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# Comparison of Mercury in Water, Bottom Sediment, and Zooplankton in Two Front Range Reservoirs in Colorado, 2008–09

Scientific Investigations Report 2010–5037

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

**Cover.** Pueblo Reservoir in south-central Colorado. Photograph by Robert Stogner.

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

**U.S. Department of the Interior**
KEN SALAZAR, Secretary

**U.S. Geological Survey**
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# Conversion Factors

| Multiply | By | To obtain |
|---|---|---|
| | Length | |
| inch (in.) | 2.54 | centimeter (cm) |
| foot (ft) | 0.3048 | meter (m) |
| mile (mi) | 1.609 | kilometer (km) |
| | Area | |
| acre | 0.004047 | square kilometer ($km^2$) |
| | Volume | |
| ounce, fluid (fl. oz) | 0.02957 | liter (L) |
| gallon (gal) | 3.785 | liter (L) |
| acre-foot (acre-ft) | 1,233 | cubic meter ($m^3$) |
| | Mass | |
| ounce, avoirdupois (oz) | 28.35 | gram (g) |
| pound, avoirdupois (lb) | 0.4536 | kilogram (kg) |

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

$$°F=(1.8×°C)+32$$

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L) or nanograms per liter (ng/L). Mercury concentrations in sediment and zooplankton are given in nanograms per gram (ng/g) dry weight and concentrations in fish are reported in micrograms per gram (µg/g) wet weight.

# Comparison of Mercury in Water, Bottom Sediment, and Zooplankton in Two Front Range Reservoirs in Colorado, 2008–09

By M. Alisa Mast and David P. Krabbenhoft


## Abstract

The U.S. Geological Survey, in cooperation with the Colorado Department of Public Health and Environment, conducted a study to investigate environmental factors that may contribute to the bioaccumulation of mercury in two Front Range reservoirs. One of the reservoirs, Brush Hollow Reservoir, currently (2009) has a fish-consumption advisory for mercury in walleye (*Stizostedion vitreum*), and the other, Pueblo Reservoir, which is nearby, does not. Water, bottom sediment, and zooplankton samples were collected during 2008 and 2009, and a sediment-incubation experiment was conducted in 2009. Total mercury concentrations were low in midlake water samples and were not substantially different between the two reservoirs. The only water samples with detectable methylmercury were collected in shallow areas of Brush Hollow Reservoir during spring. Mercury concentrations in reservoir bottom sediments were similar to those reported for stream sediments from unmined basins across the United States. Despite higher concentrations of fish-tissue mercury in Brush Hollow Reservoir, concentrations of methylmercury in sediment were as much as 3 times higher in Pueblo Reservoir. Mercury concentrations in zooplankton were at the low end of concentrations reported for temperate lakes in the Northeastern United States and were similar between sites, which may reflect the seasonal timing of sampling.

Factors affecting bioaccumulation of mercury were assessed, including mercury sources, water quality, and reservoir characteristics. Atmospheric deposition was determined to be the dominant source of mercury; however, due to the proximity of the reservoirs, atmospheric inputs likely are similar in both study areas. Water-quality constituents commonly associated with elevated concentrations of mercury in fish (pH, alkalinity, sulfate, nutrients, and dissolved organic carbon) did not appear to explain differences in fish-tissue mercury concentrations between the reservoirs. Low methylmercury concentrations in hypolimnetic water indicate low potential for increased methylmercury production following the development of anoxic conditions in summer. Based on the limited dataset, water-level fluctuations and shoreline characteristics appear to best explain differences in fish-tissue mercury concentrations between the reservoirs. Due to the shallow depth and the large annual water-level fluctuations at Brush Hollow Reservoir, proportionally larger areas of shoreline at Brush Hollow Reservoir are subjected to annual reflooding compared to Pueblo Reservoir. Moreover, presence of macrophyte beds and regrowth of terrestrial vegetation likely increase the organic content of near-shore sediments in Brush Hollow Reservoir, which may stimulate methylmercury production in littoral areas subject to reflooding. Results of a laboratory incubation experiment were consistent with this hypothesis.


## Introduction

Mercury is released to the environment primarily from anthropogenic sources (burning of fossil fuels and wastes) and is transported to most aquatic ecosystems through atmospheric pathways (U.S. Environmental Protection Agency, 1997). Mercury is of concern because it bioaccumulates in fish and can pose health risks to humans and wildlife that consume large amounts of contaminated fish. As of 2008, 48 States in the United States have issued fish-consumption advisories for mercury and 26 States have issued statewide advisories (*http://epa.gov/waterscience/fish/advisories/*). Nearly all mercury in fish occurs as methylmercury, which is a more bioavailable and toxic form of mercury that appears to be produced largely by sulfate-reducing bacteria in anoxic environments (Gilmour and others, 1992). The extent to which methylmercury bioaccumulates in fish depends not only on the nature and length of the food chain but also on landscape and water-chemistry characteristics (Driscoll and others, 2007). Greater bioaccumulation of methylmercury has been found to occur in oligotrophic lakes that have low pH and low alkalinity (Wiener and others, 2003; Chen and others, 2005) and in lakes whose watersheds are dominated by runoff from wetlands (St. Louis and others, 1994; Kolka and others, 1999). Lakes that undergo seasonal stratification can contain elevated concentrations of methylmercury following the development of anoxic conditions in the hypolimnion (Driscoll and others, 1995; Watras and others, 2005). Some studies have reported lower mercury accumulation in nutrient-rich water bodies due to biodilution of mercury under algal-bloom conditions (Pickhardt and others, 2002). Mercury in fish commonly is elevated in man-made reservoirs compared to natural lakes. In newly created reservoirs, the initial flooding of organic-rich soils results in elevated mercury concentrations in fish for 10 to 20 years after the reservoir is created (Bodaly and others, 2007). Mercury accumulation also appears to be elevated in established reservoirs that experience annual water-level fluctuations related to water storage, power generation, or flood control (Sorensen and others, 2005) and natural lakes that experience large water-level fluctuations related to climate (Selch and others, 2007).

In 2004, the Colorado Department of Public Health and Environment (CDPHE) initiated a 5-year study to test fish tissue (fillets) for mercury in water bodies across the State (*http://www.cdphe.state.co.us/wq/fishcon/index.html*, accessed January 2010). Of the 94 water bodies tested as of August 2008, nearly one-quarter had one or more fish species that exceeded the Colorado tissue criterion for mercury of 0.5 microgram per gram wet weight (µg/g ww) for the protection of human health (*http://www.cdphe.state.co.us/wq/fishcon/index.html*, accessed January 2010). As a result of the tissue study and a growing public awareness of mercury contamination in Colorado, the U.S. Geological Survey (USGS), in cooperation with the CDPHE, conducted a study to investigate environmental factors that might contribute to the bioaccumulation of mercury in fish. Two reservoirs in Colorado were selected for the study—one that has a current (2009) fish-consumption advisory for mercury in walleye (*Stizostedion vitreum*) and one that does not. Because of the large number of lakes and reservoirs in the State, the results of this study may be useful to resource managers in identifying untested water bodies that are at greatest risk for mercury contamination. Additionally, insight gained from this study also may be useful in the development of management strategies to lower methylmercury production in Colorado reservoirs and reduce mercury available to fish.

## Purpose and Scope

The purpose of this report is to compare mercury concentrations in water, bottom sediment, and zooplankton samples collected from two Front Range reservoirs in Colorado during 2008 and 2009 and to evaluate factors that may be contributing to bioaccumulation of mercury in fish. Additionally, this report presents results of a sediment-incubation experiment conducted in 2009 to evaluate the methylation potential of sediments in these two reservoirs. The two reservoirs, Brush Hollow and Pueblo Reservoirs (fig. 1), are located in the Arkansas River drainage within 20 miles of each other yet have very different fish-tissue mercury concentrations. Mercury concentrations in walleye, which is the top predator fish in each reservoir, are below analytical detection in tissue samples from Pueblo Reservoir but exceeded the fish-tissue criterion for the State of Colorado in some tissue samples from Brush Hollow Reservoir.

## Description of Study Area

Pueblo Reservoir is approximately 3 miles northwest of Pueblo, Colorado (fig. 1*A*), and has a total storage capacity of 357,678 acre-feet (Bureau of Reclamation, 1977). The reservoir, which began filling in 1974, was created to store water for municipal, industrial, and irrigation uses but also provides flood control, recreational activities, sport fishing, and wildlife habitat for the region (Lewis and Edelmann, 1994). At full pool, the reservoir is about 9 miles long and ranges in width from 0.3 to about 2.2 miles and has a maximum depth of 155 feet near the dam (Bureau of Reclamation, 1972). Nearly all the inflow to the reservoir is from the Arkansas River, and more than one-half of the inflow occurs during May through July (Lewis and Edelmann, 1994). Annual storage typically peaks in April then decreases through the summer and early autumn months because of decreased inflow and large downstream demands for irrigation water (fig. 2). The reservoir inundates four large canyons and parts of several small tributaries. The shoreline is irregular and rocky and the reservoir is underlain by flat-lying shales, sandstones, and limestones (Galloway and others, 2008). Vegetation is sparse with scattered willows, grasses, and cottonwoods growing in ravines and on small sandy beaches. The reservoir supports both cold- and warm-water fisheries and is routinely stocked with rainbow trout, cutbow trout, walleye, bass, wiper, and channel catfish (*http://wildlife.state.co.us/Fishing/Reports/FisherySurveySummaries/*, accessed January 2010).

Brush Hollow Reservoir is 6 miles northeast of Florence, Colorado (fig. 1*B*), and has a storage capacity of 3,933 acre-feet. The reservoir was established in 1907 to store irrigation water from the Beaver Creek drainage to the east, which is delivered by way of a supply ditch that discharges near the dam. On rare occasions, rainstorms upstream from the reservoir contribute some water. The reservoir is within the Brush Hollow Wildlife Refuge and also provides recreation, sport fishing, and wildlife habitat. At full pool, the reservoir is about 0.9 mile long and 0.3 mile wide and has a maximum depth of 45 feet near the dam. The reservoir is subject to extreme annual fluctuations in water level due to water management activities and in many years is drawn down to the minimum allowable pool of 25 feet near the dam (D. Krieger, Colorado Division of Wildlife, oral commun., 2008). Annual storage typically peaks in April around 4,000 acre-feet then declines rapidly, reaching a minimum of less than 1,000 acre-feet by midsummer (fig. 2). The reservoir is situated on flat-lying shale and limestone units (Scott and others, 1978), and vegetation around the reservoir is dominated by cottonwoods, grasses, and sagebrush. Beds of aquatic macrophytes grow in shallow areas along the northern end of the reservoir when it is at full pool. The reservoir is managed as a warm-water and seasonal trout fishery and is routinely stocked with rainbow

