A Comparison of Water Quality Data Collected from Two Washington Rivers by the Department of Ecology and the U.S. Geological Survey

Abstract

Results collected by integrated sampling (U.S. Geological Survey, USGS) and by single grab sampling (Washington State Department of Ecology, Ecology) were compared at two stations, the Palouse River at Hooper and the Yakima River at Kiona. About 10 years of matching (same year and month) data exist at each station for each monitoring program. The purpose of this analysis is to compare these two independent data sets.

In general, single point grab samples provided results similar to the more intensive and expensive integrated sampling method for the Palouse and Yakima rivers when comparing concentrations of water quality constituents. Sampling methodology should not significantly affect conclusions based on concentrations at these stations. However, for sediment and total phosphorus, loads (concentration times discharge) calculated from grab sample results were much lower than loads calculated from integrated sampling results. This significantly low bias could lead to incorrect conclusions. If grab sample data are used to determine loads, the analyst should fully understand the potential limitations of this sampling method.

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Introduction

Prior to about October 1981, Ecology monitored water quality in Washington cooperatively with USGS. In the late 1970's, however, USGS began encouraging its cooperators to use integrated sampling methods to collect samples. Typically, integrated sampling requires that an isokinetic depth-integrating sampler (stream water approaching and entering the sampler intake does not change in velocity) be lowered through the water column, usually at 10 or more increments across the stream width. The device continuously collects water at a rate proportional to the stream flow. This technique provides more accurate average cross-sectional estimates of constituent concentrations for constituents that are not homogeneously distributed throughout the water column (sediment and total phosphorus (TP), in particular). However, there are significant practical disadvantages to this methodology compared to the single grab sample method used by Ecology. These include double the required staffing levels, much longer on-station times, and inability to collect samples at stations without safe bridge access or cableways. Ecology concluded that for our objectives the potentially improved accuracy for certain constituents did not justify the increased expense (or reduction in the number of stations sampled), and the cooperative program ended. (Current USGS procedures allow non-isokinetic sampling techniques, such as grab sampling, under certain conditions. Even then, however, the field manual states that these procedures "have limited value for collecting samples used to calculate constituent discharge" (US Geological Survey, variously dated).)

Several authors have studied the difference between grab and integrated sampling. Ging (2003) concluded that there was no significant difference at her sites except for TP, dissolved calcium, and dissolved organic carbon, though her samples sizes were very low. Lietz (1999), who also worked with relatively small sample sizes, found no difference in total nitrogen results, but concluded that "depth-integrated samples probably provide a more realistic representation of TP…than do point samples." Martin (1992) found that, of the nutrients, only TP "clearly differed between the sampling methods." Kammerer (1998), on the other hand, found no difference among monitoring programs for TP, though there were differences among monitoring programs for dissolved orthophosphate and sediment. Kammerer concluded, however, that "lab differences in general appeared to be more significant and important than sample collection methods." Yake (1979) reported that in Washington, vertical and cross-sectional variability (which is what integrated sampling techniques "integrate") was low compared to temporal and between-station variability based on the limited data available at the time. (The raw data from this analysis are available, but the analysis itself has either been lost or was never formally documented.) Except for Yake's analysis, the difference between USGS's and Ecology's monitoring programs has never been formally assessed.

An integrated sample is assumed to be both less biased and more precise than a grab sample. If the constituent being measured is horizontally or vertically stratified, as sediment and associated TP are presumed to be especially under high-flow conditions, concentrations in a near surface grab sample will be lower than in a depth-integrated sample. This bias can be significant (Leitz 1999, Kammerer 1998, and Martin 1992) and could preclude grab sample data from being used to accurately calculate annual loads of these constituents. The effect of a stratification-related bias on trend analyses is less clear, however, and may depend in part on whether the trend is occurring predominantly in the surface portion of the stratified constituent or at depth. For example, a surface grab sample may detect a trend in fine particulates sooner than would an integrated sample where the contribution of finer particulates may be overwhelmed by the heavier particles collected from deeper in the water column. Conversely, a surface grab might entirely miss trends in heavier particulates. Either sampling technique could be used for trend analysis if there is a constant bias for the period of interest.

While bias may or may not be critical depending on whether the aim of the monitoring is load estimation or trend analysis, it is always important to minimize variance. That is, the variability within a multi-year data set after accounting for variability due to explainable sources such as trends, flow, and seasonality, must be kept as small as possible. For load estimates where concentration may be estimated for unsampled time periods based on an empirical relationship with flow, the greater the unexplained variability, the wider the confidence interval about the load estimate. For trend detection, the magnitude of the trend slope that can be detected is directly proportional to the square root of the unexplained variance (Smith, et al., 1989).

Assuming a constituent's distribution is patchy (not just vertically stratified, which would not contribute variance in consistently collected samples, whichever method is used), which sampling technique will exhibit greater variability is difficult to conceptualize and will depend on how the patchiness is distributed within the stream and therefore on the particular stream and flow conditions. Depth integration, which collects a weighted average sample that integrates the patchiness in vertical, horizontal, and, because the cross section cannot be sampled instantaneously, longitudinal dimensions should be less variable if the "patchiness" is distributed equally throughout all dimensions. But it is easy to imagine greater patchiness near the bottom of a stratified river, where swirls and eddies caused by bottom obstructions are more likely to affect concentrations near the bottom than at the surface. In this case, a surface grab sample may be less variable.

This paper presents the results of a comparison of central tendency and dispersion between samples collected by USGS using depth-integrated techniques and Ecology's program using grab sampling. However, different sampling schedules, field processing, and laboratories were also used so differences may not be entirely due to the collection method. Further investigation is required to identify why differences may have occurred.

Methods

Water quality monitoring data were obtained from USGS for Washington State from their "Surface Water Data for Washington" web site http://waterdata.usgs.gov/wa/nwis/sw for nine stations where Ecology has also collected monitoring data. These data were matched to Ecology data by year/month of collection and by constituent and filtered as follows:

1) Data prior to October 1981 were deleted.
2) Data not representing at least four samples in a given water year (WY; October through September) were removed.
3) Data from months and constituents not sampled in common were removed.
4) Replicate samples were deleted from the USGS data set ("samp_type_cd"=7) unless no other USGS data were available in the month.
5) For USGS data, only Equal Width Increment (EWI) or Equal Discharge Increment (EDI)-collected sample data were retained.
6) For multiple USGS samples in a given month, only the result collected closest to the date of Ecology's sample was retained.

Satisfying the above criteria resulted in only two stations where Ecology and USGS have both been sampling for the same constituents during the same months: Palouse River at Hooper ("Hooper"; Ecology station 34A070) and Yakima at Kiona ("Kiona"; Ecology station 37A90) (Table 1).

Table 1. Constituents sampled in common by Ecology and USGS monitoring programs and evaluated in this report. The number of paired samples (samples collected in the same year and month) is also shown.

