some heavy construction and has shown a steady decrease since 2001, perhaps due to dilution by clean sediments released during the course of construction. Figure 10F shows that overall arsenic concentrations have not changed substantially over three years in the upper half of the basin either (Appendix IV). Local changes were seen in sites CC40 and CC44 (Appendix IV). Site CC40 increased to a value above ERM while site CC44 declined in concentration. Concentration differences could be partially due to the difference in runoff during sampling (Figure 1). Unfortunately we do not have previous data for Scorpion Gulch and America Gulch and therefore cannot assess changes through time in the most highly concentrated areas.

**Cadmium:** Figure 14A shows that cadmium is only elevated in the upper basin and tributaries draining into Whiskeytown Lake. Figure 14B shows concentrations in lower Clear Creek are mostly at or below background. CC27 & CC31(Appendix IV), located in the Gorge, have concentrations close to the ERL (1.2 mg/kg) but are still far below the ERM (9.6 mg/kg). Figure 14C, shows that the highest concentrations of cadmium are located in the Whiskeytown tributaries. The most contaminated sites are in Whiskey Creek (19.2 mg/kg, Appendix IV), with values exceeding twice the ERM (9.6 mg/kg). Figure 14D shows that below river mile 16 all sites are at or below

background. If just taking 2003 data into consideration this would reach up to river mile 21 (Figure 14F). At ~21 river miles, sampled tributaries, including Whiskey Creek and Mad Ox Gulch, converge with Clear Creek just upstream from the lake. Concentrations from these tributaries are up to 25 times background, far exceeding levels that have toxic effects on biota. The basinwide distribution of cadmium is shown in Figures 15, 16 and 17.

Figure 14E & 14F show that overall cadmium concentrations of the Clear Creek basin have not varied substantially over the three years of this study. Figure 14E shows two sites with concentrations above the ERL in 2002. These sites had concentrations at or below background in 2001 and 2003 (Appendix IV), which suggests the change could have been due to the time of sampling or some other transient response. Figure 14F shows variable cadmium concentrations from year to year throughout the upper half of the basin. Samples collected in 2002 show a similar trend of having slightly higher values than samples collected in 2001 and 2003, again probably due to the difference in discharge previous to the sampling event (Figure 1). Unfortunately we do not have 2003 data for the site with the highest cadmium value and therefore do not know if it responded to the high flows.

**Chromium:** Figures 18A shows that chromium is fairly low in the Clear Creek drainage basin when compared to the baseline value. This is a result of the relatively high background value used for chromium that may be due to naturally elevated chromium concentrations in the tributaries chosen for background. Only one site is notably prominent, New York Gulch (WT05/NYGL, Appendix IV). However, this site is still far below the NOAA ERM (370 mg/kg). Figure 18B shows that the highest concentration in the lower half of the basin comes from one of the baseline tributaries (Appendix IV). As mentioned previously this higher value at CC28 may be due to a local geologic source of chromium. There are two other sites in the main stem that are above ERL, CC29 & CC27 (Appendix IV), both in the gorge. However, these values are both below our designated baseline. Figure 18C shows three areas at or above ERL in the Whiskeytown reach, New York Gulch (209 mg/kg), Liberty Gulch (109 mg/kg), and Brandy Creek (89.4 mg/kg, the other baseline tributary). Figure 18D shows that all

but three of the sites in the Clear Creek basin are below background, which suggests that possible chromium contamination is of little concern. In fact most sites are below the local background values. A transposed trend is seen with chromium compared to other metals where the lowest chromium concentrations are found in the tributaries of Whiskeytown and Upper Clear Creek with slightly higher values found downstream. Figures 19-21 show the aerial distribution of chromium in the basin.

Figures 18E & F show that there are two areas in which concentrations of chromium have increased over the time of this study. The two tributaries in the gorge that were used for background values and New York Gulch (Appendix IV), in Whiskeytown. New York Gulch is the highest site in the basin and could become a potential concern to biota.

**Copper:** Figure 22A shows that the greater part of the Clear Creek basin has copper concentrations just slightly above background (34 mg/kg) and ERL (40.8 mg/kg) with three tributaries in the upper half of the basin at or above ERM (270 mg/kg). Due to the scale of several plots a solid black line has been chosen to represent both background and ERL. Figure 22B shows that copper concentrations, within the lower half of the basin, are all fairly low but increase further upstream in the gorge. This data suggests that the risk of toxicity in the lower part of the basin is minimal but increases further up the basin. Figure 22C shows three tributaries are at or above ERM in the upper half of the basin. Willow Creek, Red Gulch, and Secret Squirrel Gulch (Appendix I) are located directly upstream of the lake and could have high potential for toxic effect within Whiskeytown National Recreation Area and the lake itself.

On the main stem of Clear Creek, at the town of French Gulch several tailings piles line the edges of the creek and copper concentrations increase downstream of these deposits (Appendix I). Above river mile 30.75 copper concentrations are consistently low then just beyond the French Gulch Trailer Park sites CC42, CC41, CC40 begin to gradually increase in copper. Clear Creek then converges with Willow Creek, the highest tributary, and sites CC38, CCAR, & CC39/CCBR (Appendix IV) begin to increase more rapidly in copper concentration. This data suggests that copper may be released from these tailings deposits and transported down stream then



additional more concentrated sediments join Clear Creek from Willow Creek, all of which are then transported towards the lake. This increase is very noticeable on Figure 22D. Figure 22D shows that the majority of sites within the basin are between 1 and 3 times background, three sites in the upper basin (CC37, WT12, & REDG, Appendix IV) have levels over 10 times background.

Figure 22E & F show that overall copper concentrations in the Clear Creek basin have not changed substantially since 2001, except at two sites in the gorge, (CC27 and CC31, Appendix IV). CC31, as mentioned above, is down stream of a construction site, which could be releasing clean sediments. The aerial distribution of average copper concentrations is illustrated in Figures 23-25.

**Lead:** Figure 26A shows that lead concentrations are elevated beyond baseline throughout the basin and that the highest concentrations are in the tributaries that also have the highest arsenic values (Appendix IV). Figure 26B depicts lead in the lower half of the basin, where all values are below ERL (46.7 mg/kg) except one (CC30, Appendix IV), which lies on the boundary. Although they are below values considered toxic to biota these sites are well above the measured baseline value (15.3 mg/kg). Figure 26C shows that the highest values are once again in upper Clear Creek tributaries. Similar to arsenic, the highest concentrations of lead are in Scorpion Gulch, which converges with French Gulch and then into Clear Creek at CC43, these sites have the second and third highest values, respectively (Appendix IV). Cline Gulch, America Gulch, Mad Ox, and Whiskey Creek are all similarly at or above the ERL (46.7 mg/kg). Figure 26D shows that most of the sites have lead concentrations between 2 and 10 times the local background but none are close to the ERM (218 mg/kg). This data suggests that although lead is elevated in the same sites that have elevated arsenic these sites do not show signs of potential lead effects according to NOAA criteria. Maps of the concentrations (Figure 27), enrichment factors (Figure 28) and threshold levels (Figure 29), show the spatial distribution of lead contamination in the basin.

Through time lead is behaving differently than metals previously discussed. Figures 26E and 26F show that lead concentrations have slightly increased throughout

the Clear Creek watershed. One site in the lower basin has almost doubled (CC13, Appendix IV). This site is just below the newly remidiated Reading Bar and just upstream of the site with the high arsenic value, CC14, which has remained consistent in lead concentrations since 2001 (Appendix IV). This higher concentration of site CC13 may again be due to other factors besides mining.

**Zinc:** Figure 30A shows that zinc is primarily elevated in the upper portion of the Clear Creek drainage. Figure 30B shows that although zinc is above baseline it is still fairly low by NOAA guidelines (ERL=150 mg/kg, ERM=410 mg/kg) in lower Clear Creek and the gorge. Figure 30C shows that a large number of sites in the upper part of the basin lie between the ERL and the ERM and several tributaries are above ERM. The highest zinc concentrations within the basin are in the tributaries at ~21 river miles along Whiskey Creek and Mad Ox Gulch (Appendix IV). Willow Creek also contained zinc concentrations above ERM. Figure 30D shows that the majority of sites in the upper basin range from 2-10 times the background, with tributaries far exceeding this value. Sites in the lower basin generally are from 1-3 times background and below the ERL. Aerial distribution (Figures 31-33) suggests that zinc is potentially a problem only the upper basin.

Figures 30E and 30F show that zinc concentrations have not varied substantially within the Clear Creek Basin over the time of the study except at sites CC27 and CC31 (Appendix IV). These are the only two sites in the basin that increased in zinc (and copper) concentrations in 2002 then decreased again in 2003 to similar concentrations as 2001. This data again suggests that the concentrations varied due to discharge previous to sampling.

**Mercury:** Figure 34A shows that mercury is elevated above background throughout the basin but is substantially higher in many of the tributaries upstream. Figure 34B shows that average mercury values are lower but quite variable in the lower half of the basin (Appendix IV). Most of the sites within the gorge are below ERL (0.15 mg/kg) but still above the designated baseline value (0.04 mg/kg). More variation in mercury concentration occurs in Lower Clear Creek where values are generally higher

than in the Gorge reach just upstream and lie above the ERL but are still well below the ERM. Based on the NOAA criteria these values are likely below those considered to have toxic effects on biota. Figure 34C shows that the highest values in the basin are found in four tributaries in the upper half (Appendix IV), all of which are above ERM and therefore may have high potential for toxic effects on biota. The high-mercury sites in the upper basin are mostly in French Gulch and Cline Gulch and in the main stem just downstream from the confluence with French Gulch (Appendix I). There are also high concentrations found in the lower part of Mad Ox Gulch but this appears to be very localized since samples taken above and below this site are found to be less than half the concentration of that at MDOX (Appendix IV). Figure 34D shows that the bulk of the basin has mercury concentrations between 2 and 10 times background. A small number of sites are at the background value and the high-mercury upstream tributaries have mercury concentrations reaching 20-30 times background. Mercury is elevated over background throughout the basin but may have low potential for toxic effects in many areas based on the NOAA criteria, especially the lower half of the basin (depending on the production of methylmercury from these sediments). The area at highest risk lies in the tributaries of Whiskeytown National Recreation area and Upper Clear Creek. This aerial distribution of mercury in the basin is shown in Figures 28, 29 and 30.

Figures 34E and 34F show the changes in mercury concentration over time. Figure 34E shows that of the sites sampled in 2003 there is one of particular concern, site CC01 (Appendix I and IV). This site is located directly down stream of a small active mining operation (Personal Communication from USBLM staff) and upstream of the newly remidiated section of Clear Creek at Reading Bar. The mercury concentration of this site was found to be 0.704 mg/kg in 2003 (Appendix IV) and is the only site in the Lower Clear Creek channel above ERM in the three years of sampling. Dilution of mercury seems to be occurring downstream from this site because mercury concentrations decrease exponentially through the Reading Bar reach. This high value at the farthest upstream site is in part the reason for the high variability in concentrations directly downstream. The next site upstream (~2 miles) of CC01 has much lower mercury concentrations so it is a likely that the source for the elevated

mercury at CC01 is upstream in the lowermost Clear Creek Gorge not within Lower Clear Creek proper.

**Selenium:** Figure 38A shows selenium concentrations throughout the basin collected in 2003 (selenium was not analyzed in 2001 and 2002). Concentrations through most of the Clear Creek basin are above background. About half of the sites in the basin are above the Apparent Effects Threshold (AET= 1mg/kg). The AET was used for selenium because there are no ERL and ERM values available from NOAA. The AET value is equivalent to the concentration of the highest non-toxic sample and therefore anything beyond this value would be toxic to specific biota. The value here represents concentrations above which effects would be seen on amphipods. Figure 38B shows that within the lower half of the basin the highest concentrations are within the gorge and in the Reading Bar area, concentrations decrease further downstream. Almost two-thirds of the sites are above the AET. Figure 38C show that the area of most concern are is in the tributaries at river mile 21.15, Whiskey Creek and Mad Ox Gulch, have high concentrations of selenium and may have a high potential for biomagnification and toxic effects. Concentrations reach up to 10.5 mg/kg at site WCMM and 4 mg/kg at WCUM and MXUS (Appendix IV). Figure 38D shows that Whiskey Creek is 25 times background concentrations and should be considered a potential risk for selenium toxicity. Most other sites within the basin are between 1 and 5 times background. Figure 39-41 show the basinwide distribution of selenium from the 2003 sampling period.

## **SITES OF POTENTIAL CONCERN**

**Upper Clear Creek:** Certain areas within the Upper Clear Creek basin are of more concern than others for potential effects on biota. The distribution of metals discussed above indicate that Scorpion Gulch and America Gulch along with the tributaries they flow into, French Gulch and Cline Gulch, respectively, have substantially elevated concentrations of arsenic, lead, and mercury (Figures 10C, 26C, 34C and Appendix IV)). Downstream, Willow Creek has the highest copper concentrations of the entire basin and is also the only area in the upper basin to have

zinc concentrations above the ERM (Figures 22A, 30C and Appendix IV). Cadmium concentrations in the Upper basin are somewhat elevated above background but not near the levels just downstream in the Whiskeytown reach of the study (Figure 14C). Chromium concentrations are low in this reach of the basin and therefore not likely of concern (Figure 18C). Selenium is somewhat elevated in this area with all sites having concentrations above background and several above the AET.

**Whiskeytown:** Tributaries of Whiskeytown including, Whiskey Creek, Mad Ox Gulch, Red Gulch, and Secret Squirrel Gulch have elevated concentrations of cadmium, lead, zinc, and mercury (Figures 14C, 26C, 30C, 34C, and Appendix IV). Chromium concentrations are at or below background at all sites in Whiskeytown except New York Gulch, where it is high (Figure 18C). Red Gulch and Secret Squirrel are elevated in copper (Figure 22C). Although copper is definitely still a concern in Secret Squirrel Gulch it has decreased since the 2002 sampling (Figure 22D and Appendix IV). Arsenic is somewhat elevated in the tributaries of Whiskeytown but it is not elevated as much as other contaminants (Figure 10C). The only part of the basin with substantially elevated selenium concentrations are found in the Whiskeytown reach of the basin (appendix IV). Selenium is elevated in Whiskey Creek and Mad Ox Gulch and should be considered a potential risk in these areas (Figure 38C). These tributaries ultimately flow into Whiskeytown Lake and so offer a potential metal contamination source to the lake sediment, water and biota.

**Clear Creek Gorge:** Overall, sites in the Gorge reach of the study were relatively low in metal concentrations. At the Peltier Bridge site and the site downstream of Orofino Gulch (CC27 and CC31, Appendix IV) cadmium and zinc increased in 2002 but again declined in 2003 to similar values found in 2001 (Figures 14E, 26E and Appendix IV). The changes in concentration at these two sites may be due to the difference of flows prior to sampling (Figure 1). In 2001 and 2003 sampling occurred subsequent to higher flow events while 2002 sampling occurred during a continuous low flow. At site CC27 copper progressively increased over the last three years (Appendix IV). This site has the highest average copper concentration of the

lower half of the basin but this value was still quite low compared to the ERM (Figure 22B). Unlike site CC27, copper has decreased at site CC31 since 2001. Site CC30 is somewhat elevated in lead (Figure 26B). Three sites within the gorge are elevated above AET (Figure 38B).

**Lower Clear Creek:** Due to extensive ongoing restoration efforts in Lower Clear Creek understanding metal distribution in this section of the drainage is important. Samples were collected throughout this reach to determine if metals are elevated. Overall, metal concentrations were relatively low in this part of the basin when compared to the upper basin sites, with a few local areas having metal concentrations of potential concern.

The highest concentration of mercury in Lower Clear Creek was found upstream of the newly rehabilitated area at Reading Bar (Figure 34B and Appendix I). Site CC01 (Appendix IV) is the only site in Lower Clear Creek above the ERM for mercury. This site is located just downstream of an active mine (Personal Communication from USBLM staff). The next site upstream of the mine has lower concentrations of mercury suggesting that possibly the elevated mercury at this site are originating from the lowermost gorge in the vicinity of the mine site. Concentrations found in 2002 and 2001 were much lower at this site (Appendix IV).

Several other sites in Lower Clear Creek have increased somewhat in mercury concentration over the time of the study including CC02, CC03, CC05, CC07, and CC09, while others in between have slightly decreased or stayed the same (Appendix IV). Overall, mercury concentrations of the Lower Clear Creek basin are variable, with higher values being very localized and rarely reaching the ERM for mercury.

Zinc concentrations in the lower basin are relatively low and have not varied much over the time of the study (Figure 3D). Only two sites have values at the ERL (CC13 and CC15, Appendix IV). Site CC13 was the only site in the lower basin to contain lead concentrations at the ERL in 2003 with other sites having values just slightly above background. This site also had the highest copper and chromium concentrations in the lower basin (Figures 22B, 18B, and Appendix IV). Just upstream of this site at CC14 arsenic concentrations were relatively high in 2003. This

contamination was extremely localized and probably not mining related. Chromium and selenium are not contaminants of concern in Lower Clear Creek.

## CONCLUSIONS

Examination of the distribution and changes in fine-grained bed sediments along with comparison of sediment quality guidelines and general background values can help identify areas which may have potential toxic effects on biota. In the Clear Creek basin no one metal is of concern throughout the basin but certain metals are of more concern in specific areas. Arsenic, lead and mercury are the primary concerns in the upper basin tributaries. Cadmium, lead, zinc, mercury, and selenium are the main issues in the Whiskeytown tributaries. Some copper is likely being released from the tailings piles south of French Gulch along the main stem of Clear Creek. The tributaries supply the metals mentioned above to Clear Creek where they are eventually transported and deposited into Whiskeytown Lake.

Clear Creek Gorge had relatively low concentrations of contaminants and only one site is of possible concern, sediments collected at Peltier Bridge on the main stem of Clear Creek have progressively increased in copper concentrations over the last three years, but are still relatively low when compared to the upper basin sites.

Lower Clear Creek, in general had less contamination than in the upstream sites. However, some localized areas had elevated metal concentrations. Upstream of the newly restored area at Reading Bar mercury concentrations were elevated in 2003 sampling and may be of concern. Arsenic is elevated at one point in the middle of a reach. One site, just downstream of the restoration area, has slightly elevated levels of zinc, lead, copper, and chromium.

At the basin scale, mercury was substantially elevated over background concentrations throughout the Clear Creek drainage. About three-fourths of the samples had mercury concentrations between 2 and 10 times the background values. Other contaminants including arsenic, copper, lead and zinc were commonly found between 1 and 10 times background. Chromium values tended to be the inverse of most other contaminants with the lowest concentrations found in the tributaries of the upper half of the basin, which normally contained the highest values of other metals. High

concentrations of metals are commonly found downstream of active/abandoned mines throughout the basin and they represent a substantial source of metal contamination to the headwaters of Clear Creek.

## **ACKNOWLEDGEMENTS**

Funding for this work came from two cooperative agreements between the University of Montana and the National Park Service and the U.S. Geological Survey. The data from the work for two agreements have been combined in this report to give a broader understanding of contamination in the Clark Creek watershed. Without this joint support this project would not have been possible. A special thanks goes to the staff of the University of Montana, Geology Analytical Laboratory including Heiko Langer, Donna Smith, and Nate Stevens for all their help during chemical analysis. Christine Dively and Kendall Beane-Crowder spent many hours helping in the field. Brian Collins' extensive GIS knowledge helped with map production. Many people at the various agencies working in the basin also helped extensively. Michael Harris at Western Shasta Conservation Personnel and Daniel Fehr of California Fish and Game were instrumental in helping us locate sites and sample in Lower Clear Creek. Similarly, in the upper basin, personnel at Whiskeytown National Recreation Area (WNRA) were essential to sampling within the park boundaries. Jennifer Gibson (Park Ecologist at WNRA) was instrumental in all aspects of the work in the Park and planning sampling programs. Roger Hothem and Jason May and their colleagues from the US Geological Survey were instrumental in all aspects of the fieldwork and helped sample tributaries in WNRA. We also thank all the landowners who gave permission to cross their land to sample in Clear Creek and other agency personnel who answered questions about access and locations of potential sampling sites.



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**Figure 1:** Squares located above the hydrograph represent sampling dates. Discharge data from the U.S. Geological Survey.

### Average Daily Discharge in Clear Creek at Igo, CA

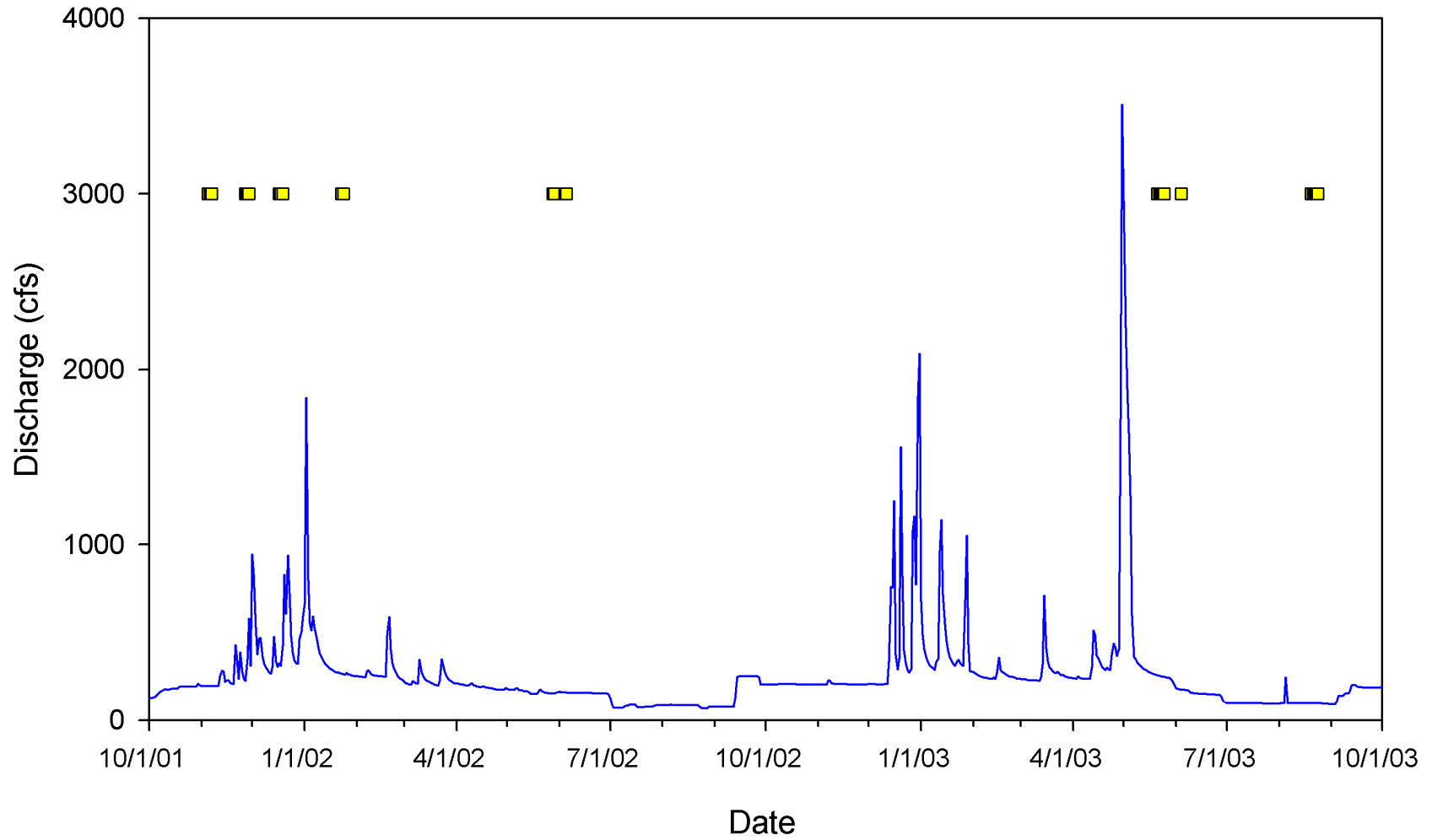


Figure 2:

### Geology of the Clear Creek Watershed

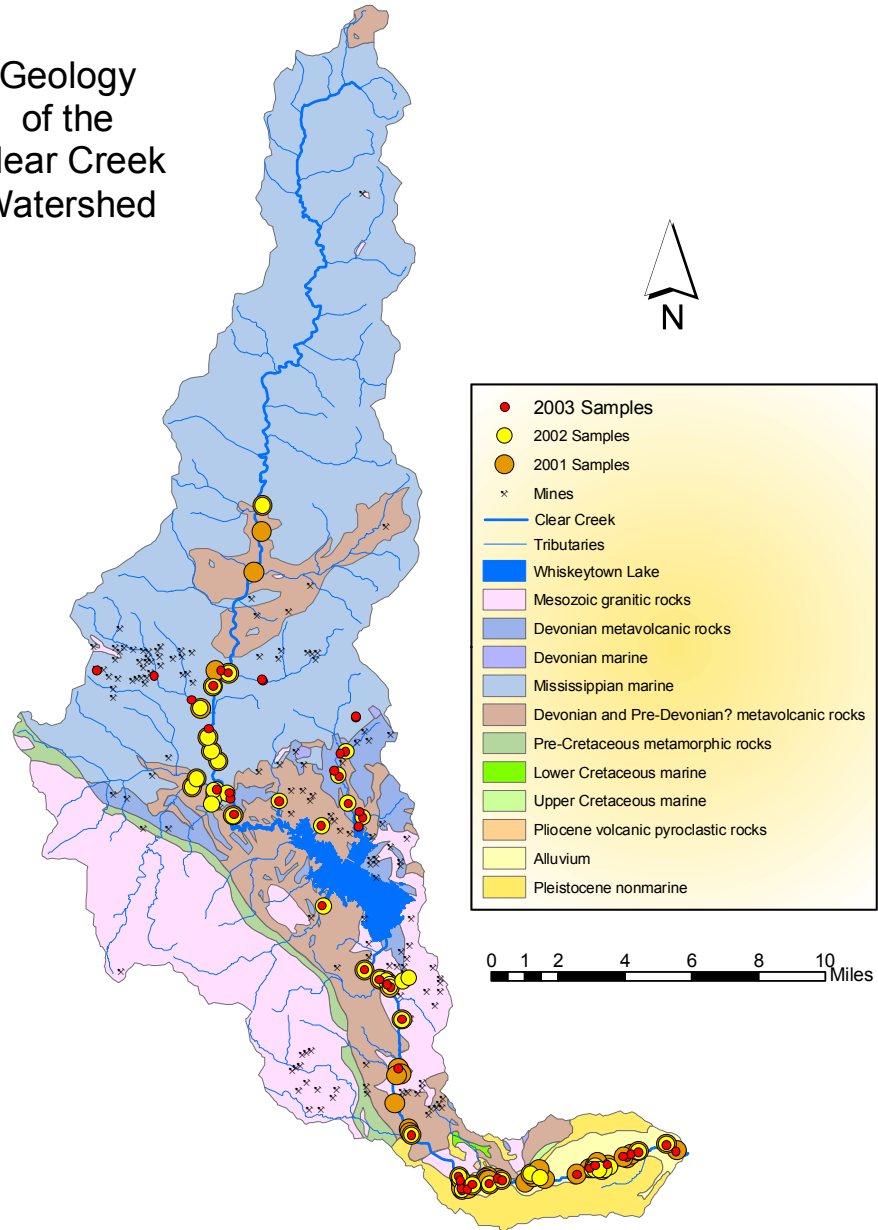


Figure 3: Sampling Locations

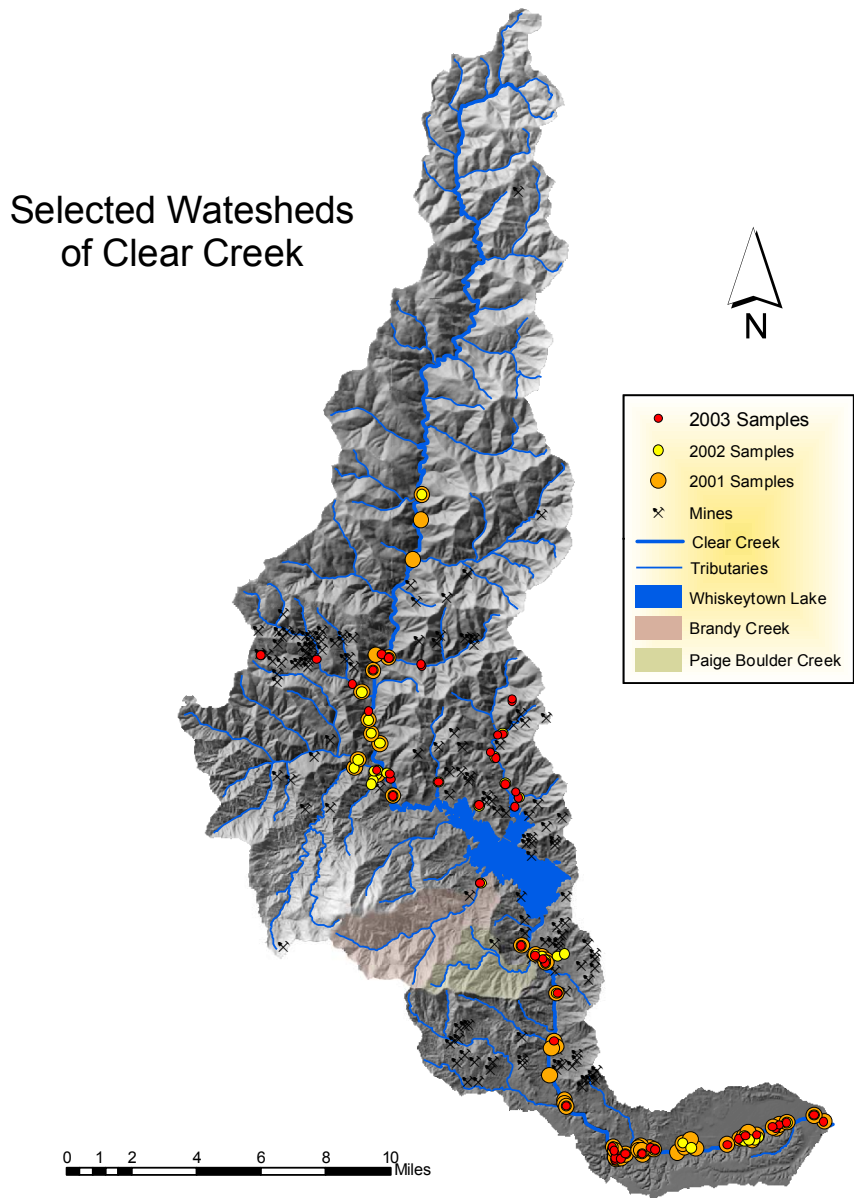


Figure 4: Sampling Reaches

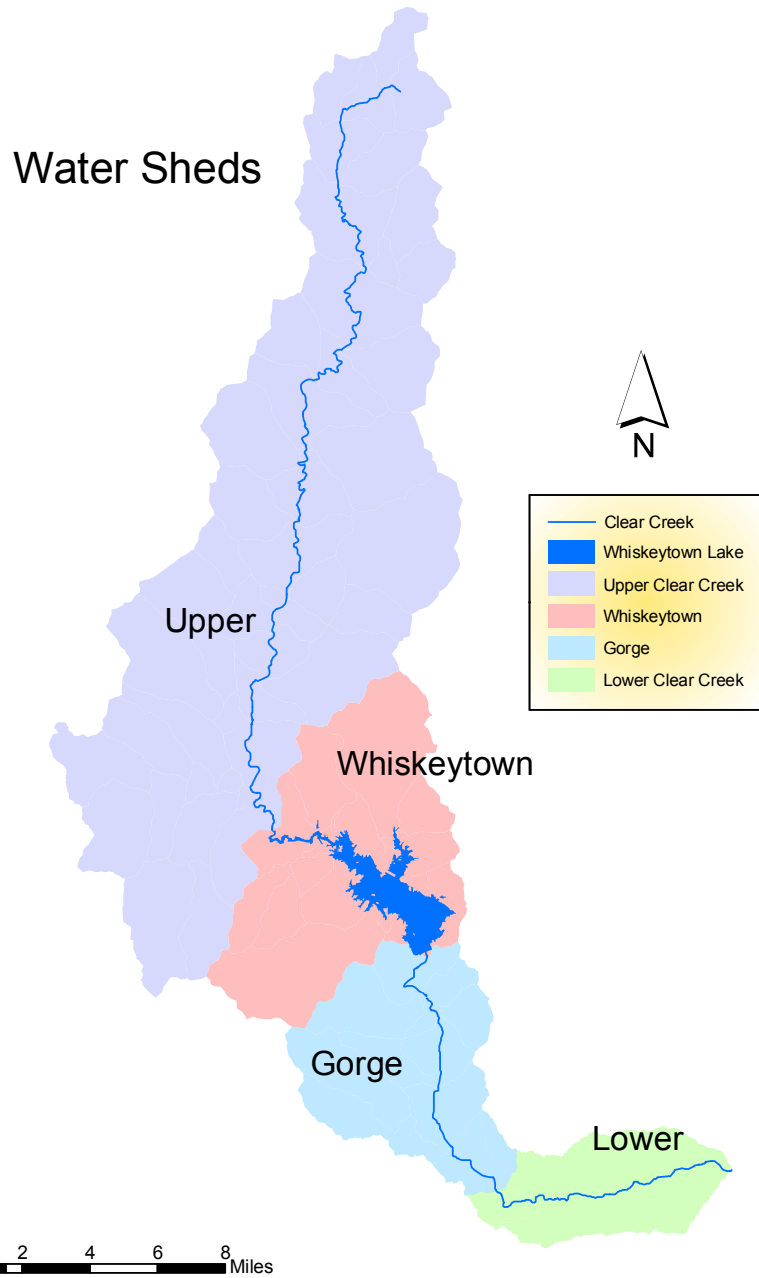


Figure 5: Upper Reach

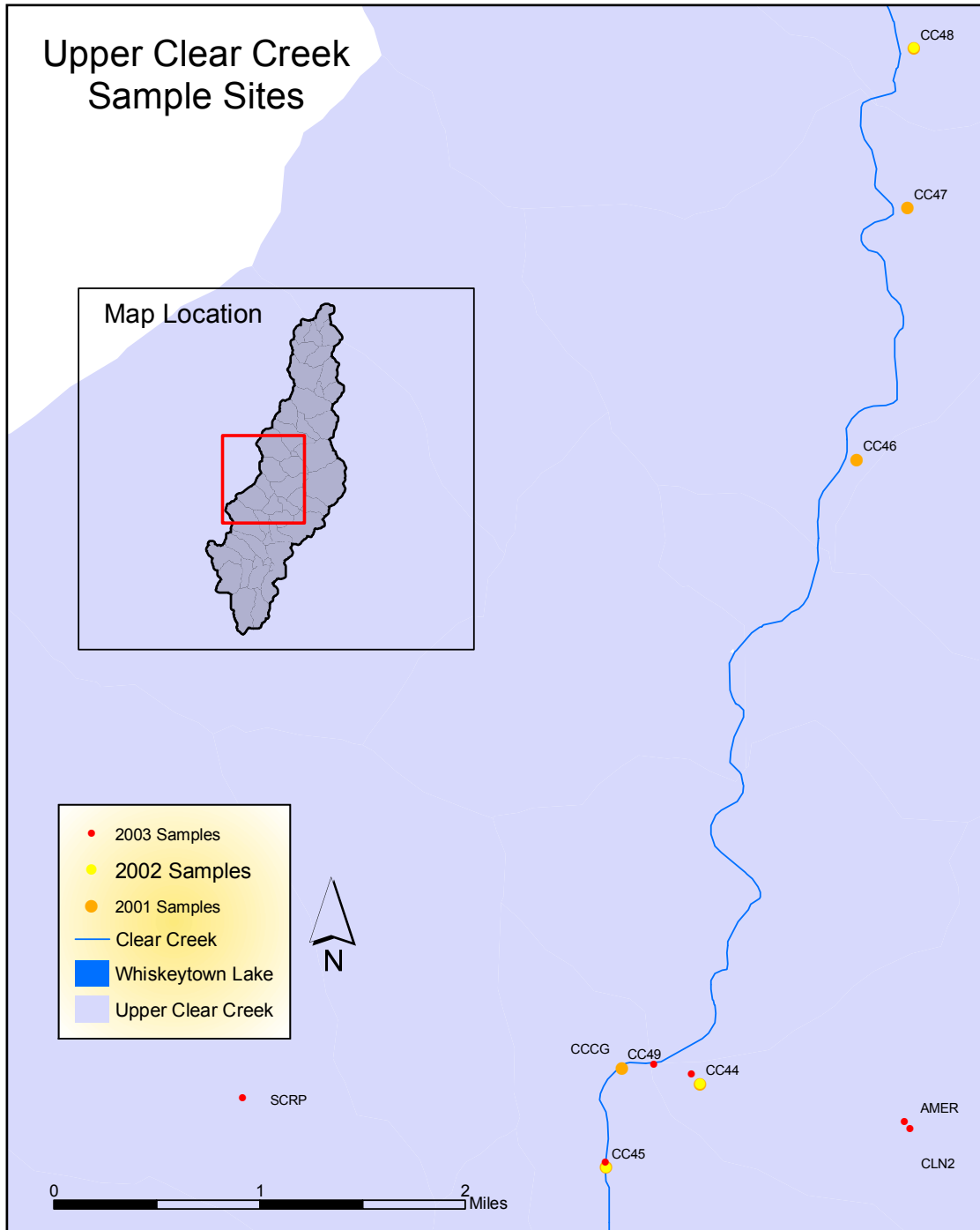


Figure 6: Upper Reach

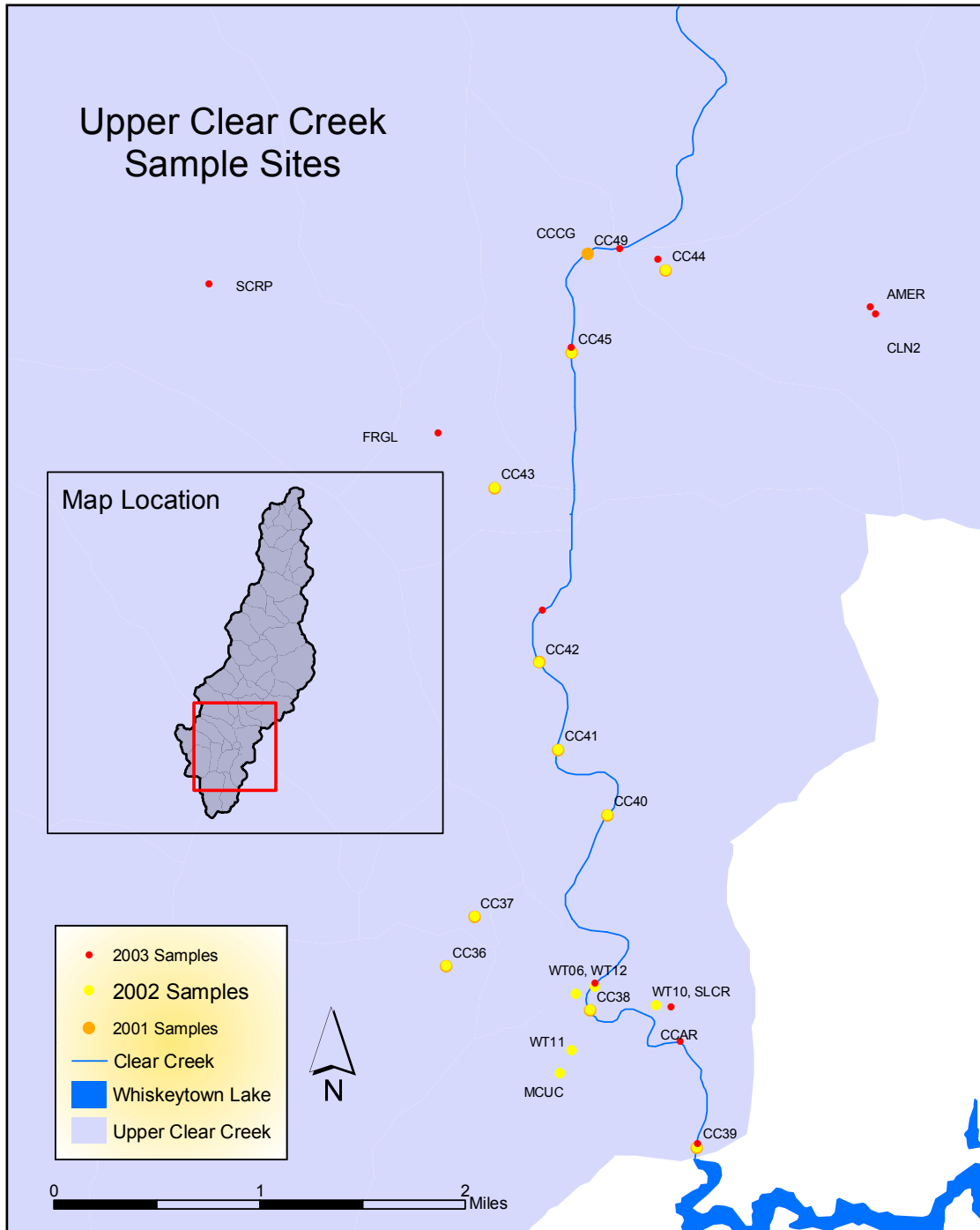




Figure 7: Whiskeytown Reach

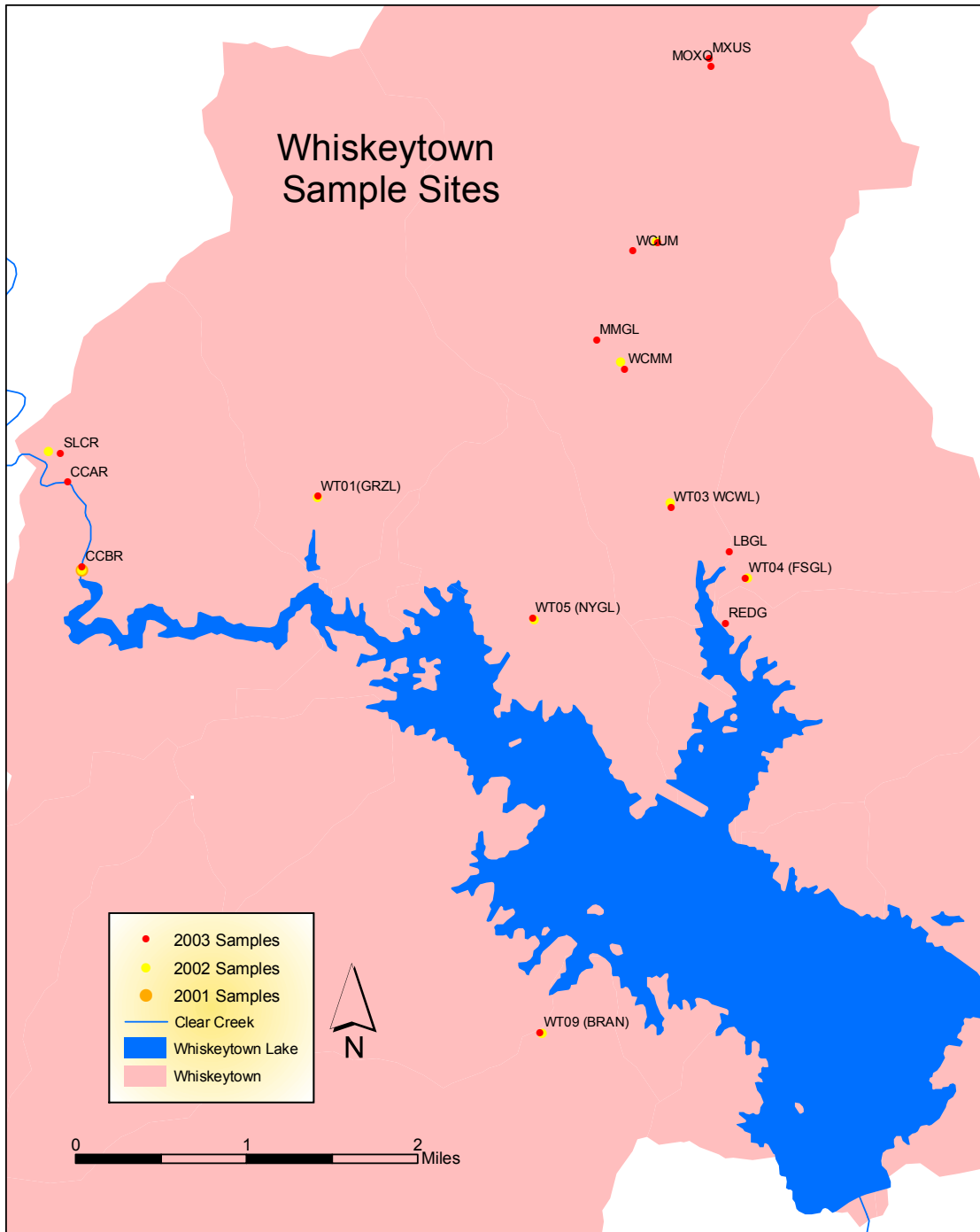


Figure 8: Gorge Reach

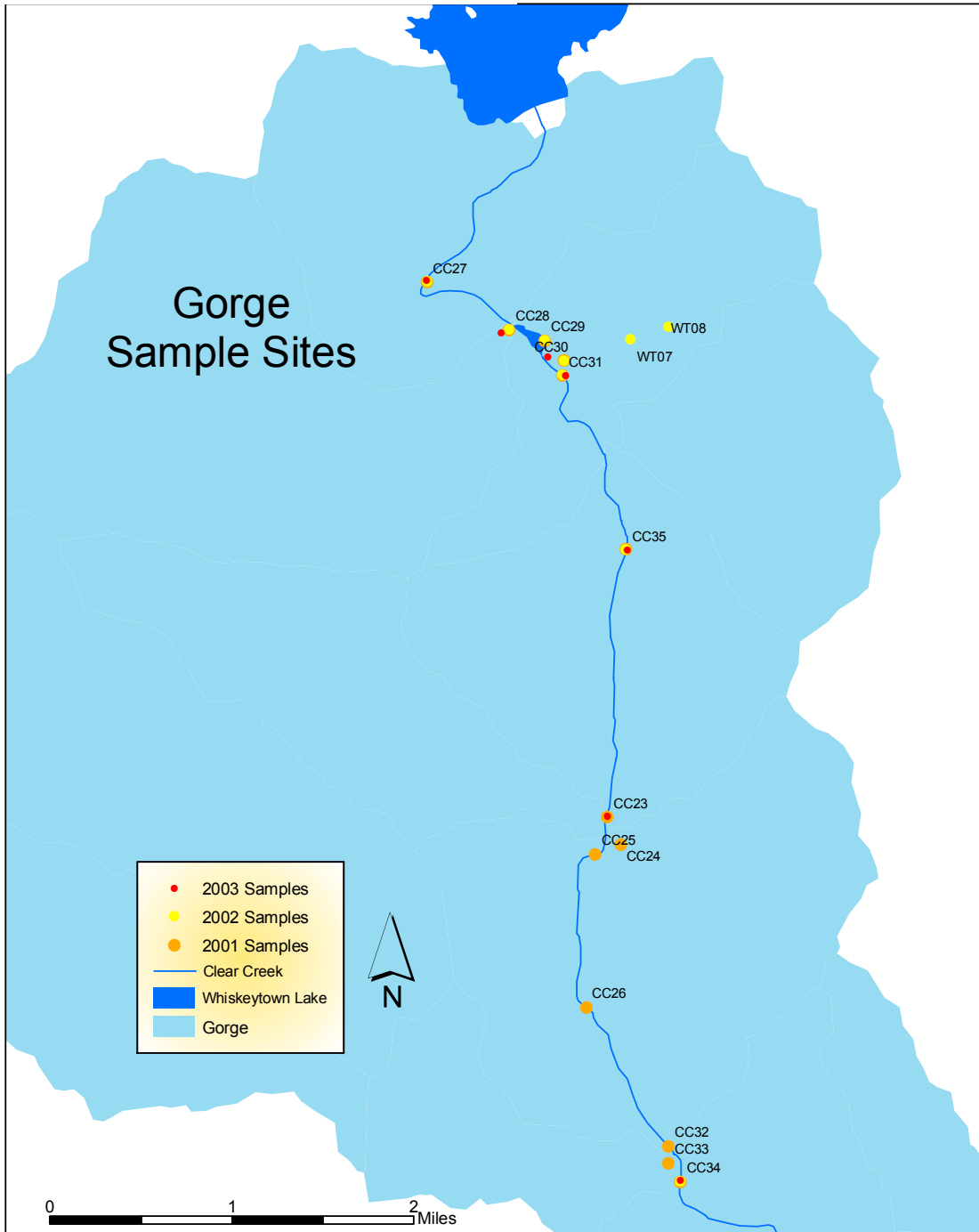


Figure 9: Lower Reach

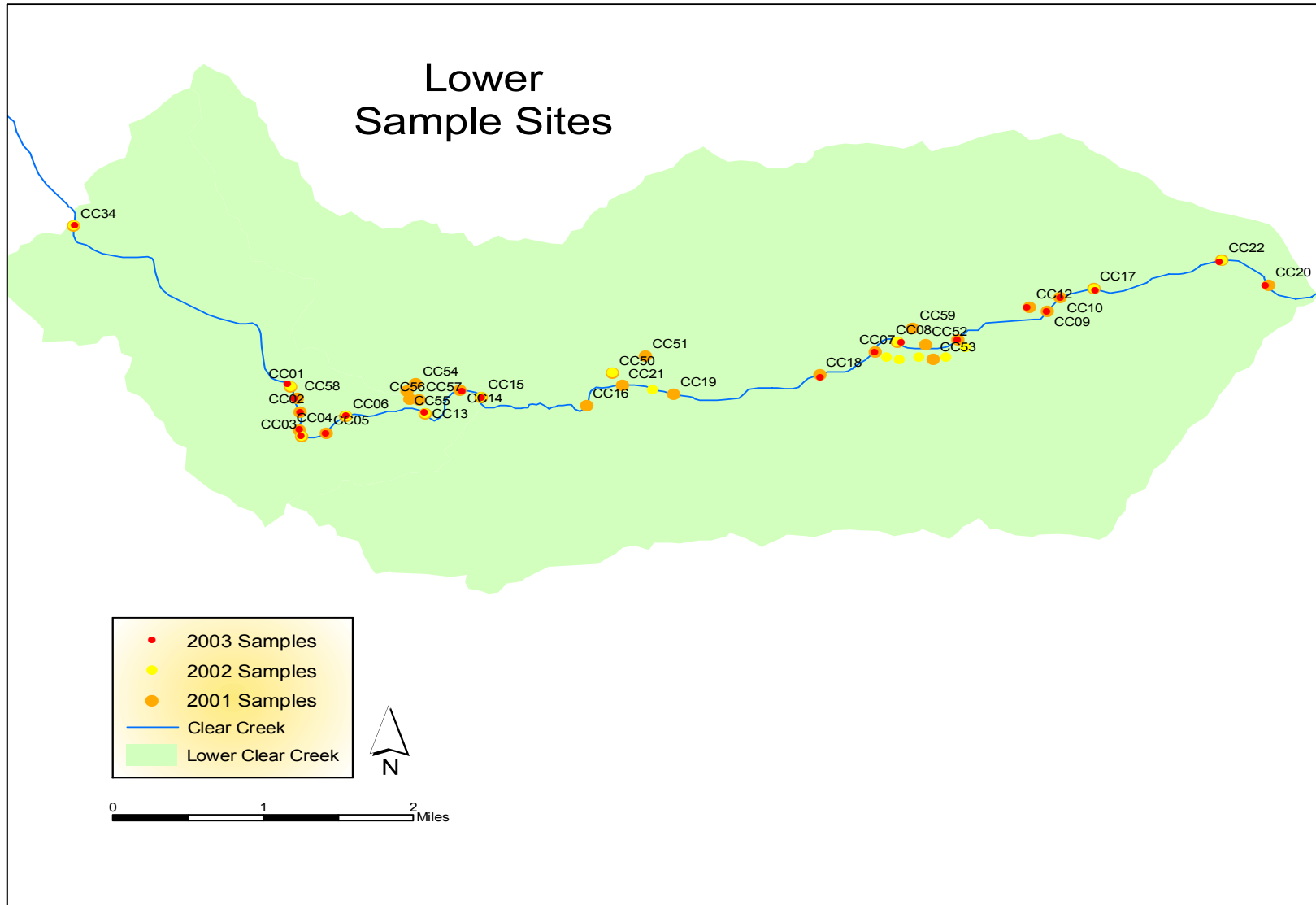


Figure 10A

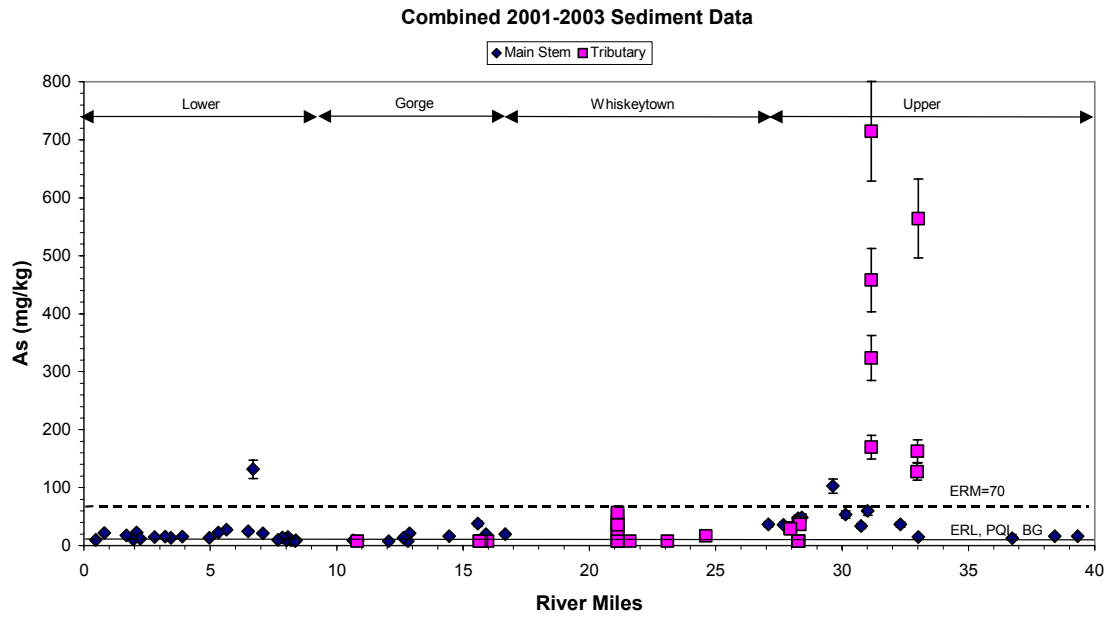


Figure 10B

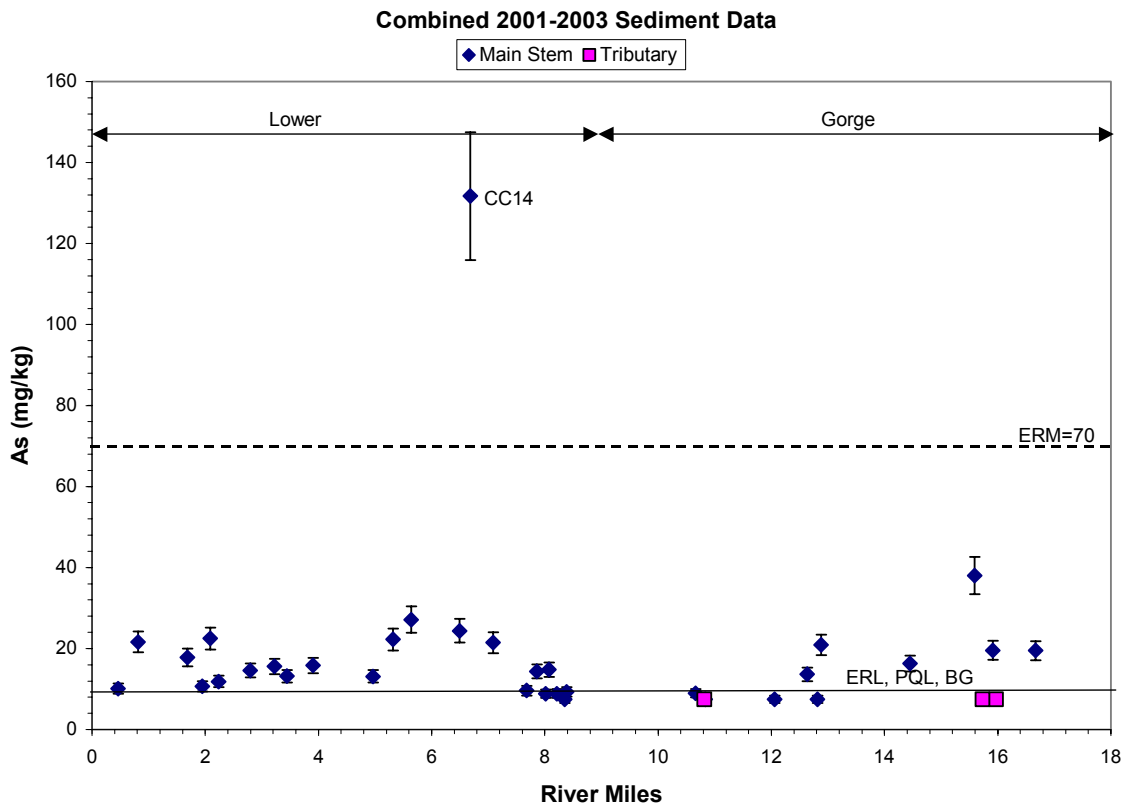


Figure 10C

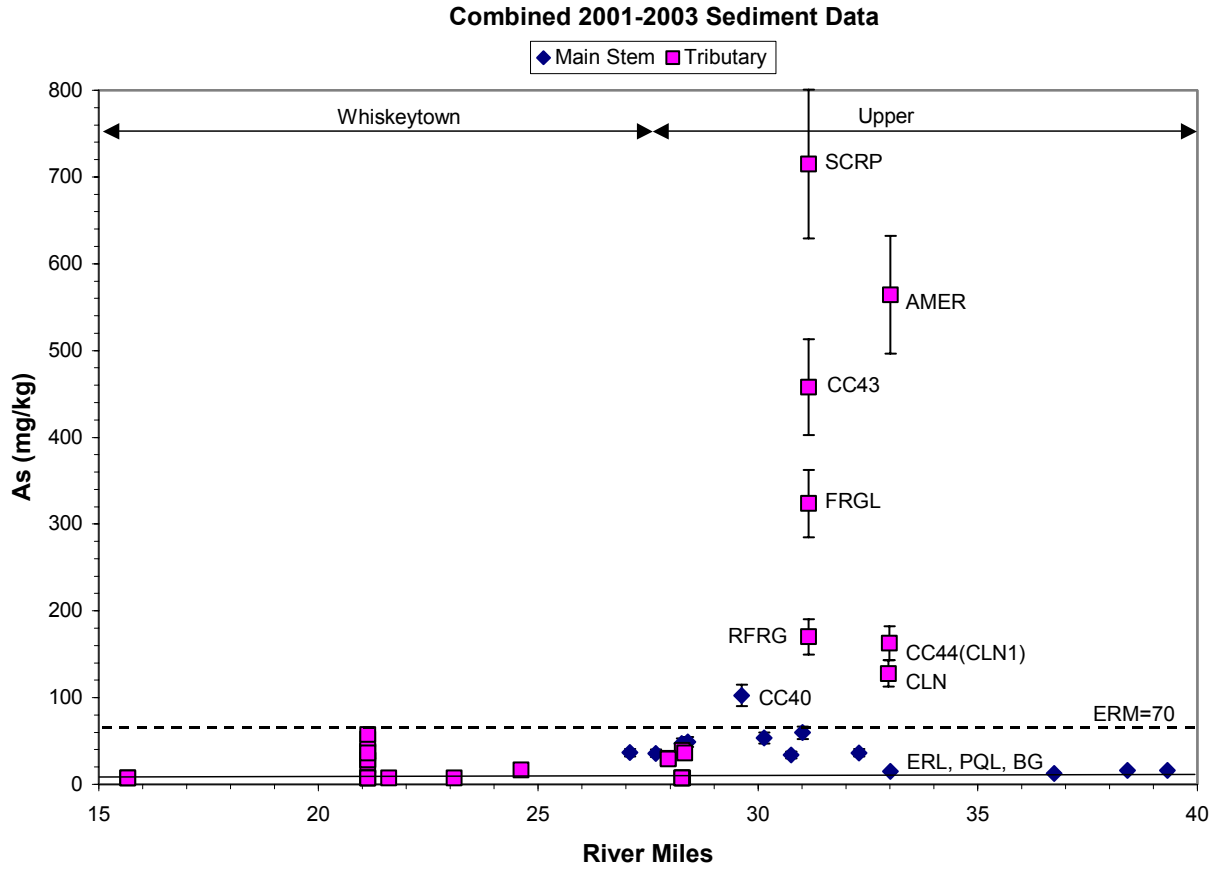


Figure 10D

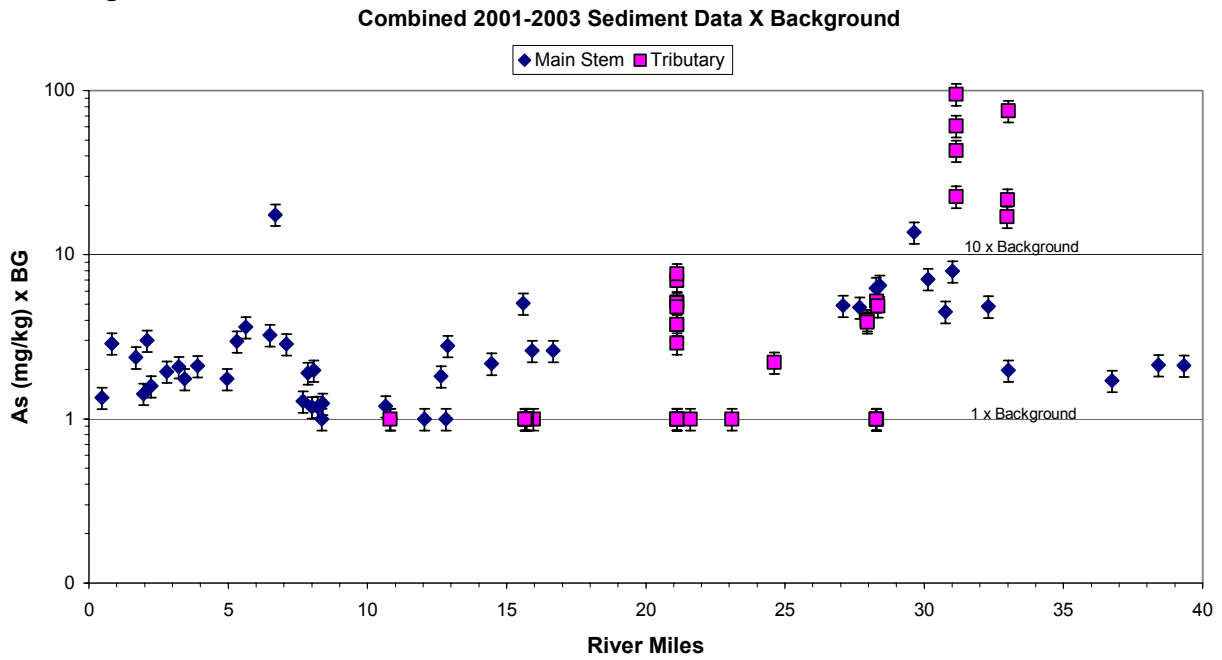


Figure 10E

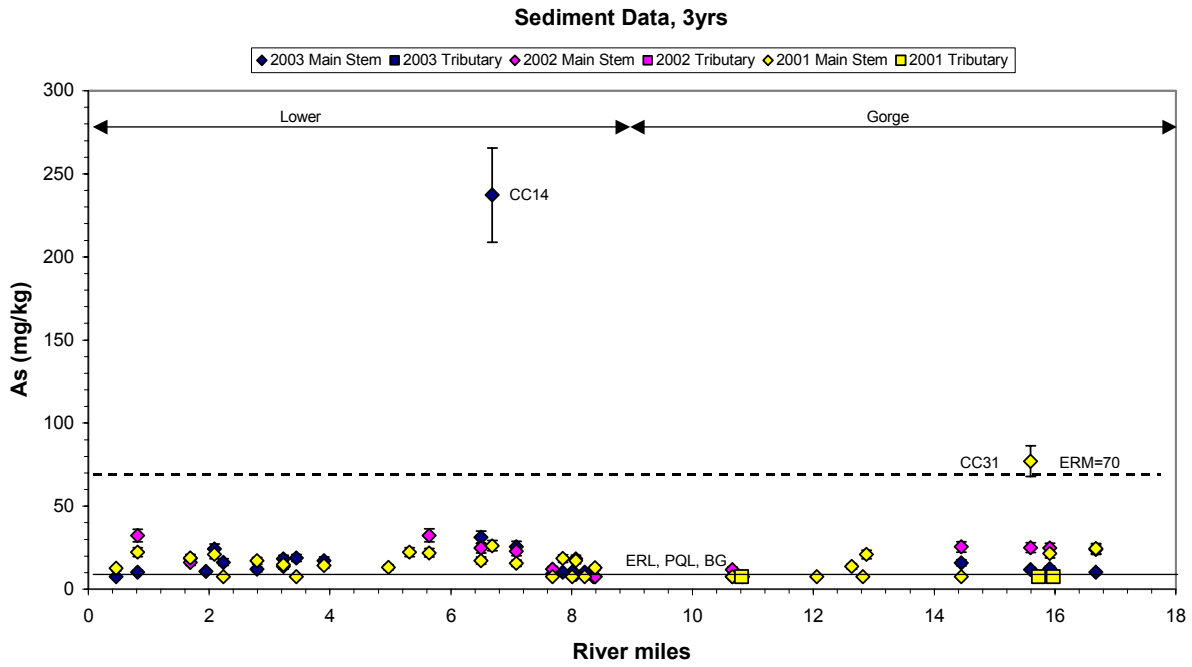


Figure 10F

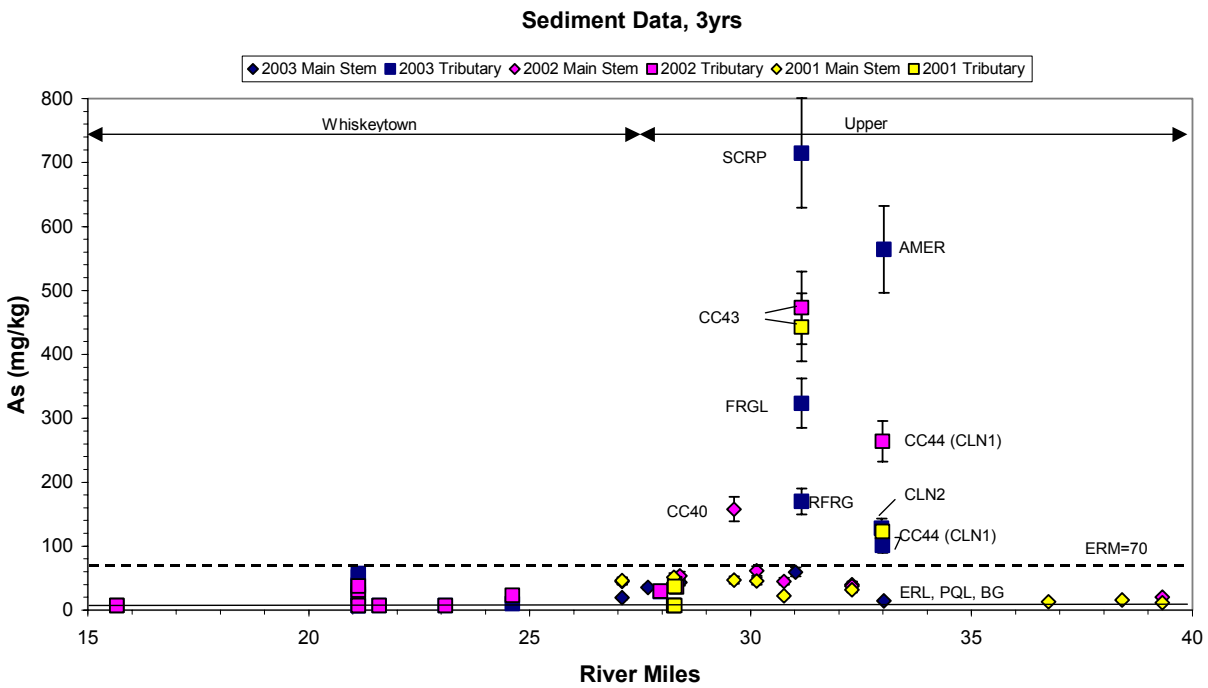


Figure 11

### Metal Concentrations: As Clear Creek Watershed, CA

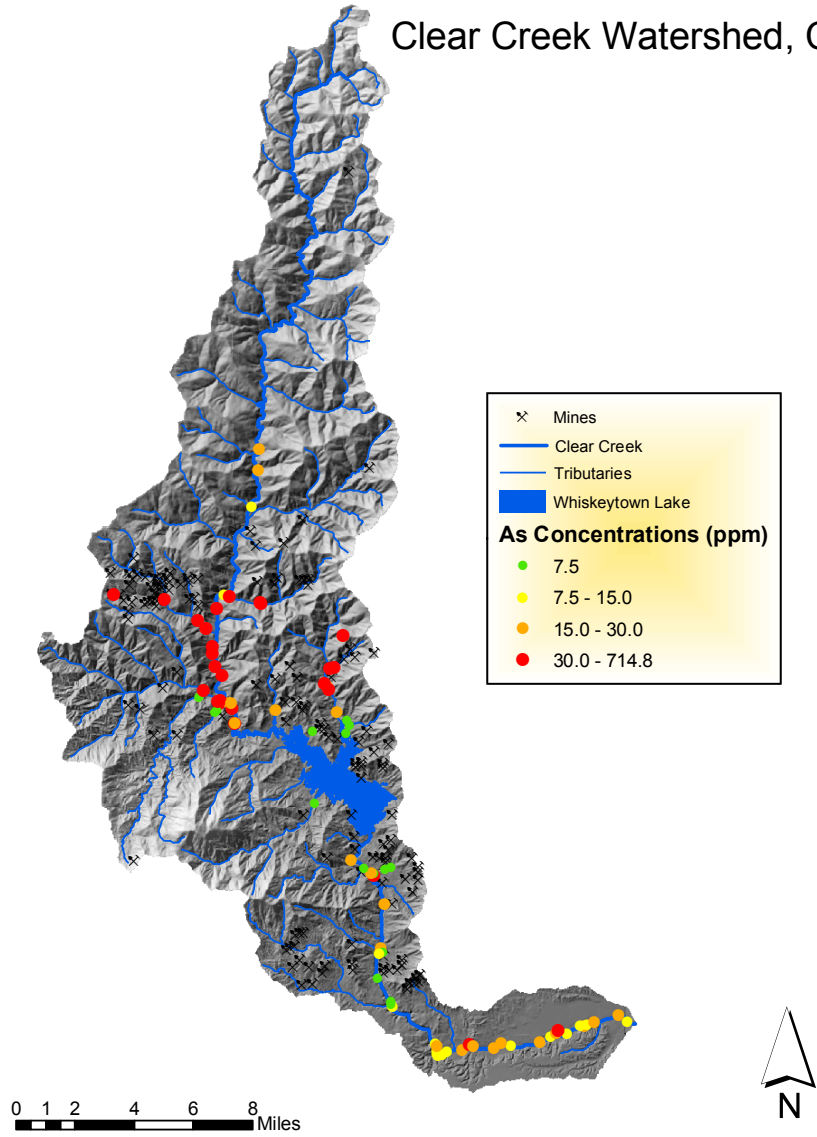


Figure 12

### Threshold Effects Concentrations: As Clear Creek Watershed, CA

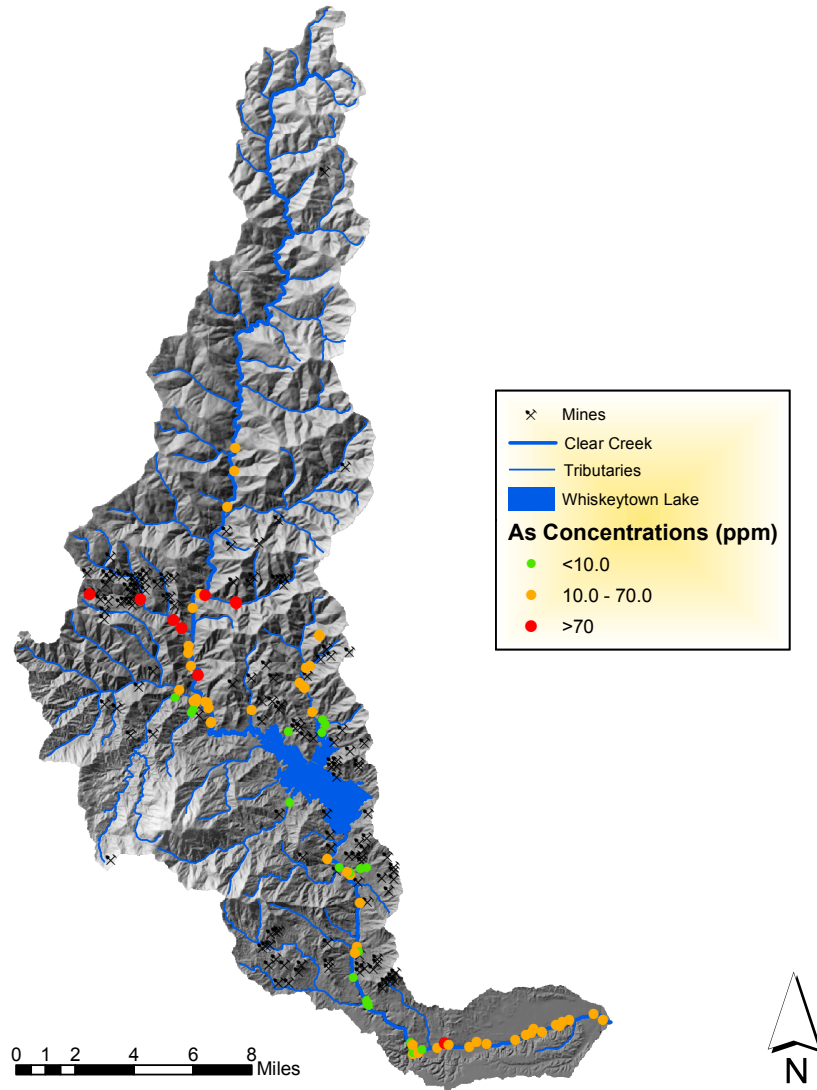




Figure 13

### Multiples of Background: As Clear Creek Watershed, CA

As Background= 7.5 ppm

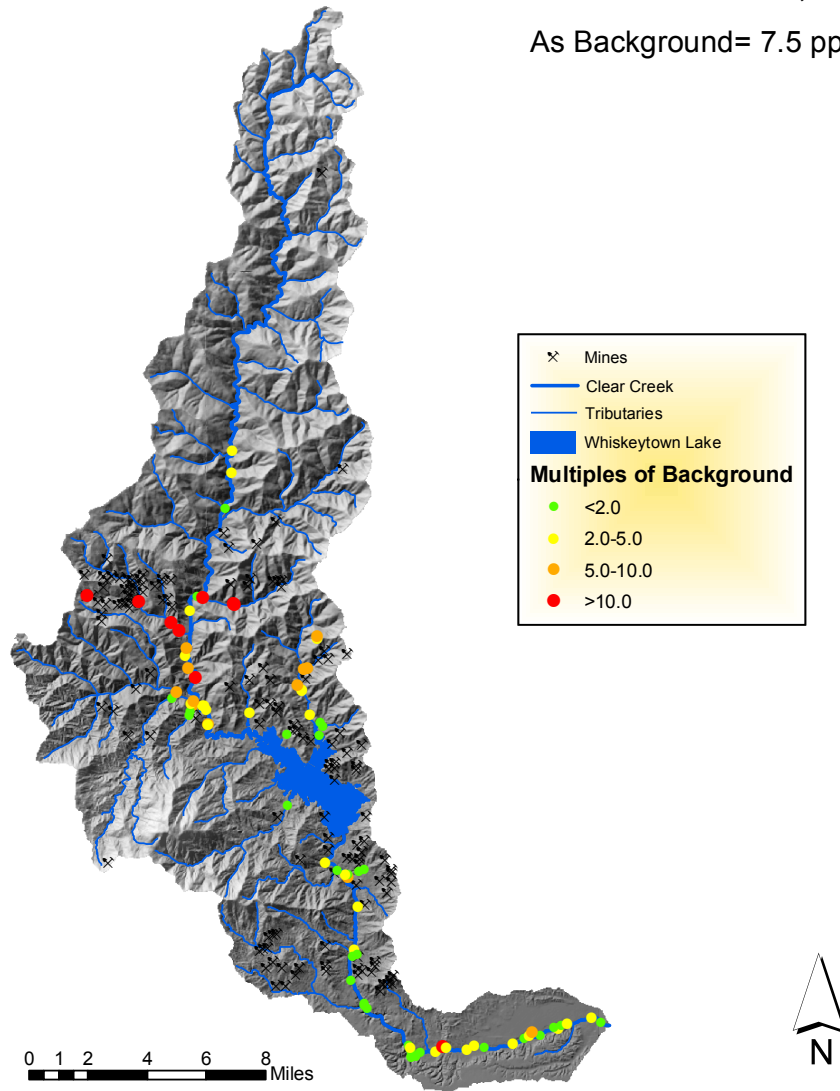


Figure 14A

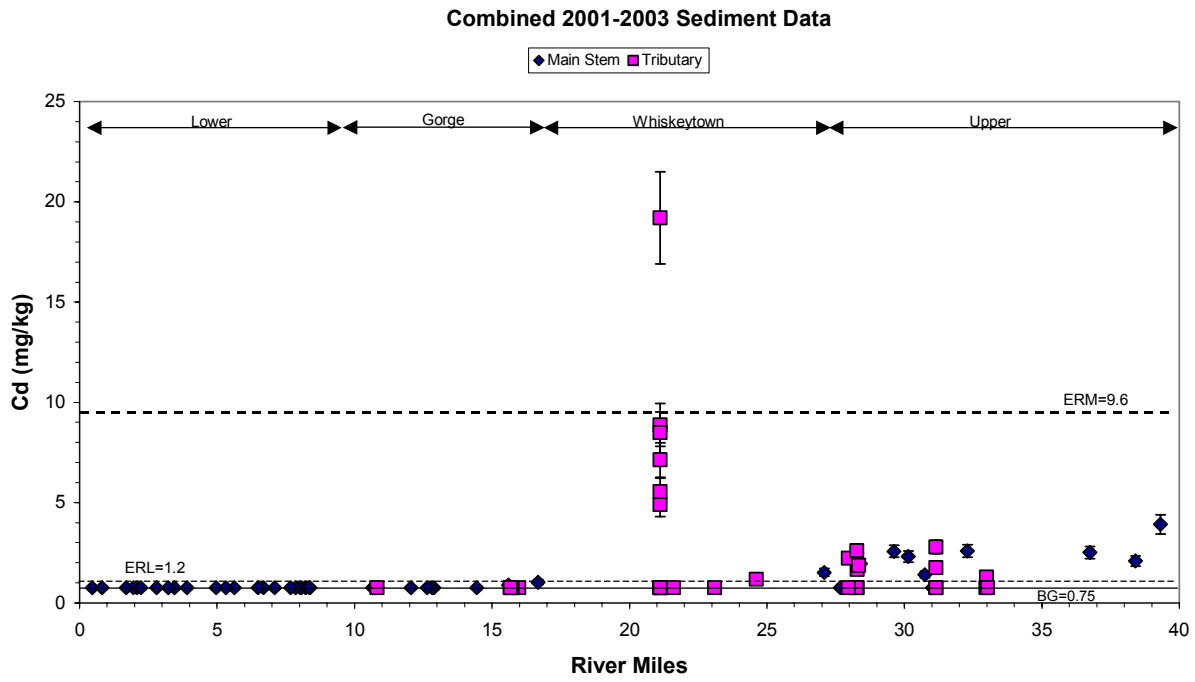
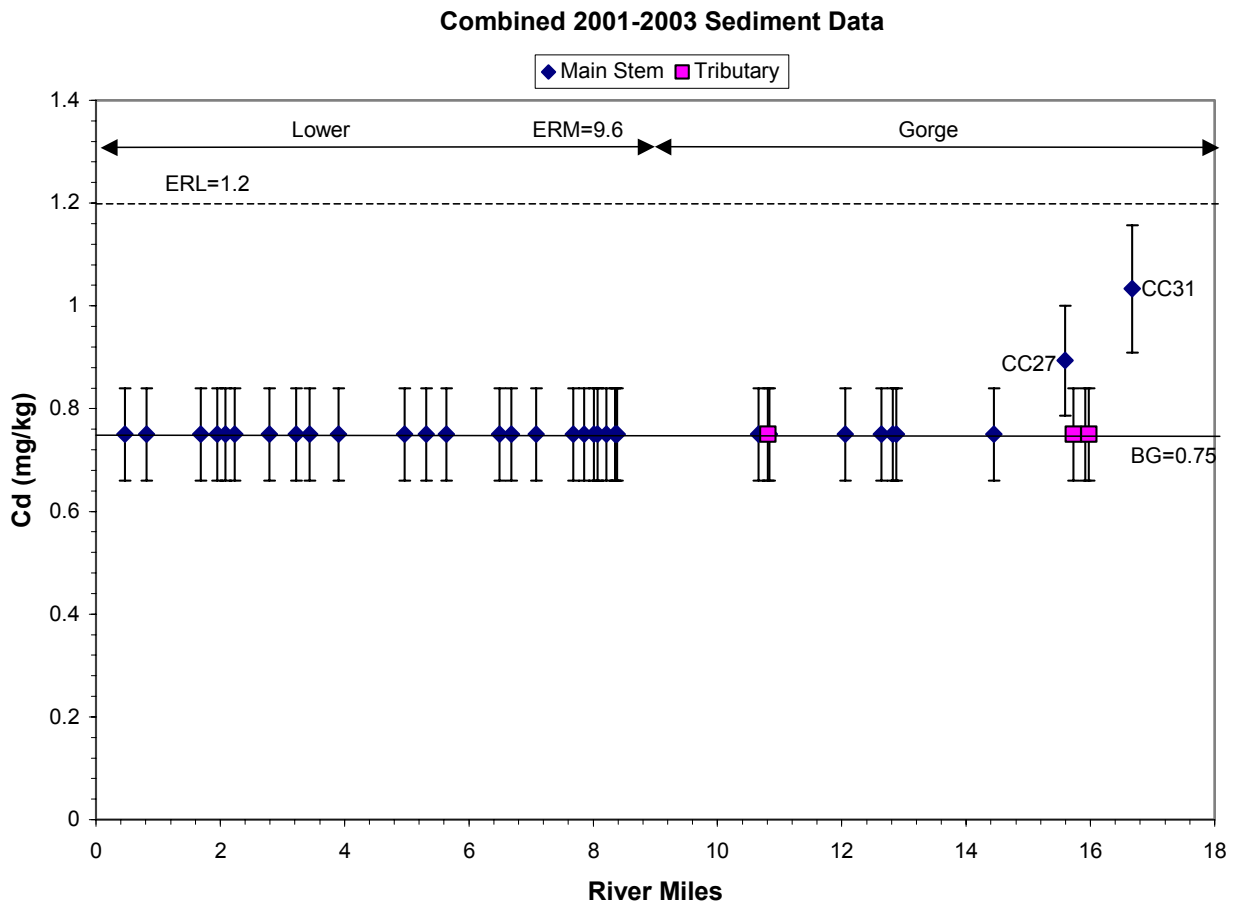