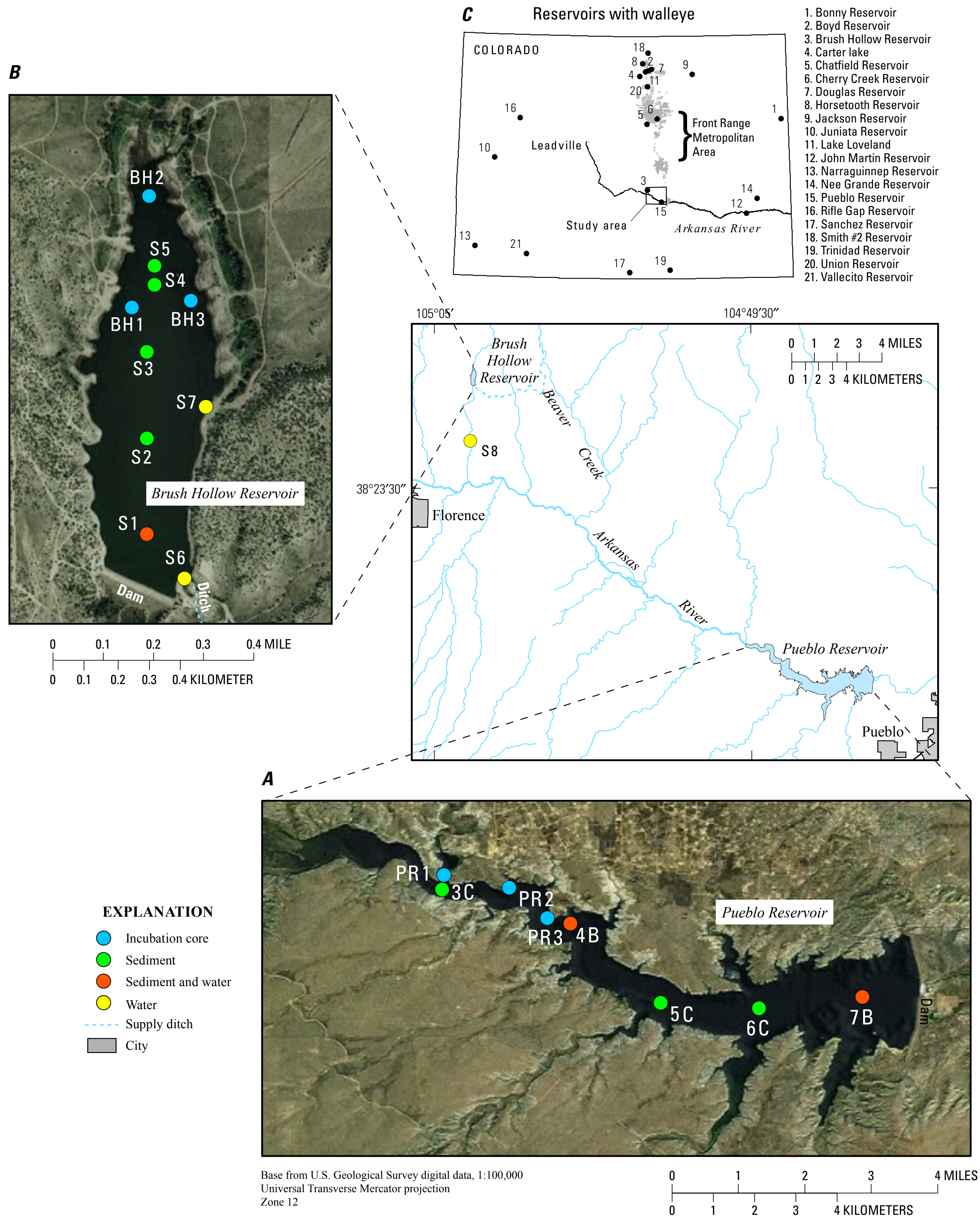


**Figure 1.** Location of study areas and sampling sites in (*A*) Pueblo Reservoir and (*B*) Brush Hollow Reservoir, and of (*C*) reservoirs with walleye (*Stizostedion vitreum*) sampled during the Colorado Department of Public Health and Environment fish-tissue mercury study.

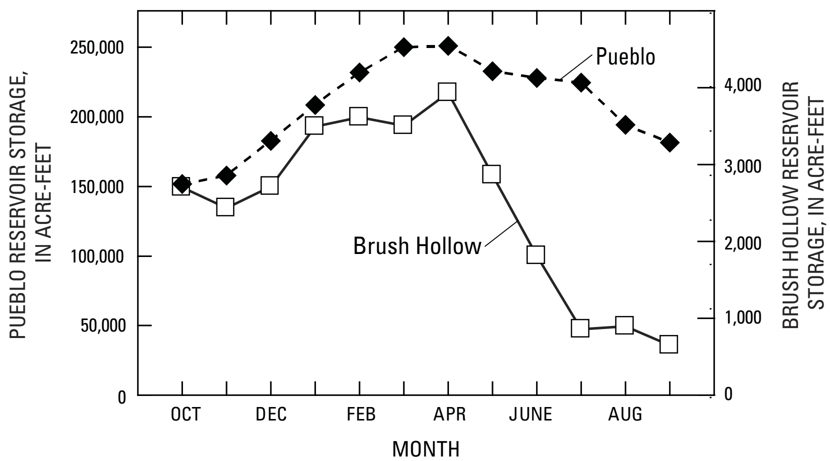


**Figure 2.** Average monthly storage in Pueblo Reservoir (1974–2008) and Brush Hollow Reservoir (1960–2008) for the period of record.

trout, cutbow trout, Snake River cutthroat, black crappie, bluegill, channel catfish, and walleye (*http://wildlife.state.co.us/Fishing/Reports/FisherySurveySummaries/*, accessed January 2010).

## Summary of Fish-Tissue Mercury in Colorado

As part of the CDPHE fish-tissue mercury study, samples were collected from 94 water bodies across the State as of August 2008, representing 38 different species of fish. Concentration data and collection methods for the CDPHE study are available online at *http://www.cdphe.state.co.us/wq/fishcon/index.html*. The most frequently collected fish species were walleye (*Stizostedion vitreum*; 17 percent), rainbow trout (*Oncorhynchus mykiss*; 10 percent), smallmouth bass (*Micropterus dolomieu*; 7 percent), northern pike (*Esox lucius*; 6 percent), black crappie (*Pomoxis nigromaculatus*; 6 percent), brown trout (*Salmo trutta*; 5 percent), largemouth bass (*Micropterus salmonoides*; 5 percent), wiper (*Morone saxatilis*; 5 percent), channel catfish (*Ictalurus punctatus*; 4 percent), and green sunfish (*Lepomis cyanellus*; 3 percent). Mercury concentrations were above analytical detection limits (0.1 µg/g ww) in 38 percent of the 3,767 fish-tissue samples analyzed. Detected concentrations ranged from 0.1 to 1.5 µg/g ww with a median concentration of 0.2 µg/g ww. Mercury concentrations varied considerably among species, with the highest concentrations in the piscivorous species such as northern pike, walleye, wiper, and bass and the lowest concentrations in forage fish such as rainbow and brook trout (fig. 3*A*). Mercury concentrations exceeded the U.S. Environmental Protection Agency criterion of 0.3 µg/g ww for protection of human health (*http://www.epa.gov/waterscience/criteria/*) in 11 percent of samples and exceeded the State of Colorado tissue criterion level of 0.5 µg/g ww in 4 percent of samples. For individual fish species, mercury concentrations also varied considerably among water bodies, particularly for piscivorous species. For example, in the 21 reservoirs with walleye (figs. 1 and 3B), nearly one-half had walleye tissue concentrations near or below analytical detection while the remainder had elevated concentrations, which in two reservoirs exceeded 0.8 µg/g ww. For the two reservoirs in this study, mercury in walleye was below detection in all tissue samples collected from Pueblo Reservoir but was detected in all tissue samples collected from Brush Hollow Reservoir, with concentrations ranging from 0.14 to 0.57 µg/g ww.

# Methods of Investigation

This section of the report describes methods of field sampling, the approach used for the sediment-incubation experiments, and laboratory analytical methods. Mercury results for quality-control samples (blanks and replicates) collected during the study also are presented. Sampling sites at the two reservoirs are listed in table 1 and shown in figure 1.

## Field Sampling

Water samples for mercury were collected at each reservoir using a Teflon Kemmerer sampler that was precleaned with 5-percent hydrochloric acid (HCl) and deionized water. Unfiltered samples were transferred to precleaned Teflon bottles and acidified in the field to 1 percent HCl by volume. During August 2008, water samples for mercury were collected from the epilimnion and hypolimnion at two locations in Pueblo Reservoir (sites 7B and 4B) and one location in Brush Hollow Reservoir (site S1) (fig. 1). One equipment blank was collected from the Kemmerer sampler and one field replicate was collected at each reservoir. Samples also were collected with the Kemmerer at all three sites for major dissolved constituents, nutrients, and dissolved organic carbon; these samples were field filtered through a 0.45-micron (µm)

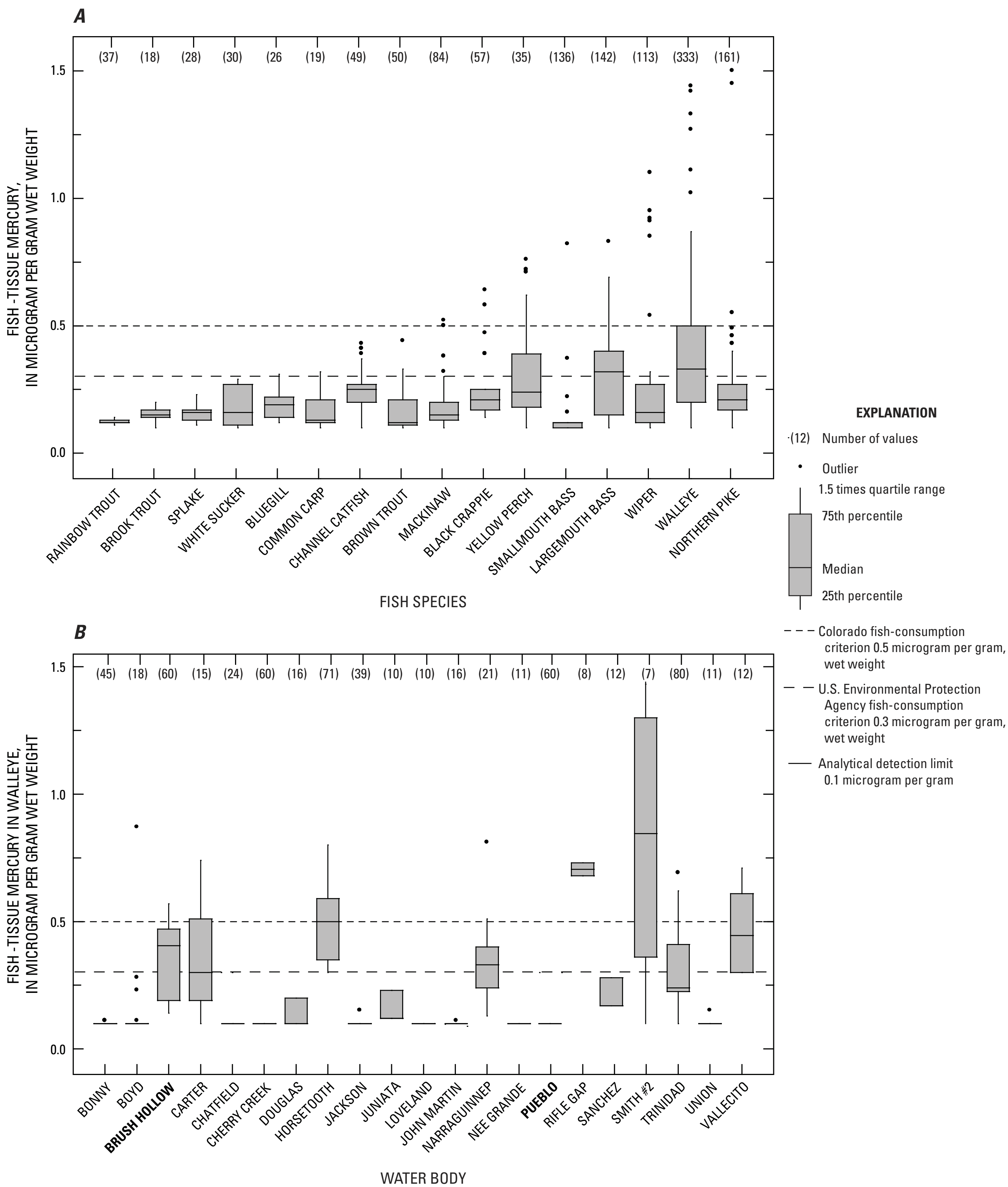


**Figure 3.** Mercury concentrations in fish tissue from selected water bodies in Colorado (*A*) for fish species with detectable concentrations and (*B*) for walleye (*Stizostedion vitreum*). [U.S. Environmental Protection Agency (USEPA) fish-consumption criterion = 0.3 microgram per gram, wet weight; Colorado fish-consumption criterion = 0.5 microgram per gram, wet weight; Analytical detection limit = 0.1 microgram per gram]

capsule filter, packed on ice, and transported to the laboratory. At each site a Secchi depth was recorded and field measurements of water temperature, specific conductance, and dissolved oxygen were made at depth intervals of 2–3 feet using a Hydrolab water-quality sonde. During 2009, additional water samples and field replicates for mercury were collected during April, May, and June. At midlake sites, samples were collected using the Kemmerer sampler, and at sites S6–S8, grab samples from the surface were collected into Teflon bottles.

