

In cooperation with the City of Wichita Falls

Physicochemical and Analytical Data for Tributary Water, Lake Water, and Lake Sediment, Lake Arrowhead, Clay and Archer Counties, Texas, 2006



Data Series 334

U.S. Department of the Interior U.S. Geological Survey

Cover.

- **Top left:** Hydrolab H20 multiparameter monitor, February 15, 2006 (photograph by David M. Holmes, U.S. Geological Survey).
- **Top right**: Collecting lake water samples, February 15, 2006 (photograph by David M. Holmes, U.S. Geological Survey).

Bottom right: West Little Post Oak Creek, October 16, 2006.

Bottom left: Subsampling lake sediment box core, August 30, 2006 (photograph by David M. Holmes, U.S. Geological Survey).

Physicochemical and Analytical Data for Tributary Water, Lake Water, and Lake Sediment, Lake Arrowhead, Clay and Archer Counties, Texas, 2006

By Jennifer T. Wilson, MaryLynn Musgrove, Monti M. Haynie, and Peter C. Van Metre

In cooperation with the City of Wichita Falls

Data Series 334

U.S. Department of the Interior U.S. Geological Survey

U.S. Department of the Interior

DIRK KEMPTHORNE, Secretary

U.S. Geological Survey

Mark D. Myers, Director

U.S. Geological Survey, Reston, Virginia: 2008

For product and ordering information: World Wide Web: http://www.usgs.gov/pubprod Telephone: 1-888-ASK-USGS

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment: World Wide Web: http://www.usgs.gov Telephone: 1-888-ASK-USGS

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted materials contained within this report.

Suggested citation:

Wilson, J.T., Musgrove, MaryLynn, Haynie, M.M., and Van Metre, P.C., 2008, Physicochemical and analytical data for tributary water, lake water, and lake sediment, Lake Arrowhead, Clay and Archer Counties, Texas, 2006: U.S. Geological Survey Data Series 334, 13 p., 2 appendixes.

Contents

Abstract	1
Introduction	1
Sampling Methods	3
Tributary Water	3
Lake Water	3
Lake Sediment	5
Analytical Methods	6
Quality Assurance	6
Field Quality Control Samples	6
Laboratory Quality Control Samples	6
Physicochemical and Analytical Data	7
Tributary Water	7
Lake Water	7
Lake Sediment	7
Summary	9
References	.13
Appendix 1—Field and Laboratory Quality Control Sample Results	

1.1. Field quality control sample results for Lake Arrowhead, Texas, 2006

1.2. Laboratory quality control sample results for lake sediment samples collected from Lake Arrowhead, Texas, 2006

Appendix 2—Physicochemical and Analytical Data

- 2.1. Physicochemical and analytical data for water samples collected from tributaries to Lake Arrowhead, Texas, 2006
- 2.2. Physicochemical and analytical data for lake water samples collected from Lake Arrowhead, Texas, 2006
- 2.3. Analytical data for lake sediment samples collected from Lake Arrowhead, Texas, 2006

Figures

1.	Map and	o showing tributary water, lake water, and lake sediment sampling sites in near Lake Arrowhead, Texas, 2006	2
2–5.	Grap	ohs showing:	
	2.	Arsenic concentration (A) over time and (B) in relation to suspended sediment concentration in tributary water samples collected near Lake Arrowhead, Texas, 2006	8
	3.	Concentrations of arsenite plus arsenate in lake water samples collected from Lake Arrowhead, Texas, 2006	9
	4.	Concentrations with depth of selected major and trace elements in lake sediment samples collected from Lake Arrowhead, Texas, 2006	10
	5.	Comparison of lake sediment trace element concentrations to consensus- based sediment quality guidelines, threshold effect concentrations, for samples collected at Lake Arrowhead, Texas, 2006	11

6.	Boxplots showing comparison of selected major and trace element
	concentrations in sediments collected from 35 lakes in the U.S. to Lake
	Arrowhead, Texas, 200612

Tables

1.	List of sampling sites and dates with types of samples collected at Lake Arrowhead, Texas, 2006	4
2.	Summary of conditions during sampling of tributaries to Lake Arrowhead, Texas, 2006	5
3.	Summary of the relative percent difference (RPD) of duplicate results for lake water samples and replicate results for sediment samples collected at Lake Arrowhead, Texas, 2006	6

Conversion Factors and Datum

SI to Inch/Pound

Multiply	Ву	To obtain	
	Length		
centimeter (cm)	0.3937	inch (in.)	
kilometer (km)	0.6214	mile (mi)	
meter (m)	3.281	foot (ft)	
micrometer (µm)	3.937 x 10 ⁻⁵	inch (in.)	
millimeter (mm)	0.03937	inch (in.)	
	Area		
hectare (ha)	2.471	acre	
	Volume		
liter (L)	33.82	ounce, fluid (fl. oz)	
microliter (µL)	0.00003	ounce, fluid (fl. oz)	
milliliter (mL)	0.034	fluid ounce (fl. oz)	

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

°F=(1.8×°C)+32

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents are given in milligrams per liter (mg/L), micrograms per liter (μ g/L), or milligrams per kilogram (mg/kg).