	34A070	37A090
Date Range:	Dec 1992-Sep 2002	Sep 1982-Sep 1994; May 1999-Sep 2002
Total paired data points	823	1094
Total co-sampled months	107	123
Constituent	No. of Pairs	No. of Pairs
Conductivity	104	121
Ammonia-nitrogen	0 [a]	45
Nitrite, dissolved	9 [a]	31 [a]
Nitrate+nitrite	0 [a]	13 [a]
Soluble reactive P, dissolved	105	118
Oxygen, dissolved	105	101
PH	105	120
Suspended solids/sediment	107	118
Temperature	105	123
Phosphorus, total	75	95
Turbidity	1 [a]	89

[a] Insufficient numbers of pairs for further analysis.

Differences in field and lab procedures between Ecology and USGS may affect results for some constituents. Ecology analyzed sediment samples using the total suspended solids method (TSS; SM2540D (APHA, 1998)), which weighs a filtered aliquot from the grab sample. USGS uses the suspended sediment concentration method (SSC; ASTM D 3977-97 (ASTM, 1999)) which uses the entire sample submitted to the lab. The latter method has been shown to return higher concentrations than the TSS method (Gray, et. al., 2000). USGS dissolved oxygen and temperature results were from point samples, not from the integrated sample. Other USGS field measurements (pH and conductivity), however, usually were from an aliquot taken by processing the integrated sample through a churn splitter (Smith, pers. comm.). Ecology methods are specified in Hallock (2003) and Hallock and Ehinger (2003). Ecology's field protocols are detailed in Ward (2002). USGS methods are described in U.S. Geological Survey (variously dated).

Although samples collected in the same year and month have been "paired" to establish comparable data sets and some paired-sample statistics have been used, most analyses are not based on paired-samples; the analyses are intended to address the respective datasets as a whole, not differences between sample pairs.

WQHydro (Aroner, 2002) was used for plotting and statistical analyses. The central tendencies of results collected by the two monitoring programs were compared using the Hodges-Lehman estimator (of central tendency) and the paired Wilcoxon signed rank test (to test for significance). The Klotz (normal scores) test was used to evaluate the equality of variances, an assumption of the Wilcoxon test. If this assumption proved false, the Anderson-Darling test was used to assess equality of central tendency. The Wilcoxon test was used rather than the parametric t-test because it does not have an assumption of normality, and it is nearly as powerful as the t-test even when the normality assumption is valid (Aroner, 2002). Quantile-quantile plots are used to further explore the relationships between monitoring programs for some constituents. The quantile-quantile plot compares USGS and Ecology results in rank-order (it does not plot "paired" samples). Trend analyses used the seasonal Kendall trend test.

The ability to detect trends depends on the unexplainable variability in the data, not on whether the central tendencies of the two sample methods are similar. A constant bias is irrelevant to trend detection. Variability was evaluated by comparing standard deviations. Seasonality and trends, which can increase variance in the data, were removed by deseasonalizing (and adding back the median) and detrending (using the Sen slope). Predicted minimum detectable trend (PredMDT) expressed as a percent of the mean was determined using equation 1 (Hallock, 2003).

$$\mathrm{Pr}\,edMDT = \frac{\mathrm{s_{obs}} * \delta}{\bar{x}} * \left(1 + \frac{\bar{x} - median}{\bar{x}}\right)^{-6} * 100\% \qquad 1)$$

where $\bar{x}$ is the mean, s_{obs} is the total standard deviation of the deseasonalized, detrended data, and δ is the "minimum relative detectable trend," which, for ten years of independent monthly data, $\alpha = 0.1$, and $\beta = 0.1$, is 0.932. The parenthetical component of equation 1 and its exponent is an empirically determined correction factor to adjust for non-normality of the data set (for its derivation, see Hallock, 2003).

Results and Discussion

Central Tendencies

On the whole, results from the two monitoring programs, Ecology and USGS, were remarkably similar with an overall difference for only a few water quality constituents (Figure 1 and Table 2). At Hooper, conductivities recorded by Ecology tended to be consistently lower than those recorded by USGS (Figure 2). There was a nearly constant offset (slope=1.02). The Hodges-Lehmann estimate of the median difference between the two datasets was 22 µS/cm. There were no obvious environmental reasons why this should be; side-by-side sampling may identify procedural causes.

During summer months, one might expect pH, temperature, and oxygen to be higher near the surface (and therefore higher in Ecology's near-surface grab samples), especially in nutrient rich, stratified streams. At Hooper, Ecology tended to record lower pH results overall (in Table 2 the "Δmedian" is positive) but during summer months, when flows and mixing are lowest; pH was, as expected, higher in the Ecology samples (Figure 3). Oxygen tended to be very similar to USGS results November through June, but summer oxygen concentrations were quite a bit higher in the Ecology data (by a median amount of 0.9 mg/L based on the Hodges-Lehmann estimator; Figure 4) even though both programs analyze oxygen from grab samples. One possible explanation for higher Ecology concentrations is that, on average, Ecology tended to sample later in the day at the Hooper station (Figure 5). This didn't seem to affect temperature, however, which was very similar in both datasets (Figure 6).

At Yakima at Kiona, there were no differences between paired Ecology and USGS data for pH, temperature, oxygen, or conductivity measurements (Table 2), though at the low end of the data range, Ecology oxygen measurements were lower than USGS's (Figure 7).

The sample site for the Palouse River at Hooper is at a deep pool below a bedrock riffle. At its lowest flows, the Palouse River becomes nearly stagnant and stratification of the pool is likely. The habitat type for the Yakima River at Kiona station is a "run". Because of this, and because low flows in the Yakima were many times higher than those in the Palouse (Figure 8), the Yakima is more likely to be mixed at low flows.

