



Investigation of Background Inorganic and Organic Arsenic in Four Washington Lakes

Abstract

During the summer and fall of 2002, arsenic data were collected from four lakes of varying geology, climate, and altitude: Black Lake (Stevens County), Conner's Lake (Okanogan County), Mountain Lake (San Juan County), and Lake Pleasant (Clallam County). These lakes, upstream from known anthropogenic arsenic inputs, provide a snapshot of background arsenic in Washington surface waters, sediments, and freshwater fish. Arsenic speciation analyses in water and fish were emphasized due to a paucity of these data from freshwater systems.

Black Lake and Mountain Lake had total inorganic arsenic concentrations in water below the National Toxics Rule (NTR) water criterion of 0.14 $\mu\text{g/L}$ for the consumption of organisms (e.g., fish). Lake Pleasant and Conner's Lake had inorganic arsenic in water from 1.2 and 13 times the NTR water criterion for consumption of organisms, respectively. At all four lakes, inorganic arsenic in water exceeded the NTR criterion of 0.018 $\mu\text{g/L}$ for the consumption of both water and organisms.

Black Lake had the lowest sediment arsenic concentrations detected in this study, and Mountain Lake had the highest. Conner's Lake and Lake Pleasant had intermediate sediment arsenic concentrations.

Only two of 21 fish tissue composites had arsenic detections: a composite of three Kokanee from Lake Pleasant had a total arsenic concentration of 180 $\mu\text{g/Kg}$, and a brown bullhead from Conner's Lake had an arsenic(III) concentration of 9 $\mu\text{g/Kg}$. The latter exceeds the NTR fish tissue criterion of 6.16 $\mu\text{g/Kg}$ for inorganic arsenic.

There is no clear relationship between arsenic concentrations in water, sediment, and fish tissue in lakes upstream from anthropogenic inputs.

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Introduction

Arsenic is a common element in the earth's crust, where it is frequently found in association with iron and in minerals containing copper, lead, or gold. Arsenic is leached from rocks and minerals by surface water and storm runoff and is released as fine dust during smelting. Dust emissions may travel many miles prior to deposition. Moore and Ramamoorthy (1984) estimate that weathering contributes 30% of global arsenic emissions, while 70% are derived from anthropogenic releases. These releases have led to measurable increases in arsenic concentrations in some surface waters.

For centuries, arsenic has been known to be an acute human poison. Ingestion of arsenic has been linked with skin, liver, bladder, and prostate cancer. Many health agencies have recognized arsenic as a human carcinogen (ATSDR, 2000). People are exposed to arsenic from a variety of sources including air, soil, and water. Another source, which may be significant, is fish consumption. Fish and shellfish, particularly marine species, are known to contain high concentrations of arsenic. Historically, much of these data have been reported for total arsenic only. Understanding the form of arsenic is important, due to the varying toxicity of inorganic and organic arsenic (Donohue and Abernathy, 2002).

Applicable standards for this current study are provided in the U.S. Environmental Protection Agency (EPA) National Toxics Rule (62 FR 42160). These standards are:

- 0.018 µg/L inorganic arsenic in water when both drinking water and organisms (e.g., fish, shellfish) are consumed.
- 0.14 µg/L inorganic arsenic in water when only organisms are consumed from the waterbody.
- 6.16 µg/Kg inorganic arsenic in organism tissues. This latter value is backcalculated from the NTR numeric water value for consumption of organisms and the NTR bioconcentration factor of 44.

The inorganic forms of arsenic are most poisonous to humans, while the organic forms vary in toxicity. Mono- and dimethyl-arsenates have low toxicity (ATSDR, 2000), while the more complex arsenobetaine, arsenocholine, and other arsenosugars are considered inert when ingested by mammals (Neff, 1997). Organic arsenicals are hydrophilic by nature and have little tendency to bioaccumulate in human tissue.

Quantitative data on arsenic concentrations and speciation in fish tissue are sparse. The currently available literature was reviewed by Donohue and Abernathy (2002). They found very few samples of freshwater fish tissue analyzed specifically for inorganic arsenic. Most prior sampling by the Department of Ecology, Environmental Assessment Program, also has not distinguished between arsenic species in freshwater species. Data on ambient concentrations and ratios of inorganic to organic arsenic in freshwater fish tissue are critical in describing the magnitude of naturally occurring arsenic concentrations. This current study emphasized this data gap as a primary objective. Secondary objectives included collecting information to

describe the magnitude of bioconcentration and/or bioaccumulation between various environmental media (water and phytoplankton) and fish tissues.

This study evaluated the levels and forms of arsenic in water, sediments, and several species of freshwater fish tissue. These data will be used to begin developing a database of typical arsenic concentrations in these media. The study establishes ambient concentrations from four lakes located upstream of known anthropogenic arsenic inputs. These concentrations have been compared to the inorganic arsenic criteria listed in the National Toxics Rule (NTR).

Study Design

Four lakes in differing geologic and hydrologic settings were selected for sampling. Black, Mountain, and Pleasant are upstream from all known anthropogenic arsenic sources, such as orchards and mines, except for global fugitive dusts. Conner's Lake is below historic mining activities in the upper watershed. For that lake, however, historic mining activities are not known to have significant arsenic discharges (Roeder, 2002).

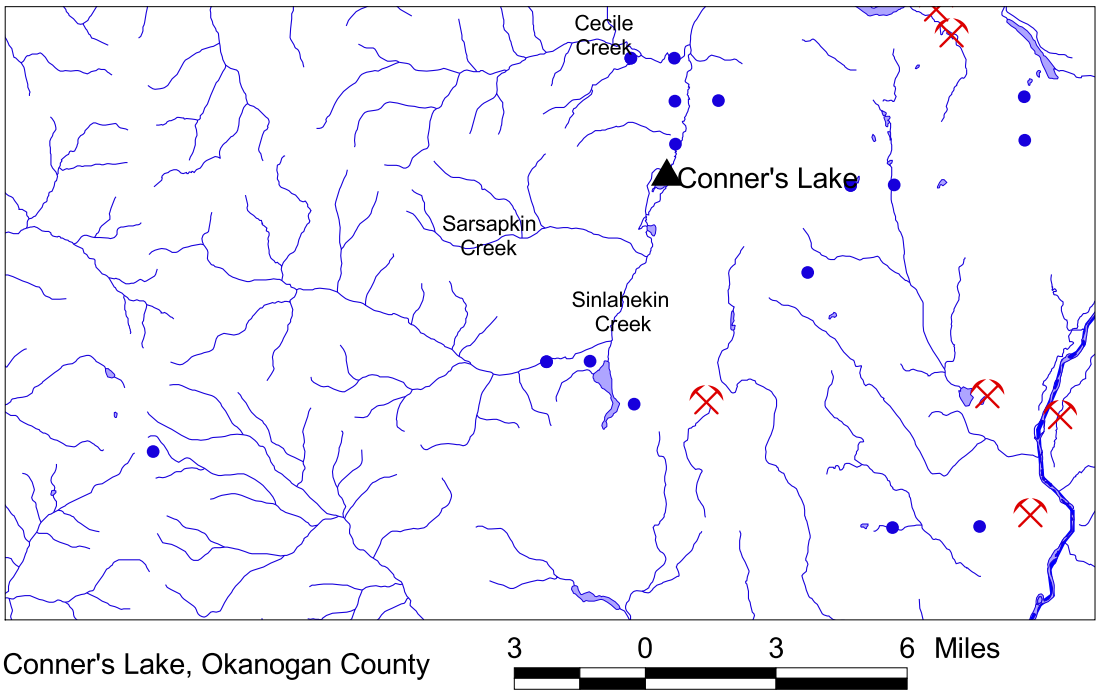
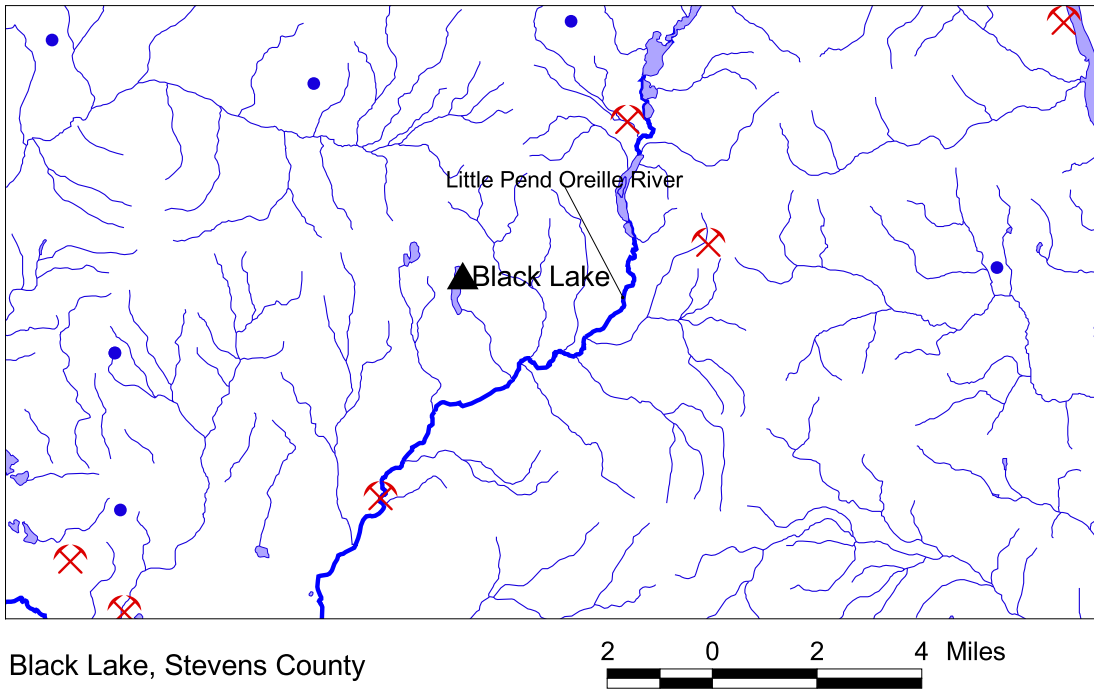
The elimination of every possible source of anthropogenic arsenic was not possible, given atmospheric sources and the intensity of prospecting and historic mining in Washington State. The database of abandoned mine sites under development by the Washington State Department of Natural Resources (DNR) was reviewed to document potential historic anthropogenic arsenic sources (Norman, 2000). Also reviewed were U.S. Geological Survey land use coverages, previous Ecology sampling activities for natural background in soils (San Juan, 1994), and sampling at abandoned mine sites (Raforth et al., 2000) to ensure that selected lakes were typical for their respective regions.