Figure 14B



Combined 2001-2003 Sediment Data

Figure 14C

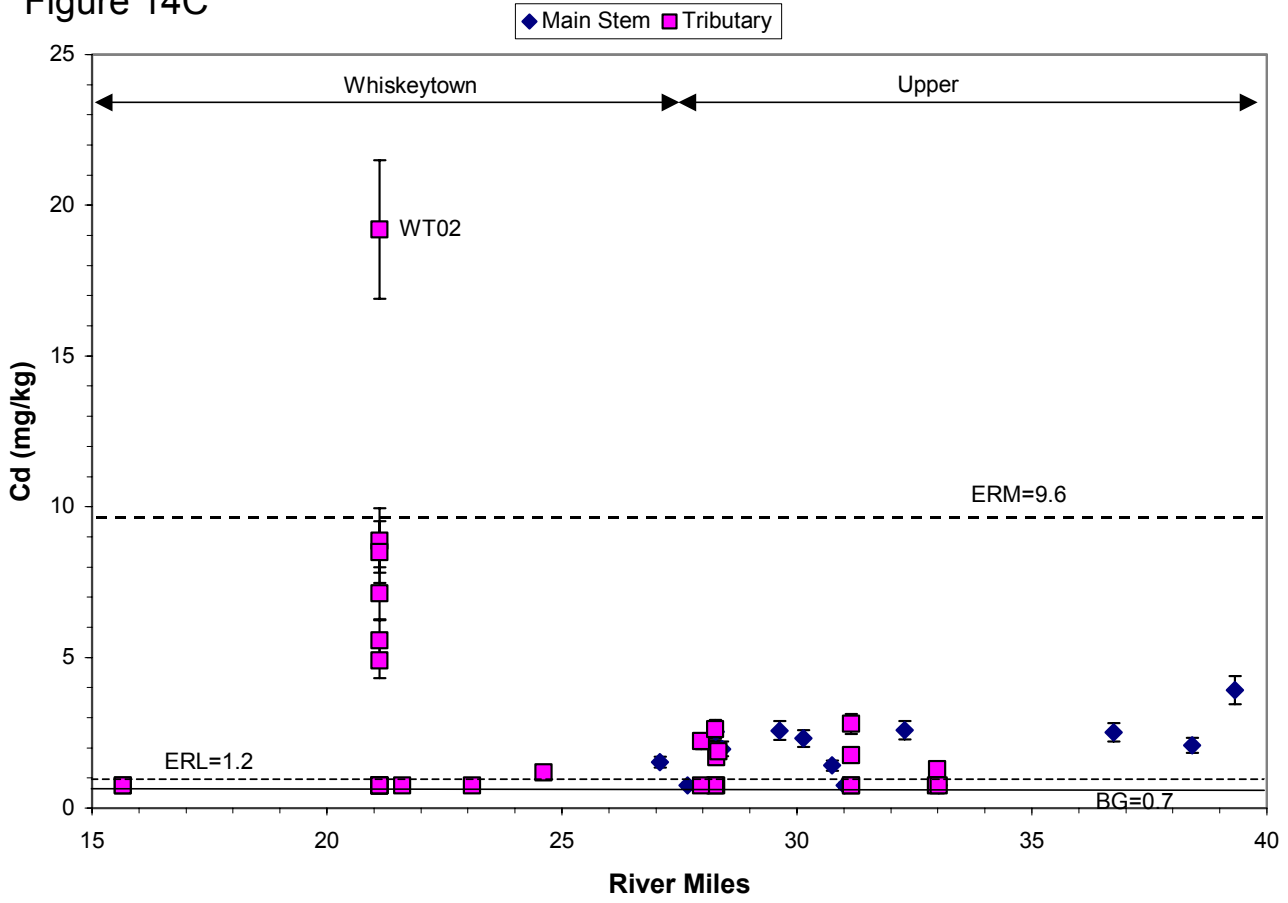


Figure 14D

Combined 2001-2003 Sediment Data x Background

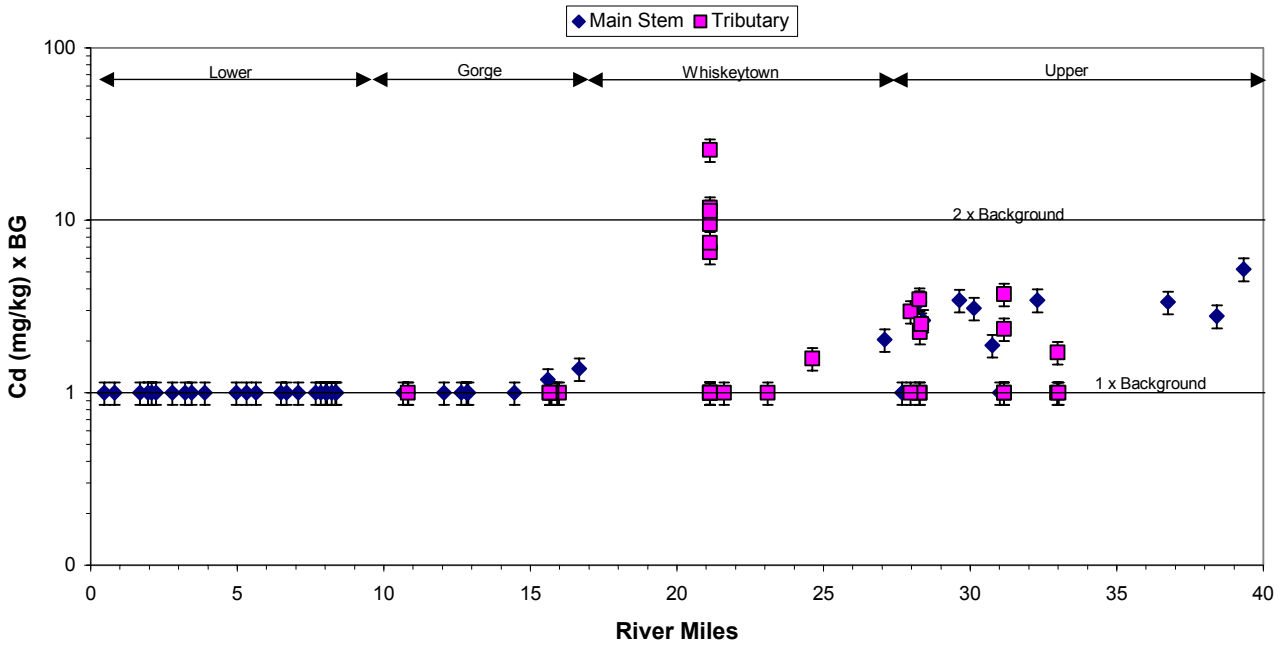


Figure 14E

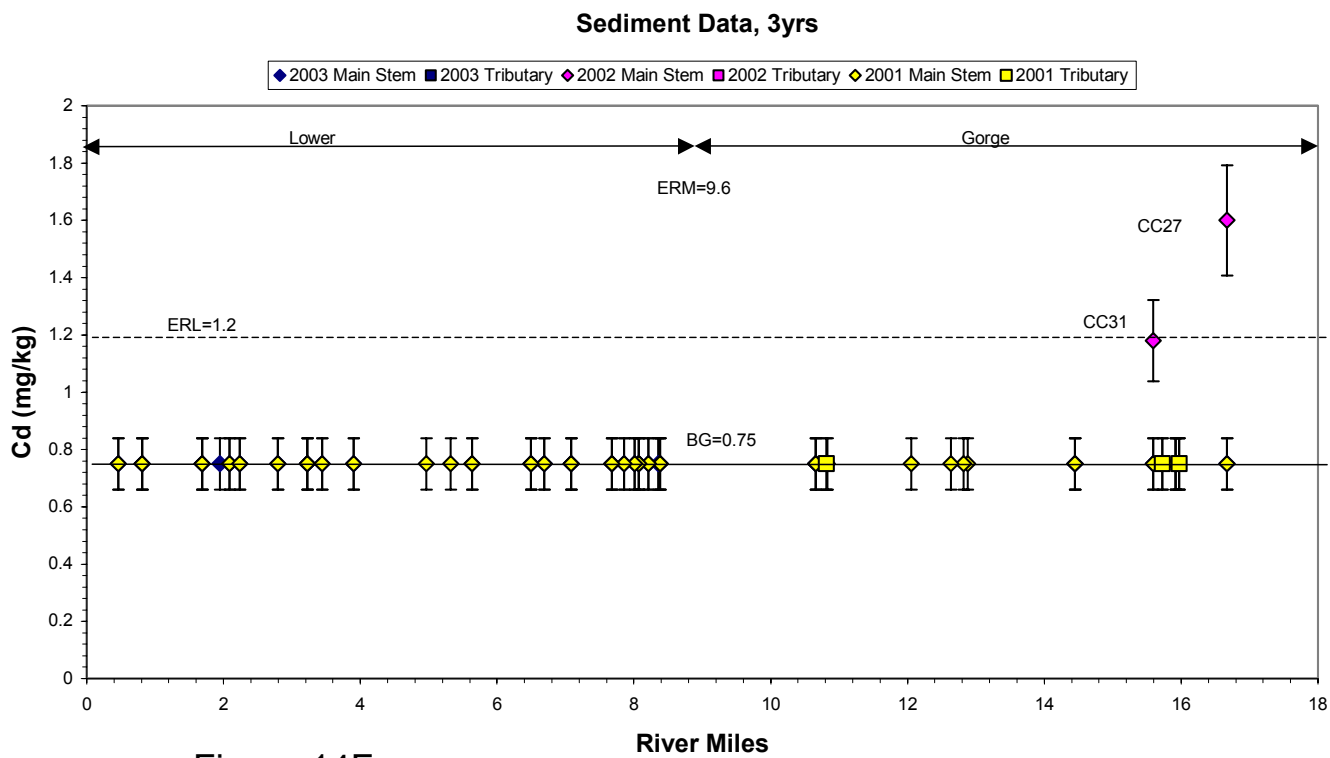


Figure 14F

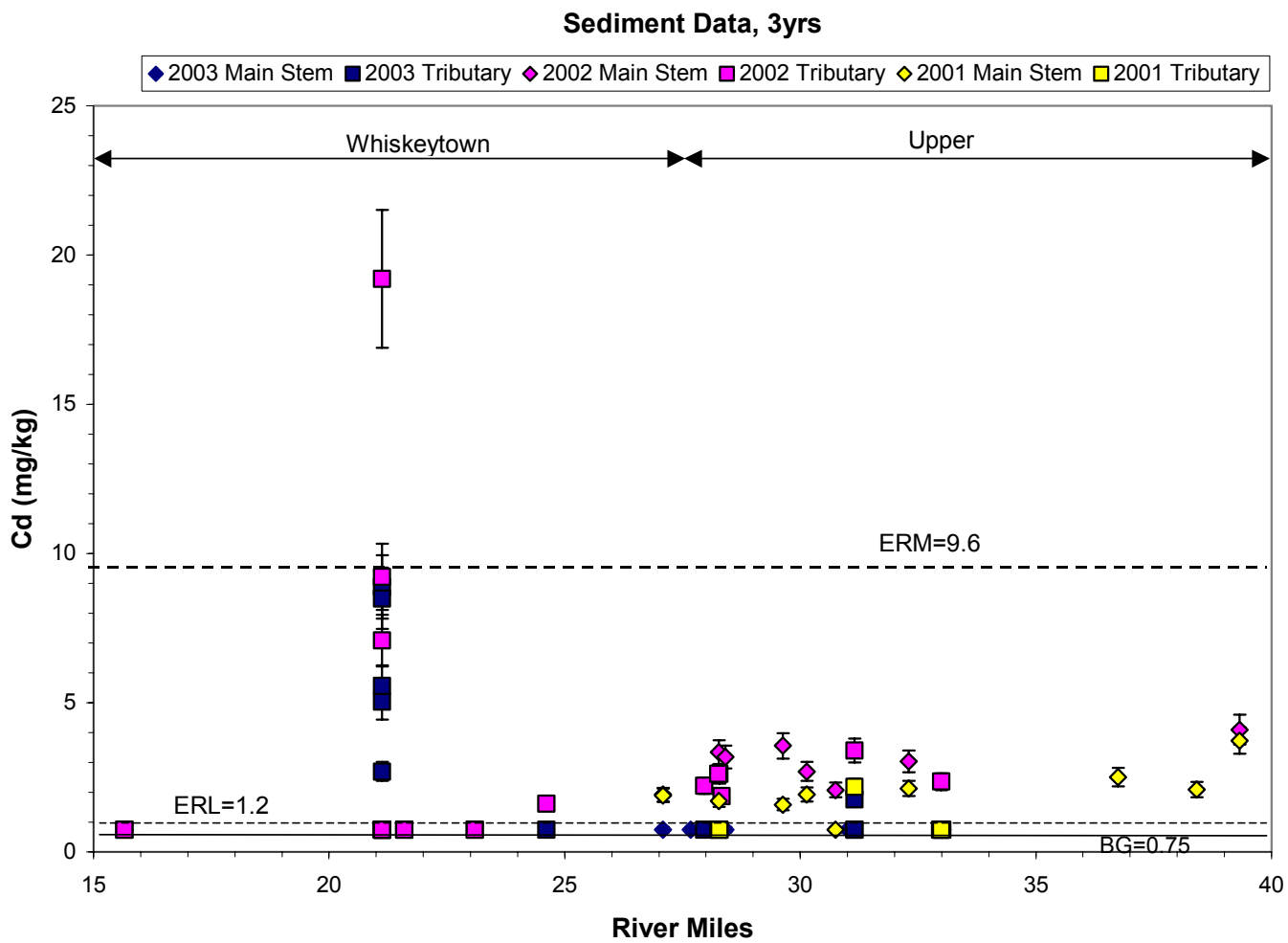


Figure 15

### Metal Concentrations: Cd Clear Creek Watershed, CA

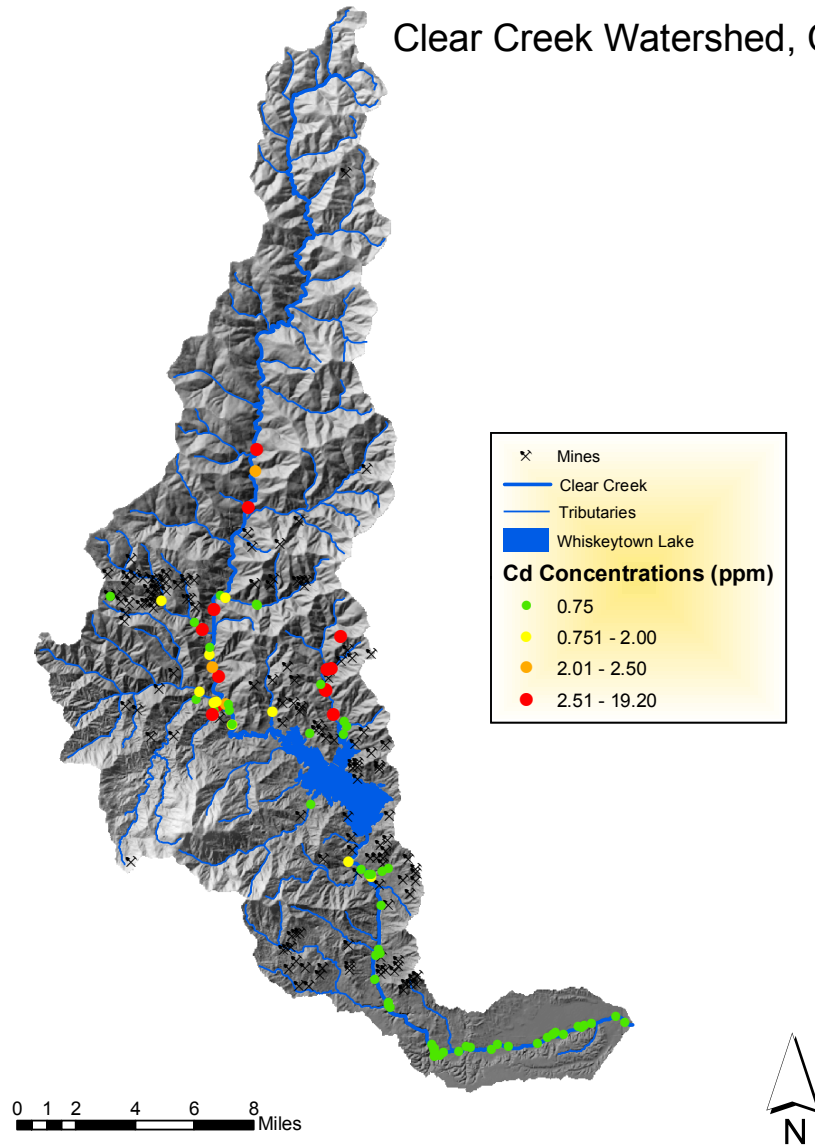


Figure 16

### Threshold Effects Concentrations: Cd Clear Creek Watershed, CA

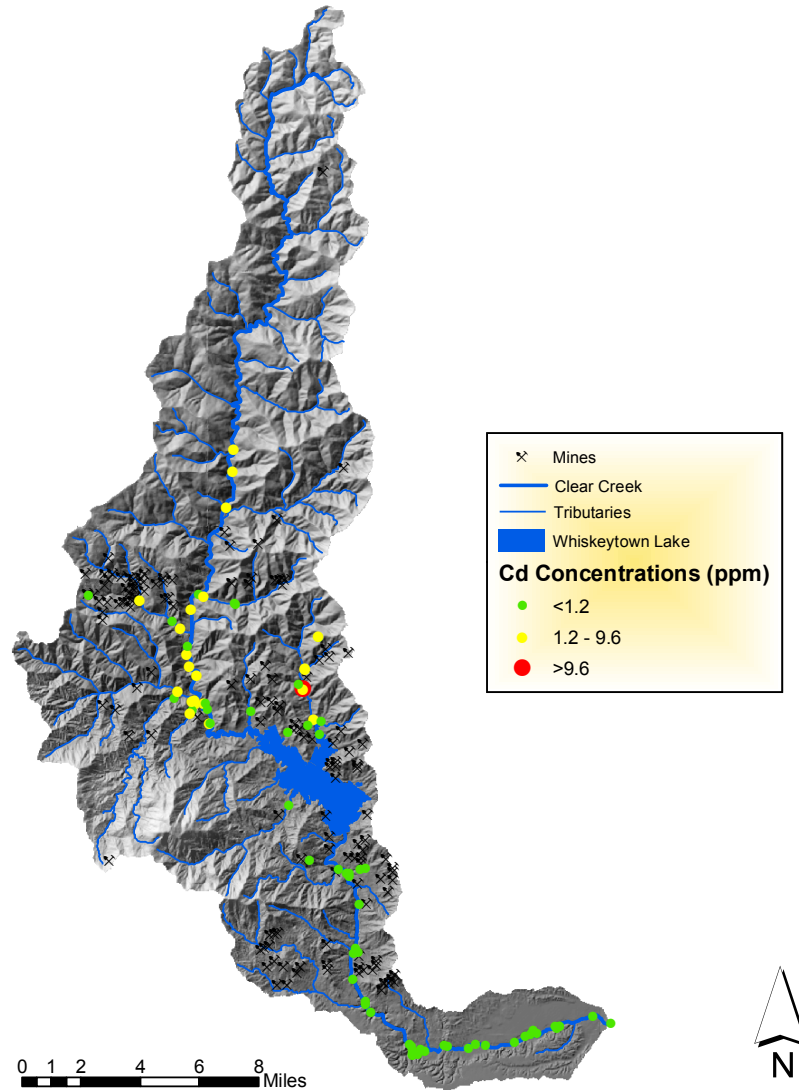


Figure 17

**Multiples of Background: Cd**  
Clear Creek Watershed, CA  
Cd Background= 0.75 ppm

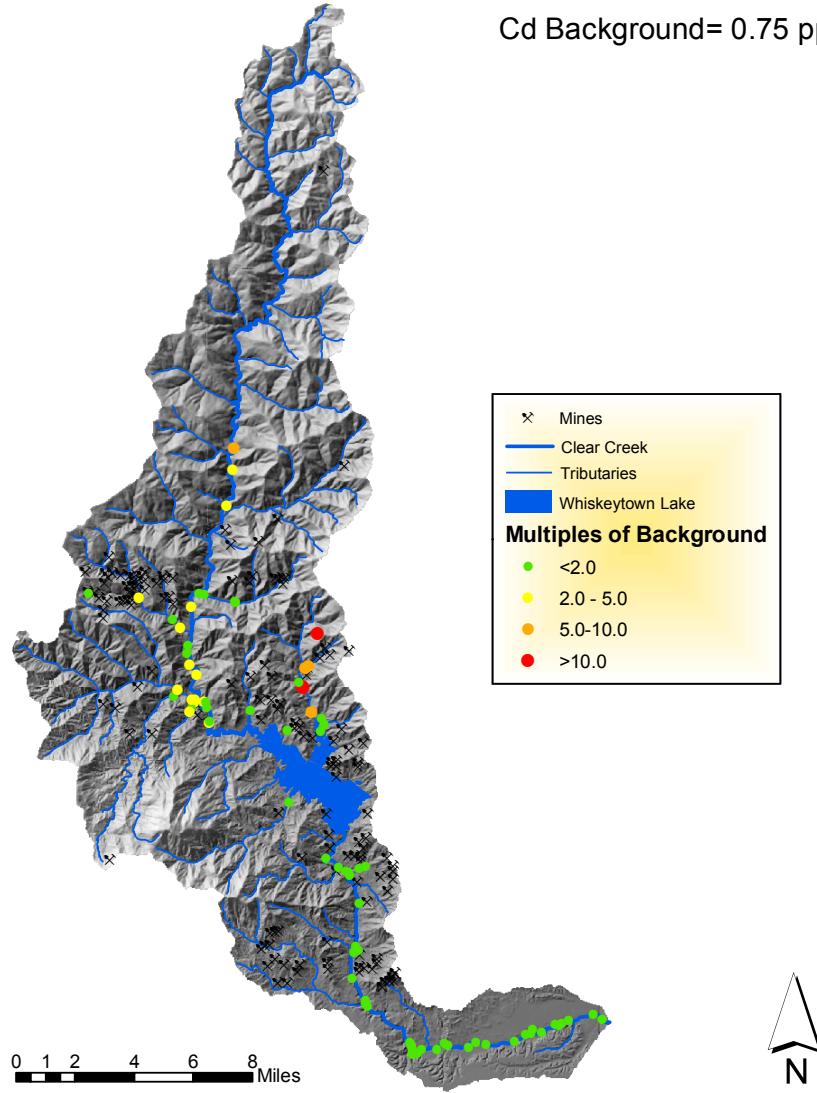


Figure 18A

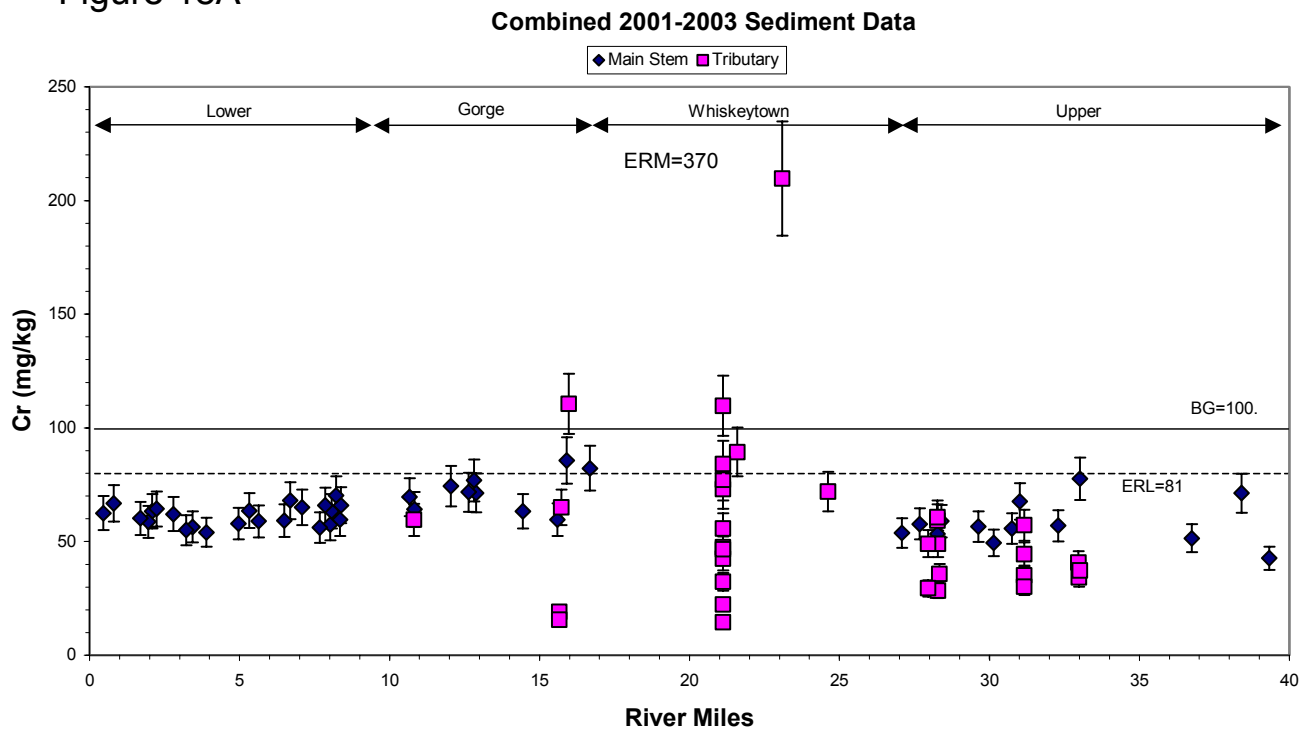


Figure 18B

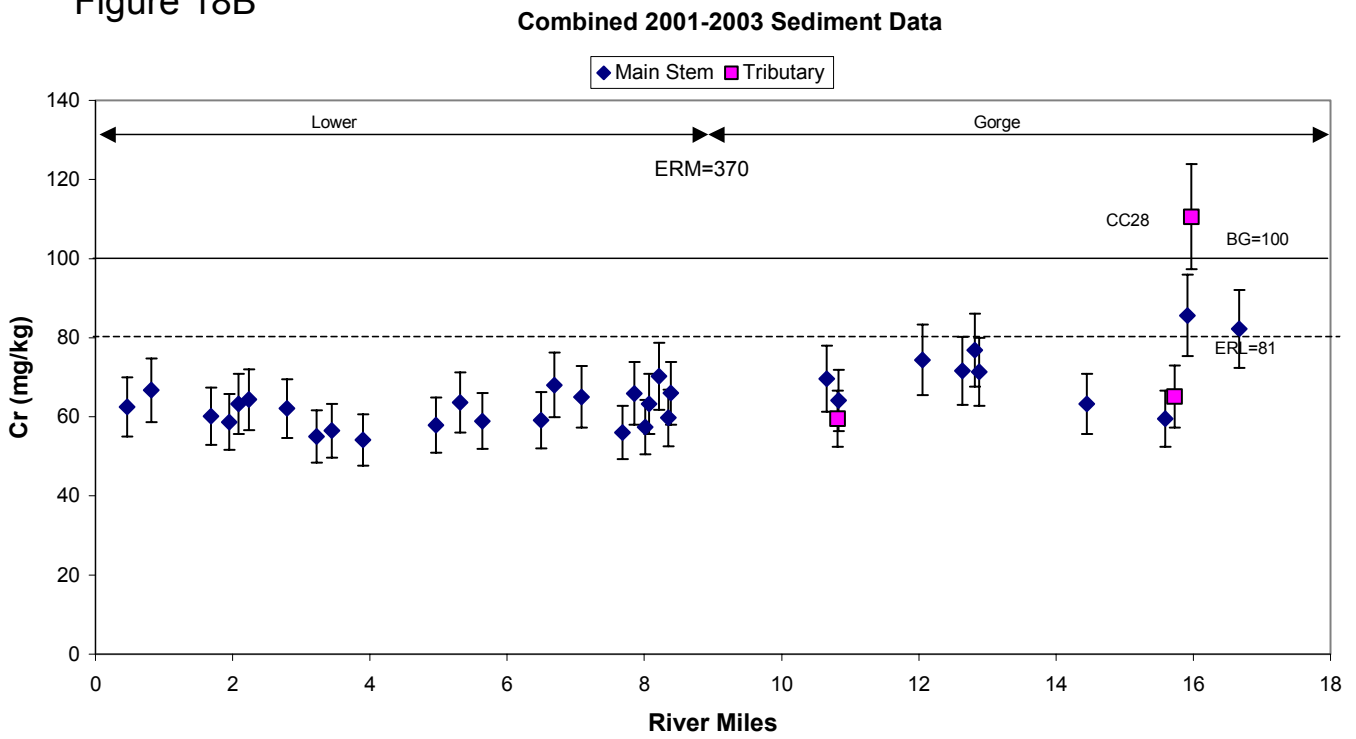




Figure 18C

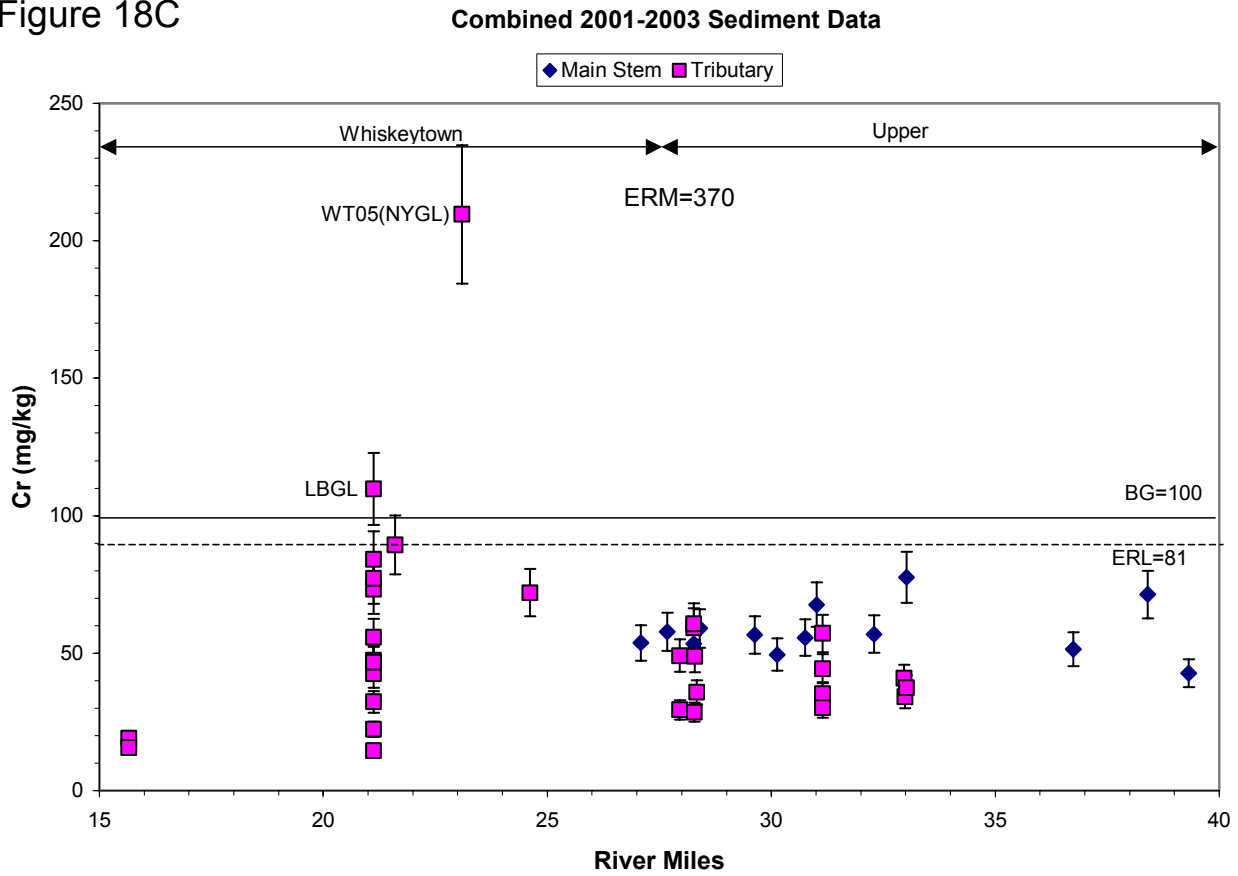


Figure 18D

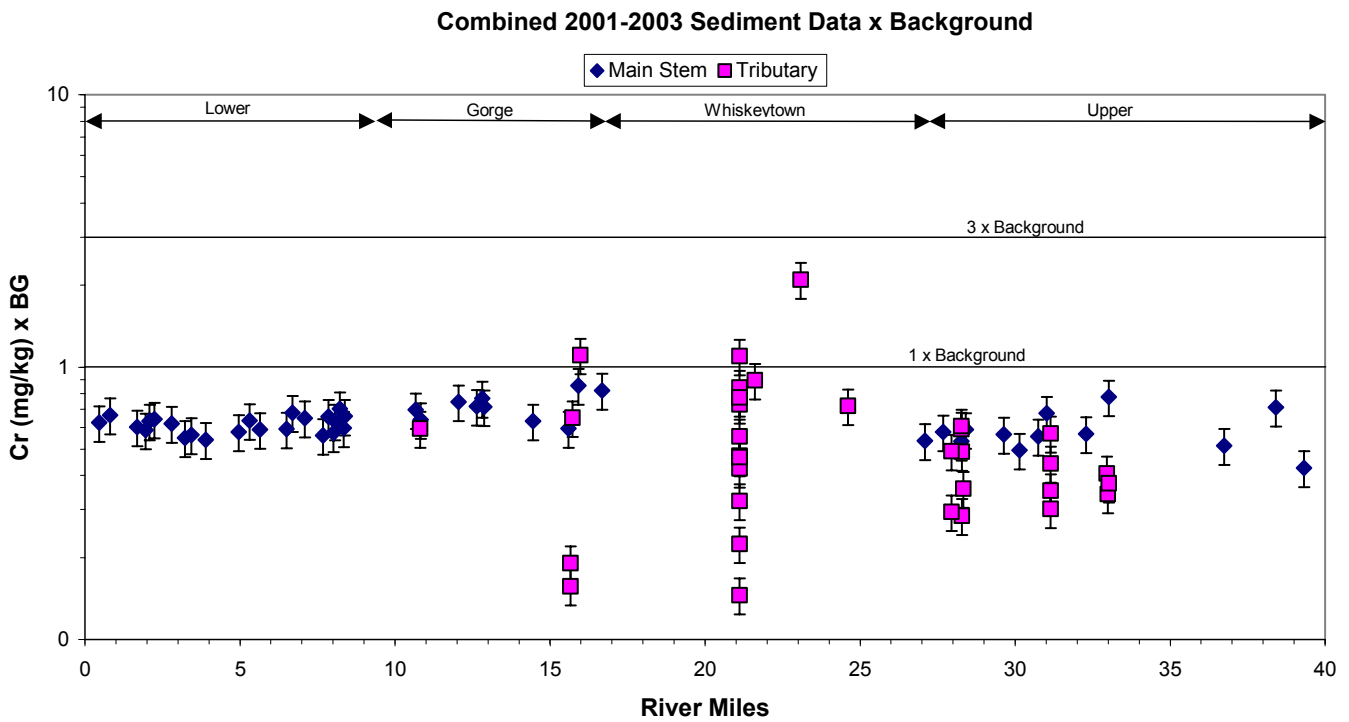


Figure 18E

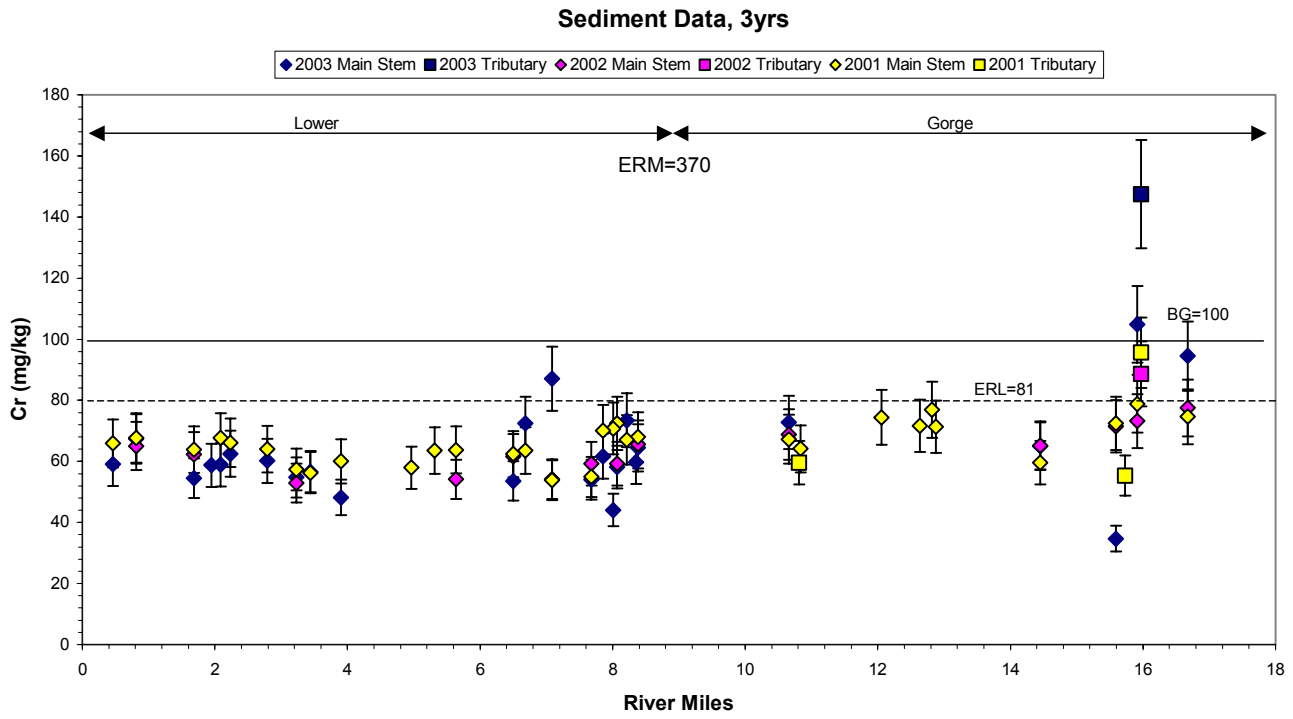


Figure 18F

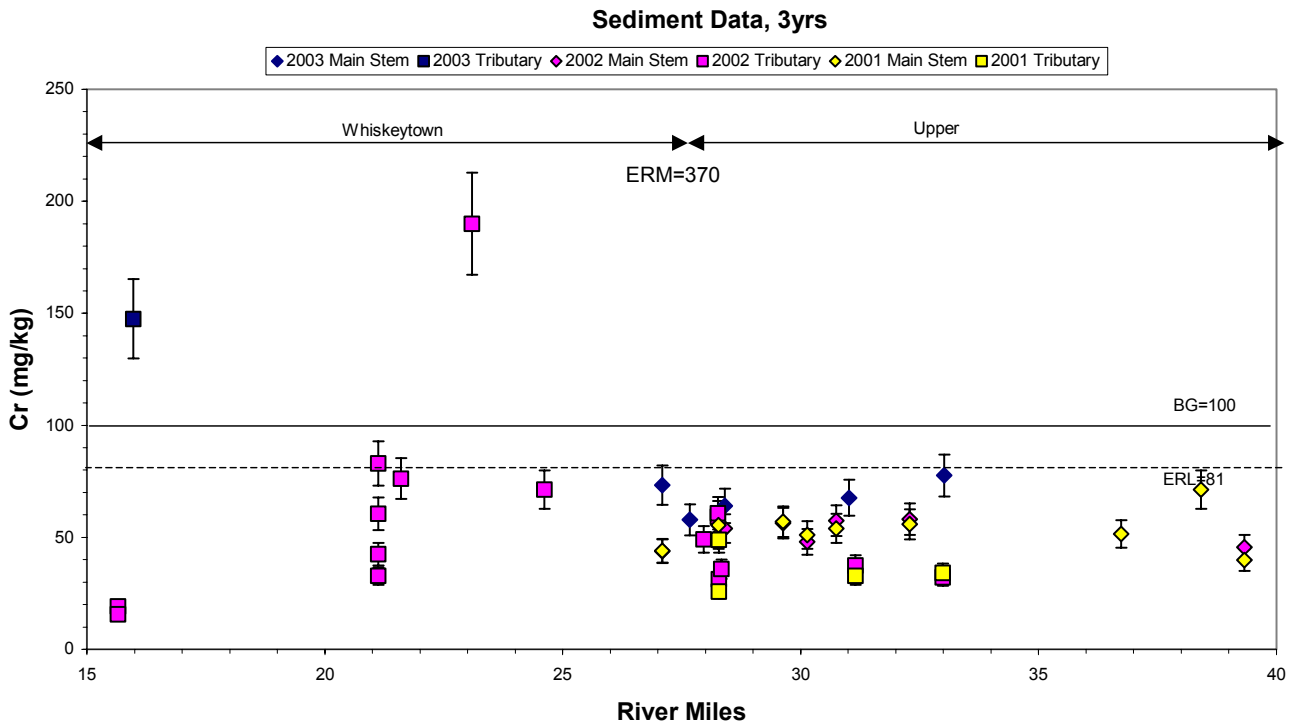


Figure 19

### Metal Concentrations: Cr Clear Creek Watershed, CA

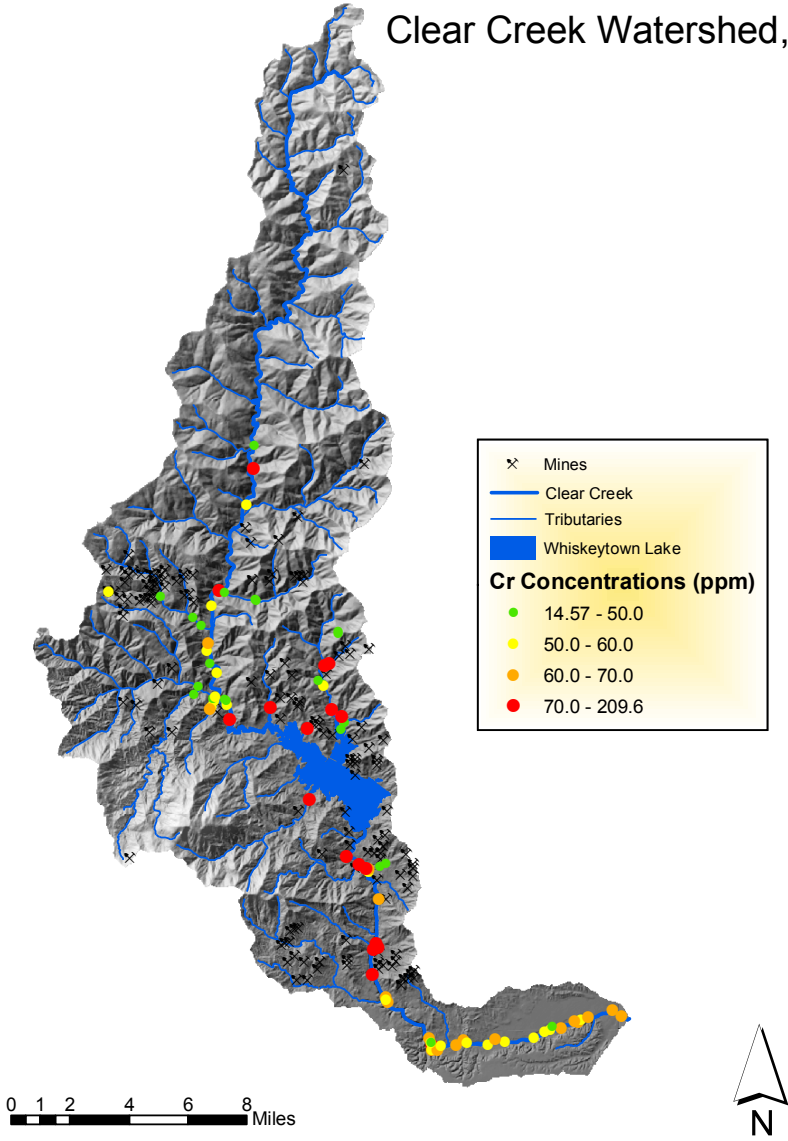


Figure 20

### Threshold Effects Concentrations: Cr Clear Creek Watershed, CA

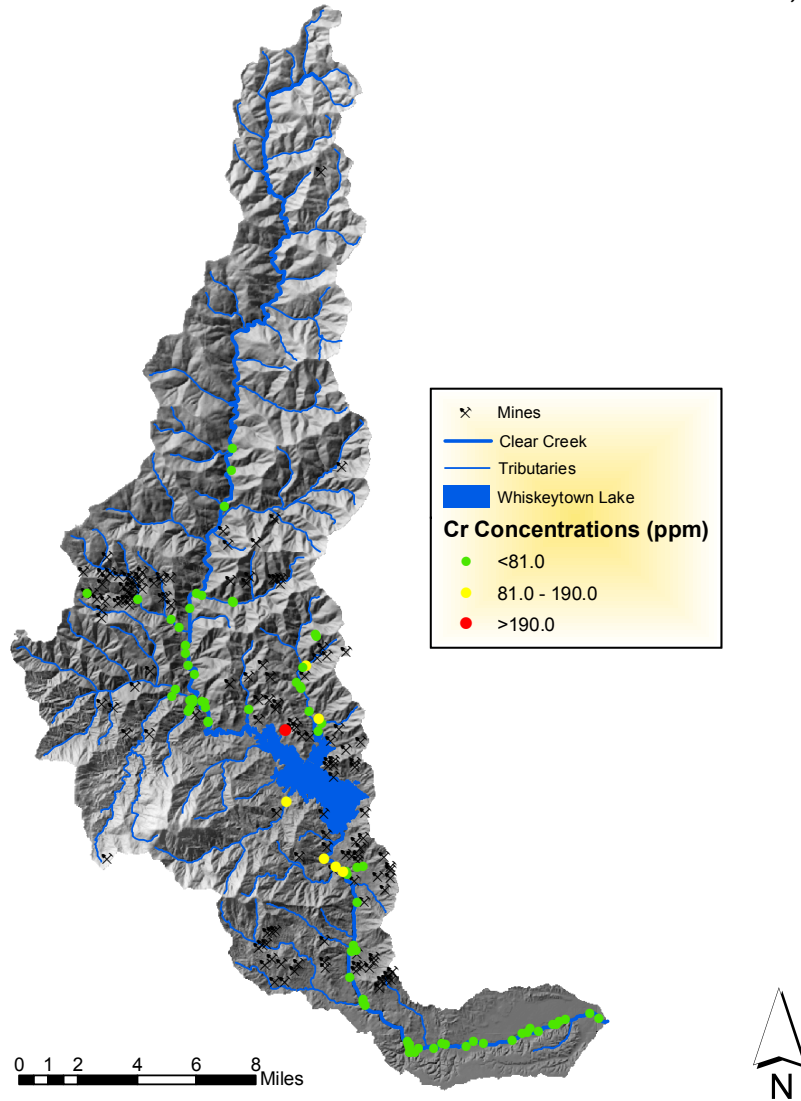


Figure 21

### Multiples of Background: Cr Clear Creek Watershed, CA

Cr Background= 100 ppm

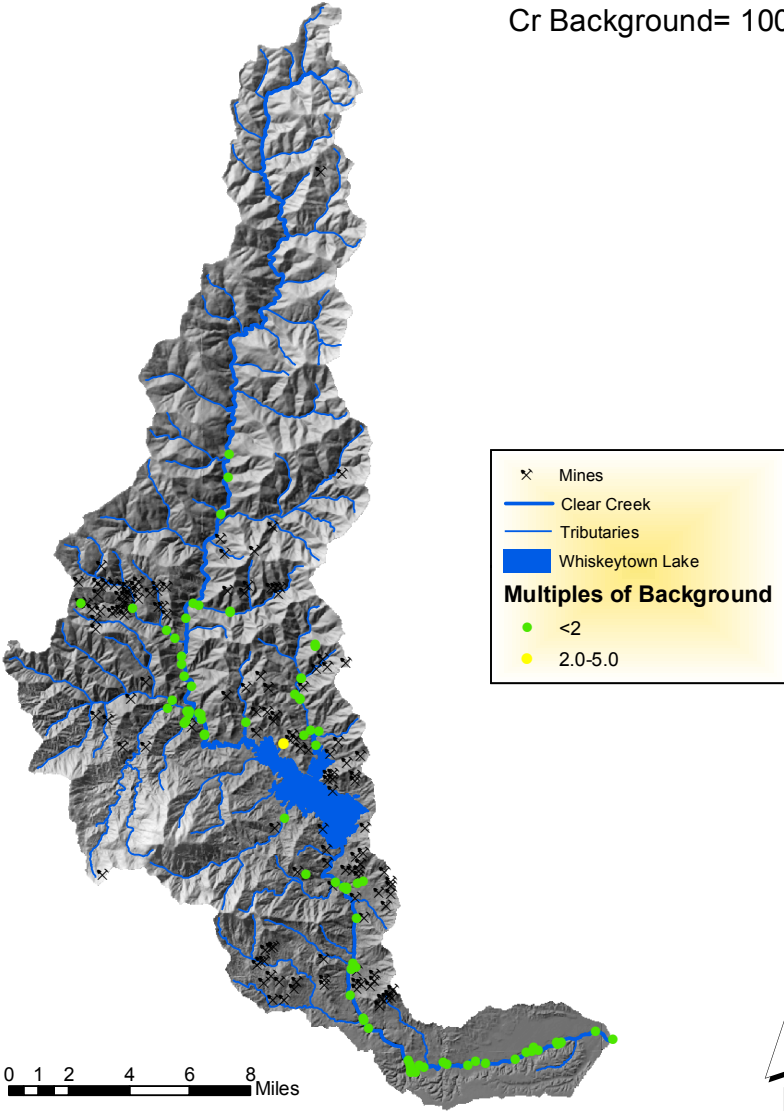


Figure 22A

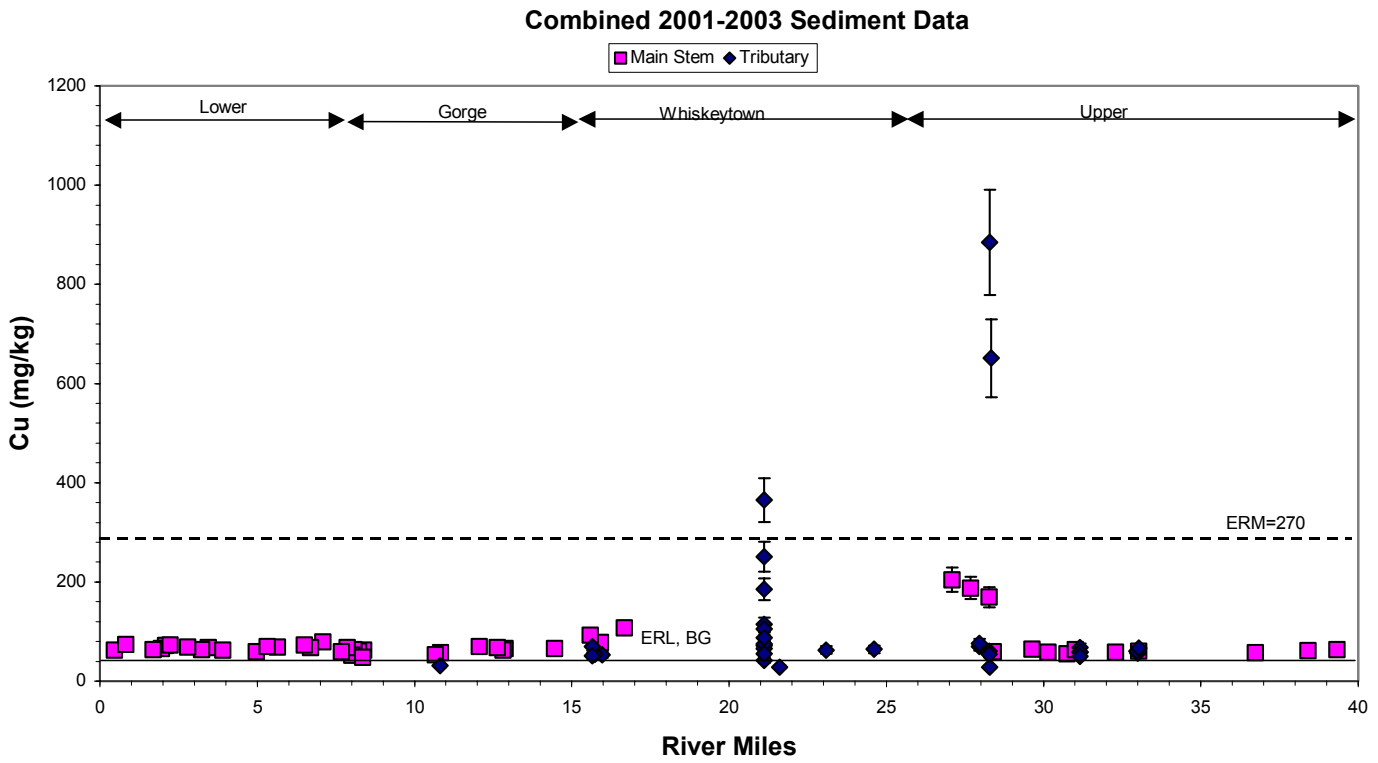


Figure 22B

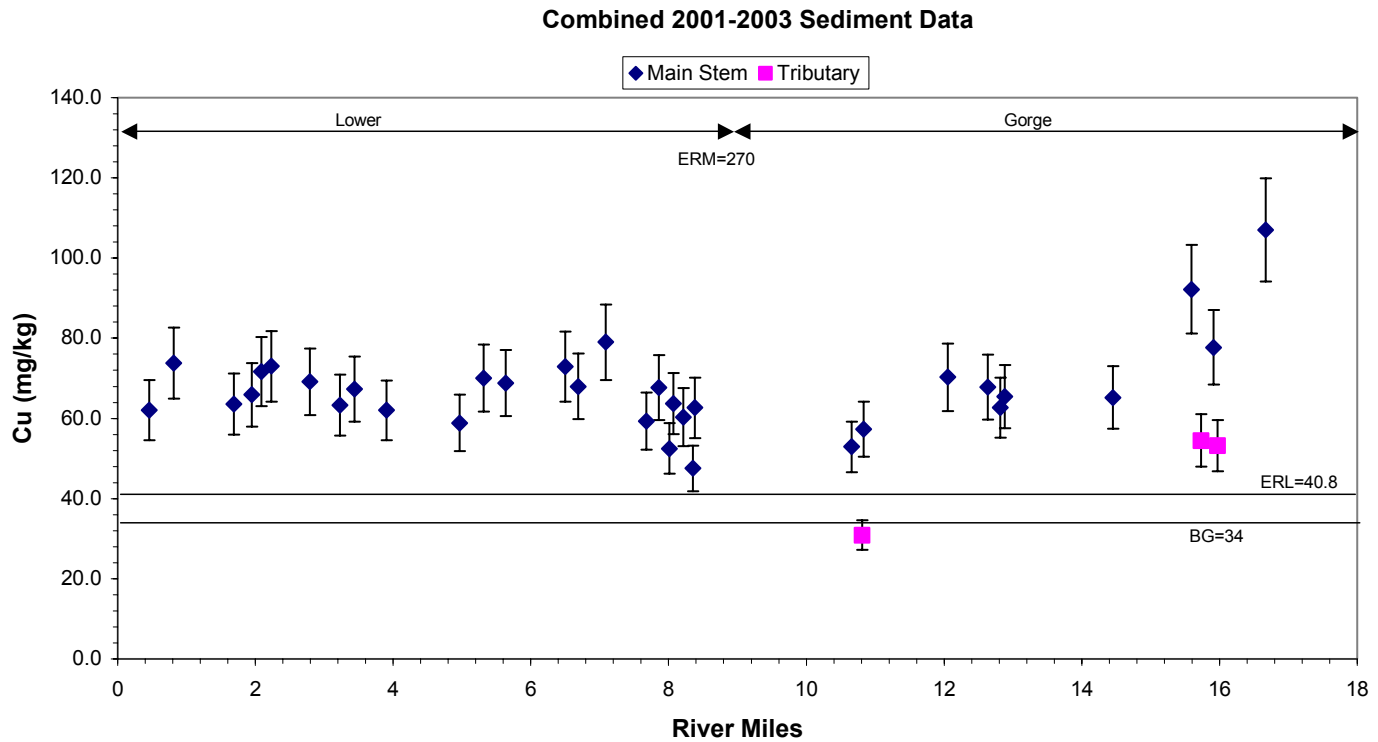


Figure 22C

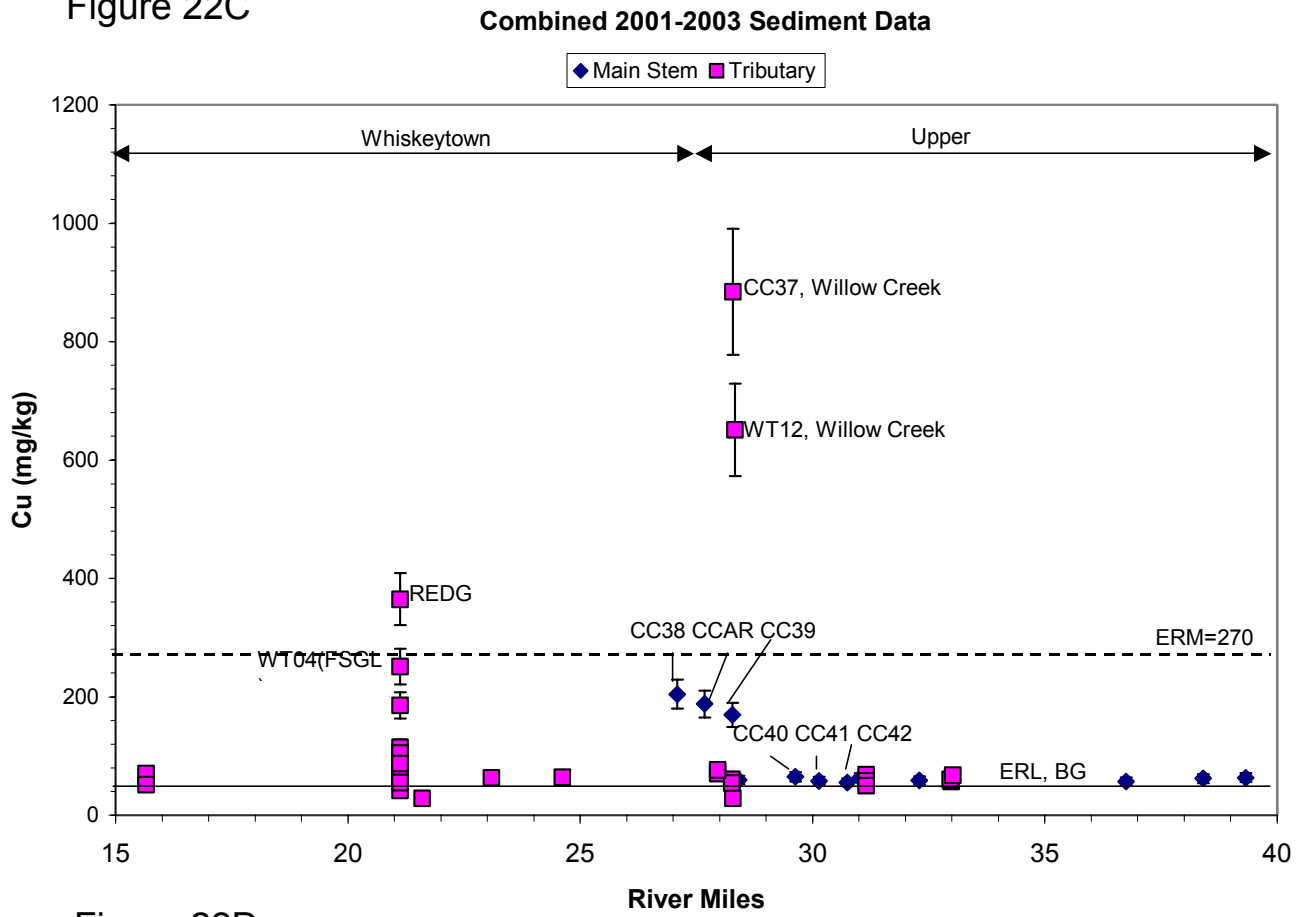


Figure 22D

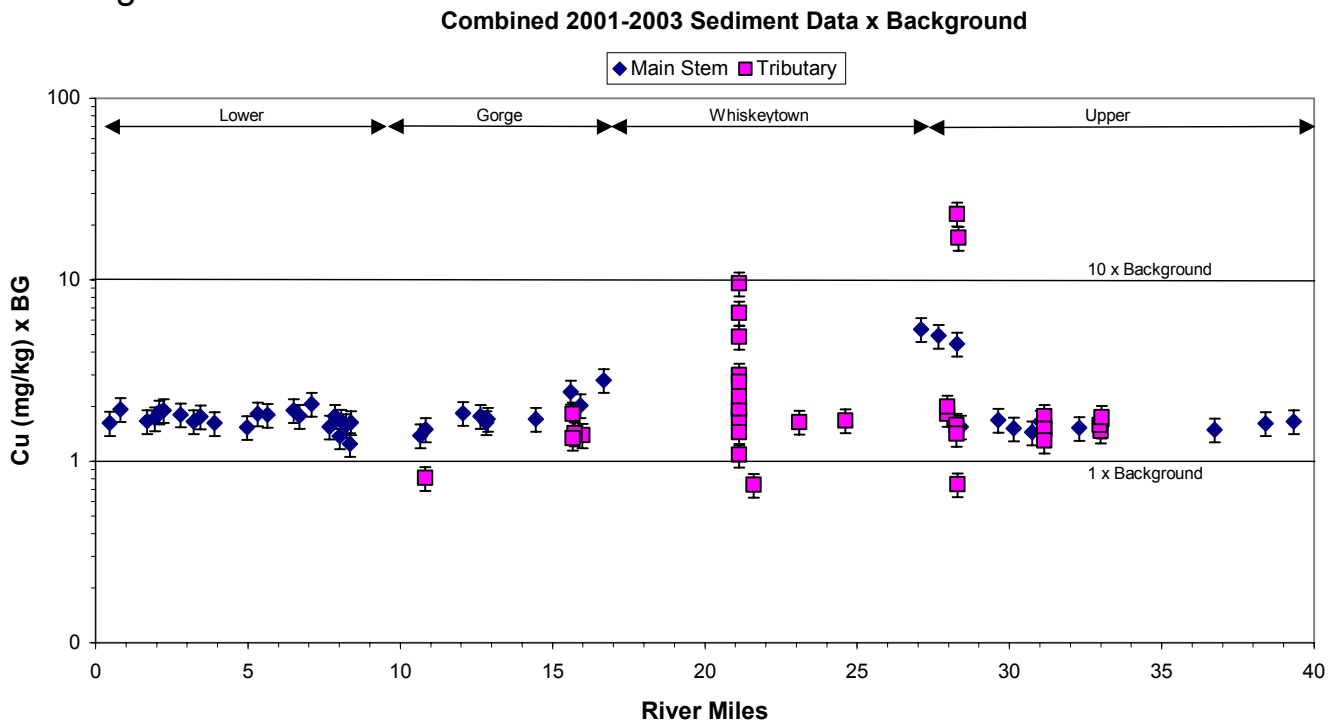


Figure 22E

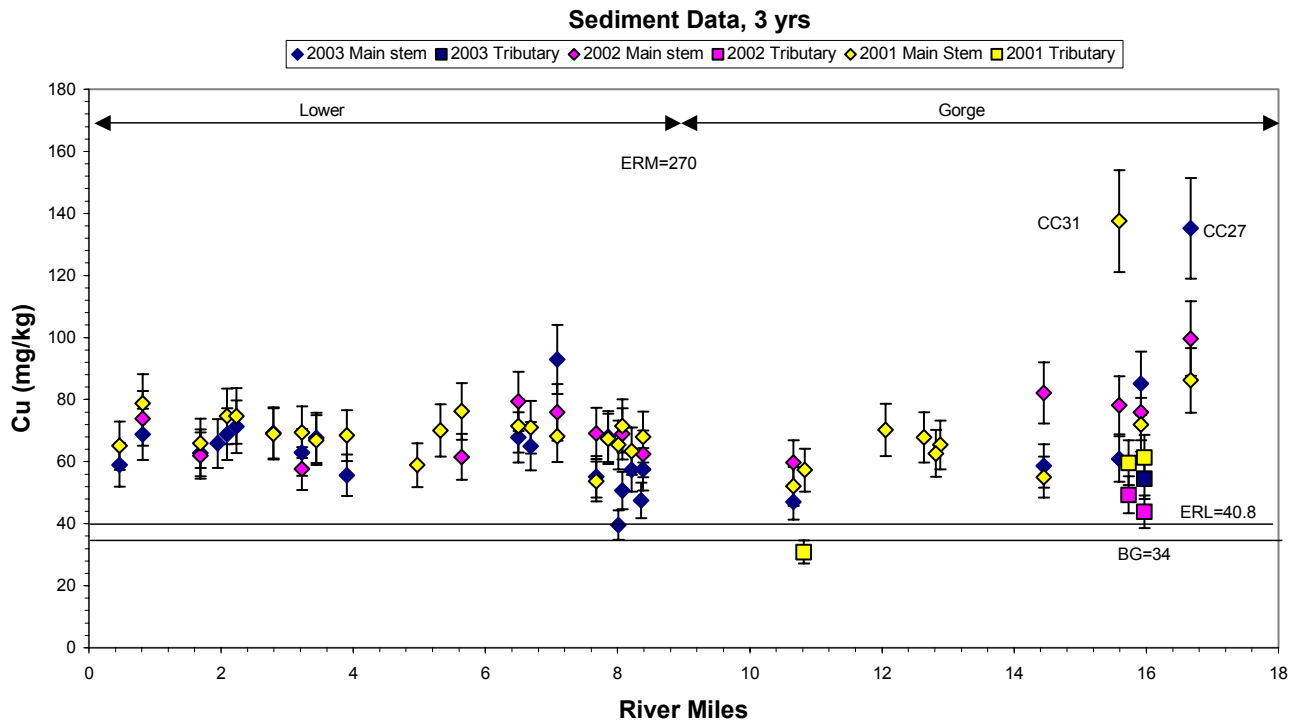


Figure 22F

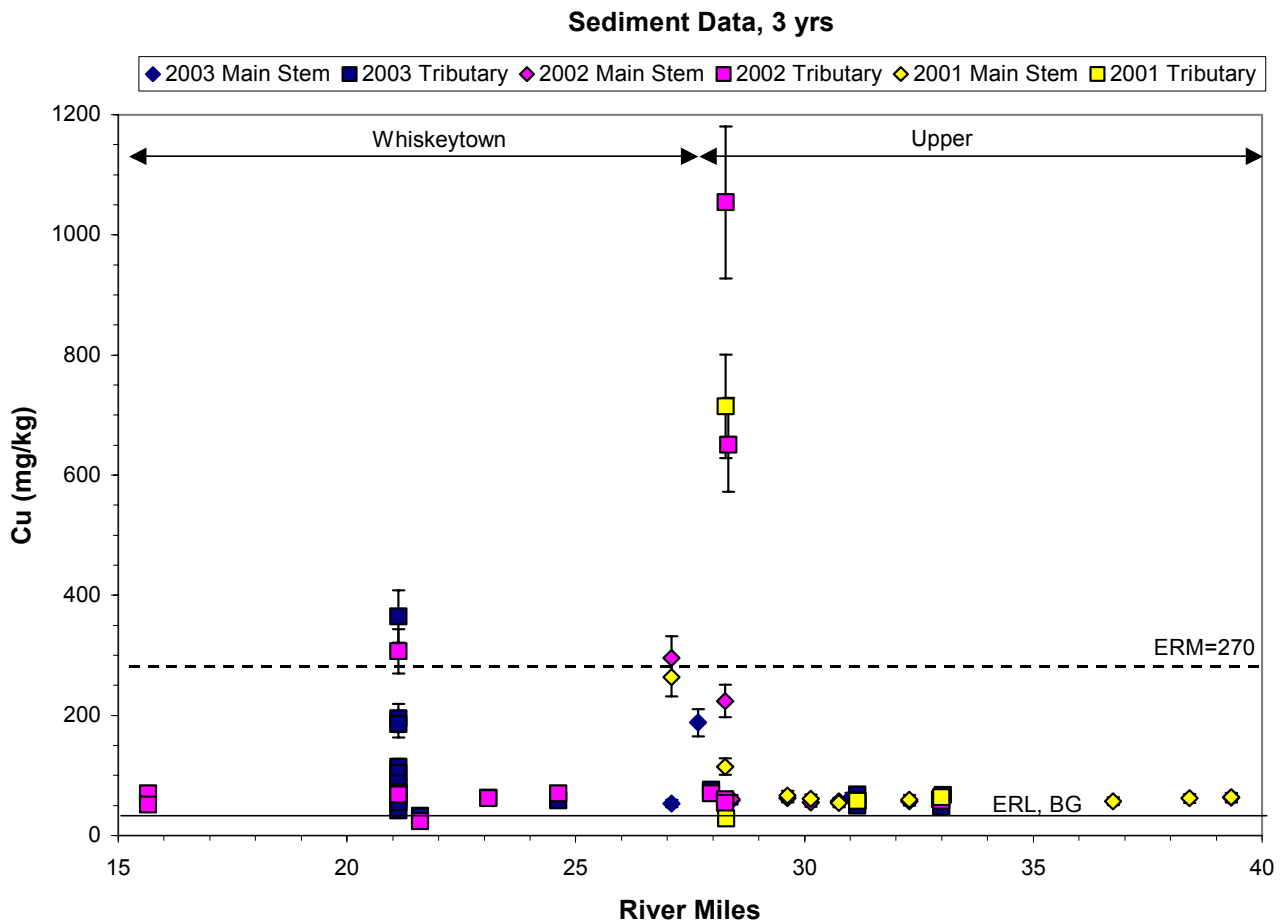




Figure 23

### Metal Concentrations: Cu Clear Creek Watershed, CA

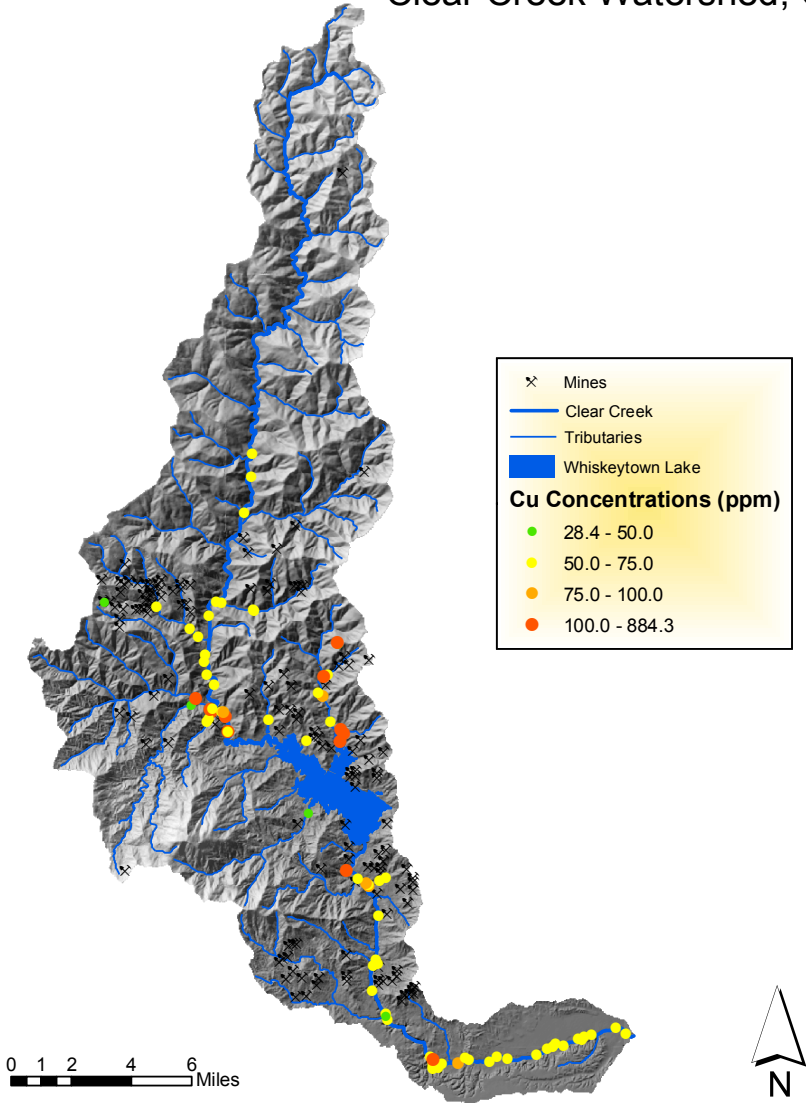


Figure 24

### Threshold Effects Concentrations: Cu Clear Creek Watershed, CA

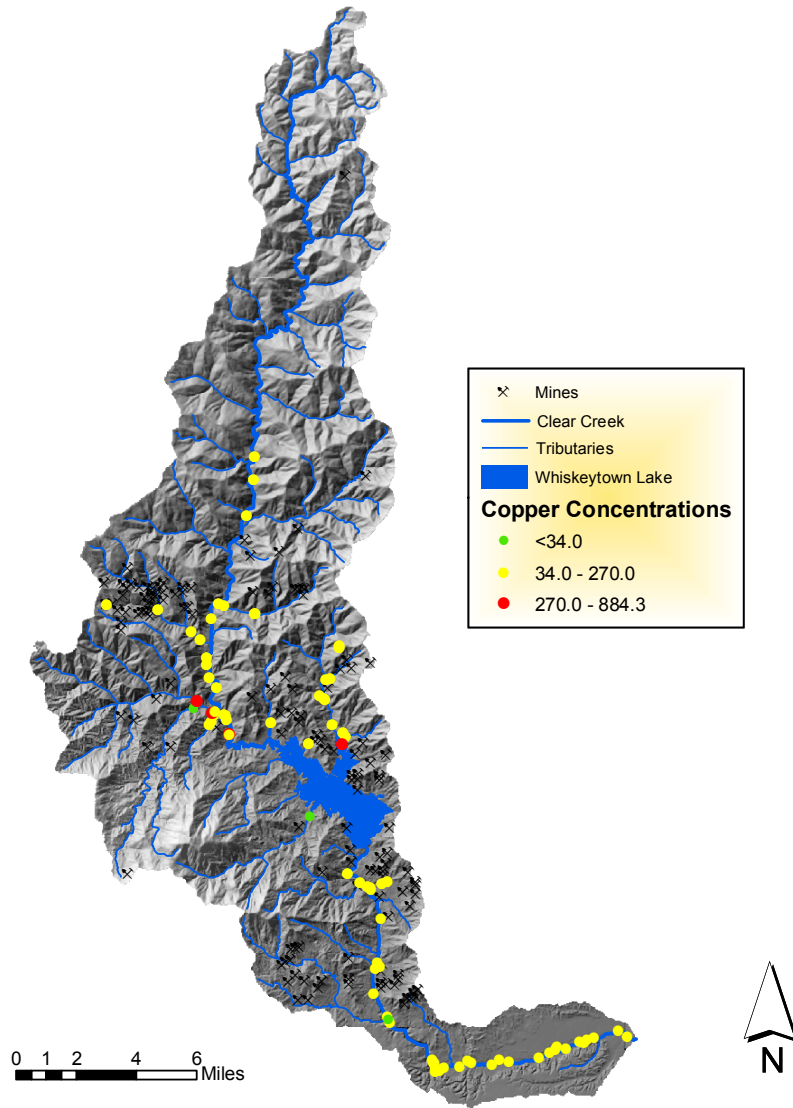


Figure 25

**Multiples of Background: Cu**  
Clear Creek Watershed, CA  
Cu Background= 40.8 ppm

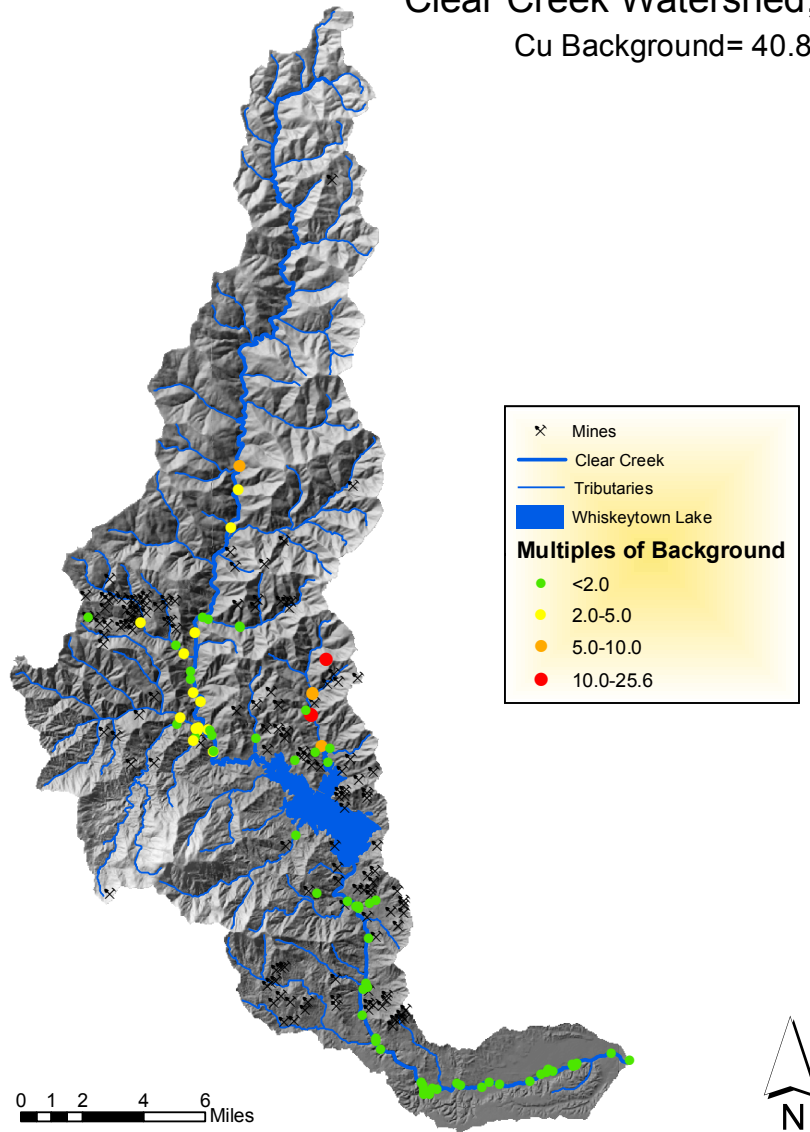


Figure 26A

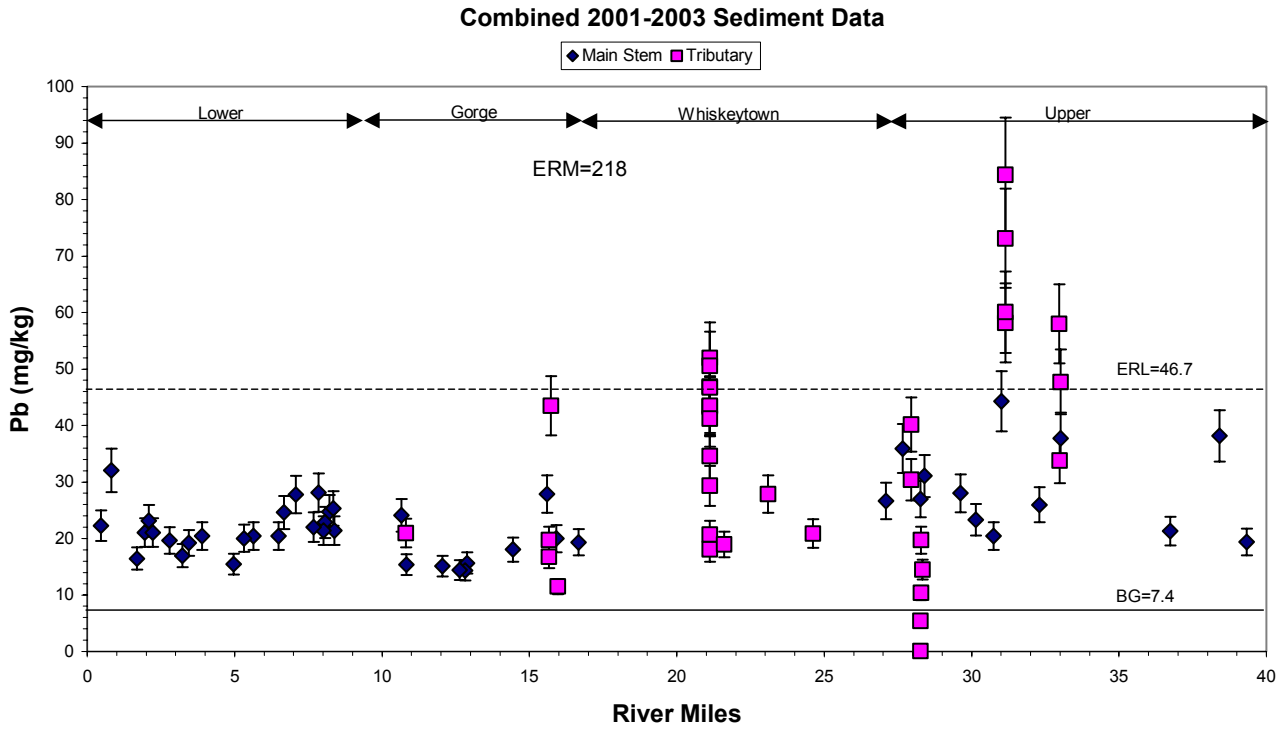


Figure 26B

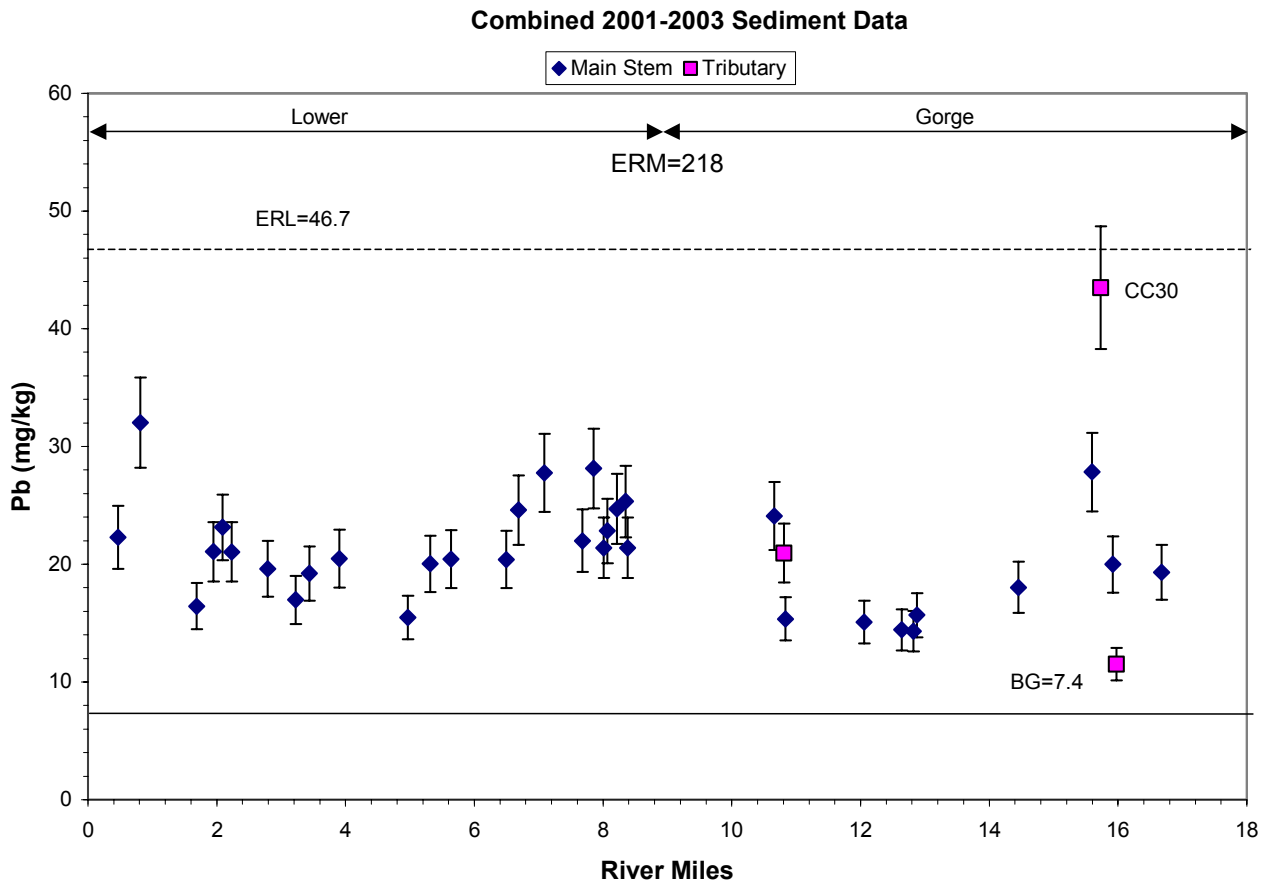


Figure 26C

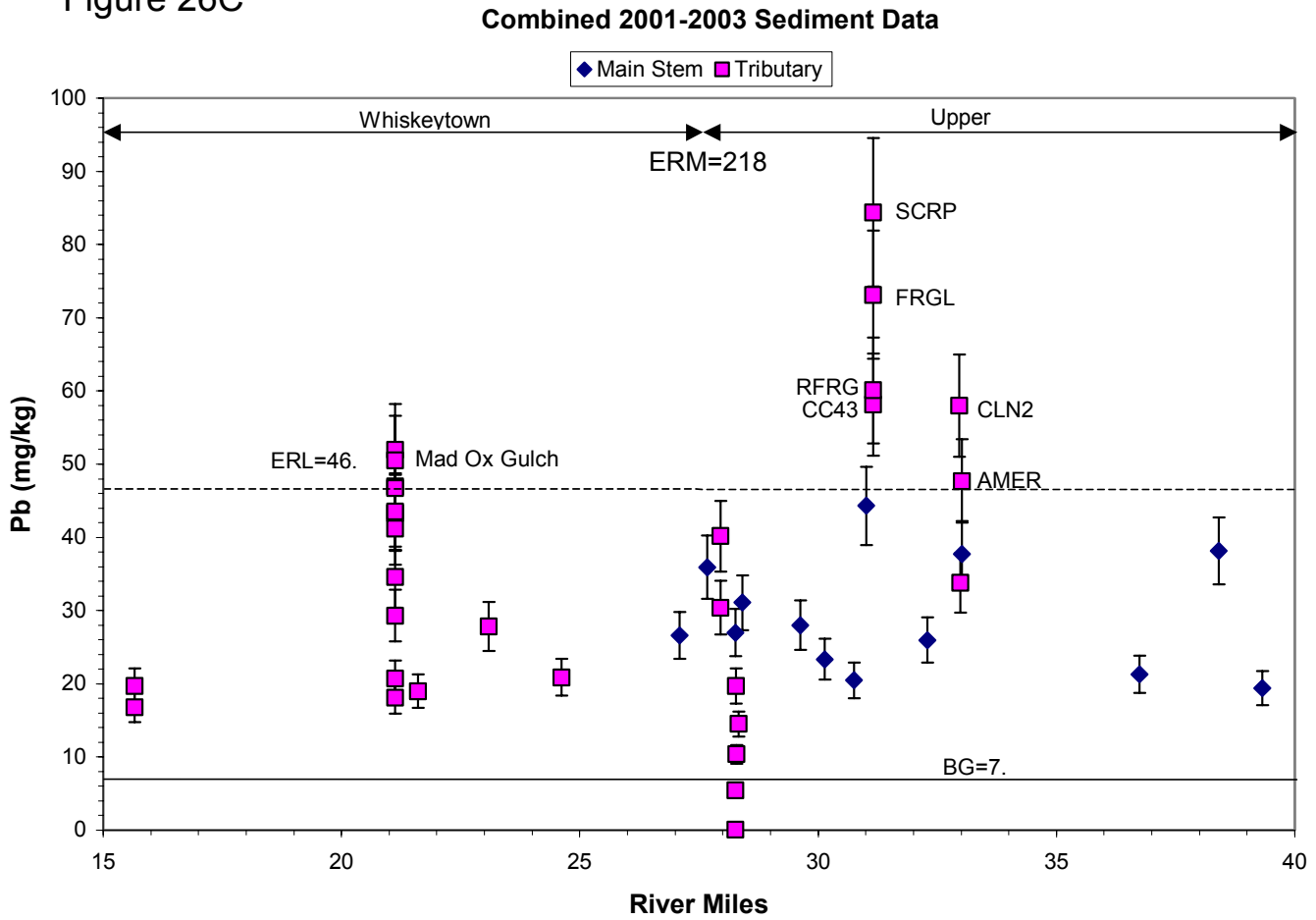


Figure 26D

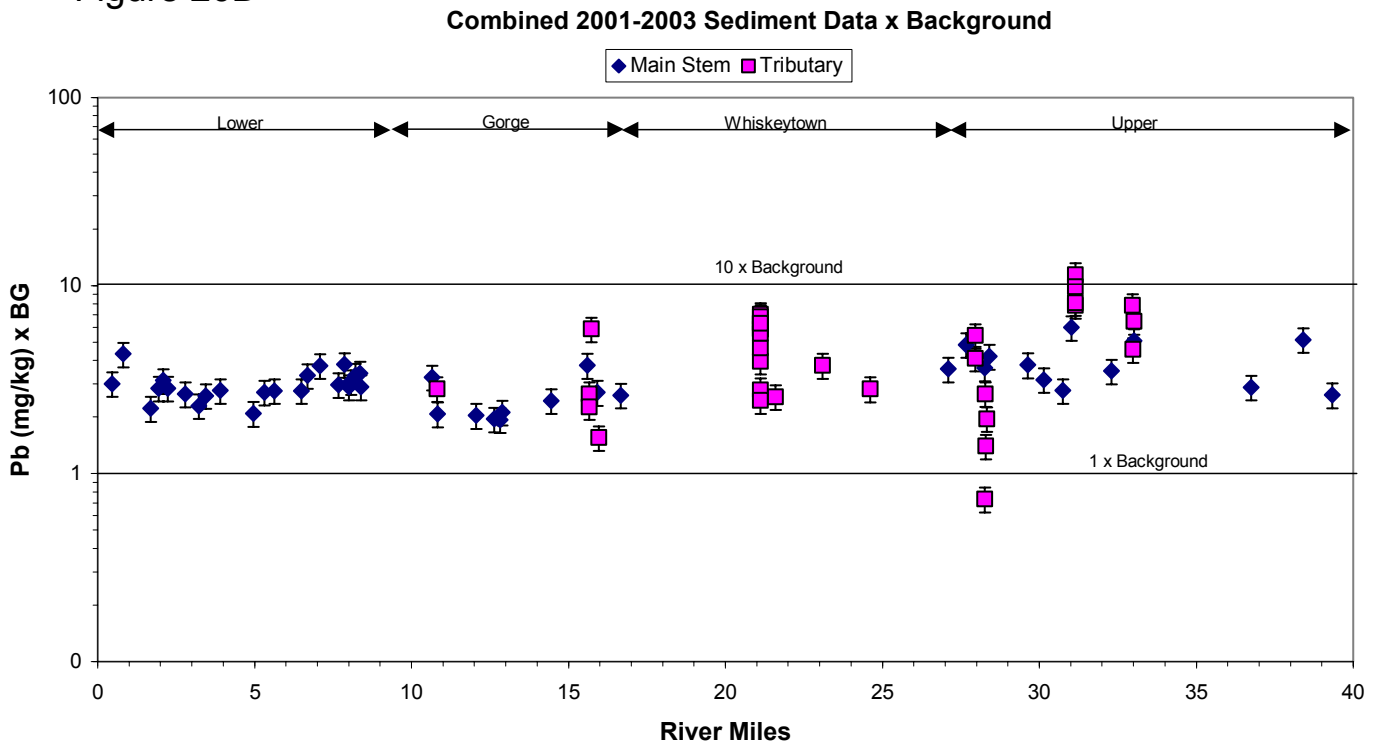


Figure 26E

Sediment Data, 3yrs

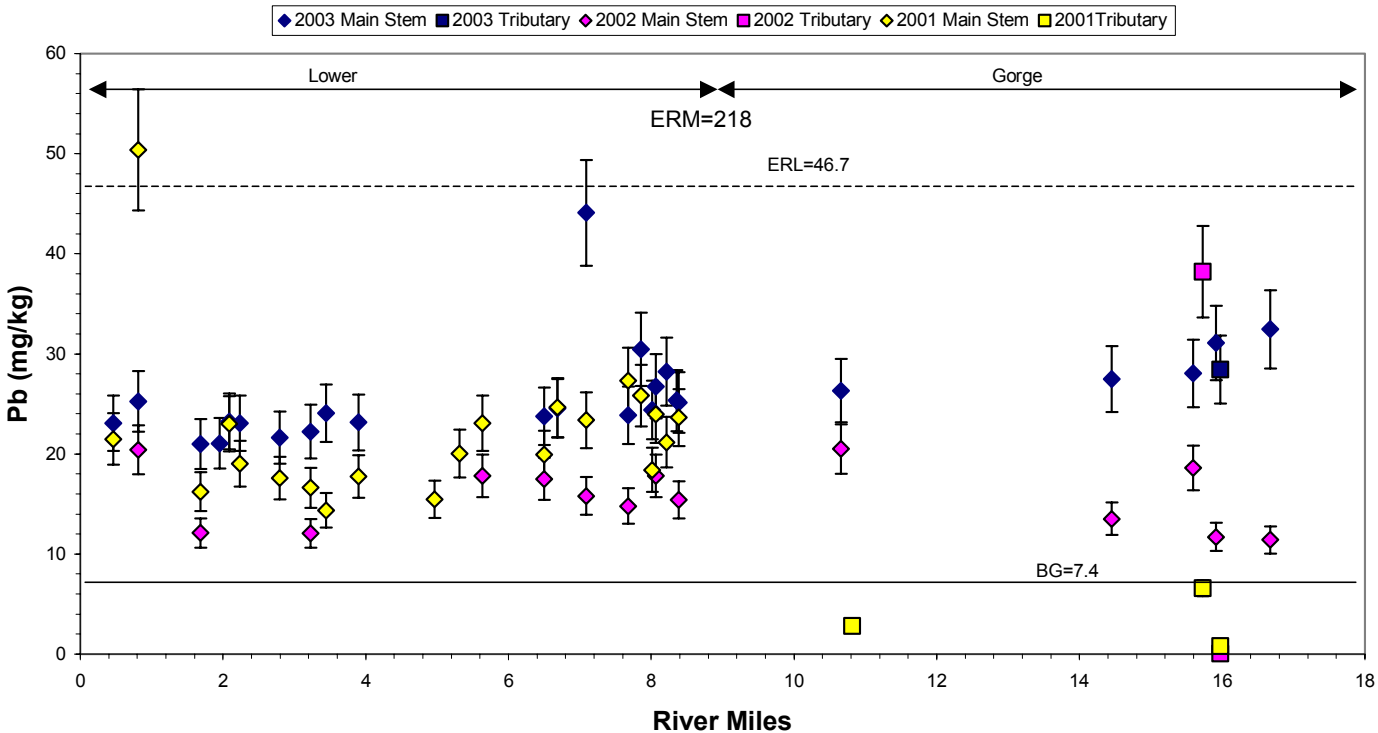


Figure 26F

Sediment Data, 3yrs

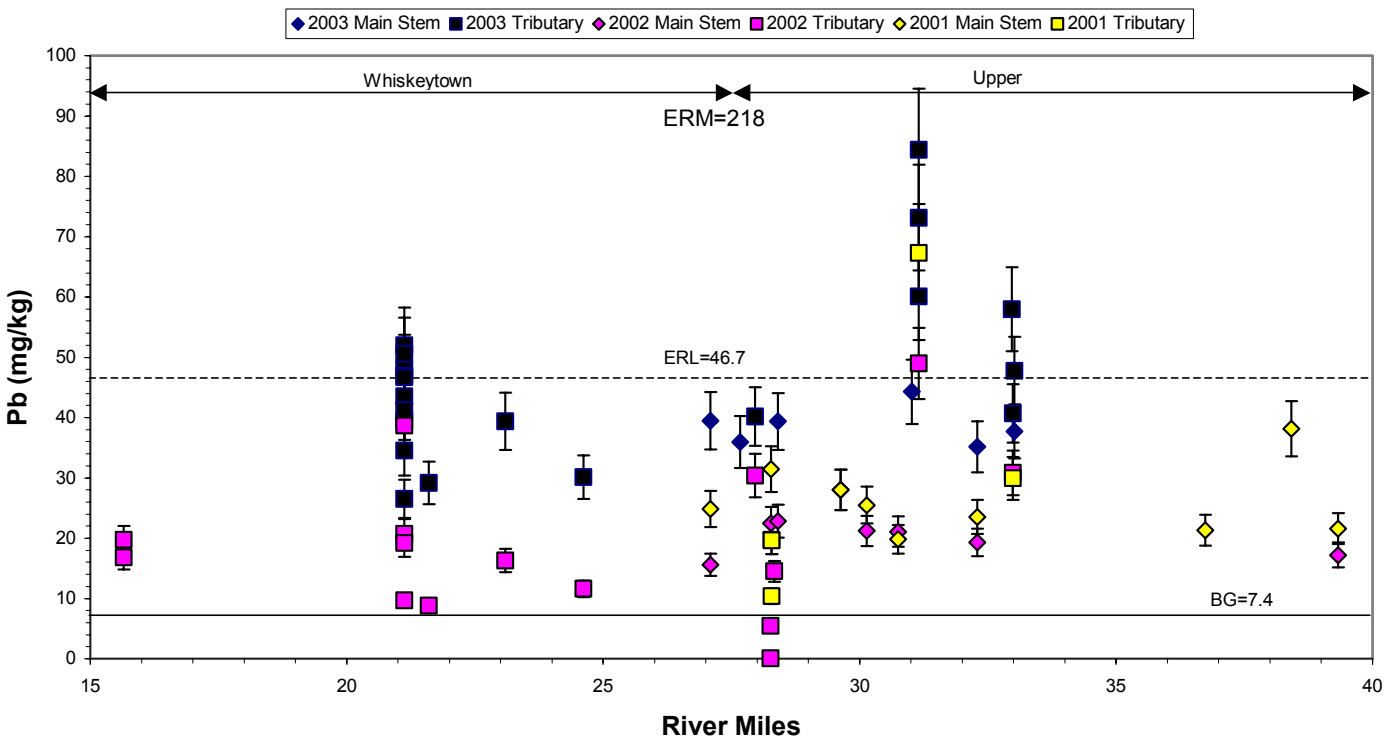


Figure 27

### Metal Concentrations: Pb Clear Creek Watershed, CA

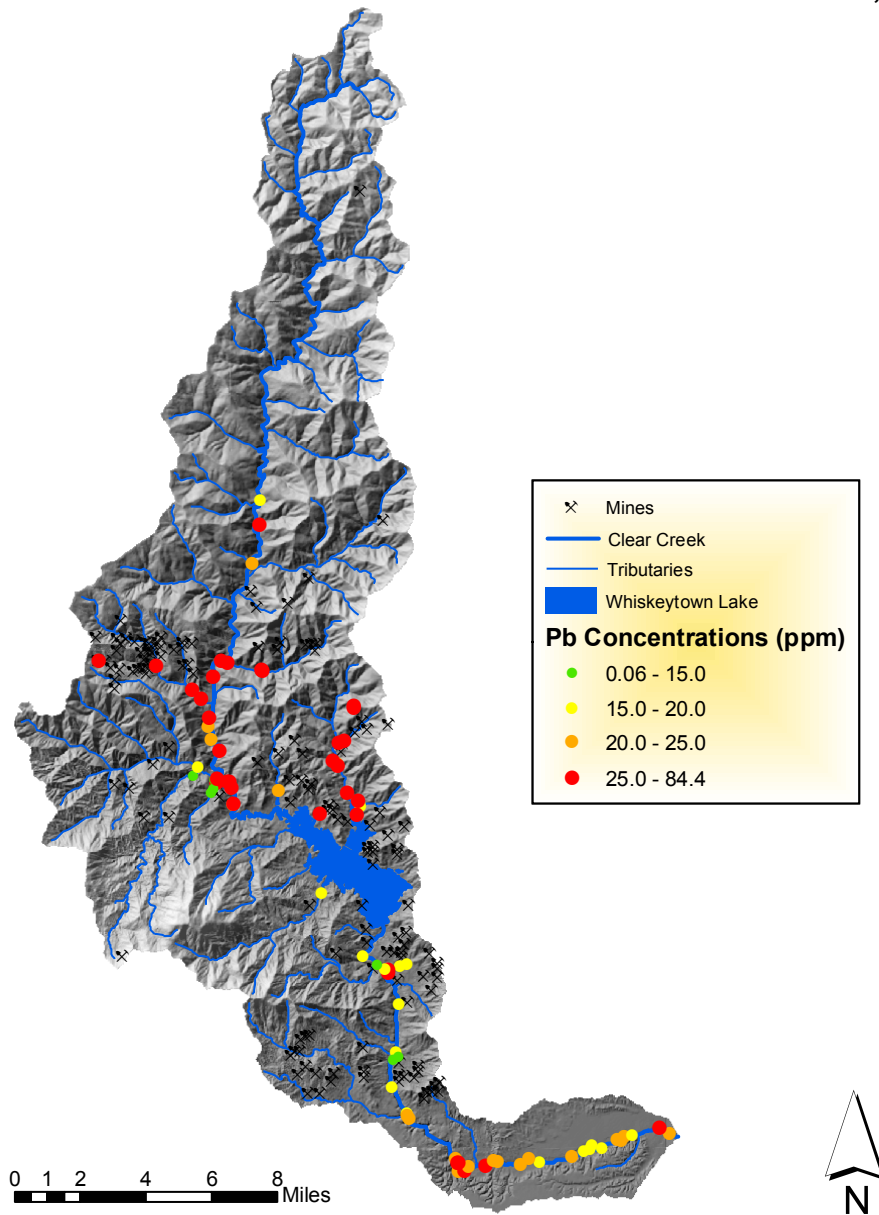


Figure 28

### Threshold Effects Concentrations: Pb Clear Creek Watershed, CA

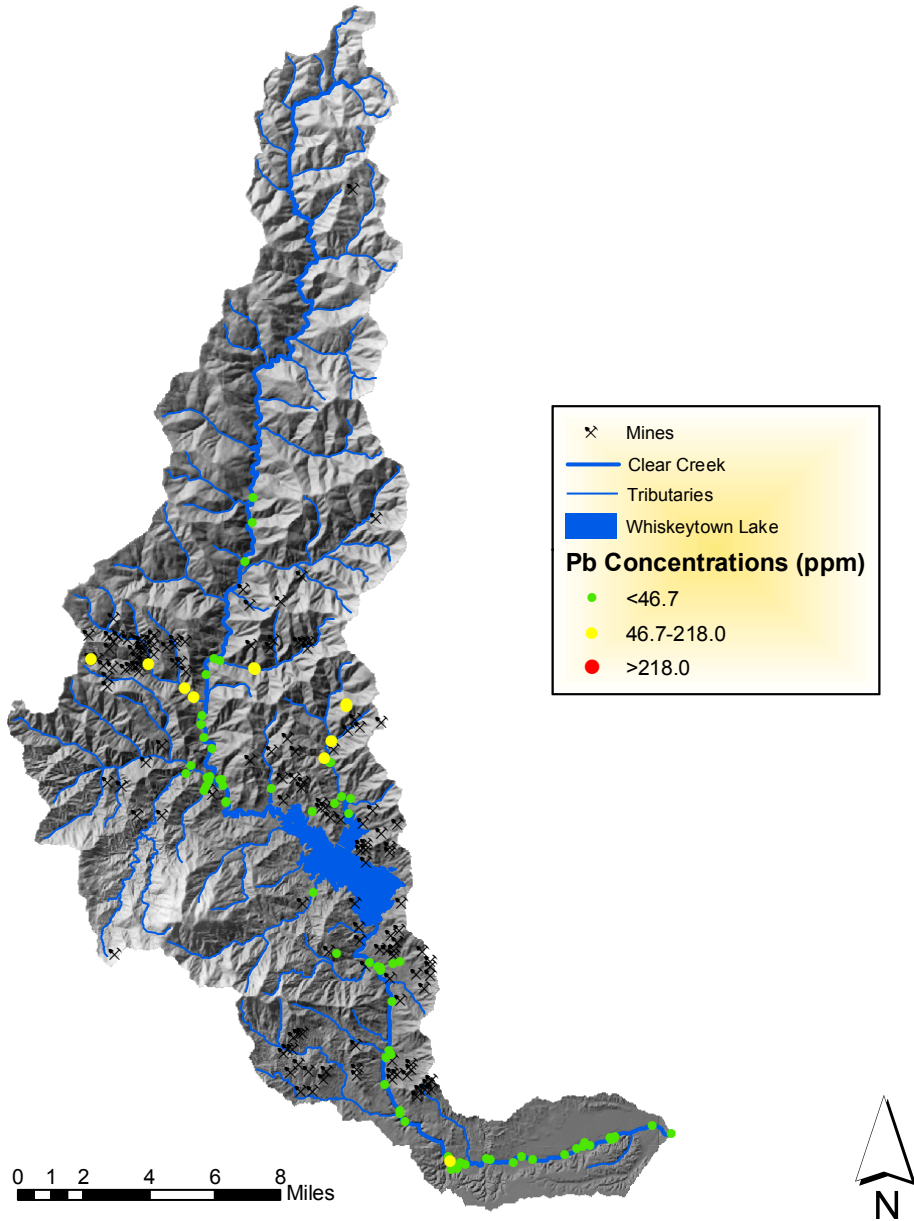




Figure 29

### Multiples of Background: Pb Clear Creek Watershed, CA

Pb Background= 15.3 ppm

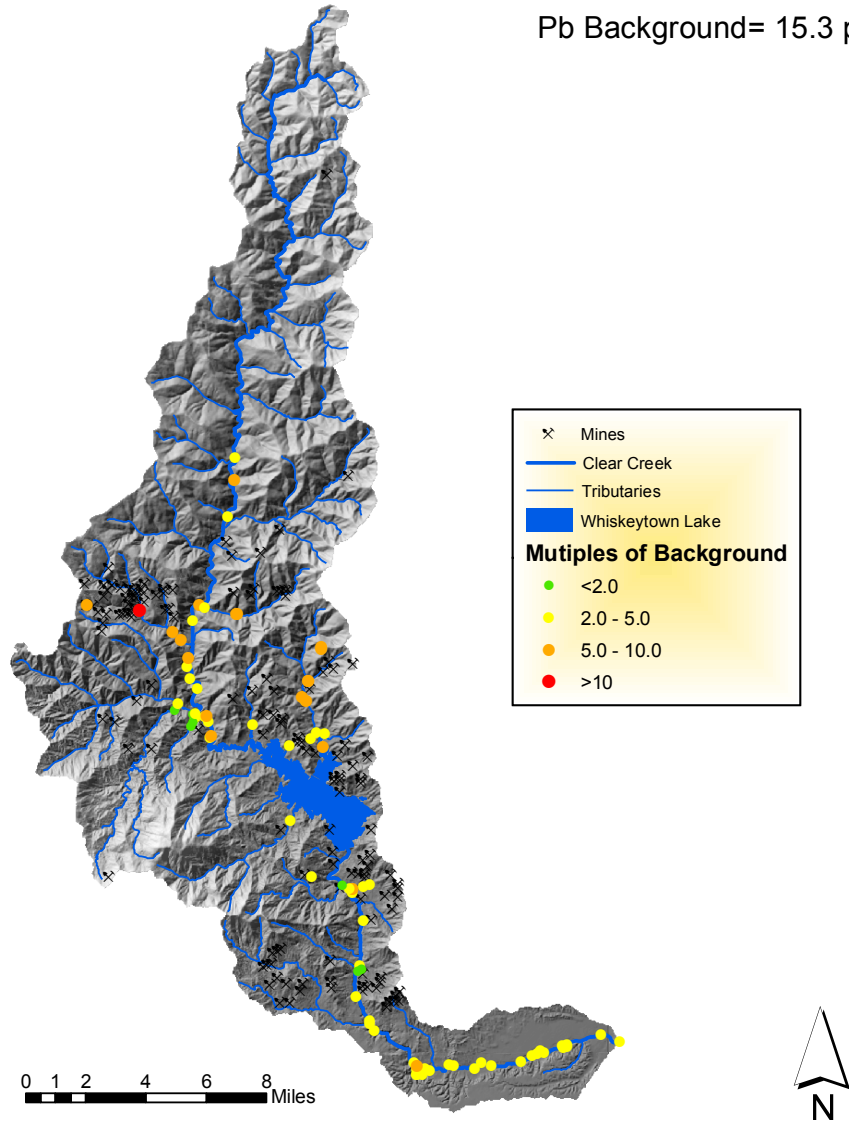


Figure 30A

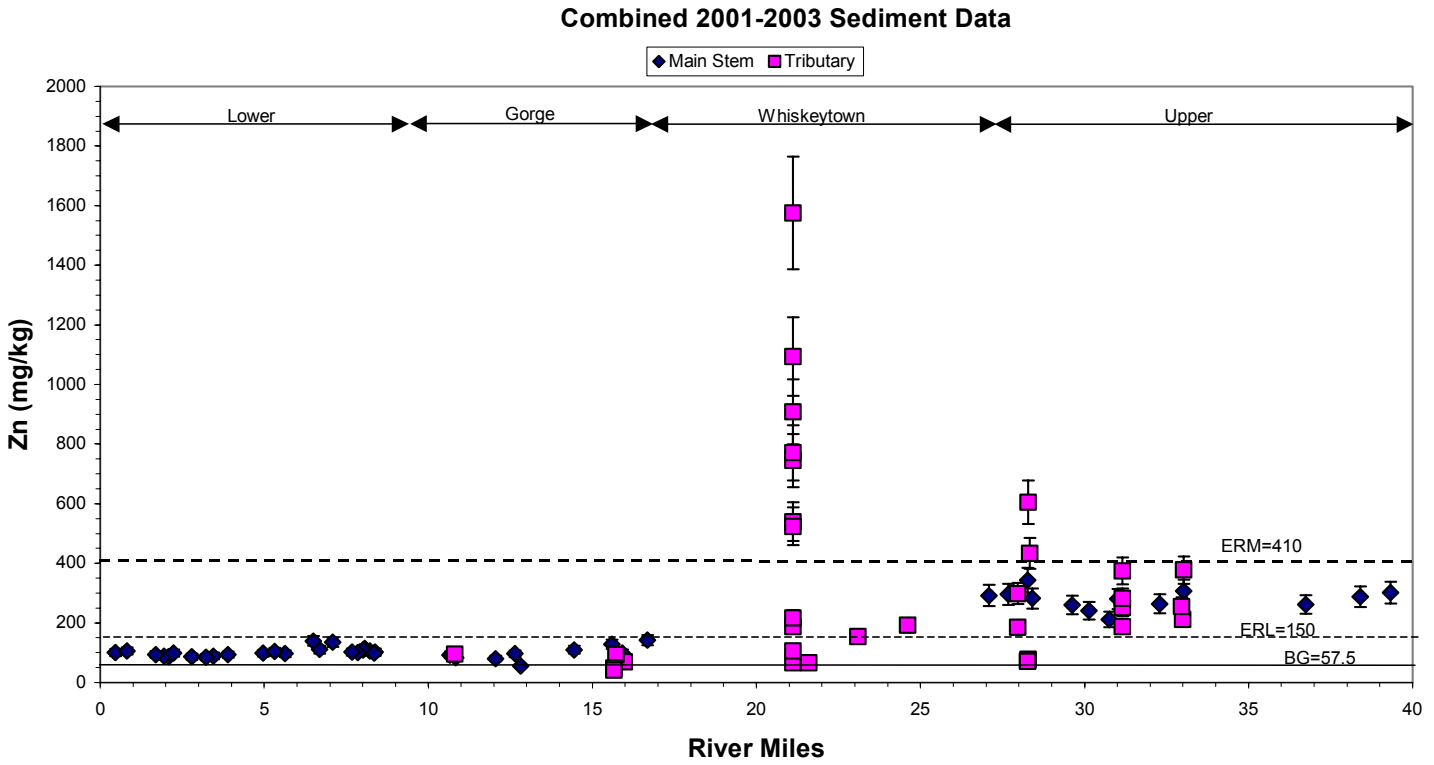


Figure 30B

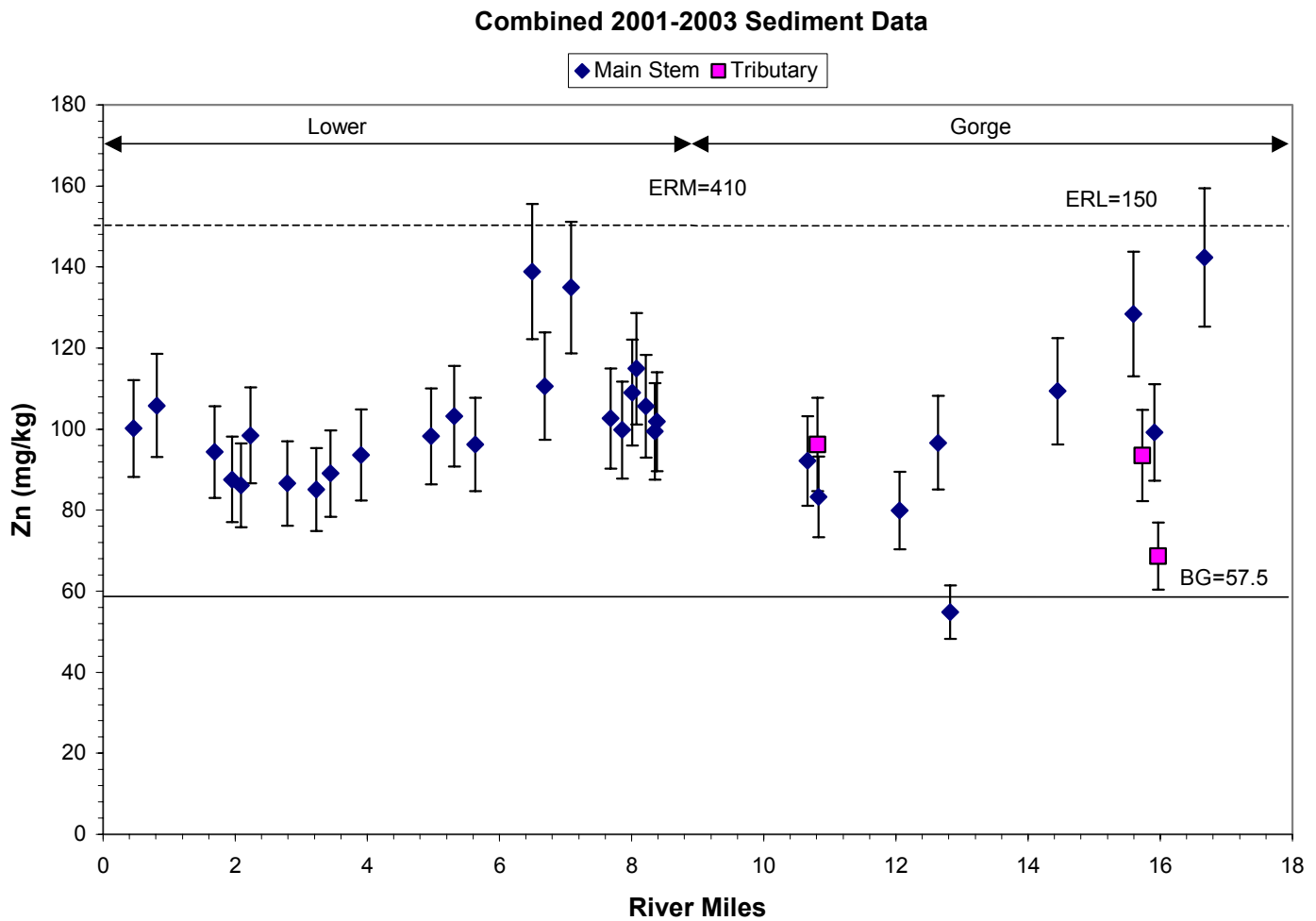


Figure 30C

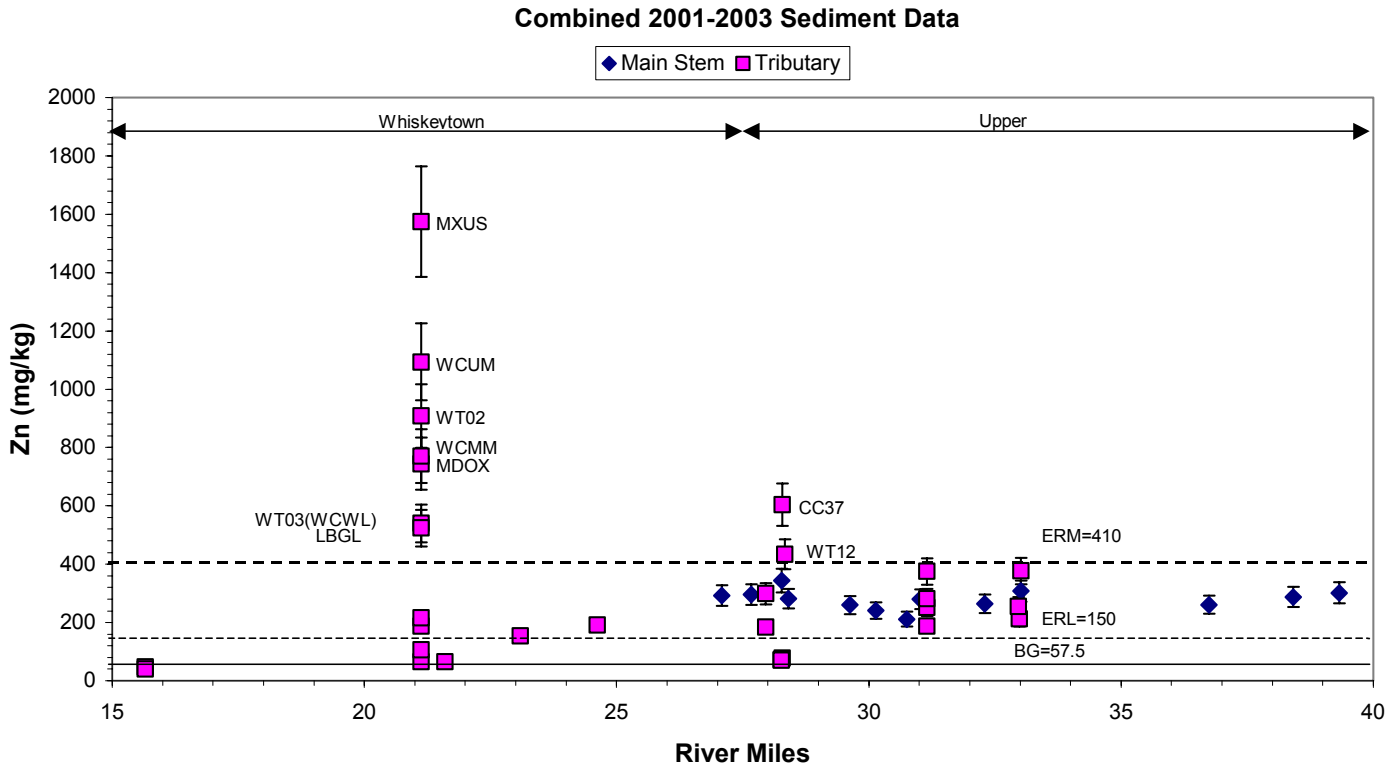


Figure 30D

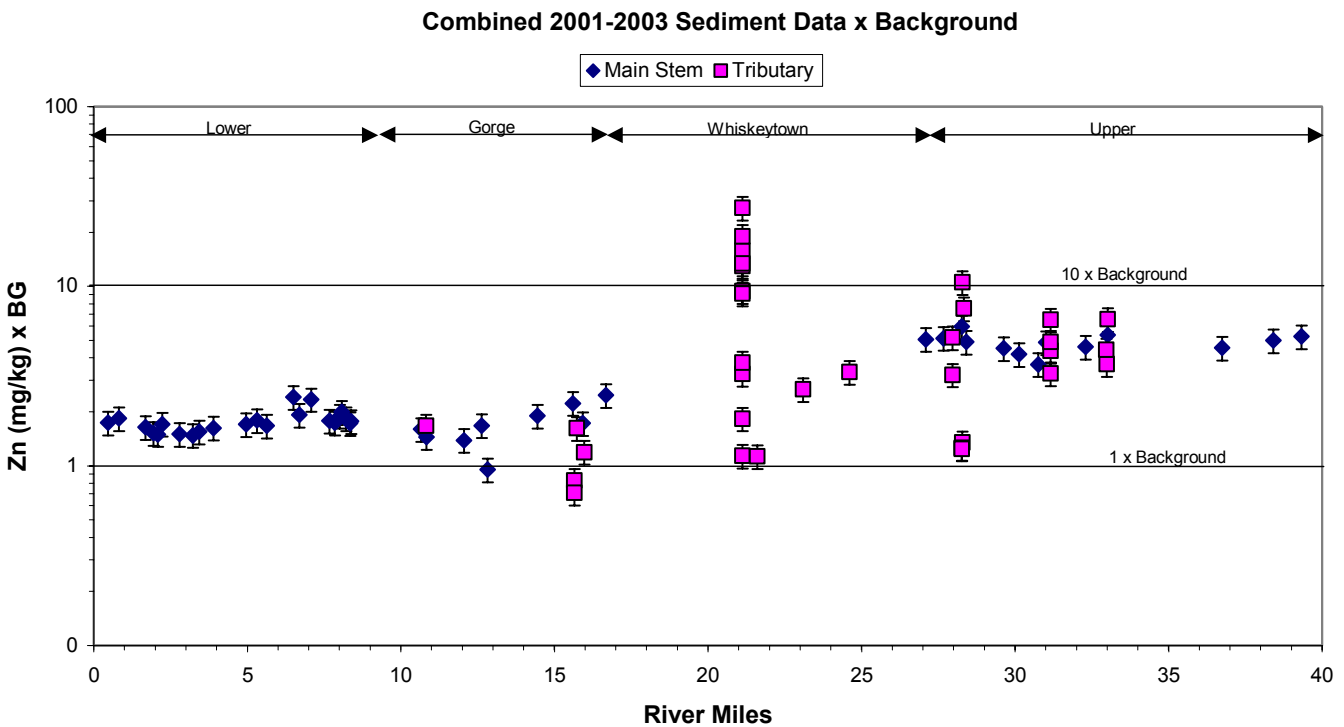


Figure 30E

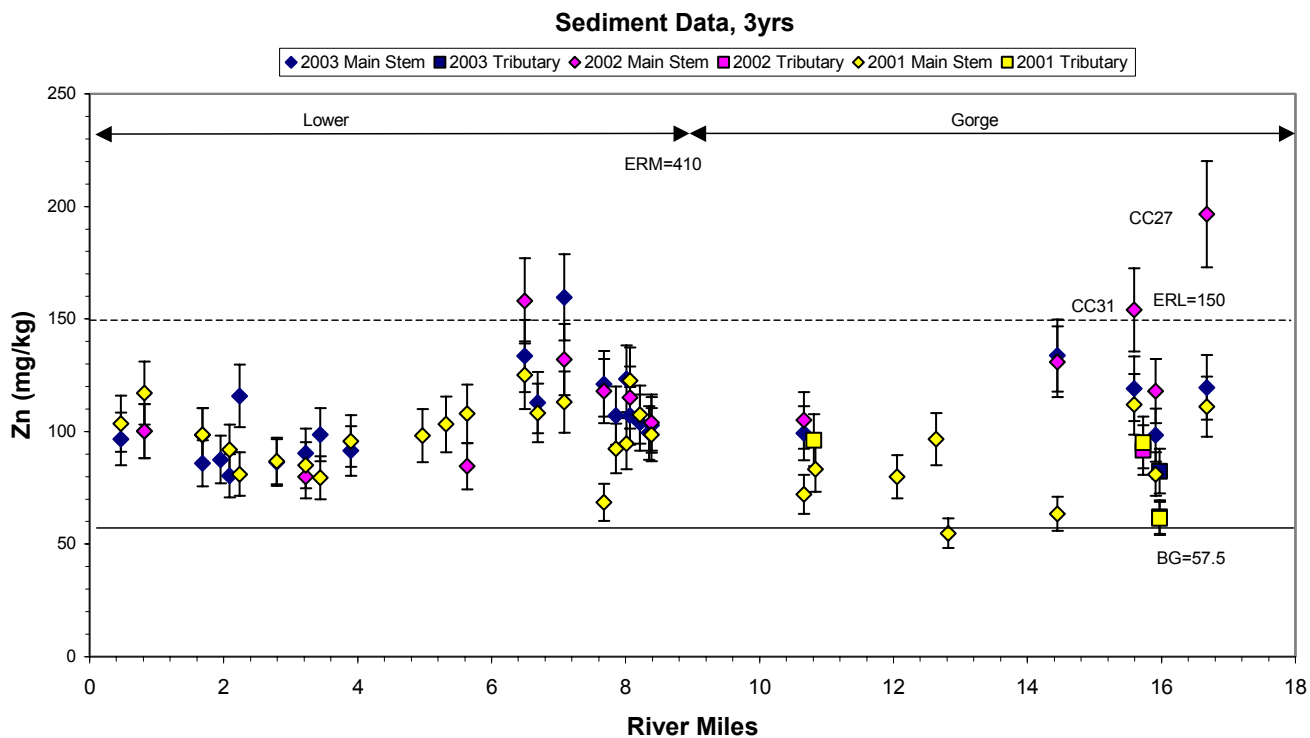


Figure 30F

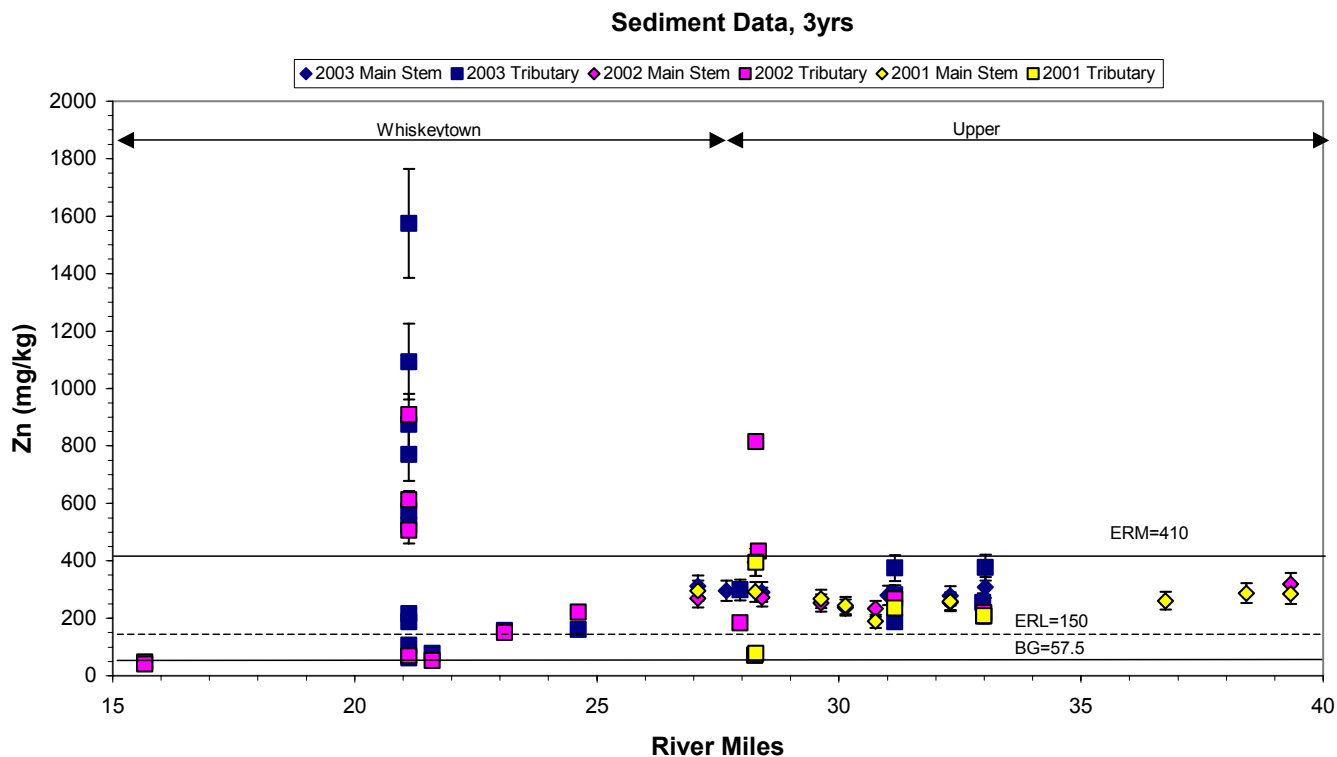


Figure 31

### Metal Concentrations: Zn Clear Creek Watershed, CA

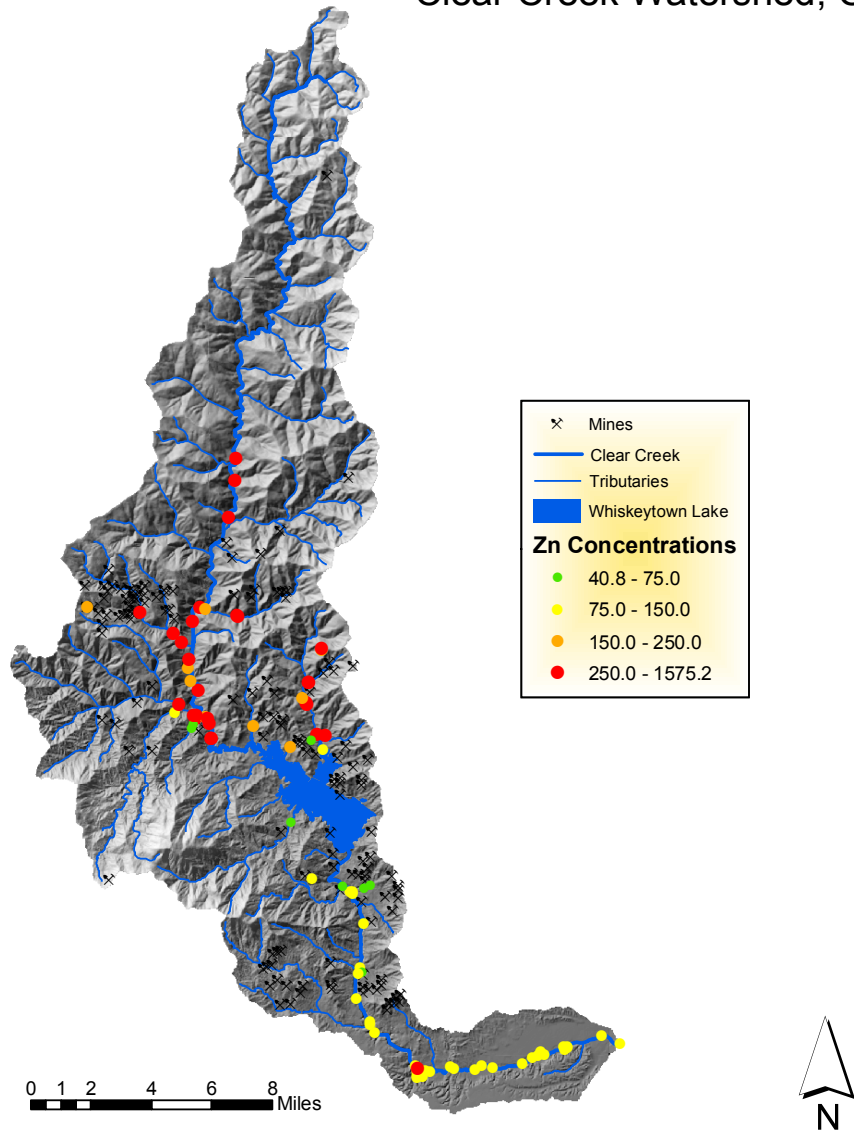


Figure 32

### Threshold Effects Concentrations: Zn Clear Creek Watershed, CA

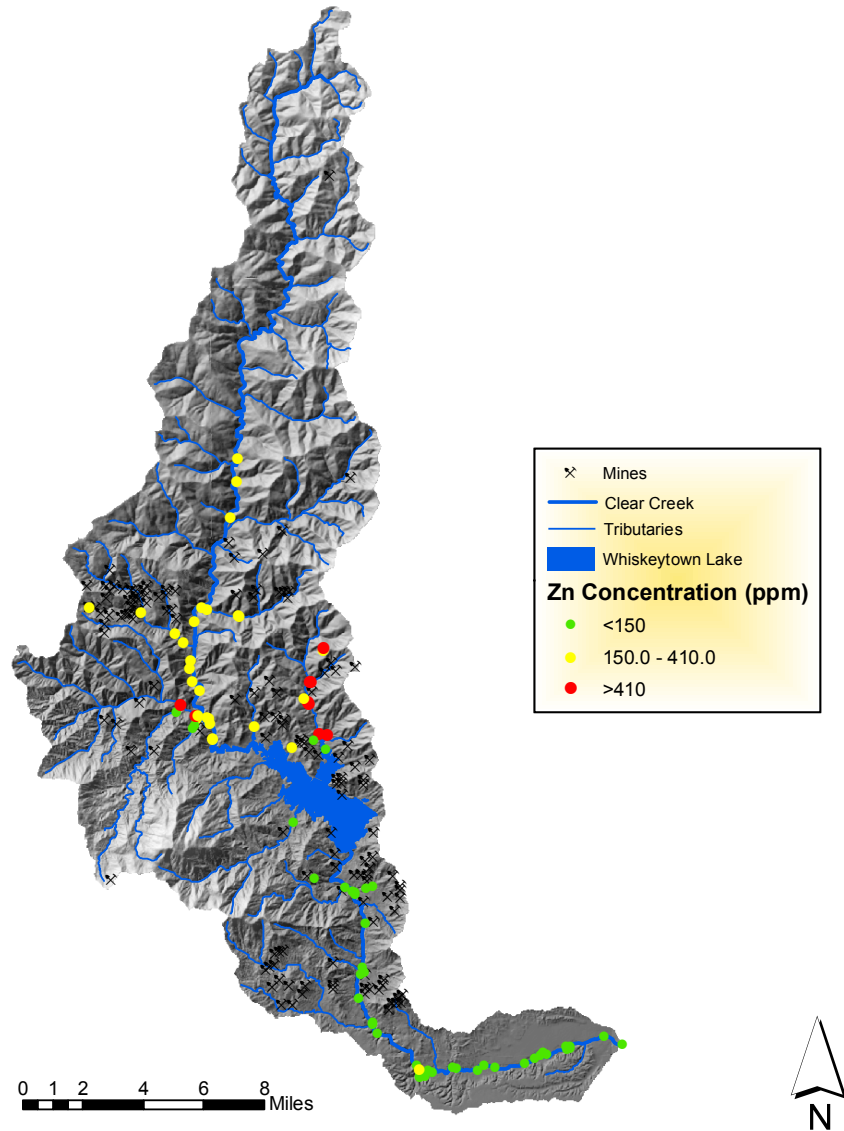


