Conducted in Cooperation with the Cities of Boise, Meridian, Nampa, and Caldwell, Idaho

Diel Fluctuations in Nutrients and Continuously-Monitored Parameters in Two Idaho Rivers

Andrew W. Tranmer and Molly S. Wood

Introduction

The U.S. Geological Survey (USGS) initiated a multi-year, water-quality monitoring effort in 2008 to evaluate nutrient inputs from the Boise River to the lower Snake River ecosystem and hydropower reservoirs. The Boise River is influenced both by recent urbanization in the Boise metropolitan area and by long-standing agricultural use in the lower part of the watershed. The Owyhee River, an agricultural basin, also enters the Snake River between Adrian and Nyssa, OR but it was not characterized in this study. In August 2009, the USGS conducted 24-hour sampling on the Snake and Boise Rivers to better understand diel variability in nutrient and chlorophyll-a concentrations and continuously-monitored parameters. Diel fluctuations in water-quality parameters may be significant in this environment because of algal growth and associated nutrient uptake, as well as irregular inflows from agricultural and municipal sources. As a result, discrete measurements may not adequately represent the range of conditions in the streams, particularly extreme values.

Figure 1. Site Photo (Parma) and Study Area Map

Methods

Samples were collected over three 24-hour periods in August 2009 at three locations near the Boise River/Snake River confluence [Boise River near Parma, ID; Snake River near Adrian, OR (7 mi upstream); Snake River at Nyssa, OR (9 mi downstream)] (figure 1). Each sampling event took place from noon one day until noon the following day. Manually-collected samples and automated measurements were analyzed to determine if current sampling techniques are adequate to evaluate compliance with water-quality standards. Light meter readings were used to define day hours (12:00-20:59 and 7:00-12:59) and night hours (21:00-6:59).

A significant change in discharge occurred over the course of the study, making flow adjustment necessary for all analyzed constituents, hereafter referred to as "flow-adjusted" concentrations (methods described in Helsel and Hirsch, 1992; MacCoy, 2004). Comparisons among nutrients and chlorophyll-a were made using the dissolved nutrient concentrations to avoid possible autocorrelation due to nutrient concentrations contained within algal cells. Statistical comparisons were made using parametric t-tests and non-parametric Mann-Whitney hypothesis tests to detect differences in means or medians. As used herein, the term "significant" denotes that the comparison was statistically significant at a level of α=0.05.

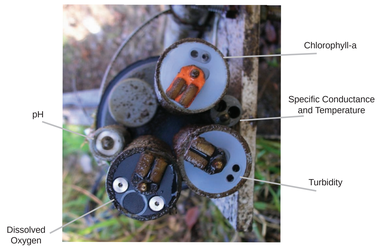

Figure 2. Continuous Water-quality Monitor Sensors

Manual samples were collected hourly using the equal-width-increment method (U.S. Geological Survey, 2006) from a bridge (DH-95 sampler) or by wading (DH-81 sampler) and were analyzed for:

- Chlorophyll-a
- Total phosphorus
- Dissolved orthophosphate as phosphorus
- Total nitrogen
- Dissolved ammonia
- Dissolved nitrite-plus-nitrate as nitrogen

Automated measurements were taken every 15 minutes from permanently-deployed, multiparameter water-quality monitors (figure 2), which recorded:

- Water temperature
- pH
- Dissolved oxygen
- Specific conductance
- Turbidity
- Chlorophyll-a fluorescence (as a surrogate for algae)

Conclusion

The study confirms that diel variation exists in the current sampling program. These significant differences make it difficult to evaluate compliance of water-quality standards for these river systems. Some built-in sampling variability may be required for the application of such standards. The diel fluctuations observed support the need for the use of automated, continuous monitors to capture timing and scale of parameters that exhibit diel fluctuations. Given site specific characteristics, a rating curve, developed using the data from the continuous water-quality monitors and samples, could be used for compliance monitoring. This may provide greater accuracy than a stochastic approach. Additionally, the monitors may be used in conjunction with automatic point samplers that respond to spikes in specific parameters, such as chlorophyll-a fluorescence, for a better understanding of pulse inputs and short-term responses within the system.

Results and Analysis

Diel fluctuations were significant for some parameters over the course of the study. Table 1 shows the parameters that were analyzed, with shaded cells representing those which were significantly higher between day and night. Nyssa, the downstream site, showed a greater number of significant diel fluctuations in measured parameters than the other sites. Correlations among nutrient and chlorophyll-a (manual samples and monitor measurements) concentrations indicate similar and dissimilar conditions exist in the two river systems (table 2). During the study, the Boise River contributed only 11 percent of the discharge in the Snake River at the confluence, yet contained median total nitrogen and total phosphorus concentrations that were more than two and six times, respectively, those in the Snake River near Adrian. This resulted in significantly higher nutrient concentrations in the Snake River at Nyssa than near Adrian.

