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Prepared in cooperation with the U.S. Environmental Protection Agency

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

# **U.S. Department of the Interior**

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# **Conversion Factors and Abbreviations**

**Concentrations of chemical constituents** in water are given in: milligrams per liter (mg/L) » micrograms per gram ( $\mu$ g/g)  $\approx$  parts per million (ppm)

#### ABBREVIATIONS USED IN THIS REPORT

BQS	Branch of Quality Services
CV	coefficient of variation
mg/L	milligrams per liter
mL	milliliters
Р	phosphorus
SRP	soluble reactive phosphorus (orthophosphate)
SRS	standard reference sample
TDP	total dissolved phosphorus
ТР	total phosphorus
μm	micrometers
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

By Michael R. McHale<sup>1</sup> and Dennis McChesney<sup>2</sup>

# Abstract

In 2003, a study was conducted to evaluate the accuracy and precision of 10 laboratories that analyze water-quality samples for phosphorus concentrations in the Catskill Mountain region of New York State. Many environmental studies in this region rely on data from these different laboratories for water-quality analyses, and the data may be used in watershed modeling and management decisions. Therefore, it is important to determine whether the data reported by these laboratories are of comparable accuracy and precision. Each laboratory was sent 12 samples for triplicate analysis for total phosphorus, total dissolved phosphorus, and soluble reactive phosphorus. Eight of these laboratories reported results that met comparability criteria for all samples; the remaining two laboratories met comparability criteria for only about half of the analyses. Neither the analytical method used nor the sample concentration ranges appeared to affect the comparability of results. The laboratories whose results were comparable gave consistently comparable results throughout the concentration range analyzed, and the differences among methods did not diminish comparability. All laboratories had high data precision as indicated by sample triplicate results. In addition, the laboratories consistently reported total phosphorus values greater than total dissolved phosphorus values, and total dissolved phosphorus values greater than soluble reactive phosphorus values, as would be expected. The results of this study emphasize the importance of regular laboratory participation in sample-exchange programs.

## Introduction

The Catskill Mountains in southeastern New York are part of the New York City reservoir system that supplies drinking water to about 9 million people. The Catskill region has been a focus of environmental research by federal, state, county, municipal, and private researchers for several decades. These entities use a variety of laboratories and techniques for water-quality analyses; thus, it is important to establish whether the data reported by these laboratories are of comparable accuracy and precision.

In 2003, the U.S. Geological Survey (USGS), in cooperation with the U.S. Environmental Protection Agency (USEPA) conducted an interlaboratory comparison of phosphorus (P) concentrations for water samples analyzed by 10 laboratories to assess the comparability of laboratories that analyze chemical data collected in and around the Catskill Mountains of New York State. This study was part of an agricultural research project conducted by the U.S. Department of Agriculture, the USGS, and Cornell University that focused on P contamination of surface waters in the Cannonsville Reservoir watershed in southeastern New York State. The project used three laboratories: U.S. Geological Survey National Water Quality Laboratory in Denver, Colo., U.S. Department of Agriculture Agricultural Research Service in State College, Pa., and Cornell University Department of Agricultural Engineering in Ithaca, N.Y. The USEPA, which funded the project through the New York City Department of Environmental Protection and the Watershed Agricultural Council, required documentation that the three laboratories used in the project provide comparable P results because the data were combined to model P movement and transformation within the watershed. Six additional laboratories that analyze stream-water samples from the Catskill region were invited to participate in this comparison, and a 10th laboratory, the University of Puerto Rico, asked that their laboratory be included to evaluate its accuracy and precision.

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#### **Objectives**

The objectives of this study were to (1) evaluate the performance of the 10 participating laboratories in terms of their reported P concentrations in terms of accuracy and precision, (2) identify analytical problems any of the participating laboratories may be having, and (3) assess whether the concentrations reported by the 10 laboratories for the same samples were comparable for three phosphorus components-total phosphorus (TP), total dissolved phosphorus (TDP), and soluble reactive phosphorus (SRP), sometimes referred to as orthophosphate.

#### **Purpose and Scope**

This report describes sample preparation, sample distribution, and statistical methods used to assess comparability among laboratories, and reports the results of the comparison.

### **Methods**

Each laboratory was sent 12 samples, all of which were analyzed in triplicate for each analyte by each laboratory except where sample volume was insufficient, to provide a measure of analytical precision. The analytical methods used by each laboratory are summarized in table 1. The laboratories were randomly assigned numbers of 1 through 10; these numbers are used here for data presentation and do not coincide with the order in which the laboratories are listed in table 1. The laboratories participated in this study on condition that the results would be reported anonymously.

#### Sample Preparation

Each laboratory was sent stream-water samples and laboratory-prepared water samples in two rounds. The laboratory-prepared samples were obtained from the USGS Standard Reference Sample (SRS) program, an interlaboratory analytical evaluation program that includes more than 275 USGS and non-USGS laboratories. Program samples are prepared twice annually and shipped to participating laboratories, and a report is produced detailing results of each evaluation. The SRS program has been in operation since 1962.

Sample distribution for this study occurred in two rounds; during the first round in the spring of 2003, the USGS sent three SRS samples and one stream-water sample to each of the 10 laboratories. The SRS program sample numbers were N-77, which was prepared with deionized water and N-78, which was prepared in a natural water matrix (water collected from Bear Creek east of Kittredge, Colo.). A detailed description of SRS sample preparation is given in Woodworth and Connor (2003). Sample N-77 was shipped in a concentrated form for sample stability, and the laboratories were asked to

dilute the sample by a factor of 10 before analyzing. The third SRS sample was a second aliquot of SRS sample N-77 that the laboratories were not asked to dilute; the laboratories were unaware that both aliquots represented the same SRS sample. The fourth sample was a stream-water sample collected at the USGS streamgage 01421618, Town Brook southeast of Hobart (table 2).

The USGS sent the second round of samples during the summer of 2003. This round consisted of eight samples collected from eight streams throughout the Catskill Mountains (table 2). These samples were filtered for TDP and SRP aliquots streamside through 0.4-µm cartridge filters and transported on ice to the USGS Water Quality Laboratory in Troy, N.Y., where the unfiltered TP aliquots were acidified with 1 mL of 4.5 normal sulfuric acid. Samples were refrigerated overnight and shipped on ice the next day to each participating laboratory. The samples for this study were labeled P1-P12 (table 2).

#### Statistical Methods

A z-value was calculated for each sample to rate the performance of each laboratory in relation to all other laboratories in the study. The rating for SRS samples N-77 and N-78 (labeled P1 and P2 for this study) was based on results submitted during March 2003 by all laboratories that participated in the SRS sample exchange for nutrients (71 laboratories, including the 10 that participated in this study). The z-value used is analogous to a z-score, or standard score, which is calculated as:

$$z = \frac{X - \mu}{\sigma} \tag{1}$$

where

X = value of a given sample, = the sample mean, μ

and

 $\sigma$ standard deviation.

