Water Quality Issues and Trends in the Pecos River and Glorieta Creek, Pecos National Historical Park, National Park Service: 1994 – 2009

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Stephen D. Porter and Glenn Longley

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by

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Glenn Longley, PhD; Director

In cooperation with National Park Service, Southern Plains Network
Cooperative Agreement J2122080014
Robert Bennetts, PhD; Inventory and Monitoring Network Coordinator

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Summary

- Pecos National Historical Park personnel have been collecting water quality data at three locations in the park since 1994; however, most of the results had not been entered into a data base, subjected to quality control procedures, or analyzed for environmental trends. Primary data include water temperature, dissolved oxygen, specific conductance, and pH that were collected monthly to bi-monthly, in addition to several other constituents that were monitored over limited periods of time.

- As part of an on-going cooperative agreement between the National Park Service's Southern Plains Network (SOPN) and Texas State University's Edwards Aquifer Research & Data Center (EARDC), water quality scientists obtained paper records of the data from park personnel, entered the data into a MS Excel file, conducted quality-control procedures, and analyzed the data for water quality conditions and 15-year trends. This report presents the results of the investigation; the data base (PECOS1994-2009.xls) can be obtained from http://www.eardc.txstate.edu/.

- Although the data base is sufficient to evaluate water quality trends in the Pecos River and Glorieta Creek, several quality-control issues were found with certain subsets of the data. The frequency of monitoring all parameters was low during 2000 – 02, resulting in relatively poor documentation of water quality during that time period. Unexpectedly high values for specific conductance (2008 – 09) and pH (2001 – 04), as well as lower-than expected dissolved oxygen concentrations during 2003 – 04, were assumed to be operational errors associated with instrument performance and (or) calibration. Those data were removed (formatted as "missing") from a revised data set used for assessing water quality conditions and trends.

- Water temperatures in the Pecos River and Glorieta Creek generally increased from 1994 through 2002; however, temperatures measured since 2003 possibly are indicating a downward trend. Median temperature in Glorieta Creek (Site B; 12.9 ^{o}C) was considerably higher than those at Site A or Site C on the Pecos River (8.4 ^{o}C and 8.7 ^{o}C, respectively).

- Concentrations of dissolved oxygen (DO) generally were high at all three sites, indicating favorable conditions for aquatic life. Median DO concentrations ranged from 8.7 milligrams per Liter (mg/L) in Glorieta Creek to 9.8 mg/L in the Pecos River. Concentrations were less than the New Mexico water quality criterion of 6 mg/L in about 1.3 percent of measurements in the Pecos River and about 9.4 percent of measurements in Glorieta Creek. DO concentrations and percent saturation have been decreasing in Glorieta Creek since about 2000, during lower-than-average streamflow conditions, whereas concentrations in the

Pecos River have remained relatively stable throughout the period of record.

- Specific conductance (COND), a measure of dissolved solids or salts in the water, was significantly larger in Glorieta Creek than the Pecos River. Median COND values in Glorieta Creek were more than three times the median values observed in the Pecos River, and nearly 98 percent of COND measurements in Glorieta Creek exceeded the New Mexico water quality standard of 300 microSiemens per centimeter (µS/cm). Although no temporal trends were observed for COND in the Pecos River, values in Glorieta Creek increased by more than 50 percent during 1994 – 2009.

- Although pH values, indicators of the relative acidity or alkalinity of the water, were variable during 1994 – 2009, no significant differences among sites or water quality trends were noted during the period of record. Median pH values ranged from 8.1 to 8.3 standard units, somewhat higher than expected from a landscape derived from sandstone and shale geology. New Mexico water quality criteria ($6.6 < pH < 8.8$) were not attained in about nine to 11 percent of pH measurements made in the Pecos River and about four percent of measurements in Glorieta Creek. Decreases in pH have been noted in the Pecos River and Glorieta Creek since about 2004.

- Considerations for improving water quality monitoring include developing written quality assurance and quality control procedures, entering and reviewing all new data in context with previous data ranges and water quality criteria, calibration of meters and probes with certified reference standards and (or) manufacturer recommendations, and cooperating with the New Mexico Department of the Environment concerning water quality issues that originate outside park boundaries but may adversely affect environmental quality within the park.

Acknowledgements

We commend Pecos National Historical Park personnel (e.g. Daniel Jacobs, Marten Schmitz, and Ted Benson) for supporting a water quality monitoring program over the past 15 years, and volunteers such as Ruben and Joan Lamarque of Santa Fe, New Mexico for assistance with data collection. The value of routine monitoring data for documenting changes or trends in environmental conditions often is realized only in retrospect. We thank Ted Benson, Pecos National Historical Park ranger, for supplying copies of data sheets used to record water quality measurements, stream discharge records, and related data, and Rob Bennetts, National Park Service SOPN coordinator, for assistance with conversion of data files and overall support of this project. Colleague reviews of a draft version of this manuscript by Rene Barker and Raymond Slade Jr. (EARDC) and Kristine Johnson (University of New Mexico, Albuquerque, NM) improved the quality of this report and are much appreciated.

Introduction

Background

The National Park Service (NPS) has long recognized that the protection and restoration of its water resources and associated aquatic life are critical for the continued appreciation by park visitors. Fundamental components of the NPS's Inventory and Monitoring (I & M) Program are designed to "understand, maintain, restore, and protect the inherent integrity of the natural resources" (e.g. Perkins et al. 2005; 2006). Specific objectives of the I & M Program are to: (1) inventory existing water quality data, (2) establish water quality benchmarks, (3) identify potential water quality problems, and (4) establish a water quality database for each park. In 1993, NPS's Water Resources Division initiated its Baseline Water Quality Data Inventory and Analysis Project to characterize baseline water quality information for every park with appreciable water resources.

Pecos National Historical Park (PECO) is part of the NPS's Southern Plains Network (SOPN), one of the 32 networks included in the I & M Program and one of seven networks in the Intermountain Region of the NPS. Major water resources within PECO include a 2.9 mile segment of the Pecos River and the lower 3.2 miles of Glorieta Creek, a tributary to the Pecos River that flows near the PECO headquarters, visitor's center, and ruins area (NPS 1995; Figs. 1 & 2). The Glorieta Unit of the park contains a mile-long reach of Glorieta Creek and a half-mile reach of Galisteo Creek. Sources of water quality contamination in these streams include historical mining operations and domestic wastewater effluents from point and nonpoint sources located north of the park (NPS 1995; NMED 2004). Analysis of available water quality data by the Edwards Aquifer Research & Data Center (EARDC) of Texas State University (EARDC 2007) revealed relatively good water quality conditions at most sites in the Pecos River basin during the early 1980s through the early 1990s; however, data were not reported for more recent time periods, and no monitoring sites were located within the boundaries of Pecos National Historical Park. EARDC (2007) recommended that water quality data collected since the early 1990s should be entered into a digital database, combined with historical water quality data, and evaluated for current conditions and trends, particularly at several potential monitoring sites within the park boundary.

PECO began a water quality monitoring program within the park boundary in January 1994, consisting of (generally) monthly measurements of water temperature, dissolved oxygen, pH, specific conductance, and other water quality constituents in Glorieta Creek near its confluence with the Pecos River, and from two locations in the Pecos River, upstream and downstream from the Glorieta Creek confluence. These data existed primarily as written field notes, although some attempt had been made to enter the 1994 – 97 data into a spreadsheet format. As part of an on-going cooperative agreement between SOPN and EARDC, data collected during 1994 – 2009 were entered into a MS Excel spreadsheet, evaluated with quality-control procedures, and analyzed for recent trends in water quality conditions. This report presents the results of those analyses and provides considerations for future water quality monitoring activities in PECO.