Figure 33

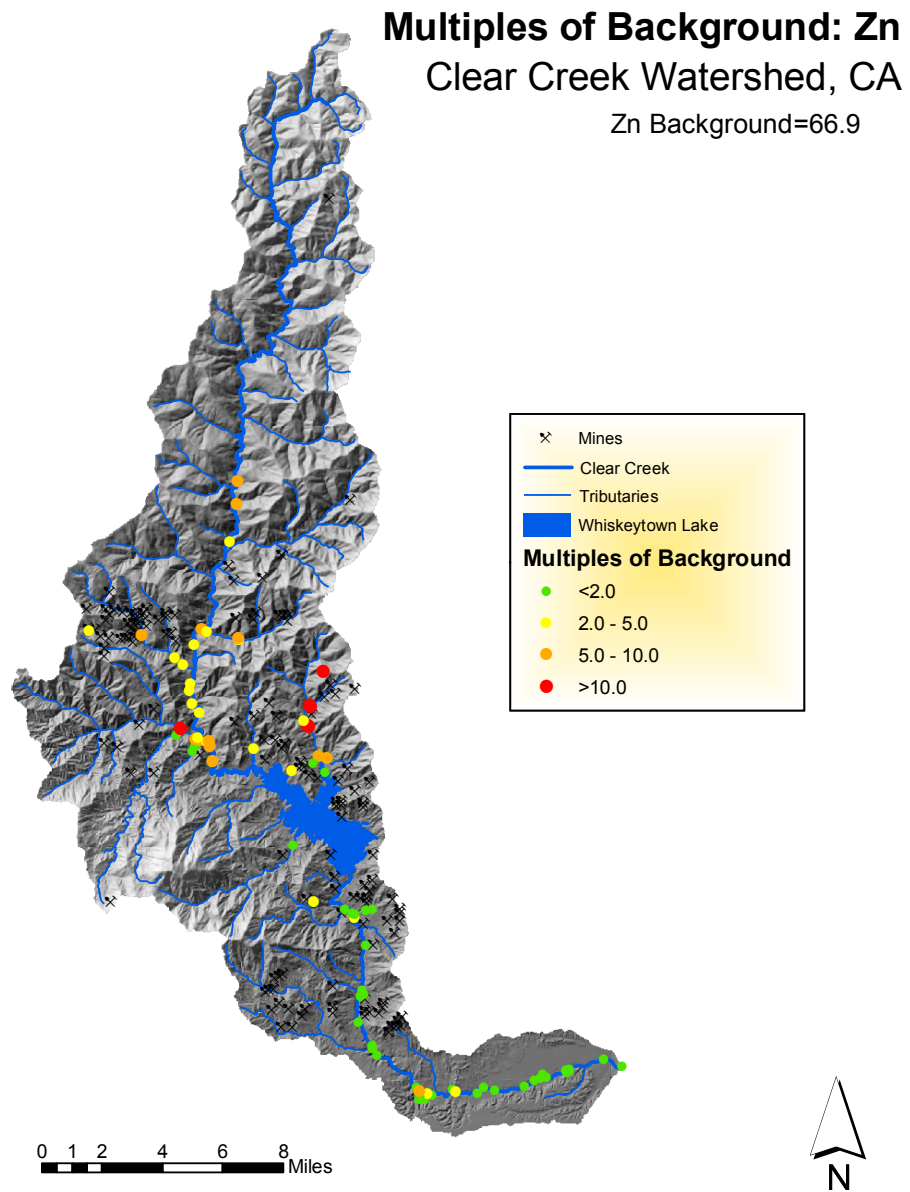


Figure 34A

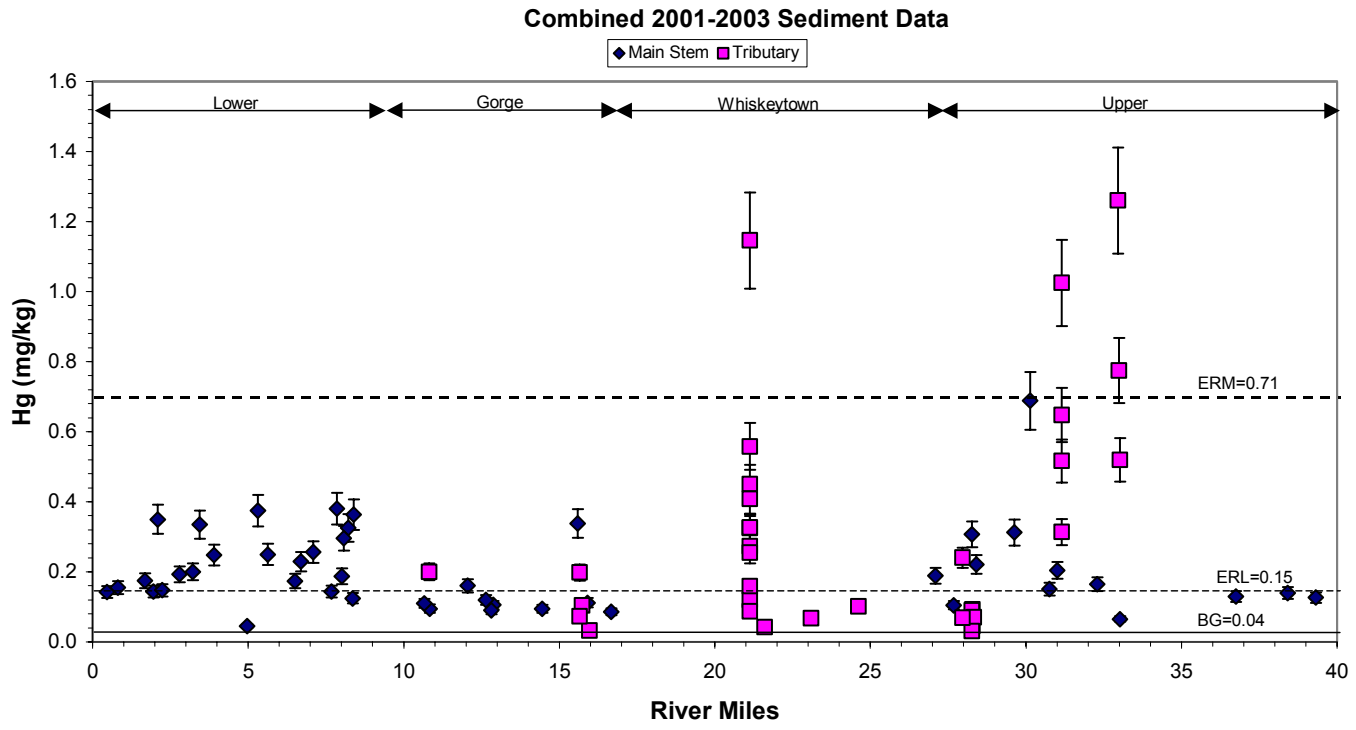


Figure 34B

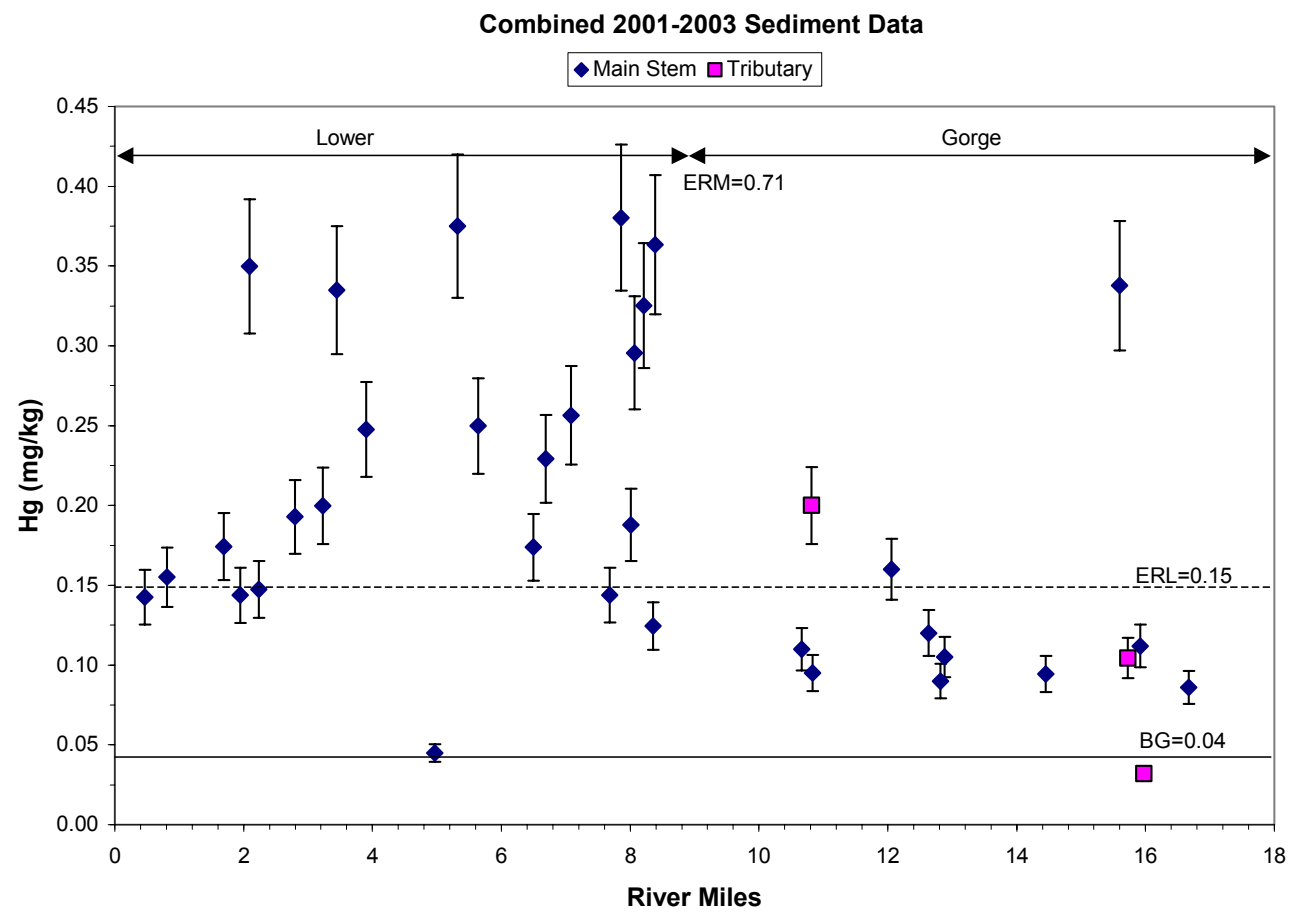




Figure 34C

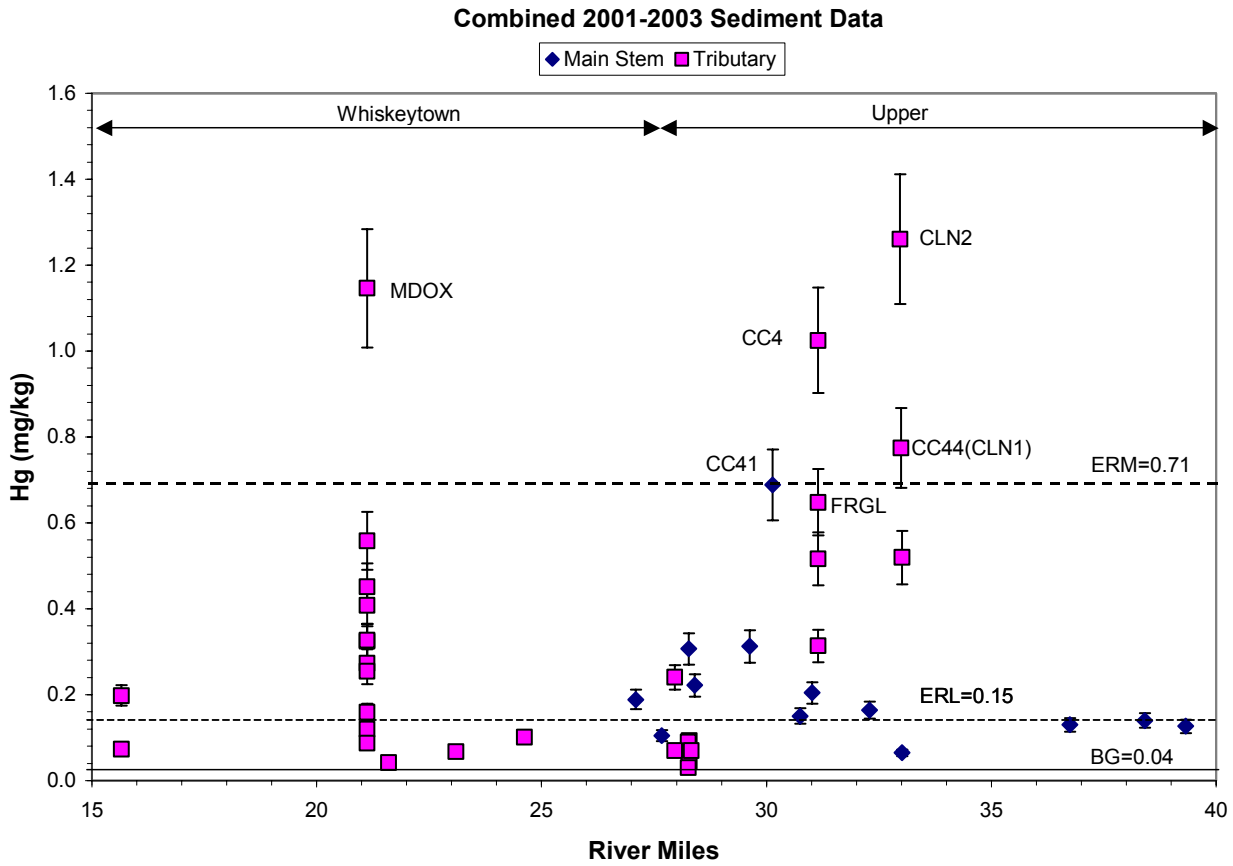


Figure 34D

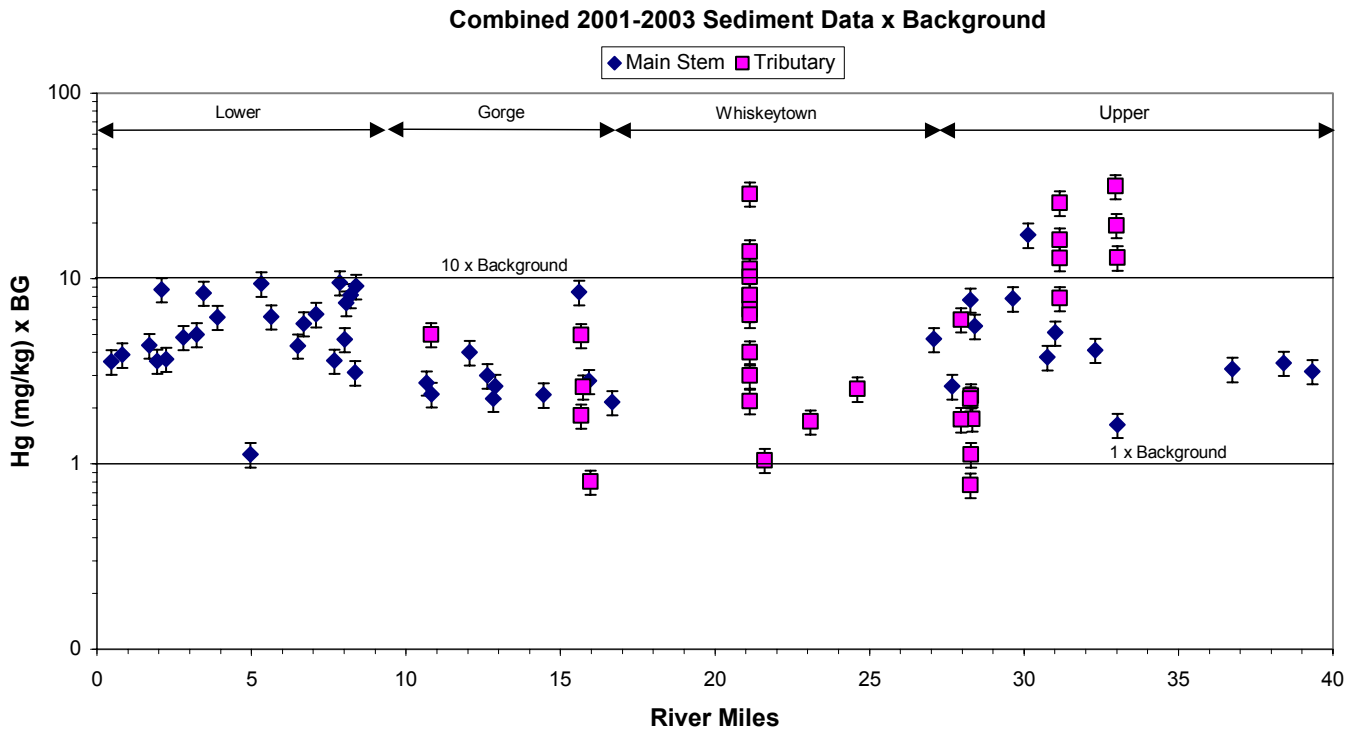


Figure 34E

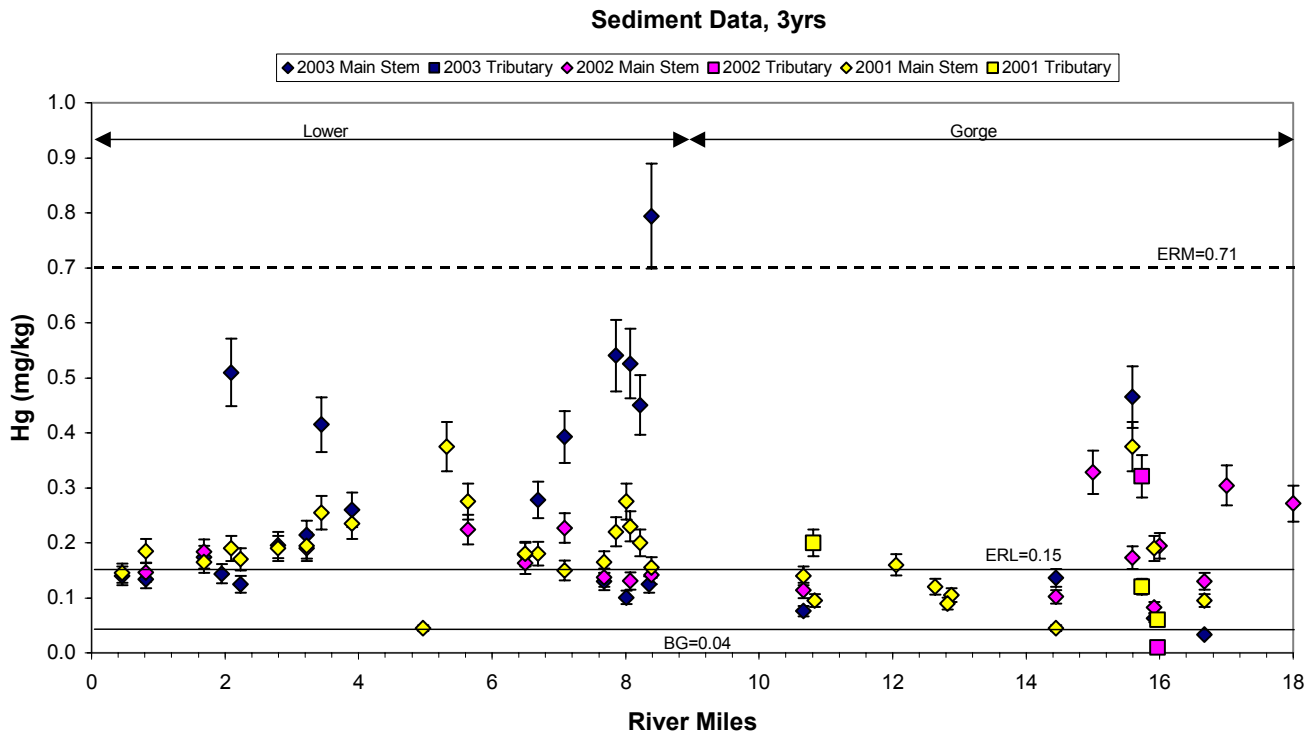


Figure 34F

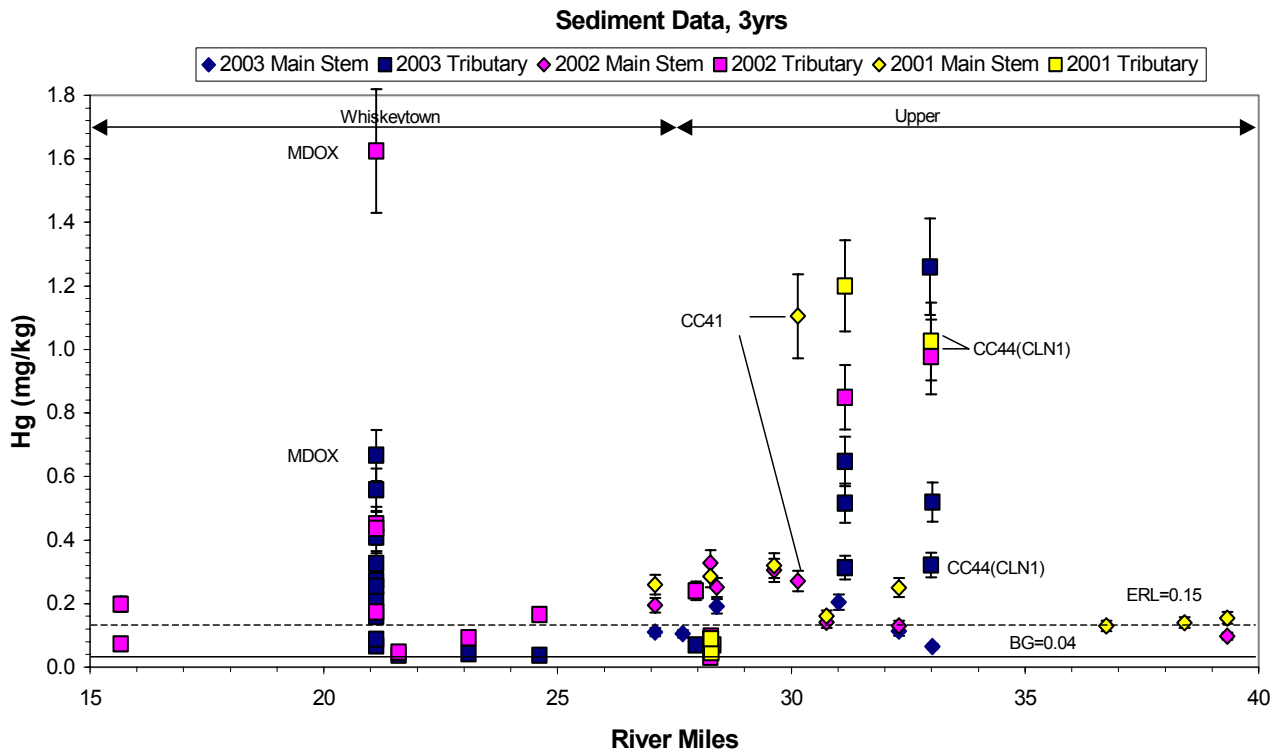


Figure 35

### Metal Concentrations: Hg Clear Creek Watershed, CA

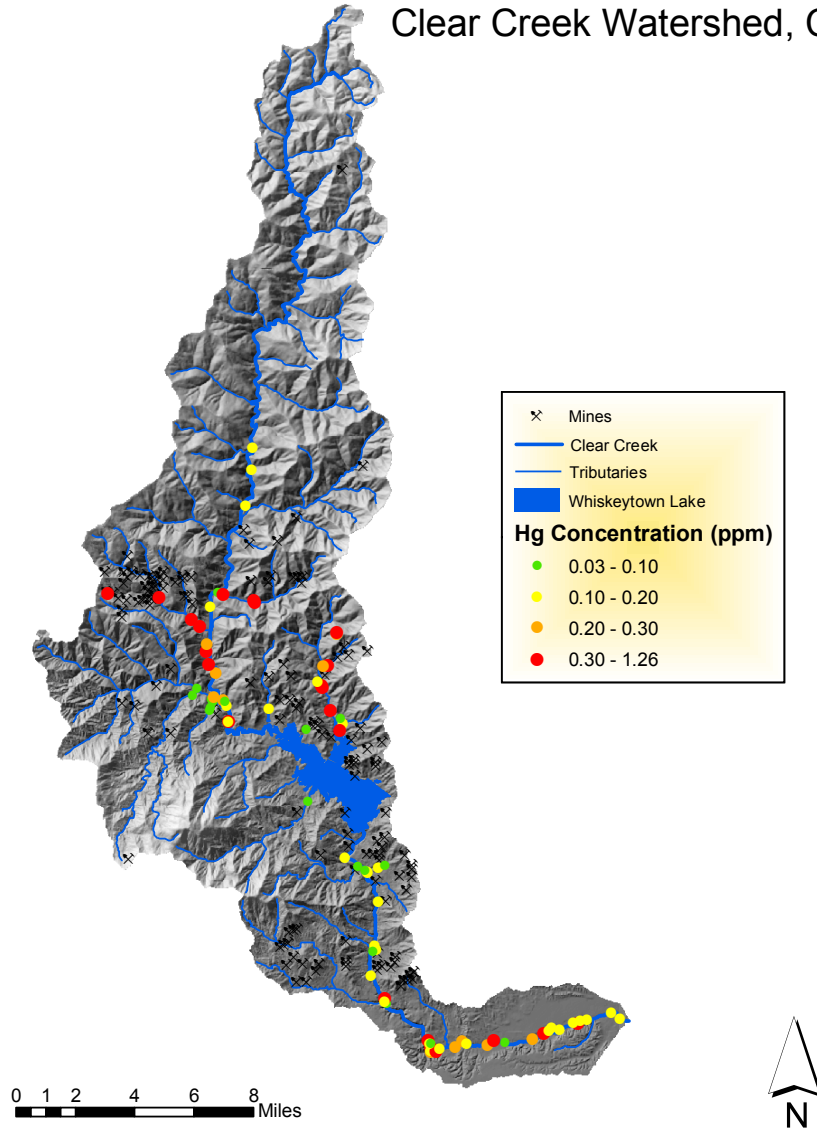


Figure 36

### Threshold Effects Concentrations: Hg Clear Creek Watershed, CA

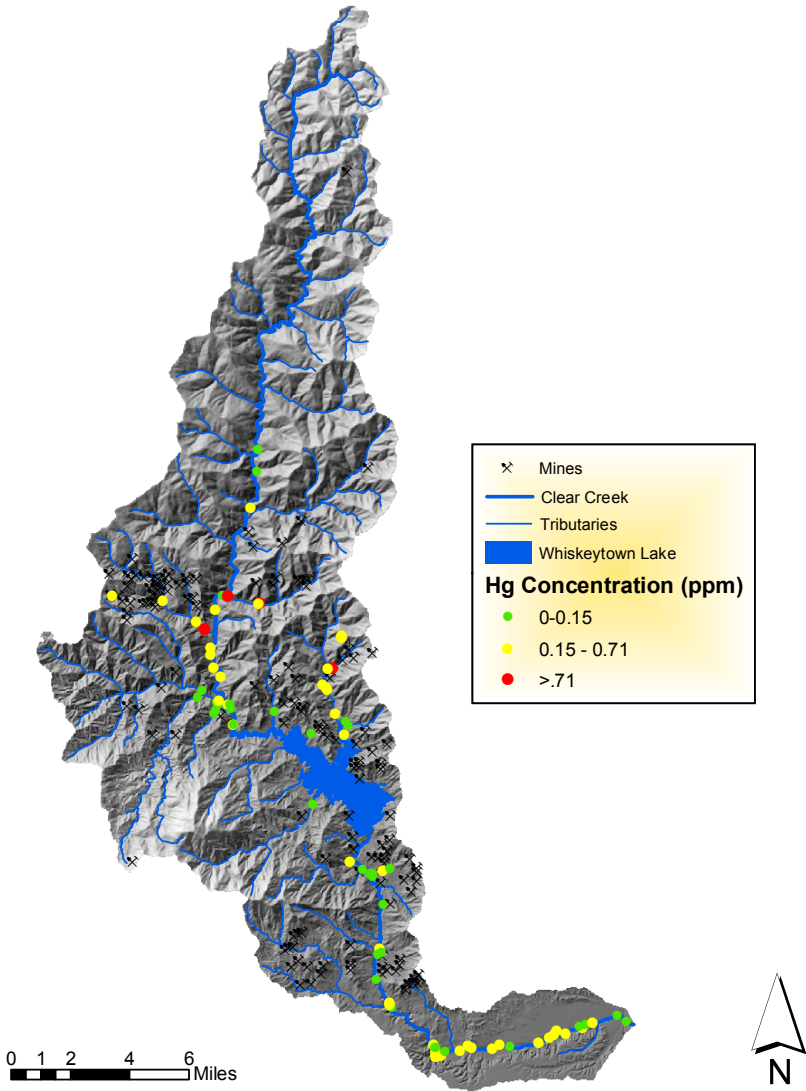


Figure 37

### Multiples of Background: Hg Clear Creek Watershed, CA

Hg Background= 0.04 ppm

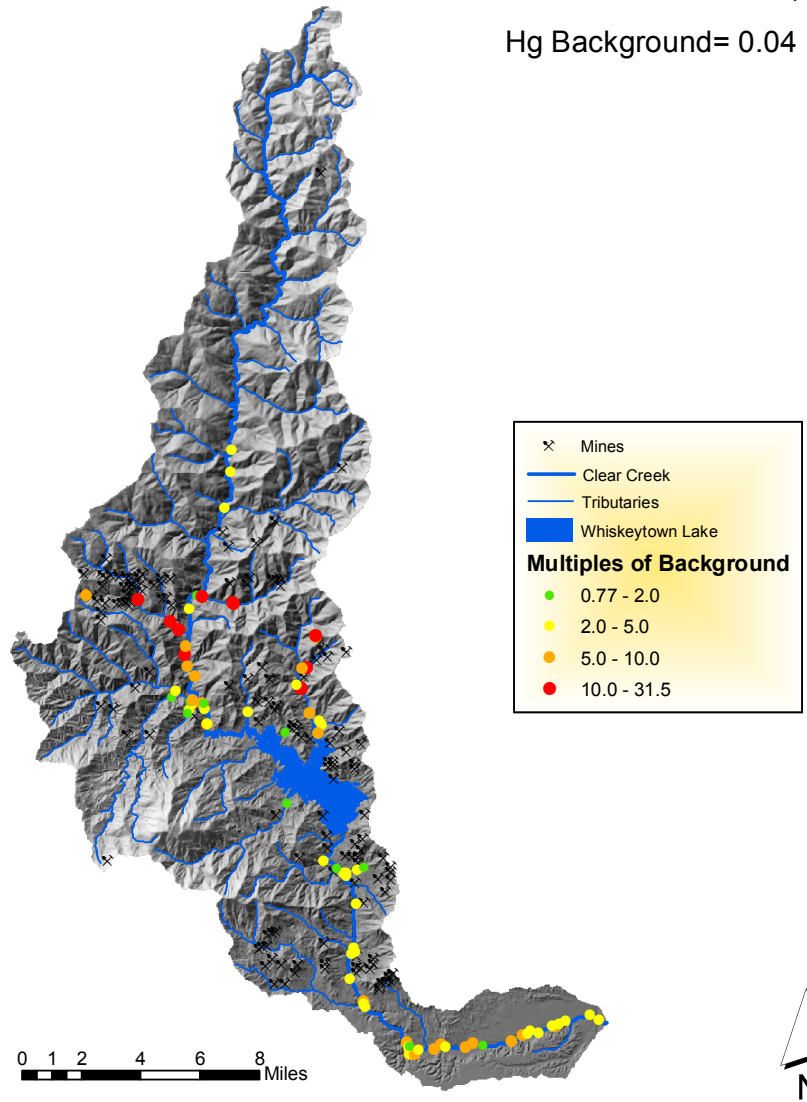


Figure 38A

2003 Sediment Data

◆ Main Stem ■ Tributary

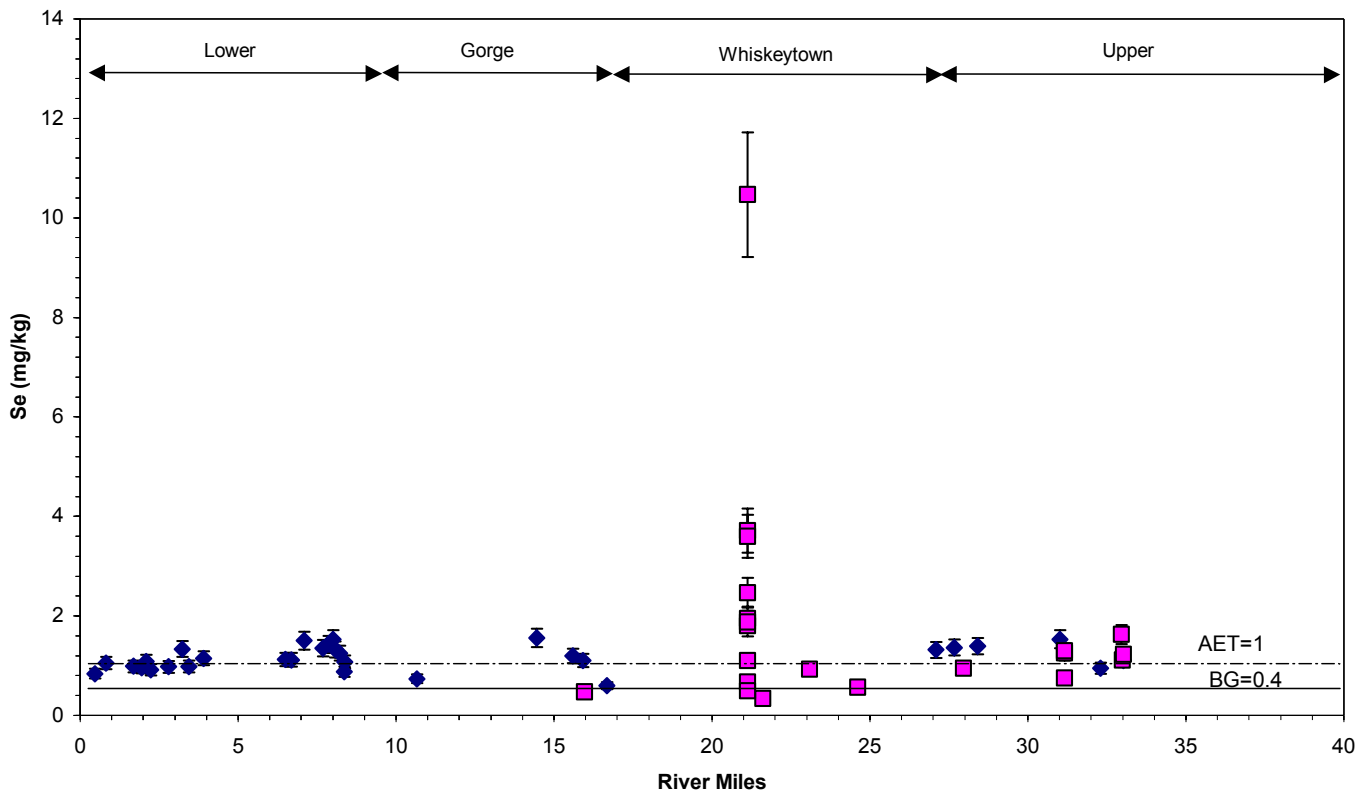


Figure 38B

2003 Sediment Data

◆ Main Stem ■ Tributary

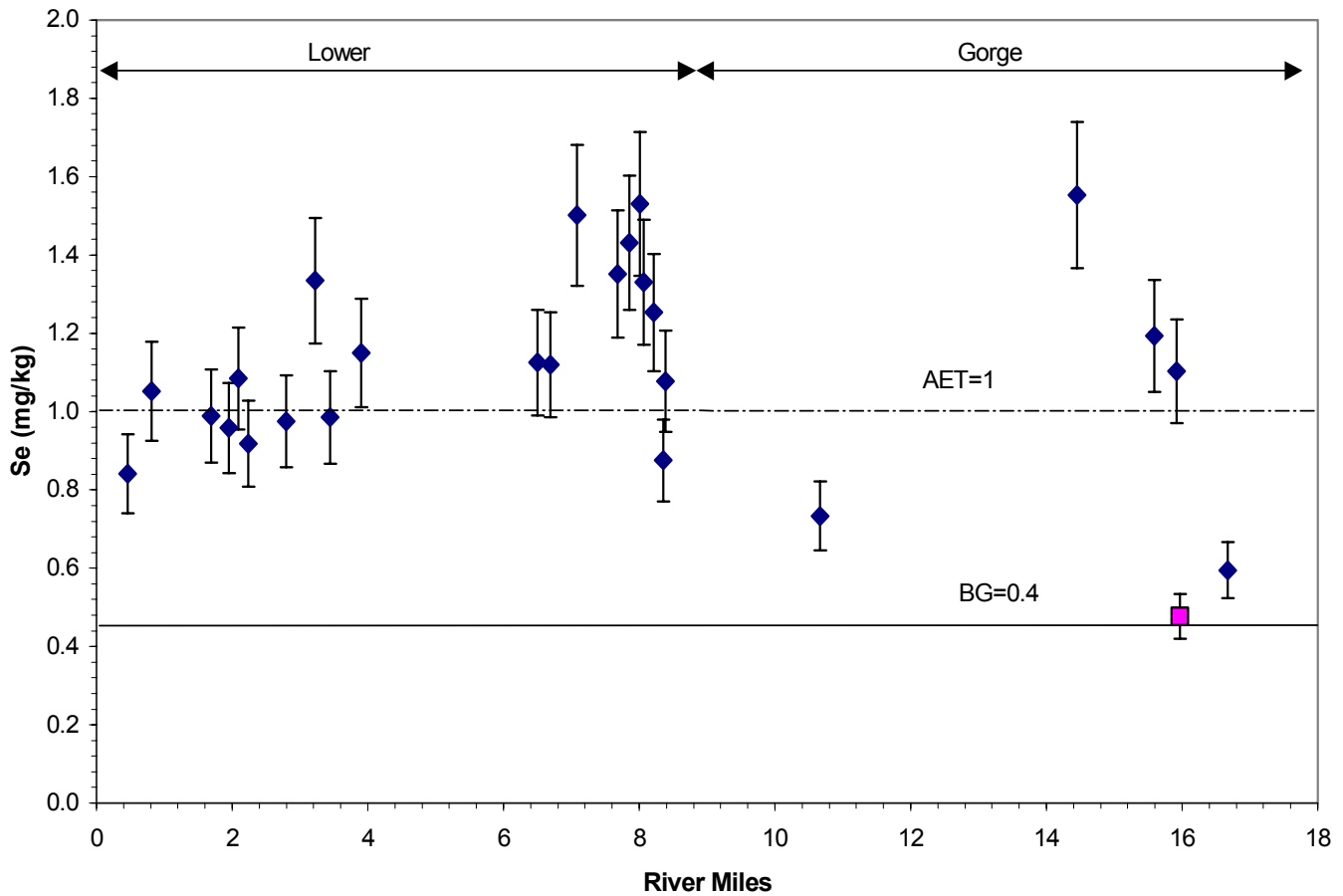


Figure 38C

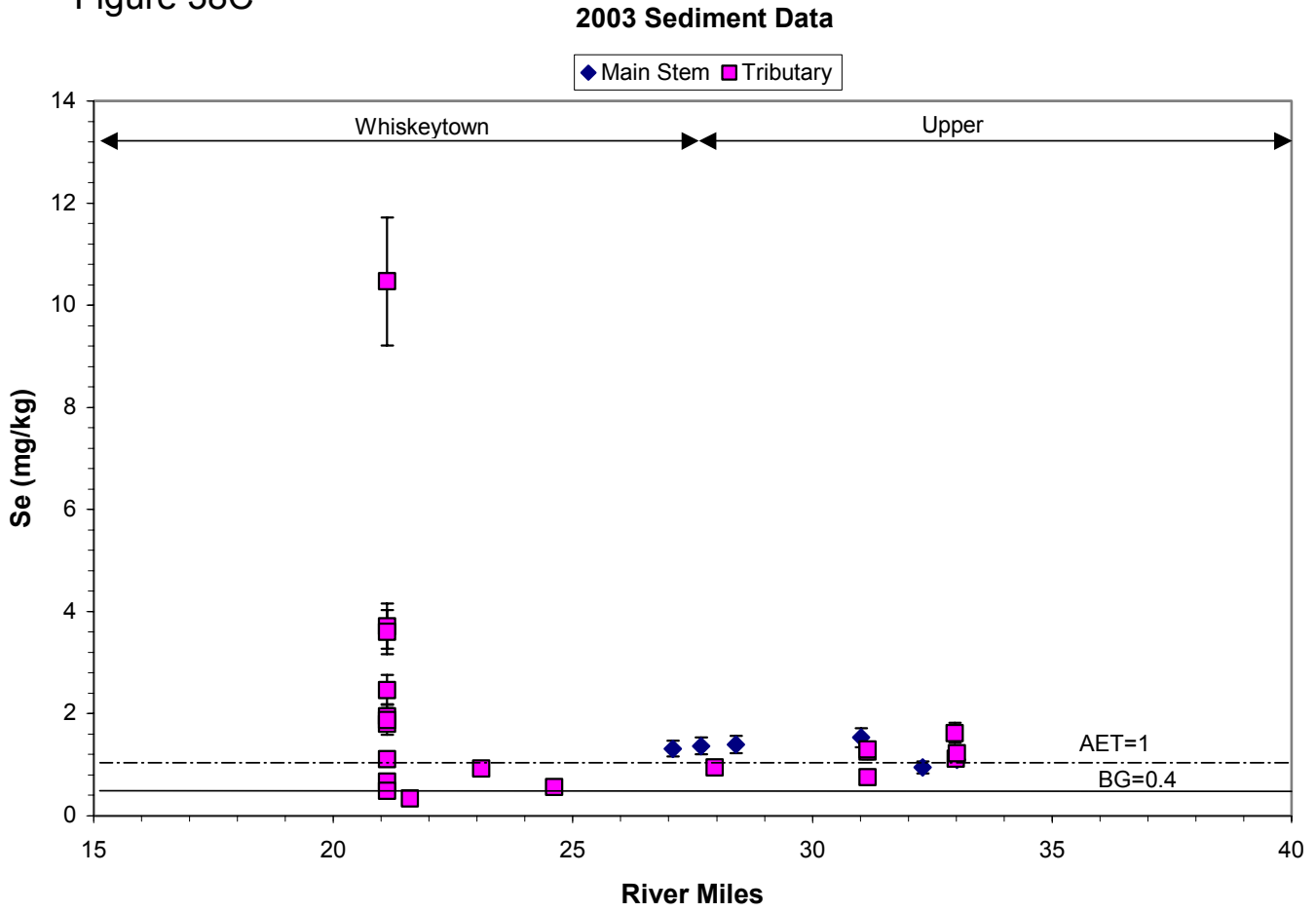


Figure 38D

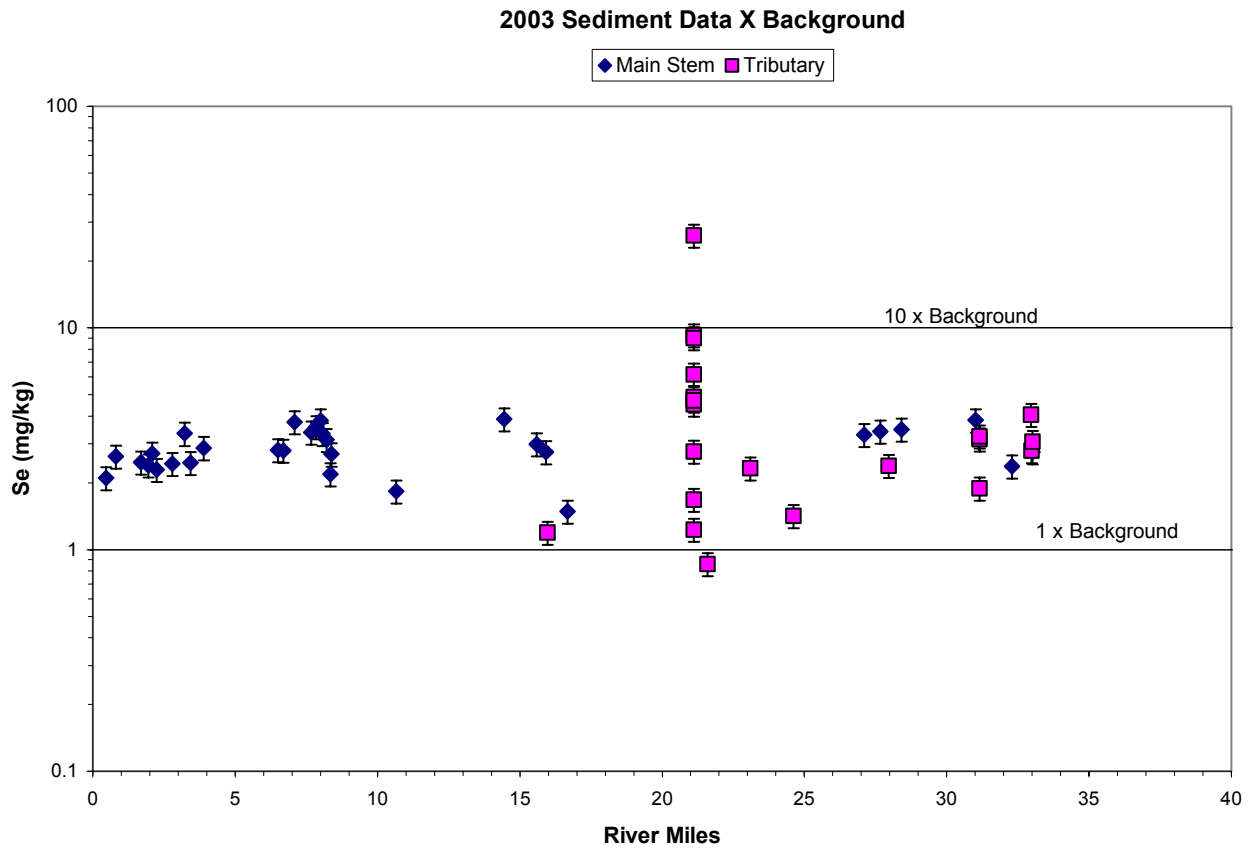


Figure 39

### Concentrations: Se Clear Creek Watershed, CA

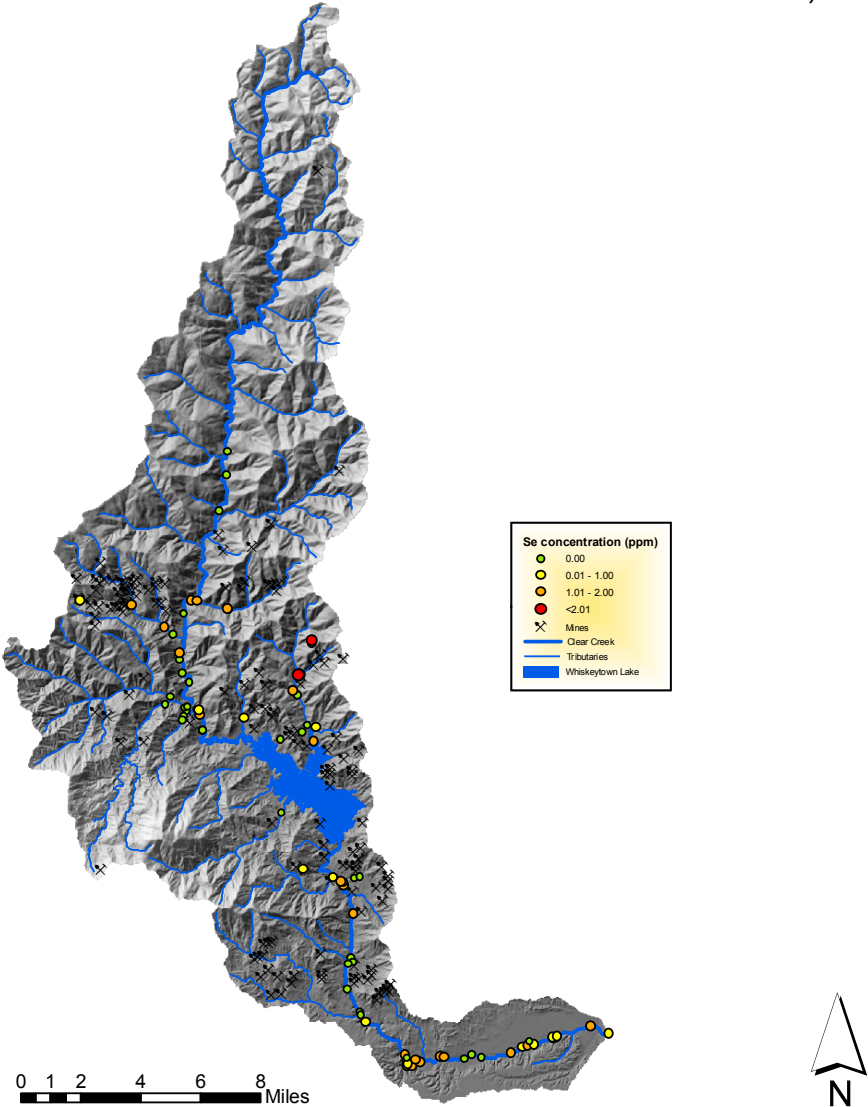




Figure 40

### Threshold Effects Concentrations: Se Clear Creek Watershed, CA

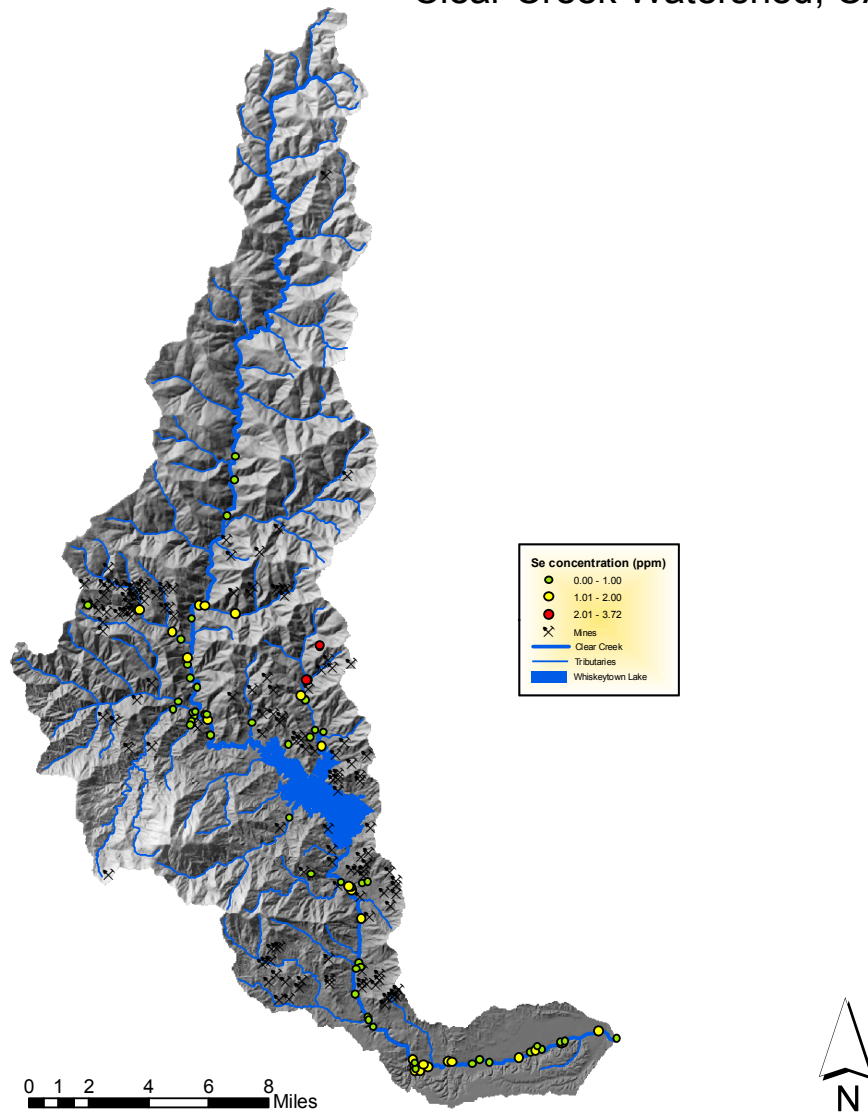
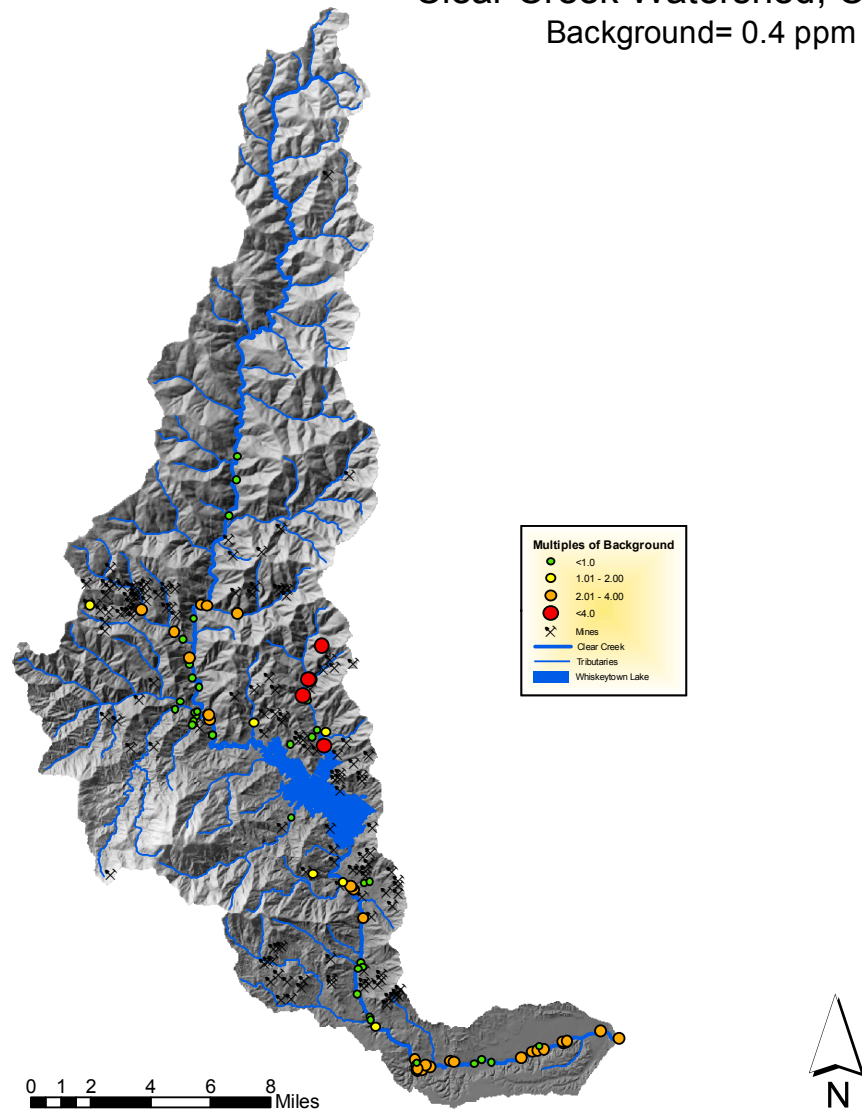


Figure 41

**Multiples of Background:Se**  
Clear Creek Watershed, CA  
Background= 0.4 ppm



## **APPENDIX I**

### **Locations of sample sites and detailed location maps for all sites sampled.**

Data points were collected with a Global Positioning System (GPS) in the field and then imported into ArcGIS. Sites are listed in the table below in UTM Zone 10-NAD27, UTM Zone 10-NAD 83, and Geographic coordinates. Several site were renamed in 2003 and this name is in parenthesis.

## Locations of samples collected in 2001

SITE	UTM Zone 10-NAD27		UTM Zone 10-NAD83		Geographic Coordinates	
	EASTING	NORTHING	EASTING_NAD83	NORTHING_NAD83	LATITUDE	LONGITUDE
CC01	542627	4482706	542556.66760	4482869.92657	40.4954421	-122.4977958
CC02	542763	4482373	542659.43372	4482551.37772	40.4925672	-122.4966045
CC03	542754	4482048	542681.75349	4482244.62233	40.4898025	-122.4963618
CC04	542787	4482137	542655.48153	4482326.55029	40.4905420	-122.4966663
CC05	542982	4482052	542943.01637	4482286.76776	40.4901687	-122.4932762
CC06	543169	4482262	543152.24214	4482502.65767	40.4921028	-122.4907928
CC07	548875	4483111	548822.56963	4483303.10157	40.4989995	-122.4238228
CC08	549134	4483210	549063.61567	4483423.94728	40.5000739	-122.4209689
CC09	550760	4483611	550667.70185	4483807.86559	40.5034360	-122.4020083
CC10	550864	4483809	550804.37338	4483981.91075	40.5049956	-122.4003814
CC11	549845	4483228	549704.40839	4483452.62755	40.5002941	-122.4134046
CC12	550544	4483673	550477.79856	4483862.94406	40.5039438	-122.4042451
CC13	544118	4482395	544004.60828	4482529.08464	40.4922961	-122.4807332
CC14	544421	4482601	544373.02718	4482819.10526	40.4948892	-122.4763656
CC15	544688	4482527	544603.33892	4482732.71745	40.4940986	-122.4736539
CC16	545795	4482425	545728.45410	4482629.57159	40.4931082	-122.4603849
CC17	551260	4483912	551163.04623	4484092.33649	40.5059683	-122.3961395
CC18	548307	4482753	548226.58564	4483011.45834	40.4964070	-122.4308782
CC19	546725	4482626	546662.83785	4482773.80313	40.4943555	-122.4493486
