

28 QUALITY ASSURANCE ASSESSMENT REPORT

BACKGROUND

Environmental monitoring and management requires the collection of highly reliable data. Data accepted for inclusion in a database must be of known quality and must meet established criteria. A Quality Assurance Program is a defined protocol for sample collection, handling, and analysis to ensure that the quality of the data collected is quantified and tracked. Quality Assurance consists of two components (*Standard Methods*, 2005):

- Quality Assessment (QA) Periodic evaluations of laboratory performance through the submission and analysis of externally provided blanks, standard solutions, duplicates, and split samples.
- Quality Control (QC) Documented operator competence, recovery of known additions, and analysis of internally provided reagent blanks, proper equipment calibration, and maintenance of control charts.

DESCRIPTION

This Quality Assurance Project Plan (QAPP) describes the procedures and quality control measures used for water quality monitoring and laboratory analyses completed in 2006 for the Minneapolis Chain of Lakes monitoring, the National Pollutant Discharge Elimination Systems (NPDES) stormwater monitoring, and other studies. The project activities for lake sampling are detailed in the Lake Monitoring Program Overview, Section 1. Stormwater monitoring procedures are explained in the Stormwater Monitoring Program Manual (MPRB, 2001).

The frequencies of quality assessment and quality control activities are set forth to ensure the validity of the database are listed in Table 28A. The QA/QC plan follows the recommendations of *Standard Methods for the Examination of Water and Wastewater* (2005).

Table 28A. Summary and frequency of QA/QC activities.

Sample type	Description	Function	Frequency
Equipment Blank	Reagent-grade deionized water subject to sample collection, processing and analysis	Used in estimating background values due to sample collection, processing and analysis	10% of samplings trips
Bottle Blank/Field Blank	Reagent-grade deionized water subject to sample processing and analysis	Used in estimating background values due to sample processing and analysis; carried in the field	Every sampling trip
Field Duplicate	Duplicate of lake sampling procedures	Used in estimating lab batch and sampling procedure precision	Every sampling trip
Blind QA/QC Audit Standard	Synthetic sample to mimic a natural sample	Used in estimating overall batch precision and lab bias	Once/Month
Laboratory Calibration Standard	Standard solution from a source other than the control standard	Used to calibrate the instrument before samples are analyzed	One/lab batch (10% of samples)
Laboratory Calibration Blank	Reagent-grade deionized water	Used in identifying signal drift and contamination of samples	One/lab batch (10% of samples)
Laboratory Reagent Blank	Reagent-grade deionized water plus reagents	Used in identifying contamination of reagents	One/lab batch (10% of samples)
Laboratory Control Standard	Standard solution from a source other than calibration standard	Used in determining accuracy and consistency of instrument calibration	One/lab batch (10% of samples)
Split Samples	Split of lake sample sent to different laboratories for analysis	Used in determining comparability	2 different lakes, twice during sampling season
Laboratory Duplicate	Split of sample aliquot	Used in determining analytical precision within batches	10% of samples (at least one per batch)
Laboratory Matrix Spike/Matrix Spike Duplicate	Known spike of sample (recovery of known additions)	Used in determining percent recovery of parameter analyzed	10% of samples (at least one per batch)

QA/QC definitions, as presented by T.A. Dillaha, et al. (1988) and *Standard Methods for the Examination of Water and Wastewater* (2005), are used in the presentation of the information in this document.

- *Precision* is a measure of the degree of agreement between independent measurements of some property. It is concerned with the closeness of the results and is usually expressed in terms of the standard deviation of the data for duplicate or replicate analyses. Precision is a measure of how close the results are together with respect to each other; not how close they are to a "true value."
- *Accuracy* is a measure of the degree of agreement of a measured value with an accepted reference or true value. It is usually expressed in terms of percent recovery of the expected value (standard solution) and is an expression of the amount of bias in the data. Accuracy is a measure of how close the results are to a known "true value."
- *Representativeness* is a measure of the degree to which data accurately and precisely represent the characteristics of the population, which is being monitored. For example, a bell curve represents a "normal" distribution of data.
- *Completeness* is a measure of the amount of valid data obtained from a measurement system compared to the amount expected to be obtained under correct normal conditions. For example, a data set for a lake will not be complete if the laboratory did not analyze all expected parameters. Completeness is usually expressed as a percent of the "true value."
- *Comparability* expresses the confidence with which one data set, measuring system, or piece of equipment can be compared with another. Data can be considered comparable if they are similar to those reported by others in the literature, data from previous years and if the analysis procedures produce results similar to those reported by other laboratories for split samples.

OBJECTIVES

The primary objective of this QAPP is to ensure and identify the completeness, representativeness, precision, accuracy, and comparability of the data collected. The following pages summarize these data characteristics for results from both field measurements and parameters analyzed by the contract lab Instrumental Research Inc. (IRI) located in Fridley, MN.

This program was designed to clearly establish which data were: 1) usable, 2) of questionable usability and needed to be flagged or 3) unusable. Quantitative data quality descriptions have been included to provide data users with background on why certain data were deemed to be questionable or unusable. This enables the data user to apply more or less stringent acceptance limits on defining usability to meet the objectives of their own analyses. Quantitative data quality indicators were calculated for each analysis method individually. In order to estimate quantitative data quality indicators on a method-by-method basis, all samples analyzed using a given method were treated as belonging to the same population (Fairless and Bates, 1989).

The QAPP set forth target frequencies for all QA/QC activities:

- Every sampling batch included analysis blanks, standards, and duplicates for each set of samples analyzed.
- Ten percent of all samples were run in duplicate.
- Ten percent of the sampling trips had equipment blanks associated with them.
- A bottle field blank was associated with every sampling trip.
- One laboratory reagent blank was analyzed for every ten samples run.
- Filter blanks were analyzed where appropriate.
- A matrix spike was analyzed with every ten samples.

Blind performance evaluation samples of known concentration were submitted to the laboratory by the MPRB monthly for analysis. The performance evaluation samples served as a quality assessment of monthly analytical runs.

IRI used the following procedures during each analytical run:

- Blanks for water and reagents (one for each) were analyzed for every 10 samples run.
- A standard of known concentration was analyzed for each analytical run.
- One spike (recovery of known additions) was analyzed for every 10 samples run.
- One duplicate sample was analyzed for every 10 samples run.