Inch/Pound to SI

Multiply	Ву	To obtain
	Flow rate	
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
foot per second (ft/s)	0.3048	meter per second (m/s)

Datum

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Blank Page

Physicochemical and Analytical Data for Tributary Water, Lake Water, and Lake Sediment, Lake Arrowhead, Clay and Archer Counties, Texas, 2006

By Jennifer T. Wilson, MaryLynn Musgrove, Monti M. Haynie, and Peter C. Van Metre

Abstract

Lake Arrowhead is a reservoir about 24 kilometers southeast of Wichita Falls, Texas, that provides drinking water for the city of Wichita Falls and surrounding areas. The U.S. Geological Survey, in cooperation with the City of Wichita Falls, did a study in 2006 to assess conditions contributing to elevated arsenic concentrations in Lake Arrowhead. This report describes the sampling and analytical methods, quality assurance, and physicochemical and analytical data. Physiochemical properties were measured in and water samples were collected from five tributaries to Lake Arrowhead (Little Wichita River, West Little Post Oak Creek, East Little Post Oak Creek, Deer Creek, and an unnamed tributary) immediately after storms. Lake water measuring and sampling were done approximately monthly from January through September 2006 at three deep-water sites and seasonally, in January and August 2006, at three shallow-water sites. Cores of lake bottom sediment were collected from five sites on August 30, 2006. Arsenic concentrations in tributary water samples ranged from 1.5 to 6.3 and 0.5 to 4.8 micrograms per liter for unfiltered and filtered samples, respectively. The highest arsenic concentrations were in samples collected from the West Little Post Oak Creek sampling site. Physicochemical properties in lake water varied with depth and season. Dissolved arsenite plus arsenate concentrations in lake water samples generally were between 3 and 5 micrograms per liter. Arsenite concentrations typically were below the laboratory reporting level of 0.6 microgram per liter. There were no detections of monomethylarsonate or dimethylarsinate. The concentration of arsenic in lake sediment samples ranged from 4.4 to 11.2 milligrams per kilogram, with a median of 6.4 milligrams per kilogram. The median arsenic concentration of the five top-interval sediment samples was 8.8 milligrams per kilogram, which generally is higher than the concentrations estimated to be on suspended sediment in the tributaries. Sediment concentrations of seven trace elements were

compared to two consensus-based sediment quality guidelines for each: the threshold effect concentration and the probable effect concentration. Arsenic concentration exceeded the threshold effect concentration in one top-interval sediment sample.

Introduction

Lake Arrowhead is a reservoir about 24 kilometers southeast of Wichita Falls, Tex., that provides drinking water for the city of Wichita Falls and surrounding areas (fig. 1). The reservoir was impounded in 1966 on the Little Wichita River, in the Red River watershed. Land use in the 162,000-hectare Lake Arrowhead watershed mainly is rural with some ranching, dairy, farming, and oil and gas production activities. Frequent detections of arsenic in the lake water, with dissolved concentrations occasionally approaching the U.S. Environmental Protection Agency (USEPA) drinking-water standard maximum contaminant level (MCL) of 10 micrograms per liter (µg/L) (Texas Commission on Environmental Quality, 2007; U.S. Environmental Protection Agency, 2001), have raised concerns among water-resource managers that arsenic concentrations might exceed drinking-water standards in the future.

The U.S. Geological Survey (USGS), in cooperation with the City of Wichita Falls, did a study in 2006 to assess conditions contributing to elevated arsenic concentrations in Lake Arrowhead. The objectives of the study were to (1) determine the primary sources, such as tributary inflows or arsenic release from lake sediment, of arsenic to Lake Arrowhead water, (2) determine seasonal variability in arsenic concentrations in deep and shallow water in Lake Arrowhead, and (3) describe arsenic concentrations in lake sediment in Lake Arrowhead. This report describes the sampling and analytical methods, quality assurance, and physicochemical and analytical data. Selected data are presented or compared graphically. All data are contained in tables in an appendix.



Sampling Methods

Field equipment and supplies were prepared at the USGS Texas Water Science Center Wichita Falls laboratory. Preparation followed the guidelines in the USGS "National Field Manual," chapter A3 (Wilde, 2004). Bottles for whole and filtered tributary and lake water samples were pre-rinsed with deionized water, filled halfway with deionized water, and stored in sealed plastic bags inside a closed container until used in the field. C-Flex tubing, which was used to pump water samples into bottles, was pre-cleaned with Liquinox laboratory soap, rinsed with warm tap water, soaked in 5-percent hydrochloric acid, rinsed with deionized water, and stored in a plastic bag until used in the field. Whatman capsule filters for tributary and lake water samples were pre-rinsed with deionized water and stored in sealed plastic bags.

Tributary Water

Water samples were collected from five tributaries to Lake Arrowhead to assess the potential of tributary inflows as a source of arsenic to the lake: Little Wichita River, West Little Post Oak Creek, East Little Post Oak Creek, Deer Creek, and an unnamed tributary (fig. 1). All five tributaries are ephemeral; therefore sampling was done immediately after storms when the streams were flowing. Three storms were sufficient for tributary water sample collection during 2006 in March, May, and October; however, Deer Creek and the unnamed tributary did not flow during the March storm (table 1).

