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Diurnal and longitudinal variations in water quality on the Big Hole River and tributaries during the drought of August, 2000

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ABSTRACT

Between August 15 and August 21, 2000, a detailed study was conducted of diurnal (24 hour) changes in environmental parameters in the Big Hole River basin, upper Missouri River watershed. Southwest Montana was experiencing a prolonged drought during this time, resulting in low flows and a total fishing ban on the popular Big Hole River. Water temperature (T), pH, dissolved oxygen (DO), specific conductivity (SC), and electrical potential (Eh) were continuously monitored with Datasonde Hydrolabs and HOBO temperature recorders at 8 locations along the main stem, as well as 4 tributary streams in the upper basin. Hydrolab data were cross-checked with manual measurements to check for calibration drift. At each location, composite samples were taken for analysis of alkalinity, organic carbon, and major and trace elements. River discharge data were supplied from 5 U.S. Geological Survey gaging stations.

All environmental parameters exhibited large and reproducible diurnal fluctuations during the summer, low-flow period of interest. For example, at Dickie Bridge (upper Big Hole River basin), pH varied from a low of 7.8 just before sunrise, to a high of 9.8 shortly after sunset, a span of 2 full log units. During the same time, DO concentrations increased from 5.6 mg/L (68.3% of atmospheric saturation at 5800' elevation) in early morning, to 10.6 mg/L (130% of saturation) in the afternoon. The other stations displayed similar diurnal trends, but not necessarily as extreme as at Dickie Bridge. The diurnal patterns are explained by the daily cycle of photosynthesis and respiration of aquatic life. Thick mats of algae clinging to rocks (periphyton) are ubiquitous in the Big Hole River, and are probably most responsible for the observed fluctuations. A longitudinal comparison of water chemistry along the entire river shows that the upper Basin (above Wise River) and the lower Basin (below Glen) showed the most extreme behavior in terms of diurnal DO and pH swings. The lower Basin also had significantly warmer water temperatures. By comparison, the middle stretch of the main stem, between Wise River and Glen, showed less range in maximum and minimum pH/DO readings. This is most likely due to the steeper gradient of the river in this region, facilitating the exchange of oxygen and carbon dioxide between water and air. The water quality of the main stem also improved below the confluence of the Wise River, the largest tributary stream in the basin.

These results have important applications to water quality studies in progress throughout Southwestern Montana. For example, large diurnal fluctuations in pH, temperature and dissolved oxygen could directly influence the concentration of dissolved nutrients (such as phosphate), as well as heavy metals (such as copper and zinc). Diurnal cycling of heavy metals has recently been documented in several drainages polluted by abandoned mines immediately to the north of the Big Hole Basin, complicating efforts to establish guidelines for total maximum daily loading (TMDL). Rapid changes in river pH and DO could conceivably be an additional source of environmental stress for trout and grayling during drought periods. Detailed diurnal monitoring studies can help identify problem areas of a particular watershed where productivity and nutrient loading are out of balance. Obviously, all of these problems are made more acute during a drought year, such as the summer of 2000.

1.0 INTRODUCTION

The Big Hole River (BHR) in southwest Montana is a world-class trout stream and home of the last self-sustaining population of fluvial arctic grayling in the lower 48 states. The BHR is one of the few major drainages in Montana that remains undammed, and is a drinking water supply for the city of Butte, Montana. Population density along the river is very sparse, with the largest towns of Melrose, Divide, Wise River, Wisdom and Jackson each containing fewer than 1000 permanent residents. Nonetheless, the watershed supports an extensive agricultural industry (mainly cattle), and is receiving increased pressure from recreation, outfitters, and land developers. This expansion has raised concerns regarding the quality and quantity of water flowing in the BHR.

Local citizen groups are actively engaged in monitoring the health of the BHR, as well as shaping policies for future land management. These groups include the Big Hole Watershed Committee (BHWC), and the Big Hole River Foundation (BHRF). Working closely with these agencies, Rich Marvin of the Montana Bureau of Mines and Geology (MBMG) has recently completed an extensive evaluation of the hydrogeology of the BHR basin, including an assessment of the impacts of irrigation on total water budgets (Marvin 1997, Marvin and Voeller, 2000). Concurrently, Chris Gammons and students at Montana Tech have undertaken studies addressing water quality concerns. Abbie Phillip (1999) investigated the effects of flood irrigation on water quality. Rebecca Ridenour (in progress) is investigating seasonal and diurnal changes in water chemistry along the main stem. The work of Rebecca Ridenour is being funded from grants by the Bureau of Land Management (BLM), the Montana Dept. of Environmental Quality (MDEQ), and the BHRF. This work has become especially significant, given that MDEQ has recently ranked the Big Hole River as the #1 priority watershed in the upper Missouri for establishment of TMDL guidelines.

This report is a summary of the results of a single, week-long study of diurnal (24 hour) variations in water-quality parameters along the Big Hole River, conducted during August 15-21, 2000. The impetus for this project was an early study by Bahls (1978), that documented substantial diurnal variations in pH and dissolved oxygen during summer low flow periods near the mouth of the BHR. The pH and dissolved oxygen (DO) content of river water were shown to increase during the day, and decrease sharply at night. Similar coupled changes in DO and pH are a common characteristic of flowing waters with high bio-productivity (Odom, 1956), and are linked to the daily cycle of photosynthesis and respiration of aquatic life. Pogue and Anderson (1995) provide a more recent example of a regional study of pH/DO fluctuations for the Willamette River, Oregon. Although a natural phenomenon, the amplitude of the diurnal variation may be greatly enhanced by anthropogenic factors, such as nutrient loading from sewage treatment plants, septic systems, or agriculture. Rapid changes in dissolved oxygen and pH may have adverse impacts on the health of aquatic organisms. In addition, large pH or DO variations could influence the mobility of other contaminants of concern, such as trace metals. Although trace metals are not widely regarded as a problem on the Big Hole River, compilations by MDEQ indicate that there have been isolated samples collected over the years that exceeded aquatic health standards for certain analytes, including copper, cadmium, lead, and zinc. Levings (1986) also reported elevated concentrations of cadmium and lithium in Steel Creek, one of the tributaries investigated in this study, and an important spawning ground for fluvial arctic grayling.

The main objective of this project was to expand on the work of Bahls (1978) by conducting a more systematic survey of diurnal variations along the entire length of the Big Hole River, including several representative tributary streams. The latter include Steel Creek, the North Fork of the Big Hole River, and Deep Creek (all believed to be important habitat for fluvial arctic grayling), as well as the Wise River (the largest single tributary to the Big Hole River). The results of our August, 2000 investigation were deemed interesting enough to publish quickly, so that other agencies and interested individuals have immediate access to the data. However, our water-quality work on the BHR is still in progress, and additional sampling and diurnal investigations are scheduled for late 2000 and 2001. The complete study will be summarized at a later date as Rebecca Ridenour's M.S. thesis.

Because of a prolonged drought and very warm weather, the Big Hole River experienced abnormally low flow during the field work of this study. August, 2000 was also marked by extensive forest fires in the upper Big Hole basin, resulting in thick smoke cover. Therefore, the results of this study should not be considered representative of a typical summer, but should instead be considered the result of a low-water year.

2.0 METHODS

During the week of August 15-21, diurnal information was collected at 8 points along the main stem of the Big Hole River, as well as at 4 tributary streams. The location and abbreviated name of each site are given in Table 1 and Figure 1. Where possible, data were collected at established U. S. Geological Survey (USGS) gaging stations. These included the NB (USGS "Glen" gage), KB (USGS "Melrose" gage), MR (USGS "Maidenrock" gage), MC (USGS "Mudd Creek" gage), and WB sites (USGS "Wisdom" gage). In all cases, measurements were taken in the center of the river or stream, directly beneath a bridge. For the NB site, the sampling site was located beneath a narrow footbridge near the "Glen" USGS gaging station, which is located several hundred yards below the Notch Bottom fishing access site. The North Fork (NF) site was located beneath the bridge that spans the southern of two adjacent stream channels. The Deep Creek site was located beneath a bridge in the NE1/4 of sec. 29, roughly 1 mile above the confluence of Deep Creek and the Big Hole River. The Wise River site was located beneath the first bridge on Highway 73, roughly 7 miles south of the town of Wise River. The other sites can be located from the legal description in Table 1.

At each site, three types of information were collected, using: 1) Datasonde Hydrolab multimeters; 2) hand-operated water-quality probes; and 3) "Hobo" temperature recorders. In addition, a composite water sample was collected at each Big Hole River station for alkalinity determination, and laboratory analysis of anions, metals, and dissolved organic carbon.

Datasonde Hydrolab multimeters were used to continuously monitor changes in water temperature (T), pH, dissolved oxygen (DO), electrical potential (Eh), and specific conductivity (SC). Four multimeters were used in this study, and each unit was calibrated according to the manufacturer's specifications on the day prior to leaving for the field. Because the DO-sensing electrode was calibrated to the local atmospheric pressure (Butte, Montana), no manual correction for elevation vs. sea level was required.

Table 1. Location of field sites and period of diurnal monitoring.

SITE NAME	ABR	LOCATION	DATE, TIME IN	DATE, TIME OUT
Big Hole River				
*Wisdom Bridge	WB	T2S,R15W,sec.33	8/15, 9:45	8/17, 9:15
*Mudd Creek Bridge	MC	T1N,R14W,sec.26	8/15, 10:45	8/17, 7:20
Dickie Bridge	DB	T1N,R12W,sec.10	8/15, 12:15	8/17, 11:55
Jerry Creek Bridge	JC	T1S,R11W,sec.1	8/15, 13:05	8/17, 10:45
*Maidenrock Bridge	MR	T1S,R9W,sec.32	8/19, 12:25	8/21, 12:25
*Kalsta Bridge	KB	T3S,R9W,sec.34	8/19, 13:15	8/21, 13:15
*Notch Bottom	NB	T5S,R8W,sec.2	8/19, 14:35	8/21, 14:40
**High Road Bridge	HR	T3S,R6W,sec.29	8/19, 15:35	8/21, 15:50
tributary streams				
Steel Creek	SC	T2S,R15W,sec.34	8/17, 9:35	8/19, 9:55
N. Fork Big Hole	NF	T1S,R15W,sec.33	8/17, 8:00	8/19, 9:10
Deep Creek	DC	T2N,R12W,sec.29	8/17, 11:15	8/19, 10:45
Wise River	WR	T1S,R12W,sec.36	8/17, 12:20	8/19, 11:25

* USGS gaging station. ** Also known as Seidensticker Bridge.

DO values expressed in terms of % oxygen saturation are valid for the elevation of the river basin, which is approximately the same as that of Butte. The Eh-sensing electrode was calibrated against fresh pH = 4 and pH = 7 buffer solutions containing quinhydrone, as per the manufacturer's specifications. The Eh values reported are automatically adjusted to SHE (Standard Hydrogen Electrode) by the Hydrolab. The multimeters were set up to record data on half-hour intervals for a period of 1 week. At each site, the Hydrolabs were placed on their side in at least 2 feet of flowing water, with the electrodes pointing downstream. The units were secured with a cable and padlock, using cinder blocks as a weight. When the equipment was returned to the laboratory, the data were downloaded and cross-checked against manual field measurements to check for calibration drift. All pH, SC, and Eh data in this report are referenced to 25°C.

To cover all 12 monitoring sites of interest, four Hydrolab units were shifted twice during the monitoring period. The exact duration of the monitoring period for each site is given in Table 1. The 4 sites on the upper Big Hole River were investigated first, between August 15 and 17. On August 17, after roughly 48 hours of continuous data collection, the Hydrolabs were shifted to the 4 tributary streams. On August 19, the units were again moved to locations on the lower Big Hole River. Extreme care was taken during handling and transport to avoid unnecessary shaking or jolting of the apparatus, which could otherwise upset the instrument calibration.

Manual measurements of T, pH, DO, SC, and Eh were collected when a Hydrolab was placed into or taken out of the water. This provided an independent quality control check on the accuracy of the Hydrolab measurements. A hand-held Orion 1230 multimeter was used with T-compensated pH, SC, DO, or Eh electrodes. Field pH was calibrated using pH 7 and pH 10 buffers at the beginning of each day and again at mid-day. The DO electrode was calibrated to air-saturation at 100% humidity immediately before each field measurement. This unit automatically adjusts for changes in barometric pressure corresponding to changes in elevation or weather. For all Eh measurements taken with the Orion meter, the necessary manual correction was made to convert from the Ag-AgCl reference cell to the Standard Hydrogen Electrode (SHE).

The agreement between our own field measurements and the Hydrolab data for pH and DO was generally good, as shown in Figures 2 and 3. Discrepancies are attributable to a combination of electrode drift and spatial heterogeneity in field parameters. For example, whereas Hydrolab readings were typically taken in the center of the stream in fairly deep water, manual readings were usually taken at the edge of the stream in shallower water. In future studies of this type, it would be advantageous to collect field parameters in exactly the same location as the Hydrolabs for a more reliable comparison. In our study, results for SC and Eh were suspect, and serious discrepancies were often noted between the field checks and the Hydrolab results. This is particularly true for Eh, in which substantial electrode drift was often noted over a 24-hour monitoring period. The Hydrolab SC and Eh results in this report should therefore be considered as semi-quantitative. The general diurnal trends are probably real, but the absolute values may be substantially in error.

"Hobo" temperature recording devices were placed in the water at each site of interest (with the exception of High Road) at the end of July, and picked up at the end of September. The Hobos were used to record river temperature at hourly intervals. These data provide an independent check on the Hydrolab temperature results, and allow a more complete comparison of river temperature, both longitudinally (from headwaters to mouth), and as a function of time. Data from each Hobo were corrected after downloading for minor temperature deviations via a user-defined calibration equation. The calibration equations were derived by placing the Hobos in an air-thermostated oven and comparing each Hobo reading vs. the true oven temperature.

At each Big Hole River site, a depth- and width-integrated water sample was collected, either on August 15 or August 16. The alkalinity of this sample was immediately determined using a HACH digital titrator, to a pH endpoint of 4.5. A portable magnetic stirrer and pH meter were used to determine the endpoint. Approximately 60 ml of each composite sample was passed through a 0.45 μm syringe filter and acidified to 2% HCl for analysis of major and trace metals via inductively coupled plasma-atomic emission spectroscopy (ICP-AES). A second filtered but unacidified sample was collected for analysis of anions (ion chromatograph) and dissolved organic carbon. Samples were also taken for analysis of nutrients, but results are not reported here. All laboratory analyses were performed by Wayne Olmstead, in the Montana Tech Central Analytical Facility. Each water analysis was input into the geochemical speciation program MINTEQ (Allison and others, 1992). MINTEQ uses the field temperature, pH and alkalinity to calculate the concentration of HCO_3^- ion, and a final charge balance. See Ridenour (in prep.) for further details.