Additional quality control measures used in the contract laboratory were as follows:

- Control charts were maintained for all routinely measured parameters and analyses were not performed unless control (reference) samples fell within the specified acceptance limits (Table 28B).
- Experienced individuals trained technicians before they were allowed to conduct analyses by themselves, and their supervisors routinely reviewed their performance.

Table 28B. 2006 IRI analytical laboratory reporting limits, the performance evaluation (PE) percent recovery acceptance limits, and relative percent difference (RPD) allowed with duplicates. NA = Not Applicable.

Parameter	Abbreviation	IRI Reporting Limits	PE % Rec Limits	Duplicate RPD Limits
Alkalinity, Total	Alk	2.0 mg/L	80-120%	±10%
Aluminum, Total/ Soluble	Al	5 µg/L	80-120%	±25%
Ammonia, Un-ionized as N	NH3	0.500 mg/L	80-120%	±10%
Arsenic, Total	As	20 µg/L	80-120%	±10%
BOD, 5 Day carbonaceous	cBOD	1.0 mg/L	80-120%	±10%
Cadmium, Total	Cd	5 µg/L	80-120%	±25%
Chloride, Total	Cl	2.0 mg/L	80-120%	±10%
Chlorophyll-a	Chl-a	1 µg/L	NA	±25%
Conductivity	Cond	2.6 µmhos/cm	80-120%	±25%
Copper, Total	Cu	5 µg/L	80-120	±25%
Fecal Coliform	FC	<1 CFU per 100mL	NA	NA
Hardness, Total as CaCO3	Hard	1.0 mg/L	80-120%	±10%
Kjeldahl Nitrogen, Total	TKN	0.500 mg/L	80-120%	±10%
Lead, Total	Pb	5 µg/L	80-120%	±25%
Manganese, Total	Mn	20 µg/L	80-120%	±25%
Nickel, Total	Ni	5 µg/L	80-120%	±25%
Nitrite+Nitrate, Total as N	NO3NO2	0.030 mg/L	80-120%	±10%
Nitrogen, Total	TN	0.500 mg/L	80-120%	±10%
pH	pH	1.00 Std. Units	80-120%	±10%
Phosphorus, Dissolved	TDP	0.010 mg/L	80-120%	±10%
Phosphorus, Total	TP	0.010 mg/L	80-120%	±10%
Silica, Reactive	Si	0.500 mg/L	NA	±10%
Solids, Total Dissolved	TDS	10.0 mg/L	80-120%	NA
Solids, Total Suspended	TSS	1.0 mg/L	80-120%	NA
Soluble Reactive Phosphorus	SRP	0.005 mg/L	70-130%	±25%
Zinc, Total	Zn	50 µg/L	80-120%	±25%

METHODS

Laboratory results and field data were entered into a spreadsheet. Data were evaluated to determine usability according to the methods below. Data were categorized into one of three levels of usability: *fully usable*, *questionable usability*, or *unusable*. To be "fully usable", the data had to meet all of the data quality criteria: *completeness*, *representativeness*, *comparability*, *precision*, and *accuracy*. Data rated as "questionable usability" met all but one of the quality criteria. Unusable data were those that were known to contain significant errors or fewer than four of the data quality criteria.

Completeness Data sets were deemed to be complete if fewer than 5% of the data were missing or not analyzed appropriately.

Representativeness Data sets were deemed to be representative if samples were collected according to the sampling schedule, and standard collection and handling methods were followed. Monitoring locations, frequencies and methods followed suggested protocol to ensure representativeness (Wedepohl et al., 1990).

Comparability Data for a given parameter were deemed to be highly comparable if the

laboratory split results for that parameter, from all three labs, had a relative percent difference of less than 20% and if reported values were consistent with past results. If the relative percent difference between labs for a given parameter was more than 20%, but the majority of data reported were within 20%, the data set for that parameter was deemed to be moderately comparable. Coefficient of variation (CV) was used as another measure of how close the laboratories were to each other.

$$\text{Coefficient of Variation (CV)} = \frac{\text{standard deviation}}{\text{mean}}$$

Precision

- Data sets were deemed precise if two criteria were met:
1. The relative percent difference of results, for each pair of duplicate analyses, was within acceptance limits for each given parameter (*Standard Methods, 2005*).
 2. The percent recovery of known standard additions met the established acceptance limits for each parameter (*Standard Methods, 2005*).

$$\text{Percent Recovery (\% Rec)} = \frac{\text{Observed Value}}{\text{Expected Value}} \times 100\%$$

Precision was further quantified by calculating the average range and standard deviation of results for duplicates.

$$\text{Relative Percent Difference (RPD)} = \frac{|X_1 - X_2|}{(X_1 + X_2)/2} \times 100\%$$

where: X_1 and X_2 are duplicate pair values; sum for all duplicates

$$\text{Average Range (R)} = \frac{\sum |X_1 - X_2|}{n}$$

where: X_1 and X_2 are duplicate pair values; sum for all duplicates,
and n = number of duplicate pairs

Standard Deviation (estimated) (SD)

R / 1.128

R=Average Range

Accuracy

Data sets were deemed accurate if the percent recovery reported for performance evaluation standards fell within the established acceptance limits for each given parameter (Table 28B) and had been deemed precise. The percent recovery estimates bias in the data set. Together, bias and precision reflect overall data set accuracy (*Standard Methods*, 2005). Low bias and high precision translates to high accuracy.

The standard solutions used for performance evaluation samples were manufactured by Environmental Resource Associates (ERA) located in Arvada, Colorado and diluted by MPRB staff to achieve the desired concentrations. ERA provided performance acceptance limits for the recovery of each analyte. These performance limits defined acceptable analytical results given the limitations of the United States Environmental Protection Agency (US EPA) approved and Standard Methods methodologies (US EPA Reports, 1980, 1985). The acceptance limits were based on data generated by laboratories in ERA's InterLab program and data from the US EPA, and closely approximated the 95% confidence interval. If a laboratory failed a blind monthly performance standard, all of the monthly data for that parameter were flagged as questionable. Laboratories were allowed $\pm 20\%$ recovery for all parameters except soluble reactive phosphorus and total dissolved phosphorus data, which were allowed $\pm 30\%$ recovery, due to the low phosphorus concentrations.