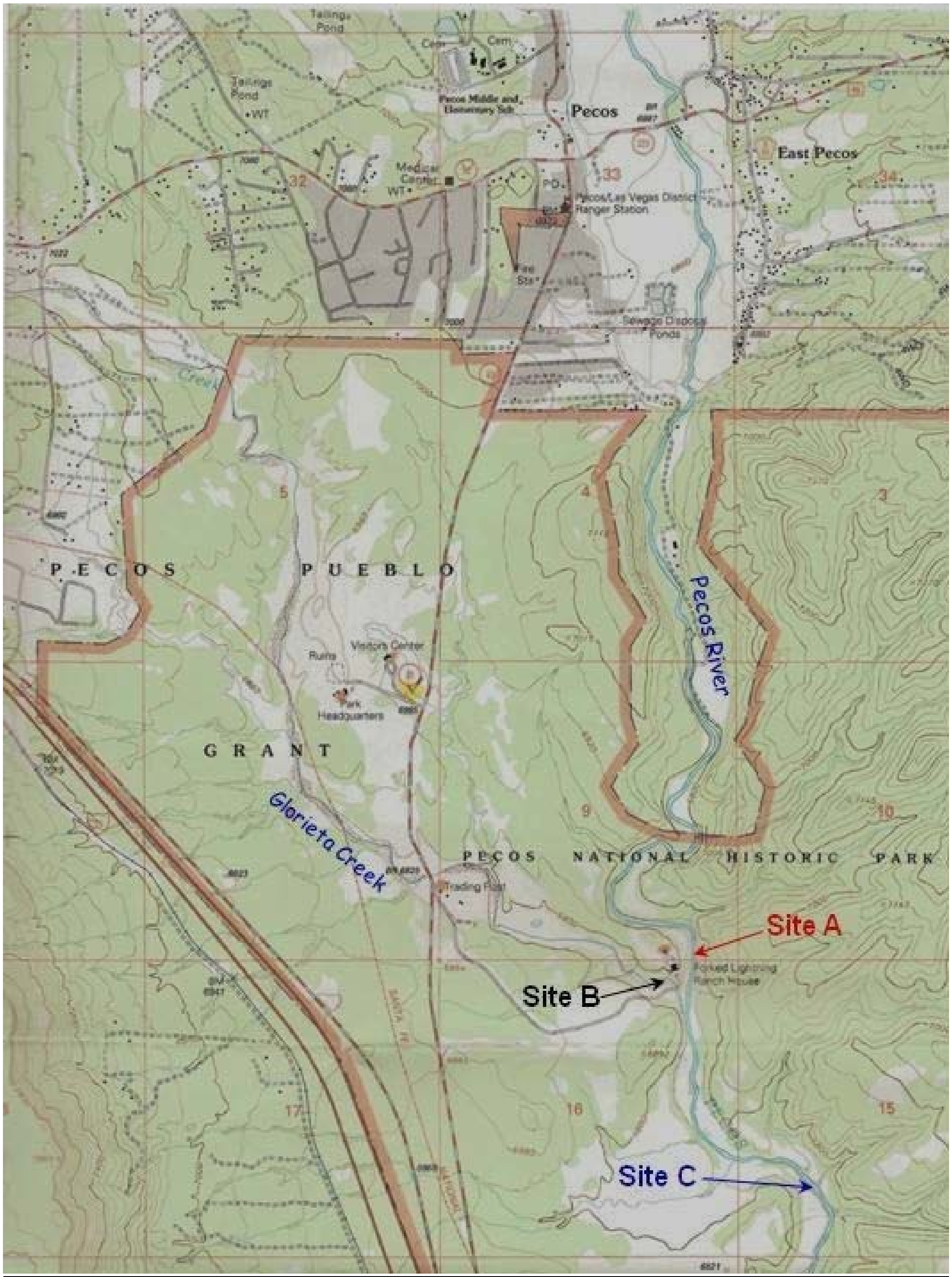

Figure 1. Locations of water quality monitoring sites in the Pecos National Historic Park.

Study Area

Pecos National Monument was established in 1965 to preserve an exceptional cultural and natural area with a long history of human settlement. From an original size of less than one-half square mile (340 acres), the National Monument was expanded into the Pecos National Historical Park in 1990, now including more than 10 square miles (6,670 acres). Most of the Pecos NHP is located within the upper Pecos River valley, bordered by the Sangre de Cristo Mountains to the north, the Tecolote Range to the east, and Glorieta Mesa to the west, approximately 25 miles southeast of Santa Fe, New Mexico. The park lies close to the terminus of the southern Rocky Mountains and near the entrance to Glorieta Pass, which connects the Rio Grande valley to the high plains and short-grass prairie of eastern New Mexico, including two Civil War battlefield sites associated with the Battle of Glorieta Pass (NPS 1995). Annual precipitation varies from 16 to 20 inches per year, with the majority falling during summer. The mean temperature ranges from a high of 80^{o} F (25^{o} C) during June through August to a low of 15^{o} F (- 9.4^{o} C) during December through February.

The upper Pecos River (headwaters to the Pecos Wilderness boundary) is located within the Santa Fe National Forest Pecos Wilderness and is relatively pristine; however, water resources downstream from the wilderness boundary have been adversely influenced by historical (1927 – 1939) hard-rock mining and milling operations, residential and commercial development, inadequate sewage treatment, illegal dumping, and suburbanization (NPS 1995). A major mining operation in the basin was the Tererro Mine, located on a 19 acre site adjacent to Willow Creek and the Pecos River about 14 miles north of PECO. Numerous mine-tailing spoil and overburden piles along Willow Creek and in the floodplain of the Pecos River are thought to be a source of high concentrations of aluminum, cadmium, copper, lead, iron, manganese, mercury, and zinc periodically measured in surface water and biota in the Pecos River (U.S. Fish and Wildlife Service 1993; Irwin 1993, 1994; NMED 2004). The former El Molino Mill Site, located on Alamitos Creek approximately one mile upstream from its confluence with the Pecos River, also is a source of heavy-metal contamination (NPS 1995). Unprocessed waste rock from the Tererro Mine site was used to construct or repair roads in the basin, resulting in additional, diffuse sources of heavy-metal contamination.

Figure 2. Glorieta Creek near confluence with the Pecos River (April 2007).

Point sources of water quality contamination include treated effluent discharges to the Pecos River from the village of Pecos wastewater-treatment plant (WWTP; 50,000 – 60,000 gallons per day), located less than two miles upstream from the PECO boundary, and the Glorieta Conference Center WWTP that discharges to Glorieta Creek approximately 8 miles upstream from the Pecos Unit boundary. During peak season (May – September), the Conference Center is capable of housing 2,500 conference participants (NPS 1995), and discharges from the Conference Center WWTP can range from 170,000 – 200,000 gallons per day.   Occasional exceedances of permit limits and (or) water quality criteria for nutrient (ammonia, nitrate + nitrite) concentrations, specific conductance, and turbidity have been observed in association with both WWTPs (NMED 2004), and considerable growths of filamentous algae have been observed in Glorieta Creek (Fig. 2), indicative of high nutrient loading (NPS 1995). Nonpoint sources of water quality contamination include numerous residential and commercial septic tanks in the basin, streambank erosion, and contaminant runoff from roads and other impervious surfaces.

Water Quality Monitoring

Water quality was monitored at three sites within the PECO boundary (Pecos Unit) beginning in January 1994. Site A (Pecos River at Ranch House: 35° 32' 14.634" N, 105° 40' 11.701" W) is located upstream from the Glorieta Creek confluence; Site B (Glorieta Creek at Ranch House: 35° 32' 5.706" N, 105° 40' 16.583" W) is located upstream from the confluence with the Pecos River; and Site C (Pecos River at Colonias Bridge: 35° 31' 28.021" N, 105° 39' 39.732" W) is located about 1.3 miles downstream from the Glorieta Creek confluence (Fig. 1). Data were obtained from PECO personnel (Ted Benson, Pecos National Historical Park Ranger, written communication) and recorded into an Excel spreadsheet file (PECOS1994-2009.xls), which is available for download at http://www.eardc.txstate.edu/.