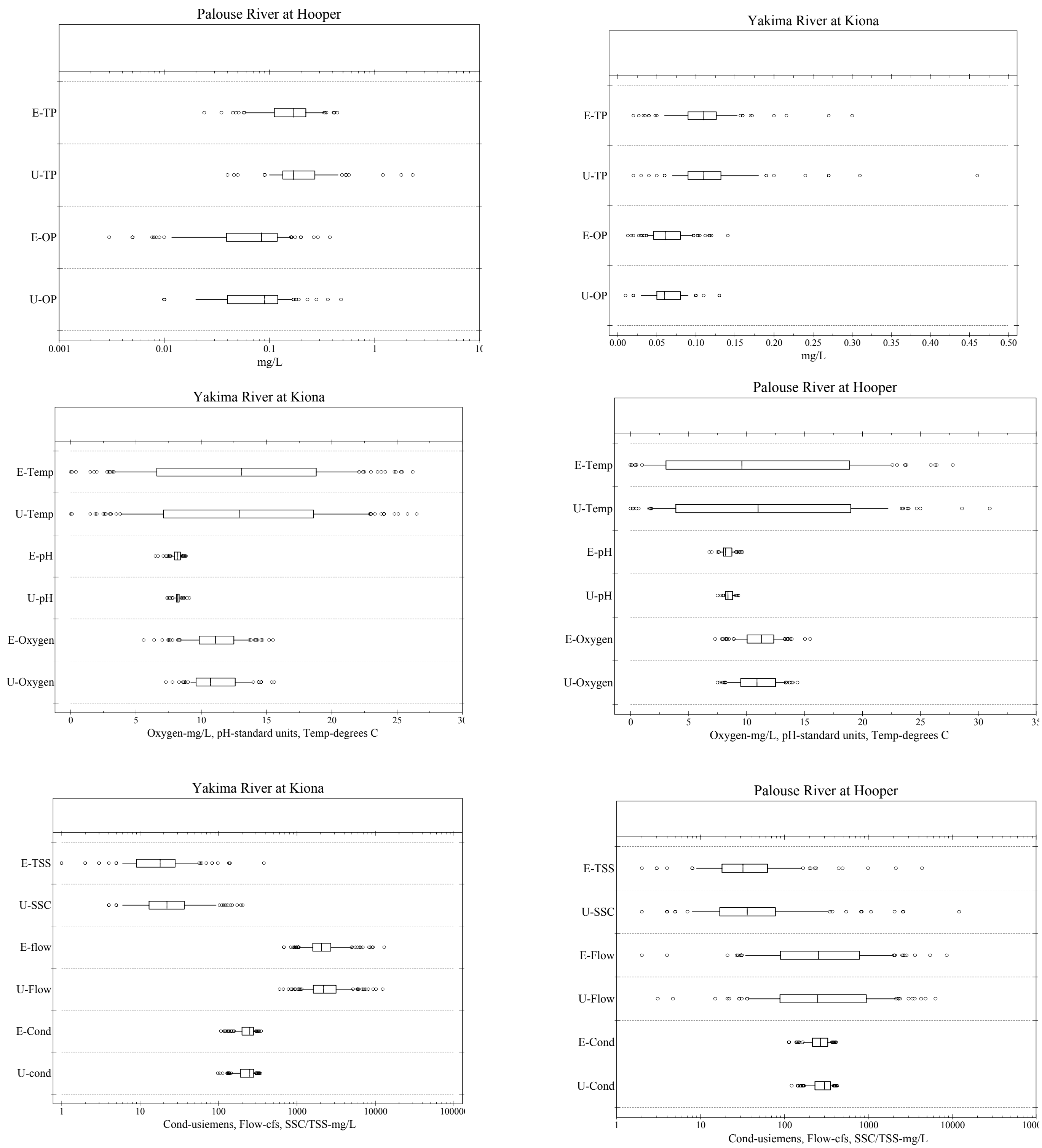


Figure 1. Horizontal box plots showing the distribution of Ecology (E-) and USGS (U-) data. Boxes enclose 50 percent of the data; the vertical bar within the box marks the median. Whiskers mark the 10th and 90th percentiles. Note that the last two graphs are plotted in logarithmic scale.

Table 2. Hodges-Lehman estimator of the difference in central tendency (Δmedian) between USGS- and Ecology-collected samples (USGS minus Ecology) and probability of significance based on the paired Wilcoxon signed rank test. (bold=significance <0.10)

	Palouse River at Hooper (34A070)			Yakima River at Kiona (37A090)		
Constituent	Δ Median	Sign.	Klotz Test	ΔMedian	Sign.	Klotz Test
Conductivity (µS/cm)	21	**<0.001**	0.93	1.0	0.721	0.74
Ammonia-nitrogen (mg/L)	Insuf. Data			0.0	0.551	0.12
Soluble reactive P (mg/L)	0.0043	0.123	0.42	-0.001	0.320	0.98
Oxygen (mg/L)	-0.20	**0.051**	0.26	0.0	0.930	0.75
pH (std. units)	0.125	**<0.001**	**<0.001** [a]	0.045	0.327	**0.007** [a]
Solids/sediment (mg/L)	2.0	0.328	**0.013** [a]	3.5	**0.004**	**0.02** [a]
Temperature (ºC)	0.45	**0.048**	0.91	0.30	0.219	0.93
Phosphorus, total (mg/L)	0.017	0.188	0.21	0.005	0.418	0.43
Turbidity (NTU)	Insuf. Data			0.30	0.603	**0.018** [a]

[a] Although the Klotz test indicates the Hodges-Lehman assumption of equal variance was violated, the Anderson-darling k-sample test yielded similar results.

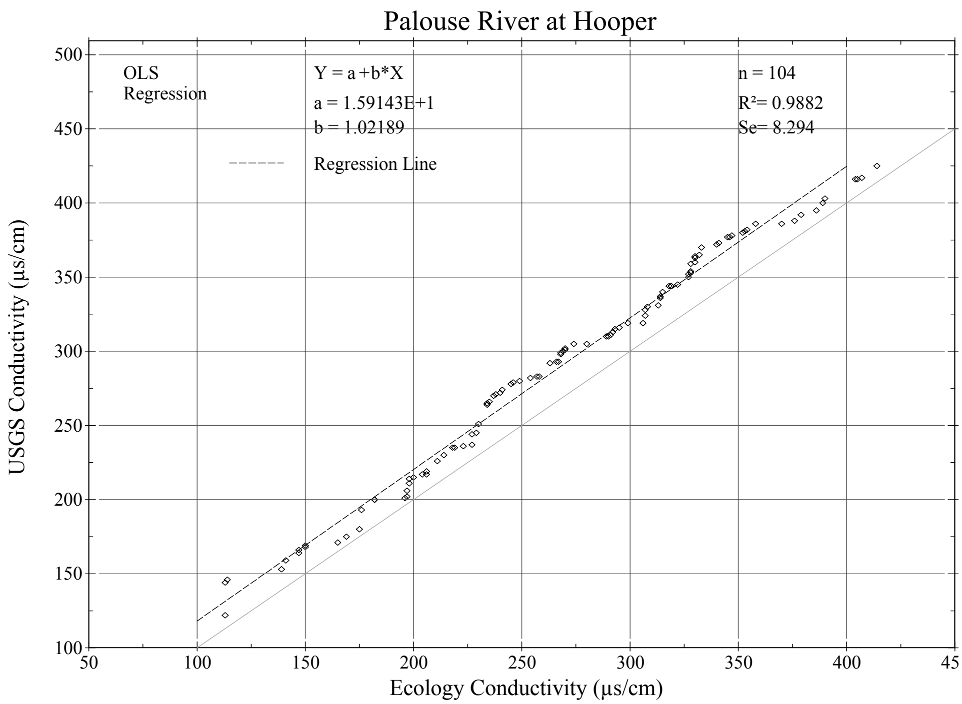


Figure 2. Quantile-quantile plot of USGS- and Ecology-collected conductivity at Palouse River at Hooper. Conductivities were consistently lower in Ecology samples.