A nonparametric equivalent of the standard score was used for this comparison. The sample median was used in place of the sample mean, and the F-pseudosigma was used in place of the standard deviation. A nonparametric statistic was used to prevent the sample distribution from affecting the results. The F-pseudosigma is calculated as the sample third quartile minus the first quartile, divided by 1.349 (50 percent of the data lies within 1.349 standard deviations from the mean). When the F-pseudosigma was less than 5 percent of the sample median, 5 percent of the sample median was used instead. The acceptability of each analysis was rated according to the following criteria:

Rating	Absolute z-value
4 (Excellent)	0.00 to 0.50
3 (Good)	0.51 to 1.00
2 (Satisfactory)	1.01 to 1.50
1 (Marginal)	1.51 to 2.00
0 (Unsatisfactory)	Greater than 2.00

Results with a rating of 2 to 4 are considered comparable to one another, and results with a rating of 1 or 0 are considered not comparable. It is important to note that for samples where there is little variation among concentrations reported by the laboratories, the z-values are sensitive to concentration differences to 3 decimal places, therefore, concentrations that are identical to 2 decimal places may have different z-values and, therefore, different ratings (table 3).

The method used to rate sample acceptability is the same as that used by the USGS program to rate laboratory performance in their SRS program. The F-pseudosigma value was greater than the median value for TP and TDP in sample P4. An F-pseudosigma value that exceeds the sample median indicates the z-value is invalid, and the rating is listed as NA (table 3).

The analytical precision for each laboratory was evaluated through the coefficient of variation (CV) calculated for each set of triplicate analyses. The coefficient of variation was calculated as:

$$CV = \frac{s}{x}(100) \tag{2}$$

where

and

s = standard deviation,  $\bar{x}$  = arithmetic mean of the triplicate samples.

The data-quality objective for all analyses is a CV of less than 10 percent.

Phosphorus concentration was also evaluated in terms of the difference between each P fraction analyzed. The TP concentration should be equal to or greater than the TDP concentration, which in turn should be equal to or greater than the SRP concentration. The difference between each P fraction was calculated for each sample sent to each laboratory to provide an indication of how accurately each laboratory analyzed the three fractions of phosphorus relative to one another.

# **Data Comparability**

A total of 1,080 values would have been reported if the laboratories had analyzed all three phosphorus fractions in triplicate for each of the 12 samples, but several factors intervened and allowed a total of only 860 reported values (table 3).

- Laboratory 2 reported nondetectable concentrations for all fractions of sample P4 (table 3).
- Laboratory 6 did not receive samples from Round 2 because of a shipping error and therefore, reported only results from Round 1.
- Laboratory 8 did not analyze the second round of samples (P5–P12) in triplicate because of a miscommunication.
- Laboratory 9 was unable to analyze the first round of samples (P1–P4) in triplicate because the sample volume was insufficient for their method.
- Laboratory 10 analyzes only for SRP (orthophosphate) and therefore, provided only those results.

Of the 860 values reported, 132 (15 percent) did not meet the comparability criteria set for the study (the absolute z-value was greater than 1.5). Of the three P fractions analyzed, SRP had the worst comparability-69 of 310 reported values (22 percent) did not meet the criteria. For TP, 37 of 276 reported values (13 percent) did not meet the comparability criteria. TDP showed the best comparability-26 of 274 reported values (9 percent) did not meet the established criteria. Two of the laboratories (Laboratories 2 and 6) failed comparability criteria for 55 percent of the values reported. Laboratories 2, 4, and 6 accounted for 80 percent of the data that did not meet comparability criteria. Three laboratories (Laboratories 5, 7, and 8) met comparability criteria for every value reported, and Laboratory 1 met the criteria for all but one value. Another three laboratories (Laboratories 3, 9, and 10) had 10 or less values that did not meet the criteria.

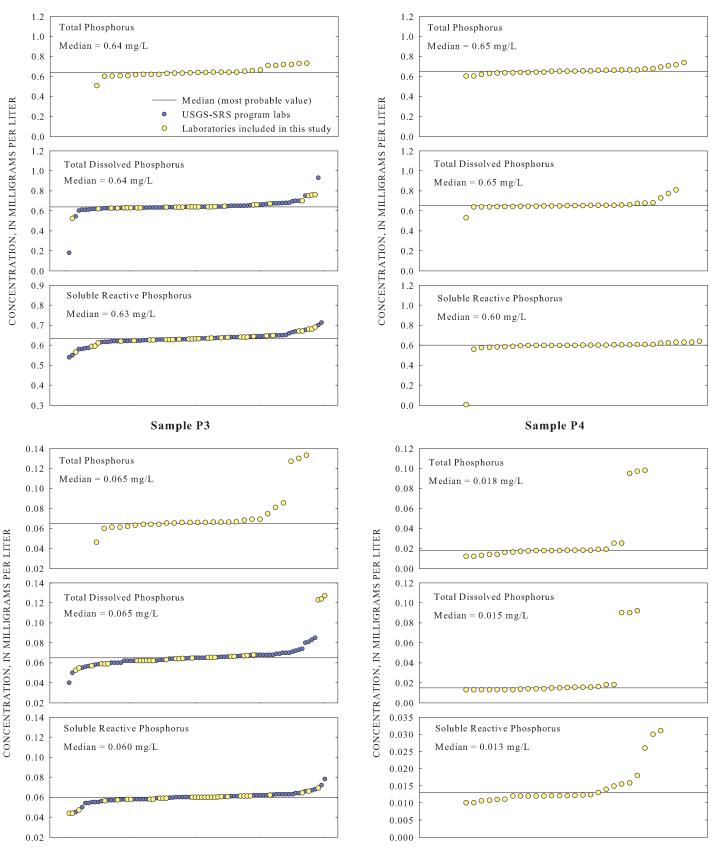
None of the laboratories showed consistently poor performance on the diluted (low-concentration) samples; of the 132 reported values that did not meet comparability criteria, only 69 had concentrations less than 0.05 mg/L. Of the 860 values reported, 512 were less than 0.05 mg/L. Therefore, low-concentration samples accounted for 60 percent of the reported values but represented only 52 percent of the values that failed the comparability criteria. Thus, laboratory performance seemed to have a greater effect than sample concentration on laboratory comparability, and laboratories that had difficulty meeting the criteria at low concentrations also had difficulty at high concentrations.

The results for the 10 laboratories that participated in this study were within the range reported for the laboratories participating in the SRS program for samples distributed and evaluated through the USGS (samples P1 and P3), except for the TDP fraction of sample P3 (fig. 1). This study generally found that for each sample, there were one or two laboratories whose reported values did not meet the comparability criteria, although not always the same one or two laboratories.

