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Water Quality Trends in the Entiat River Watershed: 2007–2010

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Abstract

A large, multiagency effort is underway in the interior Columbia River basin (ICRB) to restore salmon, trout, and char listed as threatened or endangered under the 1973 federal Endangered Species Act. Water quantity and quality are widely recognized as important components of habitat for these depleted salmonid populations. There is also broad concern about maintaining a high-quality water supply for other societal and ecosystem uses. A particularly active salmonid habitat restoration program is being conducted in the Entiat River, which drains a portion of the eastern slope of the Cascade Mountains in central Washington state. There, routine monitoring by the Washington Department of Ecology identifies pH and water temperature as water quality parameters of concern. In response, the U.S. Forest Service, Pacific Northwest Research Station is testing a more intensive approach to water quality monitoring that uses multiparameter data-logging instruments at four locations to measure fundamental water quality parameters (pH, water temperature, dissolved oxygen, and specific conductivity). This report presents results from the first 4 years of the study and discusses variation in water quality parameters with season, river discharge, and location. We demonstrate that unattended data-logging instruments effectively provide high-resolution data, which facilitate identification of forcing mechanisms such as direct solar radiation, air temperature, and river discharge. Results complement ongoing, broad-scale salmon recovery monitoring by quantifying concurrent changes in water quality. Although exploratory in nature, this study can inform future, more intensive monitoring programs.

Keywords: Water quality monitoring, salmon restoration, Columbia River basin, Entiat River.

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Introduction

An adequate supply of high-quality water is essential for the success of an ambitious, ongoing program to restore depleted salmonid populations in the largely semiarid, interior Columbia River basin (ICRB). This restoration is a cooperative effort among a number of governmental agencies, tribes, communities, and nongovernmental organizations (UCSRB 2012). The Bonneville Power Administration (BPA) is a primary sponsor of ICRB restoration efforts and is the primary funder of the National Oceanic and Atmospheric Administration (NOAA-Fisheries), Integrated Status and Effectiveness Monitoring Program (ISEMP) (BPA 2012). The ISEMP leads development of a regionwide program to assess the status of anadromous salmonid populations and their tributary habitat and to monitor effectiveness of restoration efforts (NOAA-Fisheries 2012).

Many of the entities involved in aquatic habitat restoration are also concerned with maintenance of a high-quality water supply for domestic, agricultural, industrial, recreational, and ecosystem uses. Within this context, the U.S. Forest Service, Pacific Northwest Research Station, in partnership with ISEMP, is testing an approach to status and trend monitoring of relevant water quality parameters (pH, water temperature, dissolved oxygen, and specific conductivity) in the Entiat River watershed. The Entiat is a Columbia River tributary in central Washington state (fig. 1). A particularly active program of habitat restoration is underway in the Entiat, where salmonid populations have been severely depleted (CCCD 2004). The watershed currently provides critical habitat for three salmonid populations listed under the 1973 federal Endangered Species Act (ESA), including spring Chinook salmon (*Oncorhynchus tshawytscha*) (endangered), summer steelhead (*O. mykiss*) (endangered), and bull trout (*Salvelinus confluentus*) (threatened) (CCCD 2004; UCSRB 2007, 2012).

As part of a coordinated federal and state effort to monitor compliance with the federal Clean Water Act of 1977, point measurements of water quality are taken monthly by the Washington State Department of Ecology (WDOE) near the Entiat gage, 2.5 river kilometers (RK) upstream from the river mouth (RK 2.5, fig. 1) (WDOE 2012). In the 2008 WDOE, Water Quality Assessment 305(b) Report and 303(d) List, occasional excursions of the state water quality standard for pH are documented for the period 2004 through 2006. As a result of these excursions, the lower Entiat River in the vicinity of the Entiat gage is listed as a “category 5” (impaired) water body for pH (WDOE 2008).

In addition to pH, the Entiat River, in the vicinity of the Entiat gage, is also listed in the 2008 WDOE Water Quality Assessment as a “category 4B” impaired water body for water temperature. A category 4B listing recognizes a water quality

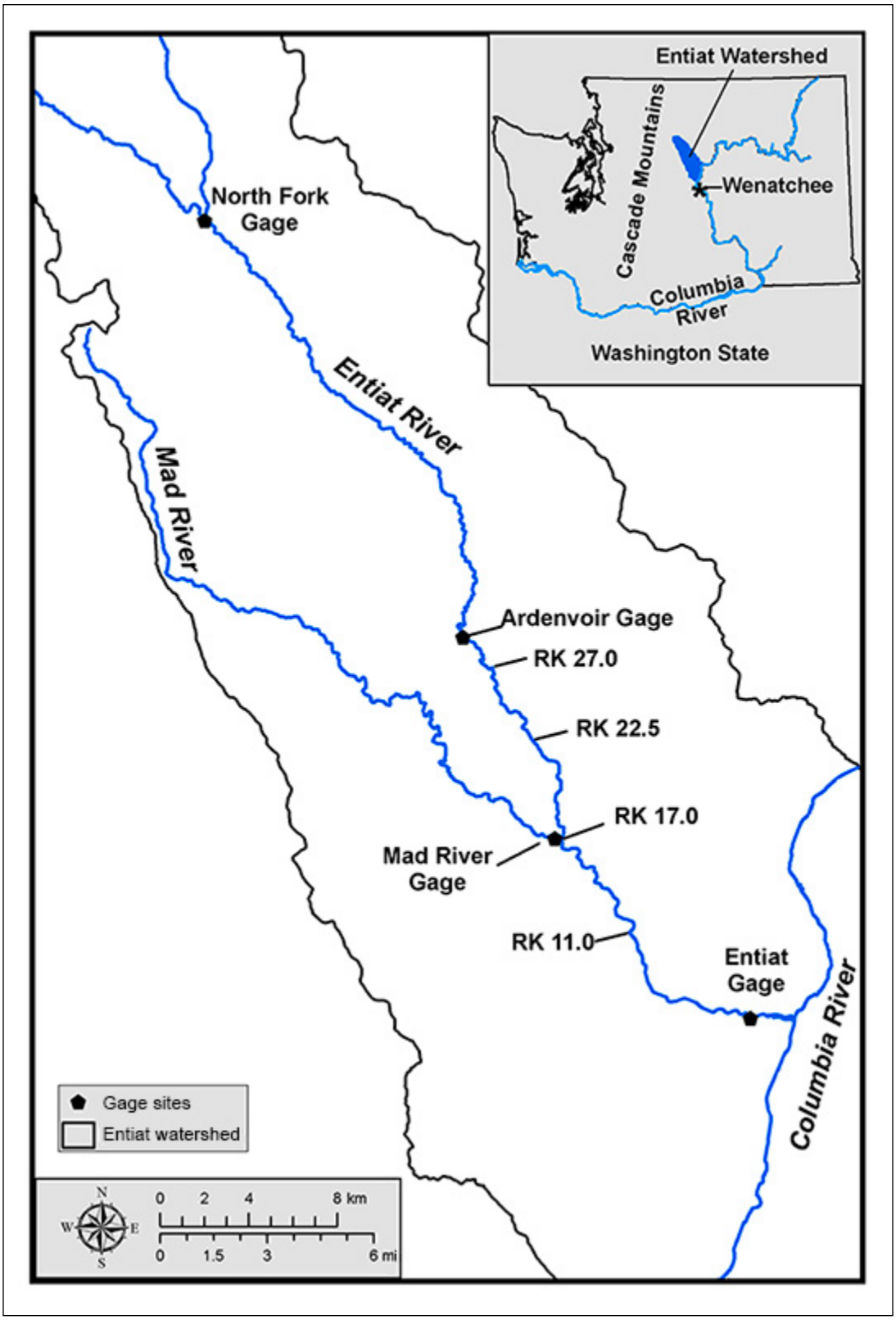

Figure 1—The Entiat River watershed. RK = river kilometer.

impairment that is being addressed by a pollution control program (WDOE 2008). During most summers, WDOE measures water temperature continuously at this station (WDOE 2012). A program of distributed water temperature monitoring is also being conducted in the Entiat and Mad Rivers by the U.S. Forest Service, Entiat Ranger District. Details of the history of water quality measurement in the Entiat watershed are presented in the Entiat Water Resource Inventory Area (WRIA) 46 Management Plan (CCCD 2004).

The focus on salmonid restoration and concern over Clean Water Act listings make water quality a matter of particular interest to the Entiat Watershed Planning Unit (EWPU), tribes, agencies, and other interested parties (CCCD 2004; NOAA-Fisheries 2012; WDOE 2008, 2012). The study reported herein is largely a response to discussions among EWPU members in 2005 and 2006 regarding the need for additional information on river pH in the watershed. Primary objectives include defining the spatial and temporal extent of high pH conditions and identifying sections of river that may contribute high pH water. The scope is broad scale and exploratory in nature, although findings may lead to more focused and detailed investigations. Results for the years 2007 through 2008 were reported in Bookter et al. (2009). The present report includes results for the years 2007 through 2010.

Measured Water Quality Parameters

pH—

The effective concentration of dissolved hydrogen ions [H+] is expressed as the logarithmic unit "pH," where pH = -log [H+]. The pH scale ranges from 0 (most acidic) to 14 (most basic). Acidic solutions have a pH less than 7.0, and basic solutions have a pH greater than 7.0. Most chemical and biochemical processes are affected by pH, and excessively high or low values can be directly detrimental to biota. Magnitude of pH affects the solubility and biological availability of nutrients, such as nitrogen, phosphorus, and other components of a river's dissolved load. A pH between 6 and 9 is generally considered an ecologically acceptable range for freshwater aquatic organisms (Hem 1985, Welch et al. 1998). The WDOE specifies a pH in the range 6.5 to 8.5 as its acceptable criterion for aquatic life in fresh water, with additional limits on human-caused variation (WDOE 2008).

Water temperature—

Water temperature is an important component of aquatic habitat. It affects chemical and biological processes, productivity, behavior, life history, and interspecies interactions. Temperature affects water chemistry by altering the rate of chemical reactions and affecting equilibria such as dissolved oxygen concentration (Allan

1995, Welch et al. 1998). The WDOE employs the 7-day average of the daily maximum temperatures as its aquatic life water temperature parameter. The average maximum temperature criterion at the Entiat gage is 17.5 °C (WDOE 2008).

Dissolved oxygen—

Dissolved oxygen (DO) is supplied to stream water by photosynthesis during daylight hours and is taken into solution from the atmosphere. It is consumed by respiration by aquatic organisms and by organic matter decomposition and other chemical processes. Dissolved oxygen concentration can also be reduced by influxes of deoxygenated ground water (Allan 1995, Welch et al. 1998). Warmer water temperatures reduce oxygen solubility and cause increased metabolic activity (growth, productivity, and respiration) and decomposition. This and the diurnal nature of photosynthesis interact to produce diurnal variation in DO concentration, which decreases at night, potentially to levels that are detrimental to certain fish species (Allan 1995, Welch et al. 1998, Williamson et al. 1997).

The U.S. Environmental Protection Agency (USEPA 1986) finds that, for the purpose of recommending criteria for salmonid waters, average DO concentrations greater than 11 mg/L are associated with no production impairment, average concentrations between 9 and 11 mg/L are associated with slight production impairment, and average concentrations between 7 and 8 mg/L are associated with severe production impairment. Hicks (2002) reviews the literature relevant to DO criteria for surface water. Brown and Hallock (2009) further discuss WDOE criteria development for DO. WDOE sets the minimum DO criterion for aquatic life in the Entiat watershed at 9.5 mg/L (Hallock 2011).

Specific conductivity—

Conductivity, a measure of the ability of a material to carry an electrical current, is the inverse of resistance, and is therefore commonly measured in units of 1/ohms called mhos or Siemens (S). Conductivity is a function of temperature. Specific conductivity (SC) is the conductivity of a solution standardized to 25 ºC. Stream water conductivity increases with higher concentrations of dissolved minerals and salts, implying increased contact with reactive bedrock or other surface or subsurface materials. It is a useful indicator of change in dissolved constituents, including soluble reactive phosphorus and nitrate nitrogen, which are important nutrients in aquatic ecosystems. Specific conductivities less than thousands of microSiemens per centimeter (µS/cm) are generally not considered harmful to aquatic biota. Specific conductivities less than 100 µS/cm are common in precipitation, and values found in potable water may be as high as 1,500 µS/cm (Hem 1985, McCutcheon et al. 1993, Welch et al. 1998). The WDOE does not have aquatic life criteria for conductivity (WDOE 2008).

Methods

Study Area

The Entiat River is located on the eastern slope of the central Cascade Mountains in the state of Washington, 55 km (34 mi) northwest of Wenatchee. It is 85 km (53 mi) long, and its drainage area is approximately 1100 km^2 (425 mi^2) (fig. 1). Wildfire, flooding, mass soil and debris movement, and land use were the primary historical disturbance processes. Land use included grazing, agriculture, timber harvesting, transport of logs within the river channel, dams for log storage ponds and hydropower generation, roading, flood plain and river channel modification projects and structures, residential development, and recreation (CCCD 2004).

Site Selection

Water quality measurement sites were located within the existing network of river gages. Specific sites were selected to maximize spatial distribution along the Entiat River and include the Mad River, the Entiat's primary tributary. This distribution was consistent with the U.S. Geological Survey (USGS), National Water Quality Assessment Program approach of making intensive measurements at a few points that integrate critical drainage areas rather than randomly selecting measurement sites (USGS 2012).

Instrumentation

In spring 2007, we deployed one In-Situ, Troll 9500[2] multiparameter, data-logging, water-quality instrument at each of four gaging stations (table 1, fig. 1). Instruments were secured in the channel inside protective 10-cm-diameter pipes. The lower 60 cm of each pipe was perforated to ensure ample water circulation around the instrument sensors. Instruments were equipped with a separate sensor for each measured water-quality parameter and programmed to record data at 15-minute intervals. Instruments were removed during winter (typically December through February) to avoid damage from river ice and redeployed the following spring when ice conditions allowed. All sensors used an EPA-approved methodology (table 2). Dissolved oxygen sensors utilized an integrated barometer with vented cable, allowing the sensor to incorporate real-time barometric pressure into calibrations and calculations of percentage of DO saturation. Following 3 years of data collection, indicating that water quality was unlikely to be a concern at the North Fork gage, measurements there were discontinued as a cost-saving measure.

[2] The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

Table 1—Location of water quality instruments in the Entiat River watershed

River gage (short name)	Gaging agency	Gage ID	River kilometer	Coordinates (lat., long.)[a]
Entiat River near Entiat (“Entiat”)	USGS[b]	12452990	2.5	47° 39' 48", 120° 14' 58"
Mad River at Ardenvoir (“Mad”)	USGS	12452800	0.64	47° 44' 13", 120° 22' 03"
Entiat River near Ardenvoir (“Ardenvoir”)	USGS	12452890	29	47° 49' 07", 120° 25' 19"
Entiat River at North Fork Campground (“North Fork”)	WDOE[c]/CCD[d]	46A170	53	47° 59' 15", 120° 34' 47"

[a] Shown in degrees, minutes, and seconds.
[b] U.S. Geological Survey.
[c] Washington State Department of Ecology.
[d] Cascadia Conservation District.

Table 2—Sensor methodology and manufacturer’s stated accuracy

Variable	Methodology	Accuracy
pH	Standard methods 4500-H+, EPA 150.2	0.1 pH units
Temperature	EPA 170.1	0.1 °C
Dissolved oxygen	In-Situ Method 1002-8-2009, EPA, ATP Case No. N05-0014, 40 CFR, Part 136.3.	0.2 mg/L
Specific conductivity	Standard methods 2510, EPA 120.1	2 µS/cm

Quality Assurance/Quality Control (QA/QC)

Reference instrument procedures—

Following initial installation and reinstallation each spring, instrument function and calibration were checked at least weekly for 2 to 4 weeks. After this initial period, instruments were inspected and data downloaded at 2-week intervals. During each site visit, a fifth multiparameter instrument, calibrated immediately before use and checked immediately afterward, was employed as a portable, hand-held reference for checking data from field instruments. Prior to recording measurements, the reference instrument was allowed to equilibrate to the stream water environment for a period of 5 to 20 minutes depending upon observed measurement stability. Field and reference instrument measurements were then recorded and compared. Field-deployed sensors were recalibrated if deviation from the reference sensor exceeded a predefined standard (table 3) or under the following conditions:

Table 3—Maximum acceptable deviations from reference sensors

Variable	Threshold deviation
pH	0.2 pH units
Temperature	0.5 °C
Dissolved oxygen	1 mg/L
Conductivity	5 µS/cm

1. Repeated, but within threshold, deviation from the reference. Typically, this occurred with each sensor one or fewer times per year.
2. Disturbance to the instrument, e.g., excessive sedimentation, biofouling, or mechanical disturbance. Sediment accumulation, commonly accompanied by biofouling, occurred each high-flow season. Following cleaning, the need for recalibration was determined by performance relative to the reference sensor. Mechanical disturbance was rare.
3. Calibration performance outside the manufacturer's standards. This commonly occurred one or fewer times per year with each sensor, and was corrected by thorough cleaning or reconditioning according to the manufacturer's guidelines.

Calibration—
Instruments were designed for field calibration at ambient, onsite temperature, elevation, and barometric pressure, thereby minimizing interruption of data collection and improving accuracy compared to offsite calibration. All calibration and testing employed the manufacturer's software and met or exceeded the manufacturer's specifications and guidelines (In-Situ 2008) as follows:

pH—A two-point pH calibration was done using buffer solutions of pH 7 and 10, thereby spanning the range of pH measured in the Entiat and Mad Rivers. The reference instrument sensor was calibrated in the lab immediately before field checks, and a one-point, pH 7 check was done immediately after returning. If this reading deviated from the standard by more than 0.2 pH units (the allowable deviation), then the reference measurements for that day were not used. If the pH calibration parameters (slope, offset, and response) were outside the manufacturer's recommended range, then the recommended sensor maintenance or replacement was performed (In-Situ 2008).

Temperature—Temperature sensors were not designed for user calibration. Therefore they were replaced if deviations from the reference sensor were not within established limits.

Dissolved oxygen—Two-point DO calibrations were done at 100 and 0 percent saturation. One-hundred percent saturation was obtained by bubbling air through deionized water. A solution of sodium sulfite provided 0 percent saturation. Following calibration, the reference sensor was checked in a 100 percent oxygen-saturated solution immediately before and after each cycle of reference checks. If measurements deviated from the standard by more than 10 percent, then the reference DO sensor was recalibrated. If the end-of-the-day measurement was outside this limit, then the reference DO readings for that day were not used. Dissolved oxygen sensors provided extremely stable results. Differences between field and reference sensors exceeding 1.0 mg/L (the allowable deviation) rarely occurred more than once during the 9-month season.

Specific conductivity—A one-point SC calibration was done using a 147-µS/cm standard. The reference sensor was calibrated in the lab immediately before and after each field session. Direct measurements of the standard solution were taken before and after each calibration. If these deviated by more than 5 µS/cm from the standard, then the sensor was recalibrated. If the end-of-the-day measurement was outside this limit, then the reference conductivity readings for that day were not used. If the calibration constant fell outside specifications, then the recommended sensor maintenance or replacement was performed and the instrument recalibrated (In-Situ 2008).

Data Processing

All data were examined for outliers or extreme variability relative to surrounding data. These cases could occur as a result of ice effects, biofouling, or other factors. Data determined to be unreliable were considered missing and not included in analyses. However, data corrected for ordinary instrument drift, as determined through reference tests and field calibrations, were considered valid, first-quality data, following Carroll et al. (2006). All data, regardless of designations or adjustments, were recorded in the database along with notes regarding reference checks, calibrations, unreliable data, or other relevant issues. Temporal trends and the timing and longevity of water quality extremes were investigated by examining time series of data measured at 15-minute intervals along with longer term means or medians (pH). Spatial trends were interpreted by comparing results across the array of instrumented sites.

Reconnaissance Surveys

Increased spatial resolution was desired to better quantify the rate of change in water quality parameters between stations. An abrupt change could suggest a local

source of water quality degradation. Therefore, water quality data from established sites were supplemented with reconnaissance-level point measurements between the Entiat and Ardenvoir gages. This included the section of river where pH and temperature measurements occasionally exceeded state water quality standards. In August 2007, we began taking point measurements at 2-week intervals with the hand-held reference instrument described previously. Locations with safe access at 11.0, 17.0 (immediately upstream of the Mad River confluence), 22.5, and 27.0 RK were identified to achieve an approximately uniform distribution along the target section of river (fig. 1). For consistency, only uninterrupted surveys proceeding upstream were included in the analyses.

For each station in each survey, the parameter value, for example pH, at that station minus the parameter value at the next upstream station was taken as the change between stations. This change was divided by the distance between stations, giving a rate of change per kilometer of river. This value was assigned to the downstream station within each pair, and medians (pH) or means were calculated for the period of record. In general, pH, water temperature, and conductivity decreased in the upstream direction, making the change between stations positive. A similar point measurement survey was done once in the Mad River during September 2008 (Bookter et al. 2010).

Temporal change in parameter values introduced uncertainty into calculations of spatial change. For example, temperature tended to increase from morning through mid to late afternoon, causing real-time spatial differences to be underestimated as measurements proceeded upstream. For parameters that increased in the upstream direction, real-time spatial differences were overestimated. Effects of these errors on calculated rates of spatial change were estimated for all parameters at the Entiat and Ardenvoir gages where diurnal variation was known. The 2009 median diurnal change per unit time was applied to the median time and distance between measurements to arrive at an estimate of the error expressed in parameter units per kilometer.

Results

pH

For the years 2007 through 2010, median-daily pH remained below 8.5 at all sites. The highest daily medians occurred at either the Entiat or the Mad gage (fig. 2). The lowest pH values occurred during periods of high river discharge, principally during the spring snowmelt period (May through June). Maximum values of pH tended to occur during low discharge periods both before (March through April) and after (August through October) the spring peak flows (fig. 2, table 4a and 4b).

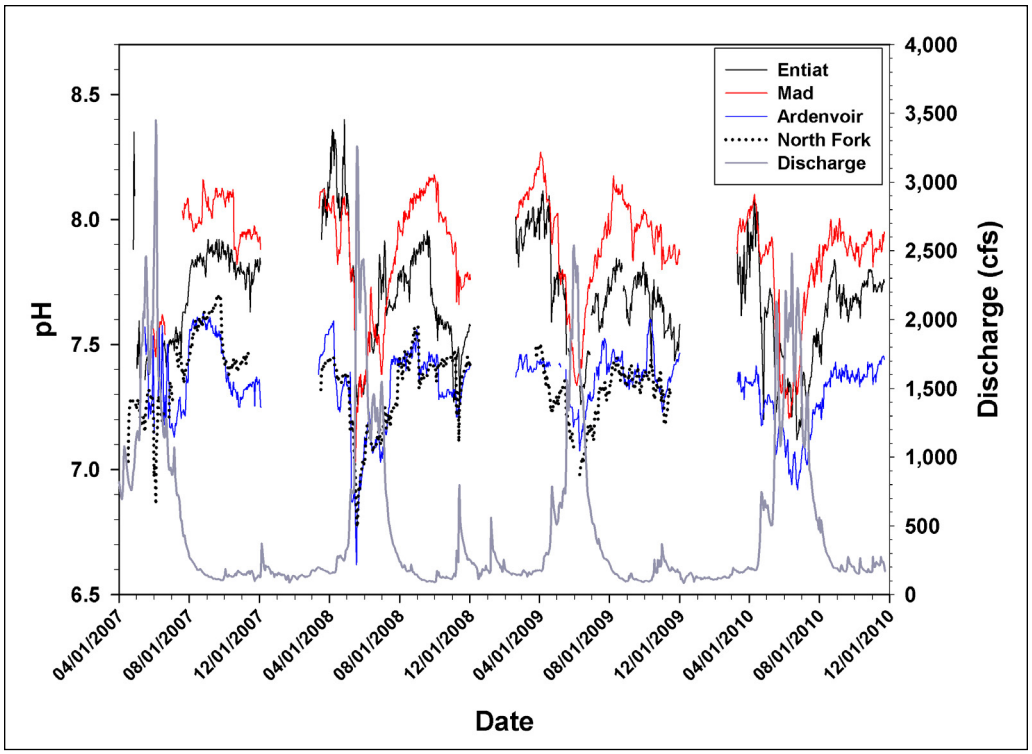

Figure 2—Median daily pH for all stations. Discharge data are from the Entiat gage.

At the Entiat and Mad gages, pH metrics were nearly always markedly higher than farther upstream at the Ardenvoir and North Fork gages. This was particularly true during periods of high pH. Variation between the two upstream gages was relatively small despite their 24-km separation (figs. 2, 3a through 3d, table 4a and 4b). Each year the highest maximum-daily pH occurred at the Entiat gage, where values commonly exceeded 8.5 during higher pH periods and reached 9.5 in rare cases. Daily-maxima remained below 8.8 at the Mad gage and below 7.9 at the Ardenvoir and North Fork gages. Daily-minima less than 7.0 were rare at all locations, reaching as low as 6.5 at the Ardenvoir gage (fig. 3a through 3d).

Each day, pH magnitude in the Entiat and Mad Rivers varied from a minimum in the early morning to a maximum in the early to mid-afternoon. Magnitude of diurnal change varied with location and season, and generally decreased in the upstream direction, following the same seasonal trends as pH magnitude (figs. 3a through 3d). Diurnal variation as large as 1.6 pH units occurred at the Entiat gage. Similar, although less extreme, variation occurred at the Mad gage. At both locations, daily maxima depart much farther from medians than do daily minima, indicating that maxima provide a poor characterization of central tendency (fig. 3a and 3b).

Table 4a—2007–2008 monthly means (or pH medians) of water quality parameters

	Entiat				Mad				Ardenvoir				North Fork			
Month	pH	Temp	DO	SC	pH	Temp	DO	SC	pH	Temp	DO	SC	pH	Temp	DO	SC
		°C	*mg/L*	*µS/cm*		*°C*	*mg/L*	*µS/cm*		*°C*	*mg/L*	*µS/cm*		*°C*	*mg/L*	*µS/cm*
May-07	7.42	7.77	12.34	52.32									7.27	4.38	11.63	32.86
Jun-07	7.47	10.06	11.59	41.19	7.57	9.19	10.98	50.34	7.31	8.54	10.90	30.57		5.77	11.27	31.57
Jul-07	7.58	15.46	10.29	52.81		15.39	9.50	87.16	7.23	12.75	10.12	36.13	7.41	9.14	10.31	33.08
Aug-07	7.82	16.89	9.89	90.28	8.05	14.62	9.64	111.3	7.58	14.30	9.56	47.45	7.57	10.14	10.02	41.13
Sep-07	7.87	14.12	9.93	113.1	8.09	11.58	10.32	122.8	7.54	12.00	10.02	55.06	7.66	7.97	10.20	46.88
Oct-07	7.84	8.01	11.51	110.5	8.04	6.16	11.60	122.1	7.32	6.50	11.18	53.82	7.42	3.77	11.55	47.30
Nov-07	7.80	3.48	12.72	108.4	7.95	2.36	12.60	128.6	7.34	2.45	12.29	53.80				
Apr-08	8.16	7.75	11.79	115.5	8.00	5.15	12.17	133.4	7.36	5.80	11.38	53.42	7.40	2.53	11.95	46.02
May-08	7.56	8.42	11.23	56.43	7.42	6.94	11.67	64.76	6.93	6.51	11.41	37.43	7.04	3.93	11.62	
Jun-08	7.50	9.67	11.18	38.99	7.51	8.49	11.25	46.77	7.12	7.92	11.10	32.79	7.12	5.72	11.46	32.11
Jul-08	7.72	15.29	9.76	52.01	7.76	14.20	9.77	76.54	7.34	12.60	9.86	38.00	7.23	9.02	10.58	34.40
Aug-08	7.80	17.30	9.05	81.74	8.03	14.79	9.65	106.0	7.47	14.61	9.25	47.30	7.48	10.22	10.18	40.52
Sep-08	7.86	13.84	9.94	111.4	8.14	11.04	10.53	118.3	7.43	11.82	9.68	54.98	7.41	8.00	10.70	46.80
Oct-08	7.58	8.15	11.15	110.9	8.02	6.17	11.73	121.7	7.33	6.59	10.97	54.90	7.44	4.06	11.61	47.22
Nov-08	7.48	4.15	12.28	76.68	7.77	3.14	12.58	92.08	7.33	3.16	12.00	45.60	7.40	1.96	11.99	41.17

DO = disolved oxygen.
SC = Specific conductivity.

Table 4b—2009–2010 Monthly means (or pH medians) of water quality parameters

	Entiat				Mad				Ardenvoir				North Fork			
Month	**pH**	**Temp**	**DO**	**SC**	**pH**	**Temp**	**DO**	**SC**	**pH**	**Temp**	**DO**	**SC**	**pH**	**Temp**	**DO**	**SC**
		°C	*mg/L*	*µS/cm*		*°C*	*mg/L*	*µS/cm*		*°C*	*mg/L*	*µS/cm*		*°C*	*mg/L*	*µS/cm*
Mar-09	7.99	4.66	12.67	114.28	8.12	2.32	13.02	132.00	7.41	3.39	11.90	55.70				
Apr-09	7.98	8.01	11.69	87.99	8.08	5.54	12.11	107.44	7.42	6.03	11.35	48.96	7.34	2.68	11.85	39.78
May-09	7.70	8.75	11.50	53.57	7.75	6.83	11.75	62.82	7.28	7.08	11.11	33.26	7.27	4.31	11.50	31.98
Jun-09	7.40	10.85	10.84	36.39	7.50	9.10	11.10	42.19	7.20	8.87	10.68	28.06	7.08	6.30	10.94	28.11
Jul-09	7.65	17.23	9.53	56.15	7.87	14.90	9.65	78.35	7.41	14.40	8.85	35.88	7.30	10.05	10.07	31.64
Aug-09	7.79	18.30	9.18	82.60	8.10	15.38	9.57	100.01	7.44	15.63	8.95	44.17	7.39	11.10	9.77	37.07
Sep-09	7.74	15.11	9.71	95.73	7.99	12.17	10.24	107.04	7.36	12.93	9.35	48.16	7.36	8.87	10.23	40.44
Oct-09	7.69	7.97	11.22	98.57	7.97	5.80	11.81	107.00	7.40	6.28	10.85	47.87	7.37	3.37	11.51	41.21
Nov-09	7.55	3.80	12.58	70.87	7.85	2.51	12.77	96.20	7.37	2.59	12.16	41.99				
Mar-10	7.81	6.80	12.16	111.54	7.98	4.23	12.38	127.36	7.35	4.85	11.38	51.96				
Apr-10	7.88	8.16	11.42	91.08	7.97	5.67	11.95	107.45	7.34	5.84	10.51	46.10				
May-10	7.48	8.29	11.45	50.59	7.68	6.49	11.76	61.13	7.17	6.33	10.68	34.68				
Jun-10	7.31	9.10	11.19	35.59	7.32	7.93	11.43	38.38	7.00	7.18	11.10	27.19				
Jul-10	7.39	13.50	10.11	40.45	7.75	13.30	10.03	63.69	7.14	10.77	9.93	29.47				
Aug-10	7.67	16.27	9.42	65.69	7.90	14.39	9.72	92.74	7.35	13.32	9.31	38.93				
Sep-10	7.68	13.95	9.91	82.13	7.91	11.41	10.43	99.33	7.37	11.48	9.60	44.55				
Oct-10	7.74	9.13	11.02	81.10	7.90	7.18	11.46	106.46	7.37	7.31	10.66	45.08				
Nov-10	7.74	5.04	12.16	68.47	7.88	3.55	12.44	93.43	7.42	3.55	11.68	41.78				

DO = disolved oxygen.
SC = Specific conductivity.

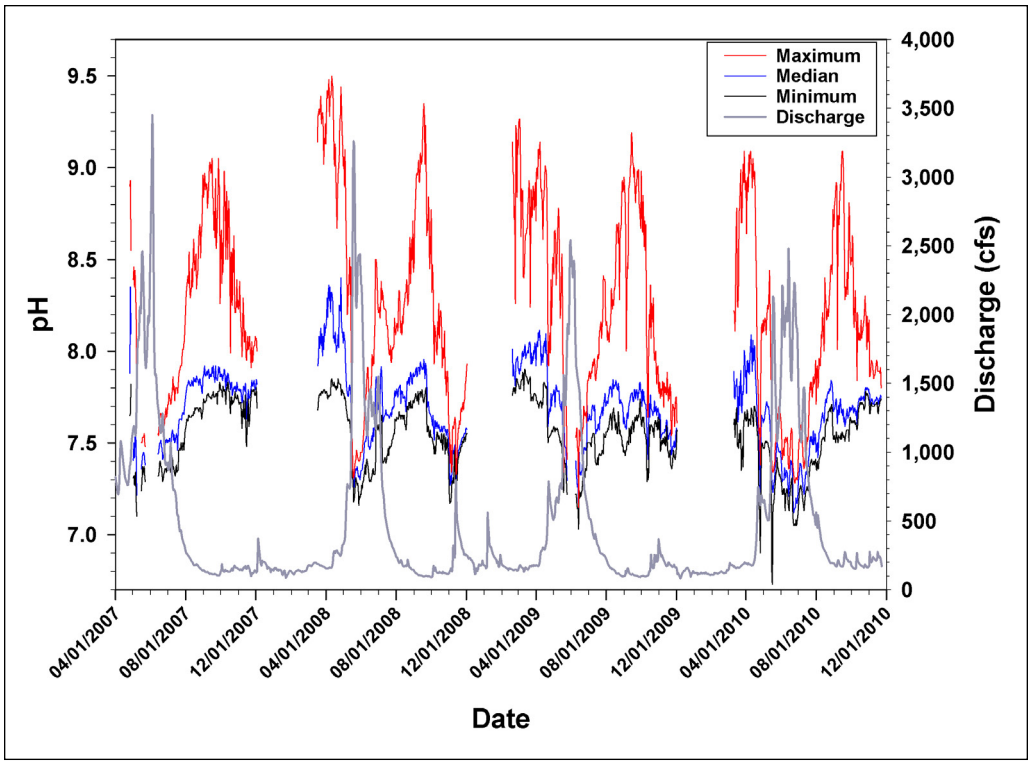

Figure 3a—Daily pH parameters and discharge at the Entiat gage.

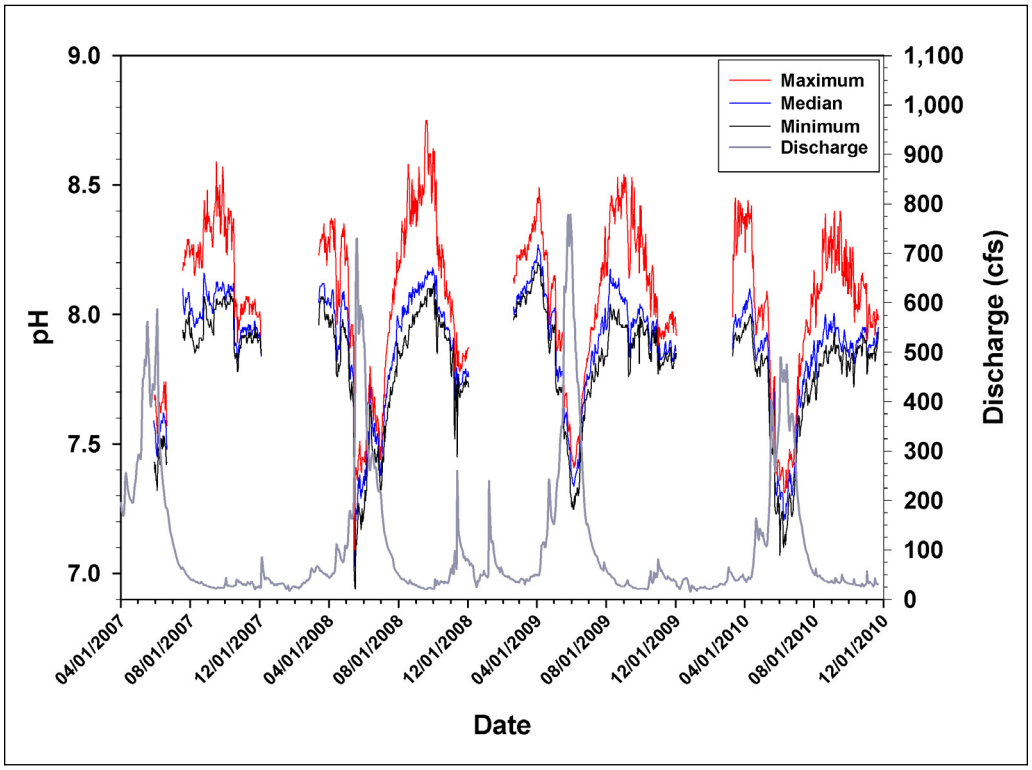

Figure 3b—Daily pH parameters and discharge at the Mad gage.

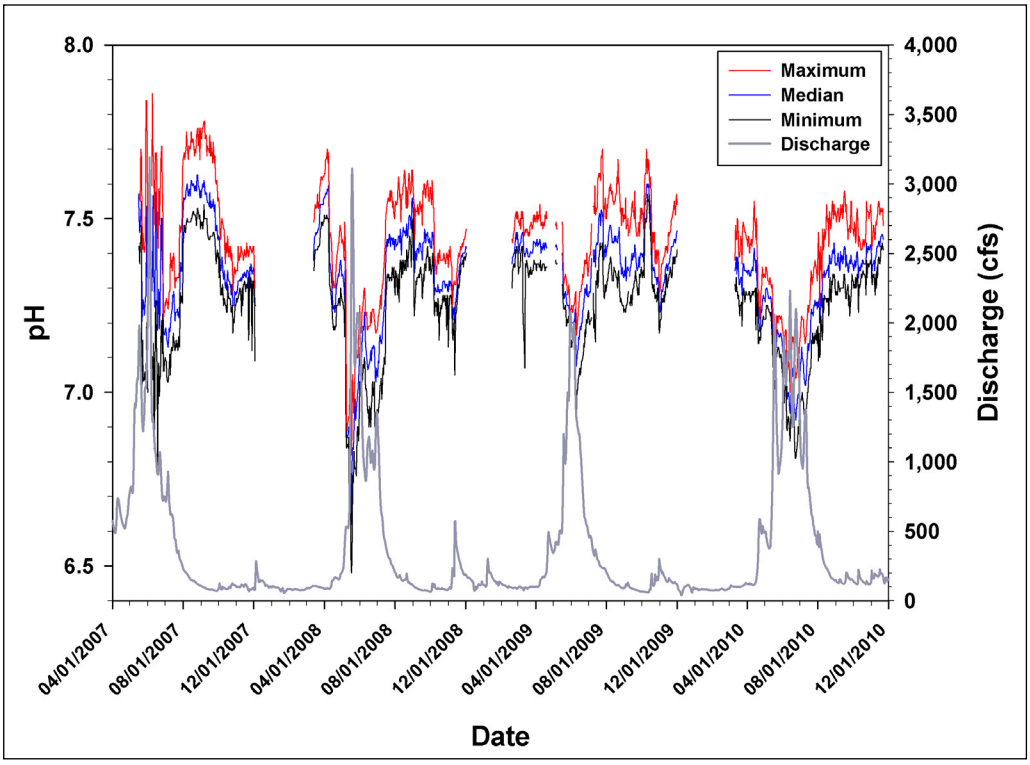

Figure 3c—Daily pH parameters and discharge at the Ardenvoir gage.

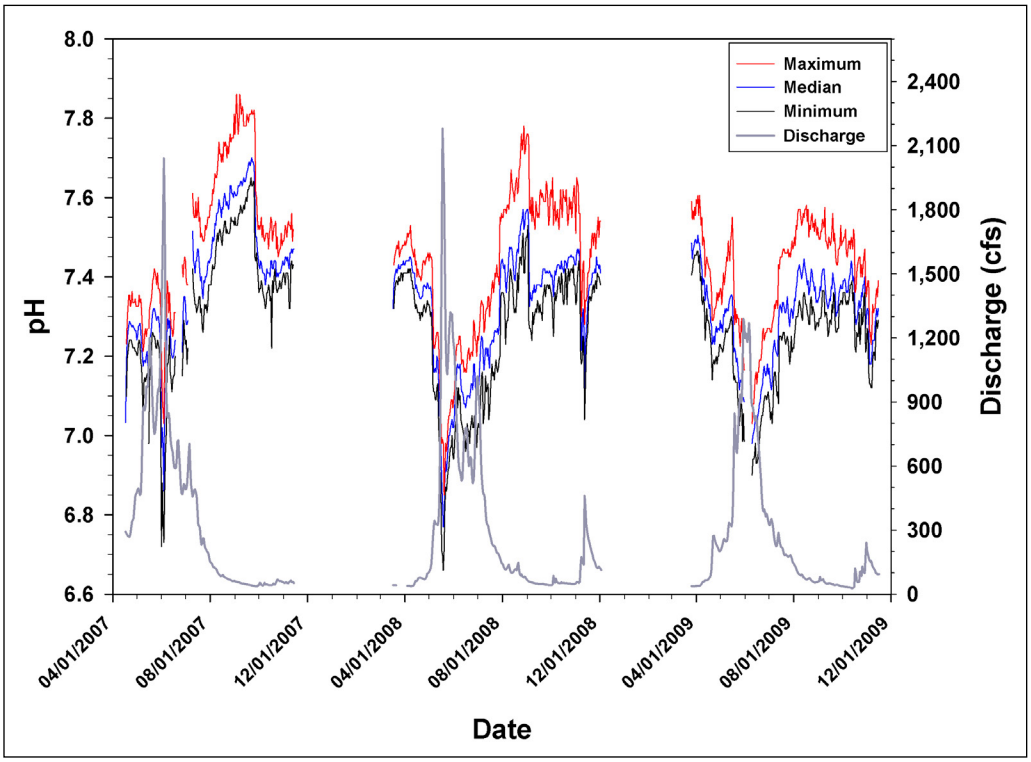

Figure 3d—Daily pH parameters and discharge at the North Fork gage.

Point measurements indicated that median rate of change in pH between the North Fork and Ardenvoir gages was negligible and only a small increase of 0.013 pH units/km occurred between the Ardenvoir and RK 27 sites (fig. 4). However, between RK 27 and the hatchery site, rate of pH increase varied from 0.02 to greater than 0.06 pH units/km. Rate of change shifted abruptly between the Hatchery site and the Entiat gage from 0.031 to -0.015 pH units/km (fig. 4). Estimated error in these rates at the Entiat and Ardenvoir gages, owing to diurnal change, was 0.004 and 0.002 pH units/km, respectively.

Water Temperature

At all stations, water temperature follows generally predictable seasonal trends, increasing steadily from near 0 °C at the beginning of each year's measurement season in the early spring. This temperature increase is slowed by the annual snowmelt-driven high flows, then resumes in early to late June as flows recede. Temperatures begin to decrease in late August or early September, and return to near 0 ºC by December (fig. 5). The highest mean-daily, maximum-daily, and

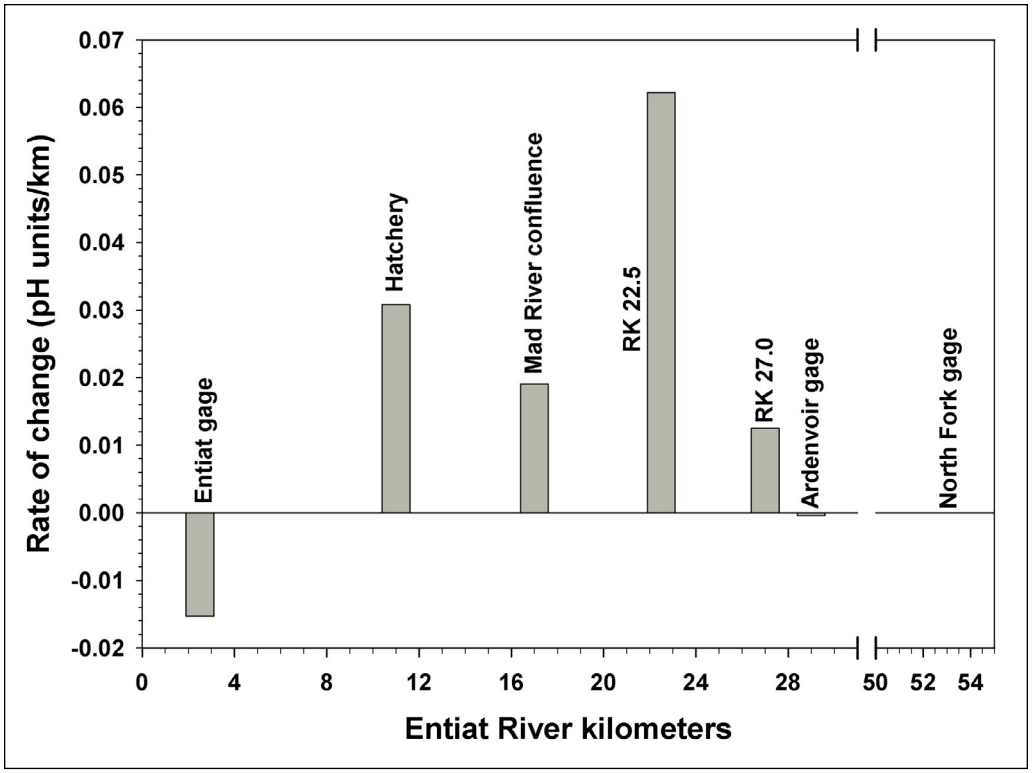

Figure 4—Median rate of spatial change in pH. The magnitude displayed is the pH at each station minus that at the closest upstream station. Thus, positive values indicate increasing pH in the downstream direction. The negative value for the Entiat station indicates decreasing pH moving downstream from the Hatchery station.

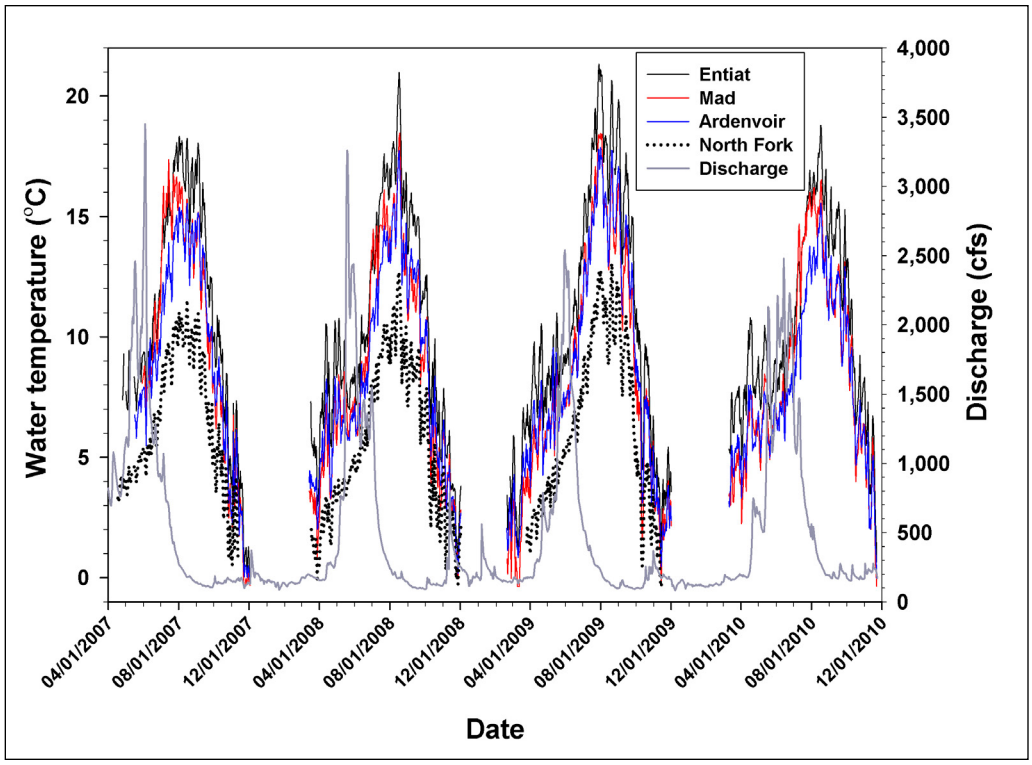

Figure 5—Mean daily water temperature for all stations. Discharge data are from the Entiat gage.

mean-monthly temperatures occur at the Entiat gage, commonly during early- to mid-August (figs. 6a through 6d, table 4a and 4b). At the Entiat gage, some maximum daily temperatures exceeded 21 ºC in all years, while in 2008 and 2009, some mean-daily temperatures reached or exceeded 21 ºC. Temperatures at the Mad gage were, in general, similar to those at the Ardenvoir gage, with mean-daily values not exceeding 19 ºC. Temperatures at the North Fork gage were consistently the coldest. Daily maxima remained below 16 ºC (fig. 5, 6a through 6d).

Water temperature increased, but at varying rates, along the Entiat River downstream from the North Fork gage. The highest estimated rates of increase occurred between the Ardenvoir gage and RK 22.5, reaching nearly 0.13 ºC/km. (fig. 7). Downstream from RK 22.5, the rate of temperature increase decreases sharply before increasing again to a moderate rate between the hatchery site and the Entiat gage (fig. 7). Error in these rates owing to diurnal variation is estimated to be 0.019 and 0.036 °C/km at the Entiat and Ardenvoir gages, respectively.

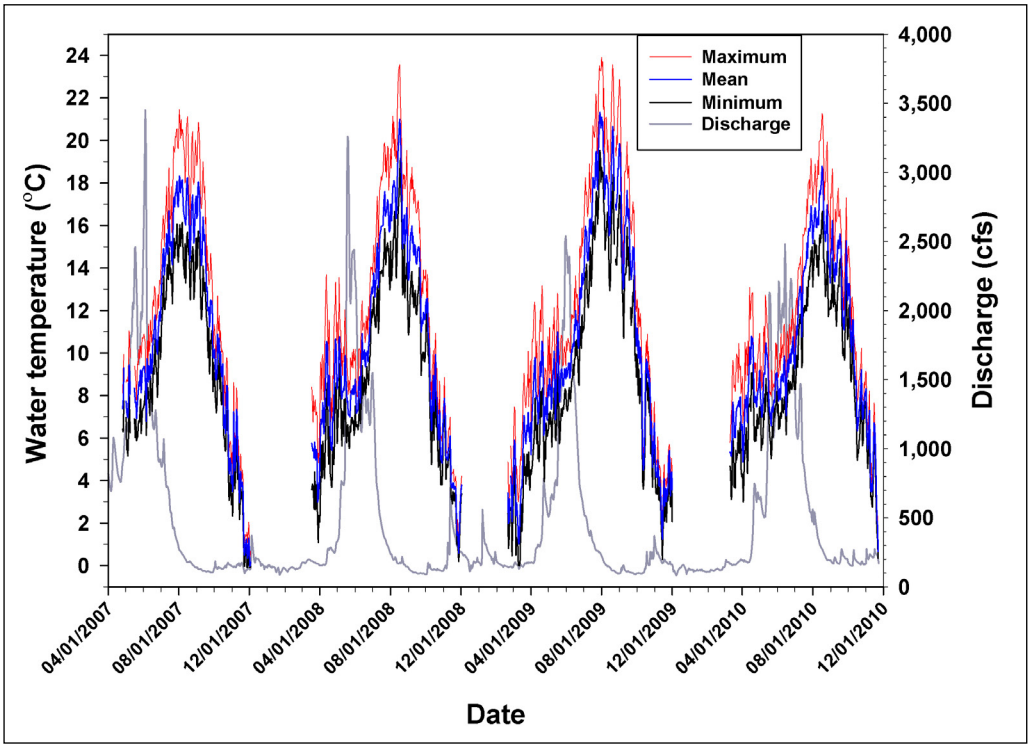

Figure 6a—Daily Water temperature parameters and discharge at the Entiat gage.

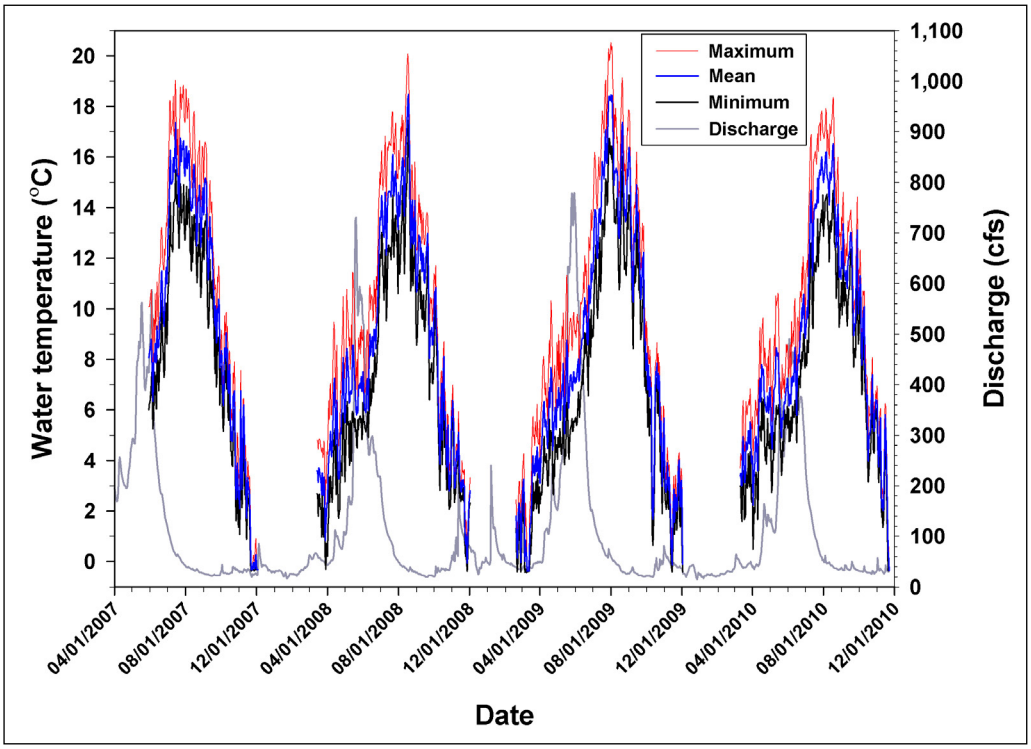

Figure 6b—Daily water temperature parameters and discharge at the Mad gage.

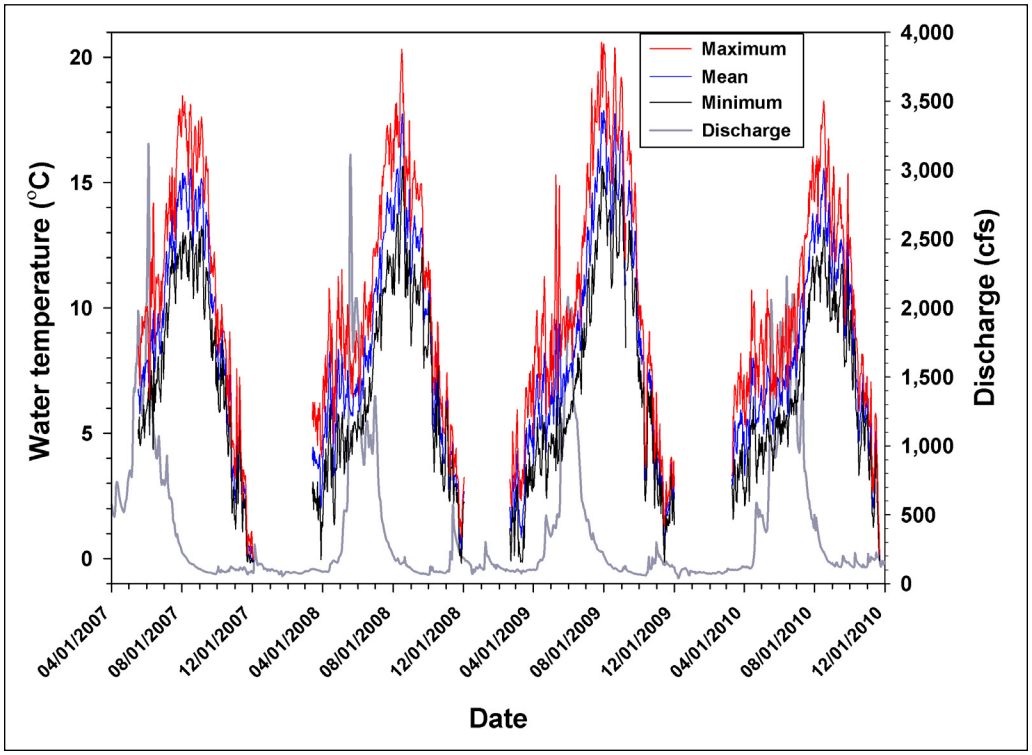

Figure 6c—Daily water temperature parameters and discharge at the Ardenvoir gage.

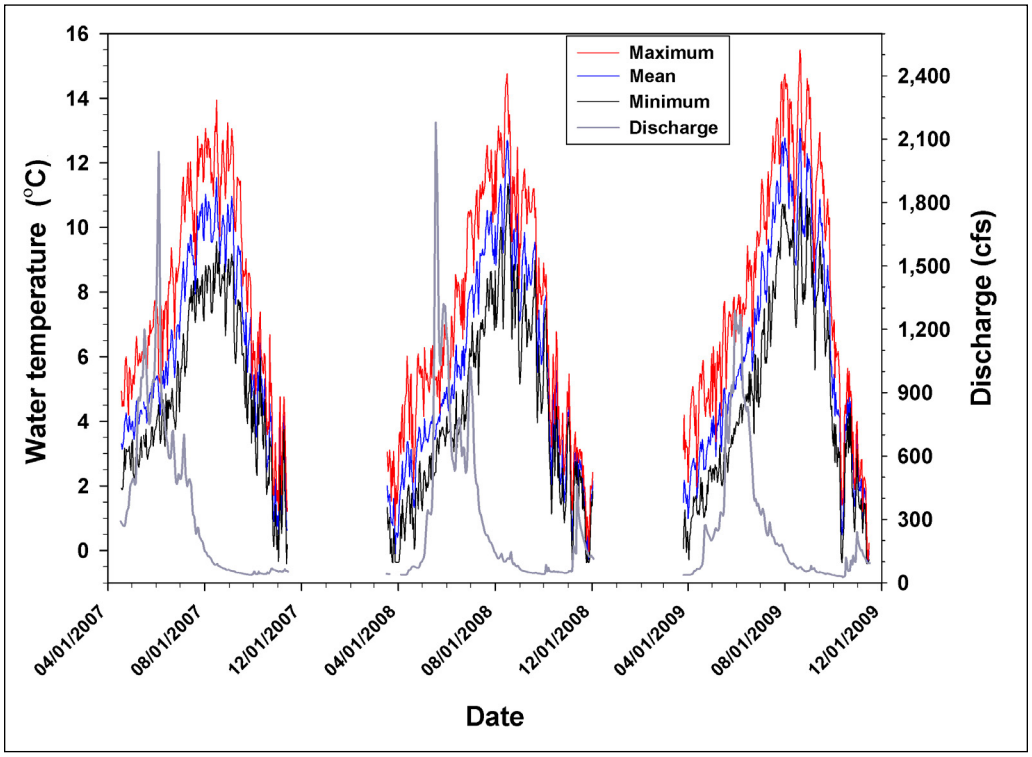

Figure 6d—Daily water temperature parameters and discharge at the North Fork gage.

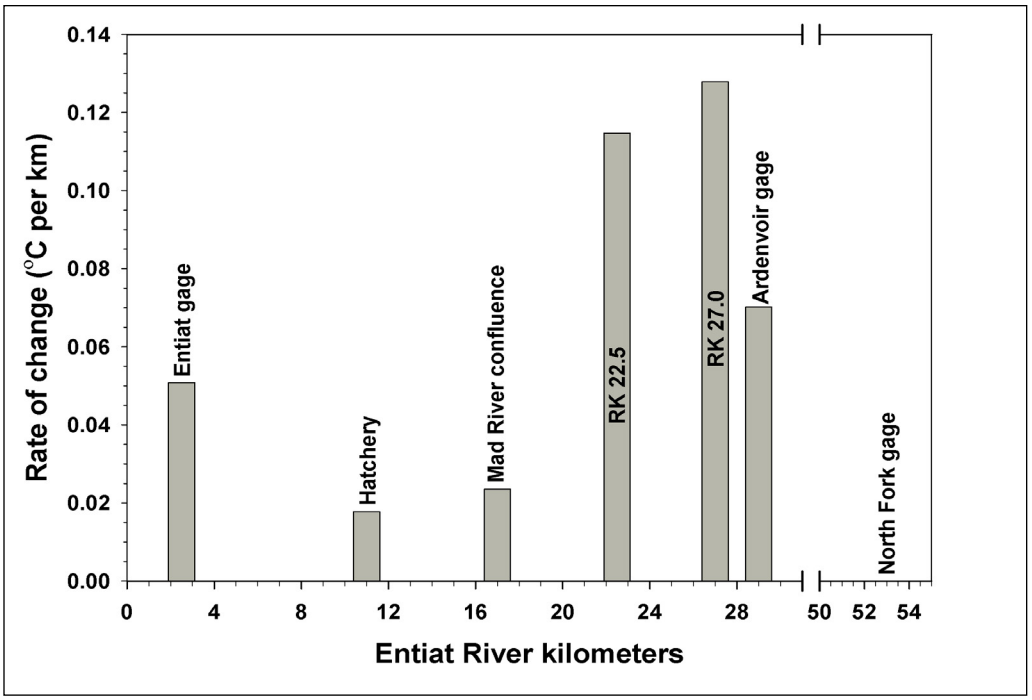

Figure 7—Mean rate of spatial change in water temperature. The magnitude displayed is the temperature at each station minus that at the closest upstream station. Thus, positive values indicate increasing temperature in the downstream direction. Rate varies among stations, nevertheless all differences are positive, indicating an uninterrupted increase in water temperature moving downstream from the North Fork gage.

Dissolved Oxygen

Except on rare occurrences, mean-daily DO concentrations varied between 8 and 14 mg/L at all measurement sites. This range spanned the WDOE minimum DO criterion for aquatic life in the Entiat watershed (9.5 mg/L) (Hallock 2011). Dissolved oxygen is inversely related to water temperature. Accordingly, the lowest DO concentrations occurred from July through September. Annual minima in DO commonly occurred from mid-July through mid-August. During this time, concentrations below 8 mg/L occurred rarely at the Entiat and Ardenvoir gages (fig. 8). Maximum DO concentrations commonly occurred during times of lowest water temperature, immediately before and after the December through February period when instruments were removed from the river (figs. 9a through 9d). Mean daily DO concentrations, expressed as a percentage of saturation, remained high throughout the measurement period. Values less than 90 percent were unusual, occurring on only a few days at all sites except the Mad gage where concentrations remained above 95 percent.

Point sampling indicated that DO changed little from the North Fork gage downstream to the Ardenvoir gage, despite a marked increase in water temperature (figs. 7 and 10). Dissolved oxygen then decreased in the downstream direction to

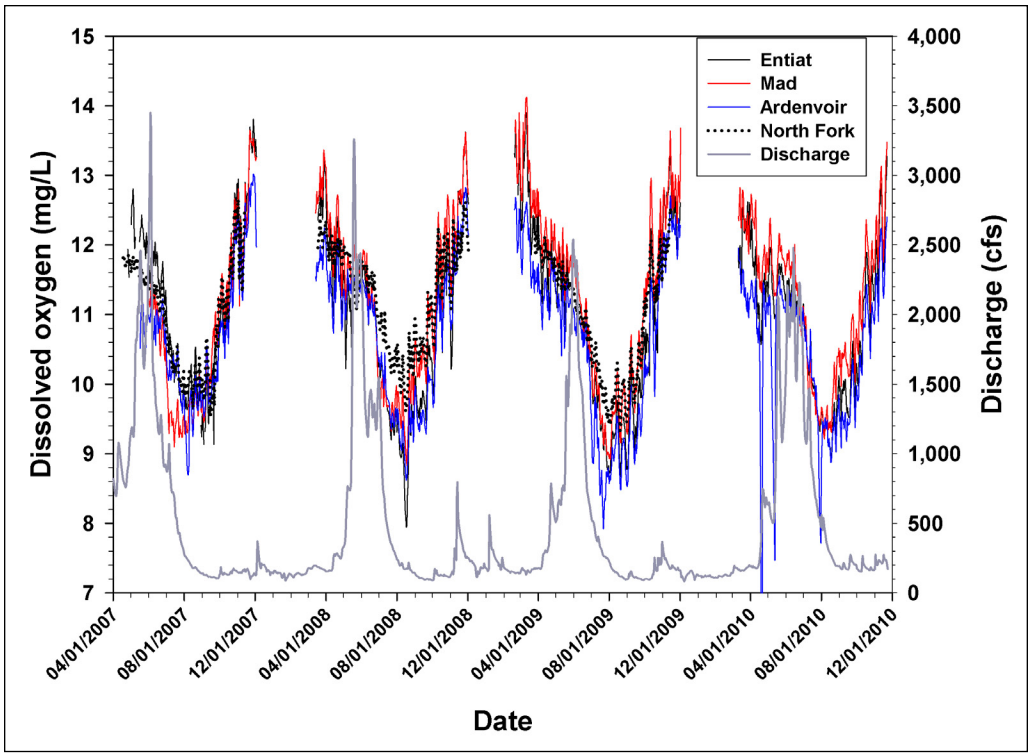

Figure 8—Mean daily dissolved oxygen for all stations. Discharge data are from the Entiat gage.

the RK 27 site before increasing sharply between RK 27 and RK 22.5. Dissolved oxygen continued to increase, although at lower rates, from RK 22.5 downstream to the hatchery site before decreasing between the hatchery site and the Entiat gage (fig. 10). Estimated error in the rate of change in DO owing to diurnal variation was 0.008 and 0.012 mg/L/km at the Entiat and Ardenvoir gages, respectively.

Specific Conductivity

At all sites and across all years, mean daily SC remained below 160 µS/cm (fig. 11). These very low levels indicated concentrations of minerals and dissolved salts well below levels that might adversely affect aquatic biota (Hem 1985, McCutcheon et al. 1993, Welch et al. 1998). Temporal trends in SC resembled those in pH in that the lowest values occurred during the peak of the snowmelt runoff period and highest values occurred during the spring and fall low-flow periods.

Spatial trends in SC were also broadly similar to pH. Both parameters were notably larger at the Entiat and Mad gages than at the Ardenvoir and North Fork gages (figs. 2 and 11). Both SC and pH changed little in the downstream direction from the North Fork gage to the Ardenvoir gage. Downstream of the Ardenvoir gage, both increased rapidly. The largest rate of increase in SC occurred in the downstream direction from the Ardenvoir gage to RK 27.0. Specific conductivity

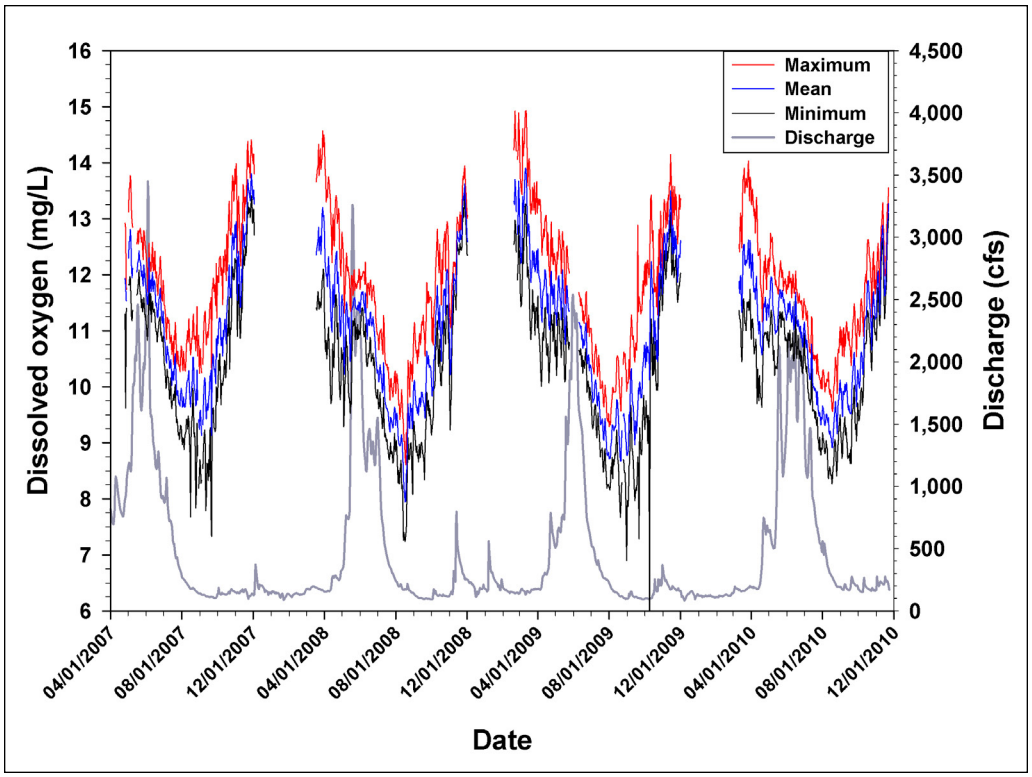

Figure 9a—Daily dissolved oxygen parameters and discharge at the Entiat gage.

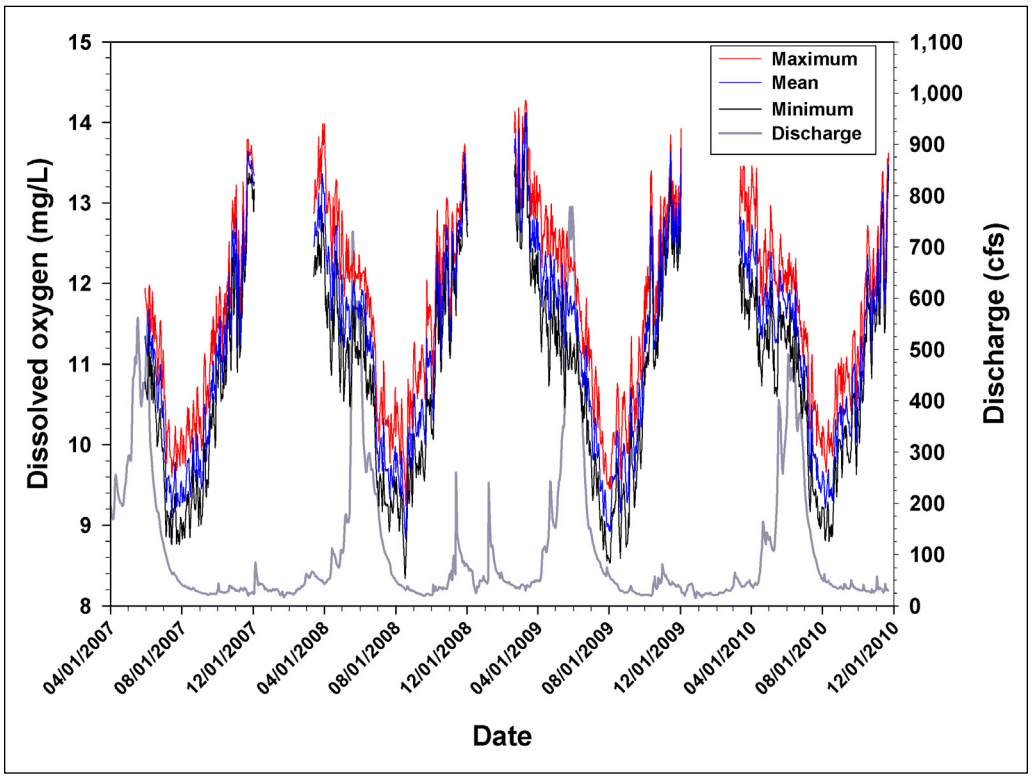

Figure 9b—Daily dissolved oxygen parameters and discharge at the Mad gage.

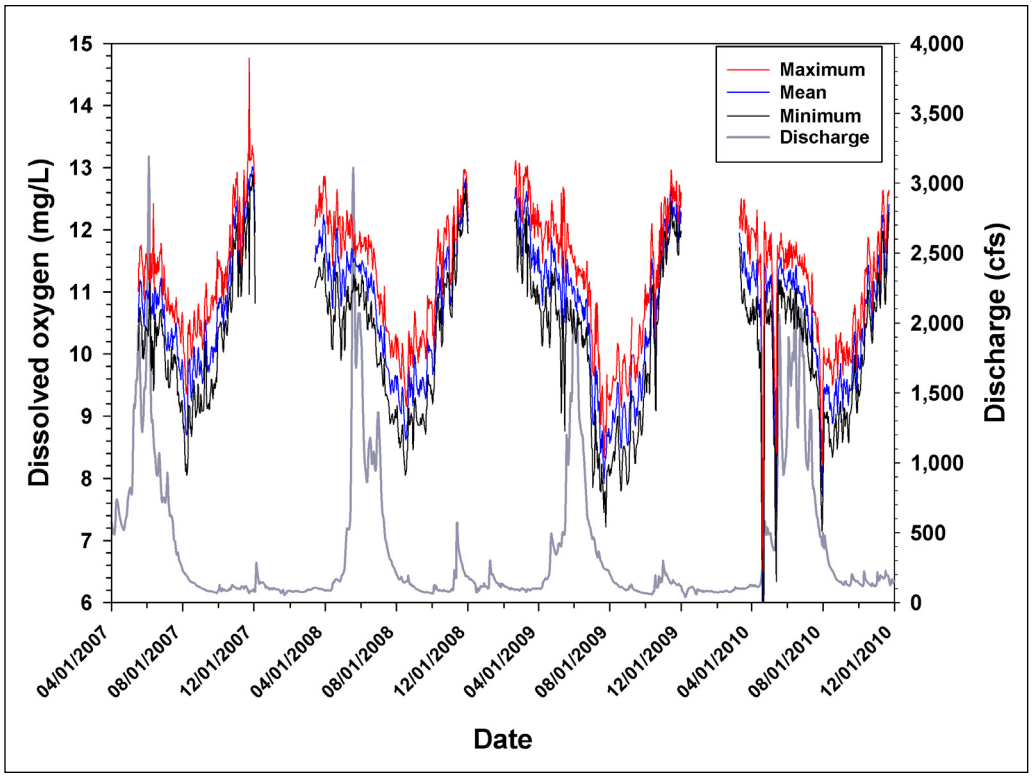

Figure 9c—Daily dissolved oxygen parameters and discharge at the Ardenvoir gage.

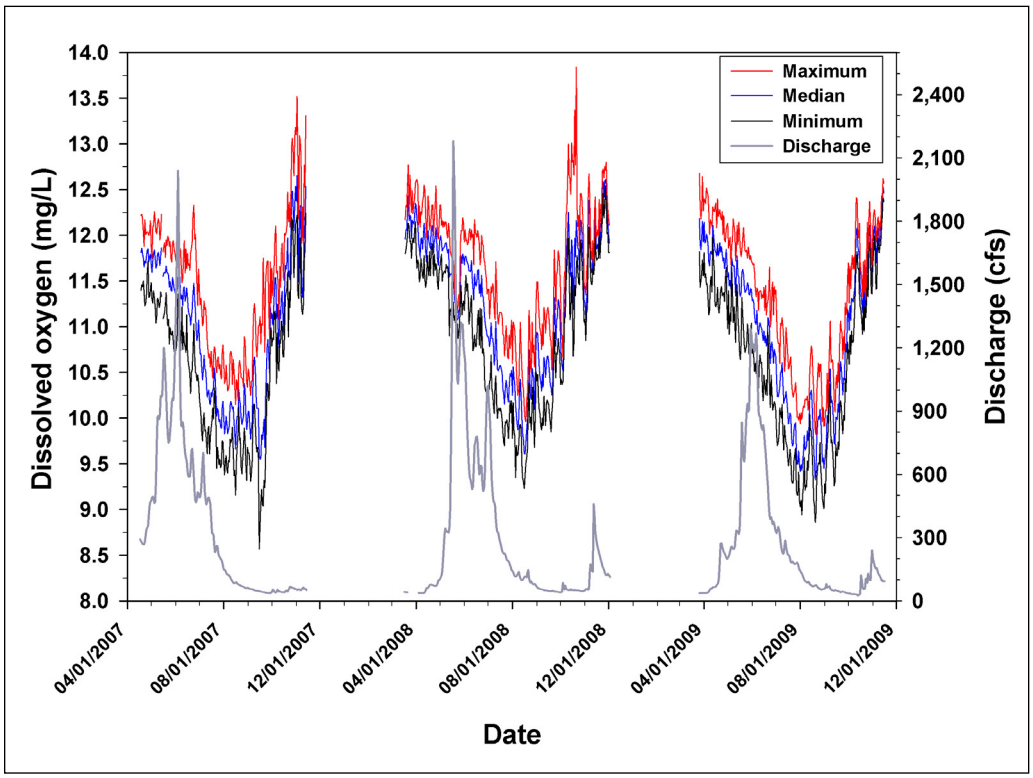

Figure 9d—Daily dissolved oxygen parameters and discharge at the North Fork gage.

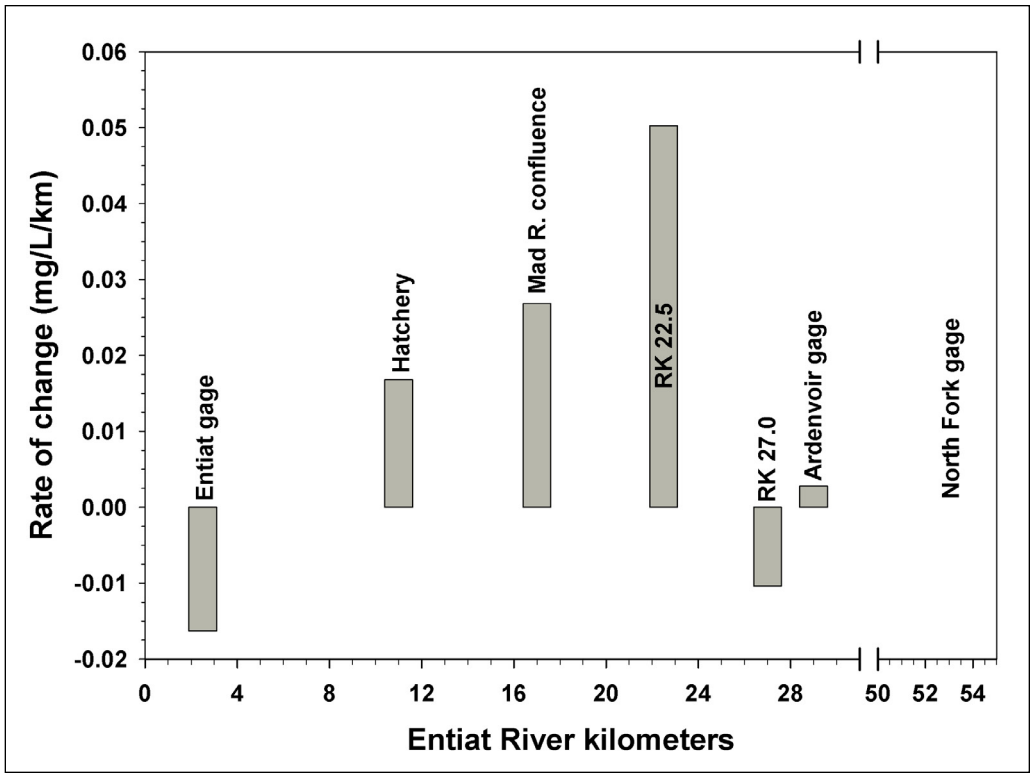

Figure 10—Mean rate of spatial change in dissolved oxygen (DO). The magnitude displayed is the DO concentration at each station minus that at the closest upstream station. Thus, positive values indicate increasing DO in the downstream direction. Negative values indicate two areas of decreasing DO moving downstream from the North Fork gage.

continued to increase at lower rates in the downstream direction to the hatchery site (fig. 12). The pattern of change in pH was similar, although the largest rate of pH increase occurred between RK 27.0 and RK 22.5 (fig. 4). The rate of change in both parameters switched from positive to negative in the downstream direction from the hatchery site to the Entiat gage (figs. 4 and 12). Error in the rate of spatial change in SC owing to diurnal variation was estimated to be 0.023 and 0.011 µS/cm/km at the Entiat and Ardenvoir gages, respectively.

Discussion

pH

Reconnaissance-level point sampling of water quality establishes that neither pH magnitude nor rate of change is spatially uniform along the Entiat River. Indeed, the rate of change can vary by a factor of five between adjacent river sections only a few kilometers in length. Furthermore, although these results cannot identify specific sources of high pH water, they can help to focus more intensive future surveys. For example, the reach between RK 27 and RK 22.5, where rate of pH increase is

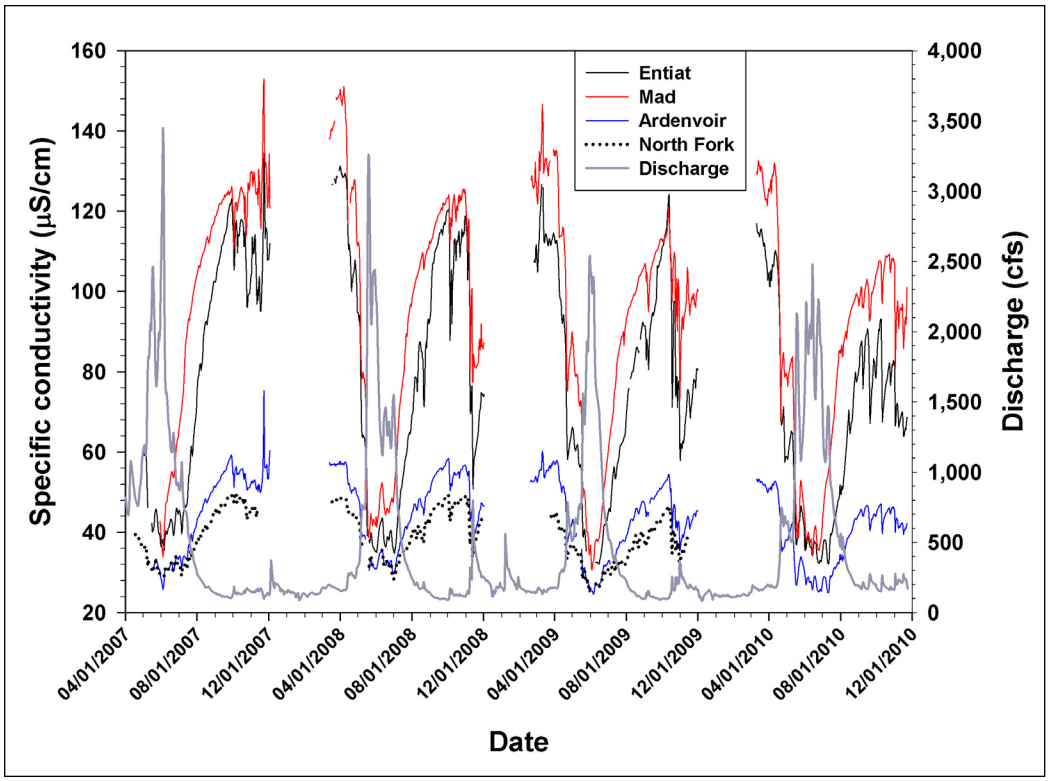

Figure 11—Mean daily specific conductivity for all stations. Discharge data are from the Entiat gage.

the highest, warrants additional investigation (fig. 4). Similarly, the high rate of pH increase between the Mad River confluence and the hatchery suggests the importance of the Mad River as a source of high-pH water (figs. 2 and 4) for the Entiat. Point measurements in September 2008 indicate a clear downstream increase in pH along the Mad River from the headwaters to the mouth (Bookter et al. 2009). The decrease in pH from the hatchery site to the Entiat gage suggests input of relatively low pH water from tributaries or ground water.

Factors that affect river pH include the watershed's soil and bedrock chemistry, water contact time with soil and bedrock, land use effects, exposure of river water to sunlight, and aquatic biological processes (Hem 1985, Welch et al. 1998). In the Entiat River, periods of high pH are correlated with either high exposure to solar radiation owing to low canopy cover (early spring) or high water temperatures (late summer and fall) (fig. 2). Both solar radiation and high water temperature are likely to increase periphyton (attached algae and other micro- and macro-organisms), photosynthesis, and productivity, which can increase pH in rivers (Welch et al. 1998, CCCD 2004). During daylight hours, periphyton photosynthesis removes carbon

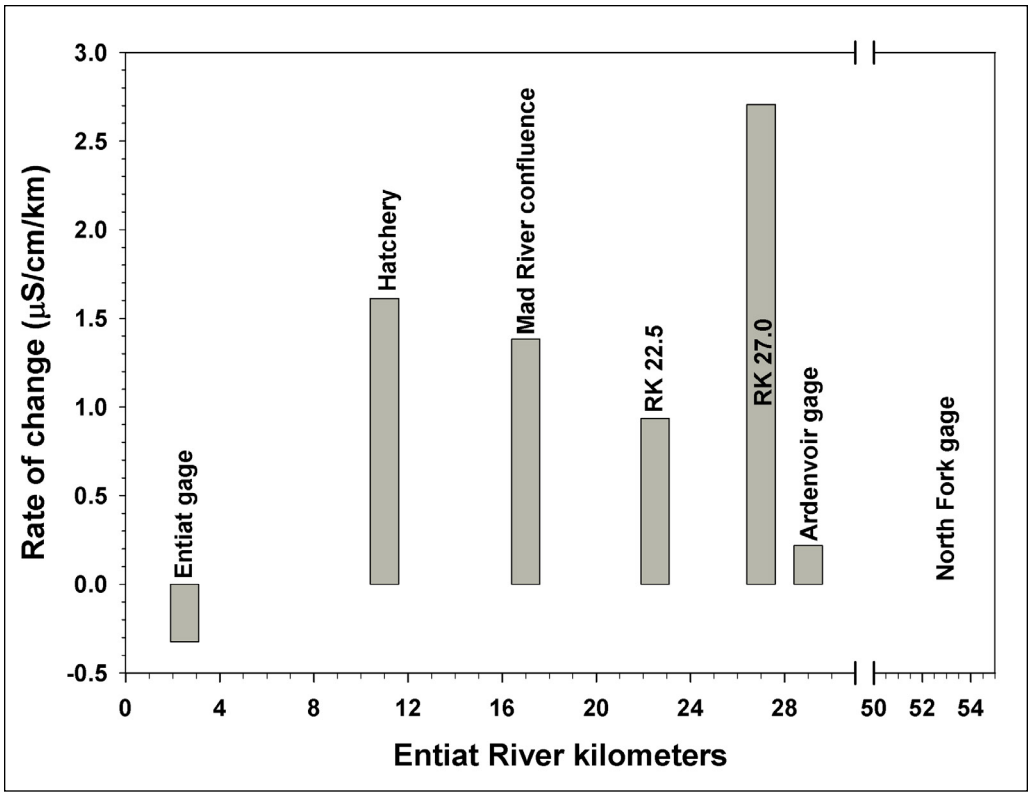

Figure 12—Mean rate of spatial change in specific conductivity (SC). The magnitude displayed is the SC at each station minus that at the closest upstream station. Thus, positive values indicate increasing SC in the downstream direction. A negative value for the Entiat station indicates decreasing SC moving downstream from the Hatchery station.

dioxide from river water, leaving free hydroxyl ions (OH-) to combine with hydrogen, thereby reducing the concentration of free hydrogen ions (H+) and increasing pH. Daytime pH values greater than 9 are common in surface water, although pH commonly drops at night as photosynthesis declines (Welch et al. 1998). Analyses of periphyton biomass in the Entiat and Mad Rivers in 2008 support a positive correlation between pH and periphyton productivity (Bookter et al. 2009).

Land use effects that can stimulate periphyton productivity include increases in water temperature and enrichment in nutrients, such as nitrogen and phosphorus. Water temperature can be increased by removal of riparian shading, water withdrawals, or delivery of high-temperature water to the river. Common sources of nutrient enrichment include nonpoint agricultural sources, septic tank effluent, and livestock waste. Soluble forms of phosphorus and nitrogen are commonly delivered to streams by runoff or irrigation return flow and can reach shallow ground water through infiltration of precipitation or irrigation water. In addition, phosphorus can be readily delivered to surface water when bound to mobile soil particles (Fuhrer et al. 2004, Welch et al. 1998, Williamson et al. 1997).

Methods of reducing nutrient enrichment and associated periphyton biomass include control of contaminant sources, maintenance of high-quality riparian habitat, and enhancement of nitrogen-fixing riparian vegetation. Invertebrate grazing is another important control on periphyton; therefore, maintenance of high-quality invertebrate habitat is important. Periphyton biomass can also be reduced by substrate disruption and scour during high flows, especially flows with high loads of entrained sediment (Fuhrer et al. 2004, Welch et al. 1998).

Although patterns of high pH in the Entiat and Mad Rivers are consistent with photosynthetic forcing, nutrient enrichment has not been identified as a concern in the WDOE monthly sampling program (WDOE 2008). Measured levels of ammonia-nitrogen, nitrate-nitrogen, total nitrogen, orthophosphate, and total phosphorus are, in general, similar to what would be expected in streams draining relatively undisturbed watersheds (McCutcheon et al. 1993). Ratios of total persulfate nitrogen to total phosphorus in this same data set range from 6.9 to 68.4 (WDOE 2008).

Even where nutrient concentrations are relatively low, periphyton biomass can respond strongly to enrichment, depending on water temperature and velocity, solar radiation, invertebrate grazing, and other factors. Concentrations of total phosphorus as low as 0.005 mg/L can cause excessive algal growth (McCutcheon et al. 1993, Murphy 1998, Welch et al. 1998). At the Entiat gage, total phosphorus concentrations that exceed the usual range of data, measured by WDOE since October 1996, include 15 values ranging from 0.017 to 0.054 mg/L (WDOE 2008). Additional, detailed investigations will be required to fully assess the distribution of nutrients and their effects on periphyton productivity and biomass, including analyses of chlorophyll-a dry mass to determine functional algal biomass (McCutcheon et al. 1993, Steinman and Lamberti 1996).

Watershed geology can have an important influence on river pH. In the Entiat valley, an accumulation of till, glacial outwash, and other alluvium creates a valley-bottom aquifer (Dixon 2003), and accumulations of till are also present in the Mad River valley (Dragovich et al. 2002, Faux and Archibald 2002, Tabor et al. 1987). These bodies of till create a setting for shallow ground water to interact chemically with the large mineral surface area present in fragmented till and outwash. Newton et al. (1987) reported that ground water pH increased substantially after exposure to a similar geologic setting in the Adirondack Mountains.

In the Entiat watershed, other opportunities for enhanced chemical interactions with ground water are provided by prominent bedrock fractures in the dominant intrusive igneous and high-grade metamorphic rocks (Dragovich et al. 2002, Tabor et al. 1987). These fractures can act as ground water storage zones and pathways. In the Mad River watershed, much of the river closely follows the contact between the Entiat pluton and the high-grade metamorphic rocks of the Mad River terrane

(Dragovich et al. 2002, Tabor et al. 1987). If bedrock has been altered by contact metamorphism or fracturing along this zone, then chemical interaction between bedrock and ground water may be enhanced. Consistent relationships between mapped geology and water chemistry are not apparent at the present spatial scales of data collection, and will remain hypothetical pending additional, detailed investigations.

Water Temperature

River and valley geomorphology may be affecting Entiat River temperatures. The highest estimated rates of water temperature increase are measured at the Ardenvoir, RK 27.0, and RK 22.5 sites. These sites are located within, or a short distance downstream of, the low-gradient "stillwater" section of the river. The broad flood plain of the stillwater section permits relatively high exposure of the river to solar radiation, and low flow velocity extends the duration of this exposure.

Although a portion of the lower Entiat River is listed as impaired owing to high water temperatures, the "category 4B" listing allows the EWPU and cooperating agencies and groups to address the impairment through a pollution control program (CCCD 2004, WDOE 2008). An active restoration strategy is being pursued in the Entiat, including measures that directly address the water temperature issue, such as riparian vegetation enhancement and reductions in both water withdrawal and return of heated agricultural water (CCCD 2004).

Dissolved Oxygen

Dissolved oxygen concentration varies inversely with water temperature, and is reduced by biologic oxygen demand, including respiration and oxygen-consuming decay processes. Dissolved oxygen increases through photosynthetic input and aeration at riffles and rapids, and is typically near saturation in forested rivers (Welch et al. 1998).

Point measurements suggest that DO is more variable in rate and direction of spatial change than the other measured water quality parameters. Although temperature increases markedly downstream from the North Fork to the Ardenvoir sites, the associated change in DO is less than measurement error (fig. 10). In this case, temperature effects may be countered by increased photosynthetic input of DO in the wide-valley, low-velocity stillwater section discussed previously. The decrease in DO from the Ardenvoir to the RK 27.0 site probably results from the associated high rate of temperature increase within the stillwater section (fig. 7). The sharp increase in DO from RK 27.0 to RK 22.5, despite continuing temperature increase, is likely caused by increased aeration, owing to steeper gradient below the stillwater section. Especially vigorous turbulent aeration occurs at RK 22.5. Dissolved oxygen continues to increase downstream through this steeper section

of river to the Hatchery site. However, increasing water temperature contributes to declining rates of DO increase. A sharp increase in temperature may drive the marked decrease in DO between the Hatchery to the Entiat gage (fig. 10).

A few unusually low DO measurements occur at the Ardenvoir gage in 2010. Each of these is a sequence of several consecutive measurements, rather than a single outlier; therefore, they are retained in the record. These likely reflect short-term biofouling of the sensor, owing to mobilization of large amounts of organic detritus by multiple runoff peaks during that year's protracted snowmelt runoff (fig. 8).

Specific Conductivity

Although conductivity in the Entiat is far too low to be a water quality concern, temporal and spatial variation can indicate changes in water sources or dissolved constituents. Increases in SC downstream of the Ardenvoir gage (fig. 12) suggest the addition of conductive solutes, possibly nutrients, which can affect biological processes. Previously noted similar spatial patterns in pH suggest a related response to an increase in solutes. Relative high conductivity and pH in the Mad River suggest that the Mad may be an important source of such constituents.

Conclusions

This report summarizes results from the first 4 years of a study testing a more intensive approach to watershed-scale, status and trend monitoring of water quality than previously employed in the Entiat River. This approach has clear advantages over the commonly applied federal Clean Water Act compliance monitoring, which is generally conducted at much lower spatial and temporal resolution. To date, results of Clean Water Act monitoring include listings for water temperature and pH. More intensive monitoring including spatially distributed measurements at points that integrate critical drainage areas within the watershed allow inferences to be made regarding the source and distribution of extreme values in water quality metrics. Measuring variation in water quality parameters at frequencies of 1 hour or less allows temporal trends and cycles to be identified that clarify the duration and severity of extreme values. This measurement intensity can be a great aid in identifying potential causes and mechanisms of water quality extremes and their relationship to other factors such as river discharge, temperature, solar exposure, or seasonality. This study further demonstrates that water quality monitoring at this intensity is logistically and economically feasible as part of the broader salmon recovery monitoring program. Although the scope is broad scale and exploratory in nature, findings will aid investigators in designing more focused and detailed studies as needed. The value of these data sets will increase and inferences will become more robust as the length of record increases.

Acknowledgments

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English Equivalents

When you know:	Multiply by:	To find:
Meters (m)	3.2808	Feet
Kilometers (km)	0.6214	Miles
Hectares (ha)	2.4711	Acres
Square kilometers (km^2)	0.3861	Square miles
Grams (g)	0.3527	Ounces
Kilograms (kg)	2.2046	Pounds
Milligrams per liter (mg/L)	0.0010	Ounces per cubic foot
Liters per second (L/s)	0.0353	Cubic feet per second (cfs)
Cubic meters per second (m^3/s)	35.3147	Cubic feet per second
Siemens or mhos	1.0000	1/ohm
MicroSiemens per centimeter (ms/cm)	2.5400	Micromhos per inch
Degrees Celsius	(1.8 ºC) + 32	Degrees Fahrenheit

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