Evaluation of Trends in pH in the Yampa River, Northwestern Colorado, 1950–2000

By Daniel T. Chafin

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To obtain
	Length	
inch	2.54	centimeter
foot (ft)	0.3048	meter
mile	1.609	kilometer
	Area	
square mile	2.590	square kilometer
	Volume	
acre-foot (acre-ft)	1,233	cubic meter
	Flow	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
	Mass	
ton per day (ton/d)	0.9072	metric ton per day
	Pressure	
atmosphere, standard (atm)	101.3	kilopascal

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

$$°F=1.8\ (°C)\ +32$$

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Altitude, as used in this report, refers to distance above or below sea level.

ADDITIONAL ABBREVIATIONS

μg/L	micrograms per liter
μmol/L	micromoles per liter
μS/cm	microsiemens per centimeter at 25 degrees Celsius
mg/L	milligrams per liter

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Abstract

In 1999, the U.S. Geological Survey began a study of pH trends in the Yampa River from near its headwaters to its mouth. The study was prompted by an apparent historical increase in measured pH at the Yampa River near Maybell, from an average of about 7.6 in the 1950's and 1960's to about 8.3 in the 1980's and 1990's. If real, further increase could cause more frequent exceedances of the Colorado water-quality standard of 9.0 and adversely affect aquatic life in the Yampa River Basin, including Dinosaur National Monument. The principal conclusion of this study is that this apparent historical increase in measured pH was caused mostly by changes in measurement protocol.

Synoptic sampling during August 16–19, 1999, a period of relatively warm weather and base flow, showed that late afternoon pH of the Yampa River ranged from 8.46 to 9.20. The largest pH (9.20) exceeded the Colorado water-quality standard and was measured at Yampa River above Elk River, about 1.8 miles downstream from the Steamboat Springs Regional Waste Water Treatment Plant outfall, where nutrient enrichment caused photosynthesis by algae to dominate. Here, the dissolved oxygen concentration was 161 percent of saturation and carbon dioxide (CO_2) was at 26 percent of saturation. At Yampa River downstream from a diversion near Hayden, 16.3 miles downstream, the effects of photosynthesis were still dominant, though attenuated by reaeration and dilution with freshwater from the Elk River. About 37.2 miles farther downstream, at Yampa River below Craig, which is about 6.2 miles downstream from the Craig Waste Water Treatment Plant, the effects of photosynthesis increased slightly, and pH rose to 8.80. Respiration plus oxidation of organic matter became dominant at Yampa River at Deerlodge Park in Dinosaur National Monument, where pH was 8.51, dissolved oxygen concentration was at 109 percent of saturation, and CO_2 was at 189 percent of saturation. Respiration plus oxidation of organic matter, though diminished, apparently extended to the mouth of the Yampa River.

Diurnal measurements on the Yampa River during August 23–26, 1999, show that the effects of photosynthesis and respiration plus oxidation of organic matter decreased downstream with distance from the developed urban area in the eastern part of the basin. Larger night-time values of pH in Dinosaur National Monument at Deerlodge Park and at the mouth of the Yampa River indicate that source waters varied with respect to capacity for respiration plus oxidation and photosynthesis, that photosynthesis was minor, and that pH was largely controlled by respiration plus oxidation of organic matter.

Synoptic sampling was repeated during March 13-16, 2000, when discharge was larger in response to late-winter melting of snow and ice at lower altitudes in the basin. Concentrations of nitrite plus nitrate were about 9 times greater in the Yampa River during March 2000 than during August 1999, and the largest increase (greater than 1,200 percent) was at Yampa River below Craig. At and downstream from Steamboat Springs, Colorado, pH at Yampa River sites averaged 8.85 during synoptic sampling in March 2000 compared to 8.70 in August 1999, with the

partial pressure of carbon dioxide gas (P_{CO_2}) averaging 67 percent of saturation (compared to 99 percent during August 1999). The apparently larger effects of photosynthesis on pH and dissolved oxygen concentrations during March 2000 compared to August 1999 probably were caused by (1) slower rates of exchange of CO_2 into and dissolved oxygen out of the river because of colder and deeper water and (2) slower rates of CO_2 production and oxygen consumption resulting from slower rates of respiration by organisms and from slower rates of aerobic decomposition of organic matter in the colder river water and streambed sediment.

Hypothetical thermodynamic simulations were done for samples collected in the lower Yampa River Basin to simulate the same amount of photosynthesis that existed at Yampa River above Elk River. These simulations indicate that maximum potential late-afternoon pH would equal about 9.1 to 9.2 (exceeding the Colorado water-quality standard of 9.0) during late-winter lowland runoff and during late-summer base flow. Additional simulations indicate that late-summer drought conditions could further raise maximum potential late-afternoon pH by about 0.1 unit, potentially causing late-afternoon pH to remain above the water-quality standard.

Flow-adjusted, two-tailed Wilcoxon-Mann-Whitney rank-sum tests were used to compare onsite measurements, constituent concentrations, and thermodynamic properties of water samples collected from Yampa River near Maybell between 1950–74 and 1975–99. These two periods were defined to represent the general periods of time before and after onsite measurements of pH were begun and to separate the earlier period of minor coal-mining activity from the period of more extensive coal mining that began in the late 1970's. Specific conductance, concentration of dissolved solids, dissolved-solids load, measured pH, and dissolved concentrations of calcium, magnesium, sodium, and sulfate were significantly greater during 1975–99. Dissolved concentrations of chloride, fluoride, and silica were significantly greater during 1950–74. Alkalinity and dissolved potassium concentration were not significantly greater during either period. The CO_2 saturation factor was significantly greater during 1950–74 (median 10.2) than during 1975–99 (median 2.5). However, hypothetical equilibration of all samples with ambient atmospheric pressure of CO_2 resulted in no significant difference in pH for the two periods. Therefore, the significantly greater measured pH values during 1975–99 cannot be attributed to the significant increase in concentrations of dissolved solids, calcium, magnesium, sodium, and sulfate, leaving decrease in the partial pressure of CO_2 as the most likely cause.

Greater dominance of rates of respiration plus oxidation of organic matter (relative to rates of photosynthesis) during 1950–74 and (or) greater dominance of rates of photosynthesis (relative to rates of respiration plus oxidation of organic matter) during 1975–99 possibly contributed to the significantly smaller measured pH values at Yampa River near Maybell during 1950–74, although these causes were not the primary cause. Most of the significant difference in measured pH between the two periods can be attributed to oxidation of organic matter in sample containers during shipping and holding prior to laboratory measurement, especially in composited samples analyzed before 1970. Laboratory measurements and underestimated onsite measurements before September 6, 1983, probably are less reliable than onsite measurements made after that date.

INTRODUCTION

In 1999, the U.S. Geological Survey (USGS) began a study of pH trends in the Yampa River from Stagecoach Reservoir near Steamboat Springs, Colorado, to its mouth, a few miles from the Utah State line (fig. 1). The study was initiated because of an apparent historical increase in measured pH values (fig. 2) at the USGS stream gage 09251000, Yampa River near Maybell, Colorado (fig. 1), since the 1960's. The data indicate that, on average, measured pH values increased from about 7.6 during the 1950's and 1960's

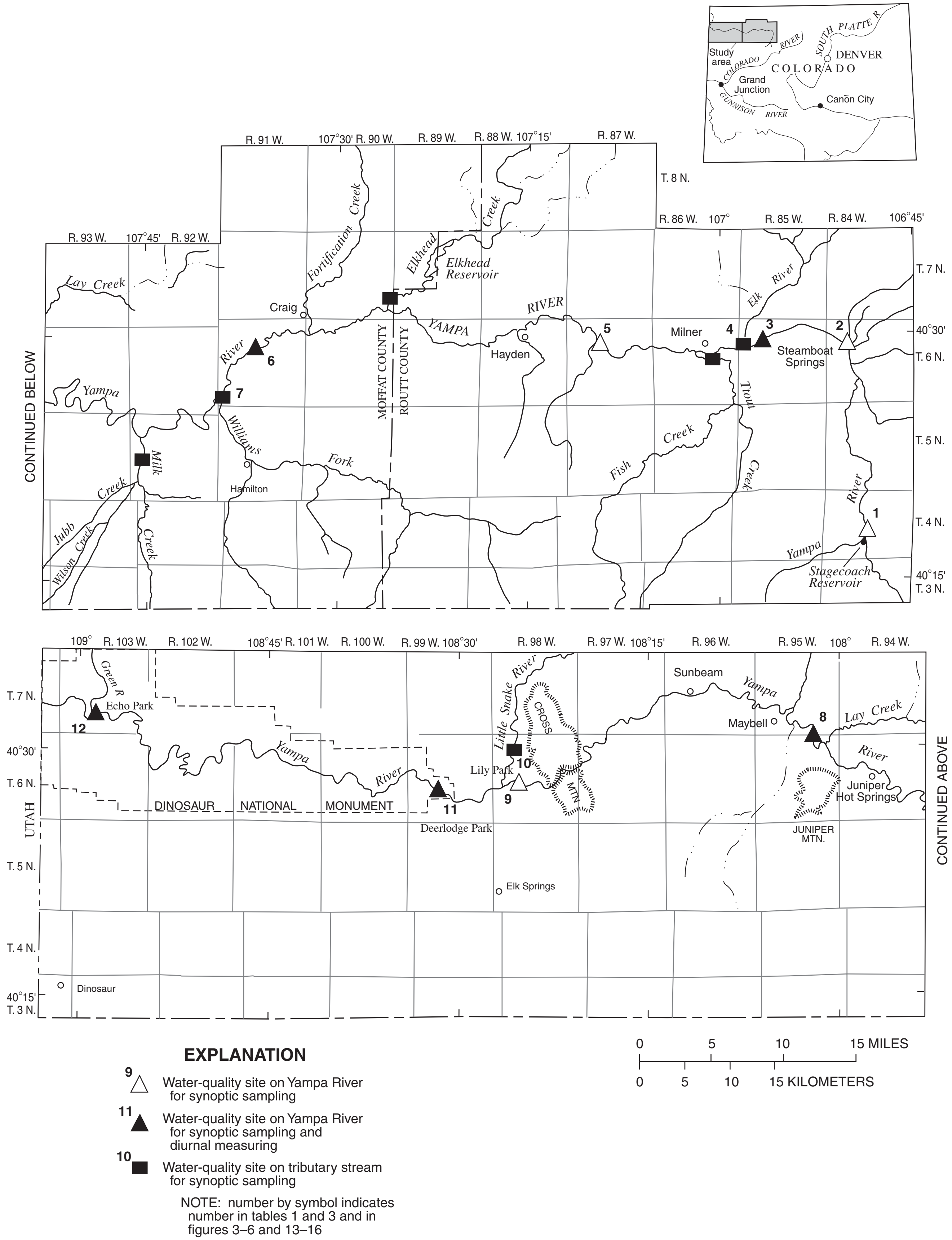

Figure 1. Study area and water-quality-sampling sites.

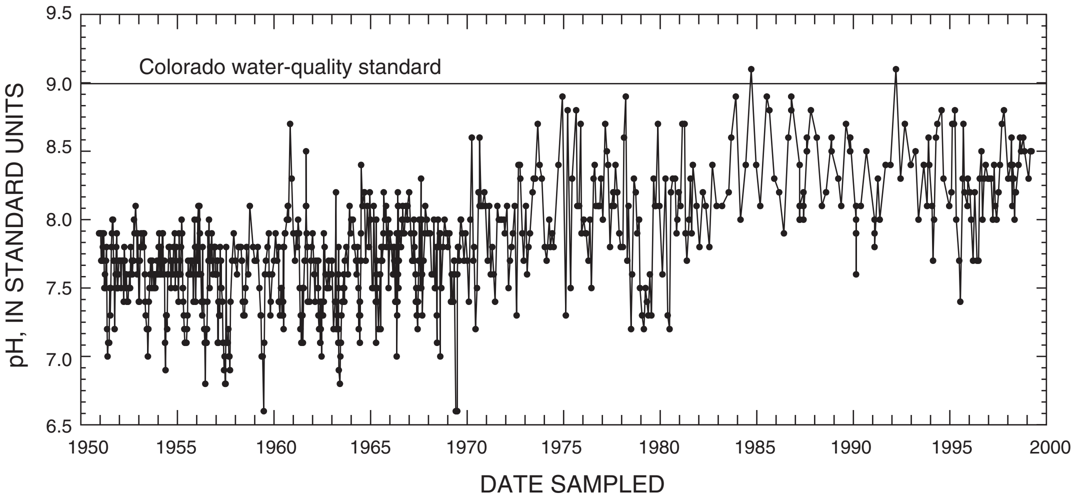

Figure 2. Temporal distribution of measured pH values at Yampa River near Maybell.

to about 8.3 during the 1980's and 1990's. If the trend is real and were to continue to the point where pH frequently exceeded the Colorado water-quality standard of 9.0, adverse effects on aquatic organisms, especially fish, would be expected. Of particular concern to the National Park Service and State and Federal fish and wildlife managers is the potential for adverse aquatic effects in Dinosaur National Monument (fig. 1).

The general objective of this study is to characterize trends in measured pH values and selected constituents in historical data and water-quality data collected for this study. Specific objectives of this study are to:

1. Characterize downstream trends in the water quality of the Yampa River at times of large pH values,
2. Estimate maximum potential pH in the lower Yampa River Basin due to enhanced photosynthesis and drought,
3. Evaluate available water-quality data for the Yampa River near Maybell for possible trends in measured pH and related constituents,
4. Determine if historical trends in measured pH values are real or the result of systematic bias in older pH data, and
5. Determine possible chemical causes of increasing measured pH values, if real.

Purpose and Scope

This report describes and tabulates synoptic and diurnal data collected for this study from selected sites along the Yampa River and main tributaries during August 1999 and March 2000. Geochemical interpretations of these data are presented. Synoptic samples are used to estimate the maximum potential diurnal pH due to photosynthesis in the lower Yampa River (including Dinosaur National Monument) for hypothetical scenarios of enhanced photosynthesis and drought. The historical water-quality data at the Yampa River near Maybell for the period 1950–99 are then interpreted statistically and geochemically to determine the nature of historically increasing, measured pH values. Finally, the report evaluates the validity of the apparent historical increase in measured pH values in the Yampa River.

Description of Study Area

The Yampa River Basin (fig. 1) is in northwestern Colorado on the west slope of the Rocky Mountains. The headwaters of the river originate at altitudes exceeding 10,000 ft south of Steamboat Springs. The highest site sampled for this study, 09237500 Yampa River below Stagecoach Reservoir (site 1 in fig. 1), is at an altitude of about 7,200 ft. The mouth of the Yampa River (site 12 in fig. 1) at the Green River a few miles east of the Utah State line is at about 5,070 ft. The climate of the study area varies from alpine in the headwaters, subalpine in the vicinity of Steamboat Springs, to semiarid in the vicinity of the river's mouth. Long-term average annual precipitation decreases from about 23 inches at Steamboat Springs to about 16 inches at Hayden (National Climate Data Center, 1983) to about 12 inches at Maybell (National Weather Service, 1985). The topography is mountainous in the vicinity of Steamboat Springs but becomes more hilly with scattered, smaller mountains west of there. The farthest downstream reach of the river is a 45-mile segment through Yampa Canyon in Dinosaur National Monument, where canyon walls rise hundreds of feet above the river.

The Yampa River near Maybell (site 8 in fig. 1) transports flow from about the upper two-thirds of the basin (3,410 square miles). This site has the longest period of record for streamflow and water-quality data for the Yampa River. Liebermann and others (1989) report that, for 1950–83, the mean annual streamflow at this site was 1,078,000 acre-ft, averaging 1,490 ft^3/s. Their plot of mean daily streamflow for this period shows snowmelt runoff beginning in late March, peaking in late May at about 7,000 ft^3/s, and ending in mid-July. The remainder of the year is characterized by base flow that usually is less than 750 ft^3/s.

The Yampa River Basin is sparsely settled. U.S. Census Bureau (2000) estimates for July 1999 indicate populations of about 17,941 persons in Routt County and about 12,714 persons in Moffat County. Most of the population is located along the Yampa River in the eastern one-third of the basin in the towns of Steamboat Springs (about 7,232 persons in July 1999), a snow-skiing resort during winter; Hayden (about 2,340 persons); and Craig (about 8,853 persons). Outside of these developed urban areas, the predominant industry is coal mining, which is located primarily in the tributary drainages south of the Yampa River between Steamboat Springs and Craig. Cattle production is the primary agricultural industry in the study area. Irrigation is not widespread.

Sample Collection and Measurements

Synoptic samples were collected at nine sites on the Yampa River and at selected tributary sites (fig. 1) during August 16–19, 1999, and during March 13–16, 2000. Synoptic samples were collected to characterize downstream trends in the water quality of the Yampa River. These sampling periods were selected because historical records for the Yampa River near Maybell indicate that measured pH values tended to be largest during August and March. The August 1999 period was chosen to determine maximum fluctuations in measured parameters due to photosynthesis during hot weather and base flow. The March 2000 period was chosen because historical data at Yampa River near Maybell indicate that measured pH values tend to be large during late-winter thaw at lower altitudes and before large discharges result from spring snowmelt at higher altitudes. Tributary sites sampled during August 1999 consisted of three rivers and three creeks; the three creeks were not sampled again in March 2000. To minimize costs and because the emphasis of this study is downstream from Steamboat Springs, tributary creeks upstream from Steamboat Springs were not sampled during either period. During August 16–19, 1999, sites on the Yampa River (except Yampa River at Steamboat Springs and at mouth) were sampled during late afternoon between 1530 and 1615 hours to assess the maximum effects of photosynthesis, which commonly causes the largest measured pH; for logistical reasons, the sites at Steamboat Springs and at mouth were sampled at 1200 hours. For logistical efficiency, tributary sites were sampled between the hours of 1200 and 1325, when the effects of photosynthesis potentially were substantial, though not maximum. During March 13–16, 2000, sites on the Yampa River (except for below Stagecoach Reservoir) were sampled between the hours of 1430 and 1530 to assess the maximum effects of photosynthesis. Tributary rivers and the site at Yampa River below Stagecoach Reservoir were sampled at 1200 hours for logistical efficiency.

All sites were measured onsite for instantaneous discharge (unless the site was at an active streamflow gage), temperature, specific conductance, measured pH, and dissolved oxygen concentration. Discharge measurements and computations were done according to procedures outlined in Rantz and others (1982). In-situ measurements for temperature, pH, and dissolved oxygen concentration were made at the centroid of streamflow. A baffling cylinder was used to prevent streamflow velocity from biasing pH measurements (which are accurate to about ±0.03 unit). Samples that were collected for laboratory determinations of dissolved concentrations of major ions, fluoride, silica, organic carbon, ammonia,

ammonia plus organic nitrogen, nitrite plus nitrate, phosphorus, and orthophosphorus were collected by the equal-width-increment method (Horowitz and others, 1994) to ensure sample representativeness. Samples were analyzed by the USGS National Water-Quality Laboratory in Denver, Colorado, using methods described by Fishman and Friedman (1989). Water-quality data resulting from synoptic sampling are presented in table 3 in the "Supplemental Information" section at the back of this report. These data are discussed in a section titled "Synoptic Sampling" in the "Summer 1999" section and in the "Winter 2000 Synoptic Sampling" section.

Diurnal measurements of temperature, specific conductance, measured pH, and dissolved oxygen concentrations were measured from the bank of five sites on the Yampa River during August 23–26, 1999. This period was chosen to represent streamflow conditions that existed during summer synoptic sampling.

The Yampa River sites (fig. 1) measured diurnally were:

1. Above Elk River, 402936106565000, site 3,
2. Below Craig, 09247600, site 6,
3. Near Maybell, 09251000, site 8,
4. At Deerlodge Park, 09260050, site 11, and
5. At mouth (Echo Park), 403136108585900, site 12.

Results of diurnal measurements are presented graphically and discussed in the subsection titled "Diurnal Measurements" in the section titled "Summer 1999."

Reconnaissance measurements of temperature, specific conductance, pH, and dissolved oxygen concentration were measured during August 30–September 3, 1999, along the Yampa River between Deerlodge Park and the mouth of the river (Echo Park). Results of these measurements are discussed in the subsection titled "Reconnaissance Measurements in Dinosaur National Monument" in the section titled "Summer 1999," except for dissolved oxygen measurements, which were discarded because of equipment malfunction.

Acknowledgments

Gratitude is extended to the people who made possible the successful completion of this study and report. Dan Beyer (Colorado State University) noticed the apparent historical increase in measured pH at Yampa River near Maybell and approached the National Park Service with his concerns. Roy Irwin (National Park Service, Fort Collins, Colorado) and Steve Petersburg (National Park Service, Dinosaur National Monument) were instrumental in initiating and conceiving the scope of the study and providing access and logistical support in the National Monument. Michael McHale (National Park Service, Dinosaur National Monument) took time away from his pressing duties during the flood-prone summer of 1999 to make water-quality measurements at the mouth of the Yampa River. Timothy Modde, Mark Fuller, and David Beers (U.S. Fish and Wildlife Service, Vernal, Utah) graciously allowed the author to join them on a fish-study float trip through Yampa Canyon in Dinosaur National Monument to make reconnaissance water-quality measurements for this study. Paul von Guerard (USGS, Grand Junction, Colorado) worked hard to promote, develop, and review the progress of this study and offered valuable technical insights. John Turk (USGS, Lakewood, Colorado) was instrumental in establishing the scope and approach of the study and authoring the study proposal. Robert Boulger, Joseph Sullivan, Jeffrey Foster, Patricia Solberg, and Kenneth Butcher (USGS, Grand Junction, Colorado), along with Richard Neam, Dennis Smits (USGS, Lakewood, Colorado), and Joseph Dungan (USGS, Meeker, Colorado), collected water-quality and hydrologic data for this study.