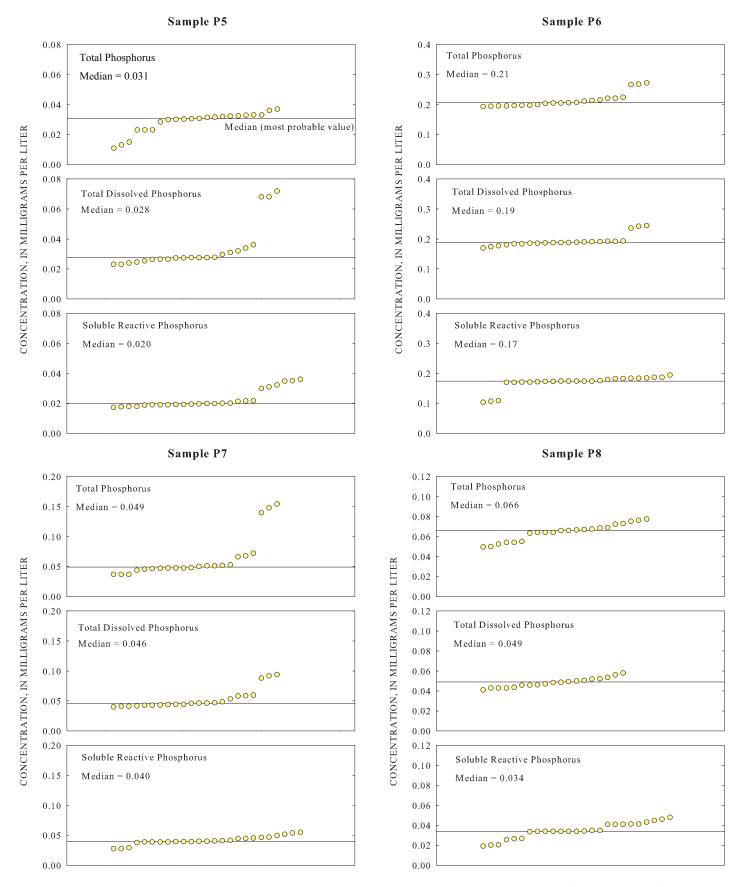
The laboratories performed well in terms of precision; only 5 of 106 sets of TP triplicates, 5 of 104 sets of TDP triplicates, and 3 of 120 sets of SRP triplicates did not meet



Sample P2



**Figure 1.** Concentrations of total phosphorus, total dissolved phosphorus, and soluble reactive phosphorus (orthophosphate) in 10-laboratory comparison of stream-water and reference samples, 2003.



**Figure 1.** Concentrations of total phosphorus, total dissolved phosphorus, and soluble reactive phosphorus (orthophosphate) in 10-laboratory comparison of stream-water and reference samples, 2003.—Continued



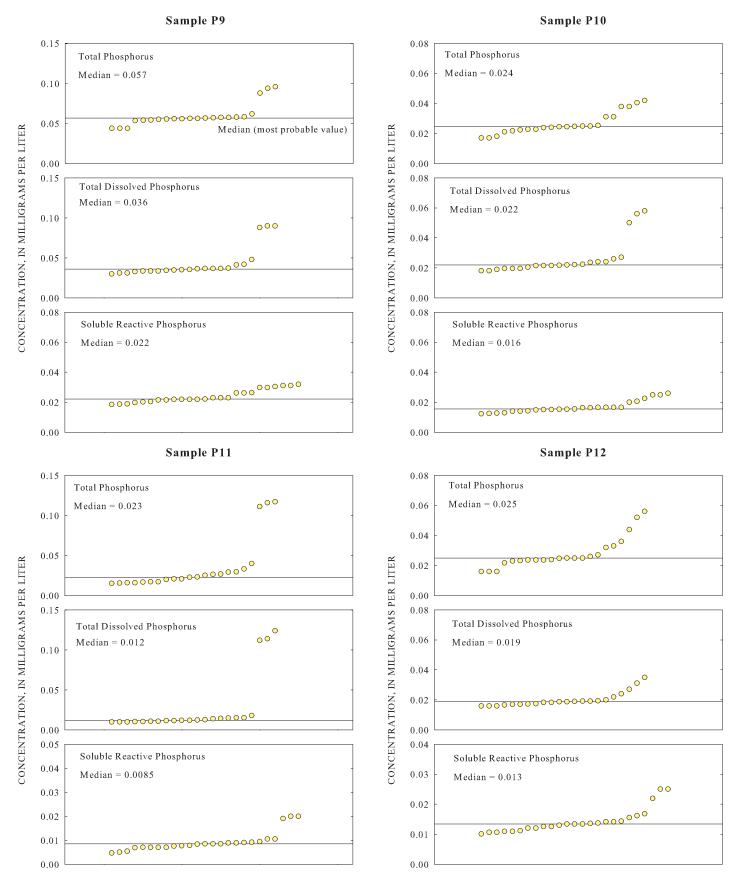
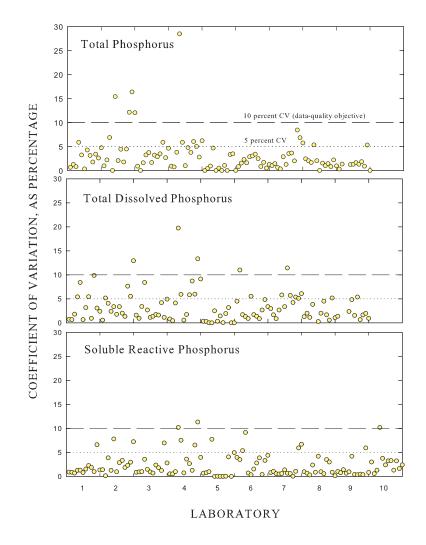


Figure 1. Concentrations of total phosphorus, total dissolved phosphorus, and soluble reactive phosphorus (orthophosphate) in 10-laboratory comparison of stream-water and reference samples, 2003.—Continued

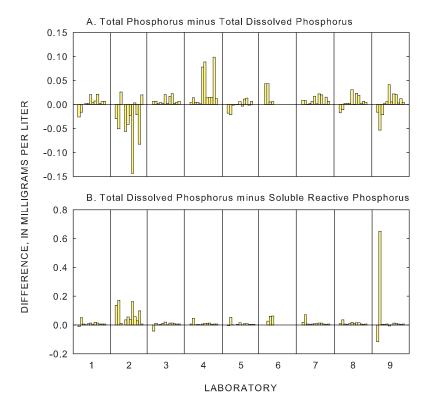
#### Data Comparability 7

the data-quality objective (a coefficient of variation less than 10 percent) (fig. 2). Even when the laboratories did not meet the comparability objective, they typically met the precision objective with the triplicate samples (table 1). In other words, the laboratories reported similar values for triplicate samples, whether or not the values were close to the median concentration for all laboratories.

The calculated differences among phosphorus fractions indicate that most of the laboratories consistently reported higher TP values than TDP values, and higher TDP values than SRP values, as expected (fig. 3). Reported TDP values that exceeded the TP value, or that were exceeded by the reported SRP value, were usually at concentrations less than 0.025 mg/L. Laboratory 2 consistently reported TP values lower than TDP values, which may indicate that the laboratory has difficulty analyzing acidified samples. Only five samples had SRP concentrations greater than the TDP concentrations, and the difference in four of those was close to zero—typically less than 0.05 mg/L.



**Figure 2.** The coefficient of variation (CV) for total phosphorus, total dissolved phosphorus, and soluble reactive phosphorus (orthophosphate) for all stream-water and reference sample triplicates reported by the 10 participating laboratories.