CC20	na	na	553032.98612	4484138.02274	40.5062624	-122.3740666
CC21	546152	4482666	546111.65067	4482886.93817	40.4954055	-122.4558445
CC22	552577	4484291	552532.52590	4484447.15903	40.5090791	-122.3799474
CC23	539692	4487810	539592.44631	4488108.31143	40.5427798	-122.5324472
CC24	539706	4487685	539710.57159	4487865.11270	40.5405833	-122.5310675
CC25	539502	4487545	539484.06340	4487775.76611	40.5397892	-122.5337478
CC26	539466	4486626	539403.03727	4486423.36307	40.5276097	-122.5347889
CC27	538051	4492677	537992.77661	4492853.81153	40.5856053	-122.5510518
CC28	538788	4492228	538722.23985	4492430.70220	40.5817598	-122.5424582
CC29	538996	4492216	539034.35993	4492337.08999	40.5809018	-122.5387761
CC30	539320	4491996	539209.19844	4492153.67094	40.5792412	-122.5367217
CC31	539327	4491813	539193.68464	4492026.95201	40.5781004	-122.5369129

**Locations of samples collected in 2001 (continued)**

<i>SITE</i>	<b>UTM Zone 10-NAD27</b>		<b>UTM Zone 10-NAD83</b>		<b>Geographic Coordinates</b>	
	<i>EASTING</i>	<i>NORTHING</i>	<i>EASTING_NAD83</i>	<i>NORTHING_NAD83</i>	<i>LATITUDE</i>	<i>LONGITUDE</i>
CC32	540290	4484952	540131.82925	4485189.82264	40.5164622	-122.5262629
CC33	540273	4484916	540136.11103	4485041.86054	40.5151290	-122.5262217
CC34	540325	4484697	540239.50122	4484877.06260	40.5136394	-122.5250118
CC35	539871	4490278	539757.36995	4490480.66953	40.5641436	-122.5303503
CC36	529530	4501470	529681.13440	4501719.11851	40.6658097	-122.6488477
CC37	530000	4501895	529901.57493	4502107.18422	40.6692977	-122.6462213
CC38	531016	4501179	530808.06487	4501374.90025	40.6626675	-122.6355323
CC39	531708	4500126	531640.53346	4500300.78258	40.6529597	-122.6257383
CC40	531059	4502674	530943.39666	4502904.44797	40.6764415	-122.6338560
CC41	530633	4503058	530555.88938	4503415.31071	40.6810580	-122.6384163
CC42	530457	4503926	530407.59388	4504098.20380	40.6872154	-122.6401380
CC43	529708	4505687	530060.44500	4505465.09450	40.6995418	-122.6441808
CC44	531531	4506994	531399.11918	4507171.38261	40.7148630	-122.6282501
CC45	530750	4506272	530664.16048	4506519.43347	40.7090176	-122.6369833
CC46	532621	4511862	532552.11297	4512081.97070	40.7590550	-122.6143441
CC47	532995	4513835	532917.60081	4514046.50092	40.7767377	-122.6099107
CC48	533060	4515047	532965.59528	4515258.52058	40.7876541	-122.6092779
CC49	530781	4507119	530788.67902	4507296.38479	40.7160122	-122.6354711
CC50	546006	4482831	546004.77679	4483041.98617	40.4968082	-122.4570944
CC51	546363	4483040	546361.76724	4483250.98958	40.4986711	-122.4528664
CC52	549436	4483206	549358.46358	4483400.74638	40.4998474	-122.4174912
CC53	549522	4483020	549444.51653	4483213.02034	40.4981511	-122.4164903
CC54	544088	4482707	543901.06948	4482902.54287	40.4956659	-122.4819290
CC55	543977	4482621	543813.33010	4482817.28734	40.4949025	-122.4829703
CC56	543844	4482544	543835.54597	4482713.35695	40.4939651	-122.4827153
CC57	543946	4482533	543936.48857	4482708.35910	40.4939147	-122.4815246
CC58	542768	4482576	542637.08426	4482719.87434	40.4940862	-122.4968569
CC59	549230	4483391	549228.69092	4483601.99467	40.5016681	-122.4190070

## Locations of samples collected in 2002

SITE	UTM Zone 10-NAD27		UTMZone 10-NAD83		Geographic Coordinates	
	EASTING	NORTHING	EASTING_NAD83	NORTHING_NAD83	LATITUDE	LONGITUDE
CC01	542627	4482706	542556.66760	4482869.92657	40.4954421	-122.4977958
CC03	542754	4482048	542681.75349	4482244.62233	40.4898025	-122.4963618