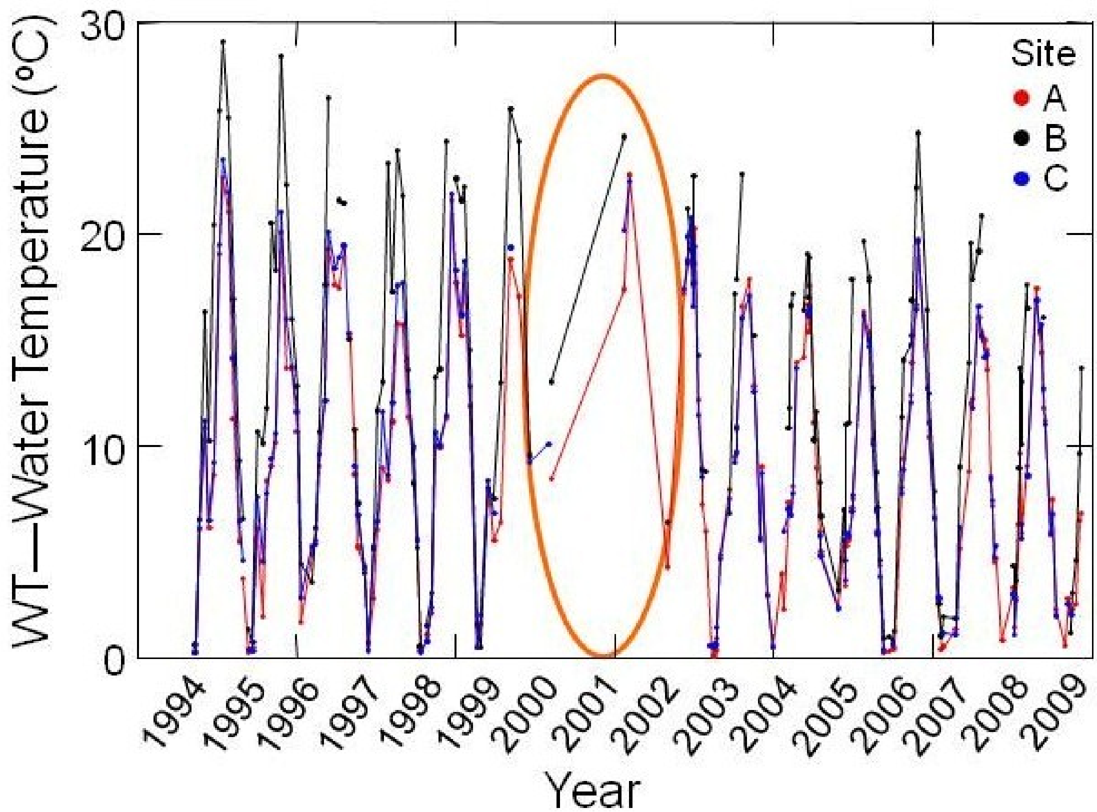

Figure 3. Water temperature in the Pecos River and Glorieta Creek during 1994 – 2009. (Orange ellipse indicates missing data.)

Figure 3 shows seasonal water temperature patterns at the three sites during 1994 – 2009 and illustrates the record of water quality monitoring during the period. Relatively few measurements were available during 2000 – 2002 (Fig. 3, orange ellipse). These data are either missing or it is possible that monitoring activities were curtailed during this period. Examination of water temperature patterns indicates higher temperatures in Glorieta

Creek than in the Pecos River during summer (Fig. 3, black lines); whereas temperatures frequently were slightly lower in the Pecos River than in Glorieta Creek during winter (Fig. 3, red or blue lines). Temperatures exceeding 20 degrees Celsius, the NMED water quality criterion for these surface waters, are common during summer months (Fig. 3). Relatively higher temperatures in Glorieta Creek during summer are probably associated with shallower water depth and relatively less flow in Glorieta Creek than in the Pecos River.

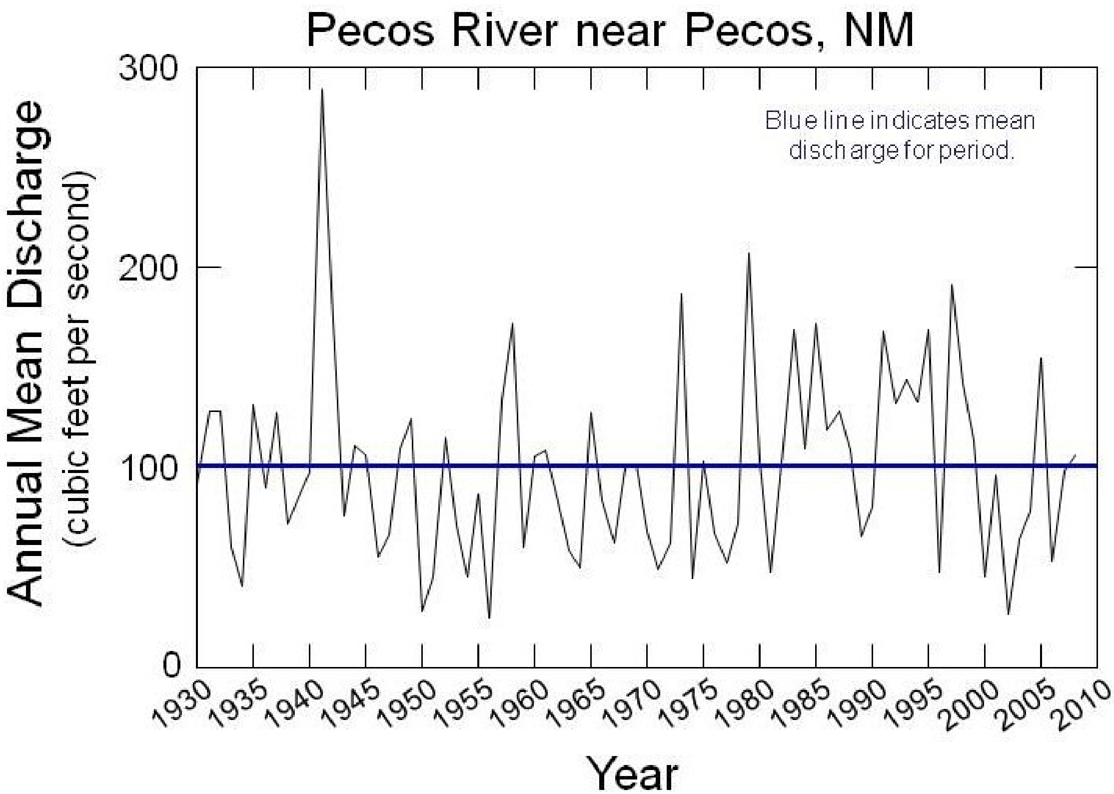

Figure 4. Annual mean discharges in the Pecos River near Pecos, New Mexico: 1930 – 2009.

The nearest U.S. Geological Survey (USGS) stream gage on the Pecos River near Pecos, New Mexico (08378500), is located about 11 miles upstream from the park. Figure 4 shows annual differences in mean discharge at this location for the period of record (1930 – present). Annual mean discharge in the Pecos River near Pecos, NM generally exceeded the long-term mean discharge (more than 100 cubic feet per second) during the early part of the monitoring period (1994-99) but was less than the long-term mean during most of 2000 – 2009 (Fig. 4). No continuous discharge records are available for Glorieta Creek; however, a limited number of concurrent discharge measurements were made at Sites A and B as part of NHP water quality monitoring activities during 1994 – 98 (above-average streamflow conditions). Comparison of discharges measured in the Pecos River (Site A) and Glorieta Creek (Site B) on the same date (refer to PECOS1994-2009.xls) indicates that the mean flow in Glorieta Creek was only about 0.5 percent of the Pecos River flow during summer months (May – September; range: 0.1% - 1.2%) and about 2.3 percent of the Pecos River flow at other times of the year (range: 0.6% - 6.8%).