The contract laboratories provided minimum detection limits (MDL) and reporting limits. The laboratory calculated the MDL based upon documented performance studies and the reporting limits are two to five times the MDL. Table 28B lists the reporting limits for analyses as provided by IRI.

RESULTS AND DISCUSSION

If the monthly performance standard failed to achieve the required percent recovery and the error was greater than two times the reporting limit, the entire month's data were flagged by underlining it. The only data that were flagged in 2006 were TKN data in the month of May. Biochemical oxygen demand performance standards were handled as a special case due to the unique nature and inherent variability within the test. These data were evaluated using the "rule of sensibility" and all of the data were deemed passing.

Completeness

The data collected in 2006 was deemed to be complete. Missing data and improper analyses accounted for less than 1% of the samples collected.

A minimum of 10% of the final data were checked by hand against the raw data sent by the laboratories to ensure there were no errors entering or transferring the data.

Representativeness

The 2006 lakes data were deemed to be representative of actual in-lake conditions. Samples were collected over the deepest point of each lake at appropriate meter depths. The duration of monitoring, sampling frequency, site location, and depth intervals sampled met or exceeded the recommendations to collect representative data and to account for seasonal changes and natural variability (Wedepohl et al., 1990), see Section 1 for details. Sample collection and handling followed established protocol for monitoring water quality as detailed in *Standard Methods for the Examination of Water and Wastewater* (2005).

NPDES stormwater samples were collected in accordance with the Stormwater Monitoring Program Manual (MPRB, 2001).

Comparability

Between Years

The 2006 lakes data were deemed to be comparable to previous years' data. In reviewing box and whisker plots of total phosphorus, Secchi transparency, and chlorophyll-*a* data (Section 2), reported values appeared to be consistent with values reported at the same times during the 2003, 2004 and 2005 monitoring seasons. The 2006 monitoring season was roughly comparable to the 2005 monitoring season.

Stormwater data for 2006 seemed to be comparable to other stormwater water data, however, it should be noted that stormwater concentrations are highly variable.

Between Laboratories

To determine "between laboratory" data comparability, lake samples were split in the field and shared with IRI, Minnehaha Creek Watershed District (MCWD), Three Rivers Park District (TRPD) and in one case Minnesota Valley Testing Laboratory (MVTL). MCWD used Maxim Technologies in Sioux Falls, South Dakota (owned by Tetra Tech) as their laboratory and TRPD uses their own in-house laboratory. The 2006 lake splits data set were deemed to be generally comparable to data analyzed by TRPD and Maxim Technologies (Table 28C). The MPRB provided split samples to the participating laboratories from two sampling events, June 20 and September 25. The results from all agency split samples are summarized in Table 28C and Figures 28A through 28D. Included in these results are the results from split samples that MCWD and TRPD submitted to IRI.

Data for a given parameter were deemed to be highly comparable if the laboratory split results for that parameter from all the laboratories, had a coefficient of variation (CV) less than 20% and if reported values were consistent with past results. Generally, if the CV between laboratories for a given parameter was more than 20%, but the majority of data reported were within 20%, then the data set for that parameter was deemed to be moderately comparable. Care must be taken when interpreting these data at very low levels or near reporting limits. For example, the CV between 1 and 2 µg/L is 47%, but the CV between 10 and 11 µg/L is 7%. Both have a difference of 1 µg/L. In Table 28C, the SRP values reported below reporting limits did not have CV's calculated if more than two laboratories were below reporting limits.

The comparability of the inter-laboratory split sample, within each of the parameters, differed considerably. Table 28D details the variability within parameters and lists the determined level of comparability for each. The comparability between years was determined by comparing 2006

values to previous year's data. The 2006 data set were comparable to previous years. The final CV calculated for SRP should not be used, due to the many below or near detection limit values (Table 28D).

Table 28C. Summary of split sample results reported by IRI, TRPD, MVTL and Maxim Technologies in 2006. CV = Coefficient of Variation. Underlined data are less than values.

Sample ID	Parameter	Units	Date	Lake	MVTL	IRI	TRPD	Maxim	CV
1	Chl-a	mg/m ³	6/20/2006	Gray's Bay		1.80	<u>5</u>	2.14	59%
2	Chl-a	mg/m ³	6/20/2006	Medicine Lk		13.2	14	16	10%
3	Chl-a	mg/m ³	6/20/2006	Wirth		15.9	20	17.1	12%
4	Chl-a	mg/m ³	9/25/2006	Gray's Bay		2	<u>5</u>	3.2	44%
5	Chl-a	mg/m ³	9/25/2006	Medicine Lk		28.7	50	61.4	36%
6	Chl-a	mg/m ³	9/25/2006	Powderhorn	9.9	2.4	7.4	6.3	48%
7	TP	mg/L	6/20/2006	Gray's Bay		0.019	0.020	0.032	31%
8	TP	mg/L	6/20/2006	Medicine Lk		0.063	0.036	0.053	27%
9	TP	mg/L	6/20/2006	Wirth		0.036	0.039	0.036	5%
10	TP	mg/L	9/25/2006	Gray's Bay		0.018	0.029	0.015	36%
11	TP	mg/L	9/25/2006	Medicine Lk		0.075	0.084	0.075	7%
12	TP	mg/L	9/25/2006	Powderhorn	0.049	0.041	0.044	0.036	13%
13	SRP	mg/L	6/20/2006	Gray's Bay		<u>0.003</u>	0.010	<u>0.005</u>	60%
14	SRP	mg/L	6/20/2006	Medicine Lk		<u>0.003</u>	<u>0.004</u>	<u>0.005</u>	25%
15	SRP	mg/L	6/20/2006	Wirth		0.005	<u>0.004</u>	0.007	29%
16	SRP	mg/L	9/25/2006	Gray's Bay		0.004	0.006	0.005	20%
17	SRP	mg/L	9/25/2006	Medicine Lk		0.012	0.012	<u>0.005</u>	42%
18	SRP	mg/L	9/25/2006	Powderhorn	0.013	0.006	0.005	<u>0.005</u>	53%
19	TN	mg/L	6/20/2006	Gray's Bay		0.543	0.770	0.707	17%
20	TN	mg/L	6/20/2006	Medicine Lk		0.656	0.800	0.899	16%
21	TN	mg/L	6/20/2006	Wirth		<u>0.500</u>	0.680	0.617	15%
22	TN	mg/L	9/25/2006	Gray's Bay		0.653	0.730	0.896	16%
23	TN	mg/L	9/25/2006	Medicine Lk		1.038	1.050	1.180	7%
24	TN	mg/L	9/25/2006	Powderhorn	1.00	0.706	0.830	0.984	16%

Table 28D. Comparability of different parameters analyzed as a part of the inter-laboratory split sample program and as compared to previous years' data. Values listed are the range and mean for the coefficient of variation between labs.