It was beyond the scope of this study to collect water samples during a 24-hour diurnal period. This is an objective of work in progress. Results will be reported by Ridenour (in prep.).

3.0 RESULTS

Before discussing diurnal trends in water quality, it is important to say a few words about the weather and river discharge levels. No precipitation was recorded during the investigation, nor in the week prior to our study. Each day was mainly sunny, although sunlight was obscured in the upper basin due to thick smoke from forest fires. Day-time high temperatures were in the upper 70's °F (upper Basin) to upper 80's (lower Basin), with lows in the 30's (upper Basin) to 40's (lower Basin). Sunrise at the Butte weather station occurred at 5:30 (Aug. 15) to 5:38 (Aug. 21). Sunset occurred at 7:38 (Aug. 15) to 7:30 (Aug. 21). There were roughly 14 hours of sunlight each day.

The summer of 2000 was a hot, low-flow year for the Big Hole River, resulting in a fishing ban for the entire river during most of August. Figure 4 shows the river discharge measured at each of the 5 USGS gaging stations from July 1 to the end of September. The period of our diurnal study is also shown. When plotted semi-logarithmically, each gaging station shows a nearly linear decrease in discharge during the month of August, typical of rivers undergoing baseflow recession. Rains in early September reversed this trend. Our study, from Aug. 15 to Aug. 21, experienced river levels that were slightly higher than the lowest discharges recorded in the year 2000.

Daily average discharge values (ft^3/sec) for the 5 USGS gaging stations during Aug. 15 to Aug. 21 are given in Table 2. Each station showed a slight decrease in flow over the project period. Also shown are historic average flows for the same dates, based on 12 years of record at the Wisdom gage, and 75 years of record at the Melrose (Kalsta Bridge) gage. These data indicate that, in 2000, river flows at both localities were roughly 60% of their historic averages. Even in a normal year, the Big Hole River experiences fairly low flows in mid-August.

Table 2. USGS stream discharge (cfs) for the period of investigation. Also shown are the historical average discharge values for the Wisdom and Melrose stations.

	Wisdom (WB)		Mudd Creek (MC)	Maidenrock (MR)	Melrose (KB)		Glen (NB)
Date	2000	'88-'99	2000	2000	2000	'24-'99	2000
15-Aug	9.4	20	49	207	150	262	136
16-Aug	9.2	17	49	203	147	247	136
17-Aug	9.1	15	50	201	148	240	138
18-Aug	9	15	48	200	146	227	149
19-Aug	9	14	48	202	146	222	153
20-Aug	8.8	14	46	194	143	218	132
21-Aug	8.7	14	45	192	138	212	129

For each of the 5 Big Hole River USGS gaging stations, discharge data were examined closely for evidence of diurnal flow patterns during the period of investigation. For 4 of the stations (WB, MC, KB, NB), there was a tendency for computed discharge to increase by a few % during the mid-day (around noon), and to decrease at night, reaching minimum values around midnight. The Maidenrock site showed a similar diurnal pattern, but with minimum discharge ~ 8:00 AM and maximum values in the early evening (~ 7:00 PM). It is unclear whether these small apparent changes in discharge are real, or are an artifact of instrument or measurement error. If they are real, they are somewhat difficult to explain. Conventional wisdom would predict that river discharge during summer low-flow conditions should decrease during the day, due to increased evapotranspiration in the river and adjacent hyporheic zone.

3.1 Water temperature

During the period of our diurnal investigation, the Big Hole River was warm, but not unusually warm, considering the summer as a whole. This is illustrated in Figure 5, which plots the temperature of the Big Hole River at Dickie Bridge recorded by a Hobo between August 1 to Sept. 29, 2000. The period of our diurnal study had water temperatures that were mid-range for the month of August. Overall, water temperature decreased slowly and steadily from early July to the second week of September, at which point a week of hot weather warmed the river up. This was followed by a sudden drop in water temperature between Sept. 20-24, due to a major cold front that brought an early snowfall to the Big Hole basin, and consequently helped to stop the spread of the forest fires.

Tables 3 and 4 summarize the average, maximum, and minimum water temperatures for each day of our investigation, at each of the sampling sites. The data in

Table 3. Average daily water temperature during the study period.

DATE	Aug. 15	Aug. 16	Aug. 17	Aug. 18	Aug. 19	Aug. 20	Aug. 21
Main Stem, Big Hole River							
Wisdom	15.4	14.5	14.4	14.6	13.8	14.0	13.4
Mudd Creek	15.1	14.5	14.9	15.2	14.3	14.6	13.8
Dickie Bridge	14.8	14.2	14.3	15.0	13.8	13.6	12.9
Jerry Creek	13.7	13.2	13.2	13.2	12.9	12.4	12.0
Maidenrock	15.4	15.1	15.0	14.6	14.3	14.0	13.8
Kalsta Bridge	16.8	16.6	16.3	16.3	15.3	15.6	15.1
Notch Bottom	17.8	17.2	16.8	15.9	15.6	15.9	15.7
High Road	-	-	-	-	-	17.4	-
Tributary Streams							
Steel Creek	14.1	13.6	13.6	13.6	12.9	13.2	12.3
N. Fork BHR	14.6	13.9	14.1	14.4	13.3	13.5	13.2
Deep Creek	13.6	13.1	13.0	13.8	13.0	13.1	12.2
Wise River	-	-	-	12.2	-	-	-

Average water temperature (from HOBO data collectors) based on each 24-hr period from August 15 through August 21, 2000.

Tables 3 and 4 are based on the Hobo temperature data with the exception of the HR and WR stations, for which only the more limited Hydrolab data were available. During the study period, the average 24 hour water temperatures at each station decreased slightly (~ 1.5 to ~ 2 degrees), with August 15 being the hottest day. In general, the tributary streams were slightly cooler than the main stem of the Big Hole River, with the exception of the BHR at Jerry Creek Bridge, which was cooler than the other river stations, presumably due to the influx of the Wise River and/or numerous springs. Differences in average temperature along the Big Hole River are discussed further in the "longitudinal variations" section.

Table 4. Maximum and minimum water temperatures recorded during the study period.

Site	Aug. 15		Aug. 16		Aug. 17		Aug. 18		Aug. 19		Aug. 20		Aug. 21	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Main Stem of Big Hole River														
WB	19.3	11.7	18.0	11.4	19.3	10.6	17.6	11.4	17.2	10.6	18.0	10.6	17.6	9.5
MC	18.9	11.2	18.2	11.2	19.7	10.5	18.9	11.9	17.8	10.9	18.5	11.2	17.8	9.7
DB	19.5	10.5	17.9	10.5	19.1	9.8	18.7	11.3	17.1	10.2	17.1	10.2	17.1	8.6
JC	17.9	9.8	16.4	9.8	17.1	9.4	15.3	10.2	16.8	9.4	14.9	9.8	16.0	8.2
MR	18.9	12.7	17.8	12.8	18.1	12.3	15.9	13.1	17.4	11.9	16.3	11.9	17.1	11.1
KB	19.3	14.2	18.1	14.6	18.9	13.8	18.1	14.9	18.1	12.7	17.1	13.8	17.4	12.3
NB	21.1	14.7	19.3	15.1	19.6	13.9	17.3	15.1	18.9	12.8	18.5	13.6	18.5	12.8
HR	-	-	-	-	-	-	-	-	22.6	-	20.9	14.6	-	13.5
Tributary Streams														
SC	19.1	9.0	18.3	9.3	19.5	8.2	17.9	9.3	17.9	8.2	17.9	9.0	17.9	7.0
NF	17.4	11.3	17.0	10.5	18.2	10.2	17.4	11.7	16.3	10.2	17.0	10.2	16.7	9.4
DC	16.5	10.0	15.0	10.4	16.5	9.6	16.1	10.8	15.4	10.0	15.8	10.8	14.6	8.8
WR	-	-	-	-	15.5	-	14.3	9.9	-	9.3	-	-	-	-

HOBO Daily maximum and minimum temperatures for each of the Big Hole River stations.

Figures 6 to 17 display the data recorded by the Hydrolabs for each of the 12 stations of interest. These same data are available in electronic form (EXCEL spreadsheet) from the senior author of this report. Superimposed on the Hydrolab data are our own manual results for T, pH, DO and SC, collected when the Hydrolabs were placed into or taken out of the water. The manual data are shown by the symbols with a gray fill, and are labeled with an (m) in each figure legend. The generally good agreement between our manual results and Hydrolab results for T, pH and DO indicate that problems related to electrode drift during the investigation were minor.

Figures 6 to 17 show that minimum water temperatures were reached shortly after sunrise (8 to 9 AM), with maximum temperatures in the late afternoon (4 to 6 PM).

3.2 pH

Diurnal pH measurements obtained from the Datasonde Hydrolabs are shown in the top diagrams of Figures 6 to 17 (note that the right y-axis is used for the pH scale). Every site showed a large and reproducible 24-hour variation in pH, with the lowest pH values recorded in early morning, and the highest during the late afternoon. Table 5 summarizes the average and extreme pH values recorded over 24 hours for each station. The Big Hole River at Dickie Bridge had the highest average pH (8.93), and also showed the largest 24-hour range, varying 2 full log units from 7.8 to 9.8. This very large variation was verified by stream-side manual pH readings during the night of Aug. 16. Most of the other BHR stations had pH variations on the order of 1 log unit during a single day-night cycle. Table 5 indicates that minimum pH values occurred in the early morning (6 to 8 AM), with maximum pH values in the late afternoon (4:30 to 7:30 PM). There seems to be a tendency for the smaller streams (including the Big Hole River at Wisdom) to reach maximum pH values earlier in the afternoon than in the main stem. Of the tributaries, Deep Creek and Wise River showed the smallest 24-hour range in pH, at 0.6 log units. These two watersheds are comparatively less impacted by agriculture (lower density of cattle), have a steeper gradient, and have slightly cooler water (Table 3). In contrast, the slow-moving Steel Creek near the town of Wisdom had a much larger pH range (1.5 log units).

Table 5. Average and extreme pH values at each sampling site.

station	date	pH min	time	pH max	time	avg. pH	pH range
Big Hole River							
WB	Aug.16	6.99	7:30 AM	7.62	4:30 PM	7.14	0.63
MC	Aug.16	7.32	8:00 AM	8.49	5:30 PM	7.91	1.17
DB	Aug.16	7.73	7:00 AM	9.77	6:00 PM	8.93	2.04
JC	Aug.16	7.68	6:30 AM	8.74	5:00 PM	8.12	1.06
MR	Aug.20	7.82	7:00 AM	8.71	5:30 PM	8.26	0.89
KB	Aug.20	7.65	7:30 AM	8.71	7:30 PM	8.16	1.06
NB	Aug.20	7.79	7:00 AM	8.63	5:30 PM	8.19	0.84
HR	Aug.20	7.82	6:30 AM	9.00	6:30 PM	8.39	1.18
Tributary Streams							
SC	Aug.18	7.06	6:30 AM	8.56	4:30 PM	7.67	1.50
NF	Aug.18	6.70	7:00 AM	7.96	4:30 PM	7.13	1.26
DC	Aug.18	7.37	6:30 AM	7.95	4:30 PM	7.57	0.58
WR	Aug.18	7.44	6:00 AM	8.00	4:30 PM	7.62	0.56

Table 6. Average and extreme dissolved oxygen values (mg/L) at each sampling site.

station	date	DO min	time	DO max	time	avg.DO	DO range
Big Hole River							
WB	Aug.16	3.66	3:00 AM	7.87	4:30 PM	5.15	4.21
MC	Aug.16	5.25	5:00 AM	10.10	4:00 PM	7.28	4.85
DB	Aug.16	5.56	11:00 PM	10.51	2:00 PM	7.96	4.95
JC	Aug.16	7.19	0:30 AM	9.86	1:00 PM	8.41	2.67
MR	Aug.20	6.75	0:30 AM	9.16	4:00 PM	7.74	2.41
KB	Aug.20	5.98	11:00 PM	8.82	1:30 PM	7.08	2.84
NB	Aug.20	6.22	5:30 AM	10.07	3:30 PM	7.82	3.85
HR	Aug.20	6.18	0:30 AM	11.79	3:30 PM	8.49	5.61
Tributary Streams							
SC	Aug.18	4.73	3:00 AM	10.91	2:00 PM	7.08	6.18
NF	Aug.18	4.86	6:00 AM	8.30	3:30 PM	6.10	3.44
DC	Aug.18	6.34	10:00 PM	8.60	11:30 AM	7.33	2.26
WR	Aug.18	7.80	8:30 PM	9.26	10:30 AM	8.40	1.46

3.3 Dissolved oxygen

Diurnal DO measurements for each sampling site are plotted in the middle diagrams of Figures 6 to 17. Each diagram has DO plotted in two ways, % of atmospheric saturation (left axis), or mg/L of dissolved O_2 (right axis). As for pH, every site showed a large and reproducible 24 hour variation in DO, with the lowest DO values recorded in the night-time hours, and the highest during the late morning to mid-afternoon. It should be noted that the solubility of oxygen in water increases with decrease in temperature. The fact that minimum DO values were recorded at night cannot be explained by temperature effects, but instead must be due to biological activity. Table 6 summarizes the average and extreme DO values at each station. Daily DO variations were largest for the main stem of the Big Hole River in the upper basin (above Dickie Bridge) and the lower basin (below Notch Bottom). The cool and swift-flowing Wise River showed the smallest variations in DO, and appears to have significantly improved the water quality of the main stem below its mouth.

Dissolved oxygen dropped below 5 mg/L each night for several stations in the Upper Basin, including the main stem at Wisdom, and the Steel Creek and North Fork tributaries. However, the Wisdom data set shows two sharp discontinuities reflecting a malfunction of the DO electrode. At Wisdom, the Hydrolab was placed in deep, slow-moving water at the tail of a long, still pool. It is possible that the anomalously low DO values (down to 3.66 mg/L) were partly due to this placement, and that higher DO values would have been measured had the Hydrolab been placed in a shallow riffle near the head of the pool. No systematic attempt was made in this study to document spatial heterogeneity in DO levels within a single stream reach (e.g., pool vs. riffle).

3.4 Specific conductivity

Diurnal SC measurements for most of the sampling sites are plotted in the bottom diagrams of Figures 6 to 17. Compared to pH and DO, the SC data collected by the Hydrolabs are considered of questionable reliability. Baseline SC was often observed to drift during the course of the investigation, and the Hydrolab data were often in significant disagreement with our own manual, freshly calibrated SC measurements. Nonetheless, the diurnal trends displayed in Figures 6 to 17 are fairly robust, and are most likely real. There is a tendency for SC to drop during the day and rise at night, with the total range being on the order of several % of the total SC value. Possible causes for these cyclic variations are discussed below.