The sampled lakes are shown on Figures 1 and 2. Locations and descriptions of the lakes are in Table 1.

Table 1. Locations and descriptions of the four sampled lakes.

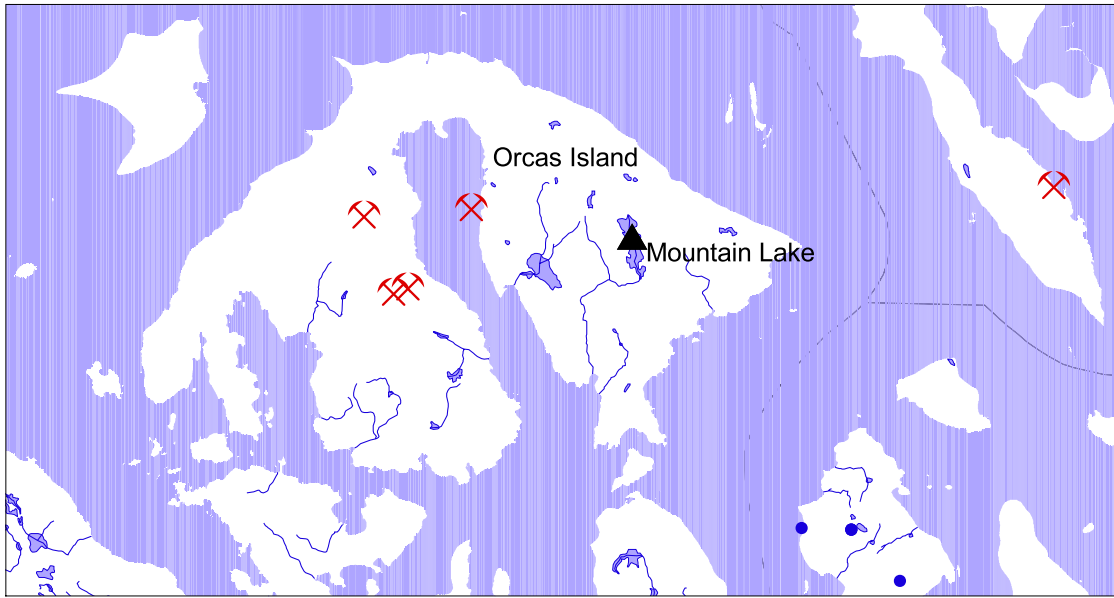
Lake	County	Elevation (ft.)	New Waterbody No.	Old Waterbody No.
Black	Stevens	3701	265WMV	WA-59-9010
Conner's	Okanogan	1557	896HNZ	WA-49-0000
Mountain	San Juan	914	115RIM	WA-02-9060
Pleasant	Clallam	390	871WBX	WA-20-9050

Arsenic concentrations in lentic systems are known to vary seasonally in response to lake stratification, oxidation-reduction potential (Eh), changes in phytoplankton composition, and/or alterations in the arsenic:phosphate ($H_2PO_4^+$) ratio (Anderson and Bruland, 1991). Phytoplankton are the most significant mechanisms for arsenic methylation and biotransformation (Maeda, 1994; Baker et al., 1983).



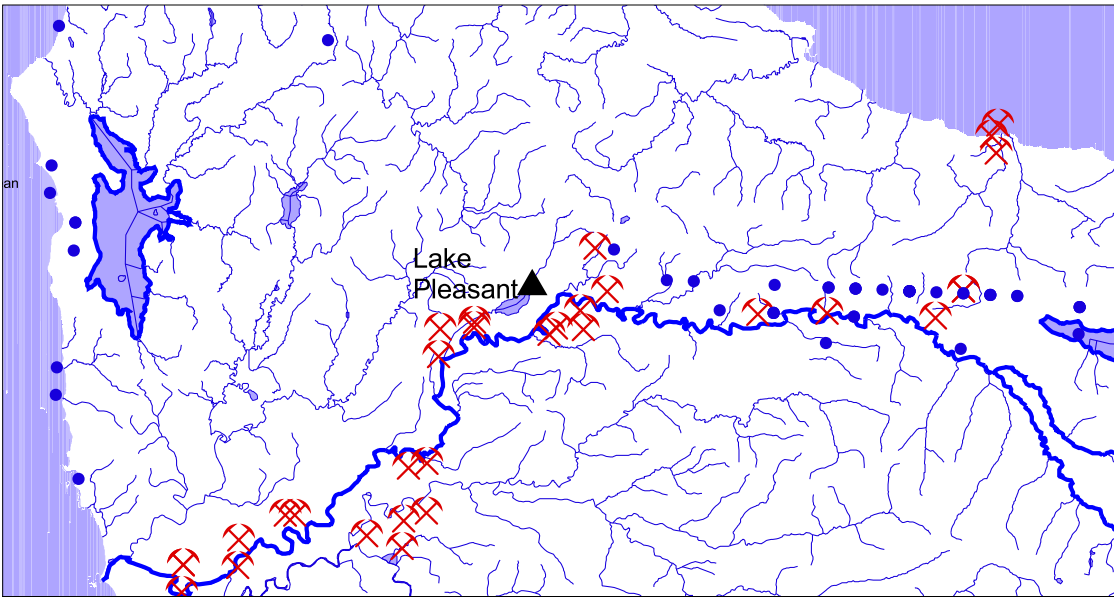
- Historic Mines (Hunting, 1956)
- ⊗ Current DNR Surface Mines
- ▲ Fish Arsenic Sampling Location

Figure 1. Eastern Washington lakes sampled for arsenic.



Mountain Lake, San Juan County

2 0 2 4 Miles



Lake Pleasant, Clallam County

5 0 5 10 Miles



- Historic Mines (Hunting, 1956)
- ⊗ Current DNR Surface Mines
- ▲ Fish Arsenic Sampling Location

Figure 2. Western Washington lakes sampled for arsenic.

Four arsenic species were analyzed during two seasons: summer (August) and fall (late November-early December) to determine the potential magnitude of seasonal cycling. Surface water and fish tissue samples also were analyzed for total arsenic by induced coupling plasma – mass spectrometry (ICP-MS) to provide data on total arsenic.

Field Methods

Water

The first surface water sampling event occurred during stratification, while the second sampling event was after fall turn-over. Waters were concurrently sampled for total phosphorus (both seasons) and chlorophyll(a) (summer only).

Waters were collected using a depth integrating bridge sampler (DH-76, US Army Corps of Engineers, Vicksburg, MS) from the entire water column. The sampler was cleaned using 10% nitric acid and deionized water prior to use. The sampler was rinsed with on-site water prior to deployment. Waters were poured from the DH-76 jar into pre-cleaned polyethylene jars with Teflon lids and preserved with 2M HCl. For filtered waters, 0.45 µm pre-cleaned disposable membrane filters were used. Personnel wore non-talc nitrile gloves during field sampling activities.

For Black Lake, the fall water sample was collected through a hole chopped in the ice and by hand dipping the bottle. This hole was close to the shoreline and in shallow water about four feet deep.

The surface waters were analyzed using the methods shown in Table 2. Brooks Rand in Seattle, Washington analyzed the waters and fish tissues for the arsenic species. Ecology’s Manchester Environmental Laboratory analyzed all other parameters.

Table 2. Surface water preparation and analytical methods.