Parameter	Coefficient of Variation		Comparability	
	2006 Range	2006 Mean	Between lab	Between years
Chl-a	10%-59%	35%	Moderate	High
TP	5%-36%	20%	Moderate	High
SRP	20%-60%	38%	Moderate	High
TN	7%-17%	15%	Moderate	High

The split samples for chlorophyll-*a* appear roughly comparable (Figure 28A). The 2006 data had similar precision in the results except sample ID number 5 where there was some scatter in the data. Chlorophyll-*a* concentrations can be extremely variable due to inherent sampling limitations and plankton patchiness. Future High Pressure Liquid Chromatography (HPLC) or fluorometric chlorophyll-*a* analysis of splits, may help determine which lab is more accurate. The average CV was 35%.

Total phosphorus splits were comparable (Figure 28B). The splits from each laboratory had similar precision results. Most of the samples were lower level samples. Scatter in the data was seen in sample ID numbers 7 and 8 where Maxim and TRPD were the outliers, respectively. Phosphorus is an important and limiting aquatic nutrient. Accurate analysis for this element is critical. The average CV for TP was 20%.

Many concentrations, of the submitted SRP split samples, were near lab reporting limits and many analyses were reported as below detectable levels (Figure 28C). Most of the samples were near or at reporting limits and scatter was not seen. The data were graphed on a log scale for visibility. IRI, TRPD and Maxim have reporting limits of 0.003 mg/L, 0.004 mg/L and 0.005 mg/L, respectively. Overall, SRP data must be deemed of questionable comparability, especially at concentrations below 0.010 mg/L. Users of these data must decide if this loss of resolution at low concentrations is of significant concern for any given data application. The average CV for SRP was 38%.

Total nitrogen splits were completed by IRI, TRPD and Maxim laboratories (Figure 28D). Significant outliers for TN were sample ID numbers 20, 22 and 23, where there was some scatter and all showed Maxim as the outlier (Figure 28D). The average CV for TN was 15%.

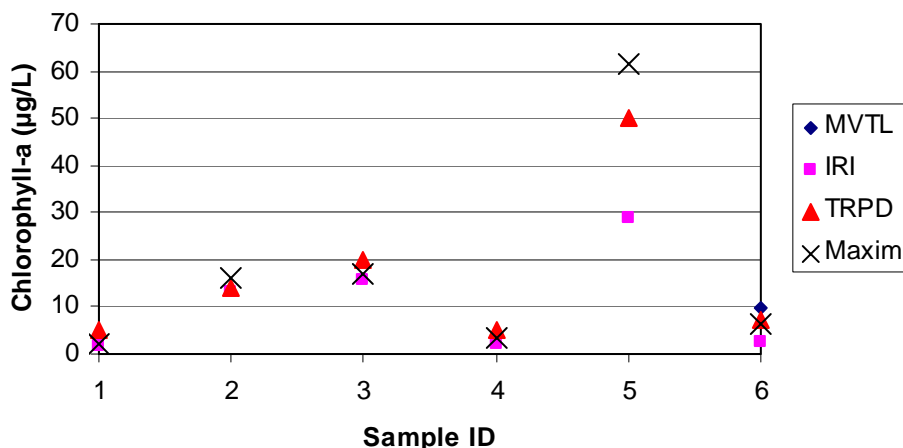


Figure 28A. Scatter plot of chlorophyll-*a* split sample results reported for 2006. See Table 28C to reference sample ID numbers with sample descriptions and results.

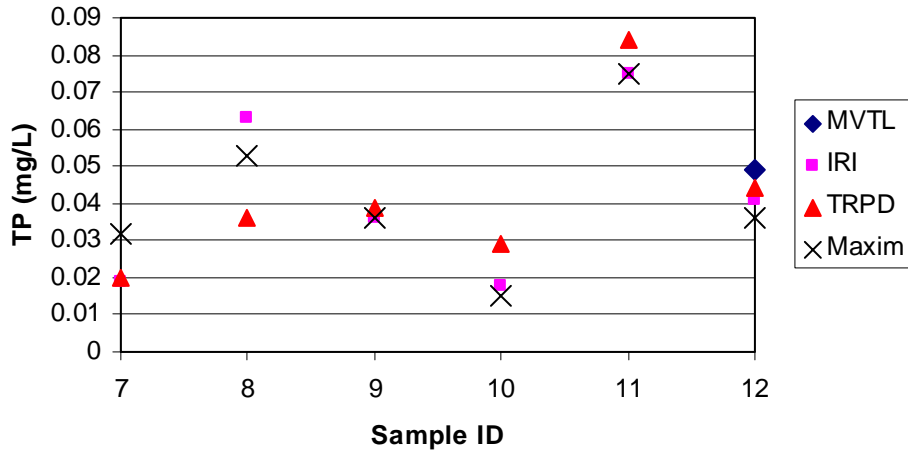


Figure 28B. Scatter plot of total TP split sample results reported for 2006. See Table 28C to reference sample ID numbers with sample descriptions and results.