Physicochemical properties (temperature, specific conductance, pH, and dissolved oxygen) were measured using a Hydrolab H20 multiparameter monitor at each site before collecting water samples for laboratory analyses. The monitor was calibrated in the field in accordance with the USGS "National Field Manual," chapter A6 (Wilde and Radtke, 2005). Samples for measuring properties were collected using either multiple vertical or single vertical methods (table 2), following the guidelines in the USGS "National Field Manual," chapter A4 (U.S. Geological Survey, 2006). Water was collected from the tributaries using a 1-liter (L) Teflon bottle and then composited in a 3-L Nalgene bottle. Samples were stored immediately on ice after collection in the field for further processing at the USGS Wichita Falls laboratory. At the laboratory, a peristaltic pump with C-Flex tubing was used to distribute the water from the 3-L Nalgene bottle to the sample bottles for both unfiltered- and filtered-sample analyses. Samples were filtered using inline Whatman capsule filters (0.45-micrometer [µm] pore size). Samples were shipped overnight on ice to the USGS National Water Quality Laboratory (NWQL) in Denver, Colo., for nutrient and arsenic analyses. Unfiltered samples were shipped to the USGS Sediment Laboratory in Baton Rouge, La., for determination of suspended sediment concentration and the silt-sand break (the proportion of material, by weight, with an equivalent particlesize diameter exceeding 63 µm) by gravimetric analysis.

Lake Water

Lake water samples were collected in deep and shallow water in Lake Arrowhead to examine spatial and temporal concentrations of arsenic in the water column over a semiannual cycle. Samples were collected approximately monthly from January through September 2006 at three deep-water sites, AC, BC, and CC (fig. 1; table 1). Samples were collected seasonally, in January and August 2006, at three shallow-water sites, DC, EC, and FC. Sampling sites AC and BC are in the lower part of the lake, sampling site CC is in the middle of the lake, and sampling sites DC, EC, and FC are in the upper part of the lake. At the deep-water sites AC, BC, and CC, samples for laboratory analyses were typically collected about 1 meter (m) below the water surface and about 1 m above the lake bottom sediment. At the shallow-water sites DC, EC, and FC, one sample was collected about 1 m below the water surface in January 2006 and two samples for laboratory analyses were collected about 0.3 m below the water surface and about 0.3 m above the lake bottom sediment in August 2006 (except site DC).

Preparation and collection of samples for the analysis of arsenic species were given special consideration. Sample collection requirements (U.S. Geological Survey, 2003) specify the use of an 8-milliliter (mL) sample bottle, filled to the top but not overflowing, and the addition of 100 microliters (μ L) of ethylenediaminetetraacetic acid (EDTA) preservative with a micropipet. Proper sample preservation while on the lake was difficult. Therefore, the EDTA preservative was added to an empty 8-mL sample bottle in the laboratory; then in the field, an empty 8-mL sample bottle was filled with filtered lake water, and the water was transferred carefully into the sample bottle containing the EDTA preservative.

Vertical profiles of physicochemical properties were measured using a Hydrolab H20 multiparameter waterquality monitor at each sampling site. The monitor was calibrated at a boat dock in accordance with the USGS "National Field Manual," chapter A6 (Wilde and Radtke, 2005). At each sampling site, the monitor was lowered into the water on a cable connected to a recording unit. The cable was marked at 0.3-m intervals to determine depth during the vertical profiling procedure. The monitor was allowed adequate time to stabilize before measurements were recorded for each property. Physicochemical properties were recorded at selected depths in the vertical profile. During dissolved oxygen measurements, the monitor was kept in motion at each measuring point by slowly raising and lowering it about 0.15 m to ensure the flow of water across the dissolved oxygen membrane. Air temperature, barometric pressure, and water transparency (measured with a Secchi disc) were recorded at each sampling site.

Lake water samples for laboratory analyses were collected at selected water depths following the guidelines in the USGS "National Field Manual," chapter A4 (U.S. Geological Survey, 2006). The samples were collected at each site using a peristaltic pump while recording the vertical profiles of physicochemical properties. The pump tubing was secured to the

4 Physicochemical and Analytical Data, Lake Arrowhead, Clay and Archer Counties, Texas, 2006

 Table 1.
 List of sampling sites and dates with types of samples collected at Lake Arrowhead, Texas, 2006.