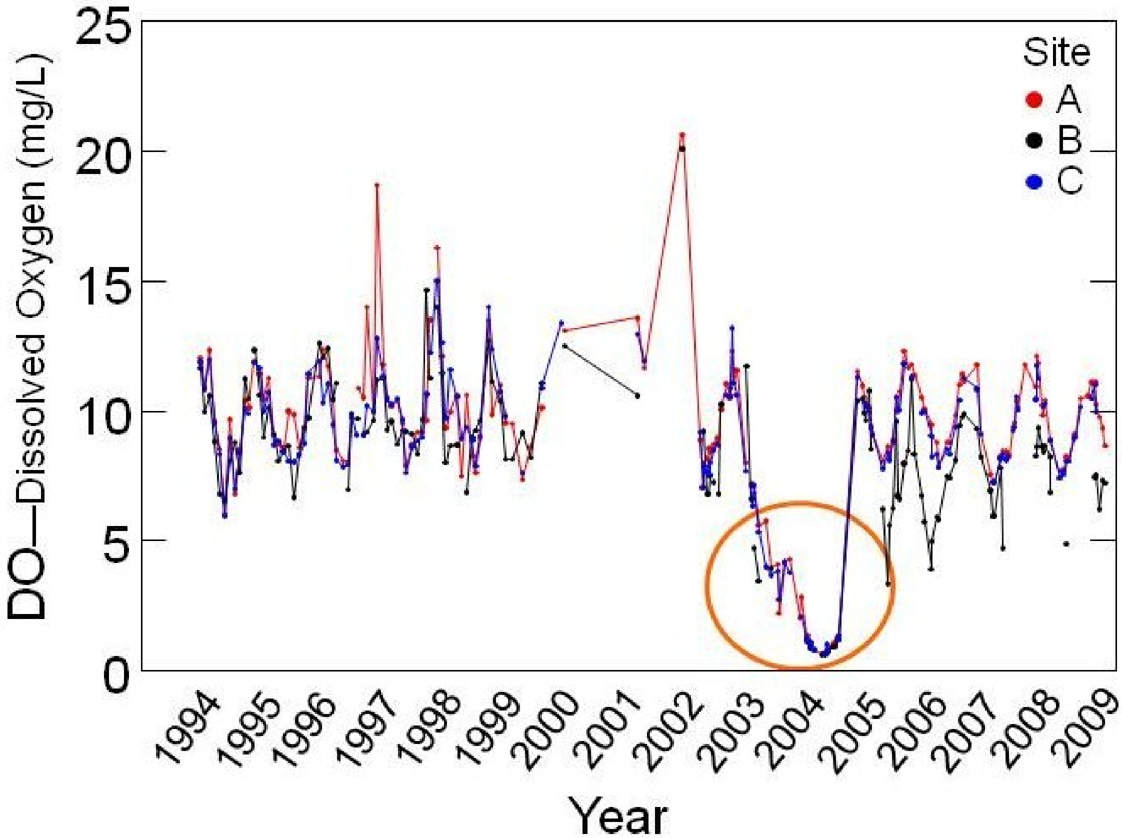

Figure 5. Dissolved oxygen concentrations in the Pecos River and Glorieta Creek during 1994 – 2009. (Orange circle indicates unexpectedly low dissolved oxygen values.)

Dissolved oxygen (DO) concentrations generally were high (favorable for aquatic life) during the 15-year monitoring period; however, unexpectedly low values were reported during 2003 – 04 at all three sites (Fig. 5). Dissolved oxygen concentrations varied seasonally (generally higher during winter and lower during summer) during the monitoring period. Low DO concentrations during 2003 – 04 appear to reflect a systematic decline in the performance of the instrument used to measure dissolved oxygen. It is unlikely that DO concentrations in the Pecos River and Glorieta Creek would have remained less than 4 milligrams per Liter (mg/L), with no seasonal variability, for such an extended period of time without obvious adverse environmental effects such as fish kills. Instrument maintenance and calibration are important components of a written quality assurance and control plan for water quality monitoring. In addition to fundamental quality control procedures presented later in this report, DO measurements less than the New Mexico water quality criterion (6 mg/L) or those associated with high DO saturation should be verified by an independent measurement made with a calibrated DO meter and probe of known quality.

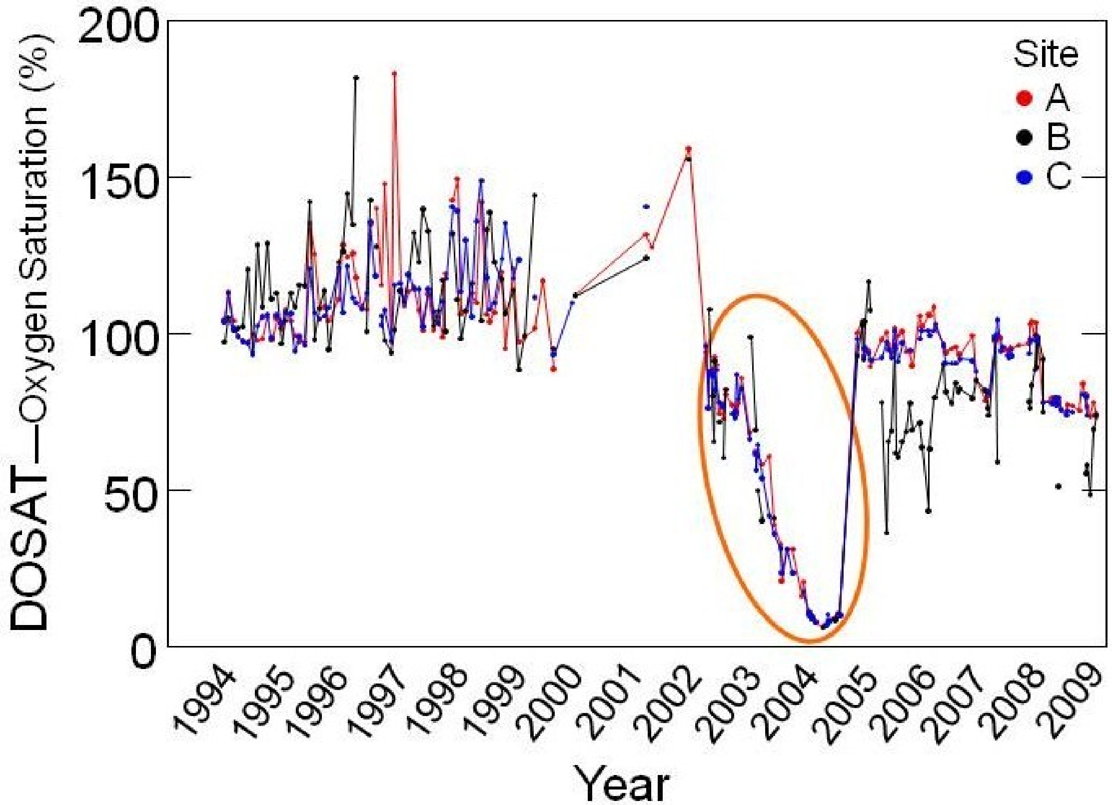

Figure 6. Oxygen saturation in the Pecos River and Glorieta Creek during 1994 – 2009. (Orange ellipse indicates lower than expected oxygen saturation)

Although DO concentrations were similar among sites during 1994 – 99, concentrations reported since 2005 have been lower in Glorieta Creek than in the Pecos River (Fig. 5; black lines). The percentage of oxygen saturation (DOSAT), a function of water temperature, atmospheric pressure, and biological and (or) chemical oxygen-demanding substances in the water, also has been lower in Glorieta Creek since 2005 relative to the middle 1990s (Fig. 6). Oxygen saturation in the Pecos River generally has been about 100 percent, which would be expected in high-gradient, high-quality streams and rivers. Many DOSAT values recorded during 1994 – 99 were higher than expected, for example, values exceeding 125 percent (Fig. 6).