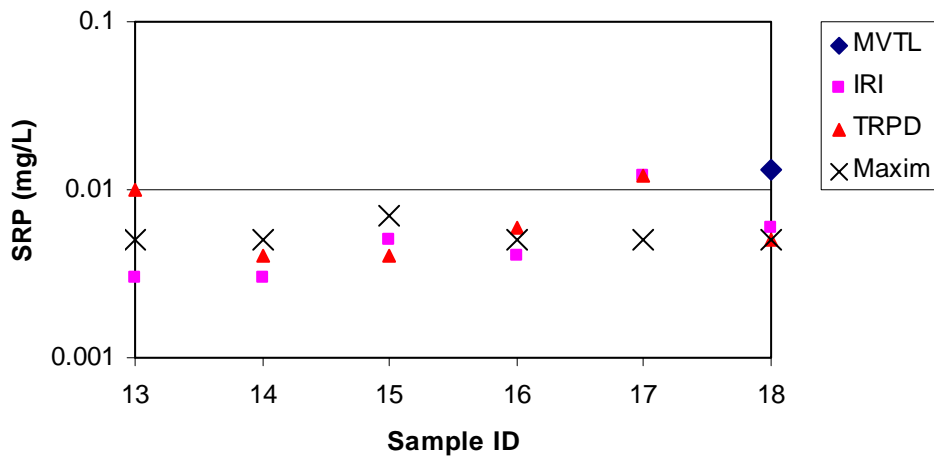


Figure 28C. Scatter plot of SRP split sample results reported for 2006. See Table 28C to reference sample ID numbers with sample descriptions and results. Note the log scale on the Y-axis. MRL = minimum reporting limit.

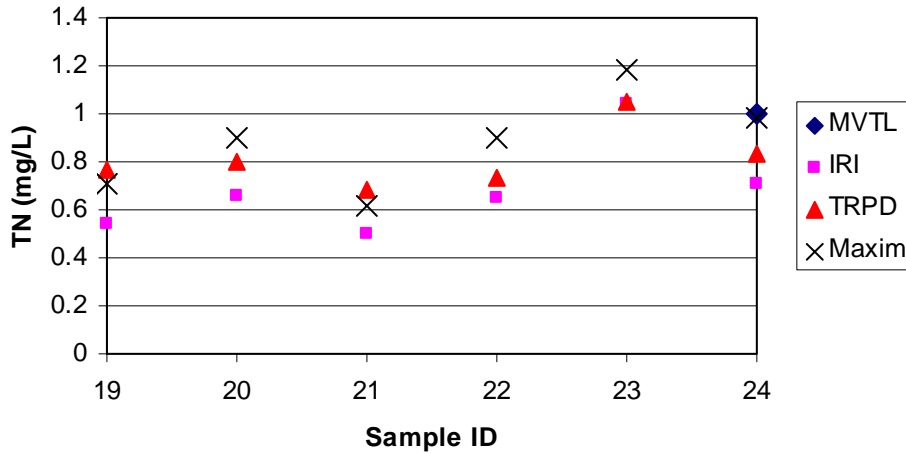


Figure 28D. Scatter plot of TN split sample results reported for 2006. See Table 28C to reference sample ID numbers with sample descriptions and results.

Precision

The first criterion used for assessing data precision was the relative percent difference (RPD) between duplicates. For reporting and calculation purposes, the average of duplicate samples was used.

Field Duplicates

Field duplicates test the reproducibility of field methods and also lake uniformity. Table 28E summarizes the results from field duplicate samples in 2006. The goal is to have the average RPD for parameters to be 10% or less. SRP duplicates are marked as >10% average RPD. When values are near the reporting limit, the RPD calculations are skewed but most times the data are considered acceptable. There were three sampling trip field duplicate failures. Brownie Lake (0-2m, 7/5/06) had Hardness values of 84 mg/L and 96 mg/L, a 13% RPD. Wirth Lake (7m, 8/15/06) had TP values of 1.052 mg/L and 0.893 mg/L, a 16% RPD. The difference may also be the result of pond sediment being disturbed by the Kemmerer sampler. It is unknown why this result occurred. Sulfates and NO3NO2 have average RPD of zero due to all of their duplicates being reported as the same value.

Lab Duplicates

IRI reported all internal QA/QC results to the MPRB. The reported RPD values, for duplicate analyses, were within acceptance limits. All duplicate analyses were deemed acceptable.

Table 28E. 2006 summary of field duplicate sample results and acceptability for IRI Laboratory.
Note: Some results reported for SRP and NO3NO2 were given as “below detection.”
For calculations, these were treated as being half to the detection limit.

Parameter	Units	Average Relative % Difference	Average Range	Std. Dev. (estimated)	Acceptable
Chl-a	µg/L	9.38	1.40	1.24	Yes
Silica	mg/L	5.15	0.15	0.13	Yes
TP	mg/L	7.57	0.01	0.01	Yes
SRP	mg/L	1.47	0.0003	0.0003	Yes
TKN	mg/L	6.31	0.07	0.06	Yes
TN	mg/L	6.70	0.05	0.05	Yes
NO3NO2	mg/L	0.000	0.000	0.0000	Yes
Alk	mg/L	4.88	4.50	3.99	Yes
Hard	mg/L	5.01	5.33	4.73	Yes
Cl	mg/L	1.38	7.00	6.21	Yes
Tot-Al	mg/L	15.6	8.87	7.86	Yes
Tot-Sol	mg/L	14.2	3.53	3.13	Yes
Sulfate	mg/L	0.000	0.000	0.0000	Yes

Performance Evaluation Samples

The second criterion for assessing data precision was percent recovery of performance evaluation samples. Performance evaluation standards were purchased from ERA. MPRB water quality staff used prepared standards mixed to “real world” concentrations for submission to the contract laboratory. Table 28F and Figures 28E through 28I summarize the performance evaluation sample results for each parameter. Of the parameters in Table 28F, TKN had a percent recovery result that did not fall within the established acceptance limits. All other performance evaluation samples fell within acceptance limits.