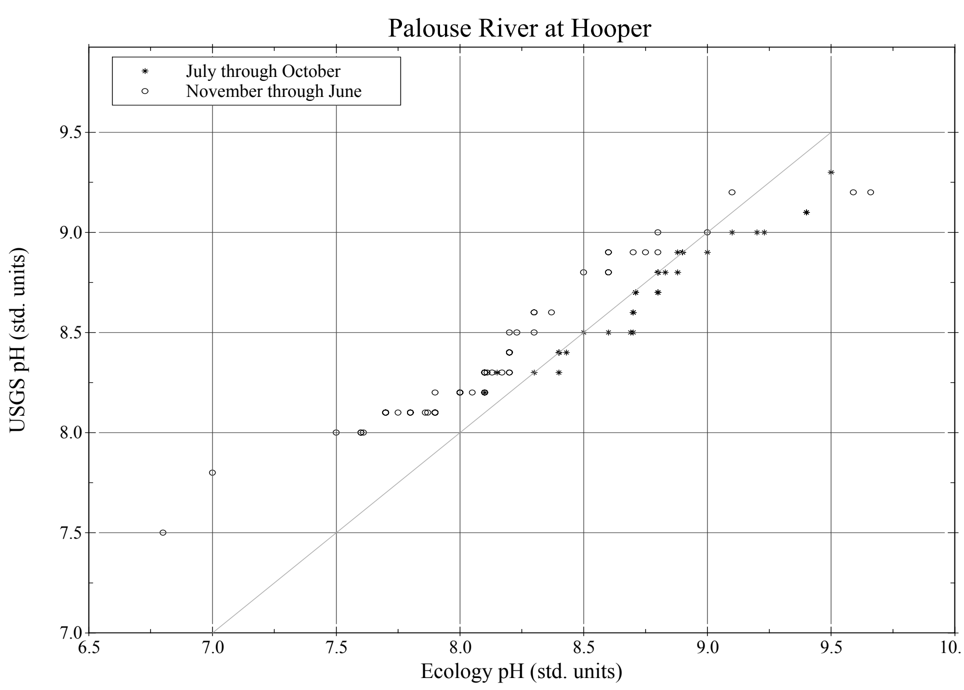


Figure 3. Quantile-quantile plot of USGS- and Ecology-collected pH at Palouse River at Hooper. Points below the 1:1 line indicate the Ecology result was larger than the USGS result. Ecology results tended to be higher during summer months and lower in the winter.

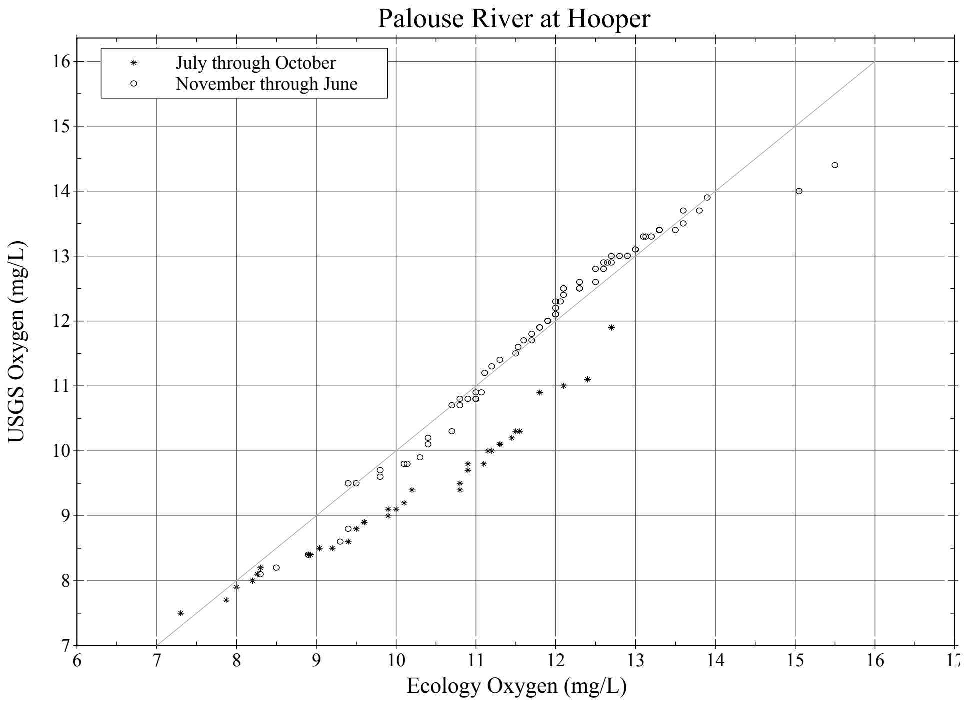


Figure 4. Quantile-quantile plot of USGS- and Ecology-collected oxygen at Palouse River at Hooper. Points below the 1:1 line indicate the Ecology result was larger than the USGS result. Ecology's summer results were consistently higher than USGS's.

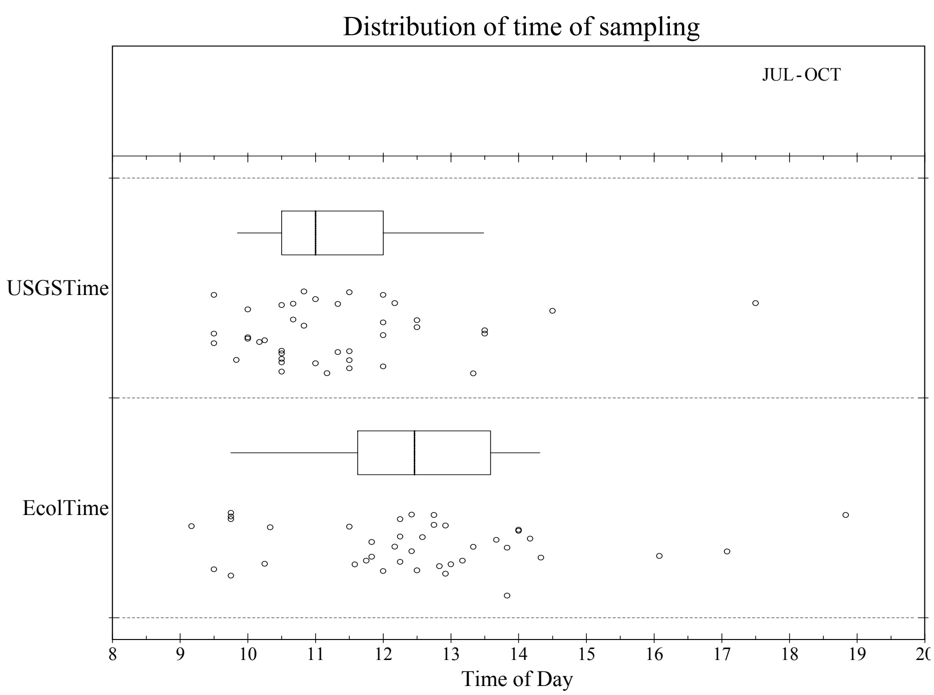


Figure 5. Time of sampling at Palouse River at Hooper by USGS and Ecology staff (summer months only). Ecology tended to sample later in the day than USGS.