**Figure 3.** Difference between phosphorus fractions in 10-laboratory comparison of phosphorus concentration in stream-water and reference samples, 2003. *(A)* Total phosphorus minus total dissolved phosphorus, and *(B)* total dissolved phosphorus minus soluble reactive phosphorus. [Laboratory 10 analyzed only for soluble reactive phosphorus]

## Conclusions

Laboratory performance has two principal measuresaccuracy and precision. Accuracy is a measure of how closely a reported concentration matches the actual concentration, whereas precision is a measure of how well a laboratory can repeat results. This study was conducted to evaluate the accuracy and precision of 10 laboratories that analyze water samples for phosphorus concentrations in research programs in the Catskill Mountain region. The laboratories compared well in consideration of the different methods used. The actual concentrations of the samples are unknown; therefore, the accuracy of each laboratory's method is also unknown. The median sample concentration from all of the laboratories is taken as the most probable value, although it is not necessarily the correct value. Thus, a laboratory could theoretically report a value that does not meet the comparability criteria and yet be the only laboratory to report the correct concentration for that sample. When the actual sample concentration is unknown, the median concentration is assumed to be close to the true value.

The differences among analytical methods used by the laboratories in this study did not appear to greatly affect laboratory performance. The laboratories whose results were least comparable used methods that differed from each other's. The three laboratories that met comparability criteria for all reported values used the same method, but other laboratories that also compared well used a variety of methods. The concentrations of the samples did not appear to greatly affect laboratory comparability. The laboratories that compared well did so at high and low concentrations, whereas the laboratories that did not meet comparability criteria had difficulty at both high and low concentrations. These results indicate that the laboratories that compared well did so regardless of method or sample concentration. This study identified a difficulty with sample digestion that one laboratory experienced during the first round of sample analysis, but this was corrected and the samples were reanalyzed. The results from the reanalysis are included in this report, and the earlier values are excluded.

All of the laboratories showed a high level of precision. Only 13 of 330 sets of triplicate analyses did not meet the data-quality objective. Data precision was expected to be high because most laboratories run triplicate samples as part of their regular quality-control procedures. Most of the laboratories also consistently reported TP values that were equal to or greater than TDP values, and TDP values equal to or greater then SRP values. The one notable exception was TP for Laboratory 2, which may indicate that the laboratory had difficulty analyzing acidified samples.

The results of this study emphasize the need for laboratories to participate in regular sample-exchange programs. Internal laboratory quality-assurance and quality-control programs can sometimes fail to identify sources of laboratory inaccuracy that would become apparent in sample-exchange programs.

## **Acknowledgments**

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# **References Cited**

Woodworth, M.T., and Connor, B.F., 2003, Results of the U.S. Geological Survey's analytical evaluation program for standard reference samples distributed in March 2003: U.S. Geological Survey Open-File Report 03–261, 114 p.

Tables 1–3

 Table 1.
 Laboratories participating in 2003 study of laboratory comparability, U.S. Environmental Protection Agency (USEPA) methods used, and method titles.

Laboratory	USEPA methods used	Method title
U.S. Geological Survey National Water Quality Laboratory	365.1	Phosphorus (All forms, colorimetric, automated, ascorbic acid)
U.S. Department of Agriculture Agricultural Research Service Laboratory at the University of Pennsylvania	365.3/365.4	Phosphorus (All forms, colorimetric, ascorbic acid, two reagent) Phosphorus (Total, colorimetric, automated, block digester AA II)
Cornell University Department of Agricultural Engineering	365.1	Phosphorus (All forms, colorimetric, automated, ascorbic acid)
New York State Department of Health Wadsworth Laboratory	365.2/365.3	Phosphorus (All forms, colorimetric, ascorbic acid, single reagent) Phosphorus (All forms, colorimetric, ascorbic acid, two reagent)
New York City Department of Environmental Protection	365.1	Phosphorus (All forms, colorimetric, automated, ascorbic acid)
Columbia Analytical Services	365.1	Phosphorus (All forms, colorimetric, automated, ascorbic acid)
Upstate Freshwater Institute	365.2	Phosphorus (All forms, colorimetric, ascorbic acid, single reagent)
Severn Trent Laboratories	365.2	Phosphorus (All forms, colorimetric, ascorbic acid, single reagent)
Academy of Natural Sciences	365.1	Phosphorus (All forms, colorimetric, automated, ascorbic acid)
University of Puerto Rico	365.1	Phosphorus (All forms, colorimetric, automated, ascorbic acid)

#### Table 2. Samples included in the interlaboratory comparison.

[USGS, U.S. Geological Survey]

Sample number	Sample description								
Round 1, April 2003									
P1	Standard Reference Sample N-78								
P2	Standard Reference Sample N-77 undiluted								
P3	Standard Reference Sample N-77 diluted by a factor of 10								
P4	USGS streamgage Town Brook southeast of Hobart, N.Y. (Gage 01421618)								
	Round 2, July 2003								
Р5	USGS streamgage Town Brook southeast of Hobart, N.Y. (Gage 01421618)								
P6	Small stream draining farmland within the Town Brook Watershed								
P7	Small stream draining farmland within the Town Brook Watershed								
P8	Small stream draining a farm within the Cannonsville Reservoir Watershed								
P9	USGS streamgage West Branch Delaware River upstream from Delhi, N.Y. (Gage 01421900)								
P10	USGS streamgage Little Delaware River near Delhi, N.Y. (Gage 01422500)								
P11	USGS streamgage East Brook east of Walton, N.Y. (Gage 01422747)								
P12	West Branch of the Delaware River at Beerston, N.Y.								

**Table 3**. Concentrations of total phosphorus, total dissolved phosphorus, and soluble reactive phosphorus (orthophosphate) for stream-water and reference samples, z-values, and ratings for the 10 laboratories involved in the 2003 comparability study.

[Conc., concentrations are in milligrams per liter (mg/L); ND, below detection limit; --, no value reported. Note that for samples where there is little variation among concentrations reported by the laboratories, the z-values are sensitive to concentration differences to 3 decimal places, therefore, concentrations that are identical to 2 decimal places may have different z-values and, therefore, different ratings]