Analyte	Preparation Methods	Preparation Method References	Analytical Method	Analytical Method Reference
Arsenic species	Field addition of 6M HCL/L for preservation as shown in the analytical methods	USEPA Method 1632	HG-CT GC-AAS, USEPA Method 1632	USEPA, 2001
Total arsenic	Field addition of 1:1 nitric acid to pH <2	--	ICP-MS	USEPA Method 600/4-79-020
Chlorophyll(a)	Filtration onto glass fiber disk, acetone extraction	APHA Standard Method 10200H(3)	USEPA Method 10200H(3)	APHA, 1991
Total phosphorus	None	4500 P-I	USEPA Method 365.3	USEPA, 1993

The project plan (Jack, 2002) outlined the collection of phytoplankton for arsenic analysis. A 20 µm plankton tow was used to collect a plankton-water concentrate. This concentrate was to be laboratory filtered to produce a solid tissue matrix for analysis on a wet-weight basis. Manchester Environmental Laboratory (MEL) used deionized water to wet 1.2 µm particle retaining glass-fiber filters for extraction of the plankton from the concentrate. MEL was unable to collect sufficient mass for analysis using these filters, due to rapid clogging of the filter media. In one case, insufficient plankton mass was available in the concentrate. Future plankton collection should tow the plankton net for at least 15-20 minutes. Future attempts at phytoplankton extraction/analysis should use durable 10 µm glass fiber filters, with the largest diameter and greatest vacuum possible.

Sediments

Surficial sediments were sampled during both study seasons using a petite Ponar sediment grab. The sediment grab was cleaned with 10% nitric acid and rinsed with on-site water prior to use. Compositing bowls and spoons were similarly cleaned and dedicated to each lake. Two grabs were selected from the approximate deepest portion of each lake with two exceptions, discussed below. The top 5 cm of sediment from each grab was composited into a stainless steel bowl.

Due to the boat drifting, grabs were not collected from exactly the same position. The summer sediment sample in Mountain Lake was taken in a cove in the lee of a small island, due to high winds on the main portion of the lake. This was in approximately 30 feet of water. The fall sediment sample from Mountain Lake was located at the 90-foot depth, closer to the 120-foot deepest portion of the lake.

For Black Lake, the fall sediment sample was collected from a shallow (4 foot deep) area along the south end of the lake near the Department of Fish and Wildlife boat ramp. The area had about 6 inches of ice cover which was broken to access the water and sediment beneath. Ice safety concerns necessitated using this shallow area to collect Black Lake's fall water and sediment samples.

Sediments were analyzed for total arsenic, total organic carbon (TOC), percent solids, and grain size by the methods shown in Table 3.

Table 3. Sediment preparation and analytical methods.

Analyte	Preparation Methods	Prep. Method References	Analytical Method	Analysis Method Reference
Total arsenic	Acid digestion per methods for ICP-MS	USEPA,1997	ICP-MS	USEPA Method 600/4-79-020
TOC	Dried at 104 ⁰ C with acid cleanup for TOC	USEPA,1997	Combustion	USEPA, 1997
% solids	None	NA	Gravimetric	USEPA 160.3
Grain size	None	NA	Sieve and Pipette	USEPA, 1996

Fish

Fish were collected from all lakes during August and early September, 2002 using gill nets or an electroshocking boat. The species and numbers of fish collected were based on availability and their potential for human consumption. Numbers and species collected are shown in Table 4.

Table 4. Fish species and average sizes.

Lake	Species	Scientific Name	Composites	Fish per Composite	Mean Total Length (mm)	Mean Weight (gms)
Black	Rainbow trout	<i>O. mykiss</i>	3	10	257	164
Conner's	Rainbow trout	<i>O. mykiss</i>	3	10	340	460
	Brown bullhead	<i>A. nebulosus</i>	3	10	167	86
Mountain	Cutthroat trout	<i>S. clarki</i>	3	4	282	197
	Kokanee	<i>O. nerka</i>	3	9	235	121
Pleasant	Cutthroat trout	<i>S. clarki</i>	3	10	231	133
	Kokanee	<i>O. nerka</i>	3	3	291	338

O. = *Oncorhynchus*

A. = *Americus*

S. = *Salmo*

Fish were wrapped in aluminum foil and transported to Ecology Headquarters on ice. Fish were frozen at -18° C until processing. Fish were descaled and rinsed with deionized water. Then equal mass aliquots of skin-on fillet tissue were removed using stainless steel knives which had been cleaned with Liquinox detergent, 10% nitric acid, and deionized water. The aliquots were homogenized with a KitchenAid® meat grinder and refrozen.

All fish tissues were analyzed for total arsenic, percent lipids, and four arsenic species as shown in Table 5. Lengths and weights for all fish collected are in Appendix A.

Table 5. Fish tissue preparation and analytical methods.

Analyte	Preparation Methods	Prep. Method References	Analytical Method	Analysis Method Reference
Total arsenic	Acid digestion per methods for ICP-MS	USEPA, 1997	ICP-MS	USEPA Method 600/4-79-020
Arsenic species	HCL digestion per methods	USEPA, 2001	HG-CT-GC-AAS	USEPA, 2001
% lipids	None	NA	Gravimetric	USEPA, 1980

Two samples of fish chow also were analyzed concurrent with the fish tissue. The chow pellets were obtained from the hatchery in Colville, Washington and stored frozen with the fish in separate polyethylene bags. They were analyzed by methods identical to the fish tissues, although they did not require homogenization in the meat grinder.

Quality Assurance Review

Surface water, sediment, and fish tissue analytical data quality has been evaluated using the data quality objectives and goals specified in Jack (2002), in their respective method descriptions, using field and laboratory duplicates, and against certified reference materials (Table 6).

Summary results from the quality assurance (QA) sample performance are presented in Table 6. In general, analytical results met the QA acceptance limits described in their respective methods. The exceptions are for dimethylarsenate (DMA) in surface water samples and monomethylarsenate (MMA) in fish tissues. These deviations are further described below.

Table 6. Quality assurance parameters.

Analyte	Average					Maximum field or lab blank concentration
	Calibration RSD	Calibration standard (% recovery)	Lab duplicate RPD	Recovery of matrix spikes (% recovery)	CRM recovery (%)	
Surface Water						
Total arsenic	-	100.4	4	108	-	<0.1 µg/L
Arsenic (inorganic)	8.7	-	3.2	94.5	80.3	0.008 J µg/L
Arsenic(III)	12.5	-	9.2	77.3	88.6	0.009 J µg/L
MMA	9.4	-	7.2	100.6	-	0.025 J µg/L
DMA	16.4	-	8.4	143.7*	-	<0.01 µg/L
Chlorophyll	-	101.1	1	-	-	<0.05 µg/L
Phosphorus	-	99.8	0	-	-	<0.01 mg/L
Sediment						
Total Arsenic	-	104.8	-	88.5	-	<0.1 mg/Kg, dry
TOC	-	95.1	8.0	-	-	<0.1%
Fish Tissue						
Total arsenic	-	102	-	104.4	96.9	<0.1 mg/Kg, wet
Arsenic (inorganic)	5.8	-	2.5	90.5	103.9	0.005 J µg/g
Arsenic(III)	16.3	-	4.5	101.8	91.8	0.002 J µg/g
MMA	4.6	-	<MDL	35.9*	106	<0.005 µg/g
DMA	10.8	-	0.1	116.6	106.5	<0.05 µg/g
% lipids	-	-	2.1	-	-	<0.01 %

- = not applicable

< = less than the noted concentration

* = outside method performance limits

J = estimated concentration

RSD = relative standard deviation

RPD = relative percent difference

CRM = certified reference material

Matrix spike recoveries for DMA in surface water sometimes exceeded the allowable method limits (75-125%). The average DMA spike recovery was 143.7%. However, in all cases the detected concentrations were very low. The excessive spike recoveries consequently led to “J” or estimated flags on the low-level DMA detections.

For MMA in fish tissues, the samples with low spike recoveries were rerun by the contract analytical laboratory. However, the reanalysis also had low spike recoveries. In a final effort to understand the reason for the low recoveries, an alternative, experimental extraction was attempted, which was unsuccessful. The contract laboratory and the reviewing chemist at Manchester Environmental Laboratory both concluded that the low spike recoveries were due to a genuine matrix interference effect. The matrix interference effects have elevated the detection limits for MMA in a number of samples.

Based on an overall review of the laboratory QA metrics, the analytical accuracy, bias, and precision goals specified in the QA Project Plan (Jack, 2002) have been met. Data are reported in the following section, with some consideration of the detection limits and relative magnitude of detections relative to detection limits.

Results

For fish tissues, only a few samples had detectable concentrations. Table 7 presents the maximum detection limit for arsenic species which were never detected and the detected concentrations for the two samples with measurable concentrations.

Table 7. Maximum detection limits and detected arsenic concentrations in fish tissue. Units are µg/Kg (wet).