3.5 Eh

Many of the Eh data sets collected by the Hydrolabs were discarded, due to severe drift, or values that were grossly in error compared to our own manual readings. The Hydrolabs showed a steady increase in baseline Eh readings over the course of the investigation, which is visible in data sets such as Maidenrock (Fig. 9), Jerry Creek (Fig. 10) and Steel Creek (Fig. 14). Superimposed on this upwards drift is a diurnal cycle in which Eh tends to decrease during the day, and increase at night. This relationship is due to the fact that pH and Eh have a negative correlation in natural waters. For two waters at equivalent relative oxidation state, an increase in pH causes Eh to drop, and vice versa (Drever, 1997). Also, it is fairly well known that the platinum electrodes used in field Eh measurements tend to malfunction in waters containing measurable quantities of dissolved oxygen, possibly due to the formation of a monolayer of Pt-oxide on the electrode surface. This problem is discussed at length by Langmuir (1997). For all of the above reasons, no firm conclusions can be drawn from the Eh information collected in this study.

3.6 Other chemical parameters

Table 7 summarizes the major element composition of water samples collected from the Big Hole River during August 15-16. Additional information was obtained on nutrients and trace metals, but is not reported here (see Ridenour, in prep., for details). The results show that the Big Hole River is essentially a Ca-(Na)-HCO_3 stream, with higher Na/Ca ratios in its upper reaches. Alkalinity values ranged from a low of 46.7 mg/L $CaCO_3$ at Wisdom Bridge, to a high of 94.2 mg/L at High Road Bridge, near the river's mouth. Dissolved organic carbon (DOC) concentrations in August were very high. With the exception of Wisdom (15 mg/L), the values were consistently between 20 and 25 mg/L of organic C. In fact, when recast on a molal basis, it can be shown that the water samples contain more dissolved carbon in organic form than as bicarbonate (the dominant form of inorganic C). The presence of elevated DOC may help to explain the charge balance errors in Table 7, which consistently show an excess of cations over anions. As discussed by Drever (1997), a large fraction of DOC in natural waters exists as humic and fulvic acids, or as lower molecular weight carboxylic acids, all of which have a tendency to develop negative charges in the pH range of the Big Hole River. Unfortunately, it is both difficult and expensive to speciate DOC. Therefore, organic ions are not routinely considered in charge balance calculations, nor are they reported in water analyses. Certain forms of DOC have been shown to increase the solubility of otherwise

Table 7. Selected water-quality data for Big Hole River samples. All data in ppm, unless otherwise noted.

Site	date/time	Ca	Mg	Na	K	SO_4	Cl	$SiO_2(aq)$
HR	Aug. 16 13:30	32.2	7.71	7.85	2.82	11.9	4.15	13.03
NB	Aug. 16 12:00	36.1	8.18	7.71	2.82	11.5	3.48	15.29
KB	Aug. 16 11:00	30.8	7.96	6.92	2.55	12.1	2.65	11.76
MR	Aug. 16 10:00	25.6	6.83	6.25	2.41	11.1	1.89	9.66
JC	Aug. 15 1:00	16.4	4.72	6.13	2.29	5.13	1.76	9.80
DB	Aug. 15 12:00	14.0	3.34	9.44	3.24	4.61	2.06	6.11
MC	Aug. 15 10:30	11.7	2.83	12.06	3.99	2.94	2.93	18.50
WB	Aug. 15 9:00	10.50	2.89	5.25	2.74	0.94	2.23	15.47

	T(C)	SC (uS/cm)	field pH	alkalinity ppm $CaCO_3$	HCO_3^-	DOC (ppm C)	TDS (ppm)	charge balance
HR	20.3	266	8.90	94.2	99.5	23.9	203.2	+8.8%
NB	17.2	281	8.26	94.0	110.2	24.8	220.1	+13.0%
KB	14.7	262	8.23	94.0	110.9	21.7	207.3	+7.6%
MR	13.0	228	8.31	81.2	95.8	25.0	184.5	+6.7%
JC	15.6	168	8.61	59.0	68.0	20.8	135.1	+7.0%
DB	16.0	163	9.02	60.5	65.1	20.2	128.1	+3.8%
MC	13.2	169	7.03	61.1	74.2	23.1	152.3	+2.8%
WB	12.4	113	6.83	46.7	56.7	15.4	112.2	+2.1%

immobile metals, such as aluminum and ferric iron (Drever, 1997). Also, DOC is an important food source for heterotrophic bacteria, and can be a major contributor to biological oxygen demand (BOD).

4.0 DISCUSSION

4.1 Causes of diurnal variations in pH and DO

Coupled diurnal variations in pH and dissolved oxygen have long been recognized for surface water bodies with high bio-productivity (Odom, 1956). During the day, photosynthesis by vascular plants, planktonic (floating) algae, and periphyton (algal masses attached to solid substrates) consumes CO_2 and produces oxygen. The overall photosynthesis reaction can be simplified as:

$$CO_2 + H_2O \;=\; CH_2O \text{ (organic C)} + O_2 \qquad (1)$$

Because CO_2 is the dominant weak acid in natural waters such as the Big Hole River, a decrease in its partial pressure causes pH to drift upward. This is illustrated by the following reaction:

$$CO_2 + H_2O = HCO_3^- + H^+ \qquad (2)$$

By LeChatelier's Principle, a decrease in CO_2 will drive reaction (2) to the left, thereby consuming protons and raising pH.

The photosynthesis reaction is thermodynamically unfavorable, and requires an additional input of energy in the form of sunlight. Thus, photosynthesis only takes place during the daylight hours, and its intensity is proportional to the intensity of sunlight. In contrast, respiration - the reverse of reaction (1) - takes place around the clock, but may be accelerated during certain periods of the day, according to species. Animals and heterotrophic bacteria rely on the energy produced from respiration for their living, whereas photosynthetic plants and algae use respiration as a secondary process in their overall metabolism. Respiration consumes oxygen and produces CO_2, and therefore tends to oppose the changes in water chemistry due to photosynthesis. However, in aquatic environments, particularly during warm summer months, the effect of photosynthesis far outweighs the effect of respiration during the day. This results in a net accumulation of DO and an increase in pH. At night, biological respiration continues in the complete absence of photosynthesis, resulting in substantial decreases in DO and pH.

Odum (1956) described a method to estimate net rates of photosynthesis and respiration in flowing waters from diurnal dissolved oxygen curves. The method assumes that the rate of accumulation of DO in a river (Q) is the combination of three fluxes: 1) production of oxygen by photosynthesis (P); 2) consumption of oxygen by respiration (R); and 3) diffusion and advection of dissolved oxygen through the water column, and across the air/water interface (D). These variables are related as follows:

$$Q = P - R \pm D \qquad (3)$$

where all units are (grams oxygen)/m^2/hr. If $P > R$, then Q is positive, and the DO content of the river will increase. If $R > P$, DO will decrease. In either case, as the DO content of the stream departs from 100% saturation, oxygen will tend to diffuse into or out of the water column to re-establish equilibrium. The rate at which oxygen will diffuse across the air/water interface depends on the chemical gradient (extent of departure from equilibrium saturation), and the gas transfer diffusion coefficient (K) of the stream. As discussed by Odum (1956), the value of K depends on the stream velocity and turbulence, and can range from 0.03 g/m^2/h for perfectly still water to > 20 g/m^2/h for cascades or waterfalls. In general, diffusion of oxygen (and carbon dioxide) will be faster in rapids or riffles, and much slower in slow-moving, laminar flow conditions. This means that changes in Q due to photosynthesis or respiration are more likely to result in large DO/pH swings for slow-moving vs. rapid water. Another consideration is stream depth. In a fertile stream environment, most photosynthesis and respiration occurs from vascular plants and periphyton (algae anchored to rocks or gravel) vs. plankton (floating algae). Thus, the total amount of active biomass is nearly independent of water depth. In mid-summer drought conditions, the ratio of river water to biomass is at a minimum, so that changes in the O_2/CO_2 flux result in very large pH/DO swings. This helps to explain why the Mudd Creek to Dickie Bridge reach of the Big Hole River exhibited the greatest DO/pH swings during the summer of 2002. The river in this reach was wide, slow-moving, and shallow, with thick mats of algae and vascular plants.

4.2 Causes of diurnal variations in SC

As previously discussed, there was a tendency for the specific conductivity of the waters investigated to decrease during the day and increase at night. For most stations, SC changes were inversely correlated with changes in both temperature and pH. This is best exemplified by the Notch Bottom data, reproduced in Figure 18. Linear regression of SC vs. pH yielded an R^2 value of 0.9853. The correlation between SC and temperature was slightly lower, at 0.9334. It should be remembered that all SC values reported in this report are temperature corrected to 25°C.

From a theoretical point of view, changes in either pH or temperature could affect the specific conductivity of a stream. Most minerals, including carbonates and oxides, are more soluble at lower pH. In addition, carbonate minerals become more soluble at lower temperature (retrograde solubility). Therefore, it is reasonable to suppose that the nightly increases in SC owe their origin to dissolution of minerals in the stream bed in response to a drop in pH and/or temperature. This hypothesis needs to be confirmed by collecting a suite of diurnal samples for chemical analysis, an activity that is planned for the summer of 2001.

4.3 Longitudinal variation in water-quality parameters

Longitudinal variations in temperature, pH, dissolved oxygen, and specific conductivity along the Big Hole River are summarized in Figures 19, 20, and 21. The x-axis of these diagrams plots river mileage, measured downstream from Wisdom. Figure 19 plots the average temperature, 24-hour temperature range, average pH, and 24-hour pH range for each Big Hole River site. The temperature data are for August 20, and are based on the Hobo records with the exception of High Road, which is based on the Hydrolab record. Because we shifted the Hydrolabs, the pH and DO data were collected on different days: August 16 for the WB, MC, DB and JC sites, and August 20 for the MR, KB, NB and HR sites.

The longitudinal profile for average temperature shows two major features: 1) a dramatic drop in river temperature between Dickie Bridge and Jerry Creek Bridge; and 2) a steady warming of the river below Jerry Creek Bridge. The first feature can be attributed to the confluence of the relatively cool Wise River and numerous groundwater springs, as well as an increase in gradient as the river passes through a deep canyon between Dewey and Melrose. The second feature is consistent with the lower elevation of the KB, NB, and HR sites, coupled with a decrease in discharge of the Big Hole River below Kalsta Bridge. It is interesting to note that the river between Wisdom and Mudd Creek, often referred to as the "thermal stretch", was no warmer than the Maidenrock site on August 20. A contributing factor for lower temperatures in the upper basin at this time could have been thicker smoke cover, caused by proximity to large fires in the National Forest northwest of Wisdom.

The longitudinal profiles for pH, also in Figure 19, show several interesting features. The river as a whole was consistently alkaline during the study period, with average pH's at most stations near or slightly above 8.0. Two notable variations from the norm were Wisdom Bridge (pH_{mean} = 7.1) and Dickie Bridge (pH_{mean} = 8.9). The very high average pH readings at Dickie Bridge during the study period are unusual for a southwest Montana stream, and are a possible concern to aquatic life. In the middle and lower river, average pH was buffered to values near 8.0, and the magnitude of the daily pH swing, although close to 1 full pH unit, was still much less than at Dickie Bridge. Surprisingly, there is no clear correlation between the amount of pH variation and the alkalinity of the river. For example, the alkalinity values of the Big Hole River at Dickie Bridge and Jerry Creek Bridge were almost identical (Table 7), and yet the former had a 2 log unit pH swing, whereas the latter had only a 1 unit swing. More likely, the pH swings at Jerry Creek were moderated by the addition of fresh, clear water from the Wise River, the largest tributary in the drainage basin. Also, the main stem has a steeper gradient below the Wise River confluence, resulting in a more effective exchange of CO_2 between water and air.

Longitudinal changes in dissolved oxygen are shown in Figure 20. Important features to note include the anomalously low average DO values at Wisdom (discussed above), and the very large range of diurnal DO values for the upper river at Mudd Creek and Dickie Bridge, as well as the lower river at Notch Bottom and High Road. Large diurnal DO fluctuations are caused by biological activity, enhanced by a flow regime that is predominantly laminar (shallow gradient with few rapids). By comparison, the "blue ribbon" stretch of the river between Jerry Creek Bridge and Kalsta Bridge had a much smaller diurnal DO range, due to the steeper gradient and turbulent nature of the Big Hole River in this reach. Also, the addition of cool, fresh water from the Wise River may have improved water quality with respect to DO levels.

Longitudinal changes in specific conductivity for the Big Hole River are shown in Figure 21. We used manual SC readings obtained on August 15-16 (Table 7) to construct this plot. Also included for comparison are the SC of the Wise River (open symbol), and a measurement from the headwaters of the Big Hole River at Saginaw Bridge (S4,T7S,R15W, see Figure 1), collected on July 13, 2000 (data point at x = -26 miles). A nearly linear trend of increasing SC with distance downstream is displayed for the Big Hole River. An exception to this trend is the plateau in SC between Mudd Creek and Jerry Creek Bridge. In this portion of the river, increases in SC are apparently offset by the confluence of numerous tributary streams with lower SC values, including LaMarche Creek, Fishtrap Creek, Seymour Creek, Deep Creek, and the Wise River.

There are several possible reasons for the observed longitudinal increases in SC. Direct evapotranspiration (ET) of river water may be a significant cause of increased salinity, especially during summer drought periods when discharge and velocity are low, water depths are shallow, and plant metabolism is at its peak. However, if ET was the only controlling factor, then one would expect a steady increase in the concentration of chloride ion, a conservative solute, with distance downstream. An examination of the data in Table 7 shows that this is not the case for the main stem above Maidenrock, although significant increases in Cl^- do occur downstream of that point. Irrigation practices are another possible influence. Flood irrigation is the major method used in the basin. Water is diverted from the main stem and tributaries, is directed by ditches and spread across the fields, and then is returned to the main stem directly as surface runoff, or indirectly as groundwater baseflow. The work of Phillip (1999) showed that the SC of irrigation water increases through the flood irrigation cycle. Because of the large number of irrigation diversions on the Big Hole River, a significant proportion of the total river flux is passed through at least one flood irrigation cycle in the mid-summer months. The SC of the main stem is undoubtedly influenced by background (non-anthropogenic) groundwater baseflow as well. Phillip (1999) showed that groundwater in the Big Hole Basin has a large range in SC, but tends to have a much higher dissolved solids content than the main stem surface waters. High SC values are often associated with wells completed in Tertiary sediments, which are widespread in the Upper and Lower Basins (Rich Marvin, pers. commun.). For example, several groundwater samples collected by Phillip (1999) in the Lower Basin near Glen had SC values in the 300-600 μS/cm range.