Sample P1										
Laboratory	Total phosphorus Sample median = 0.64 mg/L F-pseudosigma = 0.069			Sampl	issolved phos e median = 0.6 eudosigma =	54 mg/L	Soluble reactive phosphorus Sample median = 0.632 mg/L F-pseudosigma = 0.019			
-	Conc.	z-value	Rating	Conc.	z-value	Rating	Conc.	z-value	Rating	
1	0.61	0.47	4	0.63	0.19	4	0.64	0.17	4	
1	0.60	0.59	3	0.63	0.47	4	0.64	0.02	4	
1	0.60	0.56	3	0.63	0.31	4	0.65	0.36	4	
2	0.73	1.28	2	0.76	3.66	0	0.62	0.46	4	
2	0.72	1.12	2	0.75	3.47	0	0.63	0.21	4	
2	0.73	1.31	2	0.76	3.72	0	0.61	0.74	3	
3	0.63	0.15	4	0.62	0.63	3	0.68	1.44	2	
3	0.64	0.01	4	0.64	0.00	4	0.67	1.12	2	
3	0.64	0.01	4	0.63	0.31	4	0.67	1.12	2	
4	0.64	0.01	4	0.64	0.09	3	0.63	0.14	4	
4	0.63	0.12	4	0.63	0.34	3	0.63	0.27	4	
4	0.64	0.04	4	0.64	0.06	3	0.63	0.08	4	
5	0.62	0.28	4	0.64	0.03	4	0.65	0.43	4	
5	0.62	0.28	4	0.64	0.09	4	0.64	0.27	4	
5	0.62	0.28	4	0.64	0.03	4	0.64	0.17	4	
6	0.71	1.01	2	0.67	0.94	3	0.64	0.17	4	
6	0.71	1.01	2	0.70	1.88	1	0.68	1.44	2	
6	0.72	1.15	2	0.64	0.00	4	0.69	1.76	1	
7	0.67	0.36	4	0.63	0.41	4	0.63	0.17	4	
7	0.65	0.17	4	0.66	0.59	3	0.64	0.08	4	
7	0.66	0.24	4	0.66	0.66	3	0.63	0.21	4	
8	0.64	0.07	4	0.65	0.16	4	0.63	0.02	4	
8	0.62	0.33	4	0.64	0.06	4	0.63	0.21	4	
8	0.61	0.50	3	0.63	0.34	4	0.62	0.40	4	
9	0.51	1.94	1	0.52	3.66	0	0.64	0.14	4	
9										
9										
10							0.57	2.20	0	
10							0.59	1.28	2	
10							0.60	1.22	2	

Sample P2										
Laboratory	Total phosphorus Sample median = 0.65 mg/L F-pseudosigma = 0.028			Sampl	Total dissolved phosphorus Sample median = 0.65 mg/L F-pseudosigma = 0.025			Soluble reactive phosphorus Sample median = 0.60 mg/L F-pseudosigma = 0.020		
	Conc.	z-value	Rating	Conc.	z-value	Rating	Conc.	z-value	Rating	
1	0.64	0.46	4	0.64	0.42	4	0.60	0.07	4	
1	0.63	0.78	3	0.65	0.17	4	0.60	0.10	4	
1	0.62	1.03	2	0.64	0.32	4	0.59	0.37	4	
2	0.72	2.31	0	0.81	4.72	0	0.60	0.03	4	
2	0.71	1.99	1	0.77	3.65	0	0.60	0.00	4	
2	0.74	3.09	0	0.73	2.29	0	0.60	0.03	4	
3	0.65	0.00	4	0.64	0.45	4	0.63	1.00	2	
3	0.65	0.00	4	0.64	0.45	4	0.64	1.33	2	
3	0.65	0.00	4	0.65	0.14	4	0.63	1.00	2	
4	0.66	0.36	4	0.65	0.23	4	0.60	0.00	4	
4	0.67	0.53	3	0.64	0.35	4	0.60	0.07	4	
4	0.66	0.18	4	0.65	0.20	4	0.60	0.13	4	
5	0.64	0.43	4	0.66	0.08	4	0.60	0.07	4	
5	0.63	0.57	3	0.65	0.02	4	0.60	0.10	4	
5	0.63	0.64	3	0.66	0.05	4	0.61	0.23	4	
6	0.65	0.00	4	0.53	3.83	0	0.59	0.50	3	
6	0.66	0.36	4	0.65	0.14	4	0.60	0.00	4	
6	0.64	0.36	4	0.64	0.45	4	0.56	1.33	2	
7	0.69	1.49	2	0.66	0.17	4	0.60	0.17	4	
7	0.67	0.85	3	0.68	0.78	3	0.61	0.20	4	
7	0.68	0.92	3	0.68	0.72	3	0.61	0.17	4	
8	0.67	0.53	3	0.68	0.63	3	0.63	0.97	3	
8	0.64	0.32	4	0.66	0.05	4	0.62	0.70	3	
8	0.64	0.25	4	0.65	0.14	4	0.62	0.80	3	
9	0.60	1.70	1	0.66	0.02	4	0.00	19.84	0	
9	0.60	1.70	1							
9										
10							0.58	0.73	3	
10							0.58	0.67	3	
10							0.57	0.87	3	

Sample P3										
Laboratory	Total phosphorus Sample median = 0.065 mg/L F-pseudosigma = 0.014			Sample	Total dissolved phosphorus Sample median = 0.065 mg/L F-pseudosigma = 0.0044			Soluble reactive phosphorus Sample median = 0.060 mg/L F-pseudosigma = 0.0037		
-	Conc.	z-value	Rating	Conc.	z-value	Rating	Conc.	z-value	Rating	
1	0.066	0.06	4	0.067	0.40	4	0.061	0.30	4	
1	0.065	0.07	4	0.065	0.11	4	0.061	0.30	4	
1	0.066	0.00	4	0.066	0.07	4	0.060	0.11	4	
2	0.075	0.58	3	0.053	2.86	0	0.044	4.36	0	
2	0.086	1.35	2	0.057	1.87	1	0.044	4.36	0	
2	0.081	1.03	2	0.055	2.36	0	0.047	3.54	0	
3	0.062	0.30	4	0.059	1.39	2	0.059	0.27	4	
3	0.063	0.23	4	0.062	0.72	3	0.060	0.00	4	
3	0.064	0.16	4	0.063	0.49	4	0.060	0.00	4	
4	0.066	0.02	4	0.059	1.39	2	0.060	0.00	4	
4	0.069	0.19	4	0.064	0.27	4	0.059	0.27	4	
4	0.064	0.16	4	0.062	0.72	3	0.060	0.00	4	
5	0.061	0.37	4	0.062	0.72	3	0.060	0.00	4	
5	0.061	0.37	4	0.062	0.72	3	0.061	0.27	4	
5	0.060	0.44	4	0.062	0.72	3	0.061	0.27	4	
6	0.133	4.66	0	0.123	13.00	0	0.066	1.64	1	
6	0.127	4.24	0	0.127	13.89	0	0.062	0.55	3	
6	0.130	4.45	0	0.124	13.22	0	0.069	2.45	0	
7	0.066	0.03	4	0.066	0.22	4	0.060	0.00	4	
7	0.066	0.02	4	0.067	0.43	4	0.061	0.16	4	
7	0.067	0.03	4	0.066	0.20	4	0.060	0.03	4	
8	0.068	0.14	4	0.066	0.07	4	0.058	0.55	3	
8	0.066	0.00	4	0.065	0.04	4	0.058	0.60	3	
8	0.066	0.01	4	0.064	0.22	4	0.058	0.52	3	
9	0.046	1.41	2	0.068	0.58	3	0.064	1.20	2	
9										
9										
10							0.056	0.98	3	
10							0.057	0.71	3	
10							0.058	0.60	3	