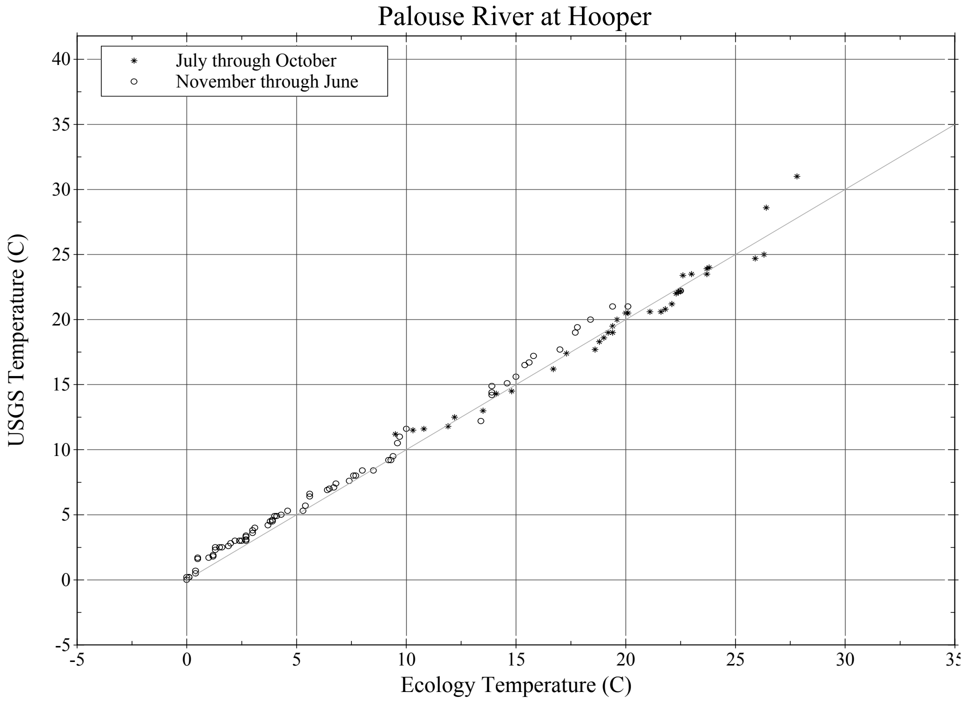


Figure 6. Quantile-quantile plot of USGS- and Ecology-collected temperature at Palouse River at Hooper. Points below the 1:1 line indicate the Ecology result was larger than the USGS result. Ecology and USGS results were similar.

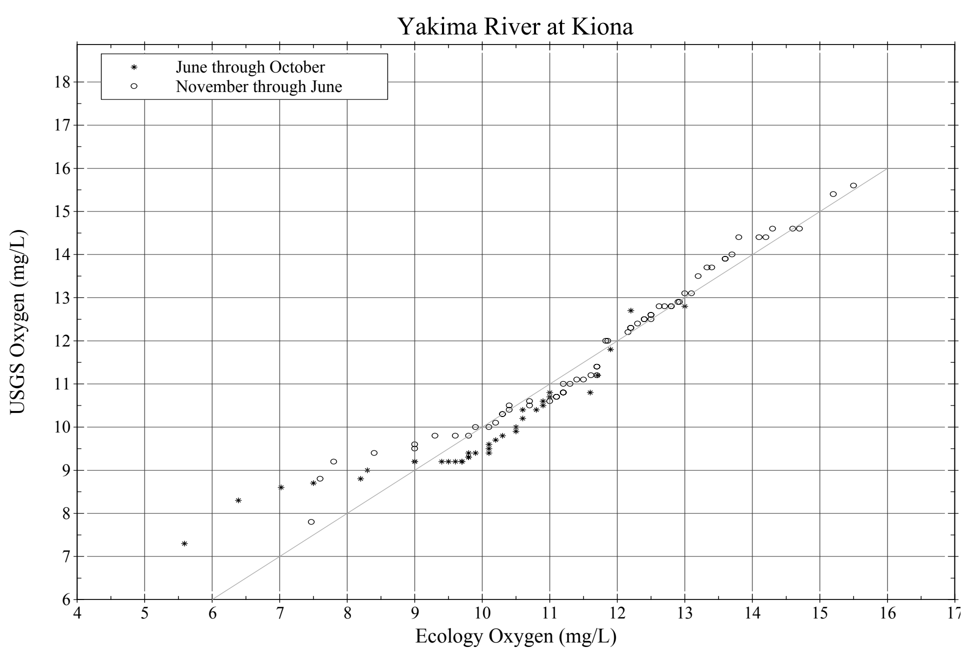


Figure 7. Quantile-quantile plot of USGS- and Ecology-collected oxygen at Yakima River at Kiona. Points below the 1:1 line indicate the Ecology result was larger than the USGS result. Ecology and USGS results were similar except at lower concentrations.