[nr, not recorded; na, not applicable]

				Total			Water
USGS station ID	Site ID	Latitude	Longitude	water depth	Sample date	Sample type	sampling depth (meters)
07214500	Little Wighits Diver	220 20' 45"	080 26' 46"	(meters)	02/10/2006	Tributary water	
07314300	Little wichita Kivei	55 59 45	98 30 40	nr	05/06/2006	Tributary water	16
				nr	10/17/2006	Tributary water	¹ .9
07314620	West Little Post Oak Creek	33° 35' 34"	98° 27' 43"	nr	03/19/2006	Tributary water	1.2
				nr	05/06/2006	Tributary water	1.5
				nr	10/16/2006	Tributary water	11.2
07314650	East Little Post Oak Creek	33° 37' 47"	98° 24' 16"	nr	03/19/2006	Tributary water	¹ .1
				nr	05/06/2006	Tributary water	1.3
				nr	10/16/2006	Tributary water	1.5
07314700	Deer Creek	33° 37' 37"	98° 19' 04"	nr	05/06/2006	Tributary water	¹ .4
				nr	10/16/2006	Tributary water	1.2
07314775	Unnamed tributary	33° 43' 11"	98° 17' 51"	nr	05/06/2006	Tributary water	1.2
				nr	10/16/2006	Tributary water	1.2
333930098244300	EC	33° 39' 30"	98° 24' 43"	3.4	01/11/2006	Lake water	1
				3.7	08/30/2006	Lake water	.3 and 3.0
334018098231100	FC	33° 40' 18"	98° 23' 11"	61	01/11/2006	Lake water	1
551010070251100	10	55 10 10	<i>y</i> 0 <i>25</i> 11	5.2	08/30/2006	Lake water	.3 and 4.9
334051098261900	DC	33° 40' 51"	98° 26' 19"	1.9	01/11/2006	Lake water	1
				1.5	08/30/2006	Lake water	.3
334308098213800	CC	33° 43' 08"	98° 21' 38"	7.6	01/11/2006	Lake water	1.0 and 7.0
				7.8	02/15/2006	Lake water	.9 and 7.0
				7.9	03/28/2006	Lake water	.9 and 7.0
				8.8	04/18/2006	Lake water	.9 and 7.0
				9.4	05/12/2006	Lake water	.9 and 8.5
				9.8 9.4	00/29/2000	Lake water	3 and 85
				9.1	08/30/2006	Lake water and sediment	.3 and 8.2
				9.1	09/25/2006	Lake water	1.5 and 8.2
334541098220600	BC	33° 45' 41"	98° 22' 06"	11.3	01/11/2006	Lake water	1.0 and 10.5
				12.0	02/15/2006	Lake water	.9 and 10.4
				11.9	03/28/2006	Lake water	.9 and 10.4
				11.9	04/18/2006	Lake water	.9 and 10.4
				11.3	06/29/2006	Lake water	.9 and 10.4
				11.0	07/19/2006	Lake water	.3 and 10.1
				10.8	08/30/2006	Lake water and sediment	.3 and 10.1
				10.7	09/25/2006	Lake water	1.5 and 9.8
334547098221200	AC	33° 45' 47"	98° 22' 12"	12.2	01/11/2006	Lake water	1.0 and 11.0
				12.2	02/15/2006	Lake water	.9 and 11.0
				11.7	04/18/2006	Lake water	.9 and 11.0
				11.9	05/12/2006	Lake water	.9 and 11.0
				11.3	06/29/2006	Lake water	.9 and 10.4
				11.0	07/19/2006	Lake water	.3 and 10.1
				10.7	08/30/2006	Lake water and sediment	.3 and 10.1
				10.7	0912312006	Lake water	1.5 and 10.1
334210098224600	UP	33° 42' 10"	98° 22' 46"	4.8	08/30/2006	Lake sediment	na
334443098204900	OF	33° 44' 43"	98° 20' 49"	8.4	08/30/2006	Lake sediment	na

¹Average sampling depth.

Table 2. Summary of conditions during sampling of tributaries to Lake Arrowhead, Texas, 2006.

Site ID	Sample date	Discharge (cubic feet per second)	Sampling method	Comments	
Little Wichita River	03/19/2006	6.9	Wading; single vertical	Flow constricted by tree limbs across channel	
Little Wichita River	05/06/2006	74	Wading; single vertical	Heavy sediment load	
Little Wichita River	10/17/2006	¹ 1.5 ft/s	Bridge; multiple vertical	Heavy sediment load with some grass debris	
West Little Post Oak Creek	03/19/2006	1.6	Wading; multiple vertical	Heavy sediment load	
West Little Post Oak Creek	05/06/2006	60 (estimate)	Wading; single vertical	Heavy sediment load	
West Little Post Oak Creek	10/16/2006	60 (estimate)	Wading; single vertical	Heavy sediment load	
East Little Post Oak Creek	03/19/2006	.8	Wading; multiple vertical	Shallow, low flow	
East Little Post Oak Creek	05/06/2006	10 to 30 (estimate)	Road/culvert; single vertical	High flow, over the road at several locations	
East Little Post Oak Creek	10/16/2006	10 to 30 (estimate)	Road/culvert; single vertical	na	
Deer Creek	03/19/2006	0	na	Dry; not sampled	
Deer Creek	05/06/2006	38	Wading; single vertical	Heavy sediment load	
Deer Creek	10/16/2006	.2	Wading; single vertical	Shallow, low flow	
Unnamed tributary	03/19/2006	0	na	Dry; not sampled	
Unnamed tributary	05/06/2006	.3	Wading; single vertical	Narrow area of flow	
Unnamed tributary	10/16/2006	.5	Wading; single vertical	na	

[ft/s, feet per second; na, not applicable]

¹Estimated flow velocity; discharge not measured.

water-quality monitor and its cable with plastic cable ties after calibration of the monitor. Deionized water and then natural lake water were pumped through the tubing before sample collection. The raw, unfiltered samples were collected first, followed by the filtered samples. Water samples were filtered using inline Whatman capsule filters (0.45-µm pore size). Samples were stored immediately on ice after collection and refrigerated upon return to the USGS Wichita Falls laboratory. Samples were shipped overnight on ice to the USGS NWQL for analysis of nutrients, iron, manganese, and arsenic species.