Sample P4										
Laboratory	Total phosphorus Sample median = 0.018 mg/L F-pseudosigma = 0.032			Sample	Total dissolved phosphorus Sample median = 0.015 mg/L F-pseudosigma = 0.030			Soluble reactive phosphorus Sample median = 0.013 mg/L F-pseudosigma = 0.0044		
-	Conc.	z-value	Rating	Conc.	z-value	Rating	Conc.	z-value	Rating	
1	0.018	0.00	4	0.014	0.04	4	0.012	0.01	4	
1	0.017	0.03	4	0.015	0.00	4	0.012	0.06	4	
1	0.016	0.06	4	0.015	0.01	4	0.012	0.01	4	
2	ND	ND	ND	ND	ND	ND	ND	ND	ND	
2	ND	ND	ND	ND	ND	ND	ND	ND	ND	
2	ND	ND	ND	ND	ND	ND	ND	ND	ND	
3	0.018	0.00	4	0.014	0.04	4	0.011	0.30	4	
3	0.018	0.00	4	0.014	0.04	4				
3										
4	0.019	0.03	4	0.013	0.07	4	0.012	0.08	4	
4	0.025	0.22	4	0.018	0.10	4	0.010	0.53	3	
4	0.014	0.12	4	0.013	0.07	4	0.012	0.08	4	
5	0.013	0.15	4	0.013	0.07	4	0.014	0.37	4	
5	0.012	0.19	4	0.013	0.07	4	0.013	0.15	4	
5	0.012	0.19	4	0.013	0.07	4	0.012	0.08	4	
6	0.095	2.40	0	0.090	2.52	0	0.031	4.19	0	
6	0.097	2.46	0	0.092	2.58	0	0.026	3.07	0	
6	0.098	2.49	0	0.090	2.52	0	0.030	3.97	0	
7	0.018	0.00	4	0.016	0.04	4	0.012	0.06	4	
7	0.018	0.00	4	0.016	0.02	4	0.012	0.03	4	
7	0.018	0.00	4	0.015	0.01	4	0.012	0.06	4	
8	0.018	0.00	4	0.014	0.04	4	0.011	0.35	4	
8	0.018	0.00	4	0.015	0.01	4	0.011	0.39	4	
8	0.016	0.05	4	0.015	0.01	4	0.011	0.28	4	
9	0.017	0.02	4				0.016	0.78	3	
9										
9										
10							0.018	1.27	2	
10							0.015	0.57	3	
10							0.016	0.71	3	

Sample P5										
Laboratory	Total phosphorus Sample median = 0.031 mg/L F-pseudosigma = 0.0070			Sample	Total dissolved phosphorus Sample median = 0.028 mg/L F-pseudosigma = 0.031			Soluble reactive phosphorus Sample median = 0.020 mg/L F-pseudosigma = 0.0020		
	Conc.	z-value	Rating	Conc.	z-value	Rating	Conc.	z-value	Rating	
1	0.032	0.22	4	0.031	0.11	4	0.020	0.00	4	
1	0.030	0.07	4	0.026	0.04	4	0.020	0.10	4	
1	0.031	0.11	4	0.030	0.07	4	0.020	0.14	4	
2	0.011	2.81	0	0.072	1.44	2	0.035	7.27	0	
2	0.015	2.24	0	0.068	1.31	2	0.036	7.76	0	
2	0.013	2.53	0	0.068	1.31	2	0.031	5.35	0	
3	0.030	0.10	4	0.028	0.01	4	0.017	1.20	2	
3	0.029	0.30	4	0.027	0.03	4	0.018	0.96	3	
3	0.031	0.01	4	0.028	0.00	4	0.018	1.06	2	
4	0.036	0.77	3	0.034	0.21	4	0.032	5.96	0	
4	0.037	0.92	3	0.036	0.27	4	0.035	7.20	0	
4	0.033	0.34	4	0.032	0.15	4	0.030	4.87	0	
5	0.023	1.09	2	0.023	0.15	4	0.019	0.43	4	
5	0.023	1.09	2	0.024	0.11	4	0.019	0.43	4	
5	0.023	1.09	2	0.023	0.15	4	0.019	0.43	4	
6										
6										
6										
7	0.032	0.14	4	0.027	0.00	4	0.020	0.19	4	
7	0.032	0.24	4	0.025	0.10	4	0.019	0.29	4	
7	0.031	0.01	4	0.025	0.07	4	0.019	0.29	4	
8	0.030	0.04	4	0.027	0.01	4	0.018	0.92	3	
8										
8										
9	0.033	0.36	4	0.026	0.04	4	0.021	0.72	3	
9	0.033	0.36	4	0.028	0.00	4	0.022	0.92	3	
9	0.032	0.26	4	0.028	0.00	4	0.022	0.82	3	
10							0.019	0.53	3	
10							0.020	0.00	4	
10							0.020	0.14	4	

Sample P6											
Laboratory	Total phosphorus Sample median = 0.21 mg/L F-pseudosigma = 0.017			Sampl	Total dissolved phosphorus Sample median = 0.19 mg/L F-pseudosigma = 0.038			Soluble reactive phosphorus Sample median = 0.17 mg/L F-pseudosigma = 0.0093			
	Conc.	z-value	Rating	Conc.	z-value	Rating	Conc.	z-value	Rating		
1	0.20	0.05	4	0.18	0.10	4	0.17	0.14	4		
1	0.21	0.03	4	0.19	0.05	4	0.17	0.39	4		
1	0.21	0.03	4	0.18	0.11	4	0.17	0.39	4		
2	0.20	0.44	4	0.24	1.46	2	0.18	1.07	2		
2	0.20	0.09	4	0.24	1.41	2	0.19	1.39	2		
2	0.20	0.56	3	0.24	1.25	2	0.19	1.39	2		
3	0.21	0.09	4	0.19	0.00	4	0.17	0.43	4		
3	0.21	0.50	4	0.19	0.08	4	0.17	0.21	4		
3	0.21	0.32	4	0.19	0.10	4	0.17	0.11	4		
4	0.27	3.90	0	0.19	0.08	4	0.18	0.90	3		
4	0.27	3.66	0	0.19	0.10	4	0.18	1.18	2		
4	0.27	3.60	0	0.19	0.05	4	0.18	1.04	2		
5	0.20	0.62	3	0.19	0.03	4	0.17	0.00	4		
5	0.19	0.68	3	0.19	0.00	4	0.17	0.00	4		
5	0.19	0.74	3	0.19	0.00	4	0.17	0.00	4		
6											
6											
6											
7	0.20	0.44	4	0.18	0.18	4	0.17	0.00	4		
7	0.20	0.62	3	0.17	0.36	4	0.17	0.43	4		
7	0.20	0.33	4	0.19	0.05	4	0.17	0.00	4		
8	0.22	1.08	2	0.19	0.13	4	0.18	0.21	4		
8											
8											
9	0.22	0.61	3	0.18	0.29	4	0.19	2.14	0		
9	0.22	0.91	3	0.19	0.03	4	0.18	0.54	3		
9	0.22	0.91	3	0.17	0.47	4	0.18	0.96	3		
10							0.10	7.47	0		
10							0.11	7.24	0		
10							0.11	6.93	0		