By combining the information in Table 7 and Table 2, it is possible to compute mass fluxes for the major chemical components at each USGS gaging station. From the difference in mass flux and discharge between adjacent stations, one can also estimate the average chemical composition of water "gained" or "lost" in each river reach. These calculations are summarized in Table 8. The top half of the table shows the calculated mass flux for each component of interest, in metric tons/day. The bottom half of the table shows the calculated chemical composition of water gained or lost in each reach. Between Wisdom Bridge and Mudd Creek, flow increased by roughly 40 cfs, and the water added was dominated by Na-Ca-bicarbonate, with a computed SC value of 197 μS/cm. According to data in Appendix G of Levings (1986), groundwater in the upper basin has a very similar Na/Ca ratio, and a median TDS value of 135 mg/L, which corresponds to a SC of roughly 186 μS/cm. Therefore, it is reasonable to infer that the observed gains in river water between Wisdom and Mudd Creek during August of 2000 were mainly due to groundwater baseflow. This is consistent with the fact that there are few major tributaries in this reach. Between the Mudd Creek and Maidenrock gaging stations, river discharge increased from 49 to 207 cfs. The hypothetical water added had SC = 247 μS/cm, and a chemistry dominated by Ca^{2+} and HCO_3^-. Numerous tributary streams enter the main stem in this reach, including the Wise River. However, most of these streams have SC < 100 μS/cm: therefore, significant inputs must have also come from irrigation returns or groundwater baseflow.

It is emphasized that the results of these mass balance calculations should not be taken too literally, as they do not take into account the possible effects of direct ET losses. For example, in the reach from Kalsta Bridge to Notch Bottom (KB-NB), there is a net loss of 11 cfs (Table 2), and mass balance calculations indicate that the lost water had an SC value of only 12 μS/cm (Table 8). The simplest explanation for these observations is that most of the 11 cfs were lost to evaporation. The larger decreases in flow (-56 cfs) between Maidenrock and Kalsta Bridge (MR-KB) are more likely due to a combination of ET losses and direct irrigation withdrawals, as the computed SC of the lost water (138 μS/cm) is closer to the actual SC of the main stem at Maidenrock (228 μS/cm). A more rigorous quantification of ET losses and their effect on chemical mass balance is in progress.

Table 8. Mass balance for selected chemical constituents.

		Mass flux (kg/day) x 10^{-3}								
Site	flow[1]	TDS	Ca	Mg	Na	K	SO_4	HCO_3	Cl	
WB	23.0	2.58	0.24	0.07	0.12	0.06	0.02	1.31	0.051	
MC	119.9	18.26	1.41	0.34	1.45	0.48	0.35	8.89	0.35	
MR	496.7	91.67	12.7	3.39	3.10	1.20	5.51	47.57	0.94	
KB	359.7	74.58	11.1	2.86	2.49	0.92	4.35	39.89	0.95	
NB	332.8	73.23	12.0	2.72	2.56	0.94	3.85	36.66	1.16	
Reach	Δ flow[1]	Composition of hypothetical water gained or lost in reach (ppm)								SC
WB-MC	96.9	161.8	16.4	3.84	18.7	5.85	4.67	106.9	4.23	197
MC-MR	376.8	194.8	29.3	7.90	4.29	1.86	13.35	100.0	1.52	247
MR-KB	-137.0	122.9	11.8	3.82	4.43	2.01	8.38	55.26	-0.08	138
KB-NB	-26.9	39.3	-27.2	4.11	-2.22	-0.68	14.70	94.40	-6.00	12.1

1 flow has units of L/day (x 10^{-6})

4.4 Significance of the results

This study documents substantial and reproducible variations in 24-hour temperature, pH, dissolved oxygen, and specific conductivity along the Big Hole River during summer, low-flow conditions. To a large extent, these fluctuations should be viewed as a normal consequence of biological activity in a highly productive stream during low water conditions. However, the very high maximum pH (9.8) and very large diurnal variation in pH (2 full log units) at Dickie Bridge suggest that productivity in certain reaches of the Big Hole River was out of balance during the summer of 2000. Such extreme swings in environmental parameters may influence the behavior of aquatic life (e.g., insects and fish), and could conceivably have deleterious health effects. For example, it has been demonstrated that high pH (> 9.5) can lead to electrolyte imbalances and reduced efficiency of ammonia excretion in rainbow trout (Wilkie and Wood, 1994; Wilkie and others, 1996), and may lead to increased trout mortality rates (Wagner and others, 1997). Likewise, it is well known that both hypoxic (low % DO saturation) or hyperoxic (unusually high % DO saturation) conditions can lead to environmental stress for salmonid species. In general, exposure to DO levels below 4 mg/L is considered harmful to trout. In this study, only the Big Hole River at Wisdom dropped below 4 mg/L DO in the late night and early morning, although a malfunction in the Hydrolab casts doubt on these results. It is likely that the cumulative stress on trout or grayling from a *combination* of high water temperature, abnormally high pH, and abnormally low or high DO would be greater than the effects of any of these variables alone.

Although not examined in this report, diurnal changes in pH, temperature, and dissolved oxygen could have a synergistic effect on the concentration of other solutes in river water, such as nutrients and trace metals. For example, photosynthesis-induced increases in pH during the day can lead to the inorganic precipitation of phosphate as an impurity in calcite. It has been suggested that this "self-cleaning" process may help river systems to regulate the growth of algae during summer months (Hartley and others, 1996). Also, large swings in pH can directly influence the fate and transport of inorganic solutes, including heavy metals. Although evidence for heavy metal contamination in the Big Hole River is sparse, nearby streams and rivers in the Clark Fork and Boulder River drainages are highly contaminated from decades of mining and smelting activities. Large diurnal variations in dissolved and total-recoverable metals, including zinc, copper, manganese, and cadmium, have been documented in these watersheds during summer, low-flow conditions (Brick and Moore, 1996; Nimick et al, 2000). In addition, significant diurnal variations in dissolved arsenic, sourced from hot springs in Yellowstone National Park, have been documented for the Madison and upper Missouri Rivers (Nimick and others, 1998). The causes of these diurnal metal fluctuations are not completely understood, but are almost certainly influenced by biologically-induced changes in river pH.

Investigators should be aware of the phenomenon of diurnal cycles in any effort to evaluate the water quality of a stream or river. The fact that pH/DO can change very rapidly during the day could weaken or invalidate conclusions based on instantaneous water-quality readings. This is especially important to keep in mind during synoptic investigations, in which a longitudinal river survey is conducted over a period of many hours or days. Based on our results, it is clear that a true "average" pH or DO measurement can only be obtained by integrating a 24-hour continuous record for a given stream reach. If continuous monitoring is not possible, an approximation of the daily maximum and minimum values may be obtained by taking measurements shortly before sunrise and in the late afternoon, respectively. In any event, instantaneous pH/DO measurements should have the time of day recorded next to them, and this information should be reported in a final publication.

4.5 Recommendations for further work

A number of follow-up studies are recommended to further understand the phenomenon of diurnal changes in water chemistry in the Big Hole River, as well as other watersheds in Southwest Montana. Important questions to be answered include:

1) What are seasonal influences on diurnal water quality changes?
2) How do diurnal changes in pH influence the concentration of dissolved nutrients and heavy metals?
3) What is the relationship between diurnal pH changes and the carbonate mass balance (e.g., alkalinity, CO_2 partial pressure, calcite saturation index) of the stream?
4) Are the large pH and DO fluctuations observed in the summer of 2000 a result of abnormally low flow conditions, or are they also seen in a "normal" year?
5) How much spatial heterogeneity exists in environmental parameters within a single stream reach, e.g., in deep pools vs. shallow riffles?
6) To what extent do diurnal changes in pH and dissolved oxygen influence the behavior and health of aquatic insects and fish?

The answers to questions 1 through 5 are objectives of work in progress by our group, and will be reported at a later date. Assessing the response of biota to diurnal changes in pH and oxygen would seem a prospective area for future research.

A final recommendation is that diurnal monitoring be considered as a monitoring tool to assess the health of streams, especially those that are sensitive to nutrient loading. Nutrient budgets in rivers are difficult to quantify by direct measurement, as the concentrations of free nitrate and orthophosphate are often extremely low or undetectable in a healthy stream. Likewise, it is somewhat laborious to directly quantify periphyton or macrophyton biomass. In contrast, it is a relatively simple process to conduct a diurnal T/pH/DO investigation. A longitudinal study of diurnal pH/DO variations could be used to define "problem areas" for a given river where bioproductivity is out of balance, resulting in DO or pH variations that exceed the healthy range of aquatic life. In addition, a comparison of diurnal pH/DO curves at the same locality from one year to the next (at similar flow and temperature conditions) could be used to help evaluate the long-term effects of changes in population density or land use (agriculture, irrigation methods, etc.) on water quality.

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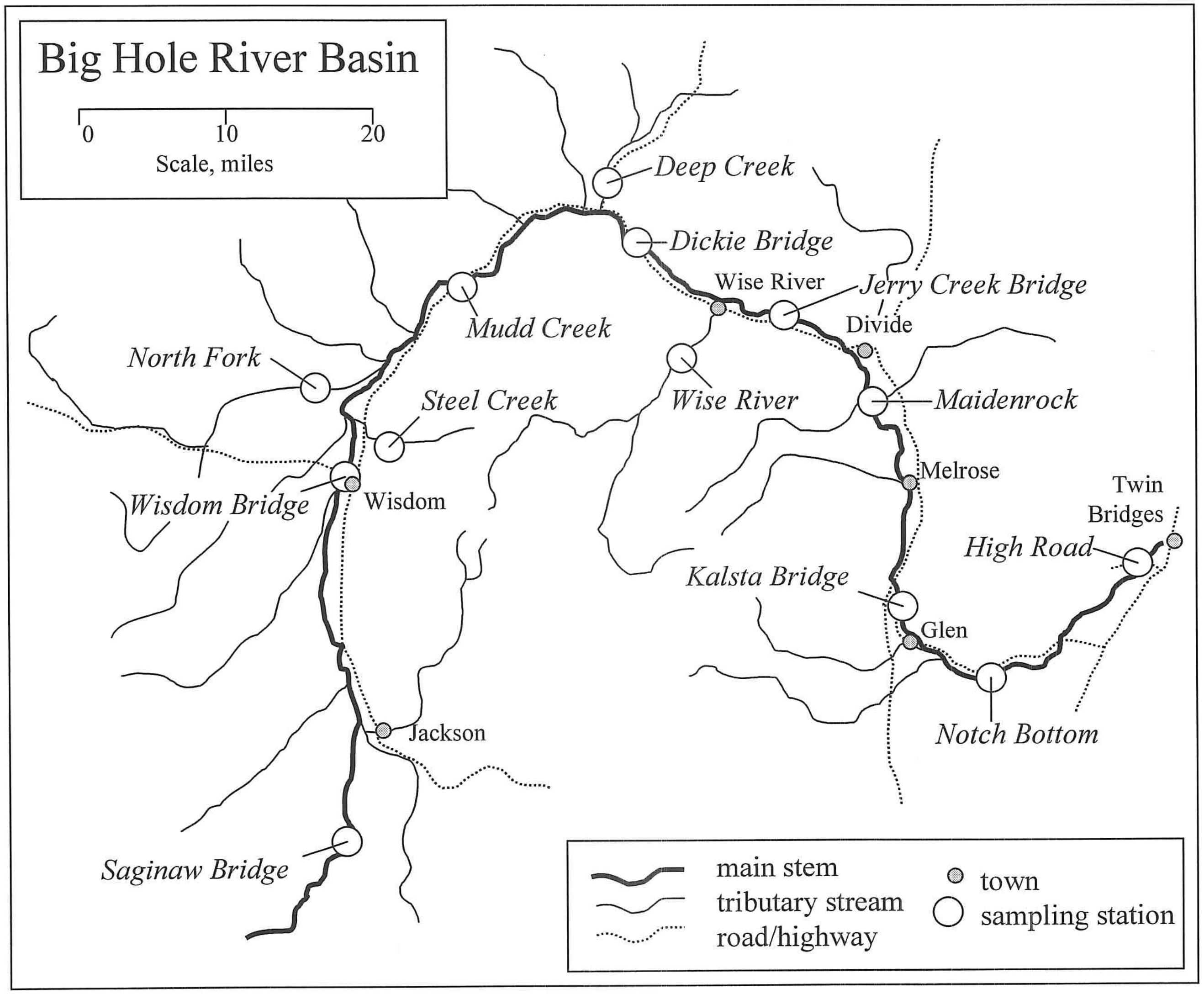

Figure 1. Location map of the Big Hole River Basin, Southwest Montana.

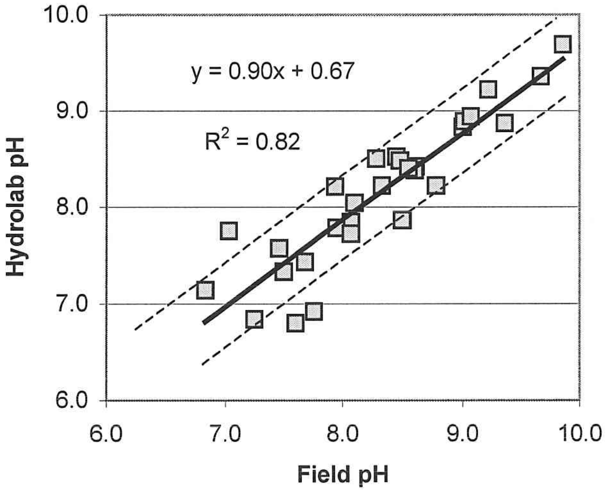

Figure 2. Field vs. Hydrolab pH. The dashed lines show ±0.5 log unit spread.

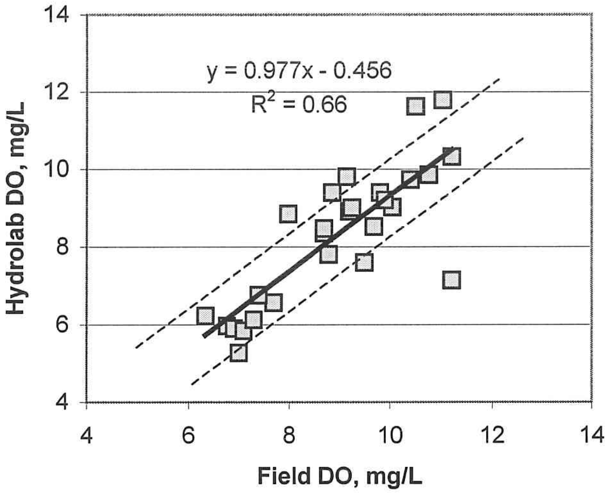

Figure 3. Field vs. Hydrolab DO. The dashed lines show ± 1 mg/L spread.