CC06	543169	4482262	543152.24214	4482502.65767	40.4921028	-122.4907928
CC08	549134	4483210	549063.61567	4483423.94728	40.5000739	-122.4209689
CC13	544118	4482395	544004.60828	4482529.08464	40.4922961	-122.4807332
CC15	544688	4482527	544603.33892	4482732.71745	40.4940986	-122.4736539
CC17	551260	4483912	551163.04623	4484092.33649	40.5059683	-122.3961395
CC22	552577	4484291	552532.52590	4484447.15903	40.5090791	-122.3799474
CC27	538051	4492677	537992.77661	4492853.81153	40.5856053	-122.5510518
CC28	538788	4492228	538722.23985	4492430.70220	40.5817598	-122.5424582
CC29	538996	4492216	539034.35993	4492337.08999	40.5809018	-122.5387761
CC30	539320	4491996	539209.19844	4492153.67094	40.5792412	-122.5367217
CC31	539327	4491813	539193.68464	4492026.95201	40.5781004	-122.5369129
CC34	540325	4484697	540239.50122	4484877.06260	40.5136394	-122.5250118
CC35	539871	4490278	539757.36995	4490480.66953	40.5641436	-122.5303503
CC36	529530	4501470	529681.13440	4501719.11851	40.6658097	-122.6488477
CC37	530000	4501895	529901.57493	4502107.18422	40.6692977	-122.6462213
CC38	531016	4501179	530808.06487	4501374.90025	40.6626675	-122.6355323
CC39	531708	4500126	531640.53346	4500300.78258	40.6529597	-122.6257383
CC40	531059	4502674	530943.39666	4502904.44797	40.6764415	-122.6338560
CC41	530633	4503058	530555.88938	4503415.31071	40.6810580	-122.6384163
CC42	530457	4503926	530407.59388	4504098.20380	40.6872154	-122.6401380
CC43	529708	4505687	530060.44500	4505465.09450	40.6995418	-122.6441808
CC44	531531	4506994	531399.11918	4507171.38261	40.7148630	-122.6282501
CC45	530750	4506272	530664.16048	4506519.43347	40.7090176	-122.6369833
CC48	533060	4515047	532965.59528	4515258.52058	40.7876541	-122.6092779
CC50	546006	4482831	546004.77679	4483041.98617	40.4968082	-122.4570944
CC66	546398	4482686	546435.12864	4482830.09134	40.4948753	-122.4520315
CC67	549859	4483164	549787.70345	4483352.04713	40.4993830	-122.4124296
CC68	549656	4483043	549580.29112	4483234.35290	40.4983352	-122.4148864
CC69	549167	4483011	548940.25874	4483233.72032	40.4983675	-122.4224394
CC70	549167	4483009	549078.21710	4483205.10668	40.4981016	-122.4208136

### Locations of samples collected in 2002 (continued)

SITE	UTM Zone 10-NAD27		UTMZone 10-NAD83		Geographic Coordinates	
	EASTING	NORTHING	EASTING_NAD83	NORTHING_NAD83	LATITUDE	LONGITUDE
CC71	549376	4483040	549291.71220	4483230.21493	40.4983151	-122.4182922
MCUC	530502	4500816	530571.32547	4500880.63290	40.6582236	-122.6383570
MDOX	536830	4503281	537045.81165	4503383.93018	40.6805093	-122.5616215
WT01	533765	4500954	533858.91969	4500981.74089	40.6590061	-122.5994619
WT02	536717	4502294	536705.90844	4502254.87107	40.6703534	-122.5657096
WT03	536978	4501740	537169.61949	4500933.73886	40.6584312	-122.5603014
WT04	537996	4500265	537896.26053	4500224.74404	40.6520112	-122.5517486
WT05	535861	4499792	535897.44372	4499830.92269	40.6485528	-122.5754132
WT06	530757	4501558	530845.88645	4501559.32068	40.6643274	-122.6350758
WT07	539729	4492350	539798.29663	4492344.45278	40.5809318	-122.5297493
WT08	540010	4492444	540129.94483	4492449.71110	40.5818640	-122.5258241
WT09	535833	4495876	535965.94751	4495953.30299	40.6136180	-122.5748246
WT10	531321	4501437	531324.96964	4501415.48845	40.6630137	-122.6294153
WT11	530455	4500847	530664.60600	4501058.28904	40.6598206	-122.6372449
WT12	530616	4501464	530696.53476	4501503.36164	40.6638289	-122.6368454