INTERPRETATION OF DATA COLLECTED FOR THIS STUDY

Data from collection of synoptic samples during August 16–19, 1999, and March 13–16, 2000, and from diurnal measurements during August 23–26, 1999, provide a framework to interpret water-quality data historically collected at the Yampa River near Maybell, including pH. In addition, reconnaissance field measurements taken on the Yampa River between Deerlodge Park and the mouth of the river (Echo Park) during August 30 through September 3, 1999, give an estimate of the maximum pH expected on the Yampa River in Dinosaur National Monument during low flow and warm weather.

Summer 1999

Data collection during summer 1999 consisted of synoptic sampling at nine Yampa River sites and six tributary sites (fig. 1), diurnal measuring at five Yampa River sites (fig. 1), and reconnaissance measuring of the Yampa River in Dinosaur National Monument between Deerlodge Park and the mouth of the river (Echo Park).

Synoptic Sampling

Synoptic samples were collected during August 16–19, 1999, at the sites listed in table 1 (and at three small creeks discussed in this section). Water-quality data resulting from this sampling are presented in table 3 in the "Supplemental Information" section at the back of this report. Samples generally were collected in the afternoon during a period of relatively low stream discharge and high temperature to assess the effects of photosynthesis, particularly on pH. Because these synoptic samples were collected over a 4-day period that was not substantially affected by rainfall, they reasonably represent a "snapshot" view of water-quality conditions along the Yampa River during afternoon hours.

Based on measured instantaneous discharges, the three main tributaries (fig. 1) augmented flow in the Yampa River at their confluences approximately by the following percentages: Elk River, 77; Williams Fork, 23; and Little Snake River, 26. In contrast, the next three largest tributaries downstream from Steamboat Springs augmented flow in the Yampa River approximately by the following percentages (based on discharges at nearest upstream Yampa River site or sum of discharges of the nearest upstream Yampa River site and nearest upstream tributary site): Trout Creek, 6.8; Elkhead Creek, 1.3; and Milk Creek, 2.1. Because of the insignificant potential of these creeks to affect water quality of the Yampa River, they will not be discussed further in this report.

During the synoptic sampling, specific conductance (fig. 3) decreased substantially from 419 μS/cm at Yampa River below Stagecoach Reservoir (site 1 in fig. 1 and table 1) to 294 μS/cm at Yampa River at Steamboat Springs (site 2) due to dilution with fresher water in tributary creeks, which substantially increased discharge from about 99 ft^3/s at site 1 to about 160 ft^3/s at site 2. Specific conductance increased slightly to 320 μS/cm at Yampa River above Elk River (site 3), which is about 1.8 miles downstream from the outfall from the Steamboat Springs Regional Waste Water Treatment Plant (SSRWWTP). Substantial dilution with fresher water (specific conductance of 102 μS/cm) from Elk River near mouth (site 4) caused a substantially smaller specific conductance of 260 μS/cm at Yampa River below diversion near Hayden (site 5). Downstream from site 5, specific conductance increased gradually to 557 μS/cm at Yampa River at mouth (site 12), primarily because of substantial contributions of saltier water from Williams Fork at mouth (site 7), with a specific

Table 1. River miles of sites sampled for this study

Site number in figures 1, 3–6, and 13–15	U.S. Geological Survey site identification	Distance from mouth of Yampa River, in river miles
1	Yampa River below Stagecoach Reservoir, 09237500	221.0
2	Yampa River at Steamboat Springs, 09239500	199.1
3	Yampa River above Elk River, 402936106565000	191.8
4	Elk River near mouth, 402914106580400	[1]190.1
5	Yampa River below diversion near Hayden, 09244410	177.2
6	Yampa River below Craig, 09247600	140.0
7	Williams Fork at mouth, 09249750	[1]135.1
8	Yampa River near Maybell, 09251000	89.0
9	Yampa River above Little Snake River, 09251100	53.0
10	Little Snake River above Yampa River, 402925108253200	[1]51.1
11	Yampa River at Deerlodge Park, 09260050	46.0
12	Yampa River at mouth (Echo Park), 403136108585900	0.0

[1]Distance is from mouth of tributary river.

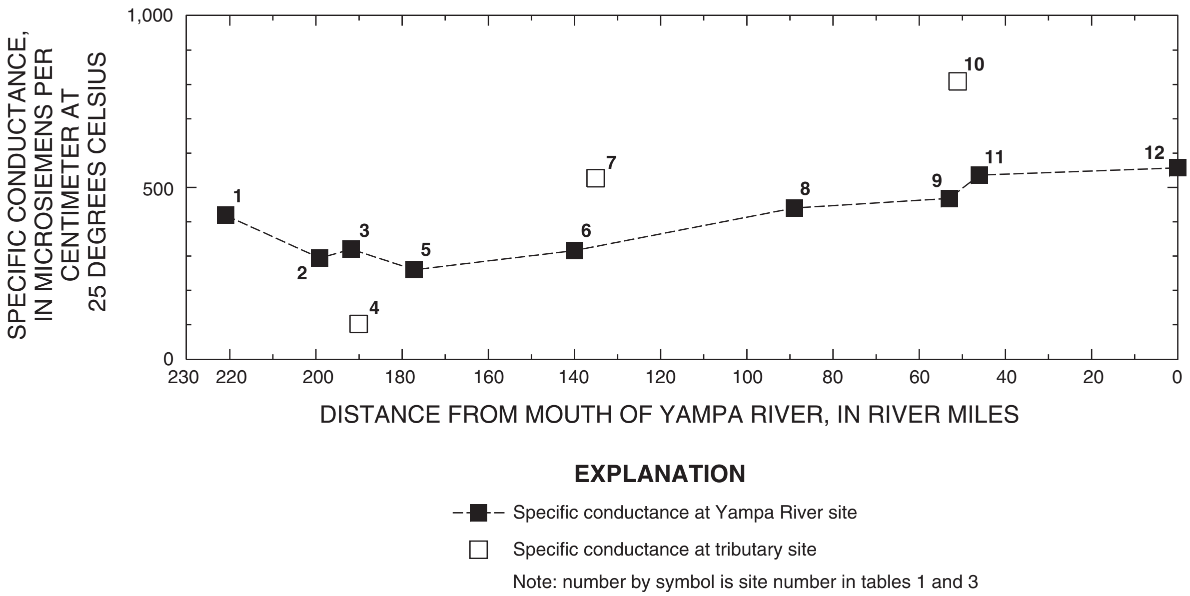

Figure 3. Specific conductance at Yampa River and tributary sites, August 16–19, 1999.

conductance of 527 µS/cm, and Little Snake River above Yampa River (site 10), with a specific conductance of 809 µS/cm. Evaporation from the river channel, irrigation return flows, sewage effluent, and inflow of saltier ground water are other potential contributors to the downstream increase in salinity.

Downstream trends in concentrations of calcium and alkalinity (fig. 4), important controls on pH and on the capacity of the waters to dissolve or precipitate calcite ($CaCO_3$), were similar to trends for specific conductance (fig. 3). Concentrations between Yampa River below Stagecoach Reservoir (site 1) and Yampa River at Steamboat Springs (site 2) were diluted by fresher water in tributary creeks. Downstream from Yampa River above Elk River (site 3), concentrations of calcium and alkalinity were substantially diluted by freshwater from the Elk River (site 4). From Yampa River below diversion near Hayden (site 5) to Yampa River at mouth (site 12), concentrations of calcium increased to 40 mg/L and alkalinity increased to 140 mg/L of alkalinity as $CaCO_3$, primarily because of inflow of more alkaline water from the Williams Fork (site 7) and the Little Snake River (site 10).

At Yampa River sites, pH (fig. 5) ranged from 8.46 to 9.20; pH ranged from 8.08 to 8.70 at the three tributary sites, which were sampled during early afternoon before pH would be expected to peak because of photosynthesis. The smallest measured pH value in the Yampa River (8.46) was at site 1, below Stagecoach Reservoir, only about 0.25 mile downstream from the dam spillway. Because this water was released from substantial depth in the reservoir, pH had little potential to be affected by the cumulative effects of photosynthesis. However, water from this site had the largest measured concentrations of dissolved ammonia (0.02 mg/L as N), dissolved nitrite plus nitrate (0.10 mg/L as N), dissolved ammonia plus organic nitrogen (0.36 mg/L as N), dissolved organic carbon (5.4 mg/L as C), and the second largest measured concentration of dissolved phosphorus (0.05 mg/L as P) at Yampa River and tributary-river sites. In addition, the rocky streambed was covered with aquatic vegetation.

The largest pH value (9.20), measured at Yampa River above Elk River (site 3), exceeded the Colorado water-quality standard of 9.0 for the upper Colorado River Basin. Site 3 is about 1.8 miles downstream from the sewage outfall from the SSRWWTP. This facility discharges about 3.9 ft^3/s of treated sewage effluent during summer daylight hours (David Jarvis, Steamboat Springs Regional Waste Water Treatment Plant, oral commun., 2000), indicating a fortyfold dilution of sewage effluent at site 3 during sampling. The river channel exhibited abundant attached algae and occasional clumps of entrained algae, indicating photosynthesis induced by nutrient enrichment from sewage effluent. The large pH was accompanied by a

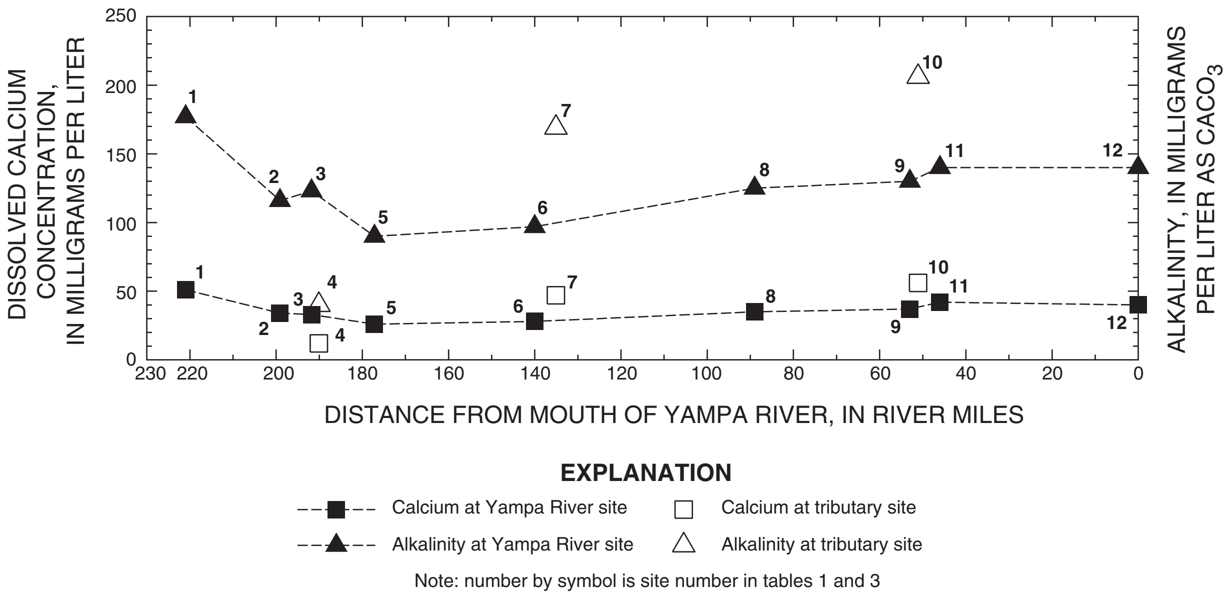

Figure 4. Concentrations of calcium and alkalinity at Yampa River and main tributary sites, August 16–19, 1999.

dissolved oxygen concentration that was 161 percent of saturation (relative to the concentration that would occur at equilibrium with the atmosphere)(fig. 5). Calculations using the thermodynamic-speciation program PHREEQC (Parkhurst, 1995) indicates that dissolved carbon dioxide gas (CO_2) (fig. 5) was undersaturated at 26 percent of the concentration that would occur at equilibrium with the atmosphere.

Drever (1982) describes the formation of algae (which represents microscopic and macroscopic plant composition) by photosynthesis:

$$106\ CO_2 + 16\ NO_3^{-} + HPO_4^{2-} + 122\ H_2O + 18\ H^{+} + (\text{trace elements, energy}) = C_{106}H_{263}O_{110}N_{16}P_1(\text{algae}) + 138\ O_2. \quad (1)$$

This equation explains the large pH value measured at site 3 by the uptake of dissolved CO_2, thus decreasing the concentration of carbonic acid (H_2CO_3) dissolved in the water, and by direct uptake of H^+ ions, which raises pH. Photosynthesis also explains the large oversaturation with dissolved oxygen. Equation 1 also shows that the formation of plant biomass depends on the availability of dissolved nitrogen and phosphorus, either of which can limit the ability of the reaction to proceed. The sample from site 3 had the largest measured concentration of dissolved phosphorus (0.06 mg/L) and the second largest (after site 1) measured concentrations of dissolved ammonia plus organic nitrogen (0.30 mg/L) and dissolved organic carbon (5.0 mg/L) of the main-stem and tributary river sites. These constituents are derived from sewage effluent, livestock waste, excretions from aquatic organisms, and other natural sources.

The effects of photosynthesis on pH and dissolved oxygen concentration were attenuated at Yampa River below diversion near Hayden (site 5) by reaeration in the approximately 16.3-mile reach downstream from the SSRWWTP and by dilution with fresher water from the Elk River (site 4). However, the relatively large pH value at site 5 (8.70) was elevated by photosynthesis, as is indicated by oversaturation with dissolved oxygen (124 percent) and undersaturation with CO_2 (69 percent) (fig. 5).

The Yampa River below Craig (site 6) is located about 6.2 miles downstream from the outfall from the Craig Waste Water Treatment Plant (CWWTP). This facility discharges about 1.9 ft^3/s of treated sewage effluent during daylight hours (Robert Frazier, Craig Waste Water Treatment Plant, oral commun., 2000). At site 6, the effects of photosynthesis were only slightly greater than at site 5. Measured pH increased slightly to 8.80, the second largest measured value (after site 3), whereas dissolved oxygen was slightly more oversaturated (131 percent) and CO_2 was more undersaturated (59 percent) than at site 5 (fig. 5). The relatively minor effects of photosynthesis on water

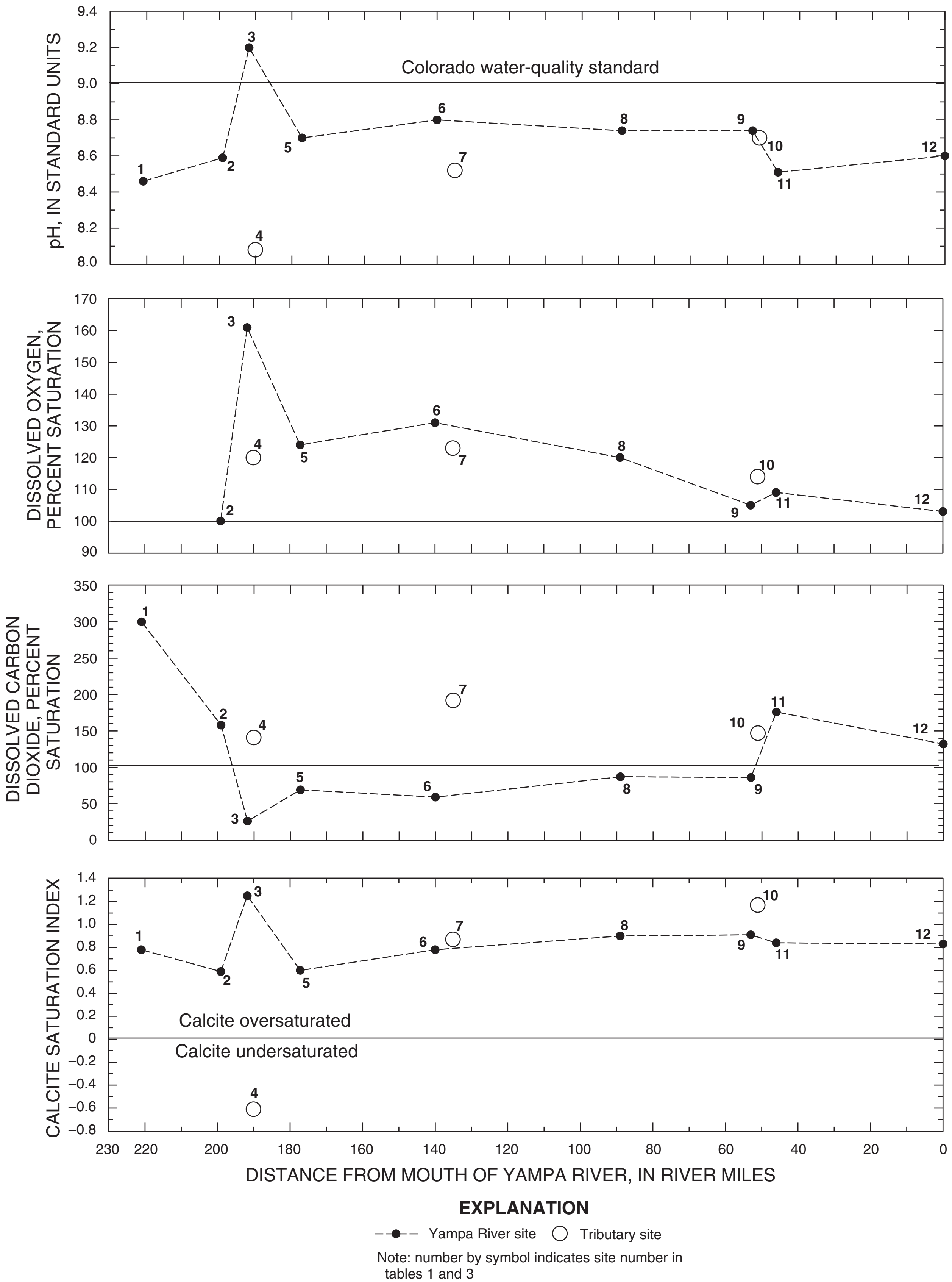

Figure 5. pH and other geochemical indicators at Yampa River and tributary sites, August 16–19, 1999.

quality at site 6 compared to the effects at site 3 were (at least partially) due to the larger dilution of sewage effluent at site 6 (about 140 times) compared to site 3 (about 40 times). Furthermore, some of the effects of photosynthesis at site 6 possibly were caused by discharge of sewage outfall from SSRWWTP, much smaller sewage discharges at Hayden and Milner, and agricultural effluent.

Downstream from site 6, the effects of photosynthesis decreased to Yampa River near Maybell (site 8) and further to Yampa River above Little Snake River (site 9). Values of pH decreased slightly to 8.74 at both sites. Dissolved oxygen concentrations became less oversaturated (120 percent at site 8 and 105 percent at site 9), and the river became only slightly undersaturated with CO_2 (87 percent of saturation at site 8 and 86 percent at site 9).

Apparently, respiration plus oxidation of plant material and organic matter (approximately the reverse of equation 1; Drever, 1982) were more dominant than photosynthesis at Yampa River at Deerlodge Park (site 11) and at Yampa River at mouth (Echo Park) (site 12). This conclusion is based on the smaller pH value measured at site 11 (8.51) and site 12 (8.60), which resulted from oversaturation of CO_2 (189 percent at site 11 and 137 percent at site 12). The apparently abrupt shift to dominance of respiration plus oxidation at site 11 compared to relative balance between photosynthesis and respiration plus oxidation at sites 8 and 9 possibly resulted (1) from inflow of nutrient-poor organic matter from the Little Snake River (site 10), (2) from arrival of water with larger concentrations of oxidizable organic matter, possibly flushed from the land surface by rain in the basin on the previous day, (3) from a reduction in aquatic-plant biomass and productivity between sites 9 and 11, or (4) from a combination of these factors. Slight oversaturation of the river water with dissolved oxygen (109 percent at site 11 and 103 percent at site 12) indicates that less photosynthesis occurred at sites 11 and 12 than at upstream sites.

Except for dissolved nitrogen as ammonia plus organic nitrogen, concentrations of dissolved nutrients (table 3) were small at Yampa River and tributary sites during August 16–19, 1999. Downstream from Yampa River below Stagecoach Reservoir (site 1), concentrations of dissolved ammonia were less than 0.02 mg/L as N, and concentrations of dissolved nitrite plus nitrate were less than 0.05 mg/L as N. Concentrations of dissolved nitrogen as ammonia plus organic nitrogen generally decreased from 0.36 mg/L as N at Yampa River below Stagecoach Reservoir (site 1) to 0.18 mg/L as N at Yampa River at mouth (site 12). These relations imply that most of the dissolved nitrogen in the Yampa River during this sampling consisted of organic (reduced) nitrogen. Downstream from Yampa River above Elk River (site 3) concentrations of dissolved phosphorus were less than 0.05 mg/L as P, and concentrations of dissolved orthophosphate were less than 0.01 mg/L as P. Bacterial mineralization (oxidation) of reduced nitrogen and phosphorus provided most of the nutrients for photosynthesis downstream from sites 3 and 6.