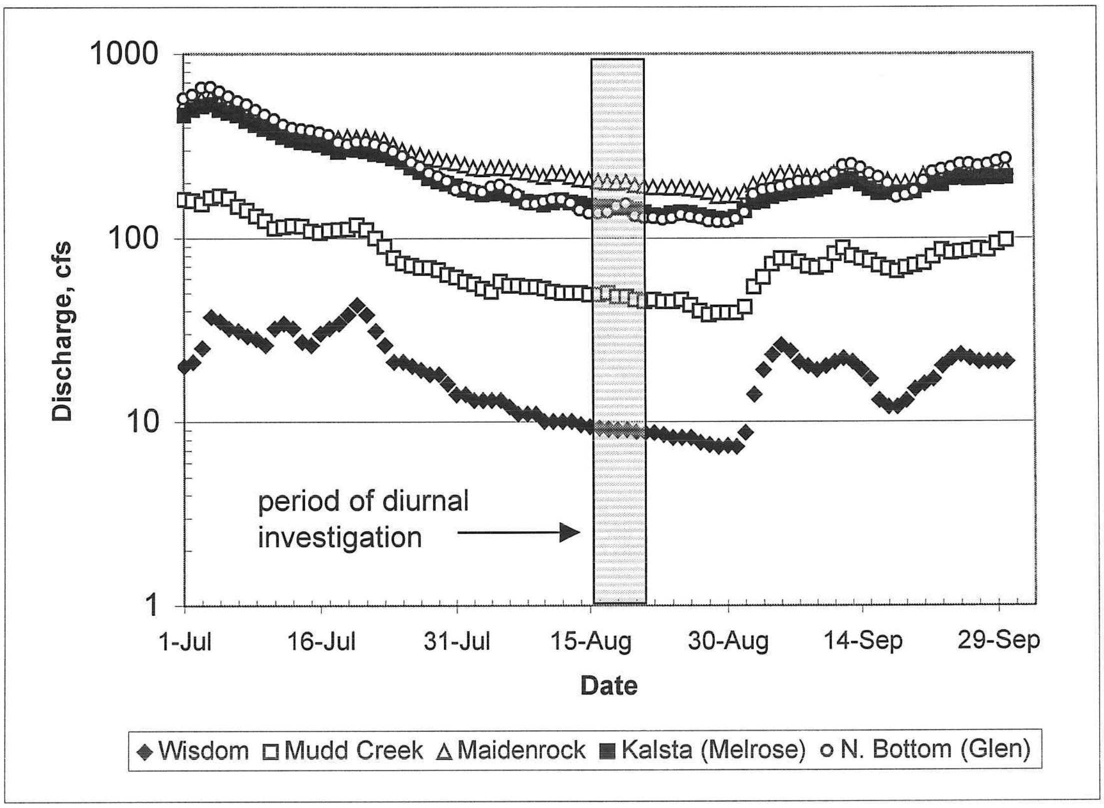

Figure 4. River discharge during the summer of 2000, showing the study period.

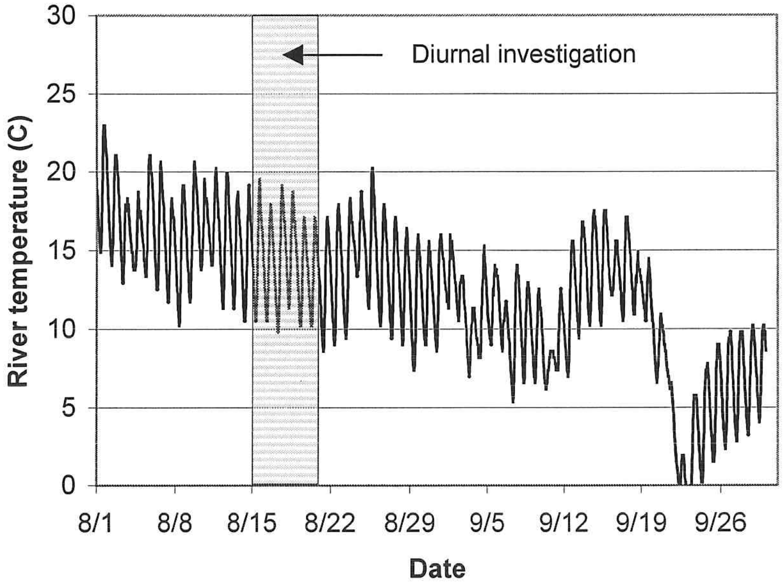

Figure 5. Water temperature of the Big Hole River at Dickie Bridge, Aug. 1 to Sept. 1, 2000.

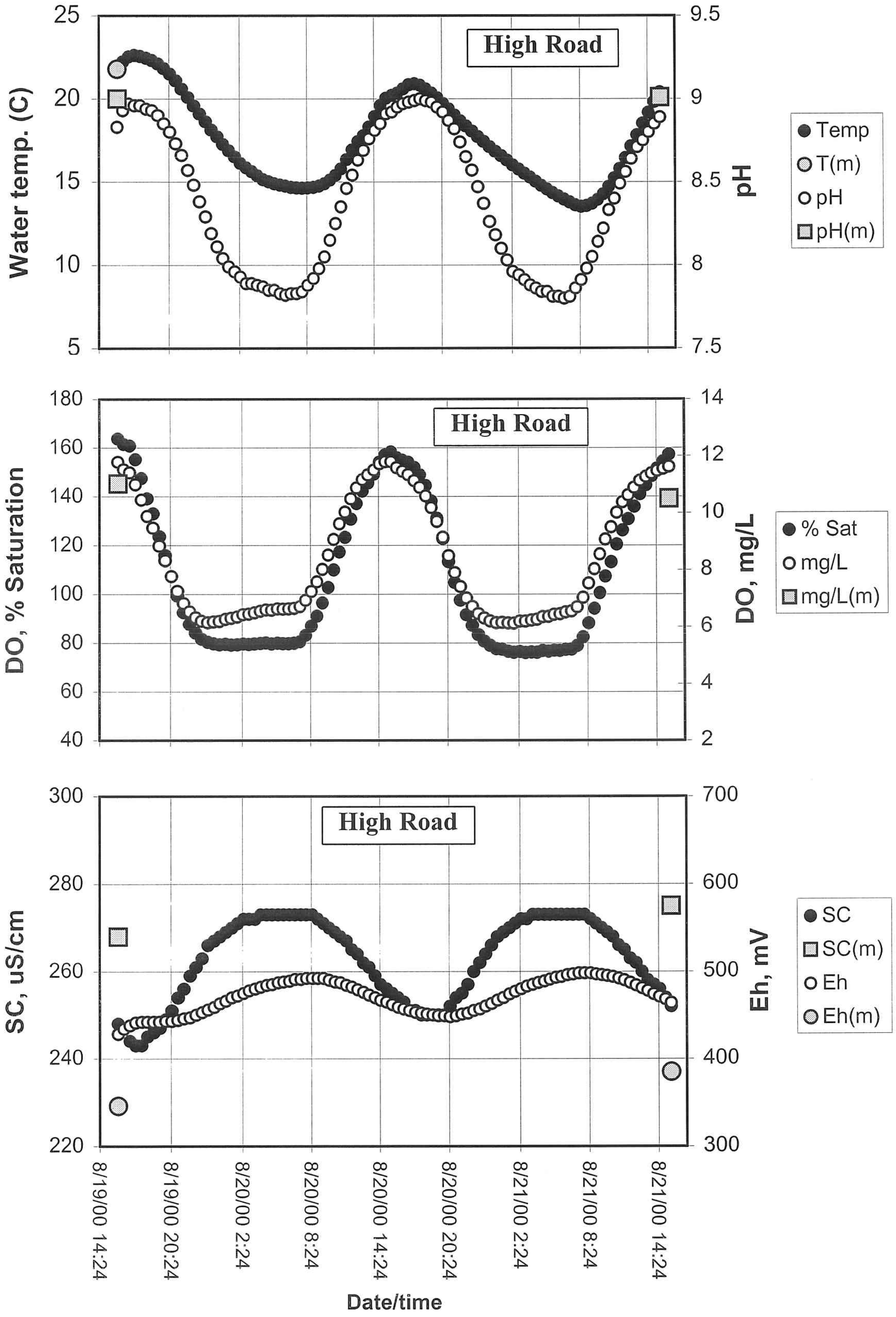

Figure 6. Hydrolab data for Big Hole River at High Road.

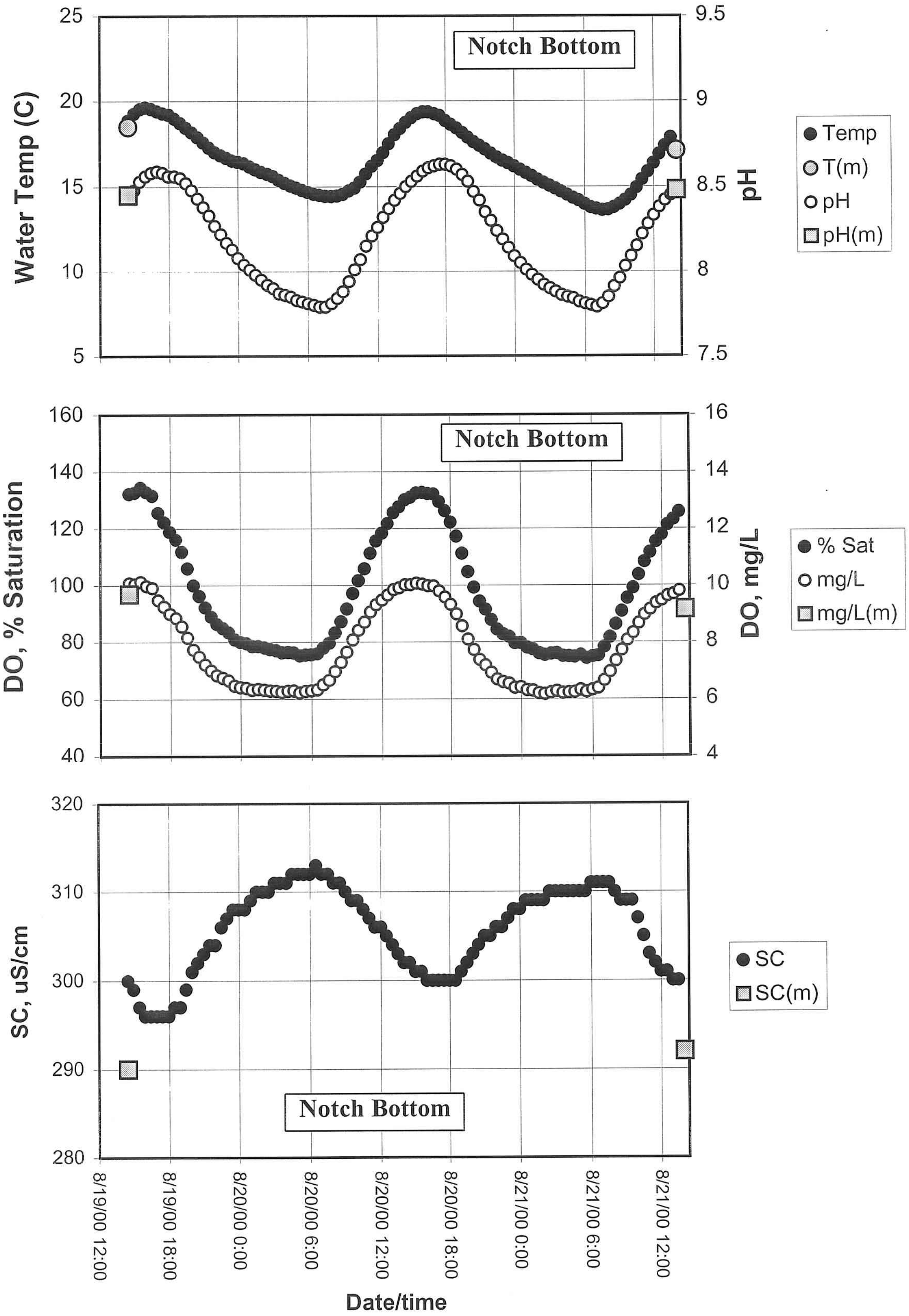

Figure 7. Hydrolab data for Big Hole River at Notch Bottom.

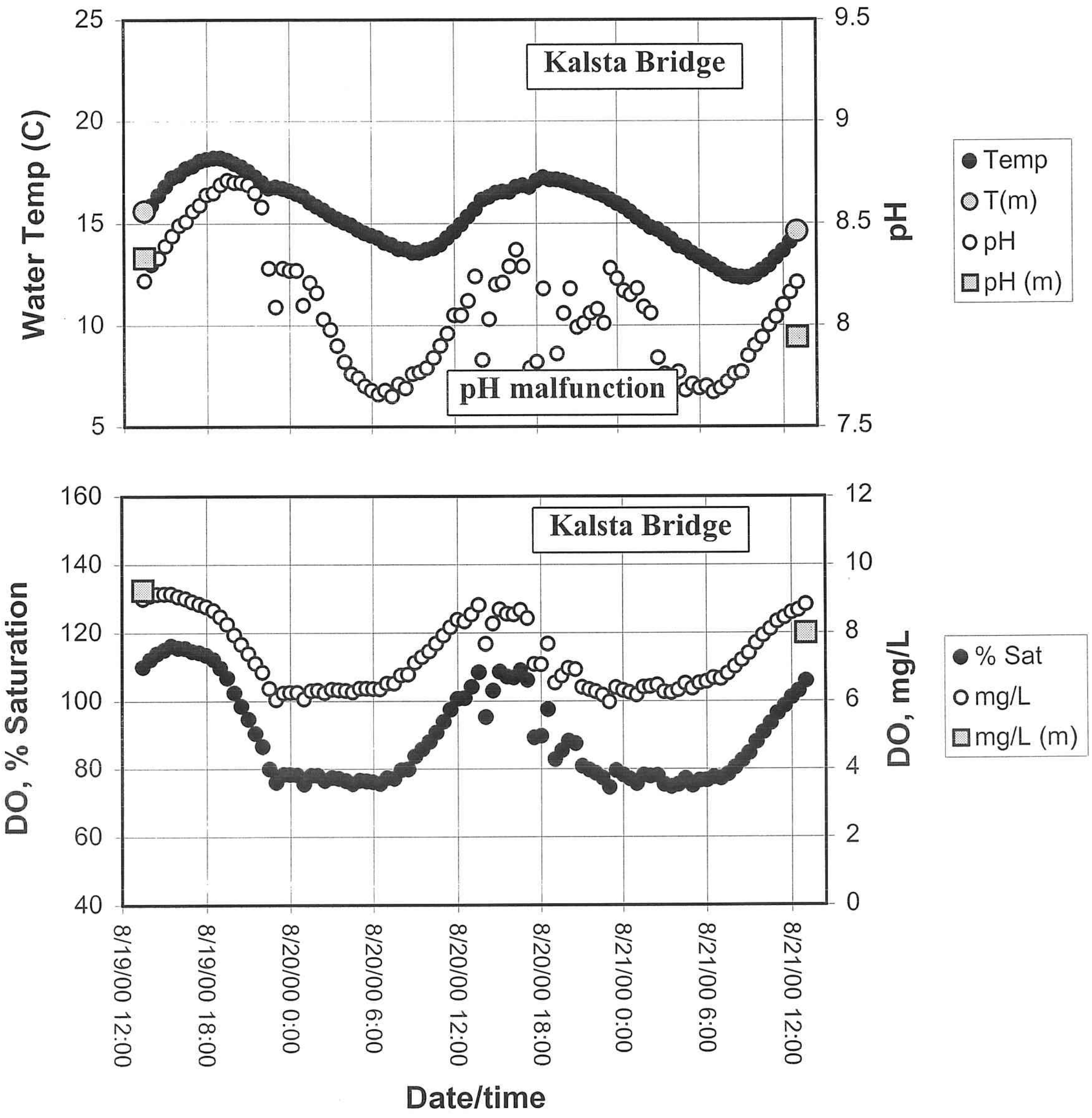

Figure 8. Hydrolab data for the Big Hole River at Kalsta Bridge. No SC or Eh data are shown, due to electrode malfunctions. There were obvious problems with pH as well, but the data are included.