## Location of samples collected in 2003

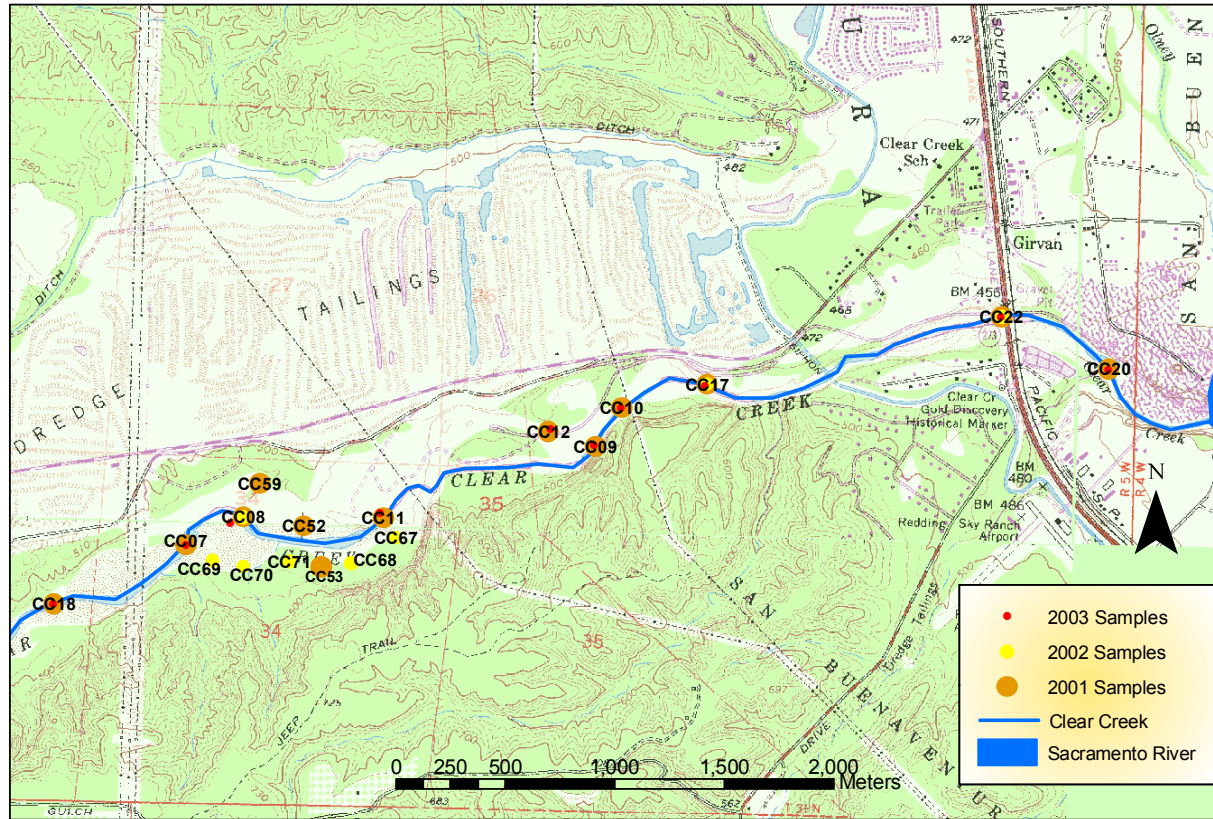
Site	UTM Zone 10-NAD27		UTM Zone 10-NAD83 Geographic Coordinates			
	EASTING	NORTHING	EASTING	NORTHING	LATITUDE	LONGITUDE
CC01	542618.2244930	4482697.6720500	542522	4482894	40.49566	-122.49820
CC02	542753.2234180	4482346.6753100	542657	4482543	40.49249	-122.49663
CC03	542762.2239090	4482054.6776400	542666	4482251	40.48986	-122.49655
CC04	542751.7053920	4482130.2273100	542655	4482327	40.49054	-122.49667
CC05	543034.2201870	4482091.6783300	542938	4482288	40.49018	-122.49334
CC06	543249.4632850	4482310.1189400	543153	4482506	40.49214	-122.49078
CC07	548910.1392070	4483097.6917700	548814	4483294	40.49892	-122.42392
CC08	549195.1350470	4483219.6918500	549099	4483416	40.50000	-122.42055
CC09	550748.6273240	4483614.9517000	550653	4483811	40.50347	-122.40219
CC10	550899.1511780	4483774.1547900	550803	4483970	40.50489	-122.40040
CC11	549793.3195380	4483255.2206100	549697	4483452	40.50028	-122.41349
CC12	550542.1141800	4483657.6927500	550446	4483854	40.50387	-122.40462
CC13	544087.7134440	4482342.4679400	543992	4482539	40.49238	-122.48089
CC14	544491.1995400	4482615.6794800	544395	4482812	40.49482	-122.47611
CC15	544701.1968990	4482534.6808700	544605	4482731	40.49408	-122.47363
CC17	551273.5421930	4483879.0475500	551177	4484075	40.50581	-122.39597
CC18	548327.1477390	4482784.6920300	548231	4482981	40.49613	-122.43083
CC20	553098.0581090	4483928.4303800	553002	4484125	40.50614	-122.37443
CC22	552599.0827820	4484232.6949000	552503	4484429	40.50892	-122.38030
CC58MAIN	542696.7050320	4482518.8439400	542600	4482715	40.49405	-122.49729
CC31	539319.1815100	4491821.5823500	539223	4492018	40.57802	-122.53657
CC34	540338.2146440	4484687.7166100	540242	4484884	40.51370	-122.52498
CC35	539867.1889980	4490278.5964900	539771	4490475	40.56409	-122.53019
CC23	539688.6483270	4487911.9264800	539592	4488108	40.54278	-122.53245
CC27	538083.2050040	4492665.0151000	537987	4492861	40.58567	-122.55112
CC29	539160.3450150	4491988.9163300	539064	4492185	40.57953	-122.53843
CC45 (FGCP)	530754.4913230	4506365.3291200	530658	4506562	40.70940	-122.63705
TRPK	530529.2408810	4504305.2541200	530433	4504502	40.69085	-122.63982



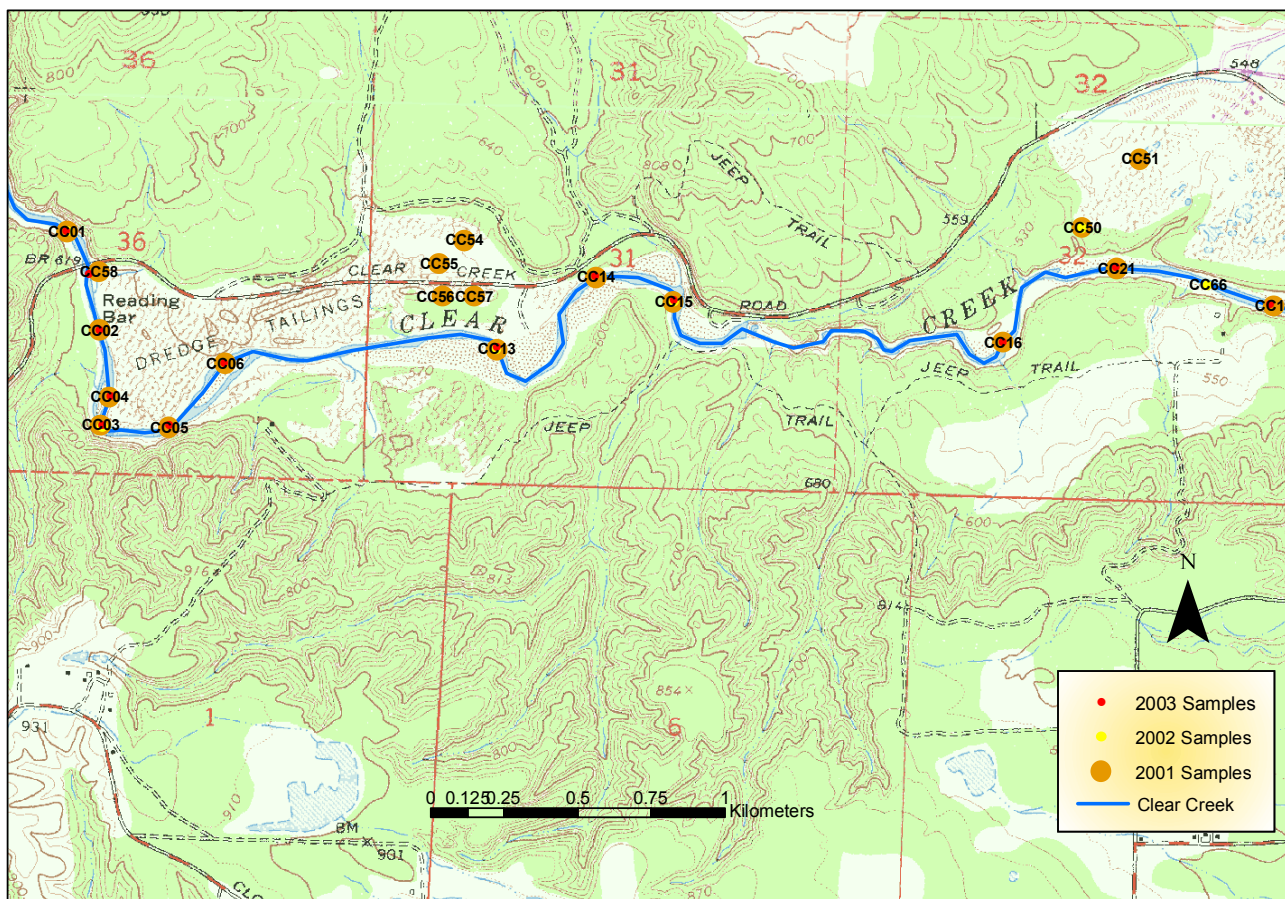
### Location of samples collected in 2003 (continued)

CCCC	531134.2130630	4507132.8460900	531038	4507329	40.71630	-122.63252
CCAR	531603.9687890	4500931.4870200	531508	4501128	40.66042	-122.62727
CCBR	531742.6249050	4500132.8431900	531646	4500329	40.65322	-122.62567
CC28	538750.1565840	4492203.2347800	538654	4492400	40.58148	-122.54327
CC44(CLN1)	531431.5865860	4507050.8416900	531335	4507247	40.71555	-122.62900
WT01(GRZL)	533958.8435400	4500795.6866600	533863	4500992	40.65910	-122.59942
WT03 (WCWL)	537272.7122530	4500689.9557100	537177	4500886	40.65800	-122.56022
WT04 (FSGL)	537973.3480180	4500023.1479100	537877	4500220	40.65197	-122.55197
WT05 (NYGL)	535972.0970000	4499648.8286200	535876	4499845	40.64868	-122.57567
WT06 (H229)	530938.5045940	4501383.8144100	530842	4501580	40.66452	-122.63512
WT09 (BRAN)	536046.0564730	4495751.2807500	535950	4495948	40.61357	-122.57501
MDOX	537144.3191650	4503181.7606800	537048	4503378	40.68046	-122.56159
REDG	537782.8885410	4499597.7000500	537687	4499794	40.64814	-122.55425
LBGL	537826.1565460	4500277.7868300	537730	4500474	40.65427	-122.55370
CLN2	533139.6403930	4506627.1789800	533044	4506824	40.71167	-122.60880
SCRP	527917.2216470	4506861.0750400	527821	4507058	40.71397	-122.67062
FRGL	529715.3663760	4505693.2269800	529619	4505890	40.70338	-122.64938
AMER	533095.7682520	4506678.7857400	533000	4506875	40.71213	-122.60932
RFRG	525136.0523550	4507117.5814800	525040	4507314	40.71637	-122.70353
MOXO	537646.6872240	4504835.5128600	537551	4505032	40.69533	-122.55555
WCUM	536913.2064690	4503098.2983600	536817	4503295	40.67972	-122.56433
MXUS	537637.8638490	4504909.4727100	537542	4505106	40.69600	-122.55565
SLCR	531539.4262340	4501201.3246100	531443	4501398	40.66285	-122.62802
WCMM	536838.8853710	4501988.4903000	536743	4502185	40.66972	-122.56528
MMGL	536579.2662180	4502264.7247500	536483	4502461	40.67222	-122.56833

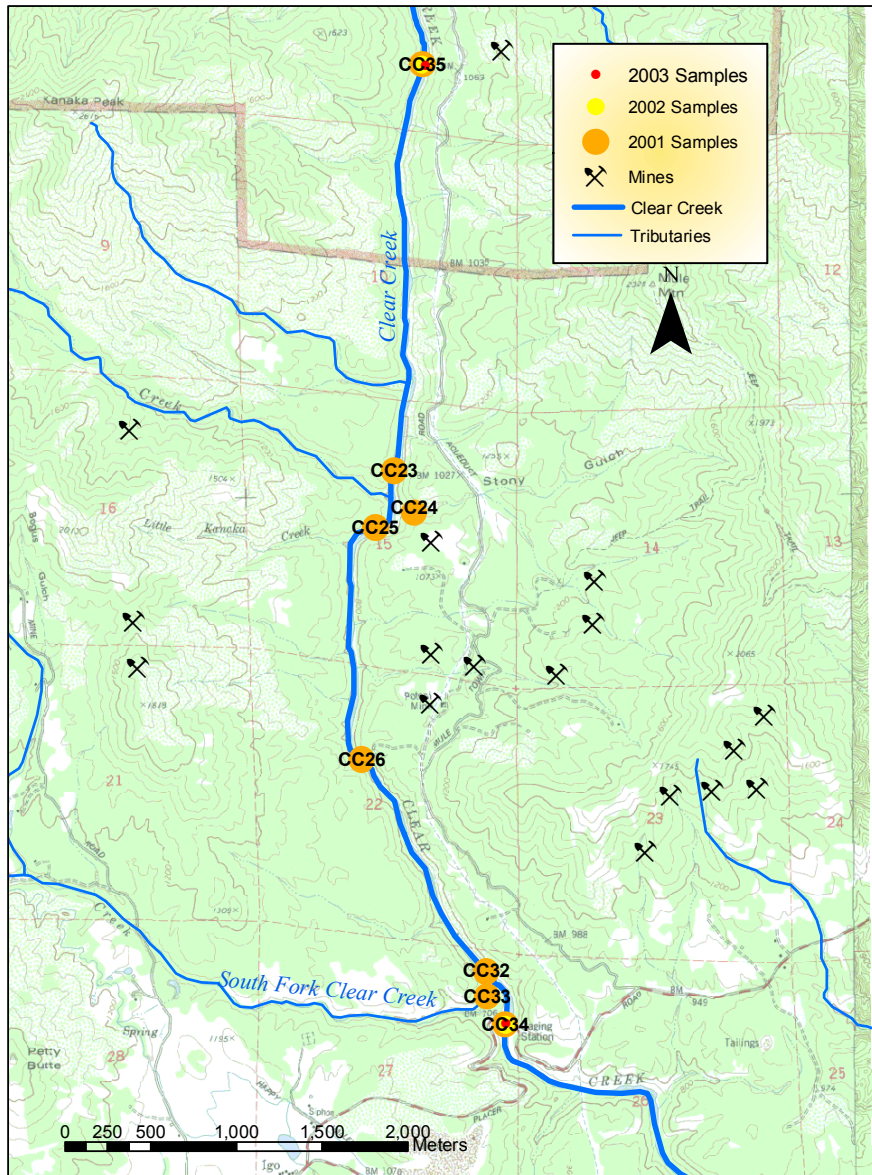
### Sample Sites CC 07-12,17,18,20,22,52,53,59,and 67-71



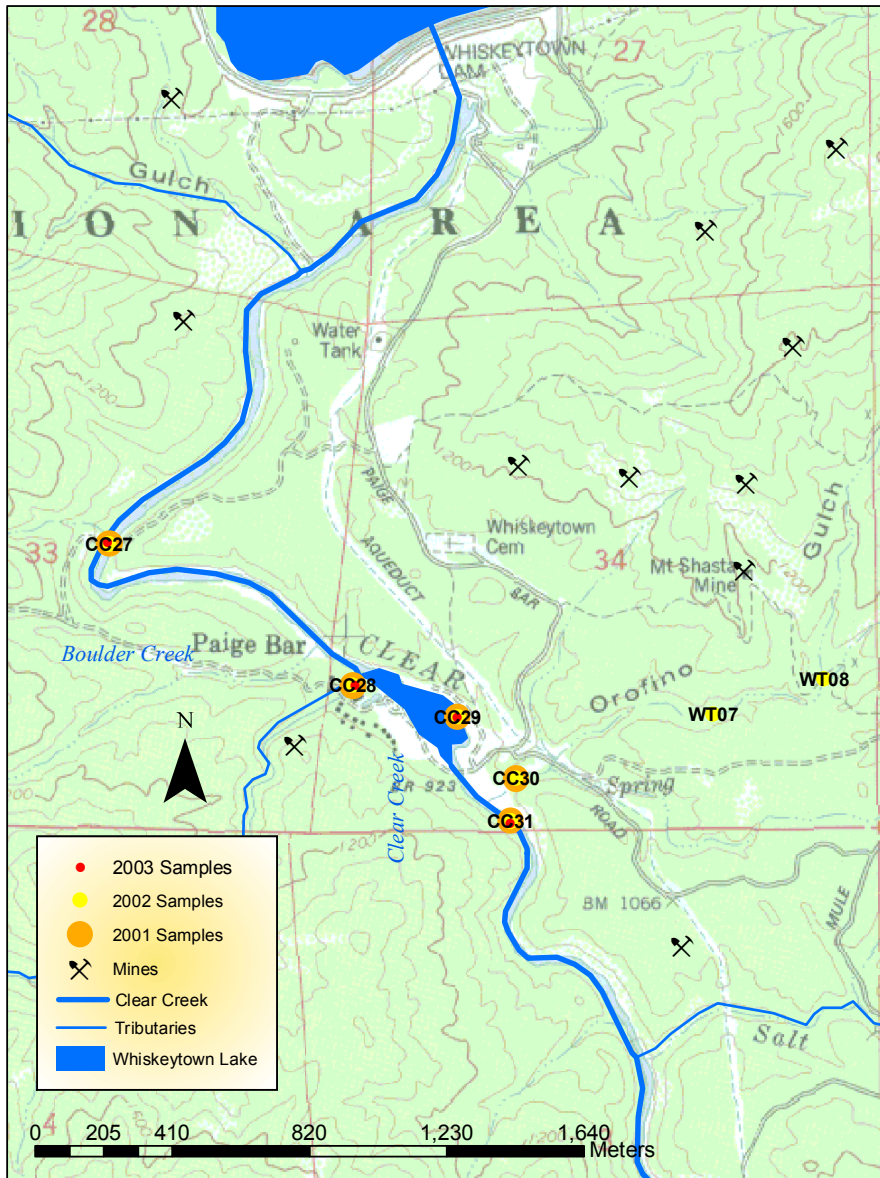
Sample Sites 1-6,13-16,19,21,50,51,54-58, and 66



# Sample Sites CC 23-26 and 32-35



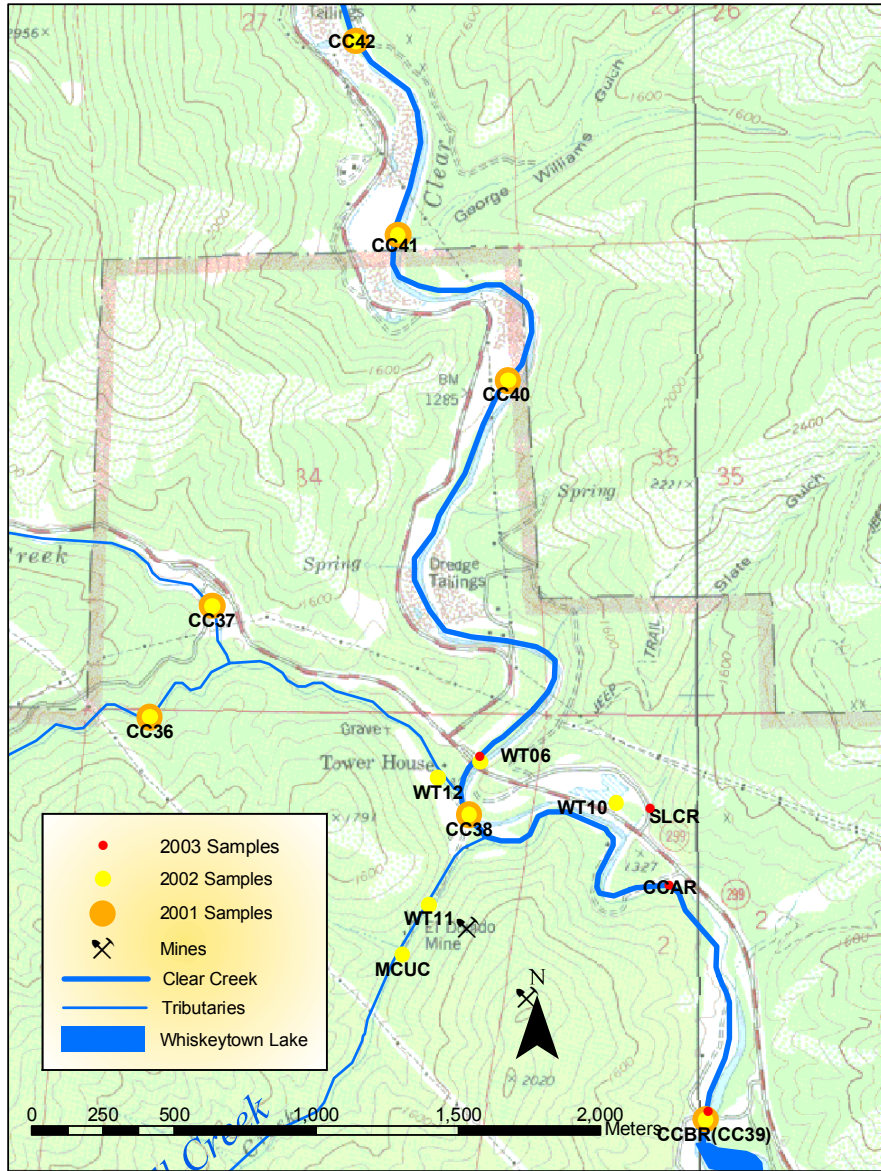
### Sample Sites CC 27-31, WT 07 and 08



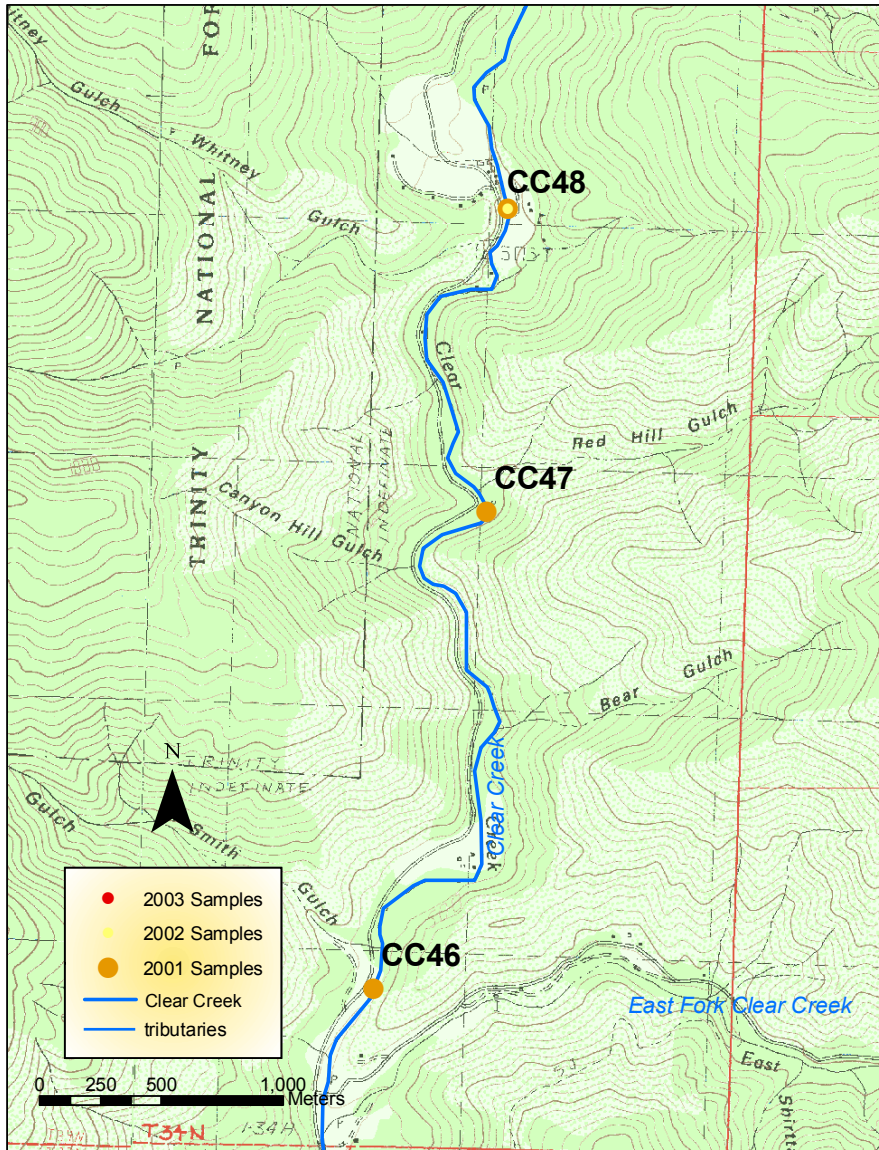
Sample Sites 36-42, WT06, WT10-WT12, MCUC, CCAR, & SLCR



Sample Sites 36-42, WT06, WT10-WT12, MCUC, CCAR, & SLCR

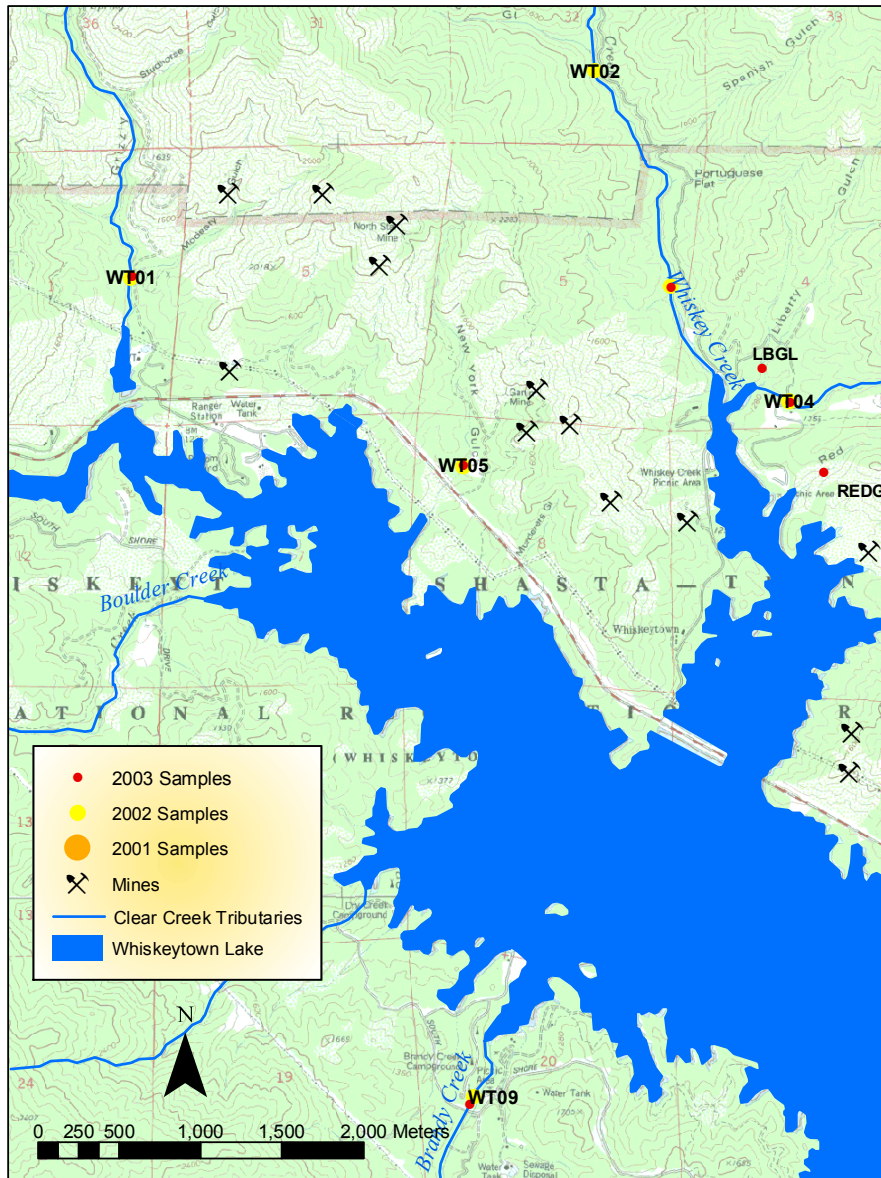


# Sample Sites CC 46-48

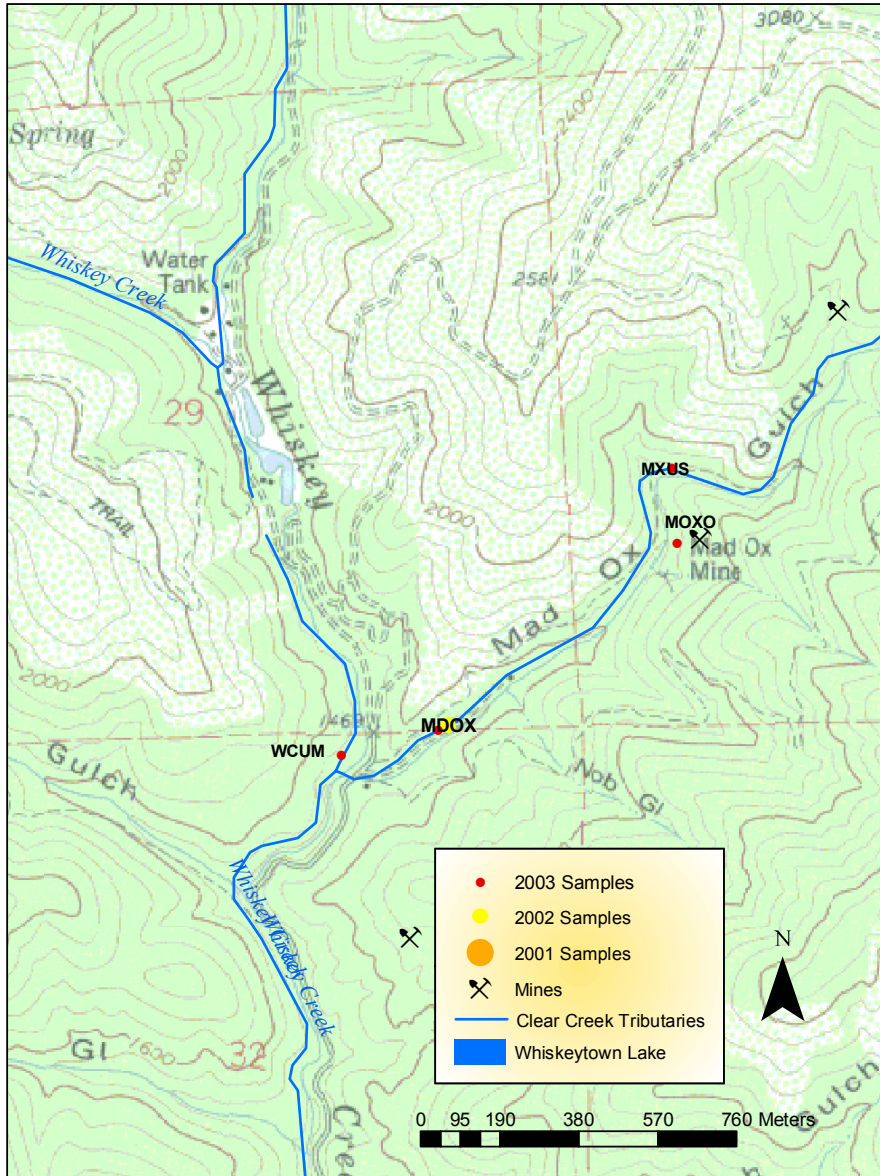




### Sample Sites WT 01-05, and 09, LBGL, REDG



# Sample Sites WCUM, MDOX, MXUS, MOXO



## **APPENDIX II**

### **Sampling and Laboratory Protocols**

Detailed field sampling methods, transport and preservation protocol, cleaning methods for sediment bottles and collection apparatus, and sample preparation and analysis procedures are listed below. Procedures include centrifuge, drying, grinding, digesting for multi-element analysis, and selenium analysis. EPA methods used for analysis are listed below, available on-line at <http://www.env-sol.com>, or can be found on the CD-ROM titled "EPA Methods and Guidance for Analysis of Water, version 2.0 Copyright 1999" by SOLUTIONS Software Corporation. Methods for selenium and mercury preparation analysis are written in full detail at the end of this appendix.

# **SAMPLE COLLECTION**

## **Clear Creek Sediment Sampling Protocol**

**Revised 10 May, 2002**

1. Locate site using 7 1/2 minute topographic maps and GPS. Write down UTM coordinates making sure to use the correct datum and record any needed coordinate data (e.g., NAD 29). Mark position of sample site on topographic map and label it with site number. Find an area that you will be able to get fine sediment from—you may have to use small pockets, rather than long reaches of channel edge. If possible (safe) collect the sample from both sides of the creek.
2. Label one 250 ml bottle with the site number. Use a letter designation for the project or area, e.g., "CCnn", where CC=Clear Creek and nn = a two digit number, e.g. 01. Follow those with a designation of A and B if a replicate sample is taken (10% of samples). Follow by the date as six digits (mmdyy, example "112201"). This will result in a number like "WT01 052802". Or "WT0123A 052802" and "WT0123B 052802"
3. Put on a pair of nitrile gloves. Make sure to keep them on for the remainder of the preparation and sampling to assure a clean sample. Each sampling setup is clean and in a Zip-Loc plastic bag. Make sure to put on the gloves before you remove it.
4. Then tape the top of the funnel (the cylindrical piece) with white vinyl tape. Put one-two layers around the "step" where the upper and lower pieces go together. This is to keep the funnel from coming apart during sieving. Two layers seem to work well, but you may have to adjust the thickness depending on the particular sieve and funnel.
5. Now put the mesh onto the bottom and push the bottom of the funnel setup over the mesh to make a tight fit. This should go together tightly, so the mesh will not slip out during sieving (that is critical).
6. Take the bottle, sieving setup and spoon to the river's edge. Take samples by scooping up fine sediment from the upper 2-3 cm of the sediment on the bed and sieving it through the mesh by stirring it with the plastic spoon. Make sure to "condition" the sieve and bottle by sieving a small amount of sediment into the bottle and dumping it before taking a sample. Continue the process until you have the bottle nearly full of slurry, about to the base of the threads. It may be difficult to get thick slurries in some areas because of the lack of fines. So, if you find a pocket of fine sediment you may have to work that well instead of moving along the bank. But, try to get as wide a sampling area as possible. Make sure to get a good, thick, opaque slurry in the bottle, other wise there will not be enough sample to do all the analyses. Also, make sure to take at least 10% duplicate samples. You can use the same sieve for both duplicate samples at the duplicate site, just label two bottles when you start as "A" and "B".

7. Once the samples are taken, dry the outside of the bottle placing it (or them if replicate sample) in the sun or by wiping with a paper towel. Then put them in a new Zip Loc plastic bag. Push out the air and seal the bag. You can put the sample label on the bag if you want. This is just to protect the label so it does not rub off during transport and shipping. Place the samples in ice in the ice chest.

8. Now, make sure to take some notes on the site: General description, lack or presence of fine sediment, any interesting features that will help locate it, etc. Then take a picture of the site that you sampled. Make sure to write down the photograph number in the notebook. Draw a simple map showing where the sample was taken at the site.

9. When finished put the dirty sieve, spoon, mesh, gloves, etc. in the plastic bag it came in and then into a white trash bag. This will make sure to keep them separated from the clean ones.

10. That is it; move to next site and repeat.

11. When you have collected the samples you can either freeze them immediately on dry ice or keep them unfrozen until you can transport them to the lab or a freezer. If the later, do not keep them unfrozen more than 72 hours, preferably less than 24 hours.

To Freeze: Put them in a freezer with the lids loose or put dry ice with them in the ice chest. But, if you do this you will have to watch them and make sure to squeeze them now and then to break up the ice to keep the ice from bulging and breaking the bottles--VERY IMPORTANT. Also, if you are going to freeze them, make sure to not fill them above the curve on the top of the bottle, or sediment and water will ooze out as the water expands. (Freezing actually made separation of the sediment easier. When they thawed, the sediment clumped together and fell out leaving very clear water above. Clearer than centrifuging the sediment alone.) If you get them frozen, then you can keep them for as long as you want before shipping otherwise transport them to the lab as soon as possible. If shipping, make sure the bottles are padded well in the bottom of the ice chest (make sure they will not slide around during shipping). Tighten the lids. You may have to let them thaw out a little bit for this because ice can seal the lids and they will leak if they thaw during transport. pack them tightly in the bottom of the ice chest, then place a layer of "blue ice" or some other form of "sealed" ice over/around the bottles. This is important to keep the water from leaking into the bottles from the melting ice. Then fill up the space above the bottles with foam or cardboard to keep the bottles from flying around if the ice chest tips over—foam is better because of the insulation. Tape up the ice chest with duct tape and address and send 2nd day air. They will stay frozen for a day or two.

Make sure to write something on the outside like, "water samples on dry ice/ice, please handle with care". Also make sure that they will arrive during the week so they do not set around over the weekend in the mail room.

## **CLEANING PROCEDURES**

### **Procedure for Cleaning 63-micrometer Sieve Apparatus**

The purpose of this procedure is to ensure proper decontamination of sediment sampling apparatus for field use in order to obtain the highest quality data. The sampling device consists of a modified, plastic "Bruckner" funnel. The top of the funnel is 135 mm in diameter. It is in two-pieces of acid resistant plastic. The top cylinder comes with a filter support base that we removed with a saber saw. For sampling plastic sieve material replaces the original plastic filter plate. A plastic spoon is used to scoop the sample into the apparatus and work it through the sieve. All these components need to be carefully washed to assure not contamination of the samples.

1. Wash apparatus (funnel, screen and plastic spoon) thoroughly with Liquanox® (or equivalent) soap.
2. Rinse apparatus with hot tap water at least three times.
3. Rinse apparatus with DI water three times.
4. Completely submerge the screen, funnel and spoon in approximately 5% Hydrochloric acid solution (v/v, e.g., 500 milliliters of concentrated HCl in 10 liters of deionized water) for 10 minutes.
5. Remove apparatus from the acid and rinse with Milli-Q water two times and then soak in clean Milli-Q water for at least 10 minutes.
6. Drain the water and dry in a clean area.
7. Place and seal complete apparatus (funnel, spoon and sieve) in clean Zip-lock plastic bag until use. Make certain to keep sealed during transport to the field and do not open until used for sampling. Always wear clean Nitrile gloves when washing and handling the apparatus to minimize contamination.

## Procedure for Cleaning Sample Bottles

Labware and sample bottles (including new bottles) are cleaned using the following "ultraclean method" to assure the complete removal of contaminants. It is important to follow the procedure completely to minimize potential of contamination of the sample. All acid solutions are made in volume of concentrated acid per volume of Milli-Q deionized water.

1. Wash labware with Liquanox soap and tap water.
2. Rinse labware with tap water at least three times making sure to remove all soap residue.
3. Rinse labware with deionized water three times.
4. Completely submerge labware in 50% Hydrochloric Acid bath for 2 hours (the bath should be designated "ultraclean " and not used for other labware).
5. Remove the labware from the acid and rinse with Milli-Q deionized water three times.
6. Submerge labware in 1% Nitric Acid solution for 24 hours.
7. Remove labware from the acid and rinse with Milli-Q deionized water three times.
8. For sample bottles, fill each with Milli-Q deionized water, dry the outside of the bottle with clean wipes and double bag them in Zip-lock plastic bags.
9. Do all the drying and storage in the laminar flow hood to minimize any contamination from dust in the air.

## **SAMPLE PREPARATION**

### **Centrifuging, Drying and Grinding**

The purpose of this procedure is to ensure the proper preparation of sediment or soil samples for digestion (e.g., using EPA Method 3050B). Make sure to follow the instructions carefully to make certain that none of the procedures used contaminate the samples.

1. If frozen, thaw the samples, if not move directly to #2.
2. Centrifuge samples at 1500 rpm for 15 minutes in a centrifuge that will hold 250 ml bottles. Make certain the centrifuge rack is balanced and the bottles will not break during centrifugation.
3. Carefully discard excess water making certain not to dump out any of the sediment accumulated on the bottom of the bottle.
4. Place the bottles in a drying oven at less than 70° C with the lids either ajar or removed. Make sure to label the lids so the proper one can be put on the bottle when the sample is dry. Leave the samples in the oven until completely dry (generally 2-4 days, depending on the moisture content). The sediment samples will form into solid pellets as they dry. To make the pulverizing process less difficult, remove the samples before they are completely dry, put on the lid and shake the sample container vigorously to loosen the forming pellet. Place them back into the oven to complete the drying process.
5. When dry place the samples in a desiccator to cool with the lids loose. Leave them in for at least 24 hours or longer if needed.
6. Remove the bottles from the desiccator and pulverize the sediment pellet in the bottle by using a thick, solid glass rod. The sediment should be a fine powder with as few lumps and clunks as possible. Make certain that the rod is clean and to wear gloves to minimize contamination. The glass rod used for pulverizing the sediment samples is immersed in a 50% HCl solution and rinsed thoroughly with de-ionized water and then dried between samples to make certain there is no carryover from one sample to the next.
7. Once ground and homogenized, transfer the samples to sealed plastic or glass vials (e.g. snap-cap vials) and store in a dessicator until sample digestion (e.g., method 3050B).



**DIGESTION**  
**Acid Digestion of Sediments, Sludges, and Soils USING THE HOT BLOCK®**  
(EPA METHOD 3050B)<sup>1</sup>

1.0 SCOPE AND APPLICATION

1.1 This method has been written to provide a digestion procedure for the preparation of sediments, sludges, and soil samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES). Samples prepared by this method may be analyzed by ICP-AES or graphite furnace atomic absorption GFAA for all the listed metals as long as the detection limits are adequate for the required end-use of the data. Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest.

Element list:

Aluminum	Magnesium
Antimony	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become “environmentally available.” By design, elements bound in silicate structures are not normally dissolved by this procedure, as they are not usually mobile in the environment. If absolute total digestion is required, use EPA Method 3052 or equivalent.

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<sup>1</sup> See Moore, 2002 for previous digest method (modified from 3050B). Using manufacturer recommended method for most 2003 samples to get lower detection limit.

## 2.0 SUMMARY OF METHOD

- 2.1 For the digestion of samples, a representative 0.25-50 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO<sub>3</sub>) until no brown fumes are given off.
- 2.2 Allow to completely cool, add hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) until remains unchanged in color.
- 2.3 Hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. The digestate is then diluted to a final volume of 50 mL and filtered. If required for aqueous samples, a separate sample aliquot shall be dried for a total percent solids determination.

## 3.0 INTERFERENCES

- 3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements in determining whether Method 3050B is applicable to a given sample type.

## 4.0 APPARATUS AND MATERIALS

- 4.1 Digestion Vessels - 55-mL.
- 4.2 Vapor recovery device – reflux cap
- 4.3 Drying ovens - able to maintain 30°C ± 4°C.
- 4.4 Temperature measurement device capable of measuring to at least 125°C with suitable precision and accuracy (e.g., thermometer, IR sensor, thermocouple, thermister, etc.)
- 4.5 FilterMate<sup>®</sup> filtering device
- 4.6 Analytical balance - capable of accurate weightings to 0.01 g.
- 4.7 Heating source – Hot Block<sup>®</sup> or equivalent constant temperature device.

## 5.0 REAGENTS

- 5.1 Trace metal grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used or at a level low enough to not effect the resulting sample concentrations.

- 5.2 Reagent Water will be used throughout the method. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified.
- 5.3 Trace metal grade Nitric acid (concentrated),  $\text{HNO}_3$ . Acid should be analyzed to determine level of impurities. If method blank is  $< \text{MDL}$  or at a level that will not effect the final sample data, the acid can be used.
- 5.4 Trace metal grade Hydrochloric acid (concentrated),  $\text{HCl}$ . Acid should be analyzed to determine level of impurities. If method blank is  $< \text{MDL}$  or at a level that will not effect the final sample data, the acid can be used.
- 5.5 Hydrogen peroxide (30%),  $\text{H}_2\text{O}_2$ . Oxidant should be analyzed to determine level of impurities. If method blank is  $< \text{MDL}$  or at a level that will not effect the final sample data, the acid can be used.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 6.1 All samples must have been collected using a sampling plan.
- 6.2 All sample containers must be demonstrated to be free of contamination at or below the reporting limit or at a level that does not effect the sample data. Plastic and glass containers are both suitable.
- 6.3 Samples should be refrigerated/frozen upon receipt and analyzed as soon as possible.
- 6.4 Because it can be difficult to obtain a representative sample with wet or damp materials, wet samples should be dried in an oven at approximately  $70\text{-}80\text{ }^\circ\text{C}$ . Once dried the samples should be crushed and/or ground to reduce subsample variability and assure a homogeneous subsample for digestion. Care must be taken to not introduce contaminants during this procedure. All grinding and crushing must be done with clean materials (i.e., acid washed).

## 7.0 PROCEDURE

- 7.1 Mix the sample thoroughly to achieve homogeneity. If appropriate and necessary, the sample can be sieved using a USS #10 sieve. All equipment used for homogenization should be metal-free if possible and cleaned between samples to minimize the potential of cross-contamination.
- 7.2 For each digestion procedure, weigh to the nearest  $0.01\text{ g}$  and transfer a  $0.25\text{ g}$  or  $0.50^2\text{ g}$  sample (dry weight) to a digestion vessel.

---

<sup>2</sup> Manufacturer recommended amount

NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. The use of an acid vapor scrubber system for waste minimization is encouraged.

- 7.3 Add 2.5 mL of concentrated HNO<sub>3</sub> and 2.5 mL of reagent water, mix the slurry, and cover with a reflux cap. Heat the sample to 95°C ± 5°C (check Hot Block<sup>®</sup> to determine actual temperature and to obtain the desired temperature of 95°C ± 5°C) and reflux for 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO<sub>3</sub>, replace the cover, and reflux for 30 minutes. Repeat this step until no brown fumes are given off. Heat samples, covered with reflux caps at 95°C ± 5°C without boiling for an additional 1 ½ hours. Do not allow the sample to go dry. Maintain a covering of solution over the bottom of the vessel at all times by adding reagent water if needed.
- 7.4 After the step in Section 7.3 has been completed and the sample has cooled completely, add 2-5 mL of D.I. water and 0.5 mL of 30% H<sub>2</sub>O<sub>2</sub>. Allow an exothermic reaction to occur, waiting 5-10 minutes. Cover the vessel with a reflux cap and return the covered vessel to the heat source for warming and to finish the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence, if needed reduce the temperature of the Hot Block by 10°C. Heat until effervescence subsides.
- 7.4 Continue to add 30% H<sub>2</sub>O<sub>2</sub> in 0.5-mL aliquots with warming until the effervescence is minimal and the color is unchanged.
- NOTE: Do not add more than a total of 2.5 mL 30% H<sub>2</sub>O<sub>2</sub>.
- 7.5 Cover the sample with a reflux cap and continue heating the acid-peroxide digestate at 95°C ± 5°C without boiling for another 30 minutes.
- 7.6 Add 5 mL conc. HCl to the sample digest and cover with a reflux cap. Reflux at 95°C ± 5°C for 15 minutes.
- 7.7 After cooling, dilute to 50 mL with water. Cap the sample containers, invert several times to mix, and allow samples to cool and settle for 18 hours.
- 7.8 Slowly filter samples using FilterMate<sup>®</sup> filtering device. The sample is now ready for analysis by FLAA or ICP-AES.

## 7.9 Calculations

7.9.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. This is done by determining the "dilution" factor of the digestion (total solution/sample weight). For the nominal weight of 0.25 g, the dilution factor will be 200. Once determined the concentration determined by FLAA or ICP-AES is multiplied by the dilution factor to determine the concentration in the sample (e.g., in mg of element per Kg of sample). If a dry weight analysis is desired for aqueous or undried samples, then the percent solids of the sample must also be determined and factored into the determination of the dilution factor.

7.9.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

## 8.0 SECOND DIGEST FOR SELINIUM ANALYSIS

8.1 To analyze Selenium using Hydride Generation Atomic Absorption Spectrometry a second digest must be performed on samples digested by EPA method 3050B (see methods below).

8.2 A dilution factor must again be considered, this time to include both digests. For the nominal weight of 0.5 g, multiply output by .24 to report the selenium concentrations in mg/kg.

## 9.0 QUALITY CONTROL

9.1 All quality control measures described below should be followed for each batch of samples or at a frequency listed below. No batch of digests should be run without quality control samples.

9.2 For each batch of samples processed, a method blank should be carried throughout the entire sample preparation and analytical process according to the frequency of at least 5% or one per digestion batch.

9.3 Spiked duplicate samples (digestion spikes) will be used to determine precision and bias. They should be digested at a frequency of 5% or at least one per batch.