Bottom sediments were collected from five sites in each reservoir in August 2008 approximately along a transect from the upstream to downstream end (fig. 1). At the time of sampling, the reservoir level at Brush Hollow Reservoir was declining and site S5 was at the northern shoreline of the reservoir. Sediments were collected using a benthos gravity corer fitted with a 2.5-inch-diameter polyethylene core tube. The cores were extruded in the field, and the top 0.75 inch of sediment was removed from the core using a plastic spatula and placed in a double polyethylene bag and homogenized. At site S4 in Brush Hollow Reservoir the surface-sediment section was split and one-half was submitted as the environmental sample and one-half as a field replicate. Four zooplankton samples were collected at each reservoir (table 1) during the August 2008 sampling event by using a zooplankton net (150-µm mesh) fitted with a Teflon cod-end assembly. Horizontal tows behind the boat were required to obtain enough sample mass for the analysis. Two samples were collected in the deepest part of each reservoir and two were collected in shallower water. The zooplankton samples were drained of most water and transferred to precleaned Teflon vials. Sediment and zooplankton samples were packed on ice and transported to the processing facility where they were frozen and shipped to the laboratory for mercury analysis.

## Sediment-Incubation Experiments

For the incubation experiments, exposed littoral sediments were cored from each reservoir at three different locations during spring of 2009 (fig. 1). A column of sediment approximately 2 inches thick and 5 inches in diameter was excavated at each sampling site by using a polyvinylchloride (PVC) ring and a ceramic knife. Care was taken not to disturb the sediment surface while the core was placed surface-side up in the bottom of a 2-liter Teflon jar. At the time of sediment collection, a sample of reservoir water was collected near the shore and filtered into a 6-liter Teflon container using an acid-rinsed 0.45-µm capsule filter. The sediment cores and water were packed on ice and transported to the laboratory and stored at 4°C until the start of the experiment. A spike of isotopically enriched inorganic mercury-201 was added to the filtered water sample and allowed to mix for 24 hours. The

**Table 1.** Sampling sites at Pueblo and Brush Hollow Reservoirs, Colorado.

[No., site number used in fig. 1; USGS, U.S. Geological Survey]

| No. | Site name | USGS station number | Sample medium |
|---|---|---|---|
| 7B | Pueblo Reservoir Site 7B | 381602104435200 | Water, sediment, zooplankton. |
| 6C | Pueblo Reservoir Site 6C | 381548104453300 | Sediment. |
| 5C | Pueblo Reservoir Site 5C | 381559104465500 | Sediment. |
| 4B | Pueblo Reservoir Site 4B | 381647104475300 | Water, sediment, zooplankton. |
| 3C | Pueblo Reservoir Site 3C | 381729104494100 | Sediment. |
| PR1 | Pueblo sediment core 1 | 381737104494501 | Incubation core. |
| PR2 | Pueblo sediment core 2 | 381726104485501 | Incubation core. |
| PR3 | Pueblo sediment core 3 | 381703104482401 | Incubation core. |
| S1 | Brush Hollow Reservoir Site S1 | 382734105030601 | Water, sediment, zooplankton. |
| S2 | Brush Hollow Reservoir Site S2 | 382744105030601 | Sediment. |
| S3 | Brush Hollow Reservoir Site S3 | 382753105030601 | Sediment, zooplankton. |
| S4 | Brush Hollow Reservoir Site S4 | 382800105030501 | Sediment. |
| S5 | Brush Hollow Reservoir Site S5 | 382802105030501 | Sediment. |
| S6 | Brush Hollow Ditch | 382729105030001 | Water. |
| S7 | Brush Hollow Reservoir nr Boat Ramp | 382747105025801 | Water. |
| S8 | Brush Hollow Creek at Hwy 50 | 382522105031701 | Water. |
| BH1 | Brush Hollow sediment core 1 | 382758105030801 | Incubation core. |
| BH2 | Brush Hollow sediment core 2 | 382809105030601 | Incubation core. |
| BH3 | Brush Hollow sediment core 3 | 382758105030001 | Incubation core. |

isotopic spike, which resulted in an initial 2 ng/L concentration of mercury-201, was added to monitor the production of methylmercury during the experiments. Each 2-liter Teflon jar was filled with the spiked water solution, which was added slowly to minimize disturbance of sediment at the bottom of the jar. The jars were closed with a screw-top lid and allowed to incubate at room temperature in the laboratory. Three samples were collected from each jar during the experiment at 2- to 3-week intervals. During sampling, the jars were opened briefly and a small volume of water was removed using Teflon tubing and a peristaltic pump. The samples were filtered in a vacuum chamber, using a 0.45-µm quartz fiber-filter, into precleaned Teflon bottles and preserved to 1 percent HCl by volume.

## Analytical Methods

All samples were analyzed for total mercury and methylmercury at the USGS Mercury Research Laboratory in Middleton, Wisconsin. Total mercury in water (both unfiltered and filtered samples) was analyzed by cold-vapor atomic fluorescence spectroscopy (CVAFS) using EPA Method 1631 Revision E (U.S. Environmental Protection Agency, 2002). Methylmercury in water (both unfiltered and filtered samples) was analyzed using the method described by DeWild and others (2001) except that detection was by inductively coupled plasma/mass spectrometry with isotope dilution instead of by CVAFS (T. Sabin, U.S. Geological Survey, written commun., 2009). The method detection limits are 0.4 nanogram per liter (ng/L) for total mercury and 0.04 ng/L for methylmercury in water. Reservoir bottom sediment and zooplankton samples were digested with acid and analyzed for total mercury and methylmercury using the method described for water, with some modifications (DeWild and others, 2004; Olund and others, 2004). The method detection limits in sediment and zooplankton are 2.0 nanograms per gram (ng/g) for total mercury and 0.02 ng/g for methylmercury. Major constituents and dissolved organic carbon in surface water were analyzed at a Colorado Water Science Center research laboratory, and nutrients were analyzed at the USGS National Water Quality Laboratory using published analytical methods (Fishman and Friedman, 1989). Percent organic carbon in sediments was determined by loss on ignition at the USGS Mercury Research Laboratory (Fishman and Friedman, 1989). Data for all field samples are stored in the USGS National Water Information System (NWIS) at *http://waterdata.usgs.gov/nwis* under USGS station numbers listed in table 1.

## Quality Control

The quality of the mercury analyses was evaluated through collection of blank and replicate samples. Two water blanks were collected during the study, one in the field using the Kemmerer sampler and one in the laboratory (for methylmercury only) using the filtration chamber (table 2). Neither sample had detectable concentrations, indicating that the potential for mercury contamination in water samples resulting from sample collection, processing, and analysis was low.

**Table 2.** Quality-control results for water samples collected during the study.

[ng/L, nanogram per liter; MDL, method detection limit; <, less than; --, not measured; RPD, relative percent difference; %, percent]

| | Methylmercury, ng/L (MDL = 0.04) | Total mercury, ng/L (MDL = 0.40) |
|---|---|---|
| Field blank | <0.04 | <0.04 |
| Laboratory filter blank | <.04 | -- |
| Pueblo Reservoir Site 7B | | |
| Environmental | <0.04 | 0.53 |
| Replicate | <.04 | .54 |
| RPD | -- | 2% |
| Environmental | <.04 | .41 |
| Replicate | <.04 | .45 |
| RPD | -- | 9% |
| Brush Hollow Reservoir Site S1 | | |
| Environmental | <0.04 | 0.60 |
| Replicate | <.04 | .64 |
| RPD | -- | 6% |
| Environmental | .050 | .60 |
| Replicate | .058 | .56 |
| RPD | 15% | 7% |

Four field replicates were collected at surface-water sites, two during 2008 and two during 2009 (table 2). The relative percent difference in concentration (calculated as the difference of the sample pairs divided by the mean of the pairs multiplied by 100) was 15 percent for the one sample with detectable methylmercury and less than 10 percent for total mercury indicating good analytical precision for mercury in water. One field replicate was collected for sediment and one for zooplankton during 2008 (table 3). The relative percent difference in these solid samples was higher for methylmercury (13 percent for sediment and 12 percent for zooplankton) than it was for total mercury (1 percent for both sediment and zooplankton), but overall the results were within the expected precision for the analytical methods used.

# Comparison of Mercury in Water, Bottom Sediment, and Zooplankton in Two Front Range Reservoirs

The following sections of the report describe the chemical characteristics of Pueblo and Brush Hollow Reservoirs and present total mercury and methylmercury concentration data for water, bottom sediment, and zooplankton samples collected during 2008 and 2009. Results of a sediment-incubation experiment conducted during 2009 also are presented.

## Chemical Characteristics

Profiles of dissolved oxygen and temperature at site 7B in Pueblo Reservoir and site S1 in Brush Hollow Reservoir are depicted in figure 4. In both reservoirs, dissolved oxygen and water temperature decreased with increasing water depth during August 2008. At site7B in Pueblo Reservoir, dissolved oxygen concentration was 0.3 milligram per liter (mg/L) at a depth of 105 feet. This is consistent with a previous study, which reported that dissolved oxygen concentrations less than 1 mg/L commonly occurred in the deepest area of Pueblo Reservoir during late summer (Lewis and Edelmann, 1994). At the shallower site 4B in Pueblo Reservoir, dissolved oxygen concentration also decreased with depth during the August sampling although concentrations did not fall below 4.0 mg/L, likely due to more efficient vertical mixing in the upstream reaches of the reservoir (Lewis and Edelmann, 1994). Pueblo Reservoir typically mixes during October (Lewis and Edelmann, 1994) and remains relatively well mixed through April; in early summer the water temperature stratifies and dissolved oxygen levels begin a seasonal decline in the hypolimnion. During late summer (August 2008) at site S1 in Brush Hollow Reservoir, dissolved oxygen concentration decreased to 1 mg/L but thermal stratification was minimal due to the shallow depth of the reservoir (fig. 4). The June 2009 profile indicates hypoxic conditions develop slightly earlier in Brush Hollow Reservoir than in Pueblo Reservoir.

Major dissolved constituents and nutrients measured in water from the two reservoirs during August 2008 are shown in table 4. Specific conductance, which is proportional to the concentration of major dissolved constituents (Hem, 1985), was slightly higher in Brush Hollow Reservoir than in Pueblo Reservoir. Calcium was the dominant cation in both reservoirs. Bicarbonate, represented as alkalinity in table 4, was the dominant anion in Pueblo Reservoir and bicarbonate and sulfate were codominant in Brush Hollow Reservoir. Silica concentrations were substantially lower in Pueblo Reservoir, particularly in the epilimnion at site 7B than in Brush Hollow Reservoir. The depletion of silica in the epilimnion likely reflects the large diatom population that is present in the reservoir during the summer (Lewis and Edelmann, 1994). Dissolved organic carbon (DOC) concentrations, which commonly are correlated with mercury in fish (Chen and others, 2005), were slightly higher in Brush Hollow Reservoir than in Pueblo Reservoir, but overall concentrations in both reservoirs were fairly low (less than 5.0 mg/L). Nitrate and phosphorus species were near or below detection levels in all but the deepest samples from Pueblo Reservoir owing to high biological uptake in the middle of summer. Total dissolved nitrogen, which was composed primarily of organic nitrogen, was as much as 2 times higher in Brush Hollow Reservoir than Pueblo Reservoir, indicating Brush Hollow is the more productive of the two reservoirs.