Table 28F. Summary of performance evaluation samples analyzed by IRI in 2006. Results in bold are outside acceptance limits. (continued on next page)

Sample ID	Parameter	Date	Known Value	Lab Value	% Recovery
1	Al	4/19/2006	194	220	114%
2	Al	5/24/2006	194	193	100%
3	Al	6/23/2006	194	195	101%
4	Al	7/21/2006	194	202	104%
5	Al	8/16/2006	656	540	82%
6	Al	9/12/2006	656	560	85%
7	Al	10/19/2006	656	660	101%
8	Al	11/21/2006	656	668	102%
9	Alk	2/28/2006	74.4	70.0	94%
10	Alk	4/19/2006	82.7	79.0	96%
11	Alk	5/24/2006	82.7	97.0	117%
12	Alk	6/23/2006	82.7	82.5	100%
13	Alk	7/21/2006	82.7	77.5	94%
14	Alk	8/16/2006	82.7	76.0	92%
15	Alk	9/12/2006	82.7	77.0	93%
16	Alk	10/19/2006	82.7	76.0	92%
17	Alk	11/21/2006	82.7	86.5	105%
18	As	2/28/2006	17.3	19.3	111%
19	As	4/19/2006	39.8	38.0	95%
20	As	5/24/2006	39.8	38.5	97%
21	As	6/23/2006	39.8	40.4	102%
22	As	7/21/2006	39.8	39.1	98%
23	As	8/16/2006	15.8	17.6	111%
24	As	9/12/2006	15.8	17.9	113%
25	As	10/19/2006	15.8	16.5	104%
26	As	11/21/2006	15.8	16.3	103%
27	BOD5C	2/28/2006	18.3	19.4	106%
28	BOD5C	3/29/2006	13.2	18.7	142%
29	BOD5C	4/19/2006	13.2	15.4	117%
30	BOD5C	5/24/2006	13.2	9.8	74%
31	BOD5C	6/23/2006	13.2	13.4	102%
32	BOD5C	7/21/2006	13.2	14.9	113%
33	BOD5C	8/16/2006	8.82	11.1	126%
34	BOD5C	9/12/2006	8.82	8.52	97%
35	BOD5C	10/19/2006	8.82	12.9	146%
36	BOD5C	11/21/2006	8.82	11.9	135%

**Table 28F. (continued) Summary of performance evaluation samples analyzed by IRI in 2006.
Results in bold are outside acceptance limits. (continued on next page)**

Sample ID	Parameter	Date	Known Value	Lab Value	% Recovery
37	Cd	2/28/2006	18.2	16.7	92%
38	Cd	3/29/2006	13.5	13.8	102%
39	Cd	4/19/2006	13.5	14.2	105%
40	Cd	5/24/2006	13.5	14.0	104%
41	Cd	6/23/2006	13.5	14.0	104%
42	Cd	7/21/2006	13.5	14.0	104%
43	Cd	8/16/2006	17.2	16.4	95%
44	Cd	9/12/2006	17.2	16.0	93%
45	Cd	10/19/2006	17.2	16.8	98%
46	Cd	11/21/2006	17.2	16.8	98%
47	Cl	2/28/2006	62.4	71.5	115%
48	Cl	3/29/2006	62.4	61.8	99%
49	Cl	4/19/2006	87.8	100	114%
50	Cl	5/24/2006	87.8	91.0	104%
51	Cl	6/23/2006	87.8	86.4	98%
52	Cl	7/21/2006	87.8	80.9	92%
53	Cl	8/16/2006	87.8	100	114%
54	Cl	9/12/2006	87.8	88.9	101%
55	Cl	10/19/2006	87.8	91.3	104%
56	Cl	11/21/2006	87.8	88.2	100%
57	Cond	2/28/2006	436	480	110%
58	Cond	3/29/2006	436	430	99%
59	cond	4/19/2006	553	430	78%
60	cond	5/24/2006	553	567	103%
61	cond	6/23/2006	553	562	102%
62	Cond	7/21/2006	553	543	98%
63	Cond	8/16/2006	553	555	100%
64	Cond	9/12/2006	553	557	101%
65	Cond	10/19/2006	553	620	112%
66	cond	11/21/2006	553	667	121%
67	Cu	2/28/2006	355	372	105%
68	Cu	3/29/2006	384	333	87%
69	Cu	4/19/2006	384	344	90%
70	Cu	5/24/2006	384	373	97%
71	Cu	6/23/2006	384	385	100%
72	Cu	7/21/2006	384	384	100%
73	Cu	8/16/2006	81.6	86.2	106%
74	Cu	9/12/2006	81.6	84.2	103%
75	Cu	10/19/2006	81.6	86.6	106%
76	Cu	11/21/2006	81.6	84.0	103%

**Table 28F. (continued) Summary of performance evaluation samples analyzed by IRI in 2006.
Results in bold are outside acceptance limits. (continued on next page)**

Sample ID	Parameter	Date	Known Value	Lab Value	% Recovery
77	Fecal Coliform	5/24/2006	119	135	113%
78	Fecal Coliform	5/24/2006	<1	<1	100%
79	Fecal Coliform	7/21/2006	114	110	96%
80	Fecal Coliform	7/21/2006	<1	<1	100%
81	Fecal Coliform	10/19/2006	209	240	115%
82	Fecal Coliform	10/19/2006	<1	<4	100%
83	Mn	2/28/2006	270	258	96%
84	Mn	4/19/2006	81.2	105	129%
85	Mn	5/24/2006	81.2	95.0	117%
86	Mn	6/23/2006	81.2	89.0	110%
87	Mn	7/21/2006	81.2	80.0	99%
88	Mn	8/16/2006	177	184	104%
89	Mn	9/12/2006	177	184	104%
90	Mn	10/19/2006	177	157	89%
91	Mn	11/21/2006	177	168	95%
92	NH3	3/29/2006	2.56	2.6	102%
93	NH3	4/19/2006	2.56	2.56	100%
94	NH3	5/24/2006	2.56	2.55	100%
95	NH3	6/23/2006	2.56	2.54	99%
96	NH3	7/21/2006	2.56	2.70	105%
97	NH3	8/16/2006	2.84	2.86	101%
98	NH3	9/12/2006	2.84	2.84	100%
99	NH3	10/19/2006	2.84	2.84	100%
100	NH3	11/21/2006	2.84	2.82	99%
101	Ni	2/28/2006	168	179	107%
102	Ni	4/19/2006	124	131	106%
103	Ni	5/24/2006	124	131	106%
104	Ni	6/23/2006	124	128	103%
105	Ni	7/21/2006	124	123	99%
106	Ni	8/16/2006	94.4	90.0	95%
107	Ni	9/12/2006	94.4	91.0	96%
108	Ni	10/19/2006	94.4	95.8	101%
109	Ni	11/21/2006	94.4	99.6	106%
110	Nox	2/28/2006	0.546	0.521	95%
111	Nox	3/29/2006	0.370	0.389	105%
112	Nox	4/19/2006	0.370	0.395	107%
113	Nox	5/24/2006	0.370	0.372	101%
114	Nox	6/23/2006	0.370	0.367	99%
115	Nox	7/21/2006	0.370	0.369	100%
116	Nox	8/16/2006	0.756	0.742	98%
117	Nox	9/12/2006	0.378	0.357	94%
118	Nox	10/19/2006	0.378	0.393	104%
119	Nox	11/21/2006	0.378	0.368	97%