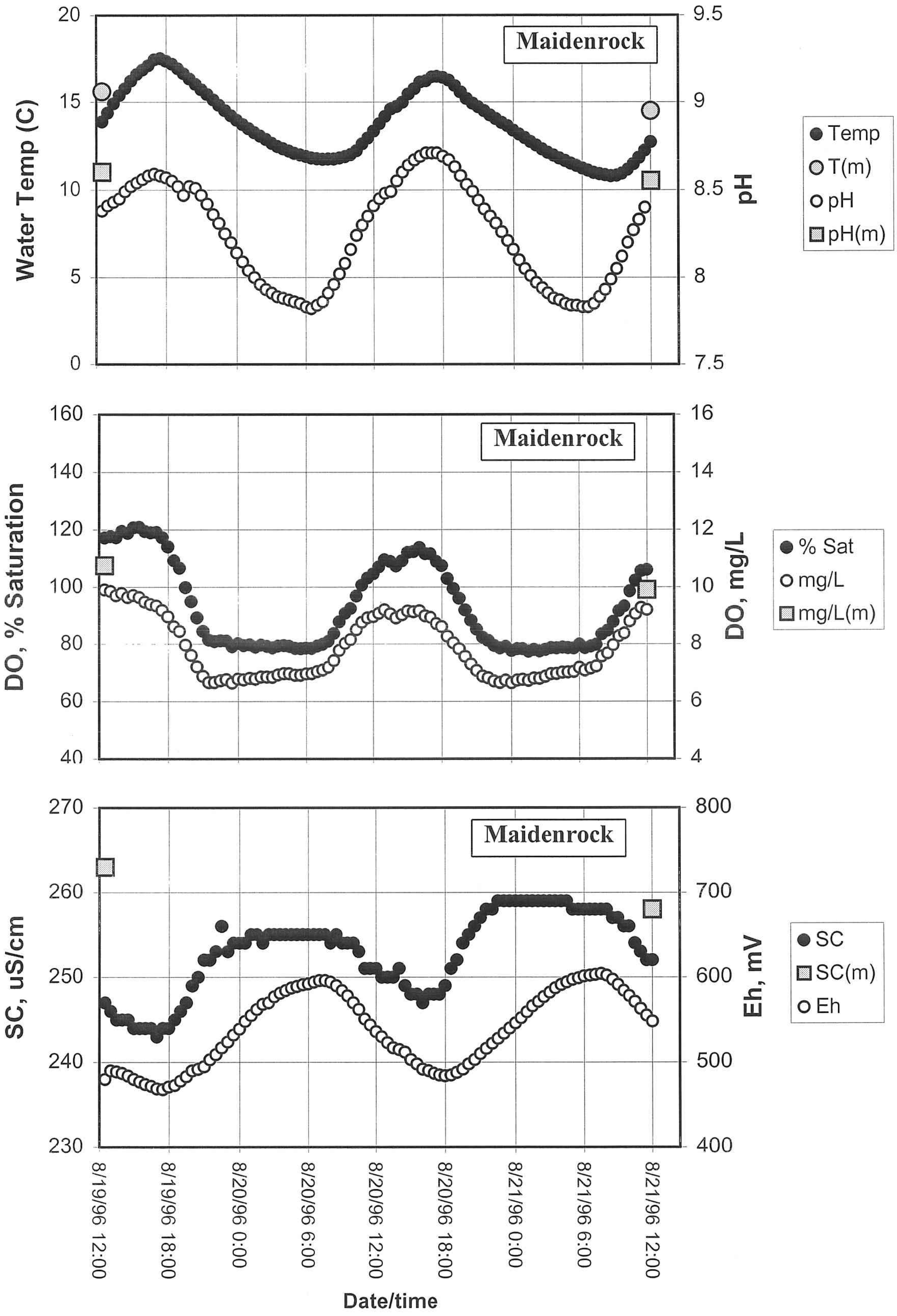

Figure 9. Hydrolab data for Big Hole River at Maidenrock.

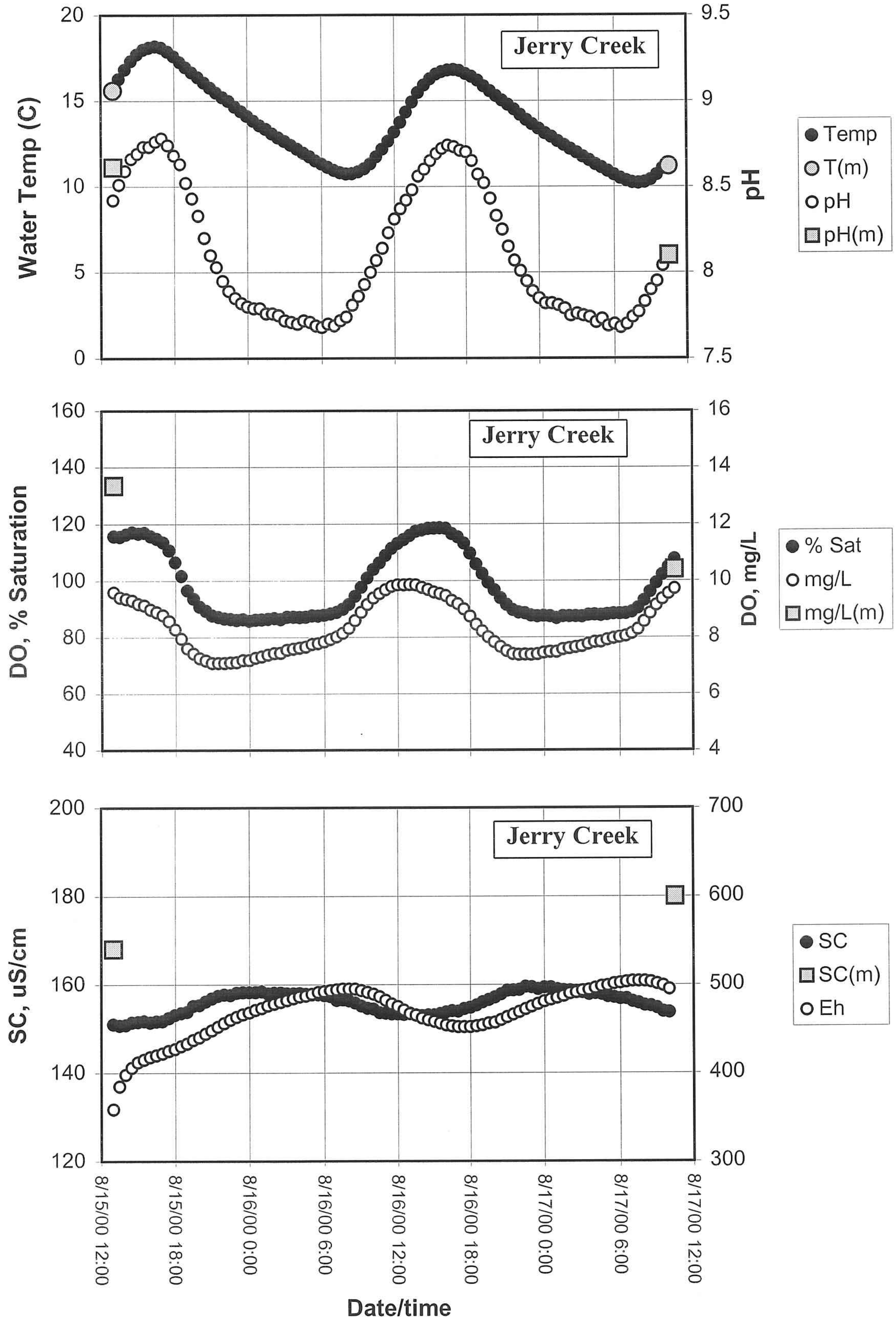

Figure 10. Hydrolab data for Big Hole River at Jerry Creek Bridge.

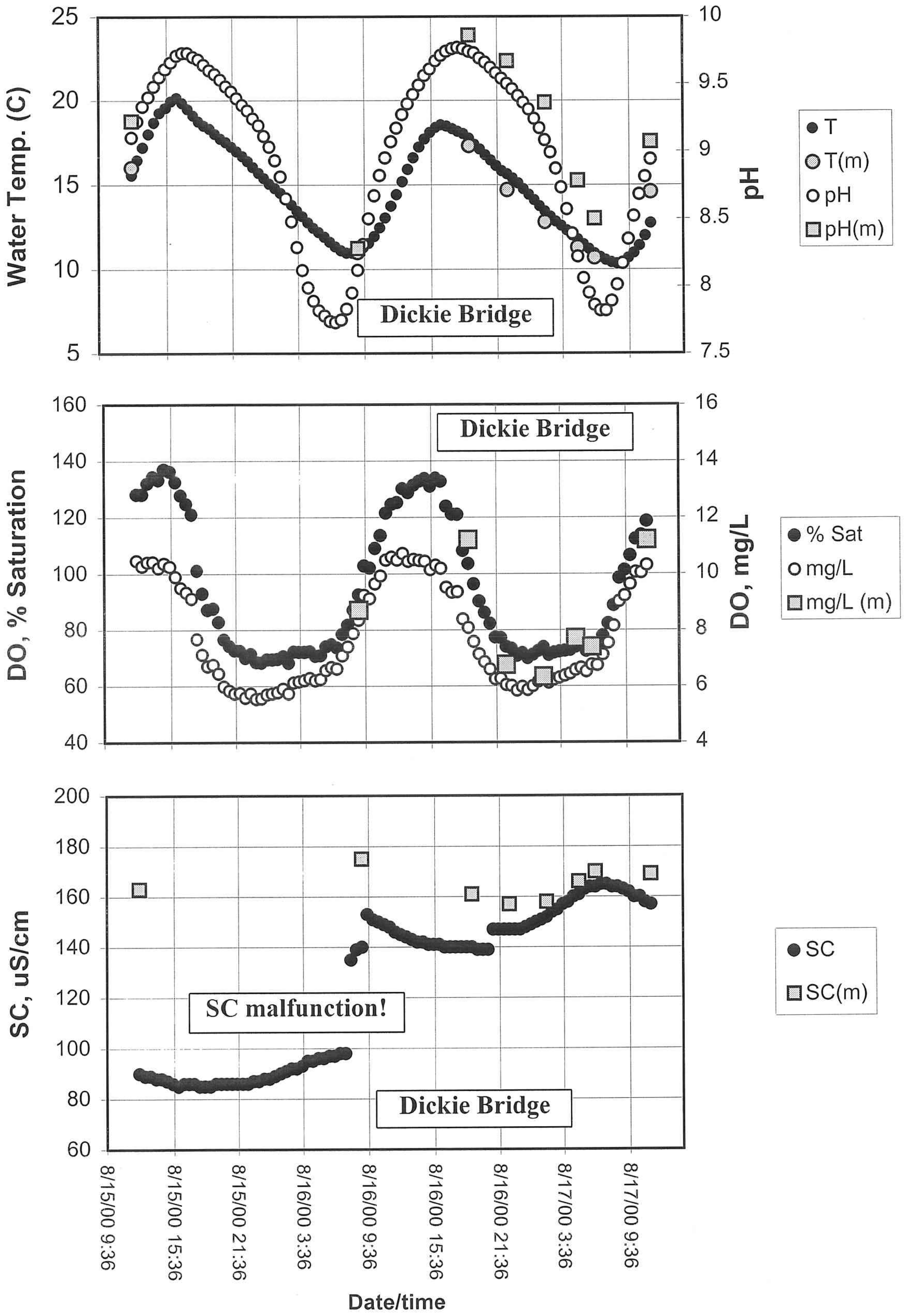

Figure 11. Hydrolab data for Big Hole River at Dickie Bridge.