Lake Sediment

Cores of lake bottom sediment were collected from five sites on August 30, 2006. Surficial sediment cores 13 to 15 centimeters (cm) long were collected from four sites, AC, CC, OF (near an onshore oil field), and UP (fig. 1; table 1) to investigate arsenic concentrations spatially. A longer sediment core, 85 cm, was collected from site BC for analysis of older sediment deposits to assess historical trends in arsenic and other trace elements. A 7.5-m-long pontoon boat with a 4.5-m A-frame and hydraulic winch was used to collect cores. Lake sediment at sites AC, CC, OF, and UP was sampled using a

14- by 14- by 30-cm stainless steel Wildco box corer. The box corer collected a 13- to 15-cm-long sediment core, which was sliced into four subsamples (0 to 2 cm, 2 to 5 cm, 5 to 10 cm, and 10 cm to bottom) on the boat immediately after collection. Sediment at site BC was sampled using a 6.7-cm-diameter steel barrel Benthos gravity corer with a polybuterate liner. The gravity corer collected 85 cm of sediment that showed a transition to thick, stiff clay near the bottom of the core (80 cm), which was interpreted as pre-reservoir material. The gravity core was held vertically until return to shore, where it was sliced into 2-cm subsamples from 1 to 10 cm down the core, and 5-cm subsamples from 10 cm to the bottom of the core. Box and gravity cores were subsampled by placing the core liner containing the sediment onto a piston and pushing the sediment up through the core liner. Measured intervals of sediment were sliced off the top of the core and placed into polypropylene sample jars for subsequent analysis. All samples were stored immediately on ice after collection and frozen upon return to the USGS Austin laboratory. Samples were freeze-dried, ground using a mortar and pestle in the USGS Austin laboratory, and then shipped to the USGS Geologic Discipline Branch of Geochemistry laboratory in Denver, Colo., for analyses of forms of carbon (organic, inorganic, and total) and major and trace elements.

Analytical Methods

Lake Arrowhead tributary water samples were analyzed for nutrients and arsenic, and lake water samples were analyzed for nutrients, iron, manganese, and arsenic species at the USGS NWQL in Denver, Colo. Nutrient analyses consisted of ammonia nitrogen, total ammonia plus organic nitrogen (Kjeldahl nitrogen), dissolved nitrite nitrogen, dissolved nitrite plus nitrate nitrogen, and total and dissolved phosphorus and orthophosphate phosphorus. Ammonia concentrations were determined by reaction with salicylate and hypochlorite and analysis by colorimetry with automated-segmented flow (Fishman, 1993). Kjeldahl nitrogen was determined using a common (Kjeldahl) digestion method with an automated photometric finish that included digest cleanup by gas diffusion (Patton and Truitt, 2000). Dissolved nitrite and dissolved nitrite plus nitrate concentrations were measured by diazotization and colorimetry with automated-segmented flow. The dissolved nitrite plus nitrate analytical method included a cadmium-reduction step before diazotization (Fishman, 1993). All forms of phosphorus were determined by semiautomated colorimetry using USEPA method 365.1 (U.S. Environmental Protection Agency, 1993). Dissolved iron and manganese concentrations were measured by inductively coupled plasmaatomic emission spectrometry (ICP-AES) (Fishman, 1993). Arsenic concentrations in whole- and filtered-water samples were measured using collision/reaction cell inductively coupled plasma-mass spectrometry (cICP-MS) (Garbarino and others, 2006). Analyses of arsenic species determined concentrations of inorganic species, arsenite (As[III]) and arsenate (As[V]), and organic species, dimethylarsinate (DMA) and monomethylarsonate (MMA). Laboratory speciation was done using an ion chromatographic column to separate the arsenic species, and analyses of the species were done using inductively coupled plasma-mass spectrometry (ICP-MS) (Garbarino and others, 2002).

Lake sediment samples from Lake Arrowhead were analyzed for forms of carbon and major and trace elements by the USGS Geologic Discipline Branch of Geochemistry laboratory in Denver, Colo. Total carbon was analyzed by combustion with an automated carbon analyzer, inorganic

Table 3.Summary of the relative percent difference (RPD) ofduplicate results for lake water samples and replicate results forsediment samples collected at Lake Arrowhead, Texas, 2006.

Constituent	Sample	RPD			
group	medium	Minimum	Maximum	Median	
Nutrients	Lake water	0	31.6	1.9	
Iron and manganese	Lake water	7.2	16.0	12.9	
Arsenic species	Lake water	.1	11.8	1.5	
Major elements	Lake sediment	.4	16.9	1.9	
Trace elements	Lake sediment	0	19.4	2.2	

carbon was determined as carbon dioxide by coulometric titration, and organic carbon was computed by difference (Taggart, 2002). Samples for major and trace element analyses were digested completely using a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids and analyzed for 37 elements by ICP-MS (Briggs and Meier, 2002).