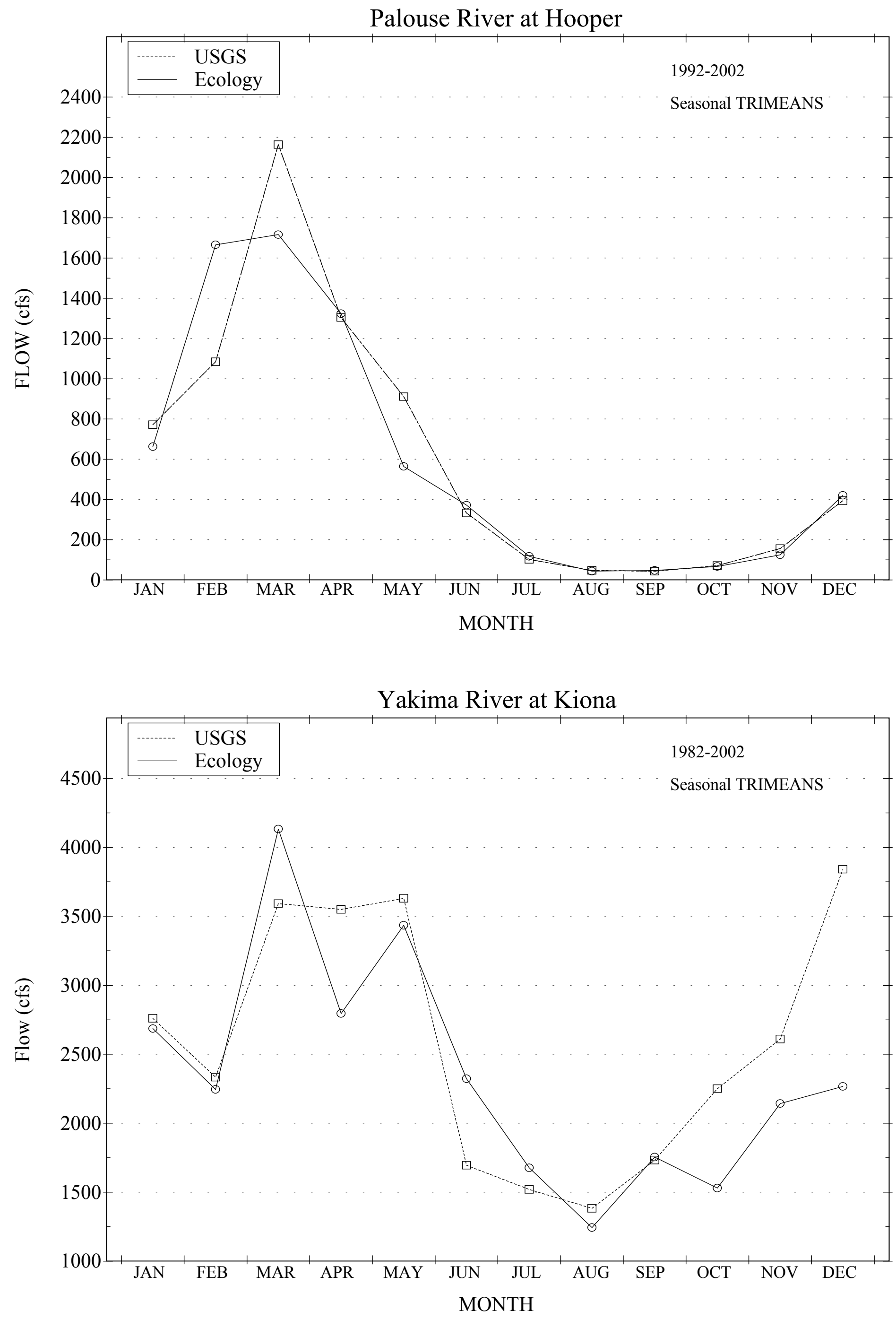


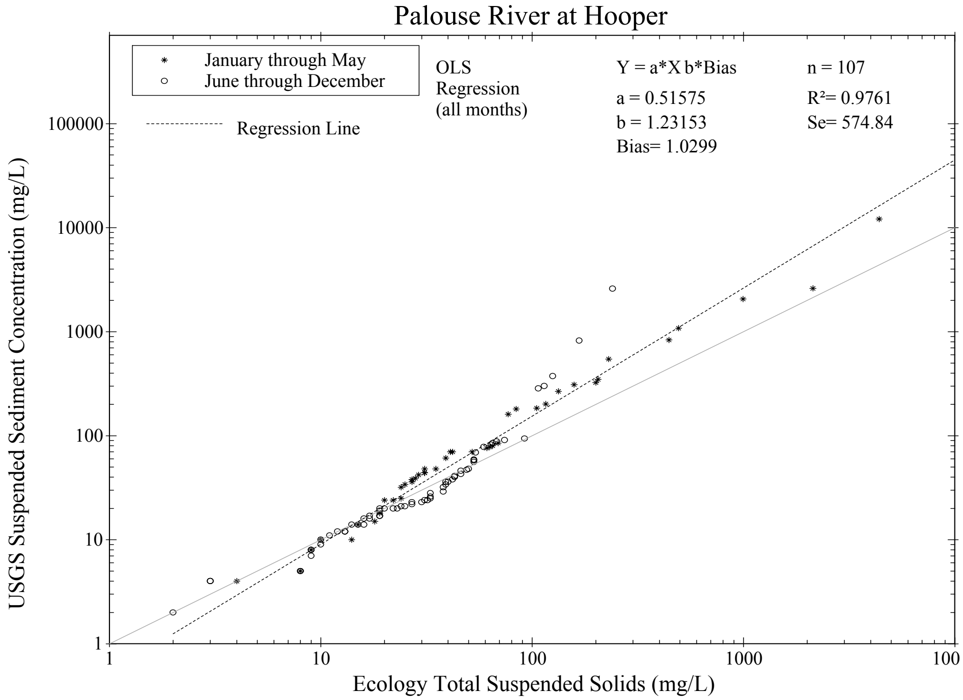
Figure 8. Monthly average (Tukey trimean) instantaneous flows associated with USGS and Ecology sampling events at Palouse River at Hooper (top) and at Yakima at Kiona (bottom).

In any case, comparisons of oxygen, pH, and temperature should be considered tentative because results were not normalized for the time of sample collection. Time of day can have a significant affect on these constituents. (However, both monitoring programs sampled, on average, at about noon at both stations. Ecology typically sampled 54 minutes later than USGS at Hooper and 19 minutes later at Kiona.)

While productivity-related constituents are more likely to be stratified during the summer months, sediment and other constituents positively correlated with flow are more likely to be stratified during high-flow months (January through May; Figure 8). (There should be no bias due to instantaneous flow measurement methodologies because USGS is the source of flow data for both monitoring programs.) However, there were no obvious pronounced seasonal effects in the relationships between Ecology and USGS sediment measures at either station (Figure 9). At Hooper, there was no significant difference overall (Table 2), though USGS results tended to be higher at higher concentrations (Figure 9, top). At Kiona, USGS concentrations were significantly higher overall compared to Ecology's (Table 2). This relationship was fairly consistent at all concentrations on a log-log plot indicating that USGS results were a constant multiple of Ecology results (slope=0.93; Figure 9, bottom).

TP was not significantly different overall between the two monitoring programs at either station (Table 2). However, at higher concentrations USGS results tended to be greater than Ecology's (Figure 10).

Average fluxes (concentration times instantaneous flow) were similar between the two monitoring programs for ammonia and ortho-phosphorus, and sediment and phosphorus fluxes were fairly similar at Kiona (Table 3). Sediment and phosphorus fluxes at Hooper calculated from Ecology data, however, were only half the fluxes calculated from USGS data. The Hooper station is below a bedrock riffle at a deep pool where sediment (and associated phosphorus) can settle out rapidly and therefore be missed in a surface grab sample. The disparity between the two monitoring programs would be even greater had loads been calculated by deriving a relationship between flow and concentration and estimating concentrations for missing days. Some of the difference in sediment results is likely attributable to the analytical method used. The SSC method used by USGS can yield significantly higher results than the TSS method used by Ecology, even if collection methods were the same (Gray, et al., 2000).