**Table 3.** Quality-control results for solid samples collected during the study.

[MDL, method detection limit; Env., environmental sample; Rep., replicate sample; RPD, relative percent difference; %, percent; concentrations in nanogram per gram dry weight]

| Constituent | MDL | Sediment | | | Zooplankton | | |
|---|---|---|---|---|---|---|---|
| | | Env. | Rep. | RPD | Env. | Rep. | RPD |
| Methylmercury | 0.02 | 0.14 | 0.16 | 13% | 13.2 | 11.7 | 12% |
| Total mercury | 2.0 | 24.6 | 24.9 | 1% | 19.8 | 19.7 | 1% |

The productivity or trophic state of the reservoirs can be directly compared using the trophic state index (TSI), which was computed based on secchi-disk depth using the method of Carlson (1977). For Pueblo Reservoir, the TSI ranged from 50 to 55, indicating the reservoir is borderline between mesotrophic and eutrophic conditions during summer (table 4). For Brush Hollow Reservoir, the TSI was 59 indicating the reservoir is slightly more productive. This perhaps is due to shallower depths and warmer water temperatures in Brush Hollow Reservoir, which can stimulate aquatic plant growth. A higher trophic level for Brush Hollow Reservoir also is indicated by the macrophyte beds that grow around the perimeter of the reservoir during early summer but are largely absent from Pueblo Reservoir.

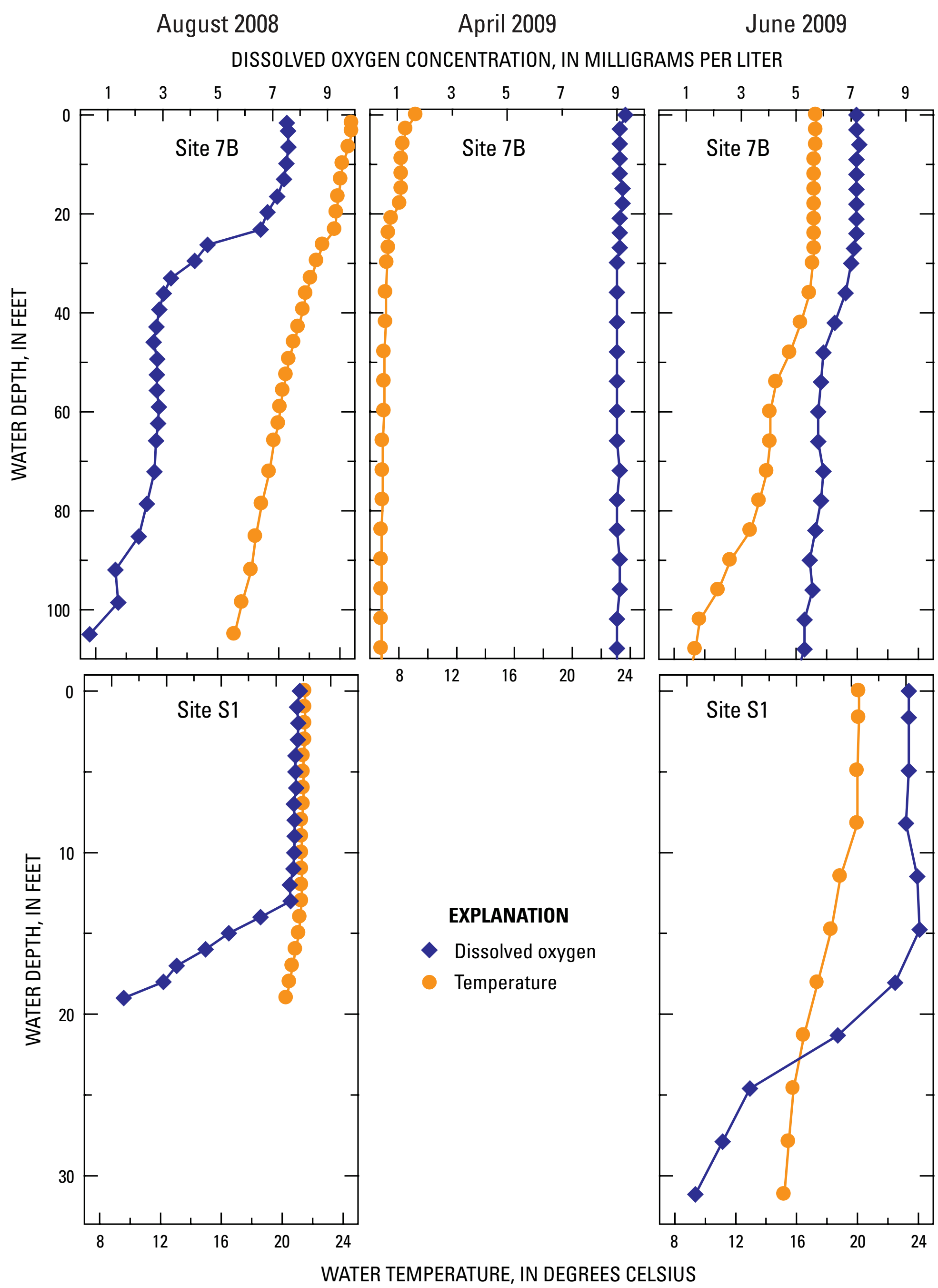


**Figure 4.** Dissolved oxygen and temperature profiles during 2008 and 2009 at site 7B in Pueblo Reservoir and site S1 in Brush Hollow Reservoir.

**Table 4.** Physical properties and dissolved constituent concentrations in water samples from Pueblo and Brush Hollow Reservoirs, Colorado.

[--, not applicable; °C, degress Celsius; µS/cm, microsiemens per centimeter at 25°C; TSI = 60 - 14.41 x ln (secchi depth x 0.3048); Concentrations in milligrams per liter; $CaCO_3$, calcium carbonate; N, nitrogen; <, less than; P, phosphorus]

| Property or constituent | Pueblo Reservoir Site 7B 08/05/2008 | | Pueblo Reservoir Site 4B 08/05/2008 | | Brush Hollow Reservoir Site S1 08/27/2008 | |
|---|---|---|---|---|---|---|
| | Epilimnion | Hypolimnion | Epilimnion | Hypolimnion | Epilimnion | Hypolimnion |
| Sampling depth, feet | 5 | 90 | 5 | 28 | 3 | 17 |
| Secchi depth, feet | 6.5 | -- | 4.5 | -- | 3.5 | -- |
| Water temperature, °C | 24.7 | 18.2 | 24.4 | 23.1 | 21.5 | 20.7 |
| Specific conductance, µS/cm | 282 | 242 | 273 | 286 | 369 | 373 |
| Oxygen, dissolved | 7.6 | 1.3 | 8.0 | 4.8 | 7.8 | 3.4 |
| pH, standard units | 8.52 | 8.11 | 8.61 | 8.30 | 8.69 | 8.29 |
| Trophic state index (TSI) | 50 | -- | 55 | -- | 59 | -- |
| Calcium, dissolved | 33.4 | 30.7 | 32.8 | 33.5 | 40.2 | 41.1 |
| Magnesium, dissolved | 8.1 | 6.3 | 7.9 | 8.1 | 7.9 | 7.9 |
| Sodium, dissolved | 10.7 | 7.6 | 10.5 | 10.9 | 22.7 | 22.8 |
| Potassium, dissolved | 1.7 | 1.4 | 1.7 | 1.7 | 2.5 | 2.5 |
| Chloride, dissolved | 4.1 | 2.7 | 3.8 | 3.9 | 5.0 | 5.0 |
| Sulfate, dissolved | 54.2 | 36.7 | 50.8 | 51.0 | 86.8 | 85.7 |
| Silica, dissolved | .4 | 6.7 | 1.5 | 2.5 | 10.0 | 10.6 |
| Alkalinity as $CaCO_3$ | 73.8 | 72.6 | 72.8 | 74.5 | 81.9 | 83.1 |
| Organic carbon, dissolved | 3.0 | 2.8 | 2.7 | 2.3 | 4.1 | 4.1 |
| Nitrate as N, dissolved | <.006 | .252 | <.006 | .021 | <.006 | <.006 |
| Total nitrogen as N, dissolved | .236 | .393 | .140 | .196 | .796 | .423 |
| Phosphorus as P, dissolved | <.006 | .014 | .008 | .006 | .006 | .005 |
| Orthophosphate as P, dissolved | .003 | .014 | .004 | .004 | <.006 | <.006 |

## Mercury in Surface Water

The range of methylmercury and total mercury concentrations measured in surface-water samples collected during the study are shown in table 5. Concentrations of methylmercury are particularly important because they are a key indicator of potential mercury exposure to aquatic organisms. Sample distribution differs somewhat between the two reservoirs because of the short duration and limited scope of this study as well as some missing methylmercury analyses, and the results need to be interpreted with some caution. In August 2008, methylmercury concentrations were below detection in all samples, and total mercury concentrations ranged narrowly from 0.53 to 0.70 ng/L, with the exception of a slightly elevated concentration (1.46 ng/L) in the deepest sample from site 7B in Pueblo Reservoir. Because concentrations were measured in unfiltered samples, the elevated total mercury concentration in the deep sample at Pueblo Reservoir in August 2008 may indicate a greater particulate fraction in the hypolimnetic water due to settling of particles from the overlying water column. During spring of 2009, concentrations of methylmercury and total mercury at the midlake sites at both reservoirs (7B and S1) were low, although methylmercury concentrations are not available for the Brush Hollow Reservoir samples collected in April 2009. Low methylmercury concentrations indicate very limited methylmercury production in the open water of both reservoirs, even during late summer when strong anoxic conditions develop in the hypolimnion.

Several additional water samples were collected from sites in and near Brush Hollow Reservoir during spring and early summer of 2009. Total mercury was measured in the supply ditch (S6) and Brush Hollow Creek (S8) to investigate other potential sources of mercury to the reservoir. The supply ditch derives water from the Beaver Creek drainage, which has headwater streams that extend into a historical mining district. The Brush Hollow Creek site, which is downstream from the reservoir, was sampled because thermal springs, which could be a potential geologic source of mercury, exist just upstream

**Table 5.** Mercury concentrations in water samples from Pueblo and Brush Hollow Reservoirs, Colorado.

[No., site number from fig. 1; MeHg, methylmercury in nanograms per liter; THg, total mercury in nanograms per liter; <, less than; --, not analyzed]

| No. | Site name | Sample date | Type | MeHg | THg |
|---|---|---|---|---|---|
| 4B | Pueblo Reservoir Site 4B | 08/05/2008 | Epilimnion | <0.04 | 0.55 |
| 4B | Pueblo Reservoir Site 4B | 08/05/2008 | Hypolimnion | <.04 | .67 |
| 7B | Pueblo Reservoir Site 7B | 08/05/2008 | Epilimnion | <.04 | .53 |
| 7B | Pueblo Reservoir Site 7B | 08/05/2008 | Hypolimnion | <.04 | 1.46 |
| S1 | Brush Hollow Reservoir Site S1 | 08/27/2008 | Epilimnion | <.04 | .60 |
| S1 | Brush Hollow Reservoir Site S1 | 08/27/2008 | Hypolimnion | <.04 | .70 |
| S1 | Brush Hollow Reservoir Site S1 | 04/23/2009 | Epilimnion | -- | .46 |
| S1 | Brush Hollow Reservoir Site S1 | 04/23/2009 | Hypolimnion | -- | .49 |
| 7B | Pueblo Reservoir Site Site 7B | 05/19/2009 | Epilimnion | <.04 | .41 |
| 7B | Pueblo Reservoir Site Site 7B | 05/19/2009 | Hypolimnion | <.04 | .40 |
| S1 | Brush Hollow Reservoir Site S1 | 06/25/2009 | Epilimnion | .05 | .60 |
| S6 | Brush Hollow Ditch | 04/23/2009 | Supply ditch | -- | 2.22 |
| S8 | Brush Hollow Creek At Hwy 50 | 04/23/2009 | Stream | -- | 1.29 |
| S7 | Brush Hollow Reservoir Nr Boat Ramp | 05/19/2009 | Shore | .16 | 2.84 |
| S7 | Brush Hollow Reservoir Nr Boat Ramp | 06/25/2009 | Shore | .09 | 1.01 |

from the sampling site. Total mercury concentrations at these two sites were slightly higher than in the reservoir water, but concentrations were still quite low, indicating inputs from land-use activities (mining) or geologic sources (springs) likely are small. Methylmercury concentrations are not available for any of the April 2009 samples due to a miscommunication with the laboratory. Two samples of reservoir water also were collected near the shoreline (site S7) in May and June 2009. Both of these samples had higher total mercury concentrations than the midlake samples from site S1 and, more importantly, both samples had detectable methylmercury concentrations, which accounted for as much as 8 percent of the total mercury. Several explanations are possible for higher methylmercury in these samples, although the limited amount of data makes interpretation difficult. Because the samples were collected near the shoreline and were unfiltered, elevated methylmercury could result from a greater particulate fraction caused by suspension of sediments by wave action in shallow areas. Another possibility is that higher methylmercury in these samples might indicate enhanced production of methylmercury in sediments in near-shore areas.