Quality Assurance

Field Quality Control Samples

Quality assurance for tributary and lake water samples involved collecting field and equipment blanks, spiked samples, and duplicate samples (appendix 1). Field blanks were collected during the January and September site visits. Equipment blanks were processed at the USGS Wichita Falls laboratory after the February lake sampling and the March tributary sampling. Field and equipment blanks used inorganic blank water from the USGS NWQL, certified with a lot number and expiration date. Field and equipment blanks were collected using the same sampling equipment and techniques and sample processing procedures used for environmental sampling.

There were three detections in the field blanks with estimated concentrations at or below the laboratory reporting level (LRL) for nitrite plus nitrate and phosphorus and the interim reporting level for ammonia (appendix 1.1). There was one detection in the equipment blanks of arsenic in unfiltered water at 0.12 μ g/L (LRL = 0.6 μ g/L). Two lake water samples were spiked in the field to determine the gain or loss, if any, of analytes resulting from matrix effects. Four lake water duplicate samples were collected during the sampling period. All field quality control samples were processed and sent to the USGS NWQL for analyses identically and concurrently with environmental samples. The maximum, minimum, and median values of relative percent difference for duplicate analyses of nutrients, iron and manganese, and arsenic species are listed in table 3. The field quality assurance results were judged acceptable.

Laboratory Quality Control Samples

Quality assurance for laboratory analyses of the lake sediment samples involved analyzing several standard reference materials (SRMs), and a blank sample and an environmental replicate sample with each batch of as many as 20 samples (appendix 1.2). The recovery of the SRMs ranged from 49 percent (cadmium) to 183 percent (niobium) with a median of 98 percent. There were no detections in the laboratory blank samples. The maximum, minimum, and median values of relative percent difference for replicate analyses of major and trace elements are listed in table 3. The laboratory quality assurance results were judged acceptable.

Physicochemical and Analytical Data

Tributary Water

Arsenic concentrations in tributary water samples varied with filtration and sampling site. Arsenic concentrations of tributary water samples were higher in unfiltered tributary water samples than in filtered samples (fig. 2A). Arsenic concentrations ranged from 1.5 to 6.3 and 0.5 to 4.8 μ g/L for unfiltered and filtered samples, respectively (appendix 2.1). The highest arsenic concentrations were in samples collected from the West Little Post Oak Creek sampling site. Suspended sediment concentrations ranged from 48 to 650 milligrams per liter (mg/L) (appendix 2.1) and typically increased with increasing discharge (table 2). Arsenic concentrations in unfiltered samples typically increased as suspended sediment concentrations increased (fig. 2B).

The concentration of arsenic transported on suspended sediment in the tributaries can be estimated using the concentration of arsenic in unfiltered and filtered water and the suspended sediment concentration. The unfiltered sample concentration minus the filtered sample concentration was multiplied by the suspended sediment concentration and converted to the same units as the lake sediment samples (milligrams per kilogram [mg/kg]) (appendix 2.1). The estimated concentration of arsenic transported on suspended sediment by the tributaries ranges from 2.3 to 11.1 mg/kg, with a median value of 5.9 mg/kg.

Lake Water

Physicochemical properties varied with depth and season. Water temperature and pH generally decreased with depth and were higher during summer and lower during winter. Lake water was alkaline with pH typically between 8.0 and 9.0 standard units. Dissolved oxygen also decreased with depth and tended to be higher in winter and lower in summer. Specific conductance typically increased with depth and was higher in summer and lower in winter.

Dissolved arsenite plus arsenate concentrations in Lake Arrowhead water samples generally were between 3 and 5 μ g/L (fig. 3). Arsenite concentrations typically were below the LRL of 0.6 μ g/L. There were no detections of monomethylarsonate or dimethylarsinate. A small but discernible seasonal cycle was evident, with higher arsenate concentrations measured in summer and lower concentrations measured in spring. There was little variation in arsenate concentrations with water depth (appendix 2.2).

Lake Sediment

The concentration of arsenic in lake sediment samples ranged from 4.4 to 11.2 mg/kg, with a median of 6.4 mg/kg.

The median arsenic concentration of the five top-interval sediment samples was 8.8 mg/kg, which generally is higher than the concentrations estimated to be on suspended sediment in the tributaries. The concentrations of selected major and trace elements (aluminum, iron, arsenic, cadmium, copper, and manganese) with depth in the gravity core collected at sampling site BC typically were lower than the concentrations in the box cores collected from sites AC, CC, OF, and UP (fig. 4). Concentrations at sites CC and OF generally decreased with depth, concentrations at sites AC and UP did not change consistently with depth, and concentrations at site BC generally increased slightly with depth (fig. 4; appendix 2.3).