Lake	Species	Arsenic by ICP-MS	Arsenic - total inorganic	Arsenic (III)	MMA	DMA
Black	Rainbow trout	100 U	3 UJ	6 UJ	5 UJ	50 U
Conner's	Rainbow trout	100 U	3 UJ	3 UJ	5 UJ	50 UJ
	Brown bullhead	100 U	9 UJ	9	5 UJ	20 UJ
Mountain	Kokanee	100 U	2 UJ	4 UJ	5 UJ	50 UJ
	Cutthroat trout	100 U	3 UJ	3 UJ	5 UJ	50 UJ
Pleasant	Cutthroat trout	100 U	5 UJ	2 UJ	5 UJ	20 UJ
	Kokanee	180	3 UJ	3 UJ	5 UJ	20 UJ

U = not detected, maximum detection limit shown

UJ = not detected, maximum estimated detection limit shown

Bold = maximum detected concentration

Black Lake has been stocked by the Washington Department of Fish and Wildlife at least twice during the past three years. This was discovered after the collection of fish (Vail, 2003). The QA Project Plan for this current study did not anticipate collecting stocked species (Jack, 2002). However, these data are presented herein to give an indication of the magnitude of arsenic

variability between stocked and unstocked species. To further evaluate the potential influence of collecting stocked species, two samples of fish chow also were analyzed. These two brands are used by all hatcheries in the state (Ebel, 2002). Table 8 illustrates the concentrations of arsenic species found in the fish chow.

Table 8. Fish chow arsenic concentrations in $\mu\text{g}/\text{Kg}$.

Brand	Total Arsenic	Arsenic – total inorganic	Arsenic (III)	MMA	DMA
SilverCup	2,640	86	74	6 J	220
NutraFeed	4,060	19	21	5 UJ	99

J = estimated concentration

UJ = estimated detection limit

Surface water arsenic concentrations ranged from non-detect to detectable levels of total inorganic, arsenic(III), and methylated arsenic species. Figure 3 illustrates the range of concentrations found. For non-detect levels, the detection limit is shown on these figures. Also shown is the numeric water quality criterion from the National Toxics Rule (NTR) for the consumption of organisms. Both the NTR criteria for consumption of water and fish ($0.018 \mu\text{g}/\text{L}$ inorganic arsenic) and the water criteria for the consumption of fish only ($0.14 \mu\text{g}/\text{L}$, inorganic arsenic) were exceeded in several lakes. Tables of all the raw laboratory results may be found in the Appendix B.

Some additional water quality parameters were collected to help evaluate potential changes and/or differences in arsenic concentrations between lakes and seasons. These include chlorophyll(a) during the August sampling event, and total phosphorus during both water sampling events. Results from these analyses are presented in Table 9.

Table 9. Ancillary water quality parameters by lake and collection date, in $\mu\text{g}/\text{L}$.

Parameter	Collection Season	Lake			
		Black	Conner's	Mountain	Pleasant
Chlorophyll(a)	Summer	3.6 J	2.5 J	0.92	5.4 J
Total Phosphorus	Summer	18	15	10 U	10 U
Total Phosphorus	Fall	22	20	10	13

J = estimated concentration

U = not detected at the concentration shown

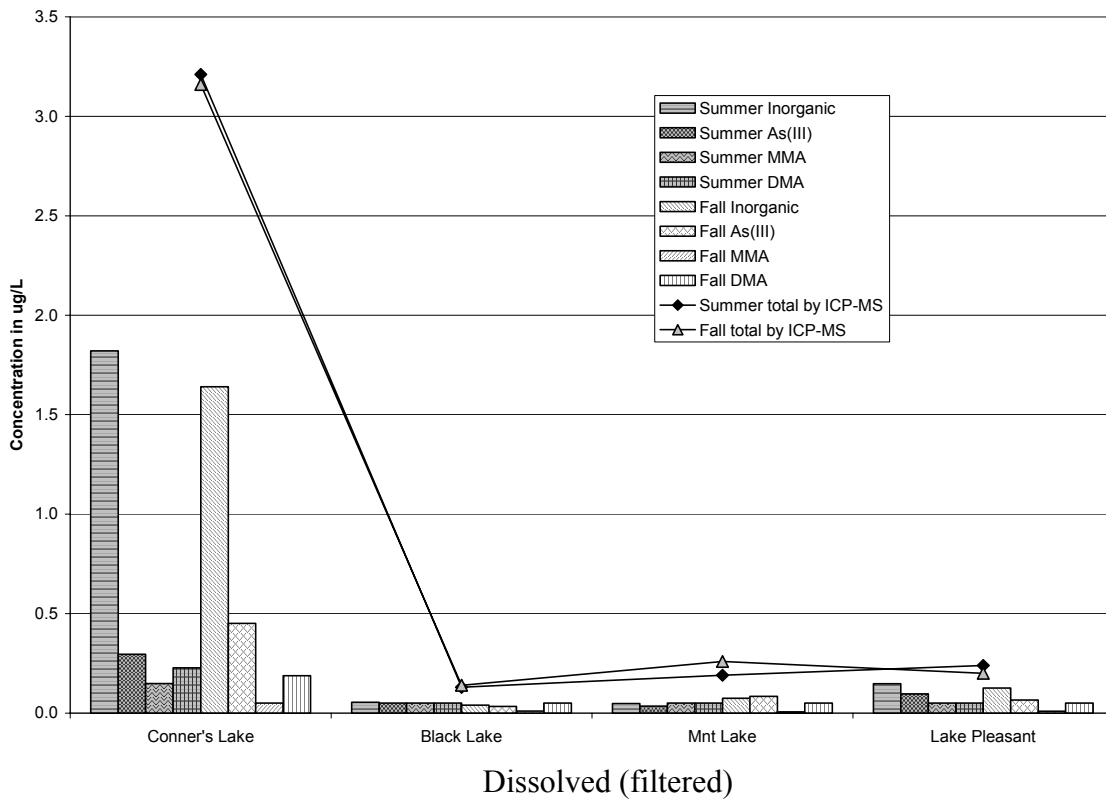
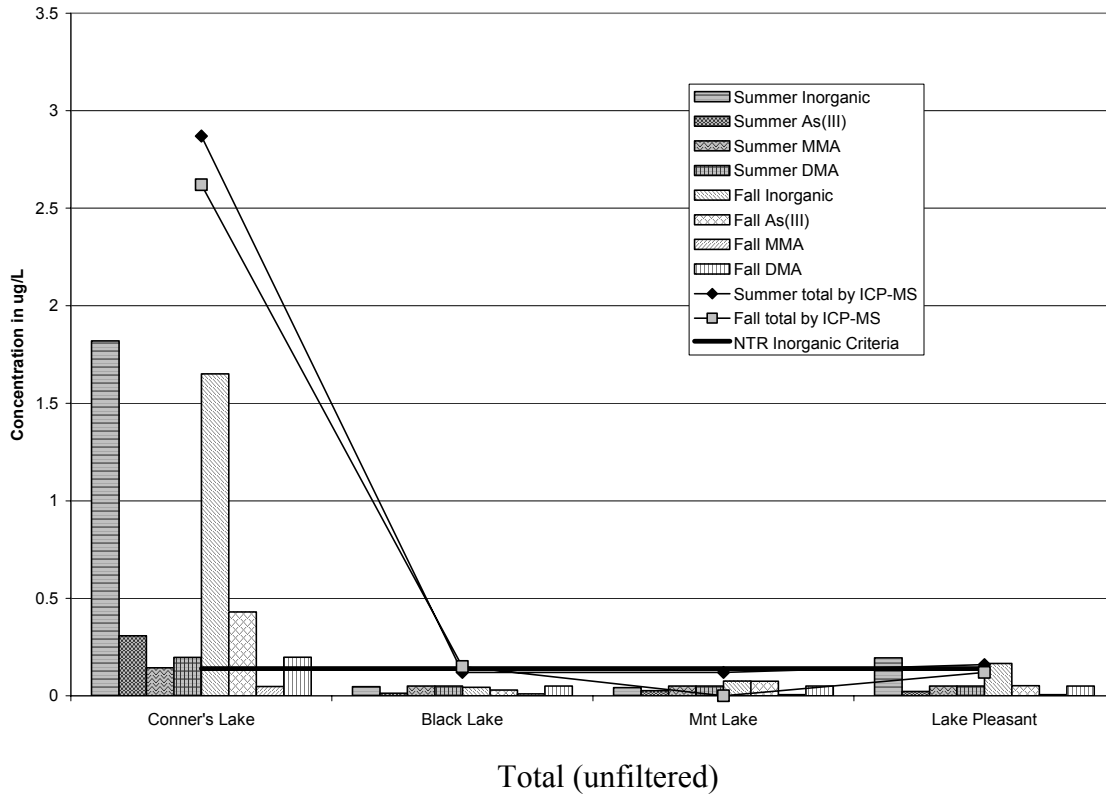


Figure 3. Total and dissolved water arsenic results.

Sediment samples were analyzed for total arsenic, grain size, and TOC. Arsenic results are provided in Table 10. Grain size and TOC results are summarized by sampling season in Figures 5 and 6.

Table 10. Sediment results by sampling season, in mg/Kg.