High oxygen saturation during daylight hours frequently is associated with accelerated, in-stream primary production of oxygen by submerged algae and other aquatic plants. Growths of algae are stimulated by enrichment of nutrients (nitrogen and phosphorus). Large growths of filamentous green algae were observed in the lower reach of Glorieta Creek during the early 1990s (NPS 1995), and above-mean stream flows during the early monitoring period may have increased the area of stream-bottom habitat for benthic algal (or macrophyte) colonization and growth. Monitoring of nutrient concentrations and benthic algae (macrophytes) should be a consideration for understanding trophic conditions in Glorieta Creek and the Pecos River, particularly with regard to WWTP discharges and non-point sources of eutrophication in the basin.

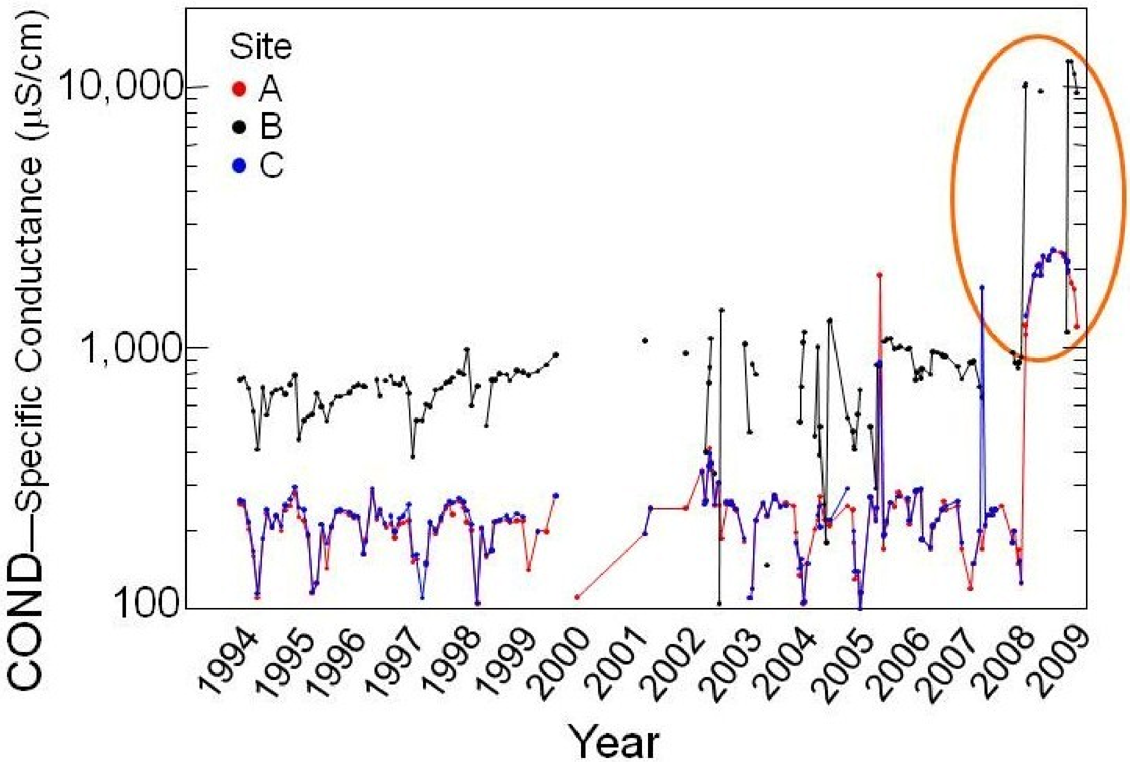

Figure 7. Specific conductance values in the Pecos River and Glorieta Creek: 1994 – 2009. (Orange ellipse indicates larger than expected values.)

Specific conductance (COND) values, a measure of dissolved solids (salts) in the water, varied seasonally at all sites, with relatively lower values recorded during periods of higher stream flow. Although COND values were significantly higher at Site B (Glorieta Creek) than at either Pecos River site (Fig. 7), values reported at all sites since 2008 have been as much as an order of magnitude larger than reported previously (e.g. Fig. 7; values *circa* 10,000 microSiemens per centimeter (μS/cm)); those values are unlikely to occur in freshwater ecosystems. We suspect that the larger-than-expected COND values are associated with instrument error and (or) calibration issues.

Median COND values for the Pecos River over the 15-year period of record were 218 μS/cm and 226 μS/cm for Sites A and C, respectively, whereas the median COND value for Glorieta Creek was 755 μS/cm (Table 1). The New Mexico water quality standard for COND for this basin is 300 μS/cm (NMED 2004). Sources of high COND in Glorieta Creek are poorly understood and warrant further investigation. On the original data sheets, COND (apparently) had been reported in units of milliSiemens per centimeter (mS/cm) since the year 2001. Those data were converted to μS/cm in the final data set by multiplying the reported value by a factor of 1,000. Specific conductance meters should be calibrated with certified standard solutions available from laboratory supply companies and results should be reported in units of μS/cm. For future monitoring, measured COND values exceeding the New Mexico water quality standard (300 μS/cm) should be verified by an independent measurement made with a calibrated COND meter and probe of known quality.

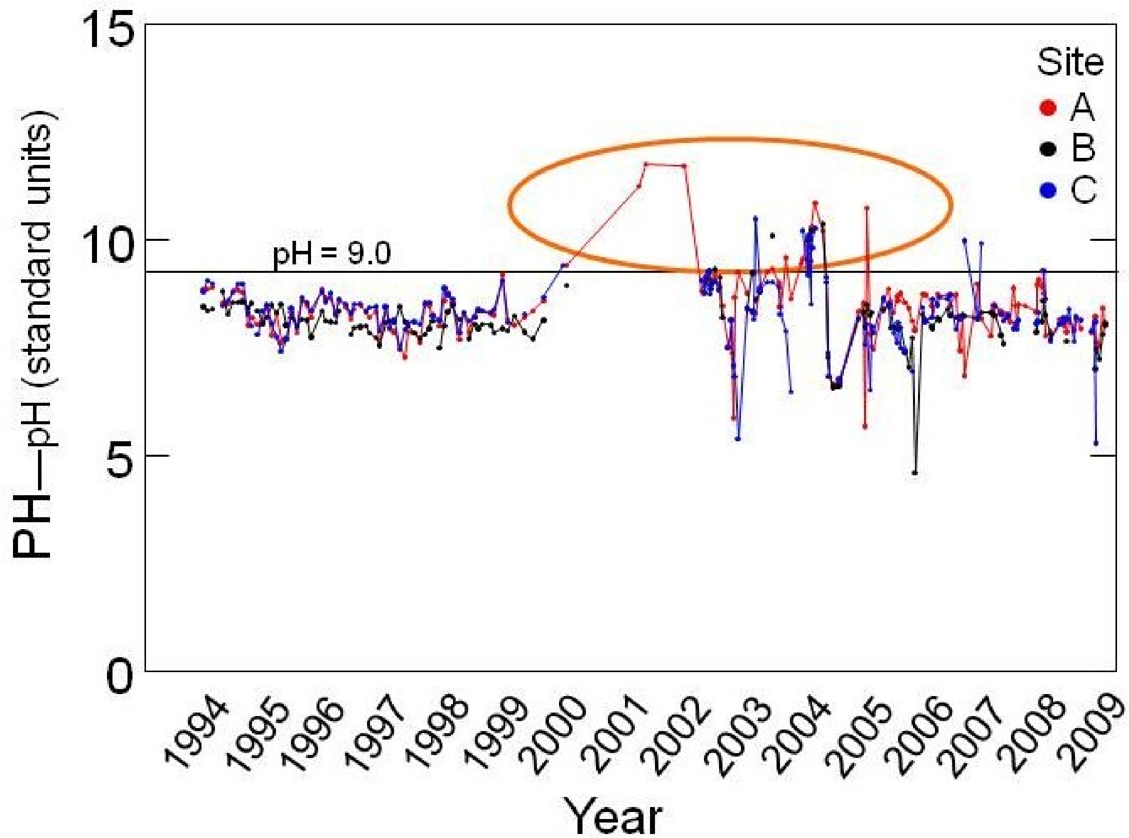

Figure 8. pH values in the Pecos River and Glorieta Creek: 1994 – 2009. (Orange ellipse indicates larger than expected pH values.)