## Mercury in Reservoir Bottom Sediment

Total mercury concentrations in bottom sediment ranged from 23.1 to 52.2 ng/g and methylmercury concentrations ranged from 0.14 to 1.30 ng/g in the samples from August 2008 (table 6). Despite higher fish-tissue mercury in Brush Hollow Reservoir, the median total mercury concentration in sediment from Pueblo Reservoir (45.8 ng/g) was nearly twice that for Brush Hollow Reservoir (26.0 ng/g), and the median methylmercury concentration in sediment from Pueblo Reservoir (0.68 ng/g) was more than 3 times that for Brush Hollow Reservoir (0.19 ng/g). Mercury concentrations in bottom sediment from both study reservoirs were similar to those reported for stream sediments collected from across the U.S. (Scudder and others, 2009). Stream sediments in unmined basins had a median total mercury concentration of 30.3 ng/g with 75 percent of sites less than 80 ng/g and a median methylmercury concentration of 0.51 ng/g with 75 percent of sites less than 2 ng/g (Scudder and others, 2009). By contrast, concentrations were substantially higher in a historical gold-mining area in California, where the median total mercury concentration in stream sediment was around 1,000 ng/g (Alpers and others, 2005). The ratios of methylmercury to total mercury concentrations in Brush Hollow and Pueblo bottom sediments ranged from 0.006 to 0.021, with the exception of the sample from site 4B, which had a higher ratio of 0.055 owing to a comparatively low total mercury concentration (table 6). The sample from site 4B was collected at the shoreline of Pueblo Reservoir and might have a greater influence from local geologic inputs compared to sediments collected on the reservoir bottom.

Patterns of mercury concentrations in bottom sediment in the two reservoirs differed as a function of water depth at the sampling site (fig. 5). In Brush Hollow Reservoir, methylmercury concentrations increase with increasing water depth with a maximum value at the deepest point of the reservoir near the

**Table 6.** Mercury concentrations in reservoir-bottom sediments from Pueblo and Brush Hollow Reservoirs, Colorado.

[No., site number in figure 1; ng/g, nanograms per gram dry weight]

| No. | Site name | Collect date | Methylmercury (ng/g) | Total mercury (ng/g) | Ratio of methylmercury to total mercury | Organic carbon (percent) |
|---|---|---|---|---|---|---|
| 7B | Pueblo Reservoir 7B | 08/06/2008 | 0.61 | 49.1 | 0.012 | 10.5 |
| 6C | Pueblo Reservoir 6C | 08/06/2008 | .53 | 45.8 | .012 | 9.9 |
| 5C | Pueblo Reservoir 5C | 08/06/2008 | .68 | 40.0 | .017 | 9.7 |
| 4B | Pueblo Reservoir 4B | 08/06/2008 | 1.30 | 23.6 | .055 | 9.4 |
| 3B | Pueblo Reservoir 3C | 08/06/2008 | 1.10 | 52.2 | .021 | 10.5 |
| | **Median concentration** | | **.68** | **45.8** | **.017** | **9.9** |
| | | | | | | |
| S1 | Brush Hollow Reservoir S1 | 08/27/2008 | .54 | 34.5 | .016 | 10.8 |
| S2 | Brush Hollow Reservoir S2 | 08/27/2008 | .32 | 34.9 | .009 | 11.3 |
| S3 | Brush Hollow Reservoir S3 | 08/27/2008 | .16 | 26.0 | .006 | 9.6 |
| S4 | Brush Hollow Reservoir S4 | 08/27/2008 | .14 | 24.6 | .006 | 9.7 |
| S5 | Brush Hollow Reservoir S5 | 08/27/2008 | .19 | 23.1 | .008 | 9.0 |
| | **Median concentration** | | **.19** | **26.0** | **.008** | **9.7** |

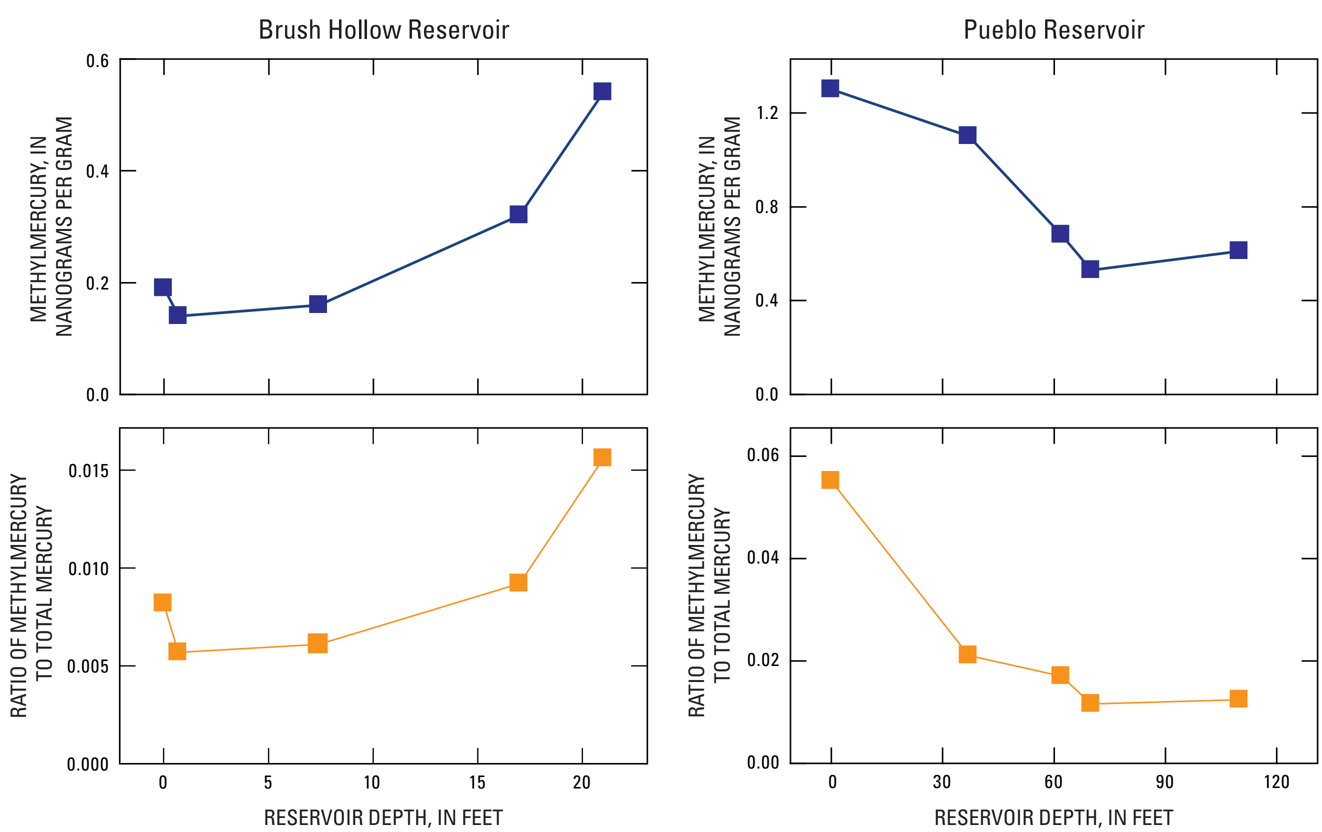


**Figure 5.** Relation of methylmercury and the ratio of methylmercury to total mercury concentrations with water depth for reservoir-bottom sediments collected during August 2008 in Pueblo and Brush Hollow Reservoirs.

dam. The ratio of methylmercury to total mercury showed a similar pattern indicating the anoxic conditions in deeper parts of the reservoir might enhance methylmercury production in sediments. Sediment in Pueblo Reservoir showed the opposite pattern with the lowest methylmercury concentrations and ratios of methylmercury to total mercury in the deepest part of the reservoir where oxygen concentrations are most depleted (fig. 5). The opposite pattern might result from the location of primary inflow sources relative to sampling sites. The main inflow to Pueblo Reservoir is from the Arkansas River that enters at the shallow end of the reservoir, whereas the main inflow to Brush Hollow Reservoir is from a ditch that enters the reservoir near the dam (fig. 1). Inputs of organically bound mercury from the inflows could increase the amount of mercury available for methylation (Wiener and others, 2006). Additionally, greater amounts of organic material in sediments deposited in areas closer to inflow sources could provide carbon for sulfate reduction, contributing to increased methylmercury production in these areas.

## Mercury in Zooplankton

Zooplankton samples were collected in both reservoirs during August 2008 to compare mercury in biota at the bottom of the food chain. Total mercury concentrations in zooplankton ranged from 19.7 to 42.8 ng/g and methylmercury concentrations ranged from 11.7 to 19.2 ng/g (fig. 6). These values are at the low end of concentrations reported for temperate lakes in the northeastern United States (Driscoll and others, 2007).

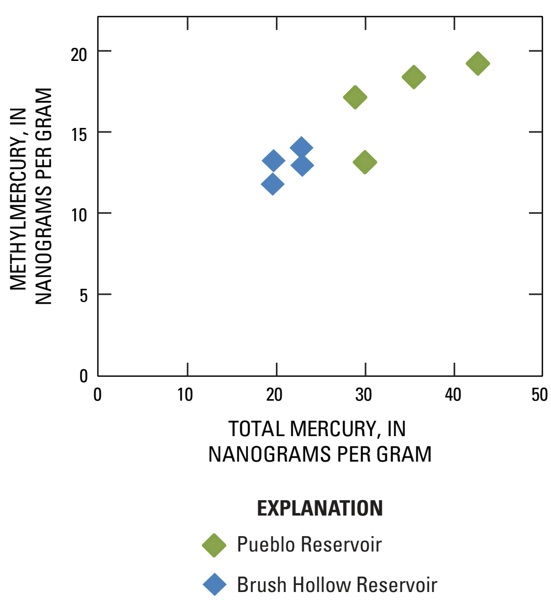


**Figure 6.** Relation between total mercury concentrations and methylmercury concentrations in zooplankton samples collected from Pueblo and Brush Hollow Reservoirs during August 2008.

Methylmercury accounted for about 61 percent of total mercury in zooplankton samples from Brush Hollow Reservoir and 50 percent in samples from Pueblo Reservoir collected during late summer. Despite higher mercury in fish at Brush Hollow Reservoir, mercury concentrations in zooplankton were higher in Pueblo Reservoir at the time of sampling, although the percentage of methylmercury was slightly higher at Brush Hollow Reservoir. The low concentrations and lack of substantial difference in concentrations between the reservoirs likely reflects the timing of sampling. Large variations in zooplankton mercury concentrations have been reported for a snowmelt-dominated reservoir in California with methylmercury concentrations in spring nearly an order of magnitude greater than during fall and winter (Stewart and others, 2008), indicating zooplankton concentrations in the study reservoirs might be different during other seasons of the year.

## Sediment-Incubation Experiments

Measurement of methylmercury production rates is one potentially effective way to reveal the influence of sediment quality across differing systems on methylmercury abundance (Marvin-DiPasquale and others, 2009). In this study, laboratory experiments were conducted to compare the methylation potential of littoral sediments from the two study reservoirs. The experiments involved incubating sediment cores collected at the shoreline with reservoir water and periodically monitoring methylmercury concentrations in the water column over a period of several weeks. A spike of inorganic mercury-201 was added to the water to monitor the production of methylmercury during the incubations.