9.4 At least 5% of the samples must be digested as duplicates or one per digestion batch.

9.5 One standard reference material must be run with each digestion batch or represent at least 5% of the number of samples digested.

9.6 All quality control data must be tracked through analyses and if not acceptable the samples re-digested or the suspect data not used.

## LIST OF ANALYTICAL METHODS USED

All methods used for analyses can be found on the CD-ROM titled "EPA Methods and Guidance for Analysis of Water, version 2.0 Copyright 1999" by SOLUTIONS Software Corporation (<http://www.env-sol.com/>). Alternatively they can be ordered from the USEPA or other vendors. Details of analytical procedures and quality control are presented in these methods. All the quality control data is presented in Appendix III.

**EPA Method 200.7:** INDUCTIVELY COUPLED PLASMA—ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES.

**Instrument:** Thermo IRIS-CID ICAPES for 2001-2003.

**Method (see below):** SELENIUM (MANUAL COLD VAPOR TECHNIQUE) FOR ATOMIC ABSORPTION SPECTROMETER.

**Instrument:** Varian Model AA-875 Atomic Absorption Spectrometer with VGA-76 Hydride Generation Unit.

Used for samples collected in 2003.

**Method 245.7(see below):** MERCURY BY COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRY.

**Instrument:** Leeman Labs Hydra AF Automated Mercury Analysis System.

Used for samples collected in 2002 and 2003.

**Method 245.1:** MERCURY (MANUAL COLD VAPOR TECHNIQUE) FOR ATOMIC ABSORPTION SPECTROMETER.

**Instrument:** Varian Model AA-875 Atomic Absorption Spectrometer with VGA-76 Hydride Generation Unit.

Used for samples collected in 2001.

Operation Procedures for  
**Preparing Standards and Samples for analysis for Mercury by CVAFS**  
University of Montana Geology Analytical Laboratory  
Last Modified 11/11/2003

**Prepare For Analyses**

**Prepare Bromine Monochloride** solution 12 hours before sample preparation.

In a fume hood use a 125 ml Teflon bottle.  
Add 100 ml concentrated HCL Trace Metals Grade  
Add clean stir bar  
Add 1.08 g. KBr Reagent Grade

Stir 1 hour

Slowly add 1.52 g KBrO<sub>3</sub> Reagent Grade  
Solution should change from yellow to red to orange  
Loosely cap bottle and stir for 1 hour before tightening cap.

Allow to stand overnight

Add 0.5% ie 0.5ml per 100 ml BrCl solution to each sample and allow samples to stand overnight.

**I. Standards**

Prepare a 100ug/L intermediate stock solution:

Use an acid washed sample tube and pipette 1.0 ml {1000 ug/L stock standard and 9.0ml 1%HCl solution.

Prepare a standard curve of appropriate standards in 1% HCl

Use the dedicated bottles, designating the midpoint of the curve as the Calibration verification standard. i.e if the curve is 5 to 100 ug/l then IPC should be 50 ug/l.

For CCV weigh an appropriate amount of 100ug/L standard into the tared 1L bottle and bring up to 1000g with 1% HCl.

For all other standards weigh an appropriate amount of 100ug/L standard into the tared 250ml bottles and bring up to 250g with 1% HCl.

**Prepare an Instrument performance Check (IPC) at the midpoint of the curve**  
i.e if the curve is 5 to 100 ug/l then IPC should be 50 ug/l.

Using the Hg 1000 mg/L **Cerilliant** stock solution:

Prepare a Hg 1mg/L (1000ug/L) stock solution:

Use an acid washed sample tube and pipette 10 ul {1000 mg/L stock standard and 9.99ml 1% HCl.

Prepare a 100ug/L intermediate stock solution:

Use an acid washed sample tube and pipette 1.0 ml {1000 ug/L stock standard and 9.0ml 1% HCl.

#### **IV. Spikes**

A spiked sample should be analyzed as a quality control measure for every set of 20 samples. Pipette 0.65 ml 100 ug/L Hg Intermediate stock into 13 mls of sample.

#### **Sample Run Order Protocol**

Calibration Check Standard

Instrument Performance Check Standard 3ppb

blank

Sample 1 through

Sample 10

Calibration Check Standard

If calibration check fails, then recalibrate and rerun previous 10 samples.

Blank

Next ten samples

Sample 11 through

Sample 20

Calibration Check Standard

If calibration check fails, then recalibrate and rerun previous 10 samples.

Blank

Etc.



Operation Procedures for  
**Analysis for Mercury by Cold Vapor Atomic Fluorescence Spectrometry**  
University of Montana Geology Analytical Laboratory  
Last Modified 11/11/2003

**Prepare Stannous Chloride solution**

In a fume hood use the dedicated 1L bottle.

Place 20 grams SnCl<sub>2</sub> in bottle.  
Add 100 ml HCl and allow salt to dissolve.  
Add 900 ml MilliQ water, allow to degas and cap.

**Turning on the Mercury Analyzer:**

Make sure there is a sufficient quantity of argon for the analyses. The Ar pressure should be ~235psi. If the gauge is approaching 100 psi, an auxiliary source of Argon may be necessary.

Turn on the argon tank and open valve on manifold leading to analyzer.

Turn on power to Mercury Analyzer. (Right side behind instrument.)

Turn on Computer Go to Hg Analysis Runner.

**Instrument Preparation**

Area counts for 100 ng/L standard should be around 40,000.

IF it has been some time since analyses have been run and/or high level samples have been analyzed and/or counts for the 100ng/L standard are significantly below 40k then the dryer tube must be cleaned and repacked.

Disconnect dryer tube and dispose of soda lime chips and glass wool.

Acid wash tube 30 minutes and bake 30 minutes in oven at 300 degrees.

Repack glass wool and soda lime followed by glass wool in tube.

Bake at 300c for 30 minutes.

Allow to cool.

Reconnect tube to lines on the front of the analyzer. Short end down. Be sure that glass wool acts as a stopper to prevent soda lime from falling into lines.

Prepare 1% HCl Blank solution for standard prep, several liters will be necessary. Use Trace Metals Grade HCL in the 2 L HDPE container marked 1% HCl.

### **Setting up instrument**

Check to see that 3 waste lines are securely inserted in empty waste carboy.

Connect lines to rinse container with 2% HCL and SnCl<sub>2</sub> solution respectively. .

In Runner menu, choose the protocol that applies to your analyses. i.e. 100 ppt 10 ppt or ppb levels. Note that flow rates may differ between protocols.

From Runner Choose protocol and turn on gas and flow will be set.

Turn on Hg lamp.

## **Calibration**

From Standards menu choose all that apply

In general standard curve occupies cups 2-7

Rep1            }  
Rep2            } YOU MUST CHOOSE ALL THREE OR IT WILL ONLY RUN ONE  
Rep3            }

### **Autorun protocol**

Go to DB

Specify

ICP cup 1

CCV cup4

Blank cup7

Every 12 analyses

### **Sample Input**

Open Rack icon

Designate all samples

Row number is cup number

After every 10 samples place a duplicate and Lspike

Save under Rack1

Go to *Samples*

*Rack1*

Starting cup# must match the rack and the Rack1 schedule

*Sample Auto.*

Check to see that CCV and IPC pass before allowing analysis to continue.

### **Shutdown**

Place tubes from rinse and stannous chloride bottles into MilliQ water and allow to pump through for several minutes.

Then allow air to pump through the lines until they are clear of liquid.

From protocol menu Turn off gas and Hg lamp.

Go to *Report, Generate Report* and choose *.WKS*. Name the file according to days run date (i.e 032103).

Empty waste container.

Turn off analyzer

Shut off Argon.

Operation Procedures for  
**Preparing Standards and Samples or EPA3050 Digestates for analysis for Selenium  
by Hydride Generation/ Atomic Absorbtion Spectrometry**  
University of Montana Geology Analytical Laboratory  
Last Modified 10/28/2003

## **I. Standards**

Using the Cerilliant Se 1000 mg/L (ppm) ICP stock solution:

Prepare a Se 1mg/L (1000ug/L) stock solution:

Partially fill a 1 L volumetric flask with Milli-Q then pipette 1 mL of Se 1000mg/L stock into the flask and fill to the line with Milli-Q.

Prepare a Se 100ug/L intermediate stock solution:

Partially fill a 1 L volumetric flask with Milli-Q then pipette 1 mL of Se 1000ug/L stock into the flask and fill to the line with Milli-Q.

Prepare a blank and 1, 3, 5 and 8 ug/L series of standards:

- 3.84 ml of [100ug/L Se] add 16.16 ml MilliQ H<sub>2</sub>O+ 14 ml T.M.G. HCl=8ug/L
- 2.40 ml of [100ug/L Se] add 18.56 ml MilliQ H<sub>2</sub>O + 14 ml T.M.G. HCl =5ug/L
- 1.44 ml of [100ug/L Se] add 17.6 ml MilliQ H<sub>2</sub>O + 14 ml T.M.G. HCl =3ug/L
- 0.48 ml of [100ug/L Se] add 19.52 ml MilliQ H<sub>2</sub>O + 14 ml T.M.G. HCl =1ug/L

## **Prepare Instrument Performance Check Standard**

Using the VHG Se 1000 mg/L (ppm) ICP stock solution:

Prepare a Se 1mg/L (1000ug/L) stock solution:

Partially fill a 1 L volumetric flask with Milli-Q then pipette 1 mL of Se 1000mg/L stock into the flask and fill to the line with Milli-Q.

Prepare a Se 100ug/L intermediate stock solution:

Partially fill a 1 L volumetric flask with Milli-Q then pipette 1 mL of Se 1000ug/L stock into the flask and fill to the line with Milli-Q.

then prepare 3ppb IPC

0.72 ml [100ug/L] stock +9.28 ml MilliQ H<sub>2</sub>O Add 14 ml of T.M.G. HCL.

## **IV. Spikes**

A spiked sample should be analyzed as a quality control measure for every set of 20 samples.

Pipette 0.72ml of 100 ug/L intermediate stock + 9.28 ml sample. Add 14 ml of T.M.G. HCL.

### **III. Sample Prep**

Pipette 10 mL of sample into a 50 ml digest vessel. Next pipette 14ml of concentrated T.M.G. HCL to achieve a 7M acid concentration.

### **V. USGS Standards**

Prepare a USGS (T142 or T145 standard in the same manner as the samples above.

### **Heat Samples to 70degrees C**

Set the hot block at 70degrees and heat samples for 1½ hours.

### **Add Urea**

After removing samples from hot block add 1g/10ml sample of urea salt. Allow sample to react and cool to room temperature before capping. Let stand 30 minutes.

### **Sample Run Order Protocol**

Calibration Check Standard 3ug/L

Instrument Performance Check Standard 3ug/L

blank

Sample 1 through

Sample 10

Calibration Check Standard 3ug/L.

If calibration check fails, then recalibrate and rerun previous 10 samples.

Blank

Matrix Spike or Matrix duplicate

Next ten samples

Sample 11 through

Sample 20

Calibration Check Standard 3ug/L.

If calibration check fails, then recalibrate and rerun previous 10 samples.

Blank

Post digestion Matrix Spike or Matrix duplicate

Operation Procedures for the  
**Analysis for Selenium by Hydride Generation/Atomic Absorption Spectrometry**  
University of Montana Geology Analytical Laboratory  
Last Modified 10/28/2003

**Turning on the AAS:**

1. Make sure there is a sufficient quantity of nitrogen for hydride generation; right gauge on the regulator needs to be at least 300psi.
2. Check to see that chimney is open. The chimney should be open about 15-20 degrees; the previously used setting of 45 degrees has been found to be too drafty and may blow the flame out.
3. Make sure the battery is connected (to the left of the AAS).
4. Locate and fill the liquid trap (the plastic container from which the two waste tubes extend is the liquid trap). To fill the liquid trap: remove the upper, vapor waste tube, and fill through opening using the milli-Q bottle with the long flexible spout. The trap is full when water begins to run out the bottom waste tube.
5. Turn on the acetylene tank and make sure oxidant is on (red lever to the left of the AAS, mounted on the wall behind the book case). Make sure the acetylene tank pressure is at least 200psi.
6. Turn on power to AAS (power button located on top left hand control panel).
7. Check lamp number through small window on top left to ensure that the Se lamp is on top in position 2; if the Se lamp is not on top rotate the lamp turret until it is.
8. Slowly adjust lamp, one click at a time, until the lamp setting is 10 milliamps.
9. Adjust the spectral band "Slit" to 1.0 (upper right control panel).
10. Place the cell in operating position by tipping it forward. Adjust the gain to single beam (SB) and acquire the appropriate setting by moving the knob until the needle is maximized on the right side of the peak scale.
11. Adjust the two knobs on the lamp (left side on lamp rotation wheel) also to maximum response.
12. Now adjust the wavelength for maximum signal on the peak meter while remaining within the scale: turn the course and fine tuning knobs corresponding to the wavelength, the needle will fluctuate and peak at the maximum response, use Gain control to reduce

scale if necessary. The reported wavelength for Se is 196.0, but usually works at approximately 196.5.

13. Change the gain back to double beam (DB).

### **Prepare For Ignition**

14. Tilt the cell back away from the burner

15. Press “Set flow” and adjust fuel to 9 (hold set flow and turn knob).

Press “air” and adjust to 39

16. Wait for ready light and press “Flame on”; using a striker located in the drawer below the AAS ignite the burner.

17. If flame doesn't come on wait for ready light and press “Flame on” again. If this doesn't work, try increasing the fuel level 2 or 3 units.

18. Allow the flame ample time to burn (30 minutes) before placing the cell in the flame to keep soot from building up on the cell. When the flame appears to be burning clean, tilt the cell into operation position and maximize the response on the ‘Peak’ window by adjusting the vertical and horizontal knobs to properly position the absorption cell.

19. Remove the cell from the flame to prevent devitrification of the cell during warm up. Allow the instrument to stabilize for at least 2 hours; check to make sure fuel and air are at 9 and 39 respectively.

### **Hooking up the Hydride Generator:**

12. 6N HCl and sodium borohydride solutions need to be made.

The sodium borohydride solution should be constructed prior to hooking up the generator to allow it to “settle”. The solution is made of 0.6% M/V NaBH<sub>4</sub> and 0.5% M/V NaOH which is 1.75g and 2.5g respectively for 500ml; 500ml will last 6 hours.

21. Now place the cell into the flame -operating position- to allow sufficient time for the cell to warm up. The cell should be warm upon completion of this procedure.

22. Connect gray tubing coming out of the absorption cell to the hydride generator.

Replace the three tubes that go around the peristaltic pump (the sample tube should be changed; the borohydride and HCl tubes may be reused if they are in good condition).

Route the tubing around pump using the upper and lower slots to the left of the pump to hold the tubing taut around the pump. Place the two smaller tubes to the inside with the larger sample tube on the outside. When the tubes are in position, close the latch to secure the tubing in the pump.

23. Nitrogen flow is regulated by a Masterflex peristaltic pump. Tubing associated with this pump rarely needs to be changed. The pump speed should be adjusted to the 7<sup>th</sup> or 8<sup>th</sup> line for best analytical results.
24. Turn on the nitrogen tank and make sure that the flow regulator on the nitrogen tank is set at the first red line on the pressure gauge ( $\leq 100$ psi).
25. Make sure waste drain tubes are draining into buckets below.
26. Turn power on both pumps. Insert the glass straws into a bottle of Milli-Q and pump Milli-Q through all 3 tubes for at least 5 minutes.
27. Check for air leaks and worn tubing. If liquids aren't being drawn properly, may need to adjust pump until air bubbles flow through smoothly. To do this, tighten platen until air bubble in line doesn't move and then back off pressure on platen slightly.
28. Place the two glass straws associated with the smaller tubes in their respective solutions; sodium borohydride and HCl. Leave the larger sample tube in Milli-Q until readings become stable.
29. Zero AAS by pressing the "CAL-ZERO" button.
30. To change the absorbance reading time to 3 second intervals, press "Time Sec", "3", then "Read".
31. Place the sample tube in the desired analyte solution. For sediment digests that have been treated with urea, DO NOT PLACE THE SIPPER ON THE BOTTOM OF THE TUBE. Hang the sipper from the edge of the sample vial so that the tip is in the clear solution and record the counts upon stabilization. Rinse the tube in milli-Q between each sample; the next analyte can be measured upon reaching the baseline.

### **System Shutdown**

32. After analysis is complete, place all three tubes into the Milli-Q water, to allow the system to rinse for at least 5 minutes.
  33. Take the tubes out of the water and allow the system to continue pumping air for 5 minutes to clear residual water from the hydride generator system. While doing this go on to step 3.
34. Shut down the flame by pressing "Flame Off"
35. Turn off the acetylene.
36. Purge the gasses from the AAS system by pressing the "Set Flow" button.



37. **Slowly** set the lamp current to zero by turning the knob counter-clockwise
38. Turn off the power on the hydride generator and unhook the pump platen and tubing.
39. Turn off the peristaltic pump controlling the nitrogen flow.
40. Turn off the nitrogen.
41. Empty the waste container.
42. Clean and acid wash the absorption cell.
  - allow the cell to cool
  - remove the cell and soak in 0.5% NaOH for 0.5 hours
  - rinse with 5.0% HCl
  - rinse well with DI
  - allow to dry in a dust free area.

## **APPENDIX III**

### **Laboratory Quality Control Summary**

Previous QA/QC data available in Moore (2002).  
Data listed in only for elements analyzed.

**NIST2704 Analysis for 2003 Samples**

	<b>Measured Mean (n=4)(mg/kg)</b>	<b>95% CI</b>	<b>Nominal Value (mg/kg)</b>	<b>95% CI (mg/kg)</b>	<b>%Meas./Nom</b>
<b>As</b>	18.3	1.7	23.4	0.80	78%
<b>Cd</b>	1.6	0.2	3.45	0.22	46%
<b>Cr</b>	84.2	4.4	135	5.0	62%
<b>Cu</b>	88.7	7.5	98.6	5.0	90%
<b>Pb</b>	158	9.2	161	17.0	98%
<b>Zn</b>	408	26.7	438	12.0	93%
<b>Hg</b>	1.3	26.2	1.47	16.7	87%
<b>Se</b>	1.19	0.05	1.12	16.3	94%

**Blank Analysis for 2003 Samples**

**Lab Blanks**

**Digest Blanks**

**Values in mg/kg**

	PQL (mg/L)	Low Smpl. Value	Number	No. < PQL	All Pass?	Number	No. < PQL	All Pass?	High Value if > PQL
<b>As</b>	<0.05	<0.05	13	13	Yes	4	4	Yes	NA
<b>Cd</b>	<0.005	<0.006	13	13	Yes	4	4	Yes	NA
<b>Cr</b>	<0.05	13.9	13	13	Yes	4	4	Yes	NA
<b>Cu</b>	<0.03	32.92	13	13	Yes	4	4	Yes	NA
<b>Hg</b>	<0.05	<0.05	13	13	Yes	4	4	Yes	NA
<b>Pb</b>	<0.04	20.55	13	13	Yes	4	4	Yes	NA
<b>Zn</b>	<0.008	62.42	13	13	Yes	4	0	No	0.0229
<b>Hg (AFS)</b>	<.0005	0.009	14	14	Yes	4	4	Yes	NA
<b>Se (AAS)</b>	<0.001	0.34	10	10	Yes	3	3	Yes	NA

### Spike Analysis for 2003 Samples

<b>Analytical Spikes Recovery</b>				<b>Method (Digest) Spikes Recovery</b>			
	<b>No.</b>	<b>Low</b>	<b>High</b>		<b>No.</b>	<b>Low</b>	<b>High</b>
<b>As</b>	6	86.2	100.4	<b>As</b>	7	84.1	99.2
<b>Cd</b>	6	79.2	87.7	<b>Cd</b>	7	75.7	89.3
<b>Cr</b>	6	88.2	97.9	<b>Cr</b>	7	85.0	103.2
<b>Cu</b>	6	89.3	100.0	<b>Cu</b>	7	87.3	104.4
<b>Pb</b>	6	81.5	89.4	<b>S</b>	7	95.1	108.8
<b>Zn</b>	6	86.8	94.5	<b>Zn</b>	7	86.5	96.5
<b>Hg (AFS)</b>	6	78.7	105	<b>Hg (AFS)</b>	6	111	163
<b>Se (AAS)</b>	5	87	103	<b>Se (AAS)</b>	3	71	79

## **Appendix IV**

### Site locations and Sample Data

Sites are listed by river mile and name for all three years. All sample data used for plots is listed by year. Data for all three years was combined and averaged for plots A, B, C, and D to determine the overall distribution of metals in the basin. Data was used as presented for plots E and F to determine changes over time. Values that are < PQL are plotted as 0.75 the PQL value. Previous data is also available in Moore (2002), along with the statistical data used to determine the length of error bars.

**Ordered by River Mile**

<b>Site Name</b>	<b>River Mile</b>	<b>Stream Name</b>
CC20	0.37	Lower Clear Creek blw Hwy 273 Bridge
CC22	0.81	Lower Clear Creek at Hwy 273 Bridge
CC17	1.69	Lower Clear Creek at rotating fish trap
CC09	2.09	Lower Clear Creek
CC12	2.23	Lower Clear Creek pond
CC11	2.79	Lower Clear Creek
CC67	2.80	Lower Clear Creek new channel
CC68	2.90	Lower Clear Creek new channel
CC53	2.99	Lower Clear Creek new channel
CC52	3.03	Lower Clear Creek pond
CC71	3.07	Lower Clear Creek new channel
CC59	3.13	Lower Clear Creek pond
CC70	3.18	Lower Clear Creek new channel
CC08	3.23	Lower Clear Creek
CC69	3.41	Lower Clear Creek new channel
CC07	3.44	Lower Clear Creek
CC18	3.90	Lower Clear Creek nr Northstate Gravel
CC19	4.96	Lower Clear Creek at Renshaw Riffle
CC66	5.10	Lower Clear Creek abv Renshaw Riffle
CC51	5.18	Lower Clear Creek pond nr old mill site
CC21	5.32	Lower Clear Creek nr old mill site
CC50	5.36	Lower Clear Creek pond nr old mill site
CC16	5.64	Lower Clear Creek blw gorge
CC15	6.50	Lower Clear Creek abv old Saeltzer Dam site
CC14	6.69	Lower Clear Creek
CC13	7.09	Lower Clear Creek nr big blue gate
CC57	7.16	Lower Clear Creek pond
CC54	7.19	Lower Clear Creek pond in Shooting Rng area
CC56	7.20	Lower Clear Creek pond
CC55	7.21	Lower Clear Creek pond in Shooting Rng area
CC06	7.68	Lower Clear Creek
CC05	7.86	Lower Clear Creek
CC04	8.01	Lower Clear Creek
CC03	8.07	Lower Clear Creek
CC02	8.21	Lower Clear Creek
CC58	8.32	Lower Clear Creek pond nr CC Rd Bridge
CC58MAIN	8.32	Lower Clear Creek main channel nr CC Rd Bridge
CC01	8.38	Lower Clear Creek abv CC Rd Bridge
CC34	10.66	Clear Creek Gorge at Placer Rd Bridge

CC33	10.80 South Fork of Clear Creek
CC32	10.83 Clear Creek Gorge abv So Fk
CC26	12.05 Clear Creek Gorge nr Grouse Mtn Ranch Rd
CC25	12.64 Clear Creek Gorge blw Stony Gulch
CC24	12.74 Stony Gulch
CC23	12.88 Clear Creek Gorge abv Kanaka Cr
CC35	14.45 Clear Creek Gorge nr BM 1053
CC31	15.59 Clear Creek blw Orofino Gulch
CC30	15.65 Orofino Gulch
WT07	15.66 Orofino Gulch
WT08	15.66 Orofino Gulch
CC29	15.92 Clear Creek Gorge abv NEED Camp Bridge
CC28	15.98 Paige Boulder Creek
CC27	16.67 Clear Creek Gorge at Peltier Bridge
WT02	21.12 Whiskey Creek
WT03	21.12 Whiskey Creek
WT04	21.12 Secret Squirrel Gulch
MDOX	21.12 Mad Ox Gulch
LBGL	21.12 Liberty Gulch
MDOX	21.12 Mad Ox Gulch
MMGL	21.12 Mad Mule Gulch
MOXO	21.12 Mad Ox Mine Outlet
MXUS	21.12 Mad Ox Gulch
REDG	21.12 Red Gulch
WCMM	21.12 Whiskey Creek downstream from Mad Mule
WCUM	21.12 Whiskey Creek upstream of Mad Ox Gulch
WT04 (FSGL)	21.12 Secret Squirrel Gulch (Foster'Gulch)
WT09(BRAN)	21.60 Brandy Creek
WT05(NYGL)	23.09 New York Gulch
WT01	24.61 Grizzly Gulch
CCAR	27.67 Upper Clear Creek US Carr PH
CC39(CCBR)	27.09 Upper Clear Creek at Power House Bridge
WT10	27.96 Mill Pond
SLCR	27.96 Slate Creek near falls
WT11	28.26 Mill Creek
MCUC	28.26 Mill Creek
CC38	28.27 Upper Clear Creek abv Mill Creek
CC36	28.33 Crystal Creek
CC37	28.33 Willow Creek
WT12	28.33 Willow Creek
WT06(H229)	28.41 Clear Creek at Highway 299
TRPK	31.01 French Gulch Trailer Park



CC40	29.63 Upper Clear Creek nr 1285
CC41	30.14 Upper Clear Creek at N-boundry of WNRA
CC42	30.75 Upper Clear Creek nr transformer station
FRGL	31.15 French Gulch
RFRG	31.15 Right Fork French Gulch
SCRP	31.15 Scorpion Gulch
CC43	31.56 French Gulch
CC45	32.30 Upper Clear Creek at FG County Park
CC49	32.85 Upper Clear Creek blw Cline Gulch
CC44(CLN1)	32.97 Cline Gulch
CLN2	32.97 Cline Gulch
AMER	33.02 America Gulch
CCCG	33.02 Clear Creek @ Cline Gulch
CC46	36.74 Upper Clear Creek
CC47	38.41 Upper Clear Creek at painted rock
CC48	39.32 Upper Clear Creek at NAWA School Bridge

**Clear Creek-2001 Sampling  
Data (mg/kg)**

<b>Site</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Hg</b>	<b>Pb</b>	<b>Zn</b>
Method:	<b>ICAPES</b>	<b>ICAPES</b>	<b>ICAPES</b>	<b>ICAPES</b>	<b>CVAAS</b>	<b>ICAPES</b>	<b>ICAPES</b>
PQL:	<b>10</b>	<b>1</b>	<b>10</b>	<b>6</b>	<b>0.06</b>	<b>8</b>	<b>1.6</b>
<b>CC20A</b>	11.0	<1	64.4	62.1	0.14	20.3	100
<b>CC20B</b>	14.2	<1	67.3	68.1	0.15	22.6	107
<b>CC22A</b>	16.9	<1	68.2	74.1	0.16	73.5	131
<b>CC22B</b>	27.8	<1	67.3	83.4	0.21	27.2	103
<b>CC17A</b>	18.4	<1	61.0	62.8	0.15	16.5	98.4
<b>CC17B</b>	19.0	<1	66.7	69.1	0.18	15.9	98.9
<b>CC09A</b>	18.4	<1	66.6	73.8	0.19	21.6	92.7
<b>CC09B</b>	23.4	<1	68.7	75.3	0.19	24.5	91.3
<b>CC11A(1)</b>	16.0	<1	62.2	68.8	0.16	16.9	86.5
<b>CC11A(2)</b>	19.4	<1	67.3	69.3	0.20	17.6	97.3
<b>CC11B(1)</b>	16.3	<1	63.0	65.7	0.27	17.6	98.5
<b>CC11B(2)</b>	14.9	<1	60.8	68.7	0.18	17.6	76.6
<b>CC53A</b>	14.2	<1	53.0	58.9	0.15	11.8	81.3
<b>CC53B</b>	<10	<1	18.6	16.6	0.16	13.6	50.5
<b>CC08A</b>	14.8	<1	59.7	72.7	0.13	17.9	86.5
<b>CC08B</b>	14.7	<1	55.0	66.2	0.26	15.4	83.7
<b>CC07A</b>	<10	<1	56.1	67.1	0.25	15.0	83.3
<b>CC07B</b>	<10	<1	56.5	66.7	0.26	13.7	75.7
<b>CC18A</b>	12.5	<1	57.5	65.5	0.22	16.9	91.6
<b>CC18B</b>	16.2	<1	62.6	71.4	0.25	18.6	100
<b>CC19A</b>	14.9	<1	59.6	61.9	0.25	16.0	106
<b>CC19B</b>	11.3	<1	56.2	55.9	ND	14.9	90.8
<b>CC21A</b>	20.7	<1	64.9	71.3	0.51	20.2	106
<b>CC21B</b>	23.7	<1	62.3	68.8	0.24	19.9	100
<b>CC16A</b>	21.1	<1	61.1	74.9	0.27	23.4	104
<b>CC16B</b>	22.7	<1	66.4	77.5	0.28	22.6	112
<b>CC15A</b>	23.0	<1	63.0	72.9	0.18	21.7	137
<b>CC15B</b>	11.6	<1	61.7	70.0	0.18	18.2	113
<b>CC14A</b>	23.5	<1	61.6	71.8	0.19	23.9	106
<b>CC14B</b>	28.9	<1	65.7	70.3	0.17	25.4	111
<b>CC13A</b>	16.9	<1	53.3	67.4	0.15	22.9	110
<b>CC13B</b>	14.5	<1	54.4	68.8	0.15	23.8	116
<b>CC05A</b>	10.5	<1	65.8	70.0	0.22	23.9	99.4
<b>CC05B</b>	26.4	<1	74.4	64.7	0.22	27.7	85.6
<b>CC03A</b>	19.6	<1	76.5	76.8	0.26	26.8	124
<b>CC03B</b>	15.1	<1	68.4	66.2	0.20	21.2	121

<b>CC02A</b>	<10	<1	61.5	56.7	0.17	19.0	85.1
<b>CC02B</b>	20.2	<1	72.6	70.2	0.23	23.3	130
<b>CC01A</b>	10.2	<1	67.5	62.7	0.16	21.7	96.2
<b>CC01B</b>	15.5	<1	68.4	73.2	0.15	25.5	101
<b>CC34A</b>	<10	<1	70.0	56.9	0.17	27.0	75.1
<b>CC34B</b>	<10	<1	64.5	47.2	0.11	24.0	69.4
<b>CC32A</b>	10.2	<1	61.6	60.4	0.10	12.6	87.5
<b>CC32B</b>	<10	<1	66.7	54.2	0.09	18.1	79.1
<b>CC26A</b>	<10	<1	78.1	70.4	0.12	15.3	65.6
<b>CC26B</b>	12.9	<1	70.7	70.1	0.20	14.9	94.3
<b>CC25A</b>	17.0	<1	74.7	71.4	0.09	14.9	118
<b>CC25B</b>	10.2	<1	68.6	64.3	0.15	14.0	74.9
<b>CC23A</b>	18.0	<1	67.8	61.6	0.10	14.2	95.3
<b>CC23B</b>	<10	<1	64.5	49.0	NA	25.2	70.9
<b>CC23B</b>	23.8	<1	74.9	69.2	0.11	17.1	115
<b>CC35A</b>	<10	<1	53.3	50.5	<0.06	13.4	59.8
<b>CC35B</b>	<10	<1	65.9	59.5	<0.06	12.8	66.9
<b>CC31A</b>	72.3	<1	86.7	80.1	0.17	30.6	83.9
<b>CC31B</b>	81.8	<1	58.2	195	0.58	43.2	140
<b>CC29A</b>	15.9	<1	75.8	69.6	0.18	16.2	74.1
<b>CC29B</b>	27.0	<1	81.9	74.3	0.20	18.0	88.2
<b>CC27A</b>	29.8	<1	71.2	92.1	0.09	14.7	87.1
<b>CC27B</b>	19.4	<1	78.0	80.3	0.10	13.4	135
<b>CC39A</b>	43.1	1.58	41.9	266	0.22	24.0	287
<b>CC39B</b>	49.0	2.22	46.3	261	0.30	25.7	303
<b>CC38A</b>	53.5	1.12	55.9	116	0.24	33.2	291
<b>CC38B</b>	49.7	2.30	55.3	114	0.33	29.7	292
<b>CC40A</b>	49.4	1.78	55.7	67.4	0.36	28.2	257
<b>CC40B</b>	44.9	1.40	58.1	66.1	0.28	27.8	277
<b>CC41A</b>	46.7	1.68	53.2	60.0	0.31	26.7	236
<b>CC41B</b>	44.5	2.18	48.8	62.1	1.90	24.3	253
<b>CC42A</b>	19.5	<1	44.4	43.6	0.13	16.8	162
<b>CC42B</b>	25.2	<1	63.5	63.9	0.19	22.9	218
<b>CC45A</b>	32.7	1.96	56.0	60.7	0.28	23.2	257
<b>CC45B</b>	30.4	2.30	55.6	59.0	0.22	23.8	262
<b>CC46A</b>	12.8	2.64	51.9	60.2	0.11	22.3	270
<b>CC46B</b>	12.8	2.38	51.0	54.0	0.15	20.4	252
<b>CC47A</b>	15.4	1.90	53.7	63.9	0.14	55.1	300
<b>CC47B</b>	16.5	2.28	88.9	60.0	0.14	21.2	276
<b>CC48A</b>	11.2	3.32	39.4	61.5	0.15	20.9	273
<b>CC48B</b>	12.4	4.14	40.3	66.0	0.16	22.3	296
<b>CC12A</b>	<10	<1	67.9	79.5	0.17	18.7	83.4

<b>CC12B</b>	<10	<1	64.4	70.0	0.17	19.3	78.9
<b>CC52A</b>	15.2	<1	47.0	57.5	0.25	13.9	78.3
<b>CC52B</b>	17.2	<1	49.4	54.6	0.21	16.4	79.3
<b>CC59A</b>	62.7	<1	47.3	69.6	0.20	19.6	101
<b>CC59B</b>	29.4	<1	50.1	61.2	0.14	18.2	100
<b>CC51A</b>	<10	<1	53.5	50.0	0.06	13.1	91.2
<b>CC51B</b>	<10	<1	48.8	48.7	0.10	11.9	81.5
<b>CC50A</b>	<10	<1	29.0	74.3	0.46	19.3	102
<b>CC50B</b>	<10	<1	29.9	69.7	2.20	28.3	109
<b>CC57A</b>	<10	<1	50.2	59.3	0.21	12.5	70.5
<b>CC54A</b>	<10	<1	38.1	54.2	0.16	105	80.6
<b>CC54B</b>	11.3	<1	63.2	85.1	0.17	91.4	143
<b>CC56A</b>	<10	<1	53.4	78.8	0.17	12.4	70.0
<b>CC56B</b>	<10	<1	55.4	83.2	0.19	13.4	74.3
<b>CC55A</b>	<10	<1	65.2	190	0.19	224	96.6
<b>CC55B</b>	10.3	<1	69.2	114	0.21	212	89.0
<b>CC06A</b>	<10	<1	60.0	52.6	0.17	24.2	75.2
<b>CC06B</b>	11.3	<1	49.9	54.7	0.16	30.4	62.1
<b>CC04A</b>	<10	<1	65.8	59.6	0.20	15.9	88.3
<b>CC04B</b>	13.2	<1	75.7	71.2	0.35	20.9	101
<b>CC58A</b>	16.6	<1	42.1	131	<0.06	44.0	424
<b>CC58B</b>	15.4	<1	44.2	94.7	<0.06	69.2	382
<b>CC33A</b>	<10	<1	62.0	32.6	0.23	21.4	106
<b>CC33B</b>	<10	<1	57.0	29.2	0.17	20.5	86.1
<b>CC24A</b>	<10	<1	74.7	53.7	0.06	14.9	47.3
<b>CC24B</b>	<10	<1	79.1	71.6	0.12	13.8	62.4
<b>CC30A</b>	<10	<1	67.8	64.1	0.12	51.8	93.1
<b>CC30B</b>	<10	<1	42.9	55.2	0.12	45.7	97.2
<b>CC28A</b>	<10	<1	95.2	49.9	0.06	<8	68.1
<b>CC28B</b>	<10	<1	96.0	72.6	<0.06	11.7	54.9
<b>CC28B</b>	<10	<1	96.2	72.2	0.06	10.3	54.5
<b>CC36A</b>	10.3	<1	48.4	27.9	<0.06	11.2	75.0
<b>CC36B</b>	<10	<1	49.4	29.2	0.06	9.6	80.5
<b>CC37A</b>	35.6	<1	26.4	692	0.09	19.8	388
<b>CC37B</b>	38.3	<1	25.1	737	0.09	19.6	403
<b>CC43A</b>	428.8	1.76	31.2	55.9	1.30	70.9	217
<b>CC43B</b>	456.4	2.62	34.5	60.2	1.10	63.7	253
<b>CC44A</b>	120.0	<1	32.0	57.3	0.85	26.8	196
<b>CC44B</b>	126.2	1.12	36.4	71.0	1.20	33.1	220

**Clear Creek-2002 Sampling Data (mg/kg)**

<b>Site</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Hg</b>	<b>Pb</b>	<b>Zn</b>
Method:	<b>ICAPES</b>	<b>ICAPES</b>	<b>ICAPES</b>	<b>ICAPES</b>	<b>CVAFS</b>	<b>ICAPES</b>	<b>ICAPES</b>
PQL:	<b>10</b>	<b>1</b>	<b>10</b>	<b>6</b>	<b>0.02</b>	<b>8</b>	<b>1.6</b>
<b>CC22A</b>	32.4	<1.0	65	74.6	0.15	20.1	99.4
<b>CC22B</b>	32.2	<1.0	65.1	73.3	0.15	20.7	101
<b>CC17</b>	16.1	<1.0	62.2	62	0.18	12.1	98.5
<b>CC67</b>	<10	<1.0	59.5	57.3	0.13	8.86	69.9
<b>CC68</b>	37.9	1.02	81.1	94.3	0.19	9.60	108
<b>CC53</b>	38.6	<1.0	69.8	70	0.10	9.4	99
<b>CC71</b>	10.7	<1.0	63.6	62.2	0.03	<8	64
<b>CC70</b>	<10	<1.0	61.1	73.1	0.05	<8	60.7
<b>CC08A</b>	16.5	<1.0	56.9	62.4	0.22	12.9	86.1
<b>CC08B</b>	11	<1.0	49	53	0.16	11.2	73.7
<b>CC69</b>	17.4	<1.0	62.6	70.1	0.11	<8	96.7
<b>CC66</b>	17	<1.0	59.7	66.1	0.35	12.8	113
<b>CC50</b>	57.2	11.6	14.6	27.3	0.27	44.3	38.4
<b>CC16</b>	32.4	<1.0	54.1	61.5	0.22	17.8	84.6
<b>CC15</b>	24.7	<1.0	61.6	79.4	0.16	17.5	158
<b>CC13</b>	23	<1.0	54.2	75.9	0.23	15.8	132
<b>CC06</b>	12.2	<1.0	59.3	69.1	0.14	14.8	118
<b>CC03</b>	18.2	<1.0	59.3	69	0.13	17.8	115
<b>CC01</b>	<10	<1.0	65.6	62.5	0.14	15.4	104
<b>CC34</b>	11.9	<1.0	68.8	59.7	0.11	20.5	105
<b>CC35</b>	25.5	<1.0	65.2	82.1	0.10	13.5	131
<b>CC31</b>	25.1	1.18	71.5	78.2	0.17	18.6	154
<b>CC29</b>	24.8	<1.0	73.2	76	0.08	11.7	118
<b>CC27A</b>	23.8	1.64	79.5	99.7	0.14	10.4	197
<b>CC27B</b>	23.9	1.56	75.5	99.6	0.12	12.4	196
<b>CC39</b>	44.8	1.92	43.8	296	0.19	15.6	269
<b>CC38</b>	42.6	3.34	51.1	224	0.33	22.5	395
<b>WT06</b>	53.8	3.18	53.9	60.2	0.25	22.8	273
<b>CC40</b>	158	3.56	56.3	62.4	0.30	28	253
<b>CC41</b>	61.2	2.7	47.9	54.9	0.27	21.2	237
<b>CC42</b>	45.2	2.08	57.4	56.5	0.14	21.1	233
<b>CC45</b>	37.5	3.04	58.1	56.7	0.13	19.3	255
<b>CC48</b>	20	4.1	45.5	62.8	0.10	17.2	319
<b>CC30</b>	<10	<1.0	34.7	49.3	0.09	38.2	91.8
<b>WT07</b>	<10	<1.0	19.1	69.8	0.20	19.7	47.9
<b>WT08</b>	<10	<1.0	15.7	51.4	0.07	16.8	40.8

<b>CC28</b>	<10	<1.0	88.7	43.9	0.03	<8	62.1
<b>WT02</b>	21.7	19.2	42.5	72	0.45	20.7	908
<b>WT03</b>	30.8	7.1	60.5	69.4	0.44	19.2	506
<b>WT04</b>	<10	<1.0	32.7	307	0.17	9.68	68.5
<b>MDOX</b>	37.3	9.22	83.0	68.3	1.63	38.6	613
<b>WT09A</b>	<10	<1.0	72.9	23.5	0.05	8.36	53.6
<b>WT09B</b>	<10	<1.0	79.6	24.1	0.05	9.22	52.5
<b>WT05</b>	<10	<1.0	190	62.5	0.09	16.3	150
<b>WT01</b>	22.9	1.62	71.3	69.7	0.17	11.6	222
<b>WT10</b>	30	2.22	49.1	69.7	0.24	30.4	185
<b>WT11A</b>	<10	<1.0	56.2	57.9	0.08	<8	68.2
<b>WT11B</b>	<10	<1.0	62.2	63.6	0.10	<8	76.4
<b>MCUC</b>	<10	2.62	60.8	54.1	0.03	5.42	71.7
<b>CC37A</b>	41.7	2.3	31	1071	0.10	19.2	810
<b>CC37B</b>	41.4	2.92	31.6	1037	0.10	20.2	818
<b>WT12</b>	36.5	1.88	35.8	651	0.07	14.5	434
<b>CC43</b>	473	3.4	37.5	58	0.85	49	267
<b>CC44</b>	264	2.36	32.2	57.3	0.98	30.8	220

**Clear Creek-2003 Sampling  
Data (mg/kg)**

Site	As	Cd	Cr	Cu	Hg	Pb	Se	Zn
Method:	<b>ICAPES</b>	<b>ICAPES</b>	<b>ICAPES</b>	<b>ICAPES</b>	<b>(AFS)</b>	<b>ICAPES</b>	<b>HGAAS</b>	<b>ICAPES</b>
PQL:	<b>0.025</b>	<b>0.004</b>	<b>0.01</b>	<b>0.01</b>	<b>.01</b>	<b>0.09</b>	<b>0.001</b>	<b>0.004</b>
AMER_A	280	b.d	38.54	53.08	0.343	39.56	0.89	309.2
AMER_B	848.4	b.d	36.26	81.02	0.696	55.86	0.9	445
BRAN(WT09)	b.d	b.d	102.56	32.92	0.009	29.18	0.34	77.06
CC01	6.83	b.d	64.46	57.51	0.79	25.14	1.08	102.9
CC02	10.28	b.d	73.44	57.31	0.90	28.23	1.25	103.9
CC03	8.82	b.d	58.09	50.64	1.05	26.75	1.33	107
CC04	10.23	b.d	44.06	39.54	0.20	24.39	1.53	123.4
CC05	10.17	b.d	61.7	68.06	1.08	30.44	1.43	107.1
CC06	9.08	b.d	54.01	55.11	0.26	23.88	1.35	121.2
CC07_A	20.32	b.d	59.5	68.66	0.17	24.95	0.95	105.4
CC07_B	17.35	b.d	53.77	66.73	1.19	23.19	1.02	91.79
CC08_A	16.21	b.d	54.57	62.29	0.45	20.55	1.21	87.31
CC08_B	20.3	b.d	54.93	63.59	0.41	23.92	1.14	93.43
CC09	24.15	b.d	58.92	68.87	1.02	23.25	2.09	80.33
CC10_A	12.16	b.d	57.61	65.64	0.31	21.24	0.9	90.49
CC10_B	9.17	b.d	59.8	66.12	0.27	20.89	1.01	84.69
CC11	12.02	b.d	60.17	69.29	0.39	21.64	2.79	86.27
CC12	16.23	b.d	62.5	71.27	0.25	23.06	0.92	115.8
CC13	25.66	b.d	87.08	92.98	0.79	44.1	1.5	159.7
CC14	237.2	b.d	72.48	64.94	0.56	24.55	1.12	112.9
CC15	31.16	b.d	53.61	67.85	0.36	23.76	1.13	133.5
CC17	18.61	b.d	54.49	62.77	0.35	20.99	1.69	85.94
CC18	17.29	b.d	48.17	55.6	0.52	23.15	1.15	91.43
CC20	7.65	b.d	59.07	59.01	0.28	23.07	0.84	96.72
CC22	10.29	b.d	67.35	68.75	0.27	25.25	0.81	100.2
CC27	10.12	b.d	94.48	135.14	0.03	32.46	0.6	119.56
CC28	b.d	b.d	147.48	54.44	0.01	28.44	0.48	82.42
CC29	12.38	b.d	104.88	85.22	0.06	31.1	1.1	98.48
CC31	11.84	b.d	74.92	60.87	0.93	28.05	1.19	119
CC34	5.97	b.d	72.71	46.98	0.15	26.32	0.73	99.29
CC35	15.94	b.d	64.91	58.62	0.27	27.47	1.55	133.8
CC58MAIN	6.87	b.d	59.72	47.54	0.25	25.33	0.88	99.46
CCAR	35.8	b.d	57.78	187.82	0.11	35.92	1.37	295.6
CCBR	19.26	b.d	73.3	53.46	0.11	39.46	1.32	311.6
CCCG	14.78	b.d	77.62	59.96	0.07	37.72	1.1	307.6

CLN1 (CC44)	101.6	b.d	36.08	47.7	0.03	40.7	1.12	207
CLN2_A	109.74	b.d	38.6	52.86	0.70	51.14	1.79	254.4
CLN2_B	145.98	b.d	43	68.08	1.82	64.86	1.46	256.8
FGCP (CC45)	40.12	b.d	59.8	182.46	0.11	35.14	0.95	278.2
FRGL	323.6	b.d	44.36	57.78	0.65	73.14	1.3	281.8
FSGL (WT04)	5.84	b.d	31.84	195.38	0.07	26.54	1.11	62.42
GRZL (WT01)	10.32	b.d	72.62	58.8	0.03	30.14	0.57	161.26
H229_A (WT06)	42.46	b.d	63.2	56.74	0.14	40.38	1.34	294
H229_B (WT06)	44.9	b.d	64.84	59.58	0.25	38.3	1.45	287.8
LBGL	6.98	b.d	109.74	185.34	0.09	34.56	0.67	524
MDOX	39.98	5.04	85.36	80.68	0.67	48	2.47	875.6
MMGL	57.34	b.d	46.66	55.2	0.16	46.72	1.88	216
MOXO_A	25.84	b.d	13.9	43.02	0.22	53.58	0.45	188.58
MOXO_B	30.06	b.d	14.8	40.6	0.32	49.4	1.56	185.06
MXUS	52.34	8.88	47.4	104.7	0.56	50.54	3.6	1575.2
NYGL (WT05)	b.d	b.d	229.2	63.24	0.04	39.38	0.93	156.86
REDG	6.02	b.d	22.4	364.8	0.33	43.52	1.8	105.48
RFRG	170.06	b.d	57.18	49.72	0.31	60.08	0.75	188
SCRP	714.8	1.76	30.14	67.9	0.52	84.4	1.26	375
SLCR	29.20	b.d	29.42	76.48	0.07	40.16	0.95	298.8
TRPK	59.64	b.d	67.66	63.18	0.20	44.30	1.53	280.2
WCMM	36.16	8.5	55.74	87.36	0.41	41.2	10.47	770.8
WCUM	38.2	5.56	77.28	114.2	0.26	46.92	3.72	1093.8
WCWL (WT03)	25.3	2.7	85.78	61.9	0.21	39.44	1.95	573.6