Table 28F. (continued) Summary of performance evaluation samples analyzed by IRI in 2006.
Results in bold are outside acceptance limits. (continued on next page)

Sample ID	Parameter	Date	Known Value	Lab Value	% Recovery
120	Pb	2/28/2006	14.7	14.5	99%
121	Pb	3/29/2006	34.6	36.5	105%
122	Pb	4/19/2006	34.6	35.9	104%
123	Pb	5/24/2006	34.6	34.9	101%
124	Pb	6/23/2006	34.6	34.8	101%
125	Pb	7/21/2006	34.6	34.8	101%
126	Pb	8/16/2006	32.7	34.7	106%
127	Pb	9/12/2006	32.7	35.2	108%
128	Pb	10/19/2006	32.7	34.9	107%
129	Pb	11/21/2006	32.7	32.0	98%
130	SRP	2/28/2006	0.090	0.095	105%
131	SRP	4/19/2006	0.018	0.018	100%
132	SRP	5/24/2006	0.018	0.019	105%
133	SRP	6/23/2006	0.018	0.02	111%
134	SRP	7/21/2006	0.018	0.018	100%
135	SRP	8/16/2006	0.087	0.087	100%
136	SRP	9/12/2006	0.044	0.044	101%
137	SRP	10/19/2006	0.044	0.044	101%
138	SRP	11/21/2006	0.044	0.044	101%
139	TDP	2/28/2006	0.090	0.092	102%
140	TDP	3/29/2006	0.018	0.018	100%
141	TDP	4/19/2006	0.018	0.018	100%
142	TDP	5/24/2006	0.090	0.094	104%
143	TDP	6/23/2006	0.090	0.088	98%
144	TDP	7/21/2006	0.090	0.089	99%
145	TDP	8/16/2006	0.218	0.224	103%
146	TDP	9/12/2006	0.218	0.221	101%
147	TDP	10/19/2006	0.218	0.227	104%
148	TDP	11/21/2006	0.218	0.237	109%
149	TDS	2/28/2006	319	347	109%
150	TDS	4/19/2006	389	411	106%
151	TDS	5/24/2006	389	412	106%
152	TDS	6/23/2006	389	408	105%
153	TDS	7/21/2006	389	399	103%
154	TDS	8/16/2006	389	411	106%
155	TDS	9/12/2006	389	405	104%
156	TDS	10/19/2006	389	372	96%
157	TDS	11/21/2006	389	384	99%
158	TKN	2/28/2006	0.568	0.607	107%
159	TKN	3/29/2006	1.09	1.03	94%
160	TKN	4/19/2006	0.436	0.501	115%
161	TKN	5/24/2006	0.436	0.587	135%
162	TKN	6/23/2006	0.436	0.416	95%
163	TKN	7/21/2006	1.09	1.14	104%
164	TKN	8/16/2006	0.915	0.98	107%
165	TKN	9/12/2006	0.915	0.795	87%
166	TKN	10/19/2006	0.915	0.867	95%
167	TKN	11/21/2006	0.915	0.888	97%

Table 28F. (continued) Summary of performance evaluation samples analyzed by IRI in 2006. Results in bold are outside acceptance limits. TP01 and TP02 are high level and low level Total Phosphorus samples, respectively.

Sample ID	Parameter	Date	Known Value	Lab Value	% Recovery
168	TN	2/28/2006	0.568	0.53	93%
169	TN	4/19/2006	0.436	0.429	98%
170	TN	5/24/2006	0.436	0.392	90%
171	TN	6/23/2006	0.436	0.455	104%
172	TN	7/21/2006	1.09	1.021	94%
173	TN	8/16/2006	0.915	0.997	109%
174	TN	9/12/2006	0.915	0.901	98%
175	TN	10/19/2006	0.915	0.976	107%
176	Total Hardness	2/28/2006	223	224	100%
177	Total Hardness	3/29/2006	233	224	96%
178	Total Hardness	4/19/2006	208	196	94%
179	Total Hardness	5/24/2006	208	208	100%
180	Total Hardness	6/23/2006	208	208	100%
181	Total Hardness	7/21/2006	208	206	99%
182	Total Hardness	8/16/2006	208	192	92%
183	Total Hardness	9/12/2006	208	196	94%
184	Total Hardness	10/19/2006	208	224	108%
185	Total Hardness	11/21/2006	208	196	94%
186	TP01	2/28/2006	0.022	0.023	105%
187	TP01	3/29/2006	0.041	0.041	100%
188	TP01	4/19/2006	0.164	0.159	97%
189	TP01	5/24/2006	0.164	0.161	98%
190	TP01	6/23/2006	0.164	0.156	95%
191	TP01	7/21/2006	0.164	0.160	98%
192	TP01	8/16/2006	0.634	0.623	98%
193	TP01	9/12/2006	0.634	0.616	97%
194	TP01	10/19/2006	0.634	0.631	100%
195	TP02	2/28/2006	0.111	0.109	99%
196	TP02	4/19/2006	0.016	0.016	100%
197	TP02	5/24/2006	0.016	0.020	125%
198	TP02	6/23/2006	0.016	0.016	100%
199	TP02	7/21/2006	0.016	0.016	100%
200	TP02	8/16/2006	0.063	0.063	99%
201	TP02	9/12/2006	0.063	0.062	98%
202	TP02	10/19/2006	0.063	0.065	103%
203	TP02	11/21/2006	0.063	0.062	98%
204	TSS	2/28/2006	48.6	44	91%
205	TSS	3/29/2006	48.6	47	97%
206	TSS	4/19/2006	94.7	83	88%
207	TSS	5/24/2006	94.7	92	97%
208	TSS	6/23/2006	94.7	83	88%
209	TSS	7/21/2006	94.7	89	94%
210	TSS	8/16/2006	94.7	85	90%
211	TSS	9/12/2006	94.7	92	97%
212	TSS	10/19/2006	94.7	89	94%
213	TSS	11/21/2006	94.7	93	98%

Table 28F. (continued) Summary of performance evaluation samples analyzed by IRI in 2006. Results in bold are outside acceptance limits.