Median pH values at the three sites ranged from 8.1 in Glorieta Creek to 8.3 in the Pecos River (Site A; refer to Table 1), and are somewhat larger than expected for streams draining sandstone and shale strata of relatively insoluble mineralogic composition. Some of the pH values reported during 2001 – 04 were considerably larger than expected (e.g. pH larger than 10 standard units; Fig. 8). New Mexico water quality criteria indicate that pH shall be within the range of 6.6 and 8.8 standard units (NMED 2004), whereas U.S. Environmental Protection Agency criteria specify a range of 6.0 to 9.0 standard units. Values exceeding 9.0 standard units are rarely observed in freshwater ecosystems. We suspect that the larger-than-expected pH values are associated with instrument error and (or) calibration issues, and for future monitoring, we recommend that measured values not in accordance with New Mexico water quality criteria (e.g. $6.6 < pH < 8.8$) should be verified by an independent measurement made with a calibrated pH meter and probe of known quality.

The unexpected values reported for DO (9/13/2003 – 11/7/2004), COND (5/27/2008 – 5/3/2009), and pH (2001 – 2004) were removed (formatted as “missing”) in a revised data set for water quality trends analyses. Descriptive statistics for the revised data set are presented in Table 1.

Table 1. Descriptive water quality statistics for selected locations on the Pecos River and Glorieta Creek, 1994-2009. WT, water temperature (degrees Celsius); DO, dissolved oxygen (mg/L); COND, specific conductance (uS/cm); pH (standard units); DOSAT, oxygen saturation (percent).

Site A		WT	DO	COND	pH	DOSAT
Number of Data Records		180	160	161	150	159
Minimum		0.1	5.6	100	6.6	58.3
Maximum		22.8	20.7	415	9.0	183
Mean		9.0	9.9	214	8.2	99.2
Standard Dev		6.0	2.0	53	0.5	18.9
Percentiles	5%	0.4	7.3	115	7.4	73.7
	10%	0.7	7.8	141	7.6	76.8
	25%	4.5	8.6	186	8.0	89.1
Median	50%	8.4	9.8	218	8.3	98.1
	75%	13.9	11.0	249	8.6	107
	90%	17.8	11.9	270	8.8	120
	95%	19.4	12.7	283	8.9	135

Site B		WT	DO	COND	pH	DOSAT
Number of Data Records		141	127	129	125	126
Minimum		0.5	3.4	180	6.6	36.6
Maximum		29.1	20.1	1,396	9.0	181.9
Mean		12.6	8.8	757	8.1	97.4
Standard Dev		7.5	2.3	212	0.4	25.6
Percentiles	5%	1.0	5.5	408	7.1	57.7
	10%	1.8	6.2	488	7.6	64.0
	25%	6.7	7.4	640	7.9	78.4
Median	50%	12.9	8.7	755	8.1	98.8
	75%	17.9	10.0	880	8.3	113.9
	90%	22.7	11.3	1,016	8.5	131.8
	95%	24.7	12.4	1,089	8.6	140.4

Site C		WT	DO	COND	pH	DOSAT
Number of Data Records		157	140	143	133	139
Minimum		0.2	5.3	100	6.5	54.1
Maximum		23.5	15.0	880	9.0	149
Mean		9.7	9.6	223	8.2	99.0
Standard Dev		6.2	1.7	78	0.5	17.1
Percentiles	5%	0.5	7.2	113	7.0	74.1
	10%	1.1	7.7	140	7.5	76.6
	25%	5.3	8.3	188	8.0	90.7
Median	50%	8.7	9.4	226	8.2	98.4
	75%	15.2	10.6	253	8.5	108
	90%	18.7	11.8	273	8.8	119
	95%	20.0	12.5	298	8.9	133

Water Quality Trends

Water quality trends during 1994 – 2009 were evaluated using a graphical model, LOWESS (Cleveland 1979, 1981; Cleveland and Devlin (1988). LOWESS, also known as locally weighted regression analysis or locally weighted scatterplot smoothing, is a modeling method based on linear and nonlinear least-squares regression. LOWESS combines much of the simplicity of linear least-squares regression with the flexibility of nonlinear regression. It does this by fitting simple models to localized subsets of the data to derive a function that describes the deterministic part of variation in the data, point by point. One of the primary attractions of this method is that a global function is not required to fit a specific LOWESS model to the data. A polynomial function is fit to the data using weighted least-squares regression, giving greater weight to data points near where the response is being estimated and lesser weight to data points further away. For the trends produced in this report, a "tension factor" of 0.5 was used. All statistical and graphical results were produced with SYSTAT v. 11 (SYSTAT Software, Inc. 2004).

Water temperature in the Pecos River (Sites A and C) increased from 1994 through 2002; however, temperature has decreased since 2003 (Fig. 9). Water temperature in Glorieta Creek also has shown a downward trend since 2003. Median temperature in Glorieta Creek (Table 1; 12.9 ^{o}C) was higher than observed in the Pecos River where median temperature was slightly higher at Site C (8.7 ^{o}C) than at Site A (8.4 ^{o}C), but did not differ statistically.

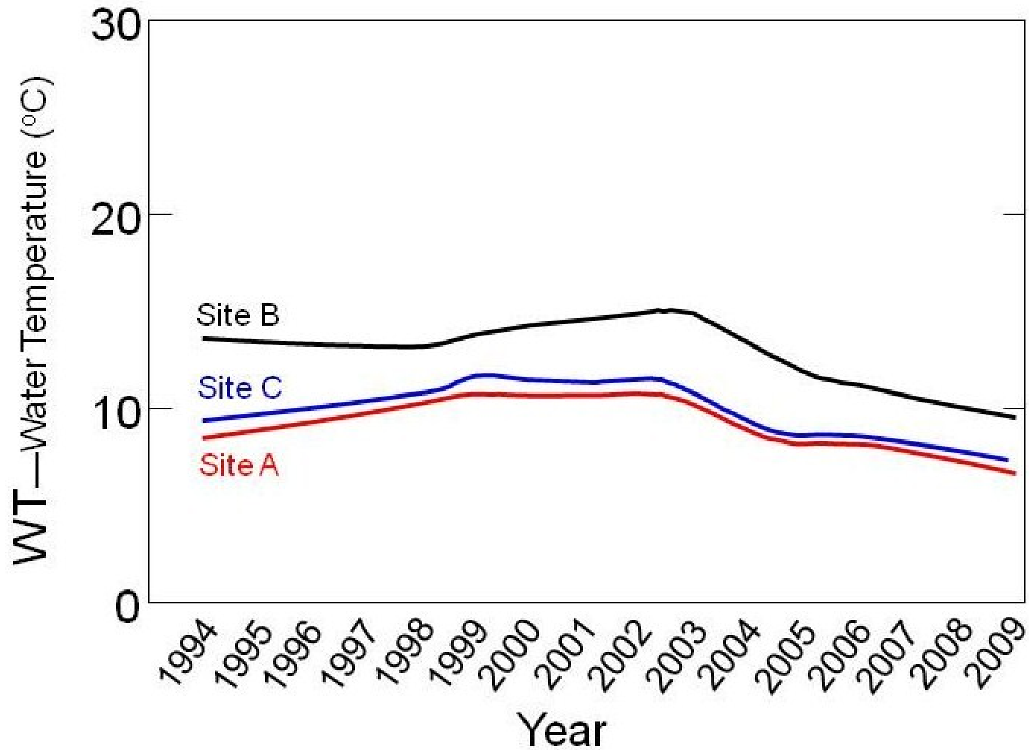

Figure 9. Water temperature trends in the Pecos River and Glorieta Creek during 1994 – 2009.

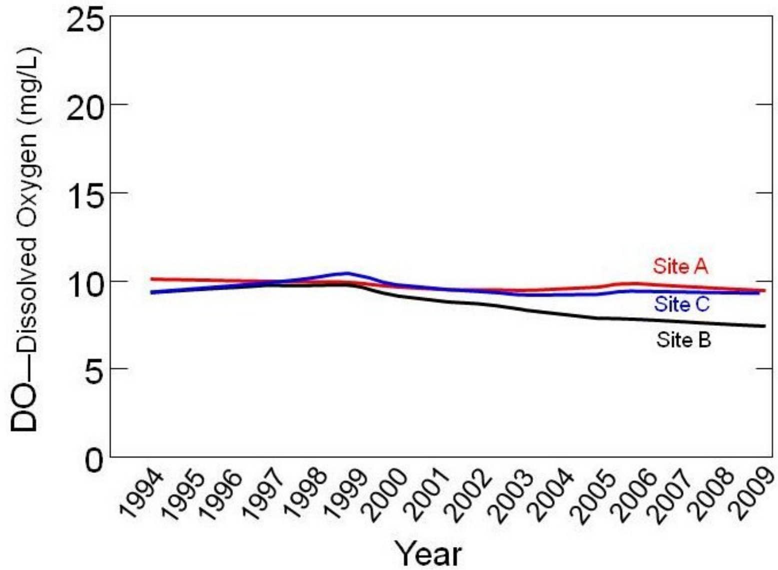

Figure 10. Dissolved oxygen trends in the Pecos River and Glorieta Creek during 1994 – 2009.

Dissolved oxygen concentrations have remained relatively uniform in the Pecos River during 1994 – 2009, whereas DO in Glorieta Creek has decreased since 1999 (Fig. 10). Median DO at the Pecos River sites was larger than observed in Glorieta Creek (Table 1). Oxygen saturation at all sites has decreased since the late 1990s, particularly in Glorieta Creek (Fig. 11), possibly in association with low streamflow conditions (Fig. 4). Apart from the unexpectedly low DO concentrations recorded during 2003 – 04 (removed from the revised, trends data set), DO concentrations were less than the New Mexico water quality criterion of 6 mg/L in about 1.3 percent of measurements in the Pecos River and about 9.4 percent of measurements in Glorieta Creek.

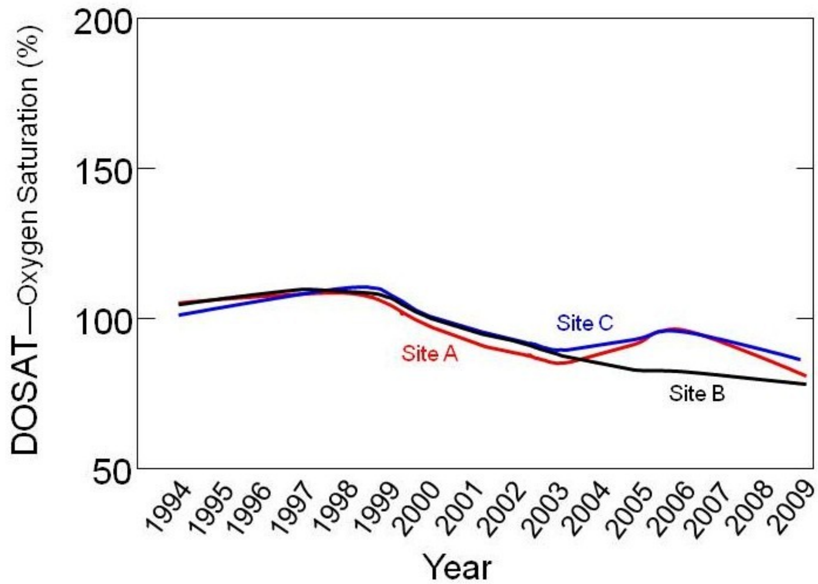

Figure 11. Oxygen saturation trends in the Pecos River and Glorieta Creek during 1994 - 2009.

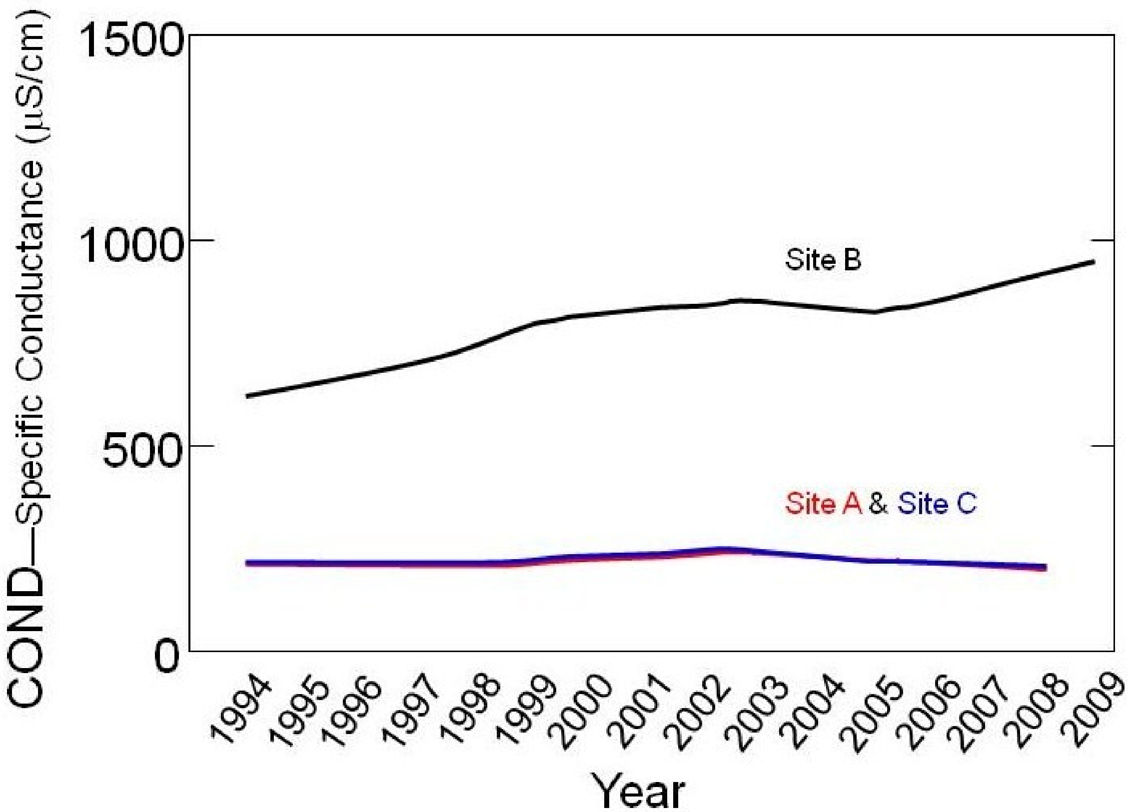

Figure 12. Specific conductance trends in the Pecos River and Glorieta Creek during 1994 - 2009.

Specific conductance values also have been relatively uniform in the Pecos River during the period of record; however, COND values in Glorieta Creek (Site B) have increased appreciably during the past 15 years (Fig. 12). Median COND values in Glorieta Creek (755 µS/cm) were more than three times the median values observed in the Pecos River (Table 1), and nearly 98 percent of COND measurements in Glorieta Creek exceeded the New Mexico water quality standard of 300 µS/cm. By contrast, less than five percent of measurements in the Pecos River (3.7 percent at Site A and 4.9 percent at Site C) exceeded the water quality standard.

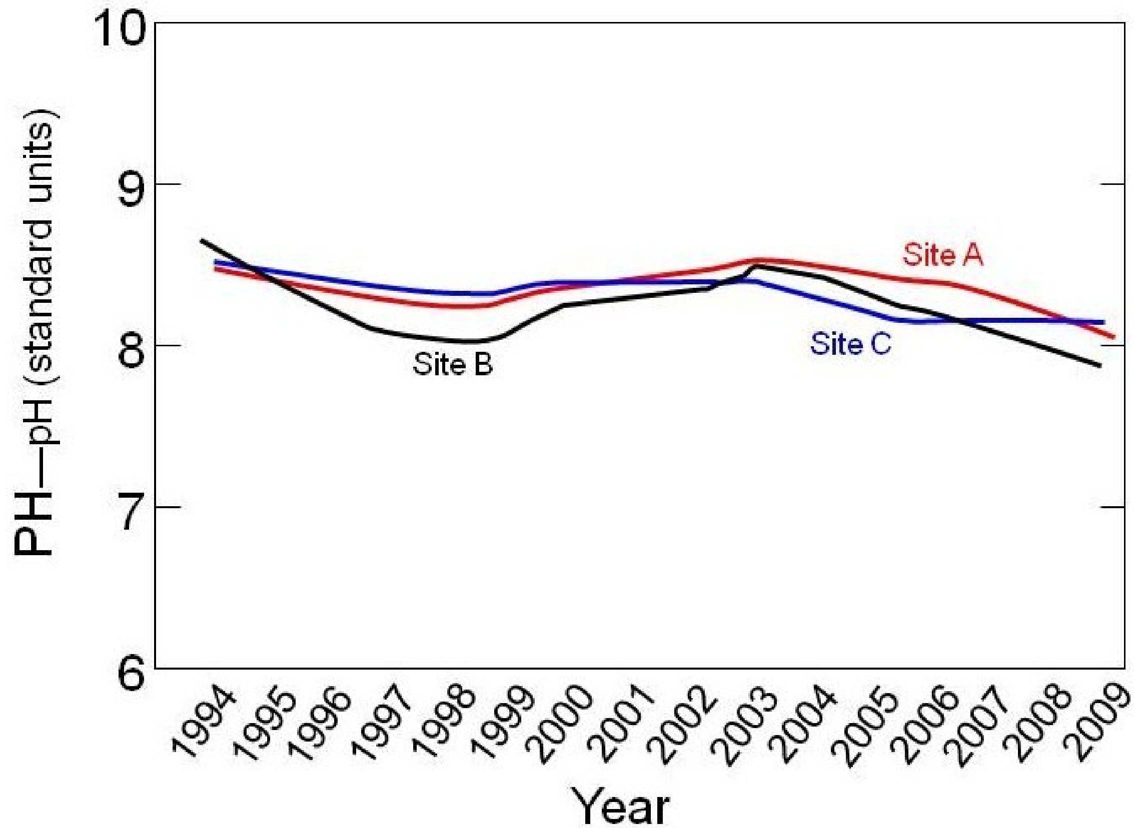

Figure 13. pH trends in the Pecos River and Glorieta Creek during 1994 – 2009.

Although pH values have varied during 1994 – 2009, no significant long-term trends were noted during the period of record (Fig. 13). Median pH values were similar among sites, ranging from 8.1 at Site B to 8.3 at Site A (Table 1). Exclusive of unexpectedly high values (pH > 9) reported during 2001 – 04, pH values did not meet New Mexico water quality standards (6.6 < pH < 8.8) in about 11 percent of measurements at Site A, four percent of measurements at Site B, and nine percent of measurements at Site C. Results of the LOWESS model suggest that pH may have declined since 2004, particularly at Sites A and B (Fig. 13). Recent (2008 – 09) pH values appear to be lower (pH about 8 standard units) than those recorded near the beginning of the monitoring period (pH around 8.5 standard units; Fig. 13).

Considerations for Improving Water Quality Monitoring

Water quality monitoring of temperature, dissolved oxygen, specific conductance, pH, and fecal-indicator bacteria is a key component of the National Park Service's Vital Sign Program in the Southern Plaines Network (Perkins et al. 2005; 2006). Oakley et al. (2003) provide general guidelines for long-term monitoring protocols that include sections describing background and objectives; sampling design; field methods; data handling, analysis, and reporting; personnel requirements and training; and operational requirements. Written quality assurance and quality control plans are a fundamental component of water quality monitoring. Quality assurance plans include consideration of manufacturer's operating manual(s) for water quality meters and probes, protocols for collecting fecal-indicator bacteria (*Escherichia coli*) samples, proper calibration of water quality meters, and training for inexperienced personnel. A quality assurance plan also considers the monitoring design and objectives. Because dissolved oxygen and pH are known to vary during daylight hours, particularly in productive streams stimulated by nutrient enrichment, the timing of field measurements should be standardized. A log book should be maintained with each water quality meter, and information concerning battery voltage (if reported) and date of last replacement or charge, calibration and repair information, the name of the investigator, date, and field remarks. Protocols for field measurements of temperature, dissolved oxygen, specific conductance, pH, turbidity, and other water quality properties are presented by Wilde (variously dated), available on-line at:
http://water.usgs.gov/owq/FieldManual/Chapter6/Ch6_contents.html.

Reference standard buffer solutions for pH and specific conductance are available from major laboratory supply companies. Two standards are recommended for pH measurements in the upper Pecos River basin, a buffer solution of pH 7.0 (blue) and pH 10.0 (yellow). Measurements of pH that are inconsistent with New Mexico water quality standards (pH less than 6.6 or more than 8.8) should be verified with a re-calibrated meter and (or) by a colleague making an independent measurement. Protocols for calibration, measurement, maintenance, and troubleshooting pH meters are presented by Ritz and Collins (2008). Similarly, two specific-conductance (conductivity) standards are recommended, a solution with a conductivity value near the New Mexico water quality criterion (300 μS/cm) and another solution with a value near the 90th percentile of the Glorieta Creek data (about 1,000 μS/cm; refer to Table 1). The standard method for reporting specific conductance is in reference to a specific temperature (25 ^{o}C). The observer should consult the manufacturer's manual to determine whether this correction is applied to the meter reading, particularly if the measurement is being made at a different temperature. Correction factors for converting readings from conductivity meters without temperature compensation are given by Radtke et al. (2005).

Dissolved oxygen meters and probes should be calibrated in accordance with manufacturer's instructions (e.g. in a water vapor saturated environment at a known temperature and atmospheric pressure). Protocols for calibration, measurement, maintenance, and troubleshooting dissolved-oxygen meters are presented by Lewis

(2006). Values less than the New Mexico water quality criterion (6 mg/L) should be verified with a re-calibrated meter and (or) by a colleague making an independent measurement. Unexpectedly high values (more than 12 mg/L or 120 percent oxygen saturation) also should be verified in a similar manner. A table listing the solubility of oxygen in water at various temperatures and atmospheric pressures is presented by Lewis (2006).

Quality control plans are designed to evaluate the accuracy and precision of water quality measurements. Repeated measures and independent colleague measurements are examples of quality control practices. Precision of water quality measurements can be estimated by obtaining three consecutive readings and calculating the coefficient of variation (relative standard deviation) by dividing the standard deviation by the mean of the three readings, then multiplying by 100 to express results as a percentage. Water quality data should be entered into a digital data base as soon as practical following field activities. Newly acquired data should be evaluated with reference to historical data ranges to identify potential errors or outliers in sufficient time to repeat field measurements, if necessary. Consistent, verifiable violations of water quality standards or criteria should be reported and discussed with New Mexico Department of Environment personnel.

Potential stream eutrophication issues in Glorieta Creek, and possibly in the Pecos River, were suggested by observations of frequent high percentages of oxygen saturation during 1994-99, as well as by comments made concerning excessive growths of filamentous algae during the same time period (NPS 1995). Collection and analysis of samples for nutrient concentrations, benthic algal biomass and species dominance, and macroinvertebrate community structure should be considered to evaluate nutrient and organic enrichment in streams within the boundary of the NHP. Continuous, hourly monitoring of dissolved oxygen and pH can provide estimates of stream metabolism, for example: rates of oxygen production by algae and (or) macrophytes (photosynthesis) and rates of oxygen demand by stream microorganisms (respiration).

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