Lake	Total Arsenic	
	Summer	Fall
Black	4.9	1.5
Conner's	25.0	24.4
Mountain	13.4	25.4
Pleasant	7.2	6.5

Total solids in these sediments were relatively low for all lakes, ranging from about 10 to 25%. Most of the lake sediments were predominantly silt, although Black Lake did have a high proportion of clay in the summer sample, collected from the central, deep portion of the lake. The sediment collected from the shallow, weedy area near the boat ramp in the fall had a much higher sand content.

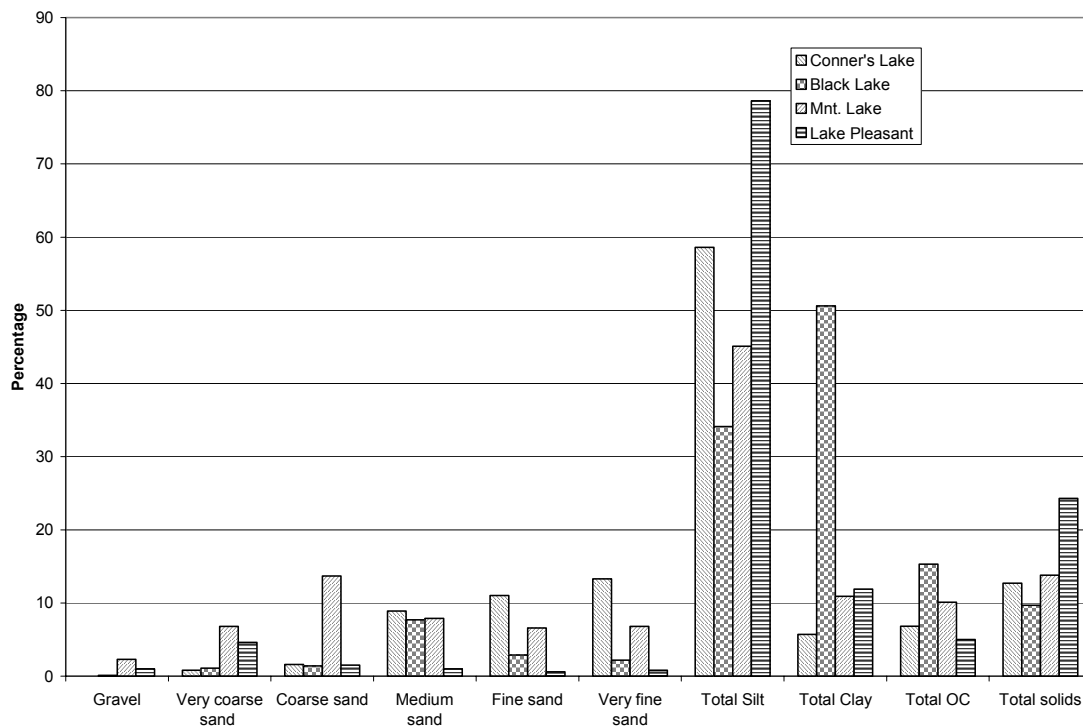


Figure 4. Grain size, TOC, and total solids percentages by lake for summer 2002 sediment samples.

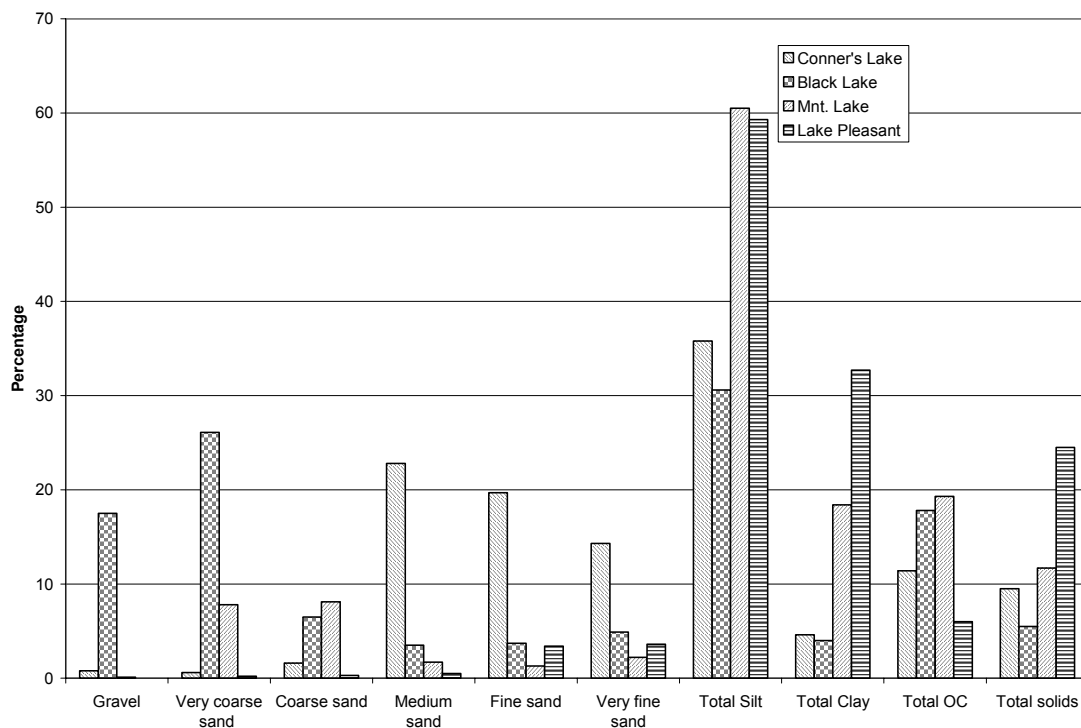


Figure 5. Grain size, TOC, and total solids percentages by lake for fall 2002 sediment samples.

Discussion

Black Lake

Both the summer and fall 2002 sampling events at Black Lake in Stevens County had levels of inorganic arsenic in unfiltered surface waters below the NTR regulatory standard for consumption of organisms (e.g., fish). The total arsenic concentrations rose very slightly from summer to fall, possibly due to a die-off in phytoplankton. This hypothesis is also supported by the rise in total phosphorus concentrations from August to early December.

Geologically, Black Lake is surrounded by Cretaceous, two-mica granites and schists. The lake's valley is underlain by glacial outwash, till, and drift. Based on reviews of the current DNR mine database and historic mining resources, no prospecting or excavation has occurred in the Black Lake watershed. The soil parent materials are not known to have high concentrations of pyritic minerals; iron oxide percentages range from 3% to about 8% (Pettijohn et al., 1973). There are no orchards or agricultural lands. Current land use in the watershed is undeveloped forestland, vacation homes, and a small resort. Consequently, arsenic concentrations in sediments are the lowest found in this study, between 1.5 and 4.9 mg/Kg.

Arsenic concentrations in rainbow trout fillets from Black Lake were all non-detect. The detection limits were at or below the relevant criterion of 6.16 µg/Kg inorganic Arsenic backcalculated from the NTR water (organism consumption only) criterion. These low levels are unexpected because the Washington Department of Fish and Wildlife (WDFW) plants about 9,000 catchable-sized rainbow trout in Black Lake annually (Vail, 2003). The stocking occurs in late April, weather and ice conditions permitting. These fish are fed trout chow in the hatchery, and this chow has relatively large quantities of arsenic. SilverCup trout chow had 2.64 mg/Kg total arsenic, and NurtaFeed chow had 4.06 mg/Kg total arsenic.

The bulk of the arsenic in both trout chow brands appears to be in more complex organo-arsenicals such as arsenobetaine and arsenocholine. The concentration of DMA, the highest arsenic species detected in either chow sample, was only 0.22 mg/Kg. This represents about 8% of SilverCup's total arsenic. The arsenic found in the trout chow used by WDFW is either unavailable for uptake in the juvenile trout gut, or was depurated during the four-month interval between planting and Ecology's fish collection. Some of the fish in Ecology's composites may have been resident in Black Lake longer than four months, due to carryover from the prior year's stocking, and their depuration period may be longer.

Oladimeji et al. (1979) found an 80% reduction in arsenic residues in whole rainbow trout within 96 hours of administration of an oral dose of isotope 74 arsenic. Based on this study, a four-month depuration period would be sufficient to virtually eliminate any increased arsenic burden produced in hatchery-raised, catchable-sized trout due to trout chow. In any case, rainbow trout stocked into low arsenic waterbodies do not, in this case, present a human health consumption issue.

Conner's Lake

Water samples were consistently elevated above the NTR numeric criteria at Conner's Lake in the Sinlahekin drainage. These water concentrations were also the highest found in this study. The total arsenic concentrations determined by ICP-MS varied little between summer and fall of 2002, with concentrations ranging between 2.62 and 3.21 µg/L. Filtered waters were always greater than unfiltered waters. The reason for this phenomenon is unknown, although it is probably a laboratory artifact, as speciated arsenic results did not exhibit this relationship.