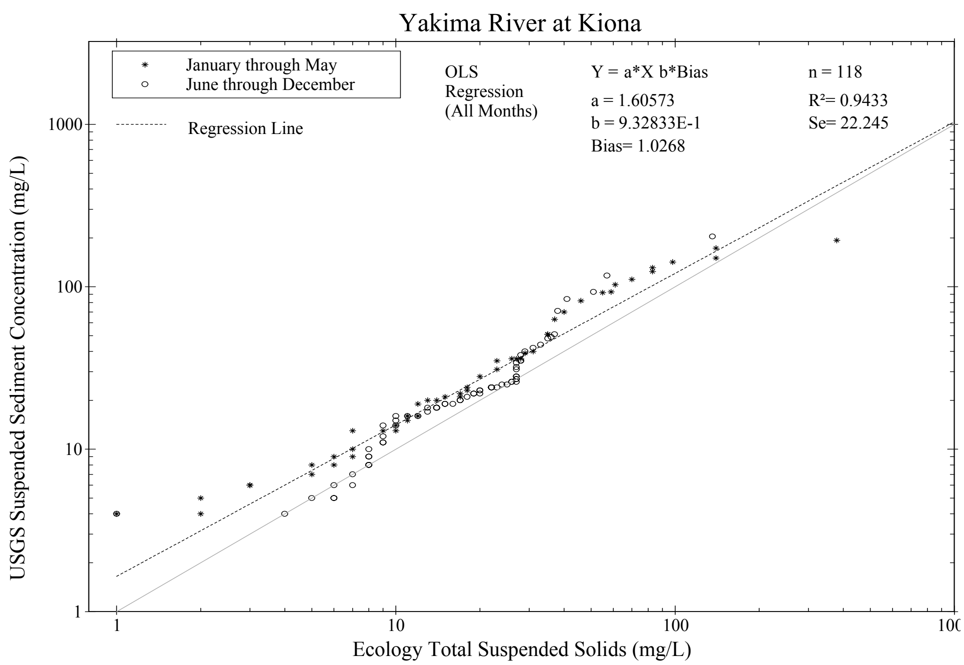


Figure 9. Quantile-quantile plot of USGS-collected SSC and Ecology-collected TSS concentration at Palouse River at Hooper (top) and Yakima River at Kiona (bottom). Points below the 1:1 line indicate the Ecology result was larger than the USGS result. Ecology results tended to be lower than USGS results.

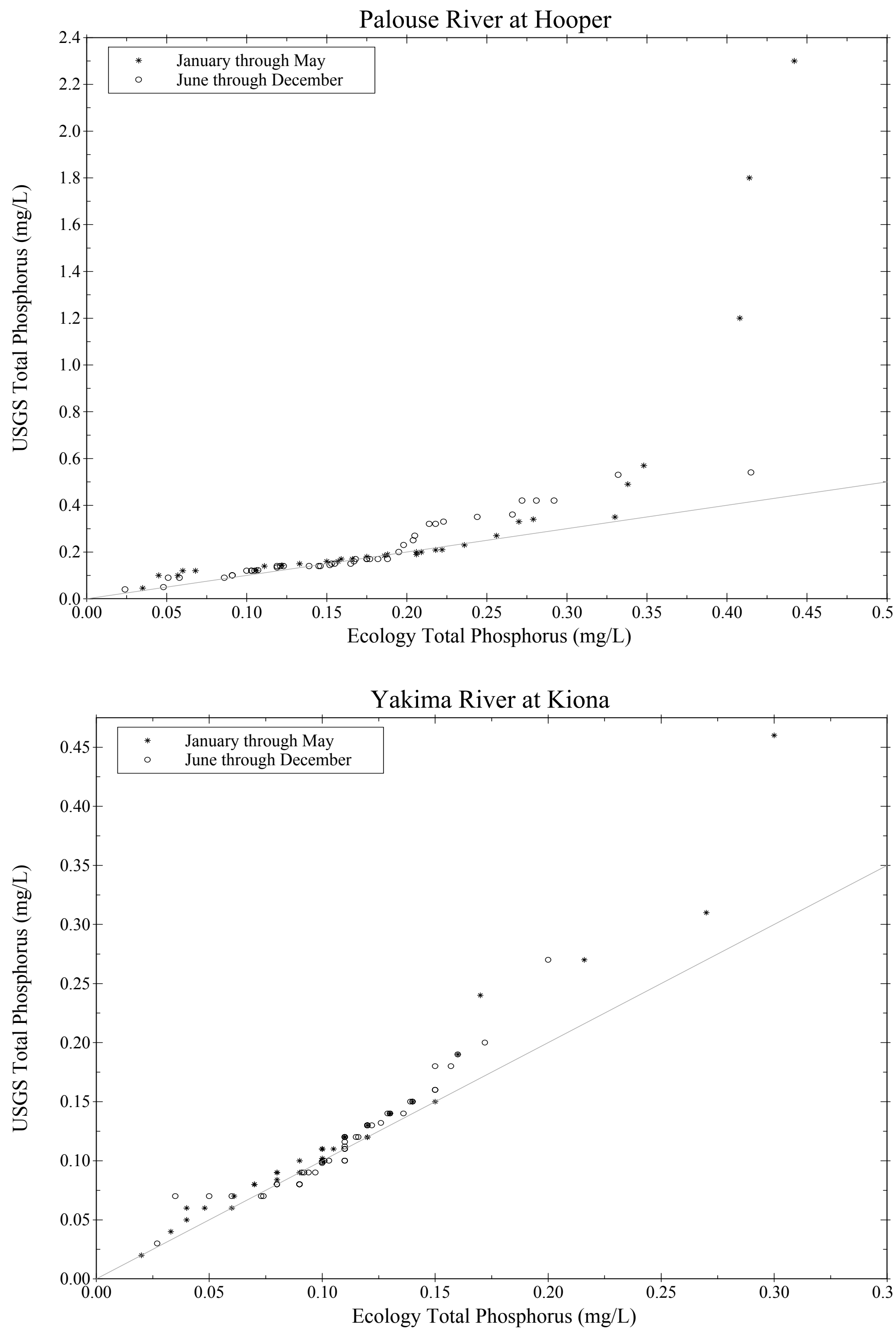


Figure 10. Quantile-quantile plot of USGS- and Ecology-collected TP concentration at Palouse River at Hooper (top) and Yakima River at Kiona (bottom). Points below the 1:1 line indicate the Ecology result was larger than the USGS result. Results were similar except at high concentrations.

Table 3. Average annual flux calculated from USGS and Ecology data sets. (Units are kg per year; calculated as the average of monthly results in mg/L times instantaneous flows in cfs times a unit conversion factor of 893).

	Palouse River at Hooper (34A070)			Yakima River at Kiona (37A090)		
Constituent	USGS Annual Flux (kg/yr)	Ecology Annual Flux (kg/yr)	Ecol. as pct of USGS	USGS Annual Flux (kg/yr)	Ecology Annual Flux (kg/yr)	Ecol. as pct of USGS
Ammonia-N	Insufficient Data			9.06×10^4	1.10×10^5	121.4%
Soluble react. P	6.69×10^4	6.45×10^4	96.4%	1.38×10^5	1.34×10^5	97.1%
Solids/sediment	6.13×10^8	2.78×10^8	45.4%	1.43×10^8	1.17×10^8	81.8%
Phosphorus, total	3.27×10^5	1.71×10^5	52.3%	3.44×10^5	2.77×10^5	80.5%

Variance

The dispersion was similar for both monitoring programs for most water quality constituent results. The standard deviation of Ecology's solids and TP data from the Palouse River and turbidity from the Yakima River tended to be lower than USGS's because USGS concentrations were greater at the high end of the concentration range (Table 4). The highest Ecology TP concentration from the Palouse River was 0.44 mg/L, while nearly ten percent of USGS results were greater than that (Figure 11).

The more important question is how sensitive the respective data sets are for detecting trends. Minimum detectable trends, expressed as a percent of the mean concentration, were very similar for most constituents—although this technique is only an approximation when data are not normally distributed. Trend power differed by more than a few percentage points only for sediment in the Yakima River and TP in the Palouse River; in both cases, the USGS dataset exhibited greater power.

At Kiona, USGS sediment data displayed a significant trend ($p<0.001$, slope=-1.0 mg/L per year) while Ecology data did not ($p=0.09$, slope=-0.3 mg/L per year).