Changes in methylmercury concentrations relative to duration of the experiment in days are presented in figure 7 for the three sediment cores collected from each reservoir. The sample at day 0 is the methylmercury concentration in the spiked water sample for both the mercury-201 tracer and the ambient mercury that was contained in the surface water at the time of sampling. For all the incubations, the fastest rate of accumulation of ambient methylmercury occurred during the first two weeks of the experiment. For ambient methylmercury, the Brush Hollow Reservoir incubations yielded considerably more methylmercury (about 4 to 10 times) than those of the Pueblo Reservoir (fig. 7), although appreciable variability is exhibited among individual Brush Hollow samples. The initial increase in aqueous methylmercury indicates that either methylmercury contained in the sediment cores was released to the overlying solution or that wetting stimulated methylmercury production in the sediment, which then diffused into the water column. Like ambient methylmercury, methylmercury-201 showed a rapid appearance during the first two weeks of the experiment, especially for the Brush Hollow samples (see bottom panels of fig. 7), which have about 2 times greater methylmercury-201 at any particular time during the experiment. The appearance of methylmercury-201 in solution is direct evidence that these sediments support the

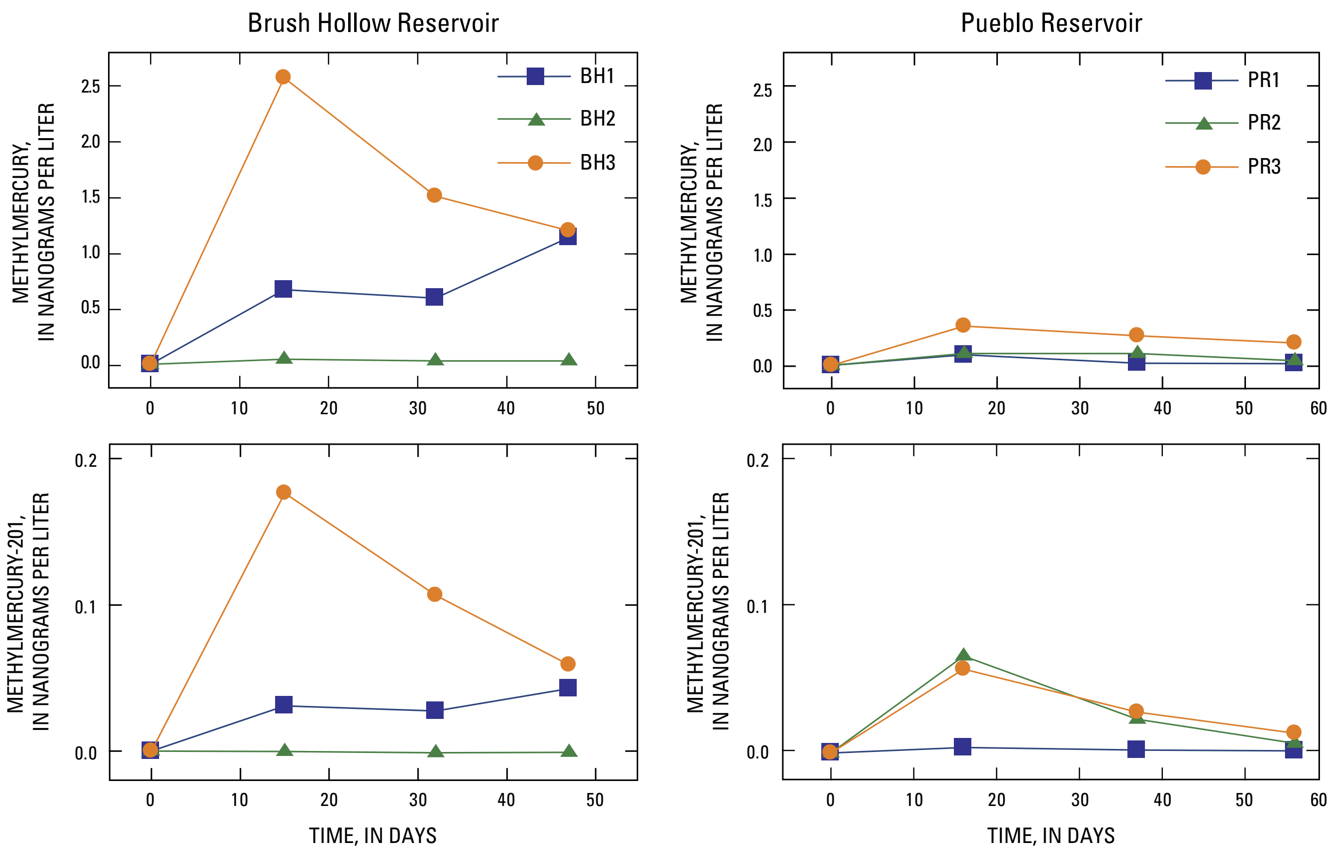


**Figure 7.** Methylmercury concentration relative to duration of the experiment in days for the sediment-incubation experiments.

methylation process because the isotopic tracer was added as inorganic mercury. For the most part, the methylmercury-201 production profiles mirrored those of the ambient methylmercury, supporting the notion that the observed ambient methylmercury production profiles reflect newly produced methylmercury, as opposed to previously existing methylmercury contained in the sediment at the time of sampling. Even though the sediments were exposed (above the water level) when they were collected, some methylmercury was produced once they were rewetted, indicating that drying of sediments did not inhibit methylation upon rewetting. In fact, other studies have shown that drying and rewetting of soils may actually stimulate methylation (Gilmour, 2003). Based on the incubation results, the near-shore sediments from Brush Hollow Reservoir appear to have a substantially greater potential (about 2–10 times) to yield methylmercury to the water column than those from Pueblo Reservoir when reflooding occurs. The difference in experimental results from these two reservoirs seems largely to be explained by the greater organic carbon content of the sediments from Brush Hollow. Overall, a strong positive correlation was found between the maximum methylmercury concentration observed from each experiment and the organic carbon content of the sediment ($r^2 = 0.86$) (fig. 8). It is interesting to note that all the experiments (with the exception of core BH1) showed decreasing or steady methylmercury

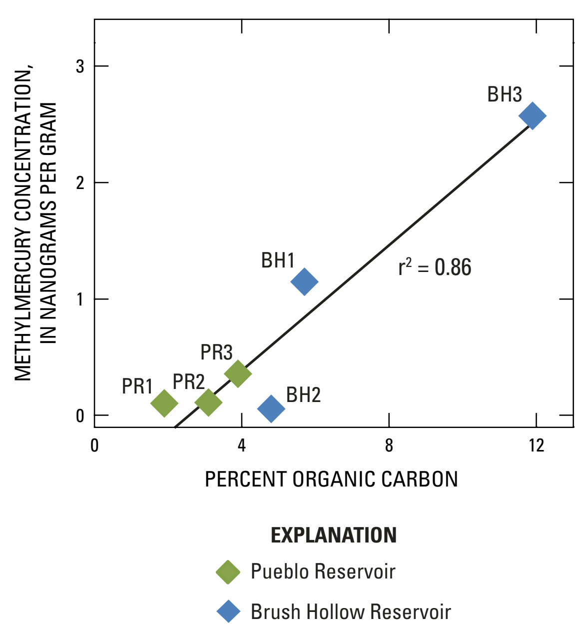


**Figure 8.** Relation between maximum methylmercury concentration in water and organic-carbon content of cores in sediment-incubation experiments.

concentrations during the latter part of the experiment. These time profiles indicate that the net methylmercury production declined and(or) ceased after about two weeks or that de-methylation of methylmercury accelerated over the time span of the experiment and eventually exceeded production after about two weeks.

## Factors Affecting Bioaccumulation of Mercury

One factor that can cause elevated mercury concentrations in fish is a larger mercury input from point-source discharges related to mining or urban activities or from elevated rates of atmospheric deposition (Evers and others, 2007). No industrial point sources or large urban centers exist in either of the reservoir watersheds; however, both drainage areas are affected by historical mining activities. Mining in the headwaters of Beaver Creek primarily was for gold; however, due to the nature of the ore, the gold was not reclaimed by amalgamation with mercury (*http://ccvgoldmining.com/Geology/geology.html*, accessed January 2010). The headwaters area of the Arkansas River primarily was mined for silver and, aside from one large placer deposit near Leadville, gold mining activities were limited to small placer deposits and prospects (Emmons and others, 1927; Parker, 1974). These descriptions indicate historical mining is not a major source of mercury to the study reservoirs. In addition, mercury concentrations in bottom sediments collected at each reservoir were relatively low (fig. 5), particularly when compared to sediment concentrations in mining-affected areas (Alpers and others, 2005). Thermal springs along the Arkansas River valley also were ruled out as a potential mercury source on the basis of low mercury concentration in Brush Hollow Creek at site S8 (table 5).

Given that geologic and point sources of mercury probably are minor, atmospheric deposition appears to be the dominant source of mercury accumulating in the study reservoirs. Due to the proximity of the reservoirs and the importance of regional or even global mercury sources in controlling deposition patterns (Selin and Jacob, 2008), current atmospheric deposition probably does not vary sufficiently to account for differences in fish-tissue mercury. Therefore, water-quality and (or) landscape characteristics are likely the main factors controlling bioaccumulation of mercury in the study reservoirs (Wiener and others, 2006).

Recent studies have identified several water-quality characteristics associated with elevated fish mercury, most notably pH, alkalinity, sulfate, and DOC (Chen and others, 2005). In the Northeastern United States, lakes with low pH (less than 6.0) and low alkalinity (less than 5 mg/L) tend to have elevated fish-tissue mercury levels (Driscoll and others, 2007). This does not fit the pattern for the study reservoirs, both of which have pH values above 8 and alkalinities over 70 mg/L. Sulfate has a more complicated response on mercury methylation (Wiener and others, 2003). In low-sulfate systems, added sulfate will stimulate methylation; however, in systems with high sulfate, the accumulation of sulfide (the byproduct of sulfate reduction) can inhibit methylmercury production (Gilmour and others, 1992; Benoit and others, 1999). Gilmour (2003) reported that, in the Everglades, sulfate concentrations between 1 and 10 mg/L were optimal for methylation and concentrations above 50 mg/L inhibited methylmercury production due to sulfide accumulation in pore water. The high sulfate concentrations (36.7 to 86.8 mg/L; table 4) in water in the study reservoirs indicate that high sulfate conditions are not likely a limiting factor in methylmercury production in the study reservoirs.

In temperate lakes, the strongest correlation with fish mercury typically is with DOC, which often is attributed to runoff from adjacent wetlands, as they are active areas of methylmercury production (Wiener and others, 2006). However, neither study reservoir has adjoining wetlands, indicating that DOC and methylmercury inputs from wetland sources are not influencing factors. DOC concentrations in reservoir water samples were slightly higher in Brush Hollow Reservoir than Pueblo Reservoir during August 2008 (table 4), perhaps reflecting differences in primary production. DOC can enhance the solubility and production of methylmercury but also can bind with methylmercury and reduce its bioavailability (Driscoll and others, 2007; Gorski and others, 2008). The relation between DOC and methylmercury in lakes is not always clear, especially at low concentrations (<5 mg/L). Wisconsin seepage lakes (Watras and others, 1995) show little relation between DOC and methylmercury in low-DOC lakes; whereas, high-elevation lakes across the Western United Stated reveal a positive relation (Krabbenhoft and others, 2002). This general lack of concurrence prevents us from concluding that accumulation of DOC is the main factor controlling differences in fish-tissue mercury concentrations between the study reservoirs and points to the need for more work to answer this question.

Nutrient enrichment of lakes and reservoirs also has been correlated with lower mercury levels in fish (Chen and others, 2005). This correlation is thought to occur as a result of algal blooms in productive water bodies, which reduce mercury in the food chain through the process of biodilution (Pickhardt and others, 2002). The water-quality results from August 2008 showed the opposite pattern, with higher fish mercury in the more productive reservoir (Brush Hollow), indicating that nutrient enrichment is not a major factor unless plankton growth and nutrient inputs are vastly different during other times of the year. A previous study of Pueblo Reservoir showed that phytoplankton production peaked during mid- to late summer (Lewis and Edelmann, 1994), indicating that the August results are representative of trophic conditions during the growing season.