Calculations using PHREEQC indicate that samples from all Yampa River sites, the Williams Fork (site 7), and the Little Snake River (site 10) were substantially oversaturated with calcite ($CaCO_3$) (fig. 5). This relation implies that these waters could not dissolve calcite and possibly were precipitating it. Only water from the Elk River (site 4) was undersaturated with calcite.

Geochemical calculations indicate that most of the variation in pH between Yampa River sites was caused by differences in P_{CO_2} (the effective partial pressure of CO_2 gas on the solution) and degree of oversaturation with calcite. The geochemical reaction model PHREEQC was used to simulate the effect of allowing the samples collected from Yampa River sites to equilibrate with ambient P_{CO_2} (0.00033 times ambient atmospheric pressure). The resulting pH values from the simulations are in the narrow range from 8.55 to 8.80 (fig. 6) with a relative distribution very similar to that of alkalinity concentrations (fig. 4). Once the dominating effects of undersaturation and oversaturation with CO_2 were removed, pH was largely a function of, and was proportional to, alkalinity.

Simulated equilibration with atmospheric P_{CO_2} had the greatest effect on the sample from site 3 (which was most undersaturated with dissolved CO_2 because of photosynthesis), decreasing the pH value by 0.51 unit. The simulated equilibrium also decreased the pH of water from site 5 (by 0.15 unit) and from site 6 (by 0.21 unit). Water from these sites also was undersaturated with CO_2 (fig. 5). Simulated equilibration with atmospheric CO_2 substantially increased the pH value of samples from sites that were substantially oversaturated with CO_2 (fig. 5): site 1 (by 0.34 unit);

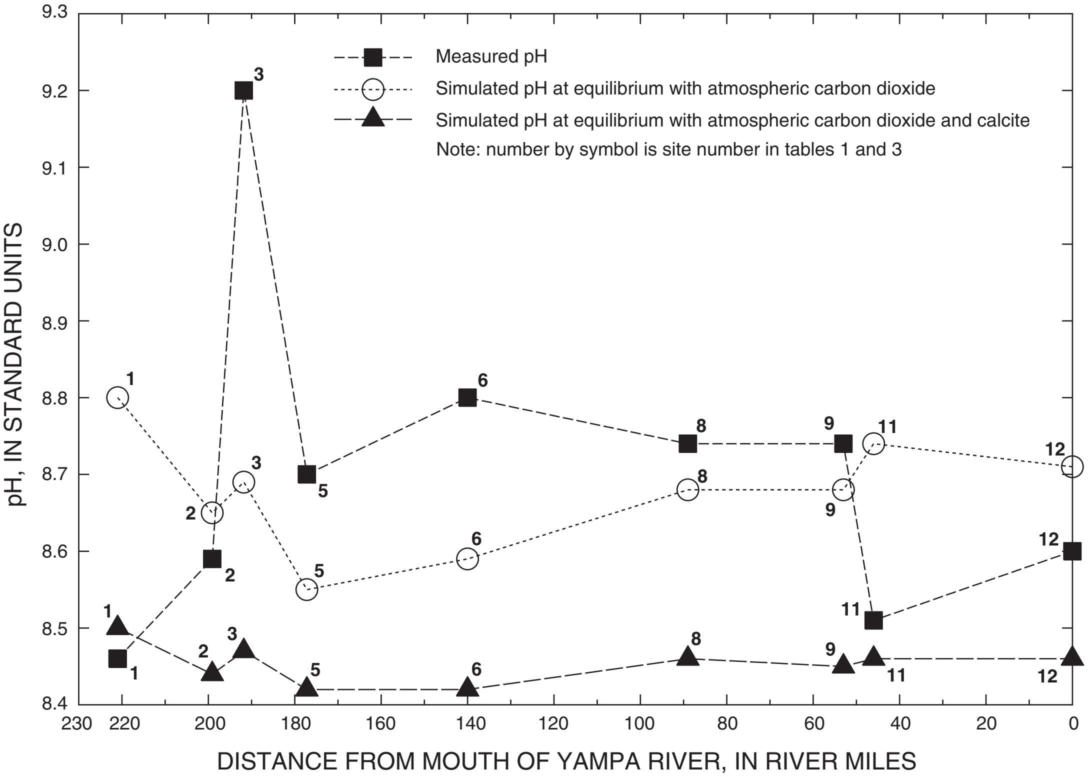

Figure 6. Measured and simulated pH at Yampa River sites, August 16–19, 1999.

site 11 (by 0.23 unit); and site 12 (by 0.11 unit). Values for pH at sites 8 and 9 were decreased slightly (by 0.06 unit) by the simulation because they were close to equilibrium with atmospheric CO_2 (fig. 5).

Further hypothetical simulations using PHREEQC to allow samples collected from Yampa River sites to precipitate enough calcite to attain equilibrium with that mineral further decreased pH values between 0.13 and 0.31 unit (compared to pH at equilibrium with atmospheric P_{CO_2}) (fig. 6). These simulations indicate that pH for Yampa River water would be restricted to the narrow range from 8.42 to 8.50 if it was in equilibrium with calcite and atmospheric CO_2.

Diurnal Measurements

Measurements at Yampa River above Elk River (site 3 in fig. 1) during August 23–24, 1999, indicated strong diurnal fluctuations in pH and dissolved oxygen concentration (fig. 7) as a result of dominance by photosynthesis during daylight and by respiration plus oxidation of organic matter during night. Values for pH ranged from a peak of 9.07 at 1500 hours in the afternoon of August 23 to a minimum of 7.92 at 0300 hours the next morning (a diurnal change of 1.15 units). Dissolved oxygen concentrations peaked at 178 percent of saturation at the same time pH peaked and attained a minimum of 66 percent of saturation at the time of minimum pH. (Because the degree of saturation of dissolved oxygen is dependent on water temperature, minimum and maximum concentration of dissolved oxygen does not exactly correspond to minimum and maximum concentration.) Specific conductance remained relatively constant at 331 to 343 µS/cm over the 23-hour period. The abrupt decrease in pH value from 9.07 at 1500 hours to 8.84 at 1600 hours apparently was caused by a 15-minute cloudy period between those measurements; this temporary inhibition of photosynthesis probably prevented pH from reaching its maximum potential that afternoon at this site, a conclusion supported by a pH of 9.20 at 1600 hours on August 18, 1999.

Diurnal measurements at Yampa River below Craig (site 6 in fig. 1) during August 23–24, 1999 (fig. 8) also indicated substantial effects of photosynthesis and respiration plus oxidation of organic matter, although not as strongly as at Yampa River above Elk River. Values for pH peaked at 8.78 at 1800 hours on August 23 and attained a minimum of 8.17 at

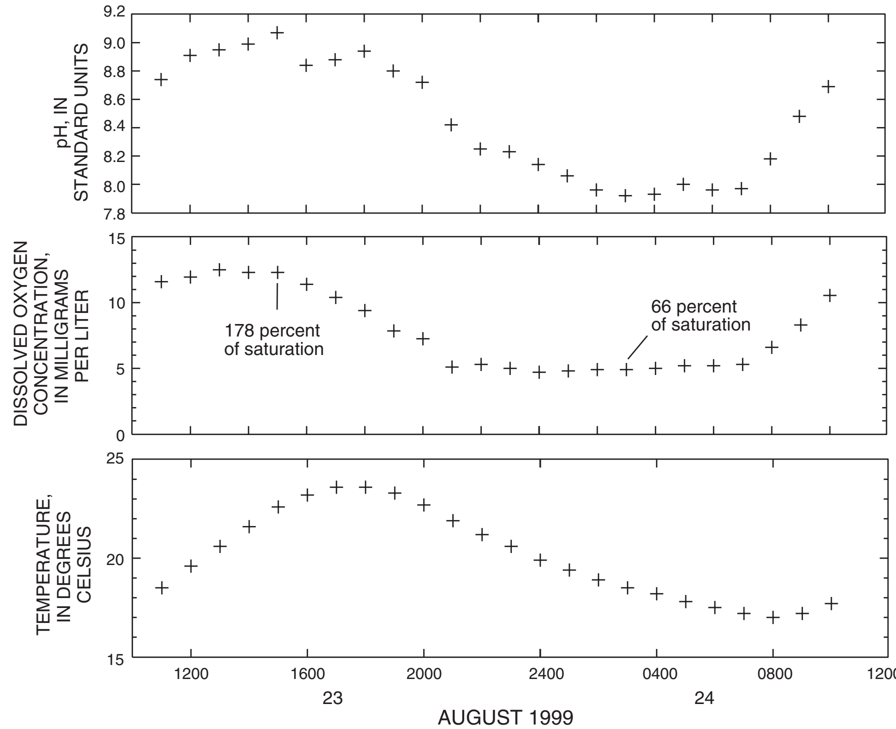

Figure 7. Diurnal measurements at Yampa River above Elk River, August 23–24, 1999.

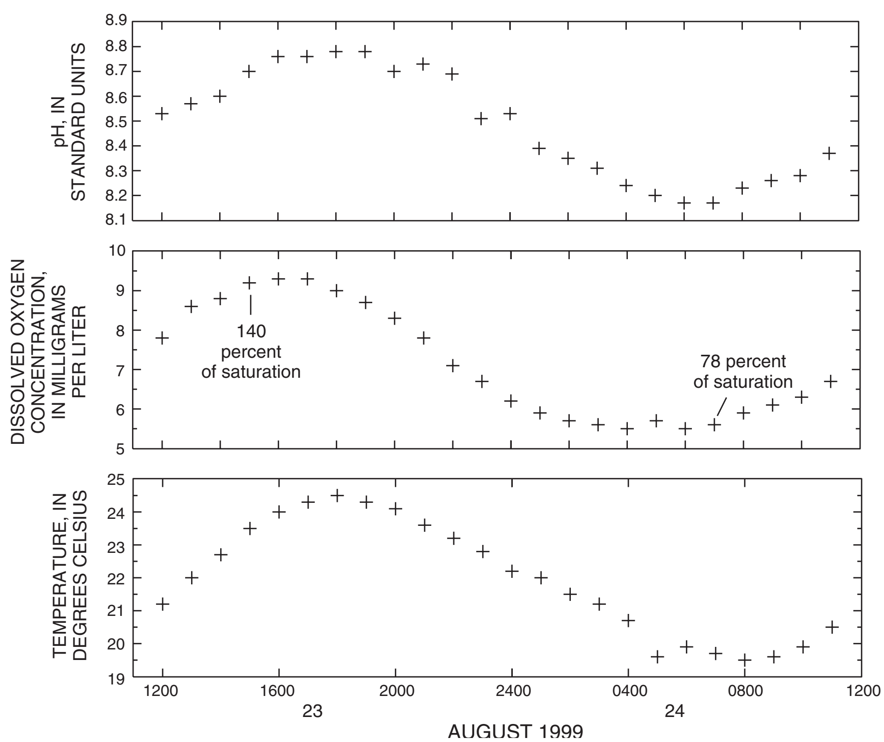

Figure 8. Diurnal measurements at Yampa River below Craig, August 23–24, 1999.

0600 hours the next day (a diurnal change of 0.61 unit). Dissolved oxygen concentration peaked at 140 percent of saturation at 1600 hours on August 23 and attained a minimum of 78 percent of saturation at 0600 hours the next day. Specific conductance ranged from 346 to 380 µS/cm.

Diurnal measurements at Yampa River near Maybell (site 8 in fig. 1) during August 23–24, 1999 (fig. 9), showed smaller effects of photosynthesis and respiration plus oxidation of organic matter than at sites 3 and 6. Values for pH peaked at 8.66 at 1900 hours on August 23 and attained a minimum of 8.52 at 0700 hours the next day (a small diurnal change of 0.14 unit). Dissolved oxygen peaked at 132 percent saturation at 1500 hours on August 23 and attained a minimum of 86 percent saturation at 0100 hours and 0600 hours the next day. Specific conductance ranged from 474 to 502 µS/cm.

Diurnal measurements at Yampa River at Deerlodge Park (site 11 in fig. 1) during August 25–26, 1999 (fig. 10), showed little or no effect of photosynthesis on pH and dissolved oxygen saturation. The smallest pH values (8.45–8.51) were measured during daylight on August 25, and the largest pH values (8.59–8.60) were measured between the hours of 2200 on August 25 and 0500 hours on August 26 (an inverted diurnal change of 0.15 unit). Dissolved oxygen concentration peaked at 106 percent of saturation at 1700 hours on August 25 and reached a minimum at 90 percent of saturation at 0700 hours the next day, with concentrations varying in the narrow range from 6.7 to 7.3 mg/L and remaining within 5 percent of saturation for most of the measuring period. Specific conductance ranged from 555 to 571 µS/cm. Cloudy weather to about 1330 hours and from about 1630 hours until after sunset on August 25 probably suppressed photosynthesis, the presence of which was weakly evidenced by the pattern of dissolved oxygen saturation. However, cloudy weather during daylight cannot account for the larger pH during night, which indicates a change in the chemistry of the water flowing past site 11.

Diurnal measurements at Yampa River at mouth (Echo Park) (site 12 in fig. 1) during August 25–26, 1999 (fig. 11), showed substantial effects of photosynthesis on dissolved oxygen concentration but not pH. Values of pH varied slightly from 8.60 to 8.70, with the largest values generally occurring between 2200 and 0200 hours. Dissolved oxygen concentrations ranged from 6.8 to 8.4 mg/L, peaking at 118 percent of saturation at 1500 hours on August 25, which indicated that photosynthesis was occurring, and attained a minimum of 93 percent of saturation at 0700 hours the next day, which indicates slight respiration plus oxidation of organic matter. Specific conductance ranged from 581 to 591 µS/cm. Except for a brief sunny period during midafternoon, cloudy weather on August 25 probably suppressed photosynthesis. As at site 11, larger pH during night indicates a change in the chemistry of the water flowing past site 12.

Diurnal measurements on the Yampa River during August 23–26, 1999, showed a general downstream decrease in the effects of photosynthesis and respiration plus oxidation of organic matter. From Yampa River above Elk River (site 3) to Yampa River below Craig (site 6) to Yampa River near Maybell (site 8), there was a decrease in maximum daily pH values (9.07 to 8.78 to 8.66), in diurnal fluctuation in pH values (1.15 to 0.61 to 0.14 units), and in maximum daily dissolved oxygen saturation (178 to 140 to 132 percent); these trends show that eutrophication of the river and the effects of photosynthesis decreased substantially upstream from site 8. In addition, the downstream increase in minimum dissolved oxygen saturation (66 to 78 to 86 percent) indicates that respiration plus oxidation of organic matter decreased substantially between sites 3 and 8. The small diurnal fluctuation in pH values (0.14 unit) at site 8 indicates that respiration plus oxidation of organic matter during afternoon hours produced CO_2 at about the same rate as it was consumed by photosynthesis; this interpretation is supported by the 89 percent of saturation with CO_2 at site 8 during synoptic sampling on August 16, 1999 (fig. 5). During night, when photosynthesis does not occur, respiration plus oxidation of organic matter, although slower because of cooler temperature, would have continued to produce CO_2 and lower pH.

Cloudy weather during most of the day when diurnal measurements were made at sites 11 and 12 made interpretation of those measurements more problematic. However, larger pH values at those sites during night (figs. 10 and 11) indicates that (1) source-water chemistry varied with respect to capacity for respiration plus oxidation of organic matter and photosynthesis and (2) photosynthesis was minor and pH was largely controlled by relative rates of CO_2 production caused by respiration plus oxidation of reactive organic matter, which would have been greater during

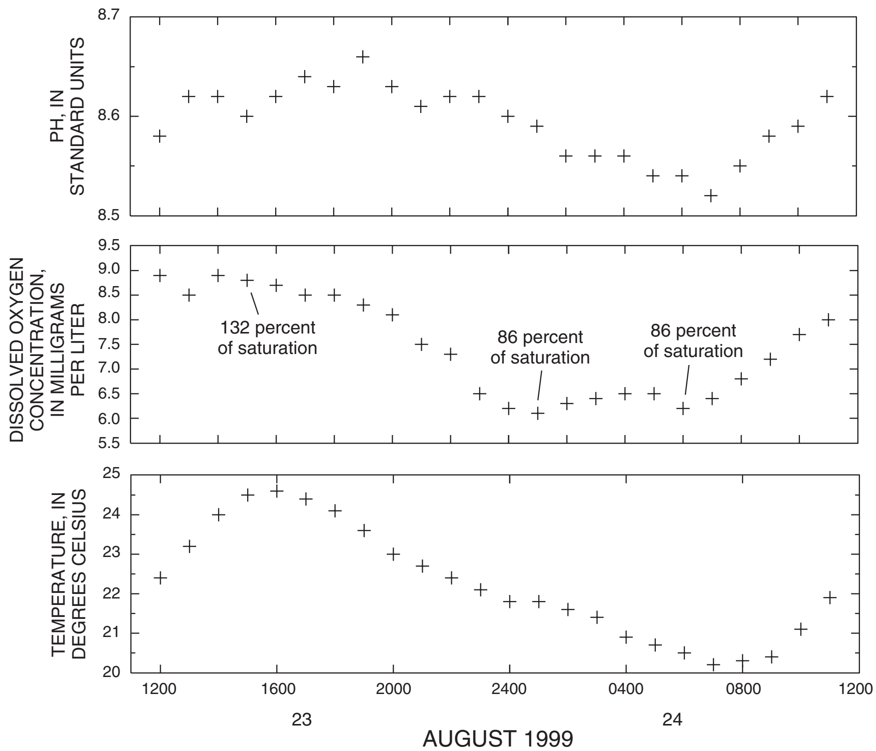

Figure 9. Diurnal measurements at Yampa River near Maybell, August 23–24, 1999.

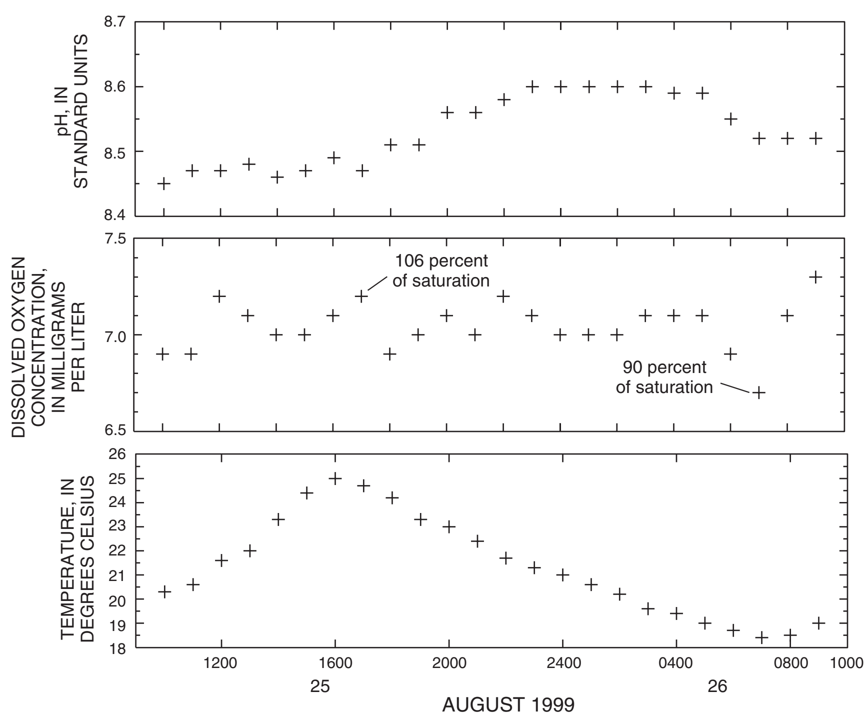

Figure 10. Diurnal measurements at Yampa River at Deerlodge Park, August 25–26, 1999.