Sample P7										
Laboratory	Total phosphorus Sample median = 0.049 mg/L F-pseudosigma = 0.014			Total dissolved phosphorus Sample median = 0.046 mg/L F-pseudosigma = 0.033			Soluble reactive phosphorus Sample median = 0.040 mg/L F-pseudosigma = 0.0047			
-	Conc.	z-value	Rating	Conc.	z-value	Rating	Conc.	z-value	Rating	
1	0.047	0.14	4	0.044	0.05	4	0.041	0.11	4	
1	0.051	0.13	4	0.044	0.07	4	0.041	0.28	4	
1	0.048	0.11	4	0.046	0.01	4	0.042	0.36	4	
2	0.068	1.30	2	0.088	1.25	2	0.055	3.21	0	
2	0.072	1.58	1	0.092	1.37	2	0.054	3.00	0	
2	0.066	1.16	2	0.094	1.43	2	0.052	2.57	0	
3	0.044	0.39	4	0.042	0.13	4	0.040	0.11	4	
3	0.046	0.27	4	0.043	0.10	4	0.040	0.00	4	
3	0.047	0.19	4	0.043	0.10	4	0.040	0.02	4	
4	0.140	6.34	0	0.058	0.35	4	0.046	1.37	2	
4	0.154	7.31	0	0.059	0.38	4	0.047	1.51	1	
4	0.148	6.90	0	0.060	0.41	4	0.050	2.06	0	
5	0.037	0.86	3	0.041	0.15	4	0.039	0.21	4	
5	0.037	0.86	3	0.041	0.15	4	0.039	0.21	4	
5	0.037	0.86	3	0.040	0.18	4	0.039	0.21	4	
6										
6										
6										
7	0.047	0.15	4	0.043	0.08	4	0.039	0.19	4	
7	0.050	0.07	4	0.053	0.21	4	0.039	0.13	4	
7	0.048	0.12	4	0.045	0.05	4	0.040	0.09	4	
8	0.048	0.07	4	0.049	0.07	4	0.038	0.43	4	
8										
8										
9	0.053	0.26	4	0.046	0.01	4	0.045	1.07	2	
9	0.052	0.19	4	0.047	0.03	4	0.045	1.07	2	
9	0.051	0.14	4	0.047	0.01	4	0.045	1.13	2	
10							0.030	2.23	0	
10							0.028	2.57	0	
10							0.028	2.58	0	

Sample P8										
Laboratory	Sample	Total phosphorus Sample median = 0.066 mg/L F-pseudosigma = 0.015			Total dissolved phosphorus Sample median = 0.049 mg/L F-pseudosigma = 0.051			Soluble reactive phosphorus Sample median = 0.034 mg/L F-pseudosigma = 0.0055		
	Conc.	z-value	Rating	Conc.	z-value	Rating	Conc.	z-value	Rating	
1	0.050	1.08	2	0.041	0.16	4	0.027	1.35	2	
1	0.050	1.10	2	0.044	0.11	4	0.027	1.31	2	
1	0.053	0.91	3	0.046	0.07	4	0.026	1.51	1	
2	0.066	0.03	4	0.212	3.22	0	0.045	2.01	0	
2	0.064	0.16	4	0.210	3.18	0	0.046	2.19	0	
2	0.066	0.03	4	0.204	3.06	0	0.048	2.55	0	
3	0.063	0.20	4	0.047	0.04	4	0.034	0.07	4	
3	0.064	0.16	4	0.048	0.02	4	0.035	0.18	4	
3	0.067	0.03	4	0.049	0.01	4	0.035	0.18	4	
4	0.067	0.04	4	0.052	0.06	4	0.041	1.32	2	
4	0.069	0.17	4	0.050	0.02	4	0.041	1.32	2	
4	0.064	0.16	4	0.056	0.14	4	0.043	1.67	1	
5	0.055	0.75	3	0.043	0.12	4	0.034	0.00	4	
5	0.054	0.82	3	0.043	0.12	4	0.034	0.00	4	
5	0.054	0.82	3	0.043	0.12	4	0.034	0.00	4	
6										
6										
6										
7	0.072	0.39	4	0.051	0.03	4	0.034	0.04	4	
7	0.068	0.13	4	0.046	0.07	4	0.034	0.04	4	
7	0.068	0.08	4	0.046	0.06	4	0.034	0.00	4	
8	0.073	0.43	4	0.050	0.01	4	0.034	0.00	4	
8										
8										
9	0.076	0.66	3	0.052	0.06	4	0.041	1.26	2	
9	0.075	0.60	3	0.054	0.09	4	0.041	1.26	2	
9	0.077	0.73	3	0.058	0.17	4	0.041	1.29	2	
10							0.021	2.45	0	
10							0.019	2.67	0	
10							0.020	2.49	0	

Sample P9										
Laboratory	Total phosphorus Sample median = 0.057 mg/L F-pseudosigma = 0.025			Total dissolved phosphorus Sample median = 0.036 mg/L F-pseudosigma = 0.040			Soluble reactive phosphorus Sample median = 0.022 mg/L F-pseudosigma = 0.0036			
-	Conc.	z-value	Rating	Conc.	z-value	Rating	Conc.	z-value	Rating	
1	0.056	0.04	4	0.036	0.01	4	0.022	0.00	4	
1	0.057	0.00	4	0.035	0.02	4	0.022	0.19	4	
1	0.058	0.04	4	0.035	0.02	4	0.022	0.19	4	
2	0.088	1.26	2	0.088	1.29	2	0.031	2.42	0	
2	0.094	1.50	1	0.090	1.34	2	0.031	2.42	0	
2	0.096	1.58	1	0.090	1.34	2	0.032	2.70	0	
3	0.057	0.02	4	0.033	0.08	4	0.020	0.66	3	
3	0.054	0.12	4	0.034	0.06	4	0.021	0.47	4	
3	0.057	0.00	4	0.034	0.05	4	0.020	0.52	3	
4	0.058	0.06	4	0.041	0.13	4	0.030	2.24	0	
4	0.055	0.06	4	0.042	0.15	4	0.030	2.07	0	
4	0.062	0.22	4	0.048	0.30	4	0.030	2.07	0	
5	0.044	0.51	3	0.030	0.15	4	0.022	0.06	4	
5	0.044	0.51	3	0.031	0.12	4	0.022	0.06	4	
5	0.044	0.51	3	0.031	0.12	4	0.022	0.06	4	
6										
6										
6										
7	0.056	0.02	4	0.036	0.01	4	0.023	0.22	4	
7	0.054	0.09	4	0.034	0.04	4	0.023	0.22	4	
7	0.054	0.11	4	0.034	0.06	4	0.023	0.22	4	
8	0.056	0.01	4	0.037	0.03	4	0.022	0.06	4	
8										
8										
9	0.058	0.04	4	0.037	0.02	4	0.026	1.16	2	
9	0.058	0.06	4	0.037	0.02	4	0.026	1.10	2	
9	0.056	0.02	4	0.037	0.01	4	0.026	1.10	2	
10							0.018	1.03	2	
10							0.019	0.95	3	
10							0.019	0.90	3	