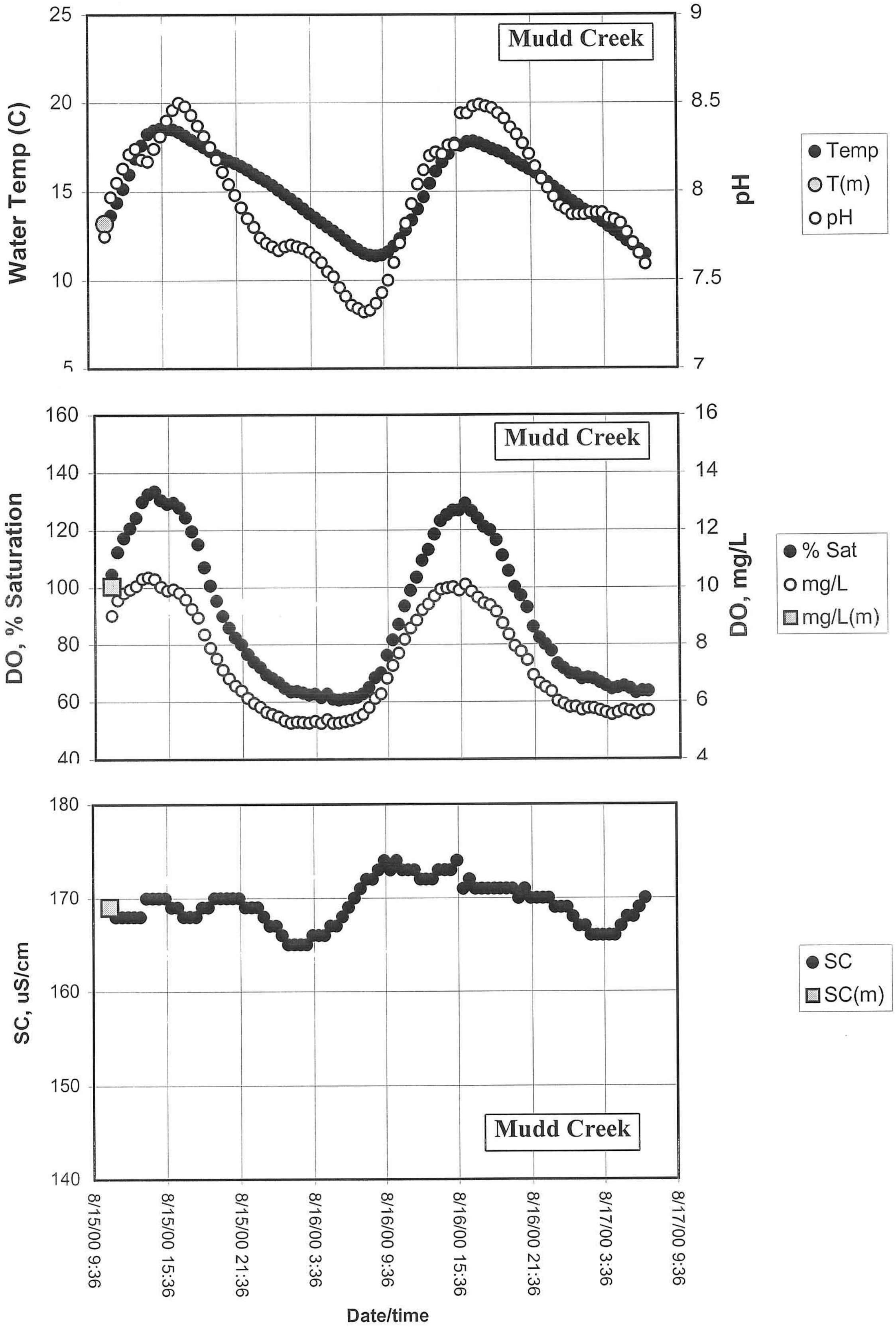

Figure 12. Hydrolab data for Big Hole River at Mudd Creek Bridge.

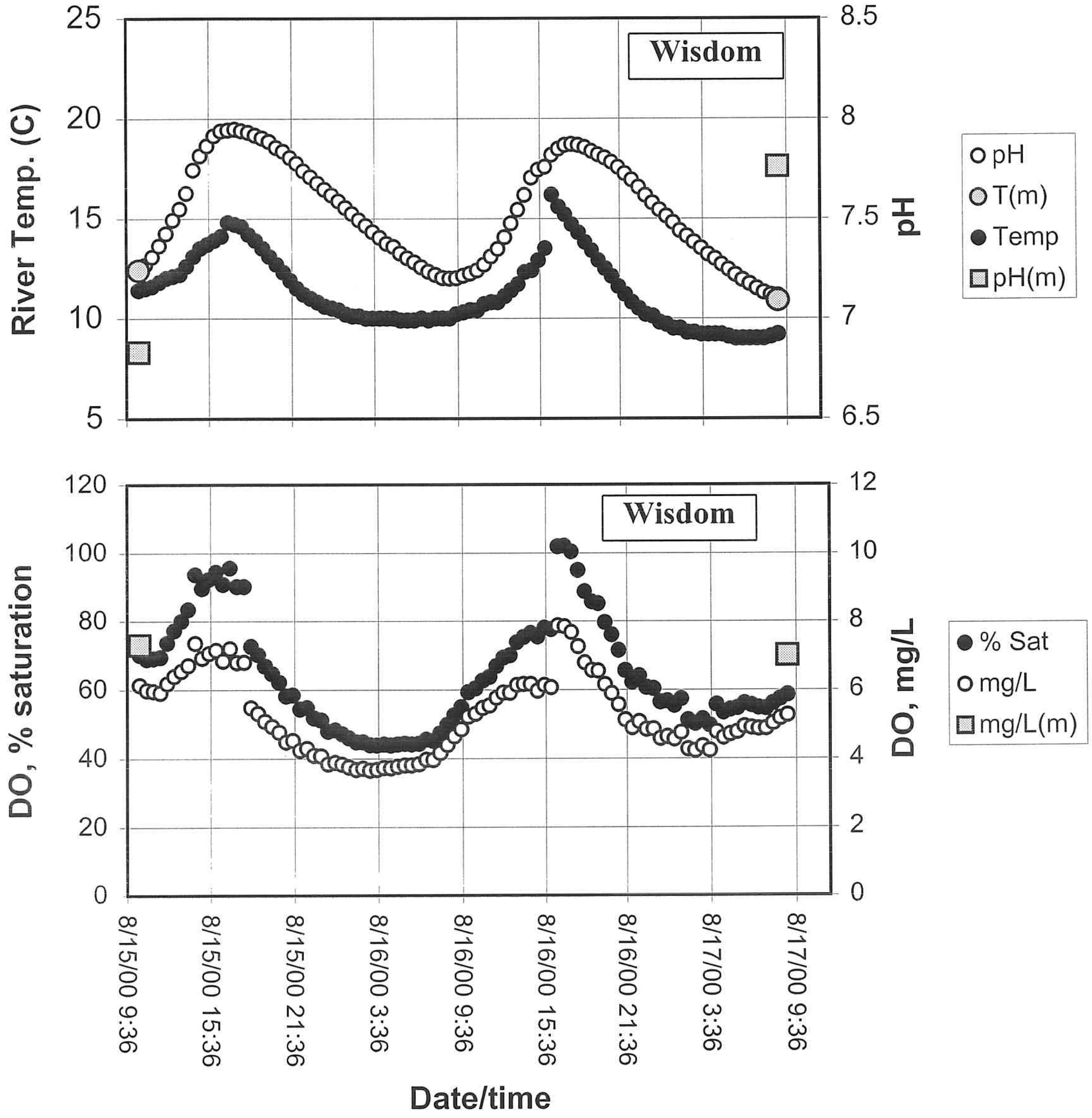

Figure 13. Hydrolab data for Big Hole River at Wisdom Bridge.
The SC and Eh data were in severe disagreement with our own manual measurements, and are not shown. There is an obvious problem with the DO and temperature data sets as well, with sharp discontinuities occuring at 6:30 in evening of the 15th, and 4:00 PM on the 16th. Our own manual DO measurements (at either end of the data set) were significantly higher than the Hydrolab results. This could be due to malfunction of the Hydrolab. However, the manual measurements were taken at the head of a long pool in a riffle section whereas the Hydrolab was placed in deep, slow-moving water at the tail of a long pool. So the DO differences could also be real. Overall, this is a questionable data set, from which few definite conclusions can be drawn.

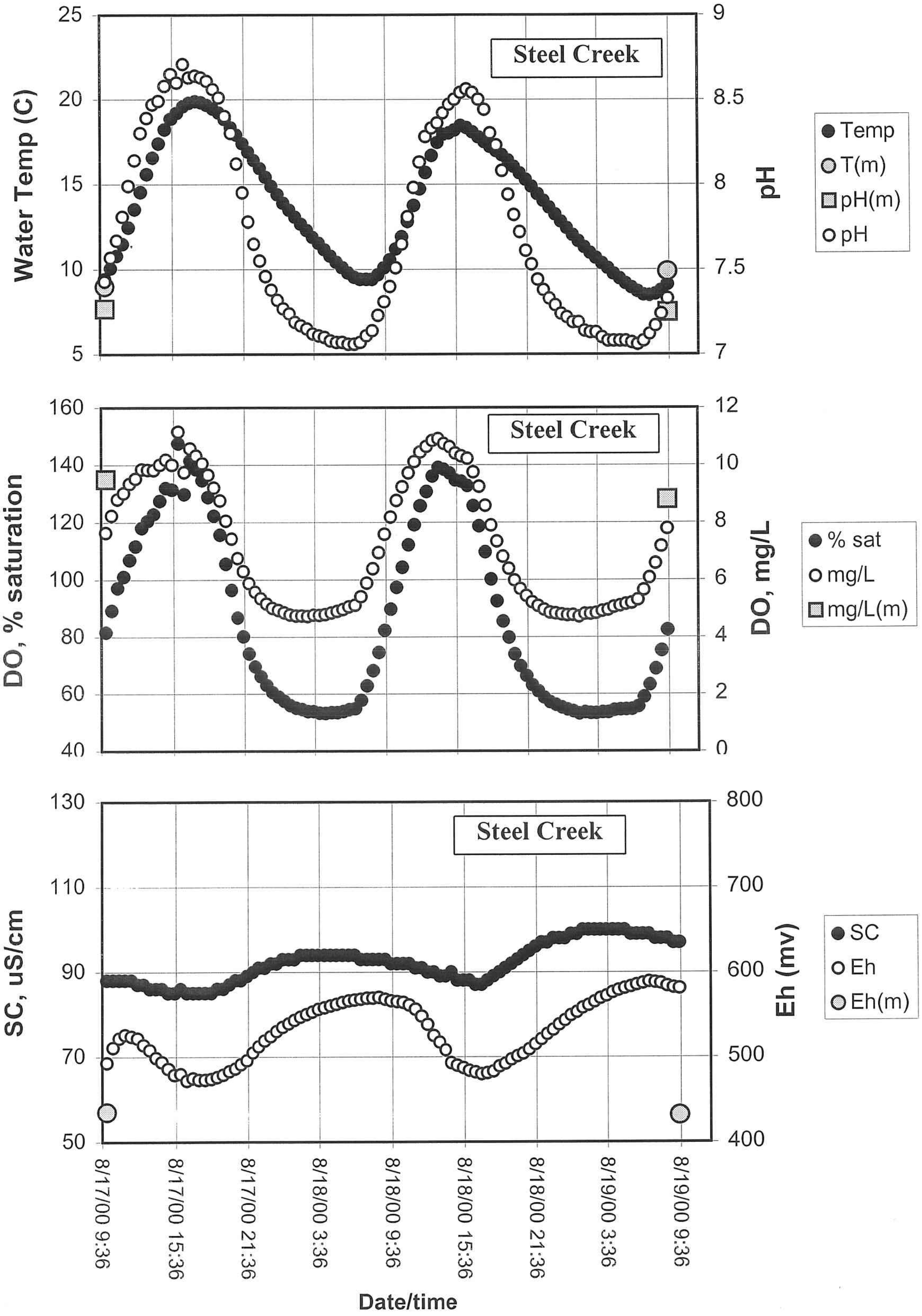

Figure 14. Hydrolab data for Steel Creek.

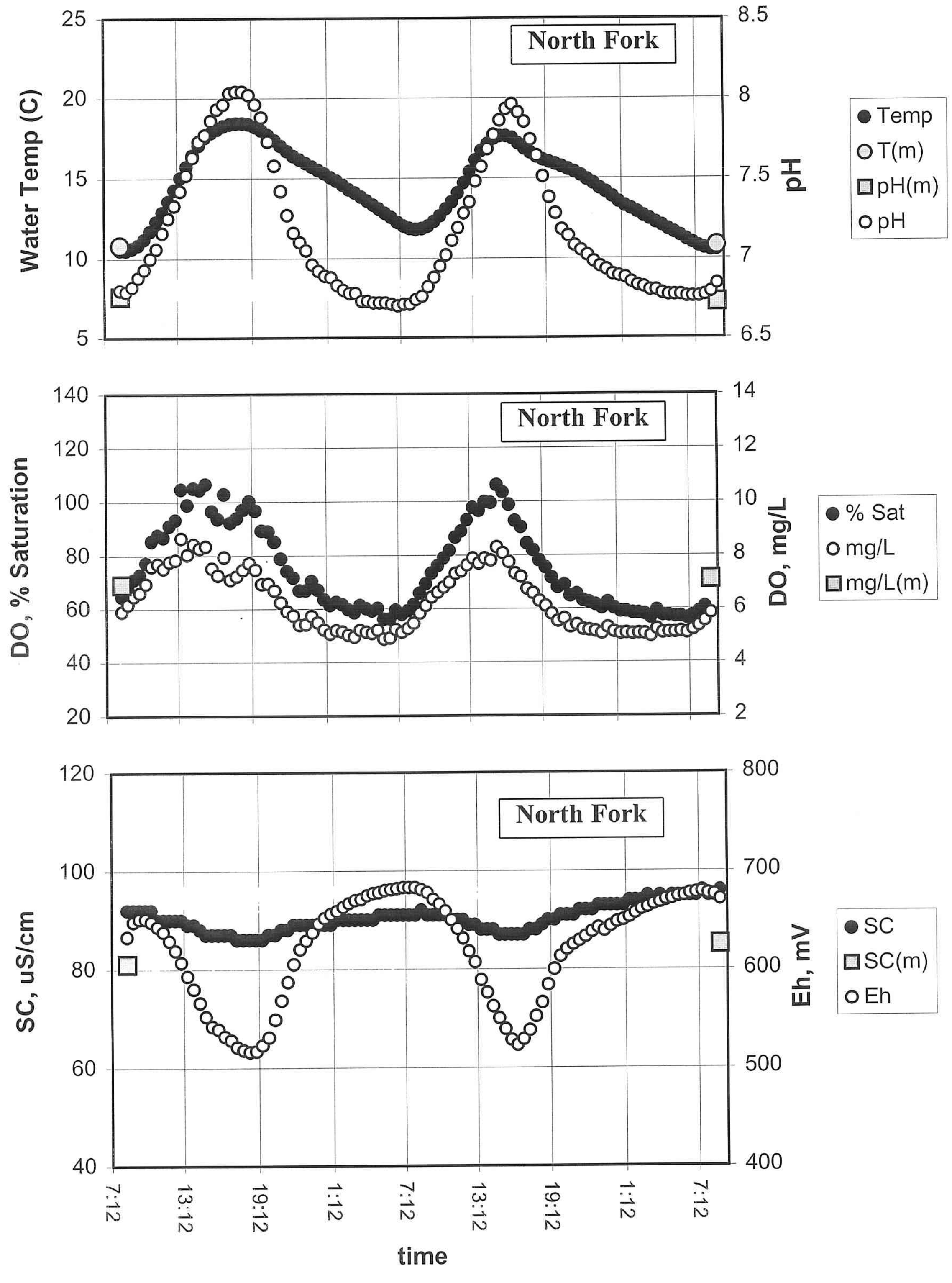

Figure 15. Hydrolab data for North Fork of Big Hole River.