Sample ID	Parameter	Date	Known Value	Lab Value	% Recovery
214	Zn	2/28/2006	299	255	85%
215	Zn	3/29/2006	241	201	83%
216	Zn	4/19/2006	241	233	97%
217	Zn	5/24/2006	241	241	100%
218	Zn	6/23/2006	241	241	100%
219	Zn	7/21/2006	241	241	100%
220	Zn	8/16/2006	391	378	97%
221	Zn	9/12/2006	391	349	89%
222	Zn	10/19/2006	391	329	84%
223	Zn	11/21/2006	391	328	84%

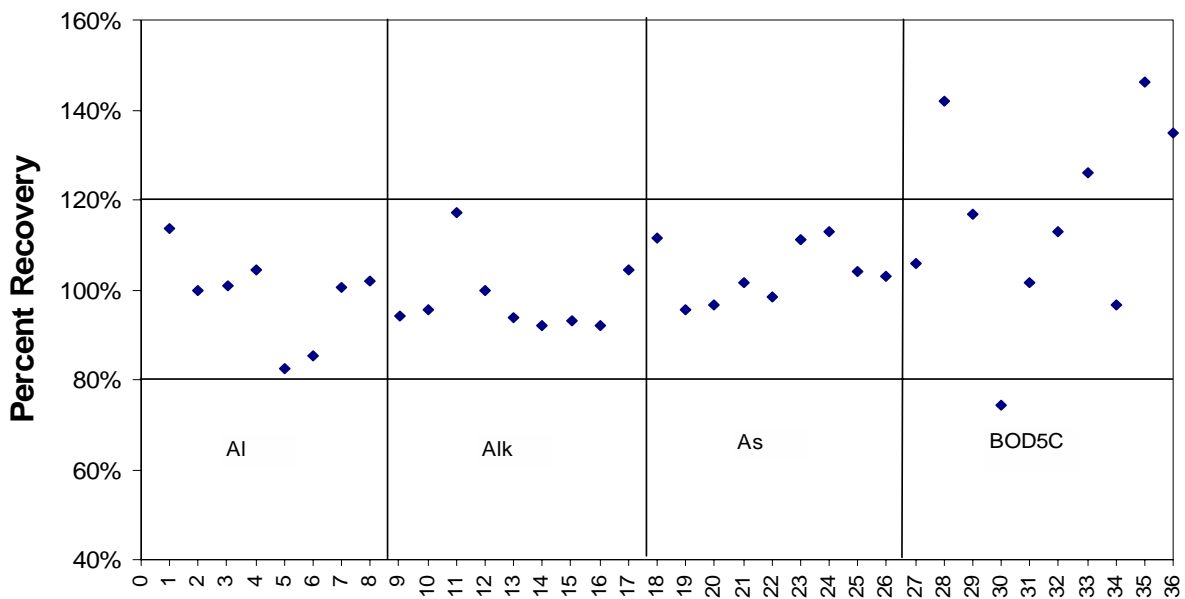


Figure 28E. Scatter plot of reported percent recoveries for performance evaluation samples in 2006. See Table 28F to reference sample ID numbers with sample descriptions and results.

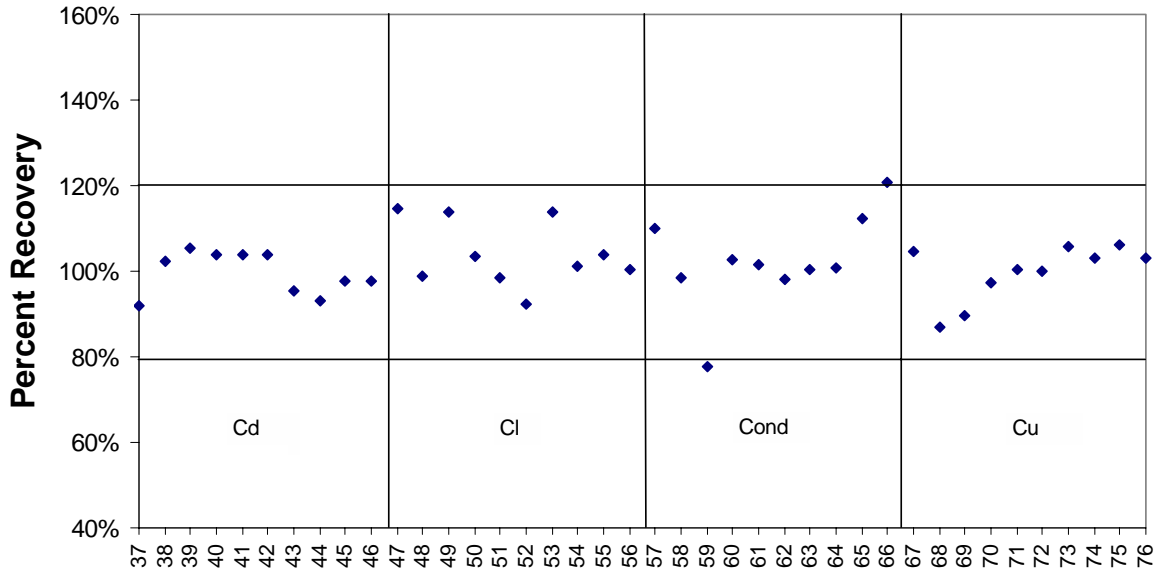


Figure 28F. Scatter plot of reported percent recoveries for performance evaluation samples in 2006. See Table 28F to reference sample ID numbers with sample descriptions and results.