Sediment concentrations can be compared to consensus-based sediment quality guidelines (SQGs) to indicate the degree of contamination of sediment. Ingersoll and others (2001) published SQGs for eight trace elements: arsenic, cadmium, chromium, copper, lead, mercury (not analyzed in this study), nickel, and zinc. Two consensus-based SQGs were defined: the threshold effect concentration (TEC) and the probable effect concentration (PEC). The TEC represents the concentration below which adverse effects to benthic biota are not expected to occur, and the PEC represents the concentration above which adverse effects to benthic biota are expected to frequently occur. These SQGs were derived through a variety of laboratory, field, and theoretical methods and are not definitive for determining sediment toxicity to benthic biota nor are they to be extrapolated to assess adverse effects to fish, aquatic plants, or humans (Long and others, 1995; MacDonald and others, 2000). No trace element concentration in lake sediment samples from Lake Arrowhead exceeded the respective PEC; however, as shown by ratios of trace element concentration to TEC greater than 1 (fig. 5), concentrations in some samples exceeded the respective TEC for arsenic, chromium, copper, lead, and nickel. Arsenic concentration exceeded the TEC of 9.79 mg/kg in only one sediment sample, the topinterval sample from the box core collected at site UP; the arsenic concentration in that sample was 11.2 mg/kg.

The concentration of major and trace elements in Lake Arrowhead lake sediment samples also can be compared to lake sediment trace element concentrations from other lakes in the United States. This comparison allows an understanding of the concentrations in Lake Arrowhead relative to other regions in the country. Van Metre and others (2006) reported concentrations of major and trace elements in sediment cores from 35 lakes in dense urban, light urban, and reference (little or no development) land-use settings across the country. Only sediment deposited after 1970, which is similar to the age of sediment sampled from Lake Arrowhead, was included in Van Metre and others (2006). Boxplots of the concentrations of arsenic, iron, and manganese for the 35 U.S. lakes by land-use setting and for Lake Arrowhead are shown in figure 6. Arsenic concentrations in Lake Arrowhead bottom sediment generally were lower than those in sediment of the other U.S. lakes for all three land-use settings. Iron concentrations in Lake Arrowhead sediment were similar to those of the U.S.



Figure 2. Arsenic concentration (A) over time and (B) in relation to suspended sediment concentration in tributary water samples collected near Lake Arrowhead, Texas, 2006.



Figure 3. Concentrations of arsenite plus arsenate in lake water samples collected from Lake Arrowhead, Texas, 2006.

reference lakes and generally lower than concentrations in sediment of U.S. lakes in urban settings. Concentrations of manganese in Lake Arrowhead sediment were slightly higher than those in the U.S. reference lakes but typically lower than those in the U.S. urban lakes.

Summary

Lake Arrowhead is a reservoir about 24 kilometers southeast of Wichita Falls, Tex., that provides drinking water for the city of Wichita Falls and surrounding areas. Arsenic has been detected frequently in the lake water and concentrations occasionally have approached the U.S. Environmental Protection Agency drinking-water standard maximum contaminant level of 10 μ g/L. The U.S. Geological Survey, in cooperation with the City of Wichita Falls, did a study in 2006 to assess conditions contributing to elevated arsenic concentrations in Lake Arrowhead. This report describes the sampling and analytical methods, quality assurance, and physicochemical and analytical data. Physiochemical properties were measured in and water samples were collected from five tributaries to Lake Arrowhead: Little Wichita River, West Little Post Oak Creek, East Little Post Oak Creek, Deer Creek, and an unnamed tributary. Tributary measuring and sampling were done immediately after storms when the streams were flowing. Lake water measuring and sampling were done approximately monthly from January through September 2006 at three deep-water sites and seasonally, in January and August 2006, at three shallow-water sites. Cores of lake bottom sediment were collected from five sites on August 30, 2006. Surficial sediment cores 13 to 15 centimeters long were collected from four sites, and a longer sediment core, 85 cm, was collected from one site.

Tributary water samples were analyzed for nutrients and arsenic, and lake water samples were analyzed for nutrients, iron, manganese, and arsenic species. Lake sediment samples were analyzed for forms of carbon and major and trace elements. Quality assurance for tributary and lake water samples involved collecting field and equipment blanks, spiked samples, and duplicate samples. Quality assurance for laboratory analyses of the lake sediment samples involved analyzing several standard reference materials, and a blank sample



Figure 4. Concentrations with depth of selected major and trace elements in lake sediment samples collected from Lake Arrowhead, Texas, 2006.



Figure 5. Comparison of lake sediment trace element concentrations to consensus-based sediment quality guidelines, threshold effect concentrations (Ingersoll and others, 2001), for samples collected at Lake Arrowhead, Texas, 2006. Samples with ratios greater than 1 have trace element concentrations that exceeded the respective threshold effect concentrations.

and an environmental replicate sample with each batch of as many as 20 samples. All quality assurance results were judged acceptable.

Arsenic concentrations in tributary samples ranged from 1.5 to 6.3 and 0.5 to 4.8 μ g/L for unfiltered and filtered samples, respectively. The highest arsenic concentrations were in samples collected from the West Little Post Oak Creek sampling site. Physicochemical properties in lake water varied with depth and season. Dissolved arsenite plus arsenate concentrations in lake water samples generally were between 3 and 5 μ g/L. Arsenite concentrations typically were below the laboratory reporting level of 0.6 μ g/L. There were no detections of monomethylarsonate or dimethylarsinate.