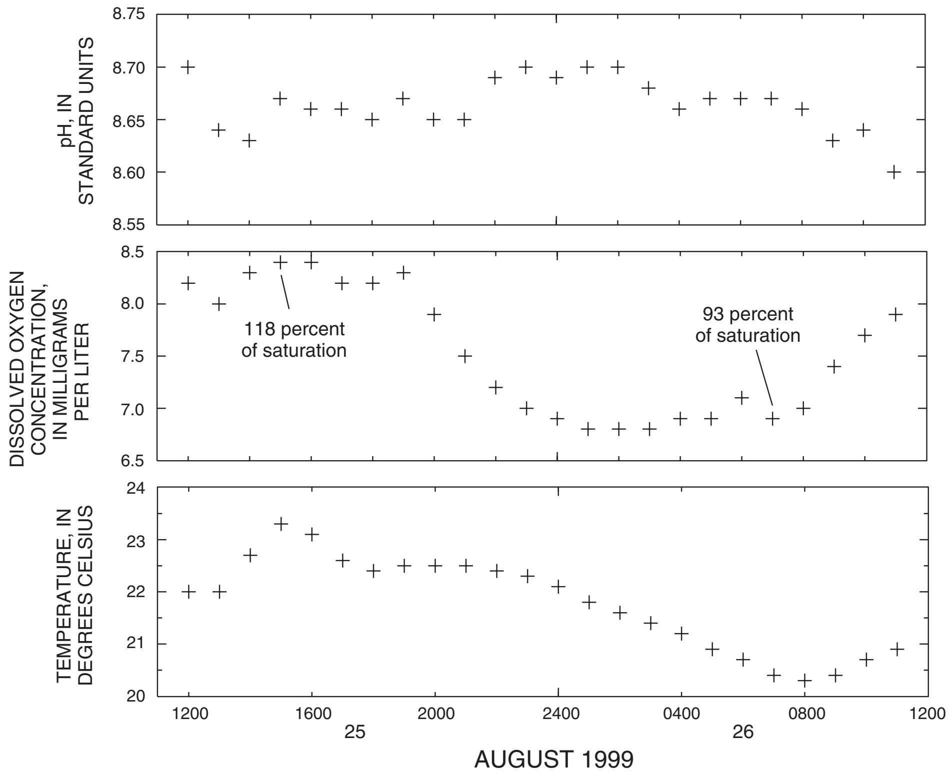

Figure 11. Diurnal measurements at Yampa River at mouth, August 25–26, 1999.

warmer daylight hours, lowering pH. The second point is supported by oversaturation of CO_2 in river water at sites 11 and 12 during synoptic sampling (fig. 5). However, this observation does not discount the possibility that variation in source-water chemistry also affected diurnal pH.

Reconnaissance Measurements in Dinosaur National Monument

Reconnaissance field measurements taken on the Yampa River between Deerlodge Park (site 11, 46 miles upstream from the mouth) and at mouth (Echo Park) (site 12) during August 30 through September 3, 1999, show pH in the narrow range of 8.43–8.77 (fig. 12), with a measurement mean of 8.63 (or 8.62 as the mean of H^+ activities). Measurements for the first 3 days indicate definite increases in pH values (0.21, 0.15, and 0.33 unit) as each day progressed, indicating possible effects of photosynthesis. The smallest diurnal change (0.15 unit on August 31) occurred on a day that was cloudy. The sky gradually progressed from sunny to cloudy on the afternoon of August 30, with a moderately hard, 30-minute rain at 2000 hours, and became sunny shortly before noon after clouds and light rain on the morning of September 1. On the fourth day, September 2, the sky was sunny for the first measurement at 0805 hours but cloudy thereafter, with a hard, 13-minute rain beginning at 1152 hours, causing brief runoff from the canyon walls; values of pH varied irregularly on this day from 8.65 to 8.77.

These pH data indicate minor or no effects of photosynthesis of the Yampa River in Dinosaur National Monument between Deerlodge Park (site 11) and Echo Park at the mouth (site 12). Aquatic vegetation was sparse and scattered in the rocky streambed of Yampa Canyon. The water had a greenish tint during the measurement period, possibly indicating entrained, microscopic plant cells (phytoplankton).

Although the first 3 days of measurement appear to indicate diurnal increases in pH values (fig. 12), these increases probably were mostly the result of downstream depletion of reactive organic matter and gradual venting of oversaturated, dissolved CO_2. Specific conductance (fig. 12) indicates that one relatively consistent parcel of water was measured during

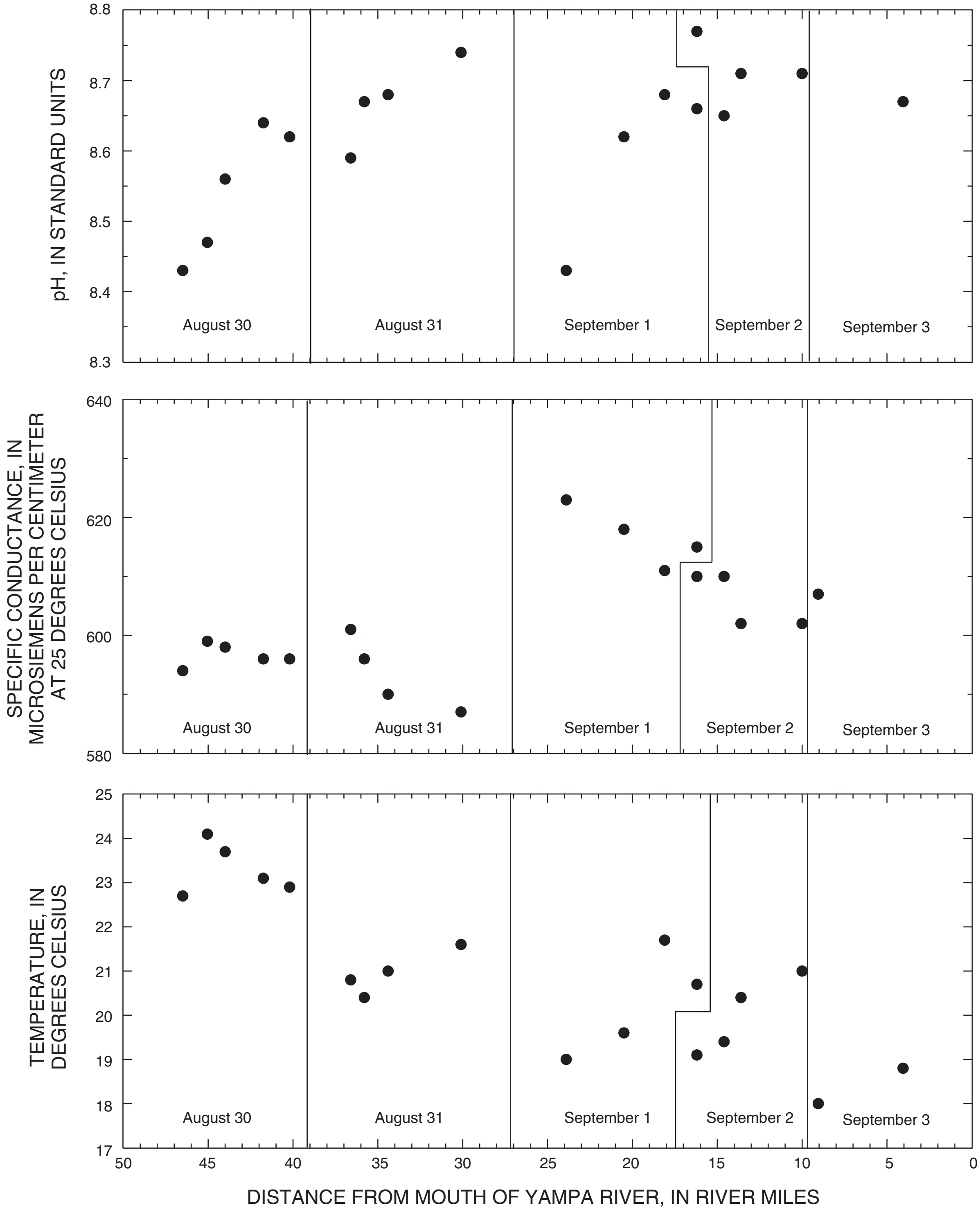

Figure 12. Reconnaissance measurements on Yampa River in Dinosaur National Monument, August 30–September 3, 1999.

August 30–31, for which pH values increased regularly (allowing for a small diurnal effect) from 8.43 to 8.74 as it flowed 15.4 miles downstream. There were no flowing tributaries or springs along this 15.4-mile reach of the river downstream from Deerlodge Park.

Another parcel of water with initially greater but decreasing salinity (specific conductance, fig. 12) was measured during September 1–3. On September 1, pH values increased from 8.43 to 8.68. The initial pH of 8.43 probably resulted from a larger concentration of reactive organic matter associated with the more saline water. This water possibly represented initial flushing of salts and organic matter from the land surface by the 30-minute rain at 2000 hours on August 30. Downriver measurement of decreasing specific conductance during September 1–3 is consistent with the arrival of fresher water that was progressively less affected by such flushing.

The stabilization of pH in the narrow range 8.66–8.77 after 1025 hours on August 31 (for the first parcel of water) and after 1205 hours on September 1 (for the second parcel) supports the hypothesis that pH between sites 11 and 12 was mostly the result of downstream depletion of reactive organic matter (the concentration of which varies with source water) and gradual venting of oversaturated, dissolved CO_2. Using results of synoptic samples collected on August 18 (site 11) and August 19 (site 12), water measured during this reconnaissance trip, if equilibrated with atmospheric P_{CO_2}, would be expected to have a pH of about 8.75 (fig. 6). Actual measurements indicate that pH value was usually smaller and that respiration plus oxidation of organic matter, not photosynthesis, was dominant during daylight in this reach of the river—a conclusion consistent with the preceding interpretation of diurnal measurements at sites 11 (fig. 10) and 12 (fig. 11). Shading of much of the river by the canyon walls probably suppressed photosynthesis.

No perennial creeks were observed during this reconnaissance trip. Only one flowing creek was measured at 1455 hours after rain on the morning of September 1 about 19.2 miles from the mouth of the river; this creek, which was flowing at about 0.2 ft^3/s, had a temperature of 25.1°C, a specific conductance of 909 μS/cm, and a pH of 8.25. After the hard, 13-minute rain at 1152 hours on the morning of September 1, waterfalls were observed to flow briefly off the canyon walls.

Several perennial springs flow between sites 11 and 12. On August 31 at 1900 hours, a spring on the south bank of the river 25.2 miles from the mouth was measured to have a temperature of 15.7°C, a specific conductance of 1,465 μS/cm, and a pH of 7.58. Discharge of this spring, which built algae terraces, was estimated to be from 0.004 to 0.01 ft^3/s. Another spring with similar discharge was observed on the north bank of the river about 25.0 miles from the mouth, but measurements were not made because of approaching darkness. The only other perennial spring observed during the reconnaissance trip was Warm Springs (on the north bank of the river, 4.05 miles upstream from the mouth), which was flowing at about 6 to 8 ft^3/s at 1155 hours on September 3, 1999. Measurements indicated a temperature of 16.2°C, a specific conductance of 1,466 μS/cm, and a pH of 8.04.

Steele and others (1978) measured pH values from 8.4 to 8.8 (with a mean of 8.6, as measured and by concentration of H^+ ions) and dissolved oxygen concentrations from 7.4 to 8.0 mg/L (90 to 108 percent of saturation) at five sites on the Yampa River between Deerlodge Park and the river's mouth during August 17–19, 1976. They measured dissolved oxygen saturations of 103, 106, and 108 percent between 1700 hours and 1900 hours on the 3 days of measurement, indicating minor photosynthesis. The range and means of pH values measured by Steele and others (1978) are essentially identical to those measured during the reconnaissance trip for this study, which was conducted when the season and discharge were similar. Dissolved oxygen saturations in 1976 generally are similar to the diurnal and synoptic measurements made for this study. Similarities in pH and dissolved oxygen saturation measured by Steele and others (1978) and measurements for this study indicate that the Yampa River in Dinosaur National Monument was not substantially different 23 years after the earlier study with respect to the effects of photosynthesis on water quality.

Winter 2000 Synoptic Sampling

Data-collection activities during winter 2000 consisted of synoptic sampling at nine Yampa River sites and three tributary sites (fig. 1). Water-quality data resulting from this sampling are presented in table 3 in the "Supplemental Information" section at the back of this report.

During synoptic sampling during March 13–16, 2000, discharge at the nine Yampa River sites was 64 percent larger on average than discharge during synoptic sampling during August 16–19, 1999. The increase in discharge between the two sampling periods generally increased downstream from –1 percent at Yampa River below Stagecoach Reservoir (site 1 in fig. 1) to 69 percent at Yampa River near Maybell (site 8) to 115 percent at Yampa River at mouth (site 12). Discharges of tributary rivers increased an average of 62 percent between the sampling periods, showing a substantial relative increase from –25 percent at Elk River near mouth (site 4) to 25 percent at Williams Fork at mouth (site 7) to 240 percent at Little Snake River above Yampa River (site 10). The downstream increase in discharge at Yampa River and tributary sites between the two sampling periods is consistent with late-winter melting of snow and ice at lower altitudes in the Yampa River Basin. This melting during March 2000 sampling caused a reversal of relative contributions of discharge to the Yampa River by tributary rivers compared to August 1999 sampling: the Elk River augmented discharge of the Yampa River by about 47 percent (77 percent during August 1999); the Williams Fork augmented it by about 20 percent (23 percent during August 1999); and the Little Snake River augmented it by about 52 percent (26 percent during August 1999).

Average specific conductance at Yampa River sites increased by 58 percent during March 2000 (fig. 13) compared to August 1999 (fig. 3); at tributary sites, average specific conductance increased by only 5 percent. Most of the increase at Yampa River sites between the two sampling periods occurred at site 6. Although average concentrations of all major ions increased at Yampa River sites during March 2000, the largest average increases were with sodium (88 percent), magnesium (93 percent), and sulfate (163 percent).

Concentrations of dissolved ammonia, dissolved phosphorus, and dissolved orthophosphorus were less than the reporting limits at all sites downstream from site 3 during both sampling periods. Average concentration of dissolved nitrogen as ammonia plus organic nitrogen at all Yampa River sites increased only 4 percent during March 2000 compared to August 1999. However, concentrations of nitrite plus nitrate at all Yampa River sites increased about 900 percent, on average (assuming that concentrations less than the reporting limit were one-half the reporting limit) during March 2000 compared to August 1999; the largest increase (greater than 1,200 percent) occurred

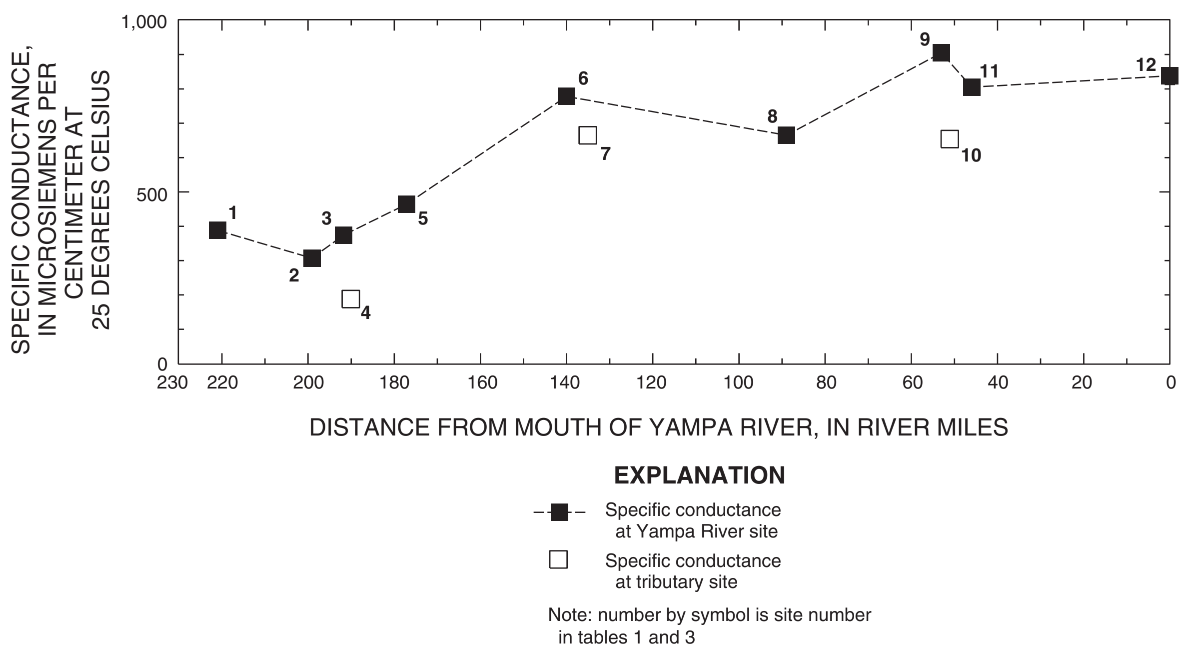

Figure 13. Specific conductance at Yampa River and tributary sites, March 13–16, 2000.

at site 6. Concentrations of dissolved organic carbon also increased an average of about 32 percent at site 6, although concentrations decreased or were about equal at sites sampled upstream from site 6. The substantial increases in specific conductance and in concentrations of nitrite plus nitrate and dissolved organic carbon at site 6 in March 2000 compared to August 1999 probably resulted from flushing of the land surface by melting snow and ice along unsampled tributaries and the Yampa River valley between sites 5 and 6 during March 2000. This hypothesis is indicated by a 133-ft^3/s increase in discharge between sites 5 and 6 during March 2000 compared to a 36-ft^3/s increase during August 1999.

Synoptic sampling during March 2000 showed a downstream distribution of pH (fig. 14) similar to the synoptic sampling during August 1999 (fig. 5). The largest difference was at Yampa River below Stagecoach Reservoir (site 1), where pH measured 7.77 in March 2000 (compared to 8.46 in August 1999). According to calculations using PHREEQC, this lower pH during March 2000 implies that CO_2 was at 1,000 percent of saturation (compared to 300 percent during August 1999), probably because of winter stratification of Stagecoach Reservoir.

Downstream from site 1, pH at Yampa River sites (fig. 14) averaged 8.85 during March 2000 (compared to 8.70 during August 1999), reflecting an average P_{CO_2} (fig. 14) of 67 percent of saturation (compared to 99 percent during August 1999). Dissolved oxygen concentrations averaged 119 percent of saturation at Yampa River sites downstream from site 1 during both sampling periods (figs. 5 and 14), but, because dissolved oxygen concentrations were about 40 percent larger at those sites during March 2000 (averaging 12.2 mg/L) than during August 1999 (averaging 8.6 mg/L), photosynthesis increased dissolved oxygen concentrations about 40 percent more during March 2000 than during August 1999. These relations indicate greater effect of photosynthesis on pH and dissolved oxygen concentrations during March 2000 than during August 1999, despite shorter days and colder water temperatures in March 2000. However, this conclusion does not imply that rates of photosynthesis were greater during March 2000. Greater increase in pH and in dissolved oxygen concentrations by photosynthesis during March 2000 probably can be attributed to (1) slower rates of exchange of CO_2 into and dissolved oxygen out of the river because of colder water temperature and deeper water and (2) slower rates of CO_2 production and oxygen consumption resulting from slower rates of respiration by organisms and of aerobic decomposition of organic matter in the colder river water and streambed sediment.

Calculations using PHREEQC indicate that synoptic samples collected at Yampa River sites during March 2000, if equilibrated with local, atmospheric P_{CO_2}, would have pH in the narrow range of 8.64 to 8.77 (average 8.69)(fig. 15), compared to 8.55 to 8.80 (average 8.67) during August 1999 (fig. 6). These calculations indicate that the high alkalinity of Yampa River water causes high pH that is further elevated by CO_2 removal during photosynthesis.

Calculations using PHREEQC indicate that synoptic samples collected at Yampa River sites (except site 1) during March 2000 were oversaturated with calcite (fig. 14); the sample from site 1 was near saturation because of relatively small pH. Excluding site 1, the average saturation index was 0.98 during March 2000, compared to 0.84 during August 1999 (fig. 5), indicating greater oversaturation during March 2000—mostly a result of higher pH, alkalinity, and concentration of calcium. Additional calculations using PHREEQC indicate that synoptic samples collected at Yampa River sites during March 2000, if equilibrated with local, atmospheric P_{CO_2} and calcite, would have pH in the narrow range of 8.43 to 8.50 (average 8.45) (fig. 15), compared to 8.42 to 8.50 (average 8.45) during August 1999 (fig. 6). The general agreement of simulated pH values for the two sampling periods indicates that pH in the Yampa River was largely controlled by degree of P_{CO_2} saturation and degree of oversaturation with calcite during both sampling periods.