Speciated arsenic results revealed that the majority of the arsenic in Conner's Lake is inorganic and in the dissolved form. The total inorganic arsenic comprised about 63% of the total arsenic as analyzed by ICP-MS. For filtered waters, the total inorganic species were about 52% of the total arsenic concentration. MMA and DMA were about 2% and 7% of the total arsenic mass, respectively. When comparing the sum of the arsenic species with the total arsenic concentration, about 72 to 59% of the arsenic was identified to form/species for total and filtered waters, respectively. This illustrates that the majority of arsenic in Conner's Lake was inorganic and dissolved. Very little seasonal variation was observed.

The sediment samples from Conner's Lake, as with the waters, had some of the highest arsenic concentrations found in this study. The concentration was 25.0 mg/Kg in summer and 24.4 mg/Kg in fall. Created by the former Washington Department of Game in 1949, Conner's

Lake is formed by a small dam, approximately 15 feet high along Sinlahekin Creek. Its sediment arsenic concentrations and sediment grain and organic carbon content are probably unusual due to the lake's origin. Forde Lake, about one mile upstream, was created in the same way and at the same time.

Geologically, the Sinlahekin drainage has potential natural and anthropogenic arsenic sources. There are four mines upstream of Conner's Lake; the summary below has been adapted from Hunting (1956). There are no lakes in the Sinlahekin watershed without historic mining activity upstream. The upstream mines are not known to discharge to surface waters (Roeder, 2002). Conner's Lake represents one of the only feasible locations to estimate potential arsenic contributions to downstream waters, such as the Similkameen River, which are on Ecology's 303(d) list as impaired for arsenic.

Following is a description of the four mines:

- The *Q.S.* mine is located about four to five stream miles upstream from Conner's Lake. This area has 24 claims for copper, gold, and silver. It is on a steep mountain slope east of Blue Lake between the 2,000 to 3,500 foot elevations. Various companies developed this deposit from 1902 until 1926. Developments included both a 1,060 and a 600 foot crosscut. A crosscut is an entry perpendicular to a mineralized vein. The deposit as a whole contained only 2.5% copper and traces of gold and silver, although some surface ores had more gold.
- The *Blue Lake* claims for copper and gold were in the same vicinity. This operation developed a 300-foot adit between 1902 and 1908. An adit is a horizontal penetration into the earth.
- *Okanogan Copper* was also nearby. This development existed in 1917. They worked heavily pyritized and metamorphosed shales for gold and copper. A 500-foot adit and two shorter adits were developed.
- *Gold Quarry* was also in the upper watershed of Conner's Lake. This development of short adits and shallow shafts worked a sparsely mineralized vein of pyrite for gold, at an indeterminate date.

These four mining activities in the upper Sinlahekin watershed have had an unknown impact on the water and sediment quality in Conner's Lake. There are no other potential human sources of arsenic upstream. Evidence of orchard land above Conner's Lake is not apparent from aerial photographs and a site drive-by. Orchards can be a significant source of arsenic to surface waters due to the historic use of lead arsenate pesticides on these lands.

Conner's Lake is in a mineralogically rich and diverse watershed, with potential natural erosion and mass wasting contributing arsenic and particulates to the creek and basins. Determining the relative contribution of natural and anthropogenic arsenic to Conner's Lake is not possible.

Ecology has sampled the major river downstream, the Similkameen, for arsenic. Ecology studies have concluded that inputs from British Columbia, Canada and potentially from sediments in Palmer Lake are predominantly responsible (Johnson, 2002a and 2002b). Palmer Lake is hydrologically unique, in that it flows northward into the Similkameen River during low and

moderate flows, and water floods southward from the Similkameen River into Palmer Lake during high flows.

Sediments in Palmer Lake ranged from 20.4 to 39.4 mg/Kg. These values bracket the 24.4 to 25.0 mg/Kg concentrations found in Conner's Lake during this investigation. The concordance of these values suggests that sediments in Palmer Lake have a high ambient arsenic concentration but may be further elevated locally due to Similkameen River inputs. Based on the preliminary results from Johnson (2002a), the sediment inputs to Palmer Lake from Sinlahekin Creek are approximately 63 to 100% of the sediment arsenic concentrations.

Surface waters from Conner's Lake had the highest arsenic concentrations found during this current investigation. August total arsenic concentrations were 2.87 $\mu\text{g/L}$ and 3.21 $\mu\text{g/L}$ for unfiltered and filtered waters analyzed by ICP-MS, respectively. Concentrations of total inorganic arsenic were between 52 and 63% of the total values. The concentrations of inorganic arsenic, 1.64 (November) and 1.82 $\mu\text{g/L}$ (August), are about 11.7 to 13 times the NTR (organism only) water criteria. It is unlikely that these exceedances of the water quality standards are due solely to the limited human activities upstream. It is more likely due to the region being heavily mineralized with pyrite-bearing rocks and copper ores.

Arsenic is frequently associated with pyrite and copper minerals due to its propensity to form mixed arsenic-iron-sulphide complexes in sediments. The Sinlahekin watershed upstream from Conner's Lake is composed of metamorphosed marine sediments including: argillite, phyllite, metawacke, intercalated hornblende, gneiss, and schists. These former marine sediments rise in steep bluffs on both the east and west sides of the creek. The valley bottom itself is composed of glacial drift. There may be colluvial materials along tributary drainages; however, the extent of these deposits is unknown. Colluvium is a talus-like deposit produced through the mass-wasting of unstable slopes.

The extent to which the four historic mines versus the in-situ geology have influenced the concentrations of arsenic in the surface waters and sediments of Conner's Lake is unknown. However, the elevated arsenic concentrations do not appear to accumulate in fish tissues. All but one of the six fish tissue samples were below the 6.16 $\mu\text{g/Kg}$ standard for inorganic arsenic in tissues. That sample, of ten brown bullhead, had 9 $\mu\text{g/Kg}$ of arsenic(III) detected. All of the other fish tissue samples had detection limits below the backcalculated NTR fish tissue value. Using the detection limits and the sole detected value, the average brown bullhead arsenic concentration is 5 $\mu\text{g/Kg}$. This level is below the NTR tissue value.

In summary, Conner's Lake appears to have considerable inputs of potential anthropogenic and natural arsenic. These inputs have elevated the concentrations of total inorganic and arsenic(III) in surface waters and surficial sediments. These elevated arsenic concentrations are not found in rainbow trout from Conner's Lake although they have been detected in brown bullhead. The mean concentrations in bullhead are under the NTR fish tissue criterion, but this mean concentration may be highly variable.

Mountain Lake

Mountain Lake on Orcas Island is the most oligotrophic lake sampled in this investigation. Its water is very clear; secchi depths and all other indicators support an oligotrophic assessment (Smith et al., 2000). Results for total arsenic in water were comparable to those found in Black Lake and are among the lowest found in this study. These concentrations ranged from less than 0.1 µg/L to 0.26 µg/L. The fact that the highest concentration was found in a filtered water sample, and the one non-detect value was in the total water sample from the same time, suggests that the filter may have been inadequately cleaned prior to use. The August water sample exhibited the same pattern; the total concentration was 0.12 µg/L and the filtered concentration was 0.19 µg/L.

The waters of Mountain Lake are used by the communities of Olga and Doe Bay as a drinking water supply. Detected concentrations of total inorganic arsenic in these surface waters were 0.042 to 0.076 µg/L. These concentrations exceed the NTR inorganic criteria (0.018 µg/L) for the consumption of water and organisms. These values do not exceed the maximum contaminant level (MCL) of 10 µg/L for drinking water or the NTR criterion of 0.14 µg/L for the consumption of organisms only.

These water concentrations are much lower than at Conner's Lake and comparable to Black Lake. This is unexpected, as the sediment arsenic concentrations were some of the highest found in this study. Summer sediment from a cove in the southwest portion of the lake had a concentration of 13.4 mg/Kg, while the fall sample from the center portion of the lake had a concentration of 25.4 mg/Kg. The latter value is the highest detected in this study.

Mountain Lake has two likely sources of this sediment arsenic:

- Seasonally, Mountain Lake experiences winds from both the north and southwest. There may be industrial aeolian arsenic sources as far north as Nanaimo, British Columbia or Port Angeles, Washington which may contribute to the arsenic found in Mountain Lake. However, there are no large known sources such as smelters.
- A more likely source is the natural geologic setting of Mountain Lake.

Orcas Island in the Mountain Lake watershed has two geological units. One is a pre-Devonian intrusive metamorphosed gabbro and the other is a mixed Cretaceous sedimentary unit. A gabbro is a rock similar to basalt. Both of these geologic parent materials are marine in origin. Because of its sedimentary nature, the Cretaceous unit is a more likely arsenic source. San Juan (1994) found arsenic concentrations between 5 and 10 mg/Kg in Orcas Island soils. These values are less than those found in Mountain Lake sediments during this study.

The differences in sediment concentrations suggests that either substantial spatial variability exists or seasonal cycling is pronounced. Distinguishing these two hypotheses is not possible with the current data set. Despite having the highest sediment arsenic concentrations found in this study and the second highest surface water arsenic concentrations, fish tissue results were all non-detect at Mountain Lake. Detection limits for the three composite samples of nine Kokanee

each and three composite samples of four cutthroat trout each were all below the NTR fish tissue criterion.