The concentration of arsenic in lake sediment samples ranged from 4.4 to 11.2 mg/kg, with a median of 6.4 mg/kg.



Figure 6. Comparison of selected major and trace element concentrations in sediments collected from 35 lakes in the U.S. (Van Metre and others, 2006) to Lake Arrowhead, Texas, 2006. [nds, nondetections, not plotted]

The median arsenic concentration of the five top-interval sediment samples was 8.8 mg/kg, which generally is higher than the concentrations estimated to be on suspended sediment in the tributaries. Sediment concentrations of seven trace elements were compared to two consensus-based sediment quality guidelines for each: the threshold effect concentra-

tion (TEC) and the probable effect concentration (PEC). No trace element concentration in sediment samples exceeded the respective PEC; however, concentrations in some samples for some trace elements exceeded the respective TEC. Arsenic concentration exceeded the TEC in one top-interval sediment sample.

References

- Briggs, P.H., and Meier, A.L., 2002, The determination of forty-two elements in geological materials by inductively coupled plasma-mass spectrometry for NAWQA, Chapter J, *in* Taggart, J.E., Jr. ed., Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey: U.S. Geological Survey Open File Report 02–223–J, p. J1–J14.
- Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory— Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.
- Garbarino, J.R., Bednar, A.J., and Burkhardt, M.R., 2002, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Arsenic speciation in naturalwater samples using laboratory and field methods: U.S. Geological Survey Water-Resources Investigations Report 02–4144, 40 p.
- Garbarino, J.R., Kanagy, L.K., and Cree, M.E., 2006, Determination of elements in natural-water, biota, sediment, and soil samples using collision/reaction cell inductively coupled plasma-mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, section B, chap. 1, 88 p.
- Ingersoll, C.G., MacDonald, D.D., Wang, N., Crane, J.L., Field, L.J., Haverland, P.S., Kemble, N.E., Lindskoog, R.A., Severn, C., and Smorong, D.E., 2001, Predictions of sediment toxicity using consensus-based freshwater sediment quality guidelines: Archives of Environmental Contamination and Toxicology, v. 41, p. 8–21.
- Long, E.R., MacDonald, D.D., Smith, S.L., and Calder, F.D., 1995, Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments: Environmental Management, v. 19, p. 81–97.
- MacDonald, D.D., Ingersoll, C.G., and Verger, T.A., 2000, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems: Archives of Environmental Contamination and Toxicology, v. 39, p. 20–31.
- Patton, C.J., and Truitt, E.P., 2000, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of ammonium plus organic nitrogen by a Kjeldahl digestion method and an automated photometric finish that includes digest cleanup by gas diffusion: U.S. Geological Survey Open File Report 00–170, 31 p.

- Potts, P.J., Tindle, A.G., and Webb, P.C., 1992, Geochemical reference material compositions—Rocks, minerals, sediments, soils, carbonates, refractories, and ores used in research and industry: Boca Raton, Fla., CRC Press, 313 p.
- Taggart, J.E., Jr., ed., 2002, Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey: U.S. Geological Survey Open File Report 02–223, accessed December 7, 2007, at *http://pubs.usgs.gov/* of/2002/ofr-02-0223/.
- Texas Commission on Environmental Quality, 2007, Texas Clean Rivers Program—Data and map resources: accessed April 30, 2007, at *http://www.tceq.state.tx.us/compliance/ monitoring/crp/data/crp-resources.html*
- U.S. Environmental Protection Agency, 1993, Method 365.1 determination of phosphorus by semi-automated colorimetry, revision 2.0, *in* O'Dell, J.W., ed, Methods for the determination of inorganic substances in environmental samples: U.S. Environmental Protection Agency EPA/600/ R–93/100.
- U.S. Environmental Protection Agency, 2001, Arsenic and clarifications to compliance and new source monitoring rule—A quick reference guide: U.S. Environmental Protection Agency, Office of Water, EPA 816–F–01–004, 2 p.
- U.S. Geological Survey, 2003, Arsenic speciation sampling instructions (version 2.0, 3/2003): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A2, accessed February 13, 2008, at *http://wwwnwql.cr.usgs.gov/usgs/as-speciation-guidance-new.pdf*
- U.S. Geological Survey, 2006, Collection of water samples (version 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, accessed December 10, 2006, at *http://pubs.water.usgs.gov/twri9A4/*.
- Van Metre, P.C., Mahler, B.J., Wilson, J.T., and Callender, Edward, 2006, Major and trace elements in 35 lake and reservoir sediment cores from across the United States, 1994–2001: U.S. Geological Survey Data Series 166, 29 p.
- Wilde, F.D., ed., 2004, Cleaning of equipment for water sampling (version 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A3, accessed December 10, 2006, at http://pubs.water.usgs.gov/twri9A3/.
- Wilde F.D., and Radtke, D.B., 2005, General information and guidelines (version 1.2): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, section 6.0, accessed December 10, 2006, at *http://pubs. water.usgs.gov/twri9A6/.*

Publishing support provided by Lafayette Publishing Service Center

Information regarding water resources in Texas is available at http://tx.usgs.gov/