Estimate of Maximum Potential Late-Afternoon pH in the Lower Yampa River Basin

Enhanced photosynthesis and increased alkalinity in the lower Yampa River Basin have the potential to increase maximum diurnal (late-afternoon) pH. To estimate maximum potential pH at water-quality sites in the lower Yampa River Basin, water-quality samples collected at Yampa River above Elk River (site 3, fig. 1) on August 18, 1999, and March 13, 2000, were selected to represent hypothetical, poten-

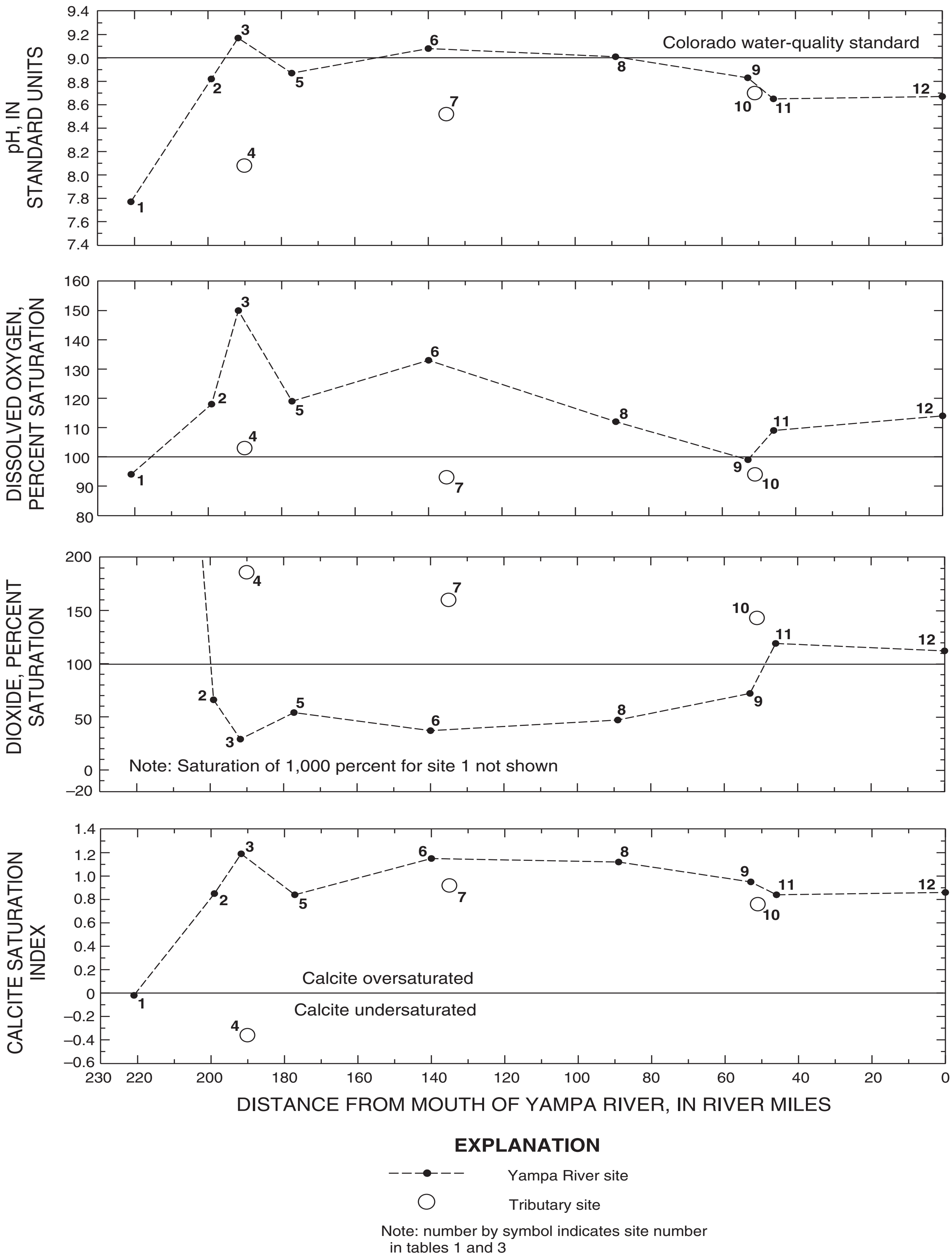

Figure 14. pH and other geochemical indicators at Yampa River and tributary sites, March 13–16, 2000.

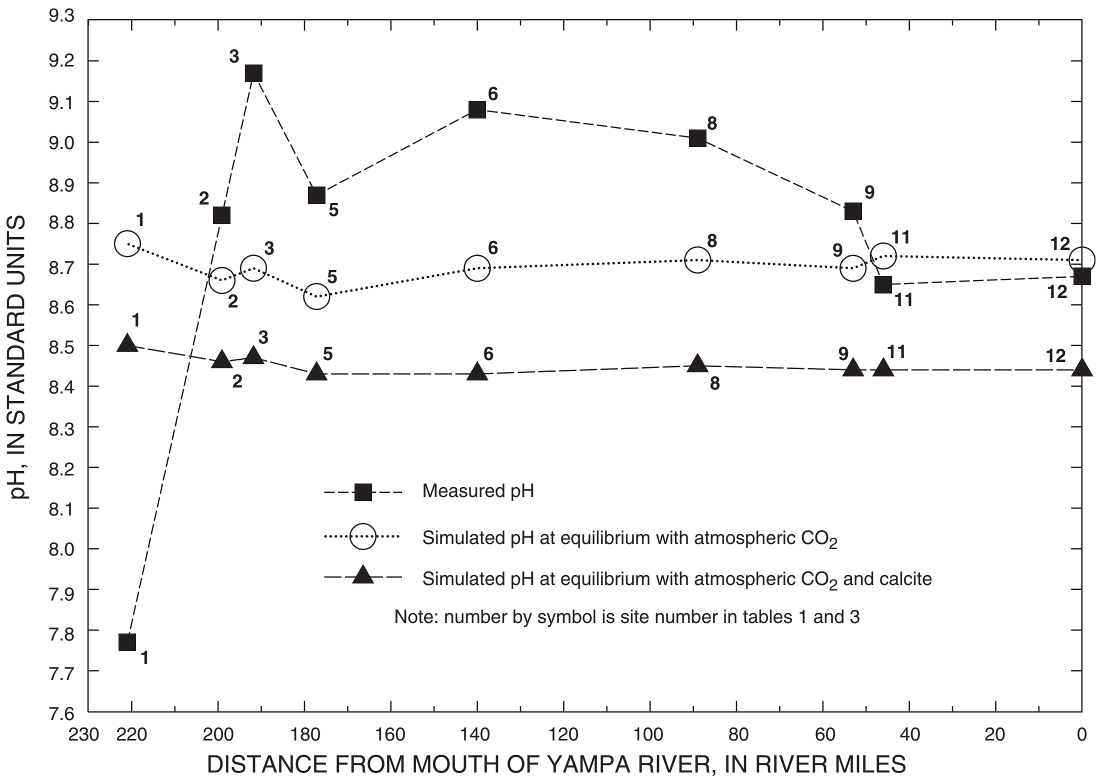

Figure 15. Measured and simulated pH at Yampa River sites, March 13–16, 2000.

tial conditions of photosynthesis in the lower basin. PHREEQC was used to calculate the difference in the concentration of CO_2 gas in the synoptic samples from site 3 at measured pH and the concentration in the samples at equilibrium with ambient atmospheric P_{CO_2}. These calculations indicate that, relative to CO_2 concentrations in equilibrium with the atmosphere at site 3, 209 µmol/L of CO_2 gas was removed from river water at site 3 by photosynthesis on August 18, 1999, and 172 µmol/L was removed on March 13, 2000. PHREEQC was then used to simulate equilibration of synoptic samples from sites 8, 9, 11, and 12 (fig. 1) with ambient atmospheric P_{CO_2} (corrected for elevation), followed by stepwise removal of 209 µmol/L of CO_2 gas from synoptic samples collected from those sites during August 16–19, 1999, and of 172 µmol/L of CO_2 gas from synoptic samples collected during March 13–16, 2000. These simulations predict pH (fig. 16) that would result from removal of the same amounts of CO_2 gas (relative to ambient CO_2 concentrations) as was removed from site 3 by photosynthesis during each sampling period. For conditions at site 3 to encroach to a given point in the lower basin, nutrient loads in the upper basin would have to increase so that algae proliferated to its maximum density in the river to that point. A deterministic, periphyton-algae, river model would be required to predict the degree of photosynthesis in the lower basin, taking into account nutrient loads, exposure to and penetration of light, channel stability, and other river characteristics. Therefore, the following simulations should not be interpreted to indicate that conditions at site 3 could actually develop at sites 8, 9, 11, and 12. For example, productivity downstream of site 11 might be limited by shading of much of the river in Yampa Canyon. Results of the simulations are shown in figure 16.

Estimates of maximum potential late-afternoon pH resulting from the simulations (fig. 16) indicate that pH hypothetically could reach values of 9.10 to 9.12 in the lower Yampa River Basin at sites 8, 9, 11, and 12 (fig. 16) during lowland runoff in late March. USGS records indicate that pH at Yampa River near Maybell was 9.1 at 1200 hours on March 17, 1992, indicating a similar amount of photosynthesis as at Yampa River above Elk River on March 13, 2000. The measured pH of 9.01 at Yampa River near Maybell on March 15, 2000 (an overcast day), indicates that about 115 µmol/L of CO_2 gas (67 percent of the 172 µmol/L removed from water at site 3 on March 13, 2000) was removed from that water. The gas-removal plots (fig. 16) indicate that pH would equal or exceed the

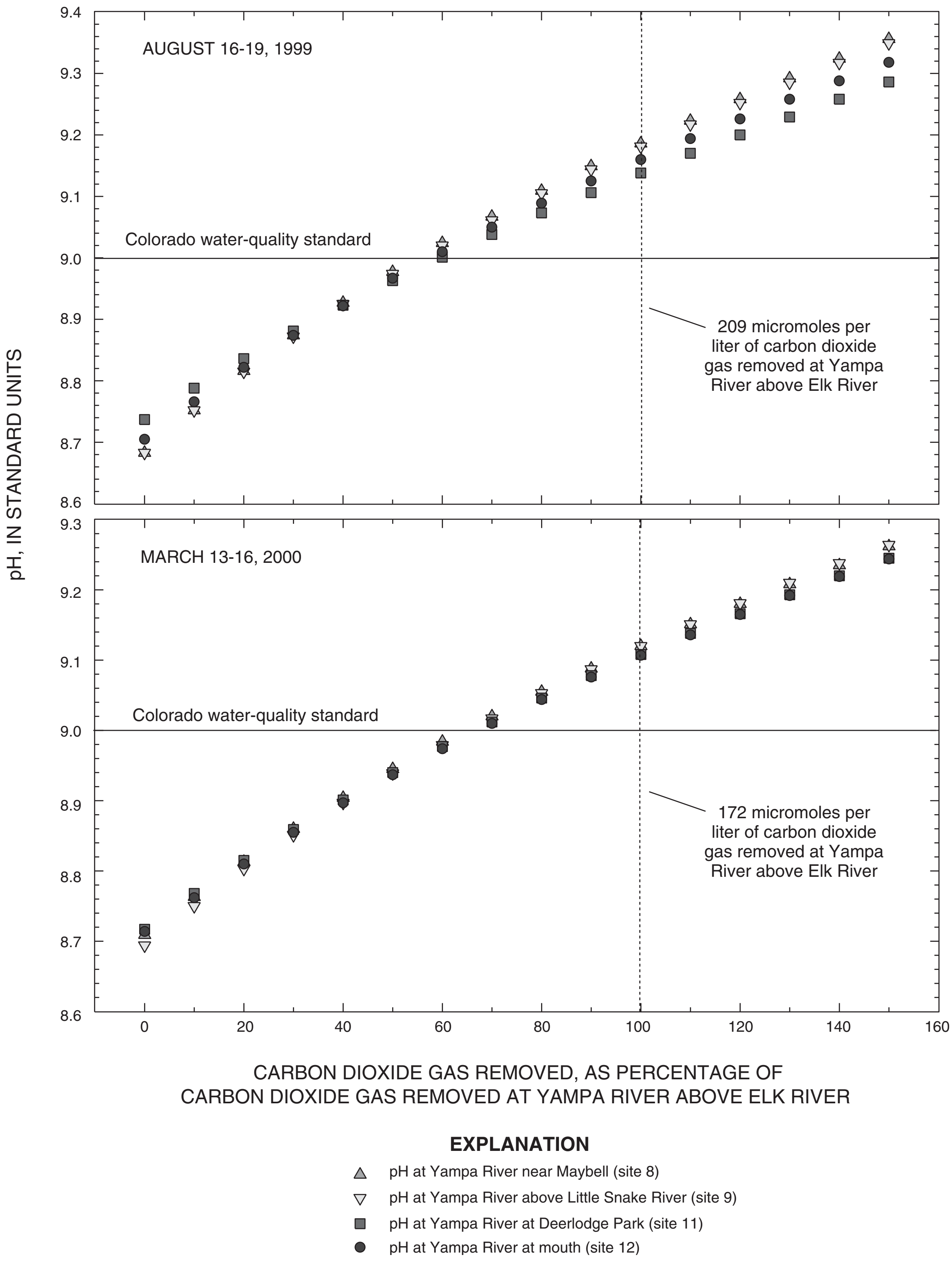

Figure 16. Simulated maximum potential pH for water-quality sites in the lower Yampa River Basin, August 16–19, 1999, and March 13–16, 2000.

Colorado water-quality standard of 9.0 if at least 67 percent of the calculated amount of CO_2 gas removed from site 3 was removed from these samples.

Hypothetically, pH could reach values of 9.14 to 9.18 at sites 8, 9, 11, and 12 during late summer (fig. 16). USGS records indicate that pH at Yampa River near Maybell was 9.1 at 1430 hours on September 18, 1984, indicating that about 75 percent as much CO_2 gas was removed by photosynthesis at that site as was removed at Yampa River above Elk River on August 18, 1999. The gas-removal plots (fig. 16) indicate that pH would equal or exceed the Colorado water-quality standard of 9.0 if at least 54 percent of the calculated amount of CO_2 gas removed from site 3 was removed from these samples.

The pH predictions in figure 16 assume that relative proportions and concentrations of major ions (especially alkalinity) remain constant. To estimate the effect of increased salinity on maximum potential late-afternoon pH, the synoptic sample collected at Yampa River at Deerlodge Park (site 11, fig. 1) on August 18, 1999, was selected for simulations of increased salinity and photosynthetic removal of CO_2 gas—conditions that might occur during prolonged drought. This sample was selected for these simulations because of its sampling location near the upstream boundary of Dinosaur National Monument and its sampling date during the time of the year when pH is at or near a seasonal maximum and when drought conditions are most likely to occur. PHREEQC was used to simulate 150 percent of constituent concentrations by evaporating one-third of the water in the sample. This concentrated sample was simulated to attain equilibrium with ambient atmospheric P_{CO_2}, followed by stepwise removal of 209 μmol/L of CO_2 gas (100 percent of the amount of CO_2 gas removed at Yampa River above Elk River on August 18, 1999). The simulation was repeated to simulate a 200-percent concentration of the original sample (by removing one-half of the sample water) and stepwise removal of 209 μmol/Lof CO_2 gas. The results of these simulations (fig. 17) show that, relative to sampled concentrations with 209 μmol/L of CO_2 gas removed (the lower curve), a 150-percent increase in constituent concentrations would cause a pH about 0.07 unit higher and a 200-percent increase (the upper curve) would cause a pH about 0.13 unit higher. Furthermore, the original sample would have a pH of 9.0 at about 60 percent of CO_2 gas removal, whereas, at 150 percent of sampled concentrations, pH would be 9.0 at about 34 percent of CO_2 gas removal, and, at 200 percent of sampled concentrations, pH would be 9.0 at about 10 percent of CO_2 gas removal. These results indicate that drought conditions potentially could cause late-afternoon pH to sustain values above the Colorado water-quality standard of 9.0.

Maximum potential late-afternoon pH (fig. 16) would be 0.03 to 0.06 unit higher for samples

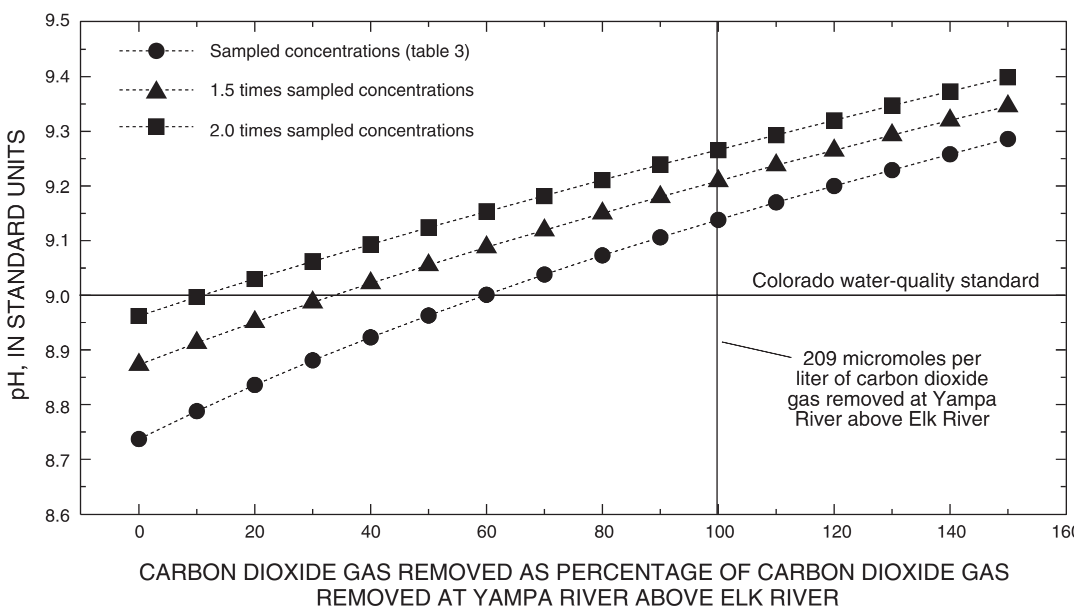

Figure 17. Simulated maximum potential pH for water sample collected at the Yampa River at Deerlodge Park on August 18, 1999, at varying salinities.

collected during August 16–19, 1999, than for samples collected during March 13–16, 2000, despite greater alkalinity during the latter period. The higher simulated pH during August 1999 can be attributed to the greater amount of CO_2 gas removed to simulate photosynthesis and the smaller solubility of dissolved CO_2 gas in the warmer water.

INTERPRETATION OF HISTORICAL DATA FROM YAMPA RIVER NEAR MAYBELL

This section describes the results of statistical hypothesis tests that were used to examine historical trends in onsite measurements, concentrations of dissolved solids and major ions, and selected thermodynamic characteristics of water-quality samples collected from the Yampa River near Maybell (site 8 in fig. 1). For this site, from November 29, 1950, through August 16, 1999, the USGS National Water Information System (NWIS) data base has 657 water-quality analyses that have sufficient data to allow thermodynamic calculations using PHREEQC. At a minimum, such calculations require pH measurement and concentrations of all major ions (except potassium, which can be neglected because of small concentrations). River discharge was not measured for one of these analyses, allowing 656 flow-adjusted analyses for statistical calculations. Through September 1, 1969, sampling times (for 413 analyses) and temperatures (for 406 analyses) were not recorded; most of these analyses were for composited samples. Missing temperatures were estimated to be the median water temperature for the month of the sampling date. Alkalinity was measured on unfiltered sample water before October 15, 1986, and on filtered water thereafter; for PHREEQC calculations, unfiltered measurements were used when filtered measurements were not available. For the periods October 9, 1980, through December 20, 1984 (25 samples), and May 15, 1991, through March 5, 1999 (61 samples), neither measurement generally was done, so alkalinity was calculated as the amount required to charge balance the solution with other ions, including potassium. For the sample collected on July 12, 1956, the concentration of the sulfate ion was calculated in a similar manner (neglecting potassium).

The Wilcoxon-Mann-Whitney rank-sum test, a nonparametric *t*-test on the joint ranks of two sample sets (Iman and Conover, 1983), was used to compare onsite measurements (including pH), constituent concentrations, and thermodynamic properties of water samples collected from Yampa River near Maybell during 1950–74 with those parameters during 1975–99. These periods of time were chosen to represent the general periods of time before and after onsite measurements of pH were begun and to separate the earlier period of minor coal-mining development from the period beginning in the late 1970’s, when coal-mining development grew rapidly. These statistical tests were done to indicate possible water-quality trends associated with the apparent historical increase in measured pH at Yampa River near Maybell and to suggest hypotheses that can be examined as possible causes of that increase.

Because concentrations of dissolved water-quality constituents usually vary inversely with discharge, if the data are not flow adjusted for hypothesis tests, unequal distributions of flow discharge between two sampling periods can cause apparent significant differences in physical measurements, concentrations of water-quality constituents, and thermodynamic properties. To adjust for the effects of flow, logarithmic values of these variables (except pH, calcite saturation index, and pH at atmospheric P_{CO_2}) were fitted by linear regression (Iman and Conover, 1983) to logarithmic values of discharge for the entire period of record, and residuals (differences between predicted and measured values) were used to conduct statistical hypothesis tests. Because pH is a logarithmic function of H^+ concentration, measured pH and pH at atmospheric P_{CO_2} were not converted to logarithms for regression. Because some calcite saturation indices are negative and cannot be converted to logarithms and because saturation indices are logarithmic quotients, calcite saturation indices were not converted to logarithms for regression.