Lake Pleasant

Surface waters from Lake Pleasant in Clallam County had relatively low levels of total arsenic. ICP-MS analyzed concentrations varied from 0.12 $\mu\text{g/L}$ to 0.24 $\mu\text{g/L}$. As with the other waterbodies sampled, filtered waters had higher concentrations than whole water samples when analyzed by ICP-MS. This pattern was not evident for speciation analysis. For whole waters, the sum of the arsenic species was greater than the ICP-MS derived concentration; this is probably due to analytical variability near the detection limits of both the ICP-MS and draft EPA Method 1632 speciation methods. Thus, the sum of the arsenic species varied from 62 to 138% of the reported ICP-MS concentration.

In both seasons, the unfiltered total inorganic arsenic concentrations exceeded the NTR level of 0.14 $\mu\text{g/L}$ for the consumption of organisms. Concentrations of all inorganic species (unfiltered) were 0.195 $\mu\text{g/L}$ in summer and 0.166 $\mu\text{g/L}$ in fall. As with the other lakes in this study, there is little evidence for pronounced seasonal cycling of arsenic into the water column or between surface waters and sediments.

Sediment arsenic concentrations in Lake Pleasant, ranging from 6.5 to 7.2 mg/Kg, were intermediate relative to the other lakes in this investigation. The lack of significant temporal variation in sediment concentrations is further evidence that seasonal cycling is relatively minor in Lake Pleasant. Lake Pleasant's sediments were predominantly silts and clays, with about 5 to 6% organic carbon. The preponderance of silts and clays reflects the underlying parent materials in the area.

The Lake Pleasant watershed is composed of mixed alluviums and two additional geologic units. One is an Oligocene-Eocene marine sedimentary siltstone, slate, or shale. The other is a layered marine conglomerate, with pillow basalts, siltstone, and sandstone. The siltstones, shales, and slates are believed to be the source of the silts and clays which dominate Lake Pleasant sediments. Despite the fact that Lake Pleasant has served as a log storage pond for a nearby lumber mill, TOC results were relatively low. Concentrations ranged from about 5% to a maximum of 6%.

Two species of fish were collected from Lake Pleasant, cutthroat trout and Kokanee. Each cutthroat composite included 10 fish, while each Kokanee composite had only three fish. Only one sample had a detection of any form of arsenic. Kokanee composite No. 3 had a total arsenic concentration of 180 $\mu\text{g/Kg}$. This sample had non-detect levels of all arsenic species when analyzed by draft EPA Method 1632. Inorganic arsenic detection limits were below the NTR criterion. The three Kokanee composites were composed of markedly different-sized fish. This is a result of the small sample size (nine fish total) collected. Composite No. 3 had two very large Kokanee, whereas the other two composite had much smaller fish. The average lengths and weights of all Kokanee composites are shown in Table 11.

Table 11. Average Kokanee sizes from Lake Pleasant.

Composite Number	Length (mm)	Weight (gms)
1	250	193
2	253	202
3	369	619

Table 11 illustrates that composite No. 3 had a mean fish weight more than twice that of either other composite. This disparity in sizes may be responsible for the differences in arsenic concentrations found. Because no identifiable arsenic species were found in this sample, the total arsenic detected by ICP-MS is probably in the form of arsenosugars, arsenobetaine, or other complex organoarsenicals.

Comparisons with Other Investigations

Ecology has collected water, sediment, and fish tissue from various locations and analyzed for total arsenic, usually by ICP-MS. These locations have often been near historic mining activities, although some sampling has been conducted in areas without intensive anthropogenic influence. Some of these data are discussed below for comparative purposes.

Raforth et al. (2000) sampled waters above and below several mines in the Conconully District in Okanogan County. This mining district is located along Salmon Creek, just downstream from Conconully Reservoir. This watershed is one drainage divide to the south of Sinlahekin Creek. Low-flow arsenic concentrations ranged from 0.48 µg/L to 2.5 µg/L. High-flow concentrations were up to 69 µg/L below the First Thought Mine. The low-flow concentrations are comparable to those found in Conner's Lake (2.62 to 3.21 µg/L).

Raforth et al. (2002) sampled waters and sediments near Big Chief Mine, about 11 miles northwest of Black Lake in Stevens County. The North Fork of Clugston Creek had less than 0.50 µg/L arsenic upstream and 0.57 µg/L downstream of the mine during low flow. During high flow, concentrations were 0.37 µg/L upstream and 0.55 µg/L downstream. These values are all elevated relative to those found at Black Lake. Black Lake had total arsenic concentrations between 0.12 and 0.15 µg/L during the summer and fall. The differences are probably due to variations in watershed mineralogy and anthropogenic inputs.

The Big Chief Mine area is composed of carbonate rocks and shallow marine sedimentary deposits. Black Lake is underlain by a granitic batholith, an igneous material. The marine nature of the Clugston Creek drainage suggests potentially increased arsenic levels in the parent materials. Igneous rocks like the Cretaceous granites and schists in the Black Lake watershed are unlikely to have significant natural arsenic sources.

This is supported by the concentrations in arsenic found in sediment upstream from Big Chief Mine. Raforth et al. (2002) reports arsenic concentrations of 7.26 mg/Kg. The current investigation found much lower concentrations in Black Lake, between 1.5 and 4.9 mg/Kg. The lower concentrations in Black Lake compared to locations upstream of mining influences in

the North Fork of Clugston Creek may be due to differences between lotic and lentic waters, although variations in parent mineralogy are a more likely explanation.

Johnson and Golding (2002) have reported arsenic concentrations from 303(d) listed and reference rivers throughout Washington State. One station was located at the DNR Campground along the Hoh River in Jefferson County. This station is 18 to 20 miles south of Lake Pleasant in Clallam County. Concentrations of total recoverable arsenic ranged from 0.10 $\mu\text{g/L}$ in June to 0.50 $\mu\text{g/L}$ in April 2002. One sample was submitted for inorganic arsenic analysis. This was the April 2002 water sample, and its total dissolved inorganic arsenic concentration was 0.092 $\mu\text{g/L}$. Therefore, 18% of the total arsenic was in the dissolved inorganic form.

This investigation found total arsenic concentrations in Lake Pleasant between 0.12 and 0.24 $\mu\text{g/L}$, which is close to those found in the Hoh River. However, the proportion of inorganic arsenic found was much higher in Lake Pleasant. This might be due to differences between lentic and lotic systems, but a more likely explanation is analytical uncertainty near the detection limit for ICP-MS. This is supported by the observation that inorganic arsenic concentrations measured by draft EPA Method 1632 were higher than total arsenic by ICP-MS values.

Conclusions

Johnson and Golding (2002) concluded that typical natural arsenic concentrations in rivers and streams were between 0.2 and 1.0 $\mu\text{g/L}$, while concentrations of 2 to 5 $\mu\text{g/L}$ were probably indicative of anthropogenic contamination. This lower range of concentrations is similar to that found at three of the four lakes sampled in this current investigation.

Conner's Lake in the Sinlahekin Creek watershed had total and speciated arsenic results within the range potentially indicative of contamination. As discussed previously, the Sinlahekin Creek watershed has some mining activities in the uppermost reaches of the watershed, above all surface water sampling locations. This lake also is located in a mineralogically rich area, with many pyritized veins and marine sediments. Differentiating between natural and anthropogenic sources of arsenic to Conner's Lake is not possible with the current data.

For the other three lakes, parent geologic materials appear to be related to arsenic concentrations in surface waters and sediments. Those lakes located in areas with marine sedimentary rocks tend to have higher arsenic concentrations than lakes underlain by igneous rocks. Surface water arsenic is not clearly related to either chlorophyll(a) or phosphorus concentrations.

Speciated arsenic in water results do not clearly relate to total arsenic derived by the ICP-MS method. Sums of species range from 50 to 185% of the total arsenic measured by ICP-MS. The wide variation is probably due to a combination of analytical uncertainty in the two methods and the presence of unquantified arsenic species.

Previous investigations (Johnson and Golding, 2002) found low levels of total inorganic arsenic relative to total recoverable arsenic in reference river stations. This current investigation found

much higher levels of total inorganic arsenic. Between 25 and 122% of the total arsenic by ICP-MS was inorganic when analyzed by draft EPA Method 1632.

Black Lake and Mountain Lake had total inorganic arsenic concentrations in surface water below the NTR water criterion of 0.14 µg/L for consumption of organisms (e.g., fish, shellfish). Lake Pleasant and Conner's Lake had surface water arsenic concentrations from 1.2 and 13 times the NTR criterion for consumption of organisms, respectively. All four lakes exceeded the NTR criterion of 0.018 µg/L for consumption of water and organisms.

Black Lake had the lowest sediment arsenic concentrations detected in this study, and Mountain Lake had the highest. Conner's Lake and Lake Pleasant had intermediate sediment arsenic concentrations.