The potential for methylmercury production may be increased in reservoirs and lakes that undergo stratification and development of anoxic conditions in the hypolimnion (Canavan and others, 2000). Buildup of methylmercury in anoxic layers can occur as a result of transformation of inorganic mercury by sulfate-reducing bacteria living in the water column or can diffuse from bottom sediments to the overlying water column (Watras and others, 2005). Anoxic conditions in the hypolimnion may also decrease rates of demethylation resulting in a net increase in methylmercury concentrations in the water column (Canavan and others, 2000). In the study reservoirs, anoxic conditions developed in the hypolimnion in midsummer, with dissolved oxygen concentrations below 4 mg/L in the deepest areas of the reservoirs (fig. 4). Methylmercury concentrations in hypolimnetic water were not detectable even during late summer (table 5), indicating stratification was not a major factor in methylmercury production or availability in either reservoir. The reason for low concentrations of methylmercury in the hypolimnion is not clear but could be related to sediment characteristics. In high-productivity reservoirs or lakes, for example, sediments may have higher levels of organic matter, which can bind inorganic mercury thus reducing the amount available for methylation (Hammerschmidt and Fitzgerald, 2004). Methylmercury production also can be inhibited in sediments with high levels of sulfide resulting from high rates of sulfate reduction (Wiener and others, 2003).

Given that water-quality characteristics do not appear to provide a clear explanation for differences in fish mercury, reservoir characteristics or water levels or both, may be plausible factors. The occurrence of elevated fish-tissue mercury concentrations in newly created reservoirs due to the initial flooding of terrestrial soils has been well established (Bodaly and others, 2007); however, a similar response has been observed for water bodies that are subject to periodic water-level fluctuations (Sorensen and others, 2005; Selch and others, 2007). One explanation is that declining water levels allow the growth of vegetation on exposed littoral areas, which then become a new carbon source when the sediments are reflooded, promoting increased microbial activity and methylmercury production. An alternate explanation is that drying of soils and sediments results in oxidation of reduced sulfur to sulfate which, when rewetted, stimulates sulfate-reducing bacteria and methylmercury production (Gilmour, 2003).

Although both study reservoirs experience annual fluctuations in storage, the overall change typically is much greater in Brush Hollow Reservoir than Pueblo Reservoir (fig. 2). Moreover, due to the shallow depth of Brush Hollow Reservoir, fluctuations in water level likely result in proportionally larger areas of exposed shoreline compared to Pueblo Reservoir, which is deep and steep sided. To evaluate this possible factor, the change in reservoir surface area (SA) resulting from annual water-level fluctuations was estimated by using Landsat 5 satellite imagery (*http://landsat.usgs.gov/*, accessed March 2010) and tools in a geographic information system (GIS). Percent change in SA was computed as SA at maximum stage minus SA at the previous minimum stage divided by the SA at maximum stage. Percent SA change was computed for each of the 3 years prior to the CDPHE fish sampling, which occurred in October 2004. In Brush Hollow Reservoir, SA changed by 54 to 67 percent over the 3-year period compared to 20 to 29 percent for Pueblo Reservoir (fig. 9). These results fit the pattern of higher fish mercury concentrations in Brush Hollow Reservoir with a greater area of exposed shoreline resulting from larger annual water-level fluctuations compared to Pueblo Reservoir.

Another factor that may affect methylmercury production in reflooded areas is the nature of the littoral sediments. Steep-sided reservoirs with organic-poor substrates can be expected to display less efficient methylmercury production than reservoirs with wide basins and large littoral areas with more organic matter (Evers and others, 2007). Shallow sediments in Brush Hollow Reservoir are rich in organic matter, particularly at the north end of the reservoir where macrophytes are present (fig. 10*A*). Moreover, because drawdown typically occurs by July (fig. 2), terrestrial plants have ample opportunity during the growing season to revegetate exposed littoral areas (note grassy areas in figure 10*A–B*). By contrast, the shoreline of Pueblo Reservoir is rocky with little organic matter and limited vegetation (fig. 10*C–D*). In addition, water levels typically reach a minimum after the growing season, providing less opportunity for regrowth of plants. The importance of organic content of littoral sediments for methylmercury production is supported by the results from the sediment-incubation experiments (fig. 7). For littoral sediments from Pueblo Reservoir, methylmercury production was uniformly low in all three incubations, whereas two of the sediment samples from Brush Hollow Reservoir produced considerably higher methylmercury concentrations. These simple experiments seem to support the hypothesis that the more organic-rich sediments in Brush Hollow Reservoir have a greater potential for methylmercury production; however, sediment-water interactions and redox conditions in the laboratory may be very different than conditions in the field and the results need to be interpreted with some caution. More extensive temporal and spatial studies of methylmercury in reservoir and sediment-pore water are needed to better understand the role of water-level manipulations on bioaccumulation of mercury in these Colorado reservoirs.

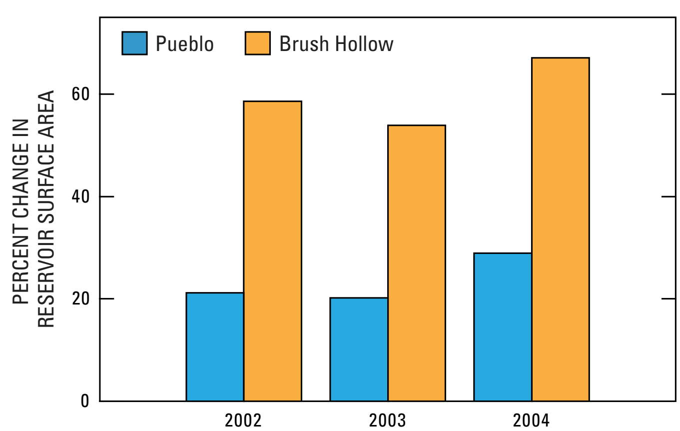


**Figure 9.** Percent change in reservoir surface area between annual minimum and maximum water level in Pueblo and Brush Hollow Reservoirs during 2002–2004.

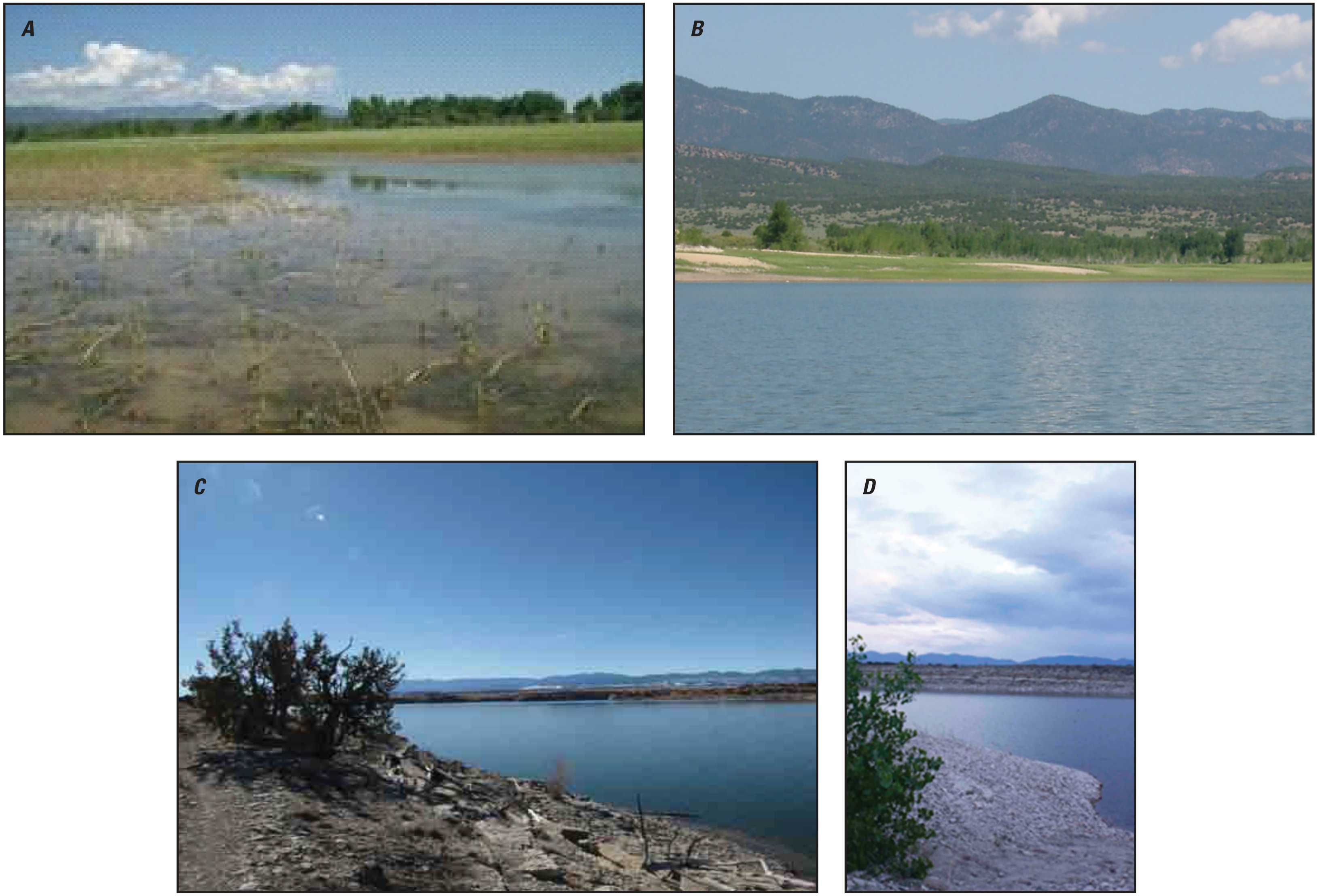


**Figure 10.** (*A*) Submerged macrophytes and (*B*) grass-covered littoral zone at north end of Brush Hollow Reservoir in late summer 2008, and (*C–D*) typical rocky shoreline at Pueblo Reservoir. Tree line in (*A*) and (*B*) delineates water level at maximum storage at Brush Hollow Reservoir.

# Summary

In 2004, the Colorado Department of Public Health and Environment (CDPHE) initiated a 5-year study to test fish tissue for mercury in water bodies across the State. Of the water bodies tested, nearly one-quarter had fish with mercury concentrations that exceeded the Colorado fish-tissue criterion for the protection of human health. As a result of the tissue study, the U.S. Geological Survey, in cooperation with the CDPHE, conducted a study to investigate environmental factors that may contribute to the bioaccumulation of mercury in two Front Range reservoirs. One of the reservoirs, Brush Hollow Reservoir, has a fish-consumption advisory for mercury in walleye (*Stizostedion vitreum*), and the other, Pueblo Reservoir, does not. This report compares mercury concentrations in water, bottom sediment, and zooplankton samples collected at the two reservoirs during 2008 and 2009, presents results from a sediment-incubation study conducted in 2009, and evaluates factors that may be affecting bioaccumulation of mercury in fish.

Methylmercury concentrations in water from the two study reservoirs were below detection in all August 2008 samples, and total mercury showed a very narrow range (0.53 to 0.70 ng/L) with the exception of a slightly elevated concentration (1.46 ng/L) in the deepest sample from Pueblo Reservoir. During spring of 2009, water from the midlake sites at both reservoirs had low concentrations of methylmercury and total mercury. Two water samples from Brush Hollow Reservoir also were collected near the shoreline in May and June 2009. Both of these samples had higher total mercury concentrations than the midlake samples and had detectable methylmercury concentrations, which accounted for as much as 8 percent of the total mercury.

Mercury concentrations in reservoir bottom sediments were similar to those reported for stream sediments from unmined basins across the United States. Bottom-sediment total mercury concentrations ranged from 23.1 to 52.2 ng/g, and methylmercury concentrations ranged from 0.14 to 1.3 ng/g. Despite higher fish-tissue mercury in Brush Hollow Reservoir, the median total mercury concentration in bottom sediment in Pueblo Reservoir was nearly twice that in Brush Hollow Reservoir, and the median methylmercury sediment concentration in Pueblo Reservoir was more than 3 times that in Brush Hollow Reservoir. Total mercury in zooplankton ranged from 19.7 to 42.8 ng/g, and methylmercury concentrations ranged from 11.7 to 19.2 ng/g. Methylmercury accounted for about 61 percent of total mercury in Brush Hollow Reservoir samples and 50 percent in Pueblo Reservoir samples during late summer. The similarity in zooplankton concentrations between sites is attributed to the timing of sampling. Mercury concentrations in zooplankton during other seasons may be very different.