Tests were set up by defining a null hypothesis (H_0) stating that the distribution of flow-regression residuals for measurements, concentrations, and properties was not significantly different for the two periods and an alternative hypothesis (H_1) stating that a significant difference did exist. A test resulting in a two-tailed significance less than or equal to 0.05 indicates that the alternative hypothesis was accepted, whereas a significance greater than 0.05 indicates that the null hypothesis was accepted. Accepting the null hypothesis does not necessarily indicate a lack of difference in sample distributions; it merely indicates that the chance of erroneously rejecting a true null

Table 2. Summary of Wilcoxon-Mann-Whitney rank-sum tests comparing flow-adjusted physical measurements, constituent concentrations, and thermodynamic properties of water samples collected from Yampa River near Maybell during 1950–74 with those measurements, concentrations, and properties collected during 1975–99

[Tests were made with a two-tailed significance level of 0.05 and a null hypothesis (H_o) defined as no significant difference between distributions of measurements, concentrations, and properties in samples collected during 1950–74 and 1975–99 and an alternative hypothesis (H_1) defined as a significant difference between measurements, concentrations, and properties; E, earlier period, 1950–74; L, later period, 1975–99; N, number of samples; *p*-value, significance level; ft^3/s, cubic feet per second; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; >, greater than; <, less than; mg/L, milligrams per liter; percent, percentage of cation (calcium, magnesium, sodium, and potassium) equivalents relative to total cation equivalents or percentage of anion (chloride, sulfate, and alkalinity) equivalents relative to total anion equivalents; saturation index, logarithm of ratio of ion activity product to solubility constant; P_{CO_2}, effective pressure of carbon dioxide gas; saturation factor, number of times solution is saturated with carbon dioxide gas compared to saturation at ambient atmospheric pressure]

Test variable	Unit	1950–74 (E)		1975–99 (L)		Test result	Test *p*-value
		Median	N	Median	N		
Specific conductance	µS/cm	469	472	530	181	H_1:L>E	<.001
pH	Standard units	7.7	473	8.2	183	H_1:L>E	<.001
Alkalinity	mg/L as $CaCO_3$	138	473	137	183	H_o	.659
Dissolved solids, sum of constituents	mg/L	287	473	317	183	H_1:L>E	<.001
Dissolved solids, total load	tons/day	280	473	371	183	H_1:L>E	<.001
Calcium	mg/L	38	473	41	183	H_1:L>E	.002
Magnesium	mg/L	16	473	20	183	H_1:L>E	<.001
Sodium	mg/L	36	473	39	183	H_1:L>E	.008
Potassium	mg/L	2.5	434	2.5	183	H_o	.226
Chloride	mg/L	18	473	14	183	H_1:E>L	<.001
Sulfate	mg/L	72	473	110	183	H_1:L>E	<.001
Fluoride	mg/L	0.3	183	0.2	183	H_1:E>L	<.001
Silica	mg/L	10	472	6.9	181	H_1:E>L	<.001
[1]Nitrate	mg/L as N	.23	448	.06	124	H_1:E>L	<.001
Calcium, fraction	Percent	40.0	473	37.4	183	H_1:E>L	<.001
Magnesium, fraction	Percent	26.4	473	31.1	183	H_1:L>E	<.001
Sodium, fraction	Percent	32.0	473	29.7	183	H_1:E>L	.008
Potassium, fraction	Percent	1.4	434	1.2	183	H_1:E>L	<.001
Chloride, fraction	Percent	10.6	473	6.4	183	H_1:E>L	<.001
Sulfate, fraction	Percent	29.1	473	40.7	183	H_1:L>E	<.001
Alkalinity, fraction	Percent	58.3	473	51.9	183	H_1:E>L	<.001
[2]Calcite saturation	Saturation index	-0.27	473	.26	183	H_1:L>E	<.001
[2]P_{CO_2} of solution	Saturation factor	10.2	473	2.5	183	H_1:E>L	<.001
[2]pH at atmospheric P_{CO_2}	Standard units	8.66	473	8.66	183	H_o	.773

[1] Late period for nitrate concentrations is 1975–94.
[2] Calculated with computer program PHREEQC (Parkhurst, 1995).

hypothesis exceeds 5 percent, given the variability in the data. When the alternative hypothesis was accepted for a variable, the mean ranks of the residuals for the two periods were inspected to determine which period had significantly greater values with respect to that variable. Results of flow-adjusted Wilcoxon-Mann-Whitney rank-sum tests are listed in table 2.

Trends in Dissolved Solids and Major Ions

Specific conductance (a measure of dissolved-solids concentration) and concentration of dissolved solids (fig. 18) were significantly greater during 1975–99 than during 1950–74 (table 2). Dissolved-solids load (discharge times dissolved-solids concentration,

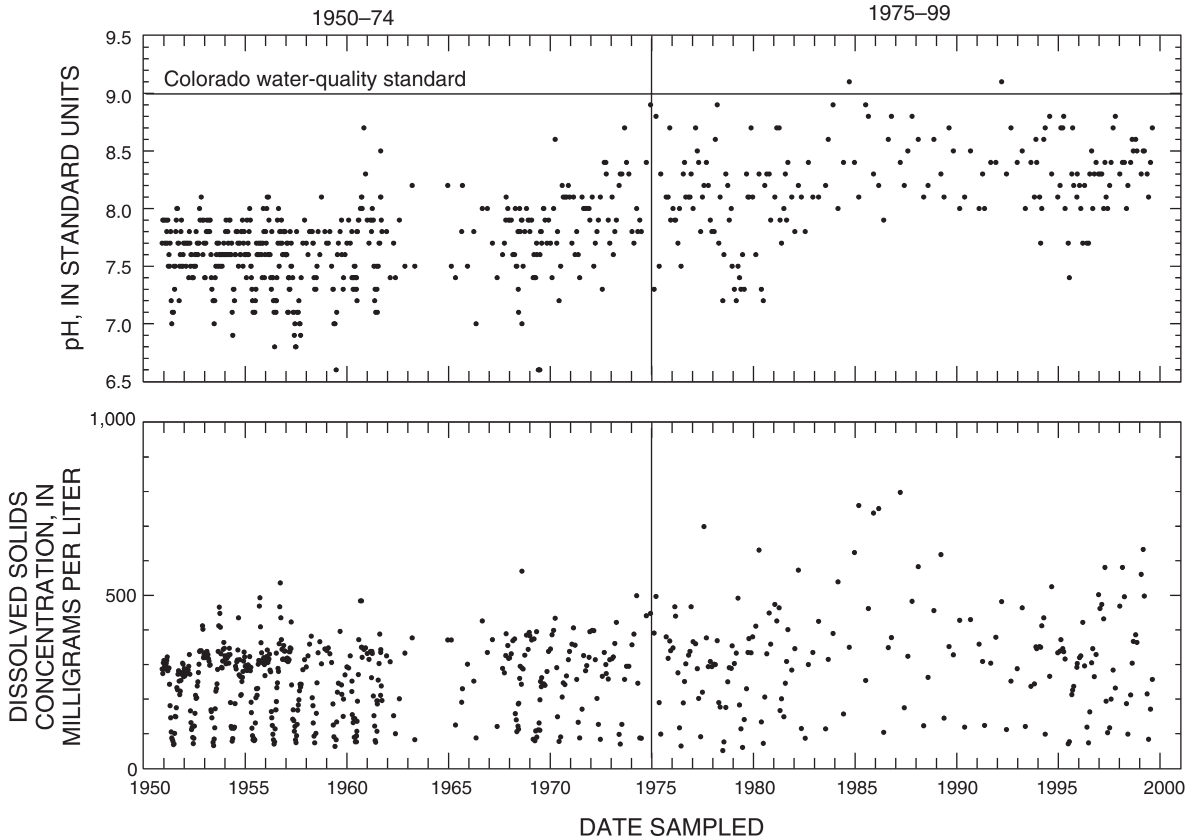

Figure 18. Temporal distribution of measured pH and dissolved solids at Yampa River near Maybell, 1950–99.

in tons per day) also had a significantly greater median value during this period. A significant increase (*p*-value <0.001) in measured pH values (fig. 18) occurred between the two periods. To a significant degree, the 1975–99 period had greater concentrations of calcium (fig. 19), magnesium (fig. 19), sodium (fig. 19), and sulfate (fig. 20). To a significant degree, the 1950–74 period had greater concentrations of chloride (fig. 19), fluoride, and silica. Alkalinity (fig. 20) and concentration of potassium (fig. 19) were not significantly different between the two periods.

The relatively large increase in median magnesium concentration (25 percent) between the two periods compared to increases in median concentrations of calcium (7.9 percent) and sodium (8.3 percent) and unchanged median concentrations of potassium caused significantly greater cation-equivalent fractions of magnesium and significantly smaller cation-equivalent fractions of calcium, sodium, and potassium during the later period (table 2). Similarly, the large increase in median sulfate concentration (52.8 percent) between the two periods compared to decreased median concentrations of chloride (22.2 percent) and alkalinity (0.7 percent) caused a significantly greater anion-equivalent fraction of sulfate and significantly smaller anion-equivalent fractions of chloride and alkalinity during the later period (table 2). Judging by median equivalent percentages (table 2), the water at Yampa River near Maybell, on average, changed from a calcium-sodium-magnesium-bicarbonate-sulfate type during 1950–74 to a calcium-magnesium-sodium-bicarbonate-sulfate type during 1975–99, with sulfate becoming more dominant.

The results of statistical hypothesis testing (table 2) are consistent with previous studies. Liebermann and others (1989) determined by monotonic-trend analysis that, at Yampa River near Maybell over the period 1951–83, median annual dissolved-solids concentration increased by 0.9 mg/L per year, a 21-percent increase (29 percent, 1.2 mg/L per year, when flow adjusted). Dissolved-solids load increased by 65 percent over the 33 years of record. In addition, they determined that annual flow-adjusted concentrations of magnesium, sodium, and sulfate were deter-

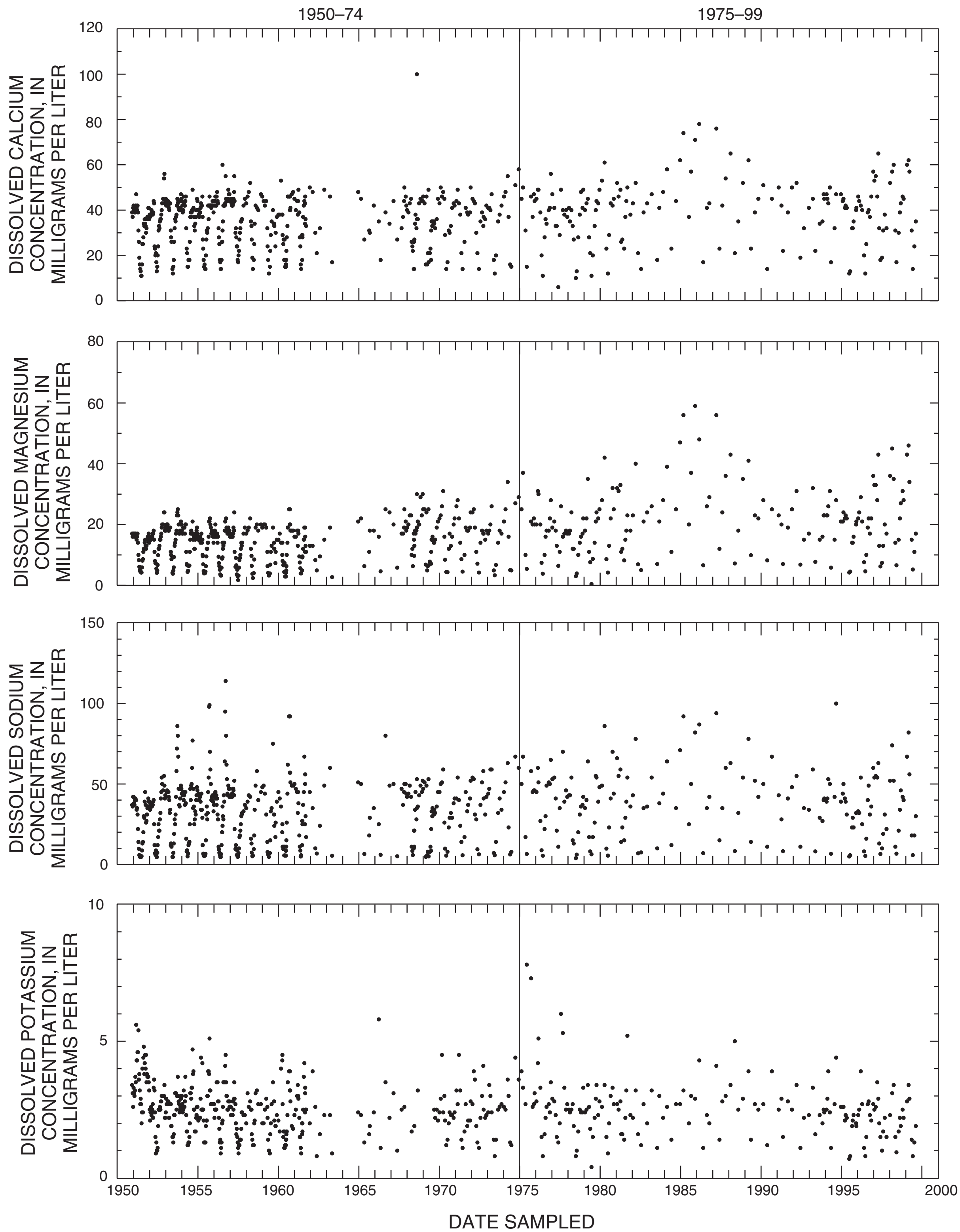

Figure 19. Temporal distribution of concentrations of major cations at Yampa River near Maybell, 1950–99.

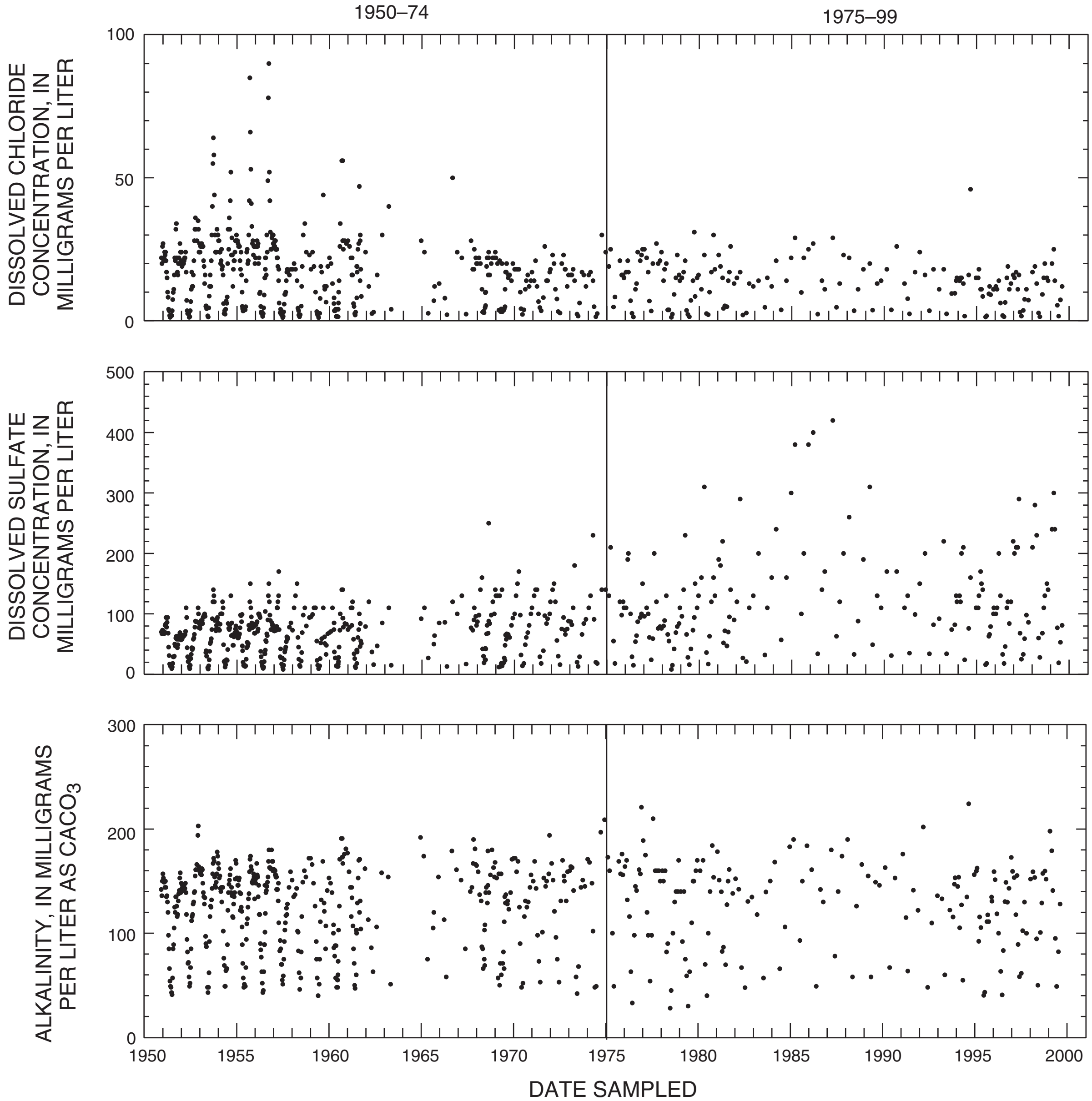

Figure 20. Temporal distribution of concentrations of major anions at Yampa River near Maybell, 1950–99.

mined to have significant upward trends for the period 1951–83. For the Yampa River near Maybell for the period 1951–96, Vaill and Butler (1999) determined significant annual increases in annual, flow-adjusted dissolved-solids concentrations (by 0.61 percent per year) and loads (by 0.57 percent per year).

Trends in Thermodynamic Properties

The coincident historical increase in measured pH and concentrations of dissolved solids (fig. 18), calcium, magnesium, sodium (fig. 19), and sulfate (fig. 20) at Yampa River near Maybell raises the question whether the increase in measured pH was caused by the increase in concentrations of these dissolved constituents. To test this possibility, various thermodynamic properties and hypothetical reactions were calculated using PHREEQC.

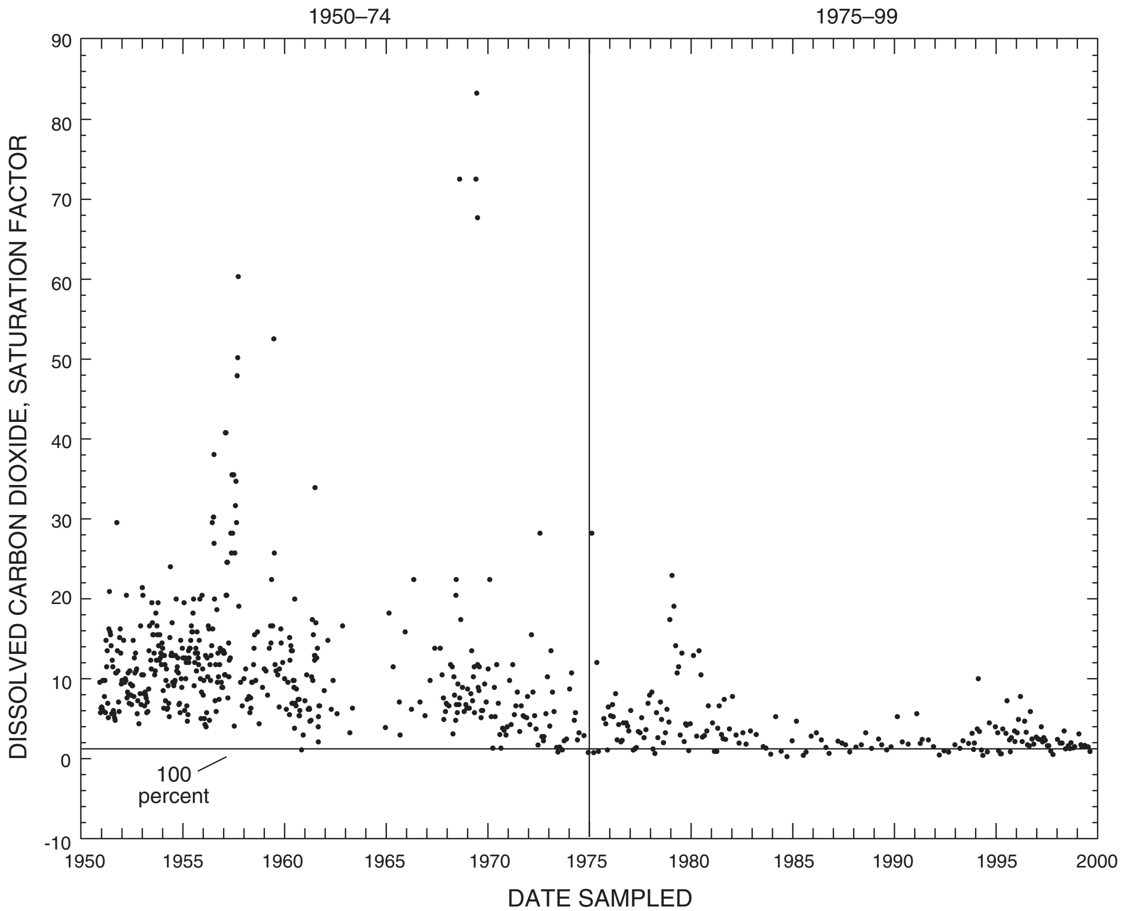

Figure 21. Temporal distribution of dissolved carbon dioxide saturation factor at Yampa River near Maybell, 1950–99.

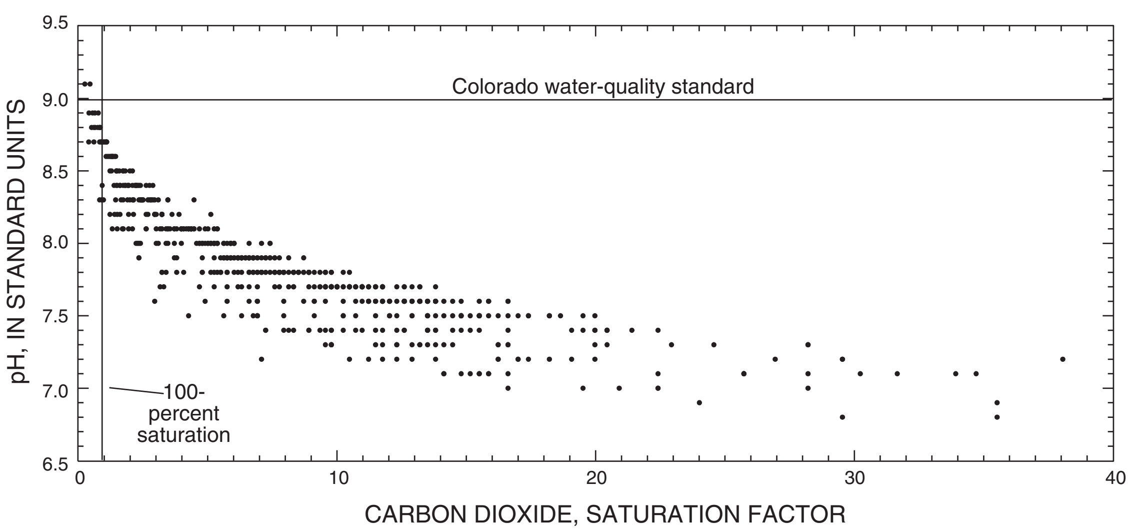

Figure 22. Relation between measured pH and dissolved carbon dioxide saturation factor at Yampa River near Maybell, 1950–99.

The CO_2 saturation factor (equals 1 when a solution is in equilibrium with atmospheric P_{CO_2}) (fig. 21) was significantly greater for the period 1950–74 (table 2), which corresponds to the significantly smaller measured pH values during that period. The inverse relation between measured pH and CO_2 saturation is shown in figure 22. Values of measured pH exceeded 8.7 only when the water was undersaturated (saturation factor less than 1), apparently indicating photosynthesis, or saturated with CO_2 (saturation factor equal to 1). Values of measured pH less than or equal to 7.5 usually had a CO_2 saturation factor exceeding 10, apparently indicating relatively large rates of respiration plus oxidation of organic matter.

PHREEQC was used to hypothetically equilibrate each sample with atmospheric P_{CO_2}. Resulting pH (fig. 23) was not significantly different between the two periods, with a median value of 8.66 during each period (table 2). Because PHREEQC accounts for concentrations of major ions during these calculations,

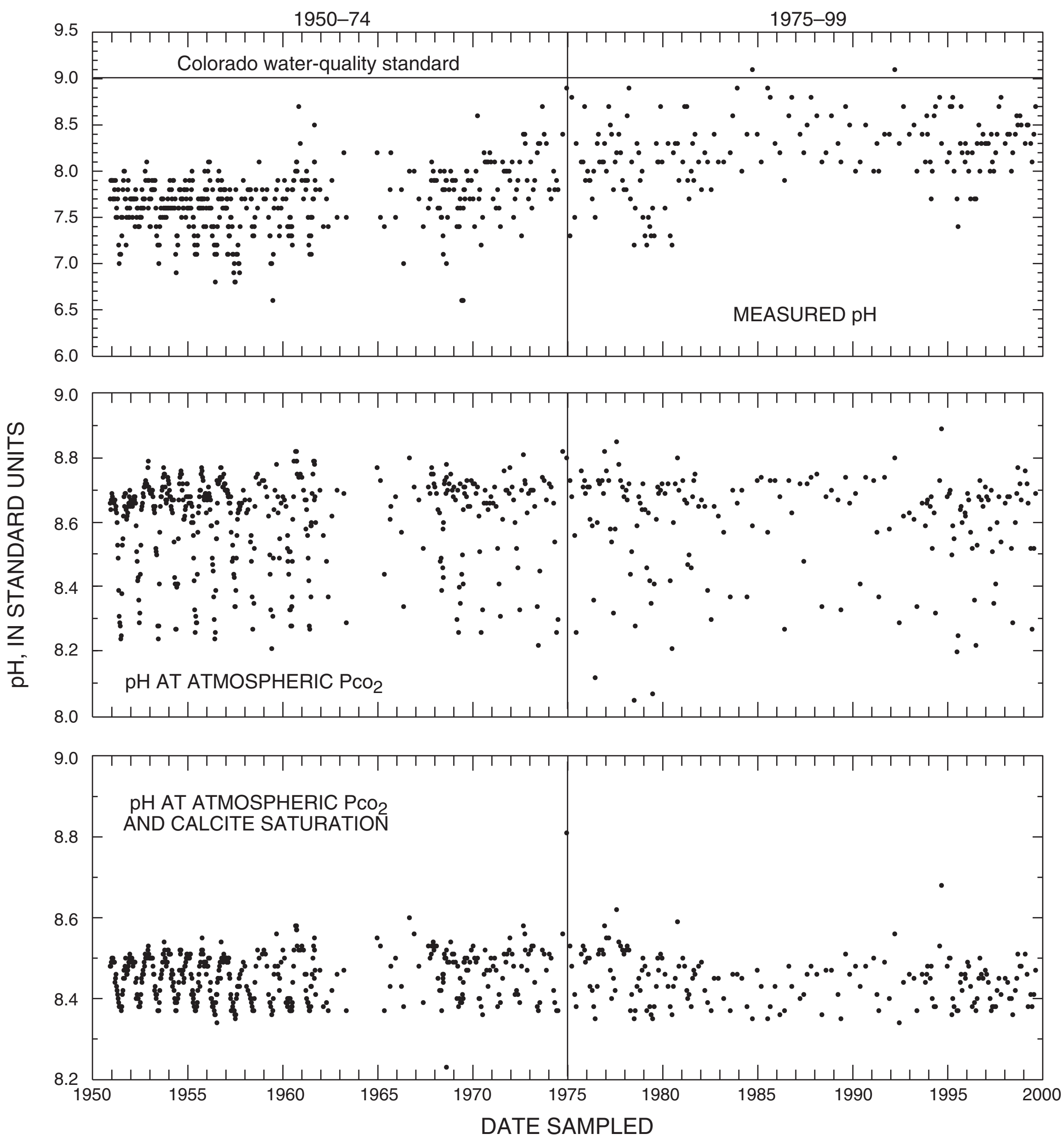

Figure 23. Temporal distribution of measured and simulated pH at Yampa River near Maybell, 1950–99.

one can conclude that significantly greater measured pH values during the 1975–99 period were not caused by the significantly greater concentrations of calcium, magnesium, sodium, and sulfate during that period.

Additional simulations using PHREEQC showed that increased concentrations of calcium, magnesium, sodium, and sulfate actually can cause a small decrease in pH. The synoptic sample collected from the Yampa River near Maybell on August 16, 1999 (table 3), was simulated to hold P_{CO_2} constant and have concentrations of these ions increased by substantial amounts: calcium, by 40 mg/L; magnesium, by 24.3 mg/L; sodium, by 23 mg/L; and sulfate, by 240 mg/L. These simulated increases caused pH values to decrease from 8.74 (measured) to 8.70. In contrast, substituting in the reaction an equivalent amount of carbonate (CO_3^{2-}) ions (150 mg/L) for sulfate (SO_4^{2-}) ions caused simulated pH to rise to 9.10, illustrating the effect of alkalinity on pH. However, because alkalinity was not significantly different between the two periods (table 2), the significant increase in measured pH values between the two periods cannot be explained by an increase in alkalinity, leaving decrease in P_{CO_2} as the most likely cause.

CAUSES OF HISTORICAL INCREASE IN MEASURED pH AT YAMPA RIVER NEAR MAYBELL

The significantly larger measured pH values at Yampa River near Maybell during 1975–99 (fig. 18, table 2) can be attributed to one or a combination of three causes: (1) substantially greater dominance of rates of respiration plus oxidation of organic matter (relative to rates of photosynthesis), raising P_{CO_2} and decreasing pH in the river during 1950–74; (2) substantially greater dominance of rates of photosynthesis (relative to rates of respiration plus oxidation of organic matter) during 1975–99, decreasing P_{CO_2} and increasing pH in the river; or (3) bacterial respiration and oxidation of organic matter, raising P_{CO_2} and decreasing pH in sample containers submitted for laboratory measurement of pH during 1950–74.

The significantly larger calculated values for P_{CO_2} during 1950–74 than during 1975–99 (discussed in the section “Trends in Thermodynamic Properties”; table 2) suggest the possibility of substantially greater dominance of rates of respiration plus oxidation of organic matter (relative to rates of photosynthesis) during that period. However, oxidation of relatively large concentrations of organic matter would have been required to substantially oversaturate river water with CO_2 during 1950–74 (fig. 21). Historical data for concentrations of dissolved and suspended organic matter are not adequate to determine if organic matter was more abundant during 1950–74 than during 1975–99, although it is possible that it was more abundant during 1950–74 before improvements in wastewater treatment at Steamboat Springs and Craig in the early 1980’s. However, in the relatively shallow, turbulent water of the Yampa River upstream from the site near Maybell, which is about 57 miles downstream from the relatively small sewage outfall at Craig, reaeration probably would usually limit CO_2 saturation factors (fig. 21) to less than 5 (compared to the median value of 10.2 for measured pH during 1950–74; table 2). Allan (1995) states that this limitation usually applies to larger European rivers, which are less exposed to the atmosphere because of greater depths. Therefore, it is unlikely that substantially greater dominance of rates of respiration plus oxidation of organic matter was the primary reason measured pH values were significantly smaller (and CO_2 saturation factor was significantly larger) during 1950–74 than during 1975–99, although it possibly was a contributing factor.

The significantly larger concentrations of nitrate during 1950–74 than during 1975–94 (table 2; fig. 24) suggest the possibility of substantially greater rates of photosynthesis during 1950–74. (This discussion assumes that lack of preservation of nitrate samples during 1950–74 did not elevate nitrate concentrations sufficiently to cause the significantly larger nitrate concentrations during that period.) This possibility is further supported by the use of phosphorus in household detergents during the 1950’s and 1960’s (Hem, 1985) and improvements in wastewater treatment at Steamboat Springs and Craig during the early 1980’s. The possibility of substantially greater rates of photosynthesis during 1950–74 than during 1975–99, if taken alone, would not account for the historical increase in measured pH at Yampa River near Maybell because it would imply greater pH during 1950–74 than during 1975–99. However, it is possible that substantially smaller rates of photosynthesis during 1975–99 would have been accompanied by substantially smaller rates of respiration plus oxidation of organic matter (because less organic matter possibly

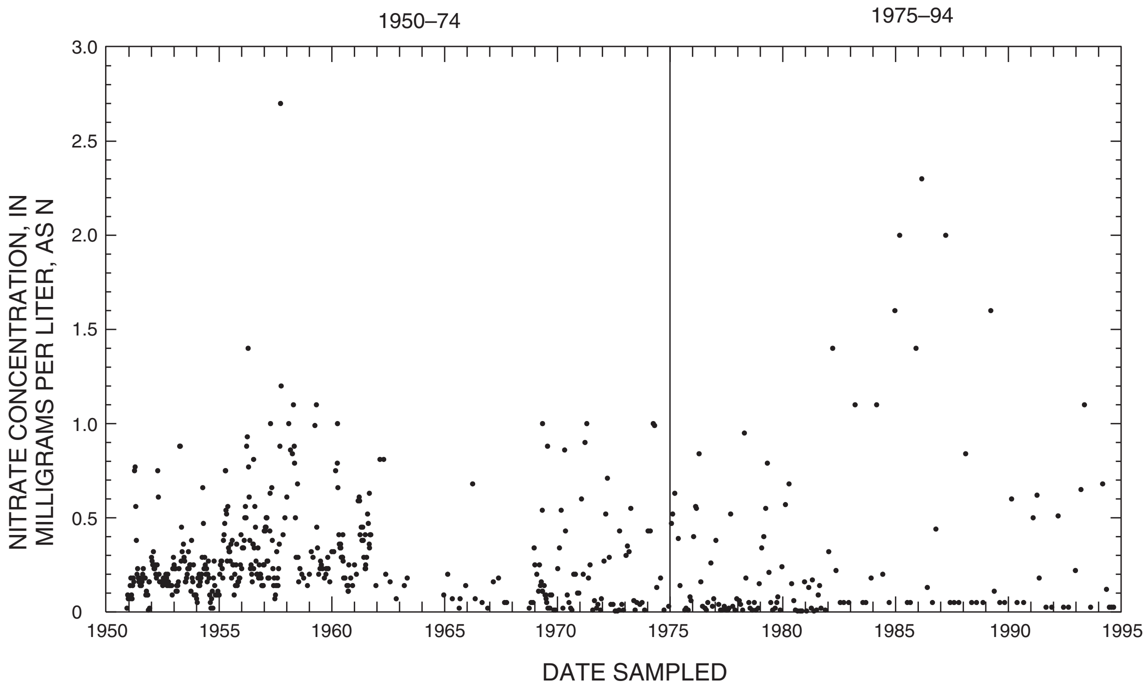

Figure 24. Temporal distribution of concentrations of nitrate at Yampa River near Maybell, 1950–94.

was discharged in sewage effluent)—at least partially offsetting or reversing the decrease in pH values caused by a possible decrease in rates of photosynthesis. In conclusion, available data are not sufficient to assess possible changes in rates of photosynthesis relative to rates of respiration plus oxidation of organic matter between 1950–74 and 1975–99.

Water-quality records indicate that the significantly smaller pH values measured at Yampa River near Maybell during 1950-74 (fig. 2) probably were caused mostly by changes in measurement procedures. The USGS National Water Information System (NWIS) data base was initiated in about 1974. Data for earlier water-quality analyses were manually loaded into the data base from hardcopy records, whereas data collected after the data base was activated was recorded into NWIS on an ongoing basis. Before the establishment of a separate parameter code for laboratory pH measurements in 1980, all prior pH measurements (whether measured onsite or in the laboratory) were recorded with the older parameter code that was designated for onsite measurements in 1980. Archived records indicate that pH measurements stored in the NWIS data base for the Yampa River near Maybell were made at the USGS regional water-quality laboratory in Salt Lake City, Utah, through June 26, 1974. Thereafter, laboratory measurements were made at the USGS Central Laboratory (currently the National Water Quality Laboratory) in Denver, Colorado. Archived records available for the period between September 2, 1974, and September 7, 1977, indicate that pH values registered in the NWIS data base were measured onsite. Although records are not available for the period between September 7, 1977, and October 9, 1980, beginning on October 9, 1980, NWIS records for samples collected at Yampa River near Maybell report values both for onsite and for laboratory pH measurements. It is reasonable to conclude that, beginning in September 1974, most pH values stored in the NWIS data base as onsite measurements were actually measured onsite (with some possible exceptions before October 9, 1980) but that, prior to September 1974, such values were actually measured in the laboratory. Laboratory measurements of pH probably were not adversely affected by deficiencies in instrumentation. Laboratory measurement of pH had become relatively reliable by the 1930's, although meters and electrodes improved considerably in the 1950's and 1960's (Hem, 1985).

Compositing of samples is another potential problem with pH values of samples collected from Yampa River near Maybell in the 1950's and 1960's. Archived records indicate that most of the samples collected during 1962–69 were composited over a period of 2 to 31 days (usually more than 5 days) and that reported pH values were measured in the laboratory. Records are not available for samples collected prior to November 1961, but it is likely that most or all samples collected before then were also composited because sampling times were not recorded. Compositing of samples increases the potential for substantial discrepancies between pH values measured onsite and those measured in the laboratory.

The primary potential problem with laboratory pH measurements of natural water samples is chemical changes that often occur in the time between sample collection and measurement. Such changes can be caused by precipitation of minerals, dissolution of minerals in sediment, oxidation/reduction reactions, or exchange of dissolved gases (especially carbon dioxide) with the atmosphere (either into or out of the sample water). When such processes occur in the sample container, the concentration of the hydrogen ion (H^+) is usually changed, and pH measured in the laboratory is not representative of the environment from which the sample was collected. During shipping and holding, bacteria can use dissolved oxygen to oxidize organic matter to produce CO_2, which lowers pH; however, photosynthesis cannot occur to consume CO_2. Sample containers would have to remain open long periods of time before the sample water could equilibrate with the partial pressure of CO_2 in the atmosphere at the laboratory. Production of CO_2 potentially was greatly enhanced in composited samples before 1970 because the sample containers were held (possibly at ambient temperature) for days to weeks. Although records indicate that onsite pH was measured between September 2, 1974, and September 7, 1977, and that, beginning on October 9, 1980, onsite and laboratory pH measurements both were recorded, anomalously large CO_2 saturation factors between September 7, 1977, and October 9, 1980 (fig. 21), suggest the possibility that these saturation factors result from laboratory measurement of pH or onsite measurement problems.

Onsite measurement, when done too rapidly to reach equilibration, can underestimate pH. At pH greater than 8.5, electrode response is sluggish in freshwater, and equilibration can take minutes. Lower temperature during winter causes substantially slower electrode equilibration. Inadequate equilibration time usually gives a low pH measurement. This problem probably was more common before late 1983 at Yampa River near Maybell. A plot of difference between onsite pH and laboratory pH (fig. 25) indicates that between October 9, 1980, and July 20, 1983, laboratory pH was usually higher than onsite pH, and after July 20, 1983, onsite pH was usually higher than laboratory pH. Onsite pH should usually be equal to or greater than laboratory pH because bacterial oxidation of organic matter usually increases P_{CO_2} in sample containers shipped to the laboratory (although this process is minimized in samples shipped and held on ice) or, if the sample was originally undersaturated with CO_2 because of photosynthesis, upon exposure to the larger (about 7 percent) atmospheric P_{CO_2} at the

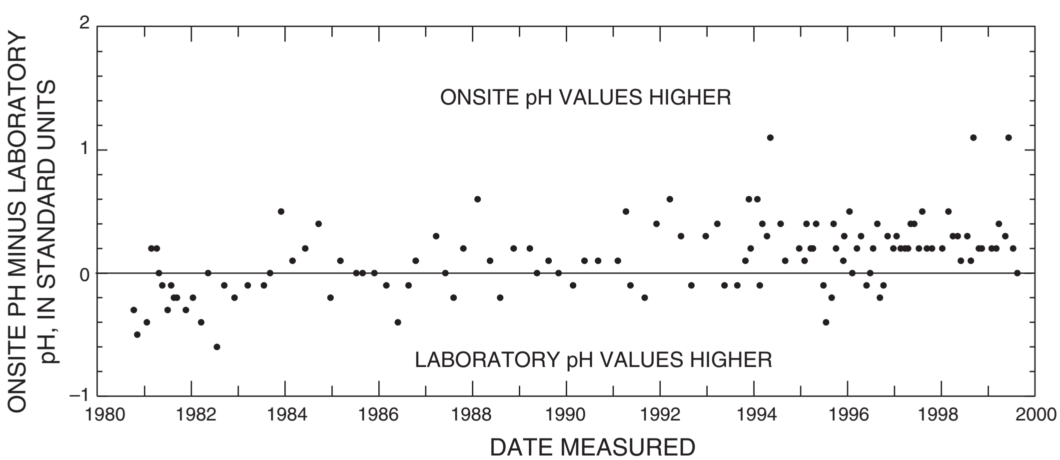

Figure 25. Temporal distribution of difference between onsite and measured laboratory pH at Yampa River near Maybell, 1980–99.

laboratory in Denver (altitude 5,510 ft) compared to the Yampa River near Maybell (altitude 5,905 ft). Therefore, considering the nature of laboratory measurements and onsite measurements made before September 6, 1983, onsite measurements made since that date are more reliable (although with some potential for measurement error, especially underestimation). This analysis emphasizes the difficulty of obtaining pH values that represent the river environment.

SUMMARY

In 1999, the U.S. Geological Survey began a study of pH trends in the Yampa River from the vicinity of its headwaters near Steamboat Springs, Colorado, to its mouth. The study was initiated because of an apparent historical increase in measured pH at the U.S. Geological Survey stream gage 09251000, Yampa River near Maybell, Colorado, from an average of about 7.6 during the 1950’s and 1960’s to about 8.3 during the 1980’s and 1990’s. This apparent increase, if real and continuing to the point where pH frequently exceeded the Colorado water-quality standard of 9.0, could cause adverse effects on aquatic organisms, especially fish, in the Yampa River Basin, including Dinosaur National Monument.

The principal conclusion of this study is that the apparent historical increase in measured pH at Yampa River near Maybell probably was caused mostly by changes in measurement procedure. The following discussion summarizes how this conclusion was reached.

Synoptic sampling of the Yampa River during August 16–19, 1999, a relatively warm, dry period of base flow, showed that late afternoon pH varied between 8.46 and 9.20. The smallest pH value (8.46) was measured downstream from Stagecoach Reservoir, about 0.25 mile downstream from the dam spillway. The largest pH value (9.20), which exceeded the Colorado water-quality standard of 9.0, was measured at Yampa River above Elk River, which is about 1.8 miles downstream from Steamboat Springs Regional Waste Water Treatment Plant. This site had the largest measured concentration of phosphorus (0.06 mg/L as P) and the second largest measured concentrations of dissolved ammonia plus organic nitrogen (0.30 mg/L as N) and dissolved organic carbon (5.0 mg/L as C). Dissolved oxygen concentration was 161 percent oversaturated, and thermodynamic calculations indicated that dissolved CO_2 was undersaturated at 26 percent relative to the concentration that would occur at equilibrium with the atmosphere. These measurements resulted from photosynthesis by algae that was induced by enrichment of nutrients from sewage effluent.

The effects of photosynthesis persisted about 16.3 miles downstream to Yampa River below diversion near Hayden, although attenuated by reaeration and dilution with freshwater from the Elk River; pH had decreased to 8.70, dissolved oxygen was oversaturated at 124 percent, and CO_2 was undersaturated at 69 percent. At Yampa River below Craig, about 6.2 miles downstream from the Craig Waste Water Treatment Plant, the effects of photosynthesis were greater, with pH at 8.80, dissolved oxygen oversaturated at 131 percent, and CO_2 undersaturated at 59 percent. The effects of photosynthesis decreased to Yampa River near Maybell and farther to Yampa River above Little Snake River, with a pH of 8.74 at both sites. Supersaturation with dissolved oxygen decreased to 120 and 105 percent, while undersaturation with CO_2 was slight at 87 and 86 percent.

Apparently, respiration plus oxidation of organic matter became dominant in Dinosaur National Monument at Yampa River at Deerlodge Park, where measurements indicated pH at 8.51 and dissolved oxygen oversaturation at 109 percent, and calculations indicated CO_2 oversaturated at 189 percent. Respiration plus oxidation of organic matter, though reduced, apparently extended to Yampa River at mouth, where pH rose to 8.60, dissolved oxygen oversaturation was 103 percent, and CO_2 oversaturation was 137 percent.

Diurnal measurements on the Yampa River during August 23–26, 1999, show that the effects of photosynthesis and respiration plus oxidation of organic matter decreased downstream. Between Yampa River above Elk River, Yampa River below Craig, and Yampa River near Maybell, maximum daily pH values decreased from 9.07 to 8.78 to 8.66, diurnal fluctuations in pH decreased from 1.15 to 0.61 to 0.14 unit, and maximum daily dissolved oxygen saturation decreased from 178 to 140 to 132 percent. These decreases indicate that the effects of photosynthesis decreased substantially upstream from the Yampa River near Maybell. Furthermore, the downstream increase in minimum dissolved oxygen saturation from 66 to 78 to 86 percent indicates that respiration plus oxidation of organic matter decreased

substantially upstream from this site. Despite cloudy skies during most of the daylight hours at Yampa River at Deerlodge Park and at Yampa River at mouth, larger night-time pH values (compared to day-time values) at those sites indicate (1) that source waters varied with respect to capacity for respiration plus oxidation of organic matter and photosynthesis and (2) that photosynthesis was minor and pH was largely controlled by relative rates of respiration plus oxidation of organic matter.

Reconnaissance field measurements taken during August 30–September 3, 1999, on the Yampa River in Dinosaur National Monument between Deerlodge Park and at mouth (Echo Park) show pH in the narrow range of 8.43–8.77 (mean 8.63), indicating little or no photosynthesis. Aquatic vegetation, mostly moss, was observed to be sparse and scattered. Measurements of pH by Steele and others (1978) during August 17–19, 1976, when the season and discharge were similar, had the same range and mean as pH measured during the reconnaissance trip for this study. In addition, their measurements of dissolved oxygen saturation during late afternoon ranged between 103 and 108 percent, indicating minor photosynthesis. Overall, similarities between measurements by Steele and others (1978) and those made for this study indicate that the Yampa River in Dinosaur National Monument was not significantly different 23 years after the earlier study with respect to the effects of photosynthesis on water quality.

Synoptic sampling was conducted during March 13–16, 2000, when late-winter melting of snow and ice at lower altitudes increased discharge substantially at most Yampa River sites compared to synoptic sampling during August 1999. Average specific conductance increased by 58 percent at Yampa River sites during March 2000 compared to August 1999, mostly because of substantial increases in concentrations of sodium (by 88 percent), magnesium (by 93 percent), and sulfate (by 163 percent); most of these increases occurred at Yampa River below Craig. Concentrations of nitrite plus nitrate were about 9 times greater during March 2000 compared to August 1999, with the largest increase (greater than 1,200 percent) also occurring at Yampa River below Craig. Concentrations of dissolved organic carbon increased an average of about 32 percent at this site, although concentrations decreased or remained relatively constant at sites sampled upstream from there. The substantial increases in specific conductance and in concentrations of nitrite plus nitrate and dissolved organic carbon at Yampa River below Craig in March 2000 compared to August 1999 probably resulted from flushing of the land surface by melting snow and ice along tributaries and the Yampa River valley between Yampa River below diversion near Hayden and Yampa River below Craig during March 2000.

At and downstream from Steamboat Springs, pH at Yampa River sites averaged 8.85 during synoptic sampling in March 1999 (compared to 8.70 in August 1999), with an average P_{CO_2} of 67 percent of saturation (compared to 99 percent during August 1999). As during August 1999, P_{CO_2} was oversaturated in the Yampa River at Deerlodge Park (119 percent) and at the mouth of the Yampa River (112 percent), although less than during August 1999 (176 and 132 percent). Dissolved oxygen concentrations averaged 119-percent saturation during both sampling periods, but the 40-percent larger concentrations during March 2000 imply a 40-percent larger increase by photosynthesis during that period. These relations indicate greater effects of photosynthesis on pH and dissolved oxygen concentrations in March 2000, despite shorter days and colder water than during August 1999. The larger effects of photosynthesis on pH and dissolved oxygen concentrations during March 2000 compared to August 1999 probably were caused by (1) slower rates of exchange of CO_2 into and dissolved oxygen out of the river because of colder and deeper water and (2) slower rates of CO_2 production and oxygen consumption resulting from slower rates of respiration by organisms and from slower oxidation of organic matter in the colder river water and streambed sediment.

Thermodynamic calculations indicate that synoptic samples collected at Yampa River sites, if equilibrated with local atmospheric P_{CO_2}, would have pH in the range 8.64 to 8.77 (average 8.69) during March 2000, compared to 8.55 to 8.80 (average 8.67) during August 1999. Additional calculations indicate that, if equilibrated with local atmospheric P_{CO_2} and with calcite, samples collected in March 2000 would have pH in the narrow range of 8.43–8.50 (average 8.45), compared to 8.42–8.50 (average 8.45) for samples collected in August 1999. These results indicate that pH in the Yampa River was largely controlled by degree of P_{CO_2} saturation and oversaturation with calcite during both sampling periods. They also show that the high alkalinity of water in the Yampa River causes relatively high pH that can be further elevated by removal of CO_2 during photosynthesis.

Hypothetical simulations were done on samples collected in the lower Yampa River Basin to simulate the same amount of photosynthesis that existed at Yampa River above Elk River. These simulations indicate that maximum potential late-afternoon pH could increase to 9.1–9.2 (exceeding the Colorado water-quality standard of 9.0) during late-winter, lowland runoff and during late-summer base flow and that pH would equal or exceed the water-quality standard if at least 67 percent of the calculated amount of CO_2 gas removed by photosynthesis from Yampa River above Elk River was removed from these samples. Additional simulations indicate that increased salinity resulting from drought conditions in the lower basin would further increase maximum potential late-afternoon pH about 0.1 unit, potentially causing late-afternoon pH to sustain values above the Colorado water-quality standard of 9.0.

Flow-adjusted, two-tailed Wilcoxon-Mann-Whitney rank-sum tests were used to compare onsite measurements, constituent concentrations, and thermodynamic properties of water samples collected from Yampa River near Maybell during 1950–74 with those parameters during 1975–99. These two periods were defined to represent the general periods of time before and after onsite measurements of pH were begun and to separate the earlier period of minor coal-mining activity from the period of more extensive coal mining, beginning in the late 1970's. Specific conductance, concentration of dissolved solids, dissolved solids load, measured pH, and dissolved concentrations of calcium, magnesium, sodium, and sulfate were significantly greater during 1975–99. Dissolved concentrations of chloride, fluoride, and silica were significantly greater during 1950–74. Alkalinity and dissolved concentration of potassium were not significantly greater during either period.

The coincident historical increase in measured pH and concentrations of dissolved solids, calcium, magnesium, sodium, and sulfate at Yampa River near Maybell raises the question whether increase in the concentrations of these dissolved constituents caused an increase in pH. To test this hypothesis, various thermodynamic properties and hypothetical reactions were calculated. During 1950–74, CO_2 was significantly more oversaturated and corresponded to the significantly smaller pH during that period. During that period, CO_2 had a median saturation factor of 10.2, compared to a median of 2.5 for 1975–99. However, after hypothetically equilibrating all samples with atmospheric P_{CO_2}, resulting pH was not significantly different between each period, with a median of 8.66 for both periods. This result indicates that larger concentrations of calcium, magnesium, sodium, and sulfate during the later period did not increase pH, leaving decrease in P_{CO_2} as the most likely cause.

Oxidation of abundant, nutrient-poor organic matter would have been required to substantially oversaturate water of the Yampa River near Maybell with CO_2 and cause significantly smaller pH during 1950–74. Inadequate data exist to characterize past concentrations of organic matter in the Yampa River. However, reaeration in the relatively shallow, turbulent water upstream from the Yampa River near Maybell site probably would usually limit CO_2 saturation factors to less than 5 (compared to the median value of 10.2 for measured pH during 1950–74). Therefore, it is unlikely that substantially larger rates of oxidation of organic matter was the main cause for the significantly smaller measured pH at Yampa River near Maybell during 1950–74, although it possibly was a contributing factor.

Significantly larger concentration of nitrate at Yampa River near Maybell during 1950–74 than during 1975–94 indicates the possibility of substantially greater rates of photosynthesis during 1950–74, which would not explain the significantly larger measured pH during 1975–99. Furthermore, substantially smaller rates of photosynthesis during 1975–99 possibly would have been more than offset by substantially smaller rates of respiration plus oxidation of organic matter, increasing pH by increasing the dominance of rates of photosynthesis relative to rates of respiration plus oxidation of organic matter. Available data are insufficient to allow assessment of possible changes in rates of photosynthesis relative to rates of respiration plus oxidation of organic matter between 1950–74 and 1975–99.

Most of the significant increase in measured pH at Yampa River near Maybell between 1950–74 and 1975–99 can be attributed to bacterial oxidation of organic matter in sample containers during shipping and holding prior to laboratory measurement, especially in composited samples collected prior to 1970. Because of this problem and the potential for underestimation of pH measured onsite before September 6, 1983, onsite measurements made after that date are more reliable.

REFERENCES CITED

Allan, J.D., 1995, Stream ecology—Structure and function of running waters: London, Chapman & Hall, 388 p.

Drever, J.I., 1982, The geochemistry of natural waters: Englewood Cliffs, N.J., Prentice-Hall, 388 p.

Fishman, M.J., and Friedman, L.C., eds., 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.

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

Horowitz, A.J., Demas, C.R., Fitzgerald, K.F., Miller, T.L., and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94–539, 57 p.

Iman, R.L., and Conover, W.J., 1983, A modern approach to statistics: New York, Wiley, 497 p.

Liebermann, T.D., Mueller, D.K., Kircher, J.E., and Choquette, A.F., 1989, Characteristics and trends of streamflow and dissolved solids in the Upper Colorado River Basin, Arizona, Colorado, New Mexico, Utah, and Wyoming: U.S. Geological Survey Water-Supply Paper 2358, 64 p.

National Climate Data Center, 1983, Climate data—Colorado annual summary: Asheville, N.C., v. 88, no. 13, 25 p.

National Weather Service, 1985, Normal annual precipitation 1931–60, Colorado: Washington, D.C., scale 1:500,000, 2 sheets.

Parkhurst, D.L., 1995, User’s guide to PHREEQC—A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 95–4227, 143 p.

Rantz, S.E., and others, 1982, Measurements and computation of streamflow: U.S. Geological Survey Water-Supply Paper 2175, v. 1 and 2, 631 p.

Steele, T.D., Wentz, D.A., and Warner, J.W., 1978, Hydrologic reconnaissance of the Yampa River during low flow, Dinosaur National Monument, northwestern Colorado: U.S. Geological Survey Open-File Report 78–226, 10 p.

U.S. Census Bureau, 2000, Population estimates for places: U.S. Census Bureau, accessed May 8, 2002, at URL http://www.census.gov/population/estimates/metro-city/placebyco/SC99T8_CO.txt

Vaill, J.E., and Butler, D.L., 1999, Streamflow and dissolved-solids trends, through 1996, in the Colorado River Basin upstream from Lake Powell—Colorado, Utah, and Wyoming: U.S. Geological Survey Water-Resources Investigations Report 99–4097, 47 p.

SUPPLEMENTAL INFORMATION

Table 3. Onsite measurements and concentrations of major and minor water-quality constituents in samples collected from Yampa River and tributary sites, August 1999 and March 2000

[deg C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; --, no data; <, less than; R, River; blw, below; abv, above; nr, near]

Station number (site number from table 1, in parentheses)	Station name	Date	Time	Discharge, cubic feet per second	Temperature, water (deg C)	Specific conductance, onsite (µS/cm)	pH, onsite (standard units)	pH, laboratory (standard units	Oxygen, dissolved (mg/L)	Alkalinity, calculated (mg/L as $CaCO_3$)	Calcium, dissolved (mg/L)
09237500(1)	Yampa R blw Stagecoach Reservoir, CO	08-19-99	1600	99	15.5	419	8.46	8.36	--	177	51
	Yampa R blw Stagecoach Reservoir, CO	03-13-00	1200	98	2.8	388	7.77	8.07	10.0	171	48
09239500(2)	Yampa R at Steamboat Springs, CO	08-19-99	1200	160	17.8	294	8.59	8.35	7.5	116	34
	Yampa R at Steamboat Springs, CO	03-13-00	1530	179	6.0	307	8.82	8.19	11.8	133	39
402936106565000(3)	Yampa R abv Elk R	08-18-99	1600	159	21.6	320	9.20	9.01	11.2	123	33
	Yampa R abv Elk R	03-13-00	1530	194	6.8	374	9.17	8.84	14.4	143	40
402914106580400(4)	Elk R nr mouth	08-18-99	1300	122	16.9	102	8.08	7.92	9.3	40	12
	Elk R nr mouth	03-14-00	1200	92	1.1	188	8.11	8.21	11.5	69	23
09244410(5)	Yampa R blw diversion, nr Hayden, CO	08-17-99	1600	237	17.4	260	8.70	8.25	9.5	90	26
	Yampa R blw diversion, nr Hayden, CO	03-14-00	1530	264	3.8	464	8.87	8.54	12.6	127	43
402816107003800	Trout Creek nr Milner, CO	08-17-99	1300	16	17.1	620	8.52	8.28	8.7	158	55
403152107260700	Elkhead Creek nr mouth	08-16-99	1325	3.3	22.9	465	8.43	8.35	8.5	137	39
09247600(6)	Yampa R blw Craig, CO	08-16-99	1640	273	21.6	316	8.80	8.55	9.2	97	28
	Yampa R blw Craig, CO	03-14-00	1500	397	5.0	778	9.08	8.62	13.8	154	56
09249750(7)	Williams Fork at mouth, nr Hamilton, CO	08-16-99	1300	63	18.0	527	8.52	8.56	9.4	169	47
	Williams Fork at mouth, nr Hamilton, CO	03-14-00	1200	79	4.5	665	8.60	8.41	9.8	199	65
402222107451600	Milk Creek nr mouth	08-17-99	1200	7.0	17.5	2,170	8.53	8.26	8.2	467	94
09251000(8)	Yampa R nr Maybell, CO	08-16-99	1615	294	21.8	440	8.74	8.69	8.5	125	35
	Yampa R nr Maybell, CO	03-15-00	1520	497	4.0	857	9.01	8.76	12.0	167	58
09251100(9)	Yampa R abv Little Snake R nr Maybell, CO	08-17-99	1615	283	19.7	468	8.74	8.59	7.8	130	37
	Yampa R abv Little Snake R nr Maybell, CO	03-15-00	1530	470	3.7	905	8.83	8.55	10.6	163	58
402925108253200(10)	Little Snake R abv Yampa R	08-18-99	1230	73	20.1	809	8.70	8.54	8.4	206	56
	Little Snake R abv Yampa R	03-15-00	1200	246	2.0	654	8.58	8.41	10.8	173	55
09260050(11)	Yampa R at Deerlodge Park, CO	08-18-99	1530	385	26.0	536	8.51	8.48	7.2	140	42
	Yampa R at Deerlodge Park, CO	03-16-00	1430	797	6.0	805	8.65	8.47	11.1	168	57
403136108585900(12)	Yampa R at mouth	08-19-99	1200	407	20.0	557	8.60	8.52	7.8	140	40
	Yampa R at mouth	03-16-00	1500	874	5.1	838	8.67	8.49	11.5	170	58

Table 3. Onsite measurements and concentrations of major and minor water-quality constituents in samples collected from Yampa River and tributary sites, August 1999 and March 2000—Continued

Station number (site number from table 1, in parentheses)	Date	Magnesium, dissolved (mg/L)	Sodium, dissolved (mg/L)	Potassium, dissolved (mg/L)	Chloride, dissolved (mg/L)	Sulfate, dissolved (mg/L)	Fluoride, dissolved (mg/L)	Silica, dissolved (mg/L as SiO_2)	Nitrogen, ammonia, dissolved (mg/L as N)	Nitrogen, NO_2+NO_3, dissolved (mg/L as N)	Nitrogen, ammonia + organic dissolved (mg/L as N)	Phosphorus, dissolved (mg/L as P)	Phosphorus, ortho, dissolved (mg/L as P)	Carbon, organic, dissolved (mg/L as C)
09237500(1)	08-19-99	17	10	2.2	1.7	43	0.13	16	0.02	0.10	0.36	0.05	0.05	5.4
	03-13-00	16	9.6	2.4	1.9	36	.11	19	.14	.28	.39	.07	.07	4.3
09239500(2)	08-19-99	11	8.3	1.8	2.3	30	.13	8.7	<.02	<.05	.29	<.05	<.01	4.7
	03-13-00	12	9.1	2.0	4.0	30	.12	15	<.02	.13	.22	<.05	.01	3.9
402936106565000(3)	08-18-99	10	19	2.4	9.6	31	.17	8.2	<.02	<.05	.30	.06	.05	5.0
	03-13-00	12	21	2.8	12	38	.17	11	<.02	.20	.26	<.05	.03	4.1
402914106580400(4)	08-18-99	2.7	2.8	.93	.82	7.8	.14	7.4	<.02	<.05	.23	<.05	<.01	1.8
	03-14-00	5.7	5.5	1.3	1.8	21	.23	10	<.02	.05	.10	<.05	<.01	2.2
09244410(5)	08-17-99	8.6	12	1.7	5.2	30	.16	5.2	<.02	<.05	.22	<.05	<.01	3.5
	03-14-00	18	24	2.2	9.6	90	.17	7.4	<.02	.10	.21	<.05	<.01	3.6
402816107003800	08-17-99	32	26	2.1	2.4	160	.12	11	<.02	<.05	.27	<.05	<.01	4.3
403152107260700	08-16-99	15	35	1.7	7.6	86	.17	11	<.02	<.05	.28	<.05	<.01	6.1
09247600(6)	08-16-99	10	18	1.8	6.5	48	.17	.39	<.02	<.05	.26	<.05	<.01	4.0
	03-14-00	35	63	2.7	17	240	.20	3.0	<.02	.60	.34	<.05	<.01	5.3
09249750(7)	08-16-99	27	24	1.8	4.7	100	.14	13	<.02	<.05	.18	<.05	<.01	3.7
	03-14-00	37	27	1.9	6.3	160	.15	12	<.02	<.05	.16	<.05	<.01	4.9
402222107451600	08-17-99	137	234	8.8	50	750	.40	13	<.02	<.05	.31	<.05	<.01	6.2
09251000(8)	08-16-99	17	30	1.9	12	81	.17	3.5	<.02	<.05	.19	<.05	<.01	3.9
	03-15-00	41	70	3.0	21	260	.20	1.5	<.02	.27	.29	<.05	<.01	5.0
09251100(9)	08-17-99	17	31	2.0	13	82	.18	5.0	<.02	<.05	.22	<.05	<.01	3.9
	03-15-00	40	72	3.1	22	270	.20	3.5	<.02	.47	.24	<.05	<.01	5.1
402925108253200(10)	08-18-99	17	95	3.6	29	160	.32	9.8	<.02	<.05	.22	<.05	<.01	4.7
	03-15-00	18	53	2.5	14	130	.26	15	<.02	<.05	.17	<.05	<.01	3.7
09260050(11)	08-18-99	18	41	2.4	16	100	.20	6.1	<.02	<.05	.22	<.05	<.01	4.1
	03-16-00	34	66	2.9	20	230	.22	6.7	<.02	.25	.31	<.05	<.01	5.4
403136108585900(12)	08-19-99	18	46	2.6	26	96	.20	6.0	<.02	<.05	.18	<.05	<.01	3.8
	03-16-00	34	72	3.2	26	230	.23	6.9	<.02	.42	<.10	<.05	<.01	5.2