Sample P10											
Laboratory	Total phosphorus Sample median = 0.024 mg/L F-pseudosigma = 0.0087			Sample	Total dissolved phosphorus Sample median = 0.022 mg/L F-pseudosigma = 0.022			Soluble reactive phosphorus Sample median = 0.016 mg/L F-pseudosigma = 0.0019			
	Conc.	z-value	Rating	Conc.	z-value	Rating	Conc.	z-value	Rating		
1	0.024	0.09	4	0.020	0.10	4	0.015	0.16	4		
1	0.023	0.24	4	0.024	0.10	4	0.015	0.11	4		
1	0.025	0.01	4	0.022	0.01	4	0.016	0.00	4		
2	0.031	1.02	2	0.050	1.25	2	0.025	5.03	0		
2	0.038	2.10	0	0.058	1.61	1	0.026	5.57	0		
2	0.031	1.02	2	0.056	1.52	1	0.025	5.03	0		
3	0.024	0.01	4	0.020	0.10	4	0.012	1.71	1		
3	0.022	0.43	4	0.021	0.02	4	0.013	1.66	1		
3	0.023	0.24	4	0.020	0.06	4	0.013	1.55	1		
4	0.038	2.10	0	0.026	0.18	4	0.023	3.78	0		
4	0.040	58.85	0	0.027	0.23	4	0.021	2.74	0		
4	0.042	2.72	0	0.024	0.10	4	0.020	2.36	0		
5	0.018	1.00	2	0.019	0.13	4	0.015	0.32	4		
5	0.017	1.16	2	0.018	0.17	4	0.014	0.86	3		
5	0.017	1.16	2	0.018	0.17	4	0.014	0.86	3		
6											
6											
6											
7	0.024	0.07	4	0.024	0.08	4	0.016	0.43	4		
7	0.025	0.04	4	0.022	0.00	4	0.017	0.59	3		
7	0.021	0.53	3	0.022	0.02	4	0.016	0.43	4		
8	0.022	0.33	4	0.020	0.10	4	0.013	1.39	2		
8											
8											
9	0.025	0.09	4	0.022	0.01	4	0.017	0.59	3		
9	0.025	0.09	4	0.022	0.02	4	0.017	0.54	3		
9	0.025	0.15	4	0.022	0.00	4	0.017	0.54	3		
10							0.015	0.27	4		
10							0.015	0.40	4		
10							0.014	0.76	3		

Sample P11										
Laboratory	Total phosphorus Sample median = 0.023 mg/L F-pseudosigma = 0.0094			Total dissolved phosphorus Sample median = 0.012 mg/L F-pseudosigma = 0.075			Soluble reactive phosphorus Sample median = 0.0085 mg/L F-pseudosigma = 0.0016			
	Conc.	z-value	Rating	Conc.	z-value	Rating	Conc.	z-value	Rating	
1	0.021	0.22	4	0.015	0.04	4	0.008	0.06	4	
1	0.021	0.24	4	0.014	0.03	4	0.009	0.25	4	
1	0.020	0.32	4	0.015	0.04	4	0.008	0.43	4	
2	0.033	1.08	2	0.112	1.33	2	0.020	7.12	0	
2	0.029	0.65	3	0.114	1.36	2	0.020	7.12	0	
2	0.040	1.82	1	0.124	1.49	2	0.019	6.50	0	
3	0.015	0.81	3	0.011	0.02	4	0.005	2.35	0	
3	0.016	0.73	3	0.011	0.02	4	0.005	1.92	1	
3	0.015	0.79	3	0.011	0.02	4	0.005	2.10	0	
4	0.116	9.89	0	0.015	0.04	4	0.009	0.02	4	
4	0.117	10.00	0	0.018	0.08	4	0.010	1.21	2	
4	0.111	9.36	0	0.014	0.03	4	0.010	1.21	2	
5	0.016	0.73	3	0.010	0.03	4	0.007	0.93	3	
5	0.017	0.62	3	0.010	0.03	4	0.007	0.93	3	
5	0.017	0.62	3	0.010	0.03	4	0.007	0.93	3	
6										
6										
6										
7	0.030	0.73	3	0.013	0.01	4	0.008	0.50	4	
7	0.026	0.37	4	0.012	0.00	4	0.007	0.99	3	
7	0.027	0.40	4	0.012	0.01	4	0.008	0.56	3	
8	0.017	0.63	3	0.011	0.02	4	0.007	0.93	3	
8										
8										
9	0.025	0.23	4	0.012	0.00	4	0.009	0.00	4	
9	0.023	0.02	4	0.012	0.00	4	0.009	0.00	4	
9	0.023	0.02	4	0.012	0.00	4	0.009	0.56	3	
10							0.009	0.29	4	
10							0.009	0.25	4	
10							0.009	0.42	4	

Sample P12										
Laboratory	Total phosphorus Sample median = 0.025 mg/L F-pseudosigma = 0.015			Total dissolved phosphorus Sample median = 0.019 mg/L F-pseudosigma = 0.0073			Soluble reactive phosphorus Sample median = 0.013 mg/L F-pseudosigma = 0.0018			
	Conc.	z-value	Rating	Conc.	z-value	Rating	Conc.	z-value	Rating	
1	0.027	0.14	4	0.018	0.05	4	0.013	0.00	4	
1	0.025	0.01	4	0.019	0.00	4	0.014	0.17	4	
1	0.025	0.00	4	0.019	0.07	4	0.013	0.00	4	
2	0.052	1.76	1	0.031	1.66	1	0.025	6.52	0	
2	0.044	1.24	2	0.035	2.21	0	0.022	4.83	0	
2	0.056	2.02	0	0.027	1.12	2	0.025	6.52	0	
3	0.025	0.01	4	0.017	0.29	4	0.010	1.85	1	
3	0.023	0.12	4	0.017	0.19	4	0.011	1.57	1	
3	0.025	0.00	4	0.018	0.05	4	0.011	1.57	1	
4	0.033	0.53	3	0.022	0.44	4	0.016	1.23	2	
4	0.032	0.46	4	0.024	0.71	3	0.017	1.95	1	
4	0.036	0.72	3	0.020	0.16	4	0.016	1.59	1	
5	0.016	0.57	3	0.016	0.38	4	0.011	1.35	2	
5	0.016	0.57	3	0.016	0.38	4	0.012	0.79	3	
5	0.016	0.57	3	0.016	0.38	4	0.012	0.79	3	
6										
6										
6										
7	0.026	0.07	4	0.019	0.01	4	0.011	1.24	2	
7	0.024	0.06	4	0.017	0.23	4	0.013	0.45	4	
7	0.023	0.11	4	0.017	0.25	4	0.013	0.45	4	
8	0.022	0.20	4	0.017	0.22	4	0.011	1.35	2	
8										
8										
9	0.024	0.07	4	0.019	0.04	4	0.014	0.56	3	
9	0.024	0.07	4	0.019	0.04	4	0.014	0.45	4	
9	0.024	0.07	4	0.019	0.00	4	0.014	0.45	4	
10							0.013	0.22	4	
10							0.013	0.03	4	
10							0.014	0.12	4	

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