However, at Hooper, the USGS TP data were more skewed than the Ecology data (mean, median, and skewness coefficient were 0.27 mg/L, 0.17 mg/L, 4.44, respectively for the USGS dataset and 0.18 mg/L, 0.17 mg/L, 0.80 for the Ecology dataset). The PredMDT estimate is sensitive to outliers and removing any one of the highest three values in the USGS data (see Figure 10, top) resulted in similar trend power for both datasets. In fact, neither monitoring program detected a trend in TP data at Hooper (USGS $p=0.29$, Ecology $p=0.23$). For most constituents, both datasets are approximately equivalent in their ability to detect trends.

Table 4. Variance in USGS and Ecology data sets expressed as standard deviation of raw data, standard deviation of deseasonalized and detrended (DS/DT) data, and predicted minimum detectable trend over a 10-year period expressed as percent of the mean.

	USGS Data Set			Ecology Data Set		
Constituent	Raw Data Std.Dev.	DS/DT Std.Dev.	Pred. Min. Det. Trend	Raw Data StdDev	DS/DT StdDev	Pred. Min. Det. Trend
Palouse River at Hooper (34A070)						
Conductivity	76.1	44.2	13%	74.0	46.0	17%
Ammonia-nitrogen	Insufficient data			Insufficient data		
Soluble reactive P	0.070	0.054	46%	0.063	0.046	52%
Oxygen	1.81	0.83	7%	1.63	1.09	9%
PH	0.36	0.27	3%	0.53	0.36	4%
Solids/sediment	1230	1223	11%	476	472	14%
Temperature	8.07	2.44	16%	8.20	2.13	9%
Phosphorus, total	0.342	0.330	23%	0.094	0.078	33%
Turbidity	Insufficient data			Insufficient data		
Yakima River at Kiona (37A090)						
Conductivity	56.7	43.6	12%	54.4	38.8	11%
Ammonia-nitrogen	0.021	0.017	43%	0.027	0.024	45%
Soluble reactive P	0.024	0.019	22%	0.024	0.020	21%
Oxygen	1.84	1.03	8%	1.94	1.27	12%
PH	0.26	0.25	3%	0.38	0.35	4%
Solids/sediment	39.7	38.0	15%	41.3	41.3	23%
Temperature	6.96	2.30	15%	7.03	2.02	13%
Phosphorus, total	0.059	0.057	32%	0.043	0.042	39%
Turbidity	10.9	10.5	24%	5.61	4.91	22%

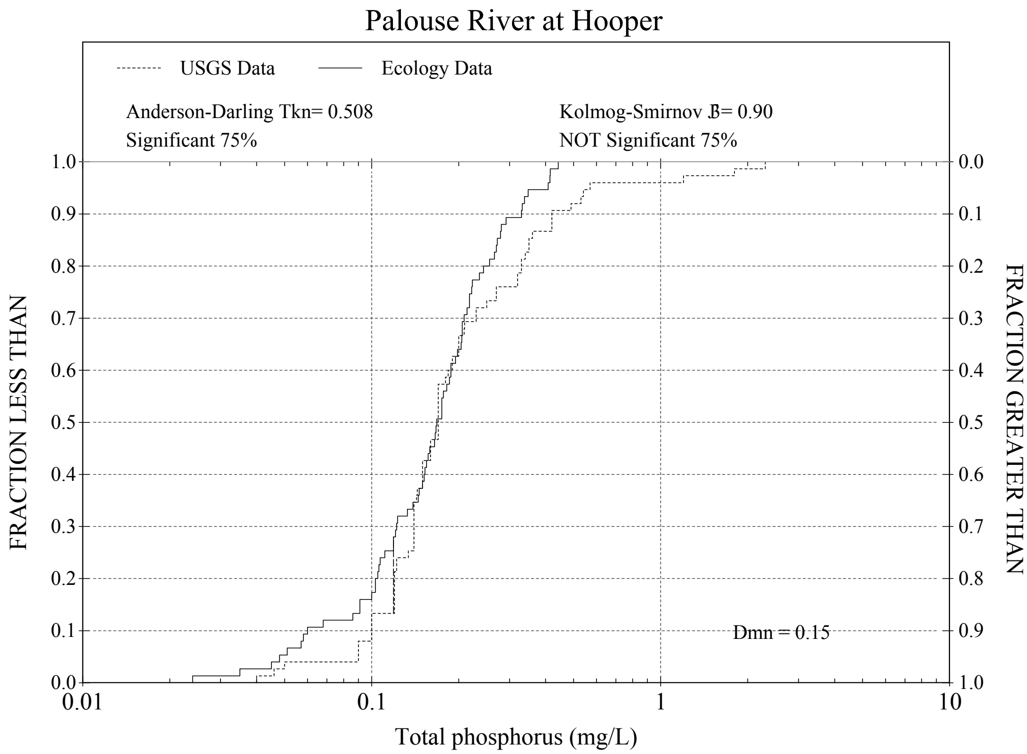


Figure 11. Cumulative distribution plot for USGS- and Ecology-collected TP data from Palouse River at Hooper. The Anderson-Darling and Kolmogorov-Smirnov tests evaluate the similarity of the distributions. Results were similar at the mid-range (30-70 percent), but Ecology results were much lower at high concentrations.

Conclusions

This report focused on two potential differences between USGS and Ecology water quality monitoring data. One potential difference is a relative bias between the two datasets. At Yakima River at Kiona, only sediment measures were significantly different overall and even for this constituent, the difference was not large. It is possible that the Yakima River at Kiona was relatively well mixed and the difference in sediment results was due as much to analytical method (SSC vs. TSS) as to sampling method (grab vs. integrated). The Palouse River at Hooper, on the other hand, where Ecology samples are taken from a deep pool, may have been stratified at *low* flows because constituents affected by solar radiation (pH, oxygen, and temperature) were significantly different in USGS and Ecology data sets. This was true primarily during the summer months when the Palouse River can become nearly stagnant. USGS oxygen and temperature results are also based on point samples, though collected upstream of the pool; for these constituents, differences in the time of sample collection may also have been a factor.

While in most cases overall results from the two monitoring programs were statistically similar, even a small bias at high concentrations and high flow periods for constituents positively correlated with flow can be magnified when calculating flux (flow times concentration). In the Yakima River, sediment and total phosphorus fluxes calculated from Ecology data were 80 percent of fluxes based on USGS data. In the Palouse River, however, fluxes based on Ecology data were only about half those based on data collected using integrating techniques. While flux may, perhaps, be calculated from Ecology data for comparative purposes, data collected using single point grab-sample methods should not be used to calculate loads for sediment-associated constituents unless the bias due to stratification is known.

Another potential difference between USGS and Ecology water quality monitoring data is their respective abilities to detect trends. The amount of variability within a dataset is a major determinant of trend power. The standard deviations and predicted minimum detectable trends for the two datasets were similar for most constituents. The USGS dataset has better power for detecting sediment trends in the Yakima River at Kiona.

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