Results of the sediment-incubation experiments showed higher methylmercury production for littoral sediments from Brush Hollow Reservoir compared to Pueblo Reservoir. The higher methylmercury production from sediments from Brush Hollow might result from the higher organic carbon content in the sediments.

Results of the study were used to evaluate factors that can affect bioaccumulation of mercury including mercury sources, water chemistry, and reservoir characteristics. Atmospheric deposition appears to be the dominant source of mercury; however, owing to the proximity of the reservoirs, deposition rates likely are similar in the two study areas. Several water-quality characteristics associated with elevated fish mercury (pH, alkalinity, sulfate, and dissolved organic carbon) were evaluated but did not provide clear explanations for differences between the reservoirs. Nutrient enrichment can result in diminished mercury accumulation in fish through biodilution; however, the opposite pattern was observed at the study sites with higher fish mercury in the more productive of the two reservoirs (Brush Hollow). Development of anoxic conditions in the hypolimnion during summer also did not appear to enhance methylmercury production in either reservoir. Water-level fluctuations and shoreline characteristics appear to best explain differences in fish-tissue mercury concentrations between the reservoirs. Due to the shallow depth of Brush Hollow Reservoir and the large annual water-level fluctuations, proportionally larger areas of shoreline are subjected to annual reflooding compared to Pueblo Reservoir. Moreover, macrophytes and regrowth of terrestrial vegetation likely increase the organic content of Brush Hollow Reservoir sediments, which may stimulate methylmercury production in reflooded sediments. Results of a laboratory incubation experiment are consistent with this hypothesis, showing higher methylmercury production for the near-shore sediments from Brush Hollow Reservoir than those from Pueblo Reservoir.

# References

Alpers, C.N., Hunerlach, M.P., May, J.T., Hothem, R.L., Taylor, H.E., Antweiler, R.C., De Wild, J.F., and Lawler, D.A., 2005, Geochemical characterization of water, sediment, and biota affected by mercury contamination and acidic drainage from historical gold mining, Greenhorn Creek, Nevada County, California, 1999–2001: U.S. Geological Survey Scientific Investigations Report 2004–5251, 278 p.

Benoit, J.M., Gilmour, C.G., Mason, R.P., and Heyes, A., 1999, Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore saters: Environmental Science and Technology, v. 33, p. 951–957.

Bodaly, R.A., Jansen, W.A., Majewski, A.R., Fudge, R.J.P., Strange, N.E., Derksen, A.J., and Green, D.J., 2007, Postimpoundment time course of increased mercury concentrations in fish in hydroelectric reservoirs of northern Manitoba, Canada: Archives of Environmental Contamination Toxicology, v. 53, no. 3, p. 379–389.

Bureau of Reclamation, 1972, Pueblo Dam and Reservoir final environmental impact statement: Denver, Final Environmental Statement FES–72–16, 81 p.

Bureau of Reclamation, 1977, Pueblo Reservoir area-capacity tables and curves: Denver, Colorado, U.S. Department of the Interior, Fryingpan-Arkansas Project, Colorado.

Canavan, C.M., Caldwell, C.A., and Bloom, N.S., 2000, Discharge of methylmercury-enriched hypolimnetic water from a stratified reservoir: The Science of the Total Environment, v. 260, p. 159–170.

Carlson, R.E., 1977, A trophic state index for lakes: Limnology and Oceanography, v. 22, no. 2, p. 361–369.

Chen, C.Y., Stemberger, R.S., Kamman, N.C., Mayes, B.M., and Folt, C.L., 2005, Patterns of mercury bioaccumulation and transfer in aquatic food webs across multi-lake studies in the northeast US: Ecotoxicology, v. 14, p. 135–147.

DeWild, J.F., Olson, M.L., and Olund, S.D., 2001, Determination of methyl mercury by aqueous phase ethylation followed by gas chromatographic separation with cold vapor atomic fluorescence detection: U.S. Geological Survey Open-File Report 2001–445, 14 p.

DeWild, J.F., Olund, S.D., Olson, M.L, and Tate, M.T., 2004, Methods for the preparation and analysis of solids and suspended solids for methylmercury: U.S. Geological Survey Techniques and Methods, book 5, chap. A7, 13 p.

Driscoll, C.T., Blette, V., Yan, C., Schofield, C.L., Munson, R., and Holsapple, J., 1995, The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack lakes: Water, Air, and Soil Pollution, v. 80, no. 1–4, p. 499–508.

Driscoll, C.T., Han, Y.J., Chen, C.Y., Evers, D.C., Lambert, K.F., Holsen, T.M., Kamman, N.C., and Munson, R.K., 2007, Mercury contamination in forest and freshwater ecosystems in the northeastern United States: BioScience, v. 57, p. 17–28.

Emmons, S.F., Irving, J.D., and Loughlin, G.F., 1927, Geology and ore deposits of the Leadville mining district, Colorado: U.S. Geological Survey Professional Paper 148, 368 p.

Evers, D.C., Han, Y.J., Driscoll, C.T., Kamman, N.C., Goodale, W.M., Lambert, K.F., Holsen, T.M., Chen, C.Y., Clair, T.A., and Butler, T.J., 2007, Biological mercury hotspots in the Northeastern United States and Southeastern Canada: BioScience, v. 57, p. 1–15.

Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

Galloway, J.M., Ortiz, R.F., Bales, J.D., and Mau, D.P., 2008, Simulation of hydrodynamics and water quality in Pueblo Reservoir, southeastern Colorado, for 1985 through 1987 and 1999 through 2002: U.S. Geological Survey Scientific Investigations Report 2008–5056, 87 p.

Gilmour, C.C., Henry, E.A., and Mitchell, R., 1992, Sulfate stimulation of mercury methylation in freshwater sediments: Environmental Science and Technology, v. 26, p. 2281–2287.

Gilmour, C.C., 2003, Status report on the effect of water quantity and quality on methylmercury production: Everglades Consolidated Report. Appendix 2B–2, *https://my.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_sfer/portlet_prevreport/ecr2003/appendices/app2b-2.pdf*, accessed January 2010.

Gorski, P.R., Armstrong, D.E., Hurley, J.P., and Krabbenhoft, D.P., 2008, Influence of natural dissolved organic carbon on the bioavailability of mercury to a freshwater alga: Environmental Pollution, v. 154, p. 116–123.

Hammerschmidt, C.R., and Fitzgerald, W.F., 2004, Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments: Environmental Science and Technology, v. 38, no. 5, p. 1487–1495.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 2254, 263 p.

Kolka, R.K., Grigal, D.F., Verry, E.S., and Nater, E.A., 1999, Mercury and organic carbon relationships in streams draining forested upland/peatland watersheds: Journal of Environmental Quality, v. 28, p. 766–775.

Krabbenhoft, D.P., Olson, M.L., Dewild, J.F., Clow, D.W., Striegl, R.S., Dornblaser, M.M., and VanMetre, Peter, 2002, Mercury loading and methylmercury production and cycling in high-altitude lakes from the western United States: Water, Air and Soil Pollution Focus, v. 2, p. 233–249.

Lewis, M.E., and Edelmann, P.R., 1994 Physical, chemical, and biological characteristics of Pueblo Reservoir, Colorado, 1985–89: U.S. Geological Survey Water-Resources Investigations Report 94–4097, 71 p.

Marvin-DiPasquale, M., Lutz, M.A., Brigham, M.E., Krabbenhoft, D.P., Aiken, G.R., Orem, W.H., and Hall, B.D., 2009, Mercury cycling in stream ecosystems. 2. Benthic methylmercury production and bed sediment pore-water partitioning: Environmental Science and Technology, v. 43, p. 2726–2732.

Olund, S.D., DeWild, J.F., Olson, M.L., and Tate, M.T., 2004, Methods for the preparation and analysis of solids and suspended solids for total mercury: U.S. Geological Survey Techniques and Methods, book 5, chap. A8, 23 p.

Parker, B.H., Jr., 1974, Gold placers of Colorado: Golden, Quarterly of the Colorado School of Mines, v. 69, no. 3, 268 p.

Pickhardt, P.C., Folt, C.L., Chen, C.Y., Klaue, B., and Blum, J.D., 2002, Algal blooms reduce the uptake of toxic methylmercury in freshwater food webs: Proceedings of the National Academy of Sciences, v. 99, p. 4419–4423.

Scott, G.R., Taylor, R.B., Epis, R.C., and Wobus, R.A., 1978, Geologic map of the Pueblo 1 degree x 2 degrees quadrangle, south-central Colorado: U.S. Geological Survey Miscellaneous Investigations Series Map I–1022, scale: 1:250,000.

Scudder, B.C., Chasar, L.C., Wentz, D.A., Bauch, N.J., Brigham, M.E., Moran, P.W., and Krabbenhoft, D.P., 2009, Mercury in fish, bed sediment, and water from streams across the United States, 1998–2005: U.S. Geological Survey Scientific Investigations Report 2009–5109, 75 p.

Selch, T.M., Hoagstrom, C.W., Weimer, E.J., Duehr, J.P., and Chipps, S.R., 2007, Influence of fluctuating water levels on mercury concentrations in adult walleye: Bulletin of Environmental Contamination and Toxicology, v. 79, no. 1, p. 36–40.

Selin, N.E., and Jacob, D.J., 2008, Seasonal and spatial patterns of mercury wet deposition in the United States—Constraints on the contribution from North American anthropogenic sources: Atmospheric Environment, v. 42, p. 5193–5204.

Sorensen, J.A., Kallemeyn, L.W., and Sydor, M., 2005, Relationship between mercury accumulation in young-of-the-year yellow perch and water-level fluctuations: Environmental Science and Technology, v. 39, p. 9237–9243.

St. Louis, V.L., Rudd, J.W.M., Kelly, C.A., Beaty, K.G., Bloom, N.S., and Flett, R.J., 1994, Importance of wetlands as sources of methylmercury to boreal forest ecosystems: Canadian Journal of Fisheries and Aquatic Science, v. 51, p. 1065–1076.

Stewart, A.R., Saiki, M.K., Kuwabara, J.S., Alpers, C.N., Marvin-DiPasquale, M., and Krabbenhoft, D.P., 2008, Influence of plankton mercury dynamics and trophic pathways on mercury concentrations of top predator fish of a mining-impacted reservoir: Canadian Journal of Fisheries and Aquatic Sciences, v. 65, no. 11, p. 2351–2366.

U.S. Environmental Protection Agency, 1997, Mercury study report to Congress: United States Environmental Protection Agency, EPA-452–97–003, Office of Air and Radiation, Washington, D.C., 1,980 p.

U.S. Environmental Protection Agency, 2002, Method 1631 Revision E—Mercury in water by oxidation, purge, and trap, and cold vapor atomic fluorescence spectrometry: United States Environmental Protection Agency, EPA–821–R–02–019, 38 p.

Watras, C.J., Morrison, K.A., Host, K., and Bloom, N.S., 1995, Concentration of mercury species in relationship to other site-specific factors in the surface waters of northern Wisconsin lakes: Limnology and Oceanography, v. 40, p. 556–565.

Watras, C.J., Morrison, K.A., Kent, A., Price, N., Regnell, O., Eckley, C., Hintelmann, H., and Hubacher, T., 2005, Sources of methylmercury to a wetland-dominated lake in northern Wisconsin: Environmental Science and Technology, v. 39, no. 13, p. 4747–4758.

Wiener, J.G., Krabbenhoft, D.P., Heinz, G.H., and Scheuhammer, A.M., 2003, Ecotoxicology of mercury, Chapter 16, *in* Hoffman, D.J., Rattner, B.A., Burton, G.A., Jr., and Cairns, J., Jr., eds., Handbook of Ecotoxicology, 2d ed.: Boca Raton, Florida, CRC Press, p. 407–461.

Wiener, J.G., Knights, B.C., Sandheinrich, M.B., Jeremiason, J.D., Brigham, M.E., Engstrom, D.R., Woodruff, L.G., Cannon, W.F., and Balogh, S.J., 2006, Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota)—Importance of atmospheric deposition and ecosystem factors: Environmental Science and Technology, v. 40, no. 20, p. 6261–6268.

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