



United States  
Department of  
Agriculture

Forest Service

Pacific Northwest  
Research Station

Research Note  
PNW-RN-563  
December 2009



# Water Quality Trends in the Entiat River Subbasin: 2007–2008

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## Abstract

Production of high-quality water is a vitally important ecosystem service in the largely semiarid interior Columbia River basin (ICRB). Communities, tribal governments, and various agencies are concerned about maintenance of this water supply for domestic, agricultural, industrial, recreational, and ecosystem uses. Water quantity and quality are widely recognized as important components of habitat for depleted salmonid populations in the ICRB where a large, multiagency effort is underway to restore salmon, trout, and char listed as threatened or endangered under the federal Endangered Species Act. A particularly active program of salmonid restoration is ongoing in the Entiat River subbasin, part of the ICRB that drains a portion of the eastern slope of the Cascade Mountains in central Washington state. In the Entiat River, monitoring of compliance with the 1977 federal Clean Water Act has identified water temperature and especially pH as water quality parameters of concern. For these reasons, agencies and others concerned with production of high-quality water and restoration of listed salmonids require meaningful and efficient approaches to water quality monitoring.

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During spring 2007, we began testing a pilot water quality monitoring strategy using multiparameter data-logging instruments. These were deployed at four locations in the Entiat River subbasin to measure fundamental water quality parameters (pH, water temperature, dissolved oxygen, and specific conductivity). In 2007 and 2008, the highest pH values occurred during the low-flow period from midsummer through the following midspring, then dropped sharply during the annual snowmelt runoff period from late spring through early summer. Water temperature began rapidly increasing during the receding limb of the annual snowmelt hydrograph. Highest mean-monthly temperatures occurred in July and August, and instantaneous maxima occurred during the period July–September. Dissolved oxygen reached its lowest levels during the period of highest water temperature in July–September. Specific conductivity remained very low at all sites throughout the year.

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

## Introduction

Production of high-quality water is a vitally important ecosystem service in the largely semiarid interior Columbia River basin (ICRB). Communities, tribes, and local, state, and federal agencies are concerned about maintenance of this water supply for domestic, agricultural, livestock, industrial, recreational, and ecosystem uses. A sufficient supply of high-quality water is also essential for an ongoing, multiagency effort to restore depleted salmonid populations in the ICRB (UCSRB 2007). The Bonneville Power Administration (BPA) is a primary sponsor of this restoration effort (BPA 2009). The BPA funds the National Oceanic and Atmospheric Administration (NOAA-Fisheries) Integrated Status and Effectiveness Monitoring Program (ISEMP). The ISEMP supports the development of a region-wide research, monitoring, and evaluation program to assess the status and trends of anadromous salmonid populations, their tributary habitat, and effects of restoration and management actions in the ICRB (NOAA-Fisheries 2009). The ISEMP tasks include supporting long-term status and trend monitoring of water quality parameters that may compromise effectiveness of salmonid restoration projects.

Within this context, The U.S. Department of Agriculture, Forest Service, Pacific Northwest Research Station, in partnership with ISEMP, is testing an approach to subbasin-scale status and trend monitoring of fundamental water quality parameters of interest to salmon recovery (pH, water temperature, dissolved oxygen (DO), and specific conductivity (SC)) in the Entiat River subbasin. The Entiat River is a tributary to the Columbia River that drains a portion of the eastern slope of the Cascade Mountains in central Washington state (fig. 1). A particularly active program of salmonid habitat restoration is underway in the Entiat subbasin,

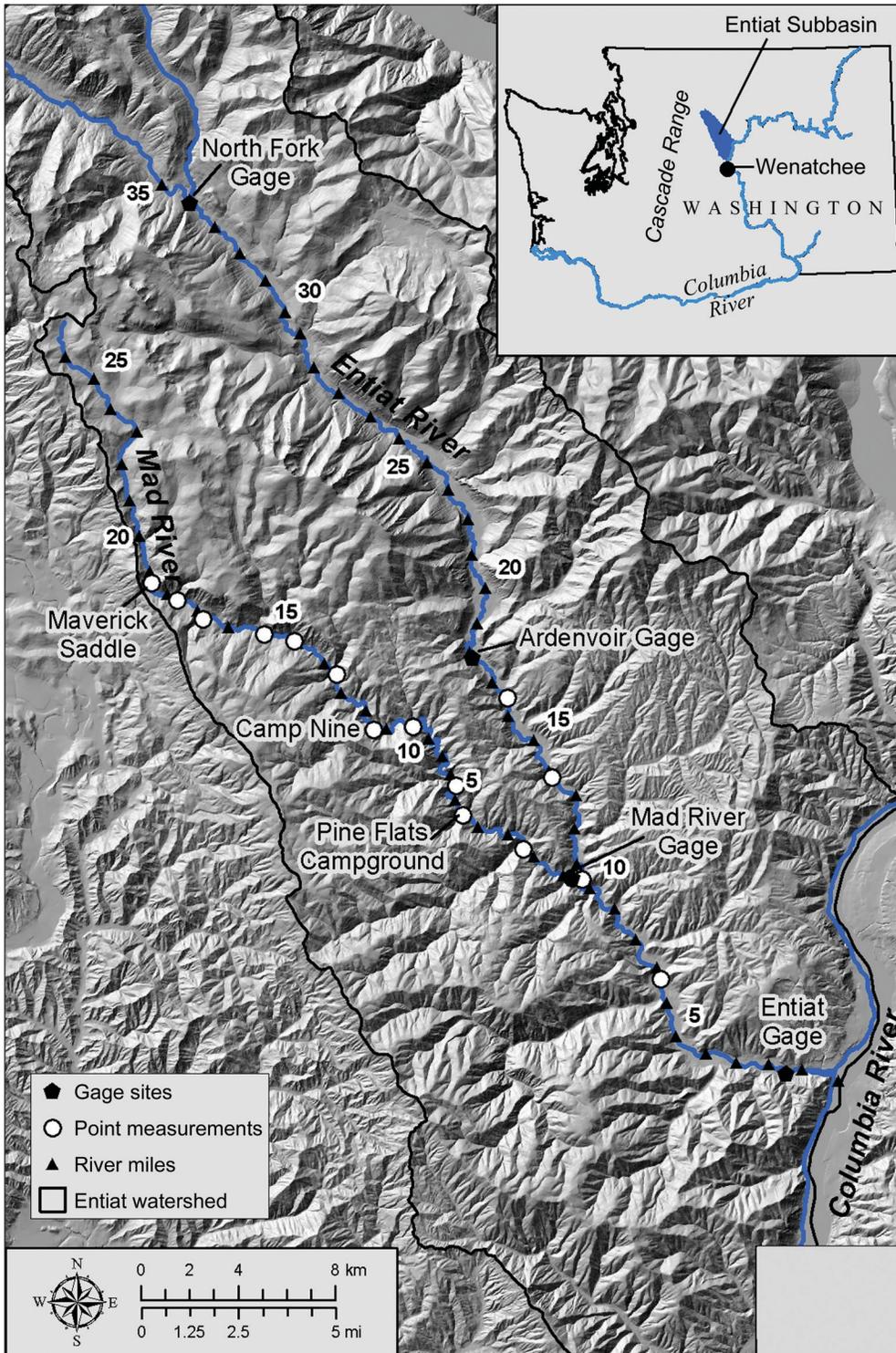


Figure 1—Location map showing measurement sites. Throughout this report, we indicate river location in miles, rather than kilometers, to be consistent with the commonly used U.S. Geological Survey topographic maps.

where all salmonid populations have been in decline since Europeans settled here (CCCD 2004). The subbasin currently provides critical habitat for three of these populations listed under the Endangered Species Act, including spring Chinook salmon (*Oncorhynchus tshawytscha*) (endangered), summer steelhead (*O. mykiss*) (endangered), and bull trout (*Salvelinus confluentus*) (threatened) (CCCD 2004, UCSRB 2007).

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 at Entiat River mile 1.4 by the Washington Department of Ecology (WDOE). Throughout this report, we indicate river location in miles, rather than kilometers, to be consistent with the commonly used U.S. Geological Survey (USGS) topographic maps. In the 2008 WDOE Water Quality Assessment 305(b) report and 303(d) list, occasional exceedances of the state water quality standard for pH are documented for the period from 2004 to 2006 (WDOE 2009). As a result of these exceedances, the lower Entiat River in the vicinity of the Entiat gage is listed as a “category 5” impaired water body for pH by WDOE. This was the only category 5 listing for the Entiat River in the 2008 WDOE report, which was approved by the U.S. Environmental Protection Agency (EPA) on January 29, 2009. A category 5 listing requires the state to prepare a total maximum daily load (TMDL) analysis, with the goal of ensuring that the impaired water body will attain water quality standards (WDOE 2009).

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 problem that is being addressed by a pollution control program; therefore, a TMDL analysis is not required (WDOE 2009). An active program of distributed water temperature monitoring is being conducted in the Entiat and Mad Rivers by the U.S. Forest Service, Entiat Ranger District. Results for 1999–2002 along with details of the history of water quality measurements in the Entiat subbasin 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 2009). This study was primarily motivated by discussions among EWPU members between summer 2005 and spring 2006 regarding the need for additional information on river pH in the Entiat subbasin. Primary objectives include defining the spatial and temporal extent of high pH values and identifying sections of river

that may contribute to high pH. The scope is broad scale and exploratory in nature, although findings may lead to more focused and detailed investigations. Initial results are presented in this report. The value of these data sets will increase and conclusions will become more robust as the length of record increases.

## pH

The effective concentration of dissolved hydrogen ions ( $H^+$ ) is, for convenience, expressed as the logarithmic unit, “pH” where  $pH = -\log(H^+)$ . The hydrogen ion concentration reflects the acidity of an aqueous solution; therefore, most chemical and biochemical processes are affected by pH. 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. Magnitude of pH affects the solubility and biological availability of nutrients, such as nitrogen and phosphorus, and other components of a river’s dissolved load, which may be harmful or beneficial to aquatic biota. A pH between about 6 and 9 is generally considered an ecologically acceptable range for freshwater aquatic organisms (Hem 1985, Welch et al. 1998). Excessively high or low pH can be directly detrimental to biota. Changes of 0.2 to 0.3 pH units can interact with temperature to significantly change the oxygen available for respiration, depending on the respiratory pigment used (hemoglobin in vertebrates and some arthropods, hemocyanin in some mollusks) (Withers 1992). The WDOE specifies the pH range 6.5 to 8.5 as its acceptable criterion for aquatic life in fresh water, with additional limits on human-caused variation (WDOE 2009).

## Water Temperature

Water temperature is a primary component of habitat for aquatic biota affecting 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 DO concentration (Hem 1985, Welch et al. 1998). The WDOE aquatic life water temperature criteria apply to the 7-day average of the daily maximum temperatures. Maximum temperature criteria in the Entiat watershed range from 12 to 17.5 °C depending on the local designated (“beneficial”) water use category (WDOE 2009).

## Dissolved Oxygen

Dissolved oxygen is supplied to stream water by photosynthesis during daylight hours and taken into solution from the atmosphere. It is consumed by respiration of aquatic organisms and by organic matter decomposition and other chemical processes. The DO content can also be reduced by influxes of deoxygenated groundwater (Hem 1985, 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 result in large diurnal variation in DO concentration, which decreases at night, potentially to levels that are detrimental to certain fish species (Hem 1985, Welch et al. 1998, Williamson et al. 1997). The WDOE minimum DO criterion for aquatic life in the Entiat watershed is either 8.0 or 9.5 mg/L depending on the local designated water use category (WDOE 2009).

### Specific Conductivity

Conductivity, a measure of the ability of a material to carry an electrical current, is the inverse of resistance, which is commonly measured in ohms. The inverse of ohms (1/ohms) is called mhos or Siemens (S). Specific conductivity is the conductivity of a solution at 25 °C. Conductivity varies with the ionic composition of stream water. Higher concentrations of minerals and dissolved salts produce higher conductivities. Therefore this parameter is a useful indicator of changes in dissolved constituents, including soluble reactive phosphorus and nitrate nitrogen, which are important nutrients in aquatic ecosystems. Conductivities less than thousands of  $\mu\text{S}$  (microSiemens)/cm are generally not considered harmful to aquatic biota (Hem 1985, McCutcheon et al. 1993, Welch et al. 1998). Specific conductivities less than 100  $\mu\text{S}/\text{cm}$  are common in precipitation, and values found in potable water may be as high as 1500  $\mu\text{S}/\text{cm}$ . The WDOE does not have aquatic life criteria for specific conductivity (WDOE 2009).

## Methods

### Project Area

The Entiat River is located on the eastern slope of the central Cascade Mountains in Washington state, 55 km (34 mi) northwest of Wenatchee. It is 85 km (53 mi) long, and its drainage area is approximately 1100 km<sup>2</sup> (425 mi<sup>2</sup>) (fig. 1). Wildfire, flooding, mass soil and debris movement, and land use have been primary historical disturbance processes. Land use has 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

Following field reconnaissance and examination of drainage network maps, measurement sites were co-located with the existing network of stream gages. This distribution was consistent with the 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. One water-quality instrument was deployed at each stream-gaging site (table 1, fig. 1). Instruments were secured in the channel inside protective, 10-cm (4-inch)-diameter pipes or other robust enclosure. A 60-cm-long section of perforated pipe was attached to the primary pipe to ensure ample water circulation around the instrument sensors.

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

River gage (short name)	Gaging agency	Gage ID	River mile	Coordinates (latitude, longitude)
Entiat River near Entiat (“Entiat”)	USGS <sup>a</sup>	12452990	1.4	47°39'48", 120°14'58"
Mad River at Ardenvoir (“Mad”)	USGS	12452800	0.4	47°44'13", 120°22'03"
Entiat River near Ardenvoir (“Ardenvoir”)	USGS	12452890	18	47°49'07", 120°25'19"
Entiat River at North Fork Campground (“North Fork”)	WDOE <sup>b</sup> /CCD <sup>c</sup>	46A170	34	47°59'15", 120°34'47"

<sup>a</sup> U.S. Geological Survey.

<sup>b</sup> Washington State Department of Ecology.

<sup>c</sup> Cascadia Conservation District.

## Instrumentation

We employed In-Situ Troll 9500<sup>2</sup> multiparameter data-logging instruments with a separate sensor for each measured water-quality parameter. All sensors used an EPA-approved or -recommended methodology (table 2). Four instruments were deployed during spring 2007 in the Entiat River subbasin and were programmed to record data at 15-minute intervals. Instruments were removed during winter (December through February) to avoid damage from river ice and redeployed the following spring as soon as ice conditions allowed.

<sup>2</sup> The use of trade names in this paper is for information and convenience of the reader. Such use does not constitute an official endorsement by the U.S. Department of Agriculture of any product to the exclusion of others that may be suitable.

**Table 2—Sensor methodology and manufacturer’s stated accuracy**

Variable	Methodology	Accuracy
pH	Standard methods 4500-H+, EPA <sup>a</sup> 150.2	0.1 pH units
Temperature	EPA 170.1	0.1 °C
Dissolved oxygen (DO)	Optical DO sensors—ASTM #D888-05, Method C <sup>b</sup>	0.2 mg/L
Specific conductivity	Standard methods 2510, EPA 120.1	0.5 percent or 2 µS/cm

Source: In-Situ, Inc. (<http://www.in-situ.com>).

<sup>a</sup> U.S. Environmental Protection Agency.

<sup>b</sup> EPA has recommended to each of its regions interim approval for the use of this method. 40 CFR part 136.5 (ATP Case No. N05-0046).

### Quality Assurance/Quality Control (QA/QC) Comparisons to a Reference Instrument

Following installation, instrument function and calibration were checked frequently for about 1 month. Following this initial period, instruments and batteries were inspected and data downloaded at 1- to 2-week intervals. During each site visit, a fifth instrument, calibrated before and after use, was used as a portable, hand-held reference for checking data from field instruments. Field-deployed sensors were recalibrated whenever deviation from reference data exceeded a predefined standard (table 3).

**Table 3—Maximum acceptable field vs. reference deviations**

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

#### Reference test procedure—

1. The reference instrument was allowed to equilibrate to the stream water environment for 5 to 20 minutes, until readings stabilized.
2. Field and reference instrument readings were recorded and compared.
3. If the difference between the field and reference readings was greater than the threshold deviation (table 3), then the field sensor was recalibrated.
4. In addition, sensor calibration was done under the following conditions:
  - A. Sustained, within-threshold deviation from the reference.
  - B. Disturbance to the instrument, e.g., sedimentation or biofouling.
  - C. Sensor performance outside manufacturer’s recommendation.

**Calibration—**

Instruments were designed to accommodate field calibration at ambient, onsite temperature, elevation, and barometric pressure, thereby improving accuracy of DO saturation measurements relative to calibration at an offsite lab. Because these instruments remained on site during calibration, interruption of data collection was minimized. All calibrations and testing were done using the manufacturer's software and specifications, thereby meeting or exceeding the manufacturer's QA/QC guidelines (<http://www.in-situ.com>).

**pH**—A two-point pH calibration was done using buffer solutions of pH 7 and 10, thereby spanning the expected range of pH in the Entiat and Mad Rivers. The reference sensor was calibrated in the lab before each day of field checks, and a one-point pH 7 check was done at the end of the day. If this reading deviated from the standard by more than 0.2 pH units (the threshold deviation), then the reference readings for that day were not used. If the pH calibration parameters (slope, offset, and response) were outside the manufacturer's recommended range, then the sensor required maintenance or replacement.

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

**Dissolved oxygen**—Two-point DO calibrations were done at 100 percent and 0 saturation. One hundred percent saturation was obtained by bubbling air through deionized water. A solution of sodium sulfite provided 0 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 in the field and the reference DO readings for that day were not used. An integrated barometer with vented cable improved the accuracy of DO calibration and the computation of percentage of oxygen saturation relative to non-vented designs by allowing the sensor to incorporate real-time barometric pressure into the calculations. In consideration of barometric pressure differences between laboratory and field sites, all DO sensors were calibrated in the field.

**Specific conductivity**—A one-point specific conductivity calibration was done using a 147- $\mu$ S/cm standard. The reference sensor was calibrated in the lab before and after each field day. Conductivity readings before and after each calibration were compared to check sensor performance. If end-of-the-day values deviated by more than 5  $\mu$ S/cm, then the reference conductivity readings for that day were

not used. If the cell constant ( $K_{\text{cell}}$ ) for the conductivity sensor fell outside the manufacturer's recommended range, then the sensor required maintenance or replacement.

## Data Processing

Time series of instantaneous data measured at 15-minute intervals and longer term means or medians (pH) were examined to investigate temporal trends and the timing and longevity of water quality extremes. Spatial variation was interpreted by comparing results across the array of instrumented sites. Particular scrutiny was applied to data that included extreme outliers, erratic fluctuations, or extreme variability relative to surrounding data. These cases occurred as a result of ice effects, biofouling, or other factors. Data determined to be unreliable were treated as missing, and not included in reporting or 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 by category in the database along with notes regarding reference checks, calibrations, unreliable data, or other relevant issues.

## Reconnaissance Data Collection

Apparent initial trends in water quality prompted additional reconnaissance-level measurements to begin to define the spatial scope of changes occurring between gages. In August 2007, we began taking point measurements between the Entiat and Ardenvoir gages at approximately 2-week intervals. We used the hand-held reference instrument discussed previously for these measurements taken in sequence at 6.8, 10.6, 14.0, and 16.8 river miles (RM) (11, 17, 22.5, and 27 km) from the mouth of the Entiat River. Seventeen to 19 measurements were taken at each location. Throughout this report, we indicate river location in miles, rather than kilometers, to be consistent with the commonly-used USGS topographic maps.

Large-scale, spatial trends in the Mad River were also of interest, not only because of high pH in the Mad River itself, but because of its potential influence on Entiat River water quality. We therefore conducted a survey of point measurements in the Mad River, as described previously for the Entiat, on September 9 and 10, 2008, a period when pH is commonly high. The Mad River survey was done on foot, requiring several hours spanning a 2-day period to complete. For this reason, pH values were corrected for diurnal change as measured at the Mad River gage from the time of the first point measurement of the day to the time of each subsequent measurement.

## Periphyton Biomass Measurements

A well-known mechanism that can contribute to elevated pH in rivers is photosynthesis by periphyton (attached algae and other micro- and macro-organisms) (Welch et al. 1998). As a preliminary test of this hypothetical linkage in the Entiat and Mad Rivers, we sampled substrate periphyton within a few meters of the Entiat, Mad, and Ardenvoir gage sites in spring (April 29), summer (July 16), and fall (October 1) of 2008. For all sampling occasions and sites, five randomly selected cobbles were removed from a riffle section and sampled for periphyton. Water depths were 1 m or less. All sites were exposed to direct or canopy-filtered sunlight for several hours each day. The sampling apparatus scraped all periphyton from a 5-cm<sup>2</sup> area. Consistent and thorough sampling was ensured by scrubbing each cobble sample area three times for 30 seconds each time, followed by a deionized water rinse between each scrub. Representative subsamples were separated from each periphyton sample for gravimetric ash-free dry mass determination, using the method of Steinman and Lamberti (1996). Subsamples were dried to a constant weight, then oxidized in a muffle furnace and reweighed. The resulting subsample weight loss was multiplied by the sample-to-subsample mass ratio to determine ash-free dry mass of the original sample.

## Results

### pH

In both 2007 and 2008 at all sites, the highest median monthly and median daily pH values occurred during either the March–April or August–September period. Both periods are characterized by relatively low discharge and high exposure to solar radiation. A sharp drop in pH occurred during the high-flow, snowmelt runoff period from late spring through early summer (table 4, fig. 2). Median daily pH was generally similar at the North Fork and Ardenvoir gages, suggesting little change in the intervening 16 RM. Similarly, during the early spring, prior to high snowmelt runoff, median daily pH tended to be similar at the Entiat and Mad River gages, where pH was consistently greater than at Ardenvoir or North Fork (table 4, fig. 2). Following the snowmelt peak runoff period, median daily pH tended to be higher at the Mad River gage than at the Entiat gage, and pH tended to be higher at the Entiat gage in the spring than during the summer-fall period. At the other gages, median daily pH before the spring snowmelt differed little from that afterward, despite higher summer and fall water temperatures (table 4, fig. 2).

**Table 4—Monthly means (medians for pH) of water quality parameters<sup>a</sup>**

Month	Entiat				Mad				Ardenvoir				North Fork			
	pH	Temp. <sup>b</sup> °C	DO <sup>c</sup> mg/L	SC <sup>d</sup> µS/cm	pH	Temp. °C	DO mg/L	SC µS/cm	pH	Temp. °C	DO mg/L	SC µS/cm	pH	Temp. °C	DO mg/L	SC µS/cm
Apr-07	8.11 <sup>e</sup>	7.55 <sup>e</sup>	11.87 <sup>e</sup>	66.69 <sup>e</sup>	—	—	—	—	—	—	—	—	7.27 <sup>f</sup>	3.74 <sup>f</sup>	11.77 <sup>f</sup>	38.31 <sup>f</sup>
May-07	7.42	7.77	12.34	52.32	7.56 <sup>e</sup>	8.15 <sup>e</sup>	11.31 <sup>e</sup>	41.84 <sup>e</sup>	7.37 <sup>f</sup>	7.01 <sup>f</sup>	10.87 <sup>f</sup>	—	7.27	4.38	11.63	32.86
Jun-07	7.47	10.06	11.59	41.19	7.57 <sup>f</sup>	9.19	10.98	50.34	7.31	8.54	10.90	30.57	7.21 <sup>f</sup>	5.77	11.27	31.57
Jul-07	7.58	15.46	10.29	52.81	8.05 <sup>f</sup>	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	7.45 <sup>f</sup>	2.10 <sup>f</sup>	12.00 <sup>f</sup>	45.57 <sup>f</sup>
Dec-07	7.83 <sup>e</sup>	0.32 <sup>e</sup>	13.37 <sup>e</sup>	109.8 <sup>e</sup>	7.92 <sup>e</sup>	0.27 <sup>e</sup>	13.24 <sup>e</sup>	126.5 <sup>e</sup>	7.31 <sup>e</sup>	0.02 <sup>e</sup>	12.40 <sup>e</sup>	57.09 <sup>e</sup>	—	—	—	—
Jan-08	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Feb-08	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Mar-08	8.05 <sup>f</sup>	4.82 <sup>f</sup>	12.71 <sup>f</sup>	128.2 <sup>e</sup>	8.10 <sup>f</sup>	2.87 <sup>f</sup>	12.86 <sup>f</sup>	144.0 <sup>f</sup>	7.50 <sup>f</sup>	3.60 <sup>f</sup>	11.82 <sup>f</sup>	56.97 <sup>f</sup>	7.42 <sup>f</sup>	1.06 <sup>f</sup>	12.16 <sup>f</sup>	48.09 <sup>f</sup>
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	36.96 <sup>f</sup>
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
Dec-08	7.58 <sup>e</sup>	3.67 <sup>e</sup>	12.61 <sup>e</sup>	74.07 <sup>e</sup>	7.78 <sup>e</sup>	2.66 <sup>e</sup>	12.75 <sup>e</sup>	87.09 <sup>e</sup>	7.42 <sup>e</sup>	2.60 <sup>e</sup>	12.16 <sup>e</sup>	46.57 <sup>e</sup>	7.42 <sup>e</sup>	1.90 <sup>e</sup>	11.96 <sup>e</sup>	42.40 <sup>e</sup>

Note: — = no data.

<sup>a</sup> Based on more than 20 days of data, unless otherwise noted.

<sup>b</sup> Water temperature.

<sup>c</sup> Dissolved oxygen.

<sup>d</sup> Specific conductivity.

<sup>e</sup> 1 to 10 days of data.

<sup>f</sup> 11 to 20 days of data.

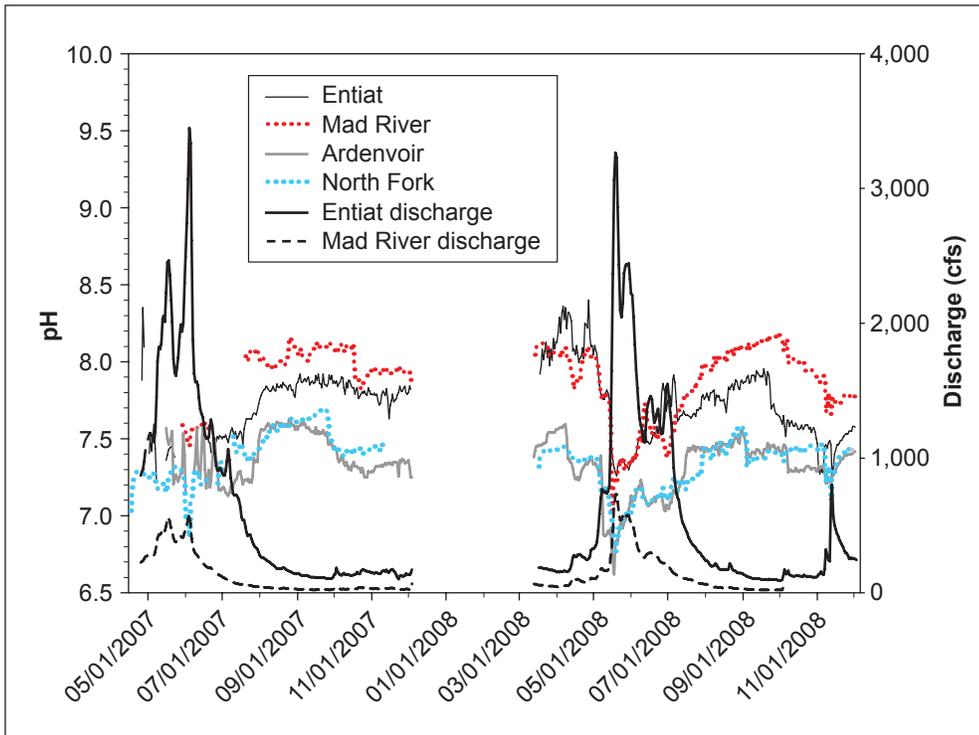


Figure 2—Median daily pH.

Overall, the highest median monthly, median daily, and maximum daily pH values were measured at the Entiat gage. At this location, instantaneous pH was as high as 9.5 in early spring 2008, and median daily pH reached a maximum of 8.3 to 8.4 in the spring of both 2007 and 2008 (fig. 3). At the Mad River gage in 2007–2008, the highest median daily values were always less than 8.2, and the greatest maximum daily pH values were in the range 8.6 to 8.8 (fig. 4). In contrast to measurements at the Entiat and Mad River gages, instantaneous pH values at the Ardenvoir and North Fork gages were always less than 7.9, and median daily pH did not exceed 7.7 (fig. 2). During periods of seasonally high pH, diurnal variation was especially large at the Entiat gage, and to a lesser degree at the Mad River gage. For example, at the Entiat gage in early April 2008, instantaneous values varied daily from approximately 7.8 in the early morning hours to a peak near 9.5 at night (fig. 5).

Point measurements taken from four locations between the Entiat and Ardenvoir gages between August 30, 2007, and October 7, 2008, supplemented gage site data. The total data set did not suggest a trend in pH among the North Fork gage, Ardenvoir gage, and the point measurement site at RM 16.8. However, downstream of RM 16.8, pH increased at varying rates along the Entiat River, including a rapid rate of increase from RM 16.8 to RM 14.0 (fig. 6). Mad River pH was markedly

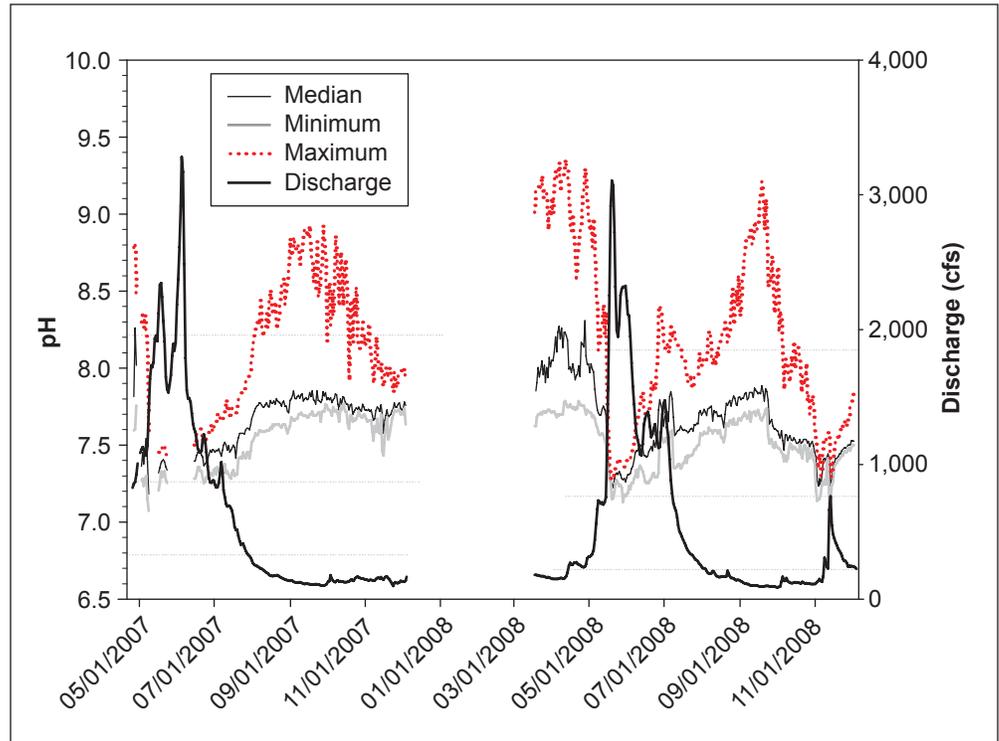


Figure 3—Daily minimum, maximum, and median pH at the Entiat gage.

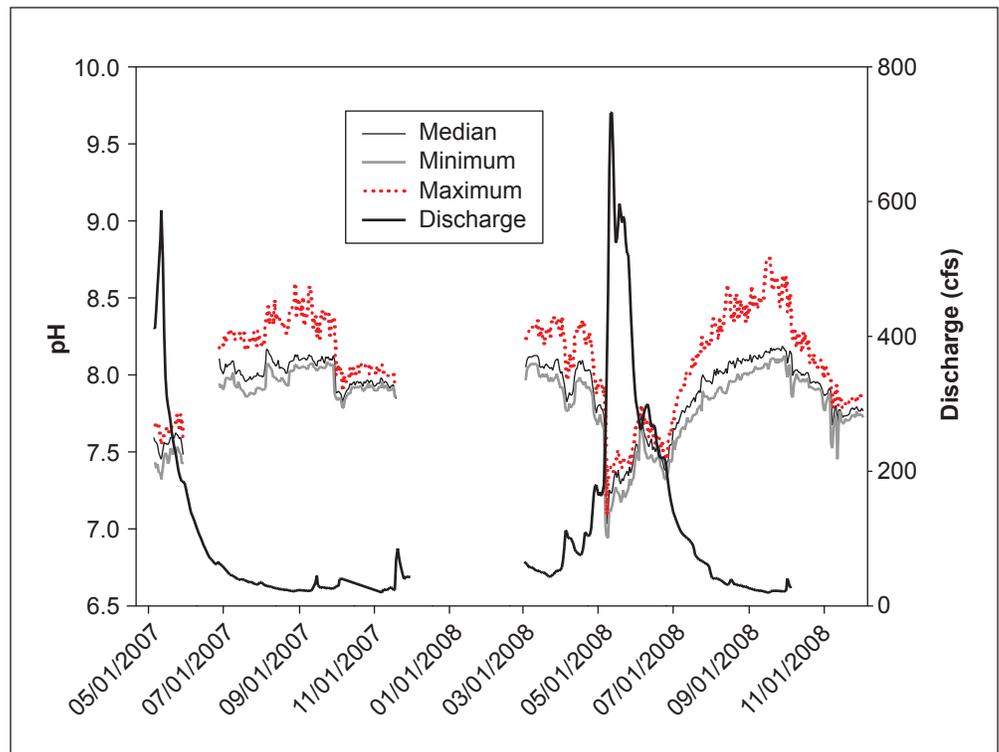


Figure 4—Daily minimum, maximum, and median pH at the Mad River gage.

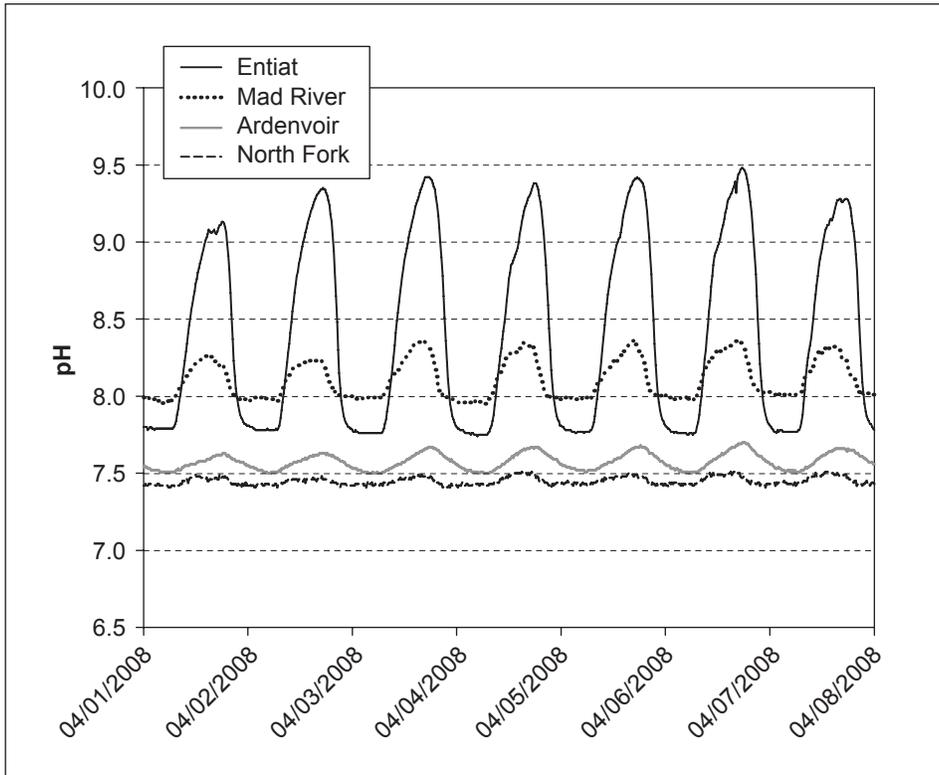


Figure 5—An example of large diurnal variation in pH at the Entiat gage.

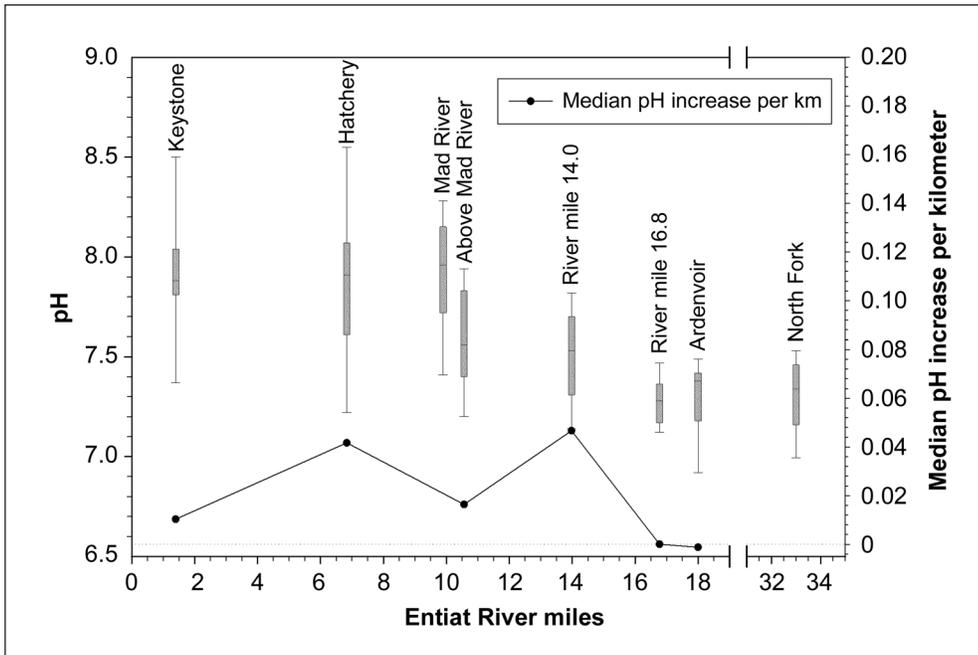


Figure 6—Entiat River pH point measurements. Box plots represent 17 to 19 pH values. Boxes contain the central 50 percent of the data values. Horizontal lines indicate the median. Horizontal error bars indicate the 10<sup>th</sup> and 90<sup>th</sup> percentiles. Dots represent the median rate of increase in pH per kilometer, relative to the next upstream measurement point.

higher than that in the Entiat River immediately upstream of their confluence. This contributed to the increase in Entiat River pH from RM 10.6 to 6.8. Downstream from RM 6.8 to the Entiat gage, median pH increase per kilometer was smaller but was still positive. This reconnaissance-level survey suggested that most of the spatial increase in pH in the Entiat River occurred within two sections: RM 16.8 to 14.0 and RM 10.6 to 6.8 (fig. 6).

Thermal infrared surveys using forward-looking infrared (FLIR) technology were flown in 2001 along both the Entiat and Mad Rivers (Watershed Sciences 2001). The FLIR technology detects thermal energy by sensing infrared radiation, allowing surface temperatures to be measured rapidly over large areas. Comparison of FLIR data to our pH surveys indicated that the Entiat River reach with rapid pH increase from RM 16.8 to 14.0 lay within a longer reach of rapid water temperature increase from RM 18-RM 12. The reach from RM 10.6 to RM 6.8 with rapid pH increase lay entirely within a reach of stable water temperature. These results do not support a possible correlation between temperature and pH increases in the Entiat River.

Point measurements along the Mad River indicated a continuous downstream increase in pH (corrected for diurnal variation). On September 9, 2008, at RM 18.7, just below Maverick Saddle on the western drainage divide, pH was 7.30 (figs. 1 and 7). From RM 18.7 to RM 10.3, pH increased at a generally steady rate to 7.76, although the rate of increase declined from RM 15.0 to RM 12.5 (fig. 7). The following morning (September 10, 2008, 09:45), corrected pH at RM 10.3 was 7.53, a large decrease from the previous afternoon. Downstream from RM 10.3, pH increased sharply to 7.68 at RM 9.0, then increased much more slowly to 7.74 at RM 4.6. From RM 4.6, pH again increased rapidly to 7.93 at the Mad River gage (fig. 7). This reconnaissance survey indicated that pH, corrected for diurnal variation, increased downstream from slightly more than 7 in the headwaters to more than 7.9 at the Mad River gage near the mouth of the river. The generally rapid rate of increase was interrupted by sections of slower increase from RM 15.0 to RM 12.5 and from RM 9.0 to RM 4.6. Within these reaches, FLIR data (Watershed Sciences 2001) indicate that water temperature increase with distance downstream was relatively weak. However, these reaches with relatively stable temperature extend into reaches where pH increased rapidly with downstream distance. Therefore, as for the Entiat River, a possible correlation between trends in pH and water temperature was not supported.

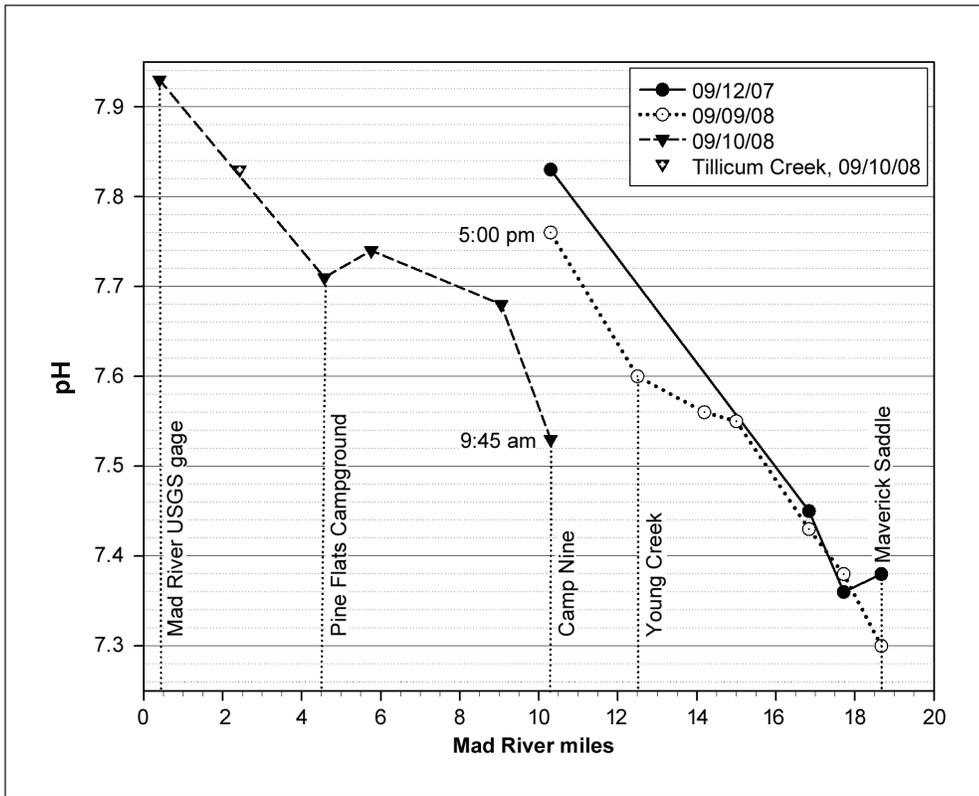


Figure 7—Mad River pH point measurements taken with a hand-held instrument during a 2008 survey. Also shown are results from a partial 2007 survey. The pH values are corrected for diurnal change as measured at the Mad River gage.

Exploratory sampling of periphyton biomass was done to look for indications of a linkage to river pH. This sampling was prompted by literature suggesting a functional relationship between high stream pH and periphyton productivity and by observations of rapid algal growth beginning in early March 2008 in the Entiat River below the Mad River confluence. The measured trend in biomass was consistent with the hypothesized correlation between pH and periphyton productivity. At both the Entiat and Mad River gages, measured periphyton biomass was at a maximum in the spring before the annual snowmelt-generated peak flow and at a minimum in July following the peak discharge and related scouring of periphyton. By the fall, biomass appeared to be recovering from the effects of spring runoff scour (table 5). At the Ardenvoir gage, periphyton biomass was not measurably affected by the spring high flow. Biomass at Ardenvoir may have been too low initially to be effectively measured by this method (table 5). Sample sizes in this reconnaissance survey were insufficient for inferential statistical analysis, so no firm conclusions can be drawn from the data collected to date.

**Table 5—Mean (n=5) and standard deviation of periphyton ash-free dry mass**

Gage		29 April 2008	16 July 2008	1 October 2008
		<i>mg/cm<sup>2</sup></i>		
Entiat	Mean	0.34 (n=4)	0.09	0.20
	SD	0.19	0.07	0.27
Mad	Mean	0.13 (n=4)	0.06	0.09
	SD	0.07	0.02	0.07
Ardenvoir	Mean	0.08	0.08	0.05
	SD	0.03	0.07	0.03

## Water Temperature

In both 2007 and 2008, water temperature began rapidly increasing during the receding limb of the annual snowmelt hydrograph. Instantaneous maxima occurred during the period July–September, and the highest mean monthly and mean daily temperatures occurred in July and August (table 4, fig. 8). Overall, the highest temperatures were measured at the Entiat gage, where instantaneous values exceeded 20 °C in both years and mean daily temperatures exceeded 20 °C in 2008 (fig. 8). Temperature at the Ardenvoir gage tended to be similar to that at the Mad River gage, although the rapid summertime temperature increase began earlier in the Mad River. In the summer and early fall, instantaneous maxima varied between 15 and 20 °C at both locations. At all sites, temperatures began to decrease in late August or early September, and fell to nearly 0 °C by December. Temperature was consistently lowest at North Fork, the farthest upstream gage (table 4, fig. 8).

## Dissolved Oxygen

Dissolved oxygen concentration is inversely related to water temperature. Accordingly, at all measurement sites the lowest concentrations were measured during the period from July through September, the months with highest water temperature and high biologic respiration. Instantaneous concentrations below 8 mg/L were unusual and were measured only at the Entiat gage. At all other sites, the instantaneous minima were between 8 and 9 mg/L, although values less than 9 mg/L were rare at the North Fork gage. Maximum instantaneous concentrations were between 13.5 and 15 mg/L at all sites. These occurred during the period from late October through April, coinciding with low water temperatures.

Mean daily DO less than 9 mg/L was unusual, but occurred at all sites other than the North Fork gage during the 2007–2008 period (fig. 9). At the Entiat gage, mean daily DO very briefly dropped below 8 mg/L in August 2008. Mean daily DO concentration, expressed in percentage of saturation, remained high throughout

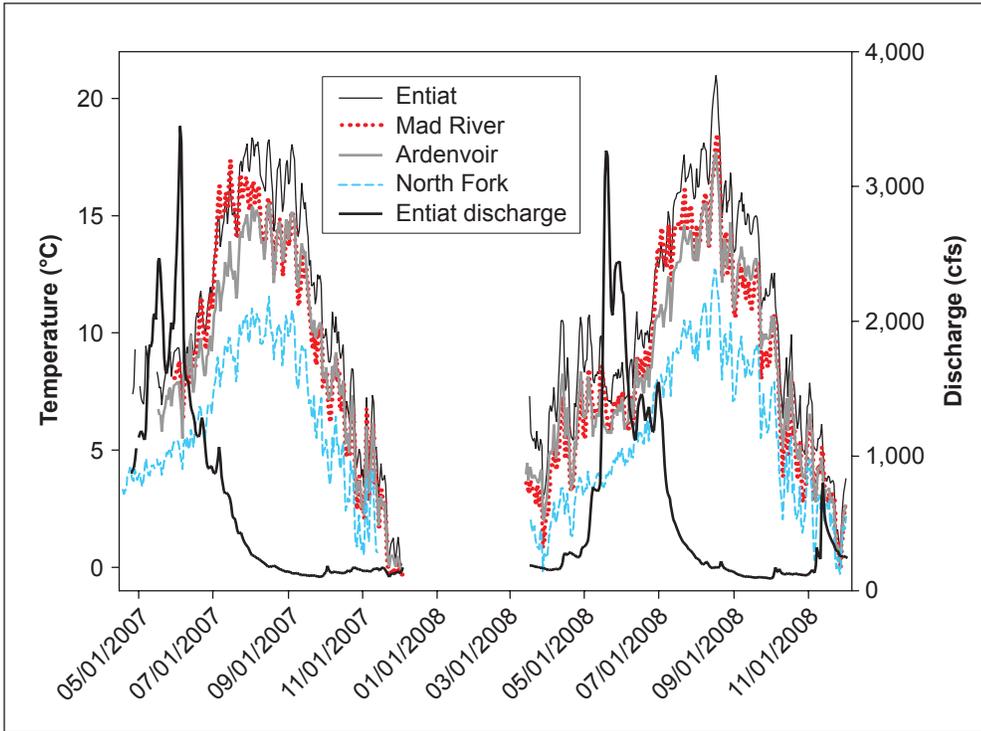


Figure 8—Mean daily water temperature.

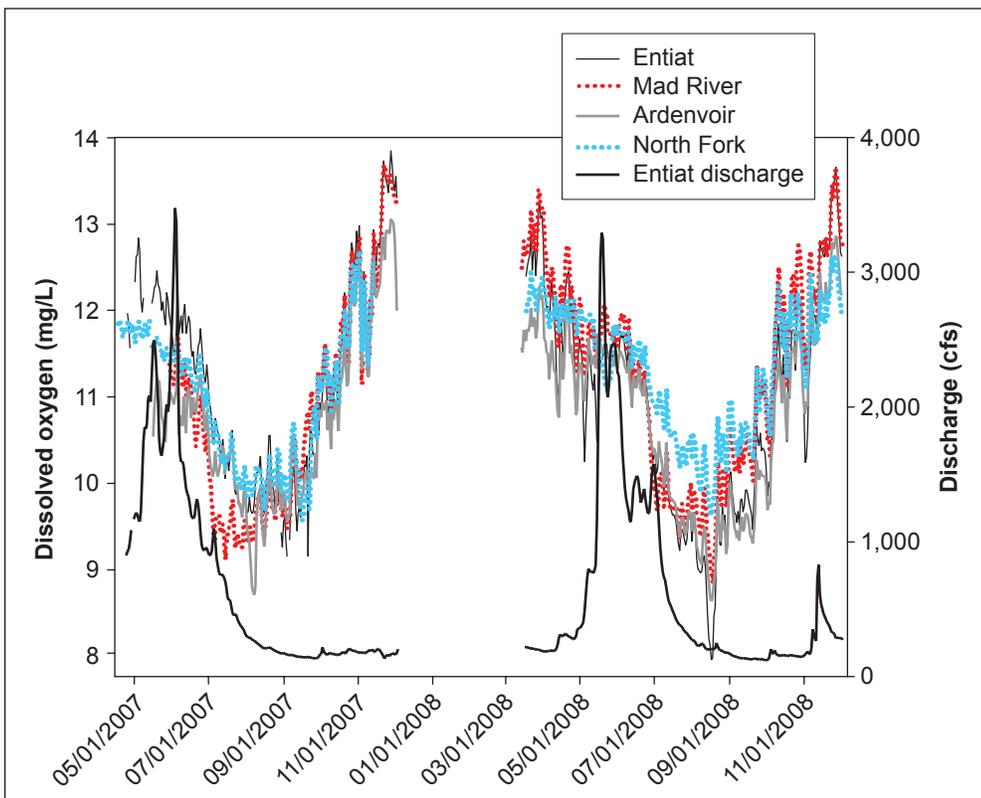


Figure 9—Mean daily dissolved oxygen.

the data collection period, never falling below 87 percent at any of the sites. Values less than 93 percent were unusual, occurring only a few days each year at all sites except the Mad River gage, where the lowest measurement was 95 percent.

### Specific Conductivity

As with pH, specific conductivity (SC) decreased sharply during the annual snowmelt-generated high-flow period. Accordingly, the lowest instantaneous and mean monthly values occurred in May and June at all sites (table 4). Highest instantaneous SC occurred in the Mad River, where values approached 160  $\mu\text{S}/\text{cm}$  in both 2007 and 2008. These values reflect high SC in Tillicum Creek, which joins the Mad River at RM 2.4. During the September 2008 reconnaissance surveys described previously, SC was measured as 156 and 89  $\mu\text{S}/\text{cm}$  in Tillicum Creek and at the Mad River gage respectively. At the Entiat gage, instantaneous and mean daily specific conductivities were somewhat lower than at the Mad River gage, but were otherwise similar (fig. 10). Instantaneous and mean daily specific conductivities at the Ardenvoir and North Fork gages were markedly lower than at the Mad and Entiat gages. Daily means rarely exceeded 60  $\mu\text{S}/\text{cm}$  at Ardenvoir or 50  $\mu\text{S}/\text{cm}$  at North Fork (fig. 10).

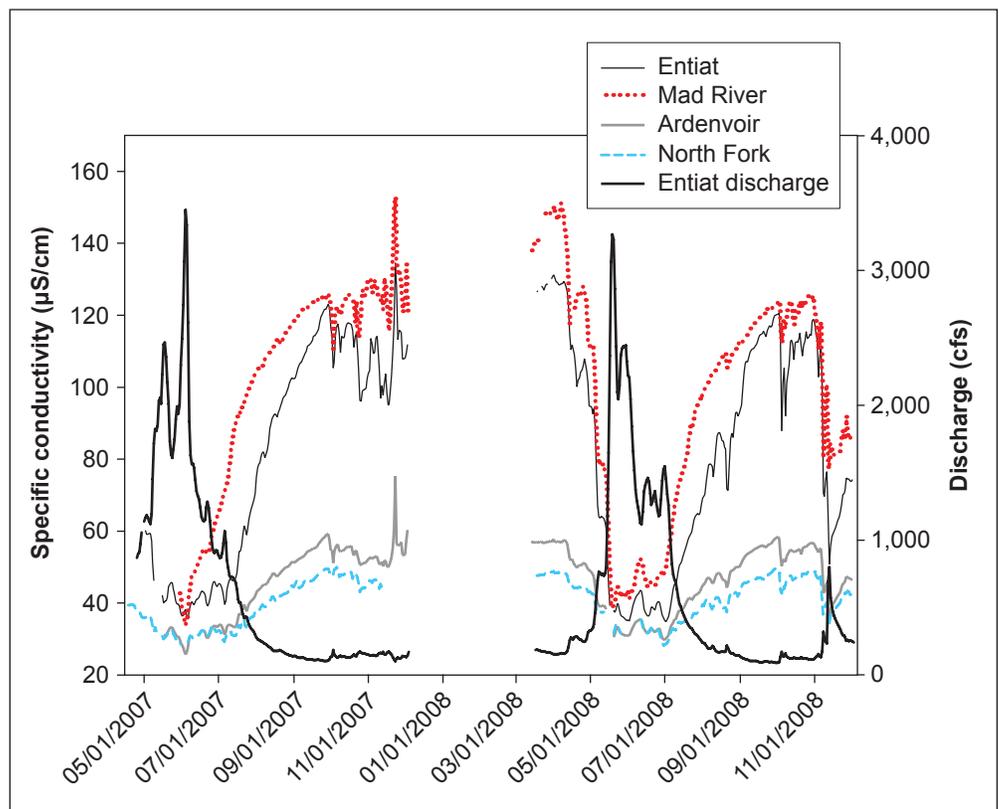


Figure 10—Mean daily specific conductivity.

## Discussion

### pH

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 biological processes (Hem 1985). Evaluation of the relative influence of these factors on observed pH is beyond the scope of this study; however, some observations may help guide future investigations. During daylight hours, periphyton photosynthesis removes carbon dioxide from river water, leaving free hydroxyl ions ( $\text{OH}^-$ ) to combine with hydrogen, thereby reducing the concentration of free hydrogen ions ( $\text{H}^+$ ) 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). Periphyton photosynthesis has been suggested as a possible cause of elevated pH in the Entiat River, where large diurnal variation in the summer may result from increased sunlight (increased photosynthesis) (CCCD 2004).

Land use effects that can stimulate periphyton productivity include enrichment in nutrients, such as nitrogen and phosphorus. 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 groundwater through infiltration of precipitation and 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 include control of contaminant sources and enhancement of nitrogen-fixing riparian vegetation. Periphyton biomass can 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). Invertebrate grazing is another important control of periphyton that interacts with nutrient availability in complex ways. Therefore, control of insecticide contamination and maintenance of high-quality invertebrate habitat can be important methods of limiting periphyton biomass (Fuhrer et al. 2004, Murphy 1998, 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 Freshwater Monitoring Unit's monthly sampling program at the Entiat gage (WDOE 2009). Concentrations of ammonia-nitrogen, nitrate-nitrogen, total nitrogen, orthophosphate, and total phosphorus measured from October

2006 through December 2008 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 2009).

Periphyton biomass can respond strongly to small concentrations of nutrients, depending on water temperature and velocity, solar radiation, invertebrate grazing, and other factors; therefore, streams with low phosphorus concentrations can be very sensitive to enrichment (Murphy 1998, Welch et al. 1998). Concentrations of total phosphorus as low as 0.005 mg/L can cause excessive algal growth (McCutcheon et al. 1993, Murphy 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 2009). Therefore, despite relatively low measured nutrient concentrations, further investigations will be required to fully assess the effects of nutrients on periphyton productivity and pH in the Entiat subbasin.

Geology can be an important factor influencing river pH. In the Entiat valley, accumulation of till, glacial outwash, and other alluvium creates a valley-bottom aquifer (Dixon 2003). This aquifer creates a setting for shallow groundwater to interact chemically with the large mineral surface area present in fragmented till and outwash. Newton et al. (1987) found that groundwater pH increased substantially after exposure to a similar geologic setting in the Adirondack Mountains. In the Mad River valley, no till is mapped farther down valley than approximately RM 20 (Dragovich et al. 2002, Tabor et al. 1987). However, Faux and Archibald (2002) noted deep glacial till in the Mad River valley bottom as far down river as Cougar Creek (approximately RM 15). This lower elevation limit of till distribution approximately coincides with the marked decline in rate of pH increase we measured from RM 15.0 to RM 12.5 (fig. 7). These and other geologic characteristics of the Entiat subbasin may warrant further investigation with respect to effects on pH, although future studies would need to consider confounding land use effects.

Bedrock characteristics in the Entiat subbasin may provide other opportunities for enhanced chemical interactions with groundwater that affect pH. These characteristics include 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 storage zones and groundwater 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 groundwater may be enhanced, potentially affecting pH. The spatial scale of our data collection did not reveal consistent relations between pH and subbasin geology as currently mapped. Possible effects of geology on water quality will remain hypothetical until more detailed investigations are done.

Wildfire is one of the major disturbance processes affecting the Entiat subbasin; however, consistent relations between mapped fire intensity (USDA FS 2009) and river pH are not apparent. For example, in the Mad River, rapid increase in pH from RM 12.5 to 9.0 correlates with a zone of high-intensity 1994 wildfire on the west side of the valley. However, similar correlations elsewhere in the subbasin are lacking. For example in the Entiat valley, areas of high and moderate 1994 fire intensity have no apparent effect on river pH between the North Fork gage and RM 16.8.

Wildfire, geology, soils, periphyton photosynthesis, and land use effects, both current and historical, all play a role in river pH in the Entiat subbasin. A thorough examination of the contribution of each of these factors will require additional investigations beginning with more detailed surveys to identify specific sources of high- or low-pH water. In addition, more intensive measurements of periphyton biomass would allow more conclusive testing of linkages to river pH. For example, analyses of chlorophyll-a dry mass in periphyton samples would further refine determination of functional algal biomass (McCutcheon et al. 1993, Steinman and Lamberti 1996). Similarly, more detailed measurements of the spatial and temporal distribution of nutrients would help define controls on periphyton productivity.

This report summarizes results from the first 2 years of a trial approach to subbasin-scale status and trend monitoring of fundamental water quality parameters important to salmon recovery in the ICRB. This approach has clear advantages over the commonly employed federal Clean Water Act compliance monitoring, which is generally conducted at much lower spatial and temporal intensity. Spatially distributed measurements at points that integrate critical drainage areas within the subbasin allow inferences to be made regarding the source and distribution of water quality extremes. This allows investigators to efficiently locate more intensive measurement programs that may be needed. 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 temporal intensity of measurement can be a great aid in identifying potential causes and mechanisms of problems and relationships to other factors such as river discharge, temperature, solar exposure, or seasonality. This study further demonstrates that water quality monitoring of this intensity is logistically and economically feasible as part of the broader salmon recovery monitoring program in the ICRB.

## Acknowledgments

This study was jointly funded by (1) The Bonneville Power Administration, Division of Environment, Fish, and Wildlife, Project number 2003-017-00, through the NOAA–Fisheries, Integrated Status and Effectiveness Monitoring Program and (2) the USDA, Forest Service, Pacific Northwest Research Station. The manuscript was improved by insightful reviews from P. Archibald, P. Bisson, and S. Wondzell.

## English Equivalents

When you know:	Multiply by:	To find:
Centimeters (cm)	0.394	Inches
Square centimeters (cm <sup>2</sup> )	0.155	Square inches
Kilometers (km)	0.6214	Miles
Square kilometers (km <sup>2</sup> )	0.3861	Square miles
Milligrams (mg)	$3.527 \times 10^{-5}$	Ounces
Milligrams per square centimeter (mg/cm <sup>2</sup> )	0.000228	Ounces per square inch
Milligrams per liter (mg/L)	0.0010	Ounces per cubic foot
Liters (L)	0.0353	Cubic feet
Cubic meters per second (m <sup>3</sup> /s)	35.315	Cubic feet per second
Siemens or mhos	1.0000	1/ohm
MicroSiemens per centimeter (μS/cm)	2.5400	Micromhos per inch
Degrees Celsius	(1.8 °C) + 32	Degrees Fahrenheit

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