Fish tissues were almost entirely non-detect for total arsenic and all species of arsenic. Detection limits were at or below NTR criteria. There were two exceptions:

- One composite of three Kokanee from Lake Pleasant had a concentration of 180 µg/Kg total arsenic. However, there were no detected arsenic species in any Lake Pleasant Kokanee samples. The fish randomly allocated to this composite were, on average, much larger than any other fish collected.
- One brown bullhead from Conner's Lake had an arsenic(III) concentrations of 9 µg/Kg. This concentration is above the NTR criteria of 6.16 µg/Kg for inorganic arsenic. Using the detection limits, the average brown bullhead concentration is below the NTR limit, but this mean may be highly variable.

Freshwater fish tissues from watersheds without current anthropogenic arsenic sources rarely have detectable concentrations of inorganic arsenic species. Detections of inorganic arsenic are cause for concern and further investigation.

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Appendix A

Table A-1. Fish sizes and weights used in composite samples.

Black Lake	Length (mm)	Weight (gms)	Used in Composite
Rainbow trout	234	114	1
Rainbow trout	226	116	1
Rainbow trout	272	180	1
Rainbow trout	233	132	1
Rainbow trout	251	177	1
Rainbow trout	273	201	1
Rainbow trout	284	205	1
Rainbow trout	243	144	1
Rainbow trout	261	162	1
Rainbow trout	256	167	1
Rainbow trout	221	104	2
Rainbow trout	253	159	2
Rainbow trout	267	177	2
Rainbow trout	283	222	2
Rainbow trout	252	147	2
Rainbow trout	242	146	2
Rainbow trout	257	163	2
Rainbow trout	282	208	2
Rainbow trout	228	134	2
Rainbow trout	280	208	2
Rainbow trout	256	172	3
Rainbow trout	239	138	3
Rainbow trout	270	173	3
Rainbow trout	224	129	3
Rainbow trout	261	155	3
Rainbow trout	288	219	3
Rainbow trout	289	181	3
Rainbow trout	252	148	3
Rainbow trout	287	183	3
Rainbow trout	255	162	3

Conner's Lake	Length (mm)	Weight (gms)	Used in Composite
Rainbow trout	357	527	1
Rainbow trout	347	506	1
Rainbow trout	355	485	1
Rainbow trout	360	568	1
Rainbow trout	321	345	1
Rainbow trout	357	500	1
Rainbow trout	381	597	1
Rainbow trout	380	586	1

Rainbow trout	246	155	1
Rainbow trout	356	536	1
Rainbow trout	338	377	2
Rainbow trout	254	185	2
Rainbow trout	312	337	2
Rainbow trout	353	476	2
Rainbow trout	330	359	2
Rainbow trout	314	327	2
Rainbow trout	376	597	2
Rainbow trout	378	570	2
Rainbow trout	368	563	2
Rainbow trout	367	619	2
Rainbow trout	255	171	3
Rainbow trout	354	524	3
Rainbow trout	272	217	3
Rainbow trout	339	416	3
Rainbow trout	323	351	3
Rainbow trout	410	781	3
Rainbow trout	361	554	3
Rainbow trout	277	236	3
Rainbow trout	386	676	3
Rainbow trout	382	657	3
Brown bullhead	204	135	1
Brown bullhead	187	88	1
Brown bullhead	210	176	1
Brown bullhead	132	33	1
Brown bullhead	118	22	1
Brown bullhead	113	31	1
Brown bullhead	247	265	1
Brown bullhead	180	93	1
Brown bullhead	169	71	1
Brown bullhead	191	103	1
Brown bullhead	175	81	2
Brown bullhead	125	26	2
Brown bullhead	186	91	2
Brown bullhead	180	84	2
Brown bullhead	203	131	2
Brown bullhead	127	30	2
Brown bullhead	113	35	2
Brown bullhead	171	75	2
Brown bullhead	126	33	2
Brown bullhead	190	110	2
Brown bullhead	125	29	3
Brown bullhead	170	74	3
Brown bullhead	135	33	3
Brown bullhead	210	154	3
Brown bullhead	189	195	3

Brown bullhead	189	105	3
Brown bullhead	128	31	3
Brown bullhead	194	100	3
Brown bullhead	128	32	3
Brown bullhead	202	124	3

Mountain Lake	Length (mm)	Weight (gms)	Used in Composite
Kokanee	243	126	1
Kokanee	250	141	1
Kokanee	197	68	1
Kokanee	167	46	1
Kokanee	234	123	1
Kokanee	242	138	1
Kokanee	255	146	1
Kokanee	240	125	1
Kokanee	228	108	1
Kokanee	255	141	2
Kokanee	222	107	2
Kokanee	246	147	2
Kokanee	233	118	2
Kokanee	241	125	2
Kokanee	245	132	2
Kokanee	243	131	2
Kokanee	223	106	2
Kokanee	258	147	2
Kokanee	192	72	3
Kokanee	166	43	Not used
Kokanee	173	49	Not used
Kokanee	194	68	3
Kokanee	245	126	3
Kokanee	246	129	3
Kokanee	240	125	3
Kokanee	256	144	3
Kokanee	253	140	3
Kokanee	247	140	3
Kokanee	242	135	3
Cutthroat trout	252	153	1
Cutthroat trout	295	197	1
Cutthroat trout	253	143	1
Cutthroat trout	310	253	1
Cutthroat trout	276	172	2
Cutthroat trout	259	166	2
Cutthroat trout	281	167	2
Cutthroat trout	284	185	2
Cutthroat trout	374	465	3
Cutthroat trout	255	136	3

Cutthroat trout	271	161	3
Cutthroat trout	271	162	3

Lake Pleasant	Length (mm)	Weight (gms)	Used in Composite
Cutthroat trout	288	222	1
Cutthroat trout	263	147	1
Cutthroat trout	182	57	1
Cutthroat trout	170	45	1
Cutthroat trout	298	237	1
Cutthroat trout	188	63	1
Cutthroat trout	363	422	1
Cutthroat trout	245	150	1
Cutthroat trout	178	59	1
Cutthroat trout	180	50	1
Cutthroat trout	240	116	2
Cutthroat trout	170	57	2
Cutthroat trout	165	50	2
Cutthroat trout	284	207	2
Cutthroat trout	175	55	2
Cutthroat trout	178	59	2
Cutthroat trout	350	378	2
Cutthroat trout	214	82	2
Cutthroat trout	183	69	2
Cutthroat trout	180	56	2
Cutthroat trout	200	73	3
Cutthroat trout	322	277	3
Cutthroat trout	306	238	3
Cutthroat trout	172	56	3
Cutthroat trout	230	104	3
Cutthroat trout	271	192	3
Cutthroat trout	262	157	3
Cutthroat trout	206	85	3
Cutthroat trout	226	106	3
Cutthroat trout	233	109	3
Kokanee	346	423	1
Kokanee	206	80	1
Kokanee	198	77	1
Kokanee	342	434	2
Kokanee	204	78	2
Kokanee	213	95	2
Kokanee	443	865	3
Kokanee	202	77	3
Kokanee	462	916	3

Appendix B

Table B-1. Sediment percent solids and TOC results by sampling season.

Lake	% solids	PSEP TOC (%)
Summer		
Black	9.7	15.3
Conner's	12.7	6.8
Mountain	13.8	10.1
Pleasant	24.3	5.0
Fall		
Black	5.5	17.8
Conner's	9.5	11.4
Mountain	11.7	19.3
Pleasant	24.5	6.0

Table B-2. Water sampling results by season.

Lake	Chlorophyll	Total Phosphorus	Arsenic by ICP-MS	Arsenic (inorganic)	Arsenic (III)	MMA	DMA
Water, unfiltered, summer							
Black	3.6 j	18	0.12	0.047 j	0.013 uj	0.05 u	0.05 u
Conner's	2.5 j	15	2.87	1.82	0.308	0.144	0.197 j
Mountain	0.92	10 u	0.12	0.042 j	0.027 uj	0.05 u	0.05 u
Pleasant	5.4 j	10 u	0.16	0.195	0.023 uj	0.05 u	0.05 u
Water, filtered, summer							
Black			0.13	0.054 j	0.05 u	0.05 u	0.05 u
Conner's			3.21	1.820	0.296	0.149	0.227 j
Mountain			0.19	0.048 j	0.035 uj	0.05 u	0.05 u
Pleasant			0.24	0.148	0.097	0.05 u	0.05 u
Water, unfiltered, fall							
Black		22	0.15	0.044	0.03 j	0.01 u	0.05 u
Conner's		20	2.62	1.65	0.43	0.048	0.198
Mountain		10 u	0.1 u	0.076	0.075	0.006 j	0.05 u
Pleasant		13	0.12	0.166	0.052	0.006 j	0.05 u
Water, filtered, fall							
Black			0.14	0.040	0.033 j	0.01 u	0.05 u
Conner's			3.16	1.640	0.451	0.05	0.188
Mountain			0.26	0.074	0.085	0.006 j	0.05 u
Pleasant			0.2	0.126	0.065	0.009 j	0.05 u

All units in µg/L

u = undetected at the limit shown

j = estimated concentration

uj = undetected, detection limit estimated