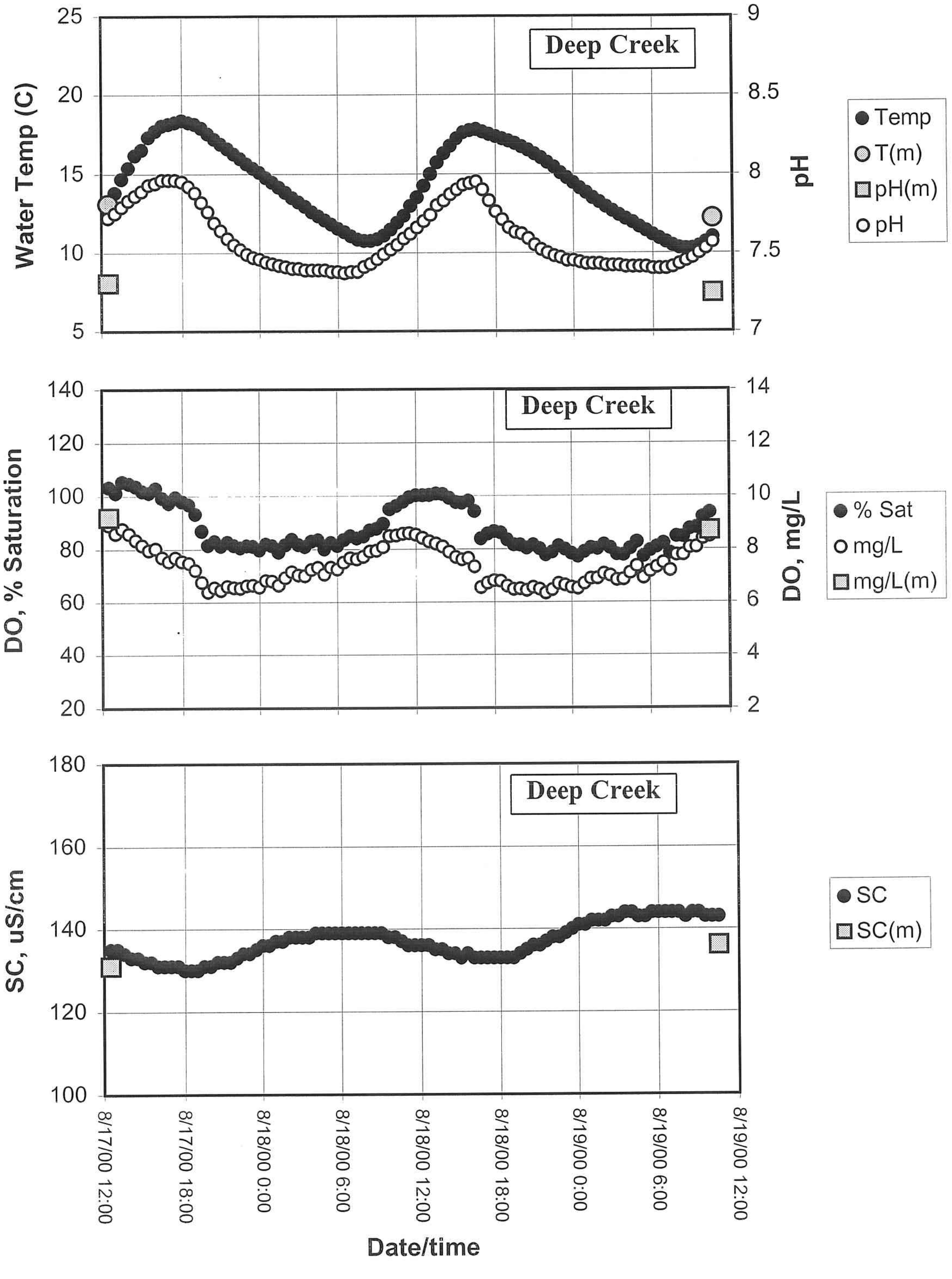

Figure 16. Hydrolab data for Deep Creek.

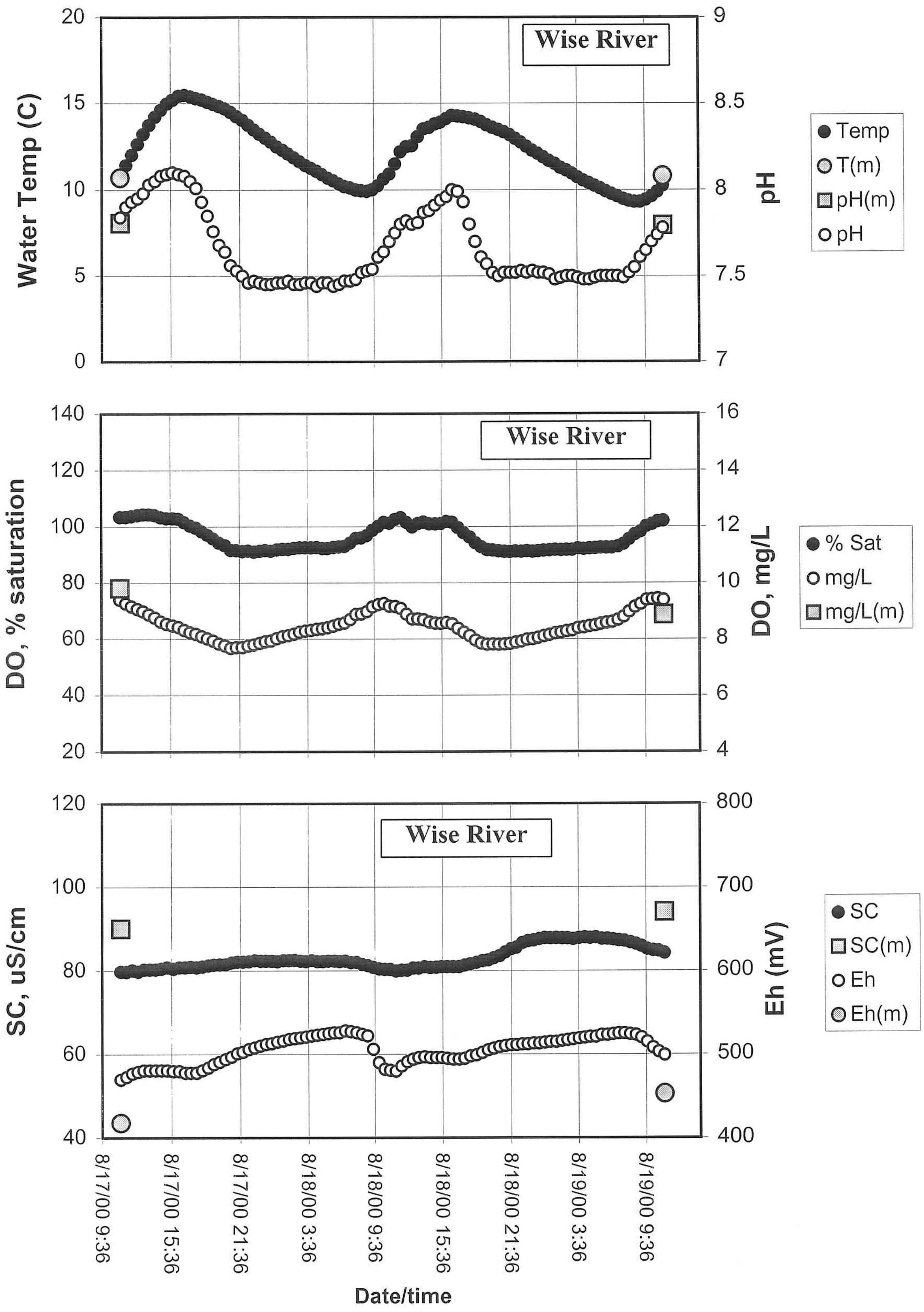

Figure 17. Hydrolab data for Wise River.

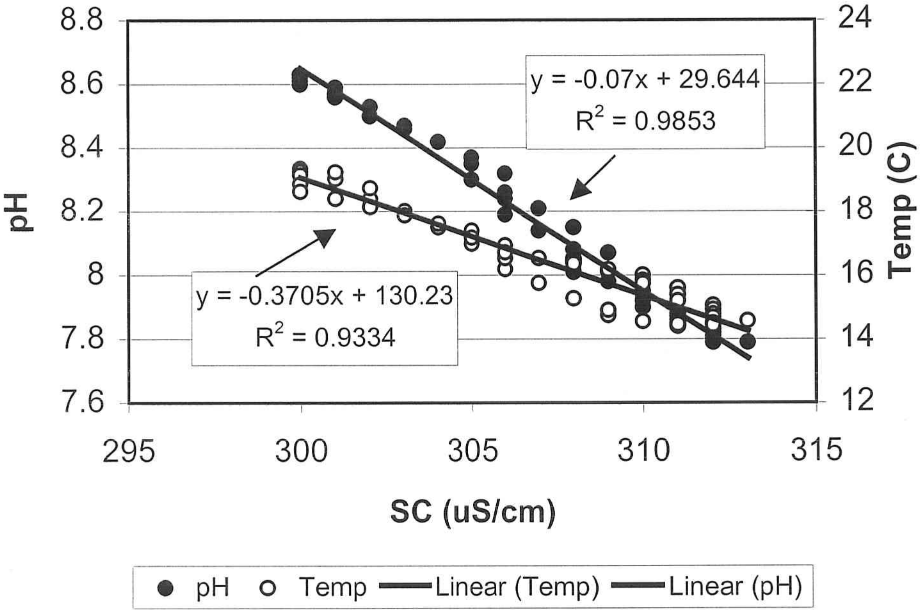

Figure 18. Correlation between specific conductivity, pH and temperature for the Big Hole River at Notch Bottom.

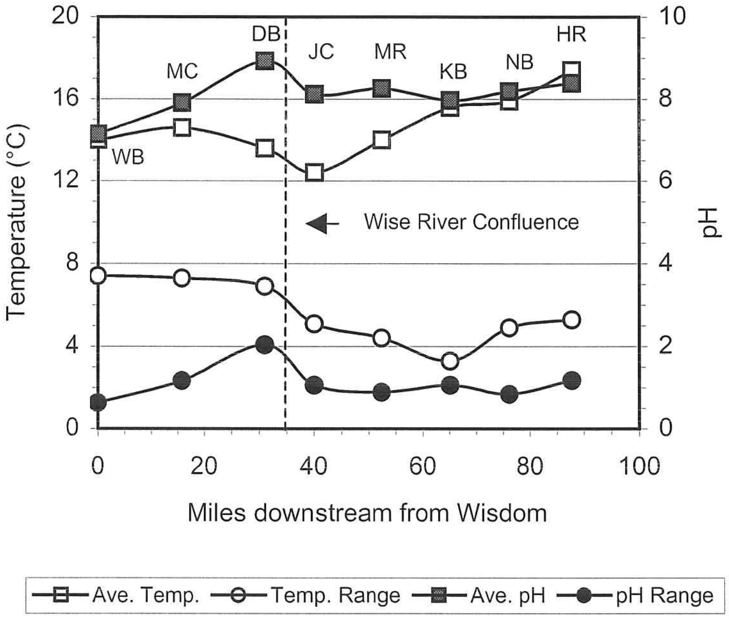

Figure 19. Longitudinal changes in temperature and pH. The x-axis plots river miles downstream from Wisdom, MT. Filled symbols are temperature data, and should be read on the left axis. Open symbols are pH data, and should be read on the right axis. Squares are daily average values, whereas circles show the total range between maximum and minimum values recorded in a single day. See Table 1 for an explanation of the abbreviations.

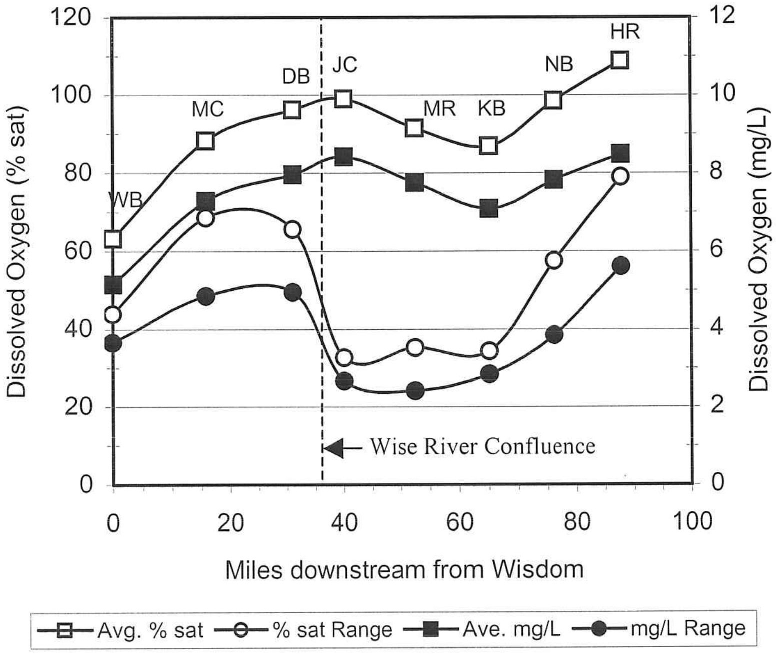

Figure 20. Longitudinal changes in dissolved oxygen. The open symbols show DO expressed in units of % saturation, and should be read on the left axis. The closed symbols show DO in units of mg/L, and should be read on the right axis. Squares show 24-hour average values, whereas circles show the total range between the maximum and minimum values recorded on a single day. See Table 1 for explanation of the abbreviations.

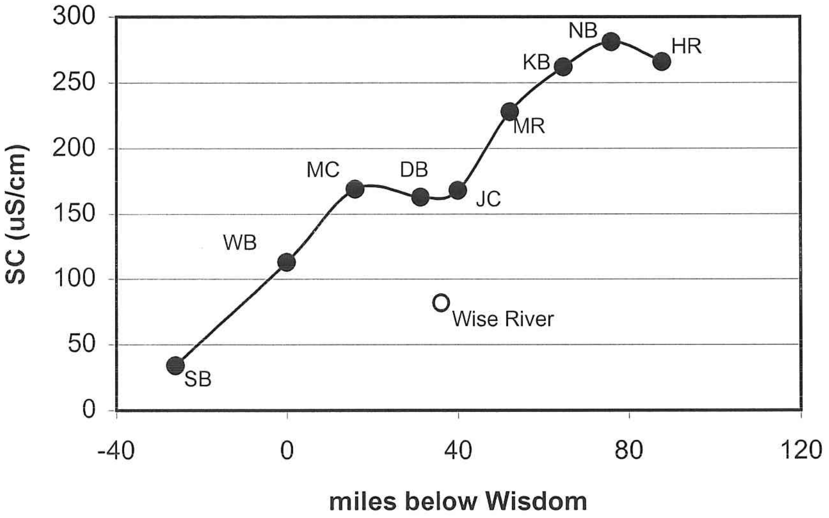

Figure 21. Longitudinal variation in specific conductivity. The SC values shown were obtained by manual measurement on August 15-16, and are believed more accurate than the Hydrolab data. The data point at -26 miles corresponds to the Big Hole River near its headwaters at Saginaw Bridge. In general, the SC of the Big Hole River increases with distance downstream. The Wise River is also shown for comparison.