Table 1. Median Diel Values — 6.23 Significantly Different Parameters (α=0.05)

	Parma		Adrian		Nyssa	
	Day	Night	Day	Night	Day	Night
Nitrate-plus-Nitrite as Nitrogen (mg/L)	**1.74**	1.70	0.57	0.58	**0.73**	0.72
Total Nitrogen (mg/L)	2.24	2.18	0.99	0.98	**1.22**	1.13
Orthophosphate as Phosphorus (mg/L)	0.24	0.24	0.02	0.01	0.04	0.04
Total Phosphorus (mg/L)	0.30	0.30	0.04	0.05	**0.08**	0.07
Chlorophyll-a (µg/L)	**9.75**	8.54	**12.74**	11.40	**13.07**	8.25
Chlorophyll-a Fluorescence (µg/L) [monitor]	9.63	9.78	**10.32**	9.10	**16.71**	11.77
Water Temperature (°C) [monitor]	20.28	**21.05**	21.91	21.79	23.34	**23.97**
Dissolved Oxygen (% sat) [monitor]	95.49	94.88	142.99	139.95	131.13	**144.12**
pH [monitor]	8.07	8.08	8.80	8.83	8.67	**8.76**
Turbidity (FNU) [monitor]	17.13	17.22	**5.75**	5.36	**8.05**	6.85

Water and air temperature

The Parma and Nyssa sites both had significantly lower water temperatures during the day than the night (table 1), indicating that the Boise and Snake Rivers were sensitive to diel temperature changes upstream of the study sites. The temperature signature at Adrian appears similar to but more muted than Nyssa (figure 3), but the differences between day and night water temperatures were not statistically significant. The lag between peak ambient air temperature and peak water temperature was 5 hours at Parma and 2-3 hours at Adrian and Nyssa. The timing of the maximum and minimum water temperatures indicates similar environmental drivers in the region with the difference between the upstream site on the Snake River (Adrian) and the downstream site (Nyssa) dependent upon ambient conditions and tributary inputs. Shallow tributaries, like the Boise and Owyhee Rivers, have greater diel swings that act to alter the temperature of the receiving water body and complicate the timing of the ambient driver.

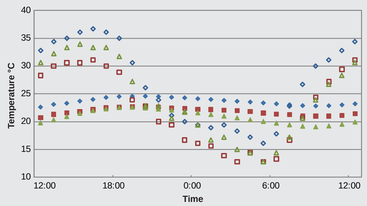

Figure 3. Diel Fluctuation of Ambient and Water Temperature

Dissolved oxygen and pH

Percent saturation of dissolved oxygen in the Snake River system fluctuated between 102% and 176%, never dropping below 100% throughout the diel cycle (figure 4). The Boise River near Parma had a narrower range of fluctuation between 78% to 128% saturation. The overall greater range in dissolved oxygen values in the Snake River system implies greater productivity of phytoplankton than in the Boise River near Parma. With high levels of soluble nutrients and moderate dissolved oxygen production, it is hypothesized that phytoplankton growth in the Boise River is limited by factors other than nutrient availability alone, and that there is a net export of underutilized nutrients to the Snake River.

The pH values do not follow traditional response trends to algal productivity in these well-buffered systems and show little fluctuation over the diel cycle. Hence, pH seems to be affected by factors other than photosynthetic activity.

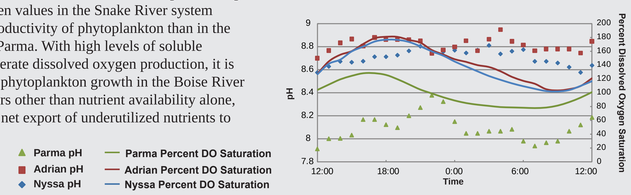

Figure 4. Diel Fluctuations of pH and Percent Dissolved Oxygen Saturation

Chlorophyll-a

Manually-collected samples showed chlorophyll-a concentrations were significantly higher during the day at all three sites. Chlorophyll-a fluorescence measurements taken by the multiparameter water-quality monitors showed significantly higher daytime values at Nyssa and Adrian and no significant difference at Parma. Elevated daytime chlorophyll-a concentrations imply algal growth and the system's associated response.

The Snake River at Nyssa, with respect to flow-adjusted chlorophyll-a concentrations, showed signs of influence from both the Snake River upstream at Adrian and the Boise River near Parma. No significant difference was detected between chlorophyll-a concentrations (manual samples) at the Nyssa and Parma sites during the study despite a much larger range of values in the Snake River [5.7-20.9 (µg/L)] than in the Boise River [6.1-11.9 (µg/L)]. Significantly greater chlorophyll-a concentrations were measured at Adrian than at Nyssa during the night period only and at Parma for both day and night periods.

Figure 5 shows a comparison of the flow-adjusted chlorophyll-a concentrations (manual samples) for all three sites. Concentrations at Nyssa follow a strong diel pattern, while those at Adrian and Parma are more muted. The Snake River acts as a lentic environment with respect to how it responds to nutrients and algal communities (Leland and others, 2001). The slow, deep flow of the Snake River lends itself to phytoplankton production within the water column, whereas the shallow pool-riffle sequences of the lower Boise River characterize an environment prone to domination by periphyton and benthic communities.

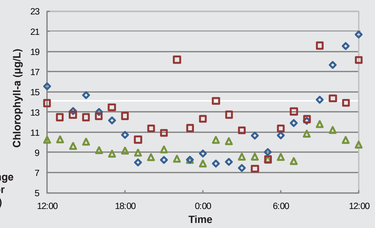

Figure 5. Flow-adjusted Chlorophyll-a (manually collected samples)

Nutrient/Chlorophyll relationship

Given the importance of dissolved nutrients to algal production, diel relations between nutrients and chlorophyll-a were examined at each site. Over the course of the study, all three sites had significant diel changes in chlorophyll-a concentrations, whereas none of the sites displayed a significant diel change in orthophosphate. Nitrite-plus-nitrate concentrations at Adrian do not significantly fluctuate over the course of 24 hours, whereas concentrations at Nyssa and Parma were greater during the day and followed a similar trend as chlorophyll-a. Orthophosphate is negatively correlated with chlorophyll-a values in the Snake River (table 2), which suggests uptake by algae. However, there were no statistically significant diel patterns in orthophosphate to correspond with diel patterns in chlorophyll-a, suggesting an overabundance of nutrients at each site. Positively-correlated diel patterns in nitrite-plus-nitrate and chlorophyll-a are probably a coincidence rather than a cause-and-effect relation. Thus, diel patterns in chlorophyll-a at these sites appear to be driven more by factors other than nutrient availability.

Table 2. Correlation Coefficients for Flow-Adjusted Chlorophyll-a Concentrations and Soluble Nutrients

	Parma		Adrian		Nyssa	
	Sample	Monitor	Sample	Monitor	Sample	Monitor
Nitrate-plus-Nitrite	0.75	-0.33	0.22	0.15	0.82	0.66
Orthophosphate	0.22	-0.59	-0.29	-0.43	-0.26	-0.25

Light availability

Turbidity, a surrogate for water clarity, was lower and more evenly distributed throughout the water column at Adrian than at Nyssa. As a result, algae may have been more vertically stratified at Nyssa, which may not be well-characterized by the sampling methodology or the deployment location of the water-quality monitor. Turbidity data follow a pattern similar to chlorophyll-a fluorescence at both Adrian and Nyssa. Because the turbidity probe measures scattering of light by any particulate matter, the presence of algae likely affects this measurement. Underwater monitoring of photosynthetically-active radiation light as well as the collection of suspended sediment samples may be a more appropriate means for measuring changes in light availability in the water column.

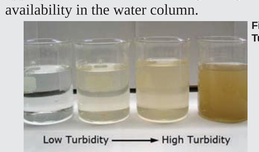

Figure 6. Turbidity Samples

Photo courtes of Fondriest Environmental: http://www.fondriest.com/science_library/turbidity.htm

To Learn More:

Andrew W. Tranmer, atranmer@usgs.gov, 208-387-1342, USGS Idaho Water Science Center
Molly S, Wood, mswood@usgs.gov, 208-387-1320, USGS Idaho Water Science Center

U.S. Department of the Interior
U.S. Geological Survey

References:

Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources: U.S. Geological Survey, Studies in Environmental Science, v. 49, 522 p.

Leland, H.V., L.R. Brown, and D.K. Mueller, 2001. Distribution of algae in the San Joaquin River, California, in relation to nutrient supply, salinity and other environmental factors. Freshwater Biology, 46, 1139-1167.

MacCoy, D.E., 2004, Water-Quality and Biological Conditions in the Lower Boise River, Ada and Canyon Counties, Idaho, 1994–2002: U.S. Geological Survey Scientific Investigations Report 2004–5128, 80 p.

U.S. Geological Survey, 2006, Collection of water samples (ver. 2.0), U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, September, accessed December 1, 2009, at http://pubs.water.usgs.gov/twri9A4/.

Idaho Department of Environmental Quality, 2004, Snake River – Hells Canyon Total Maximum Daily Load (TMDL), accessed Mar 24, 2010 at URL: http://www.deq.state.id.us/WATER/data_reports/surface_water/tmdls/snake_river_hells_canyon/snake_river_hells_canyon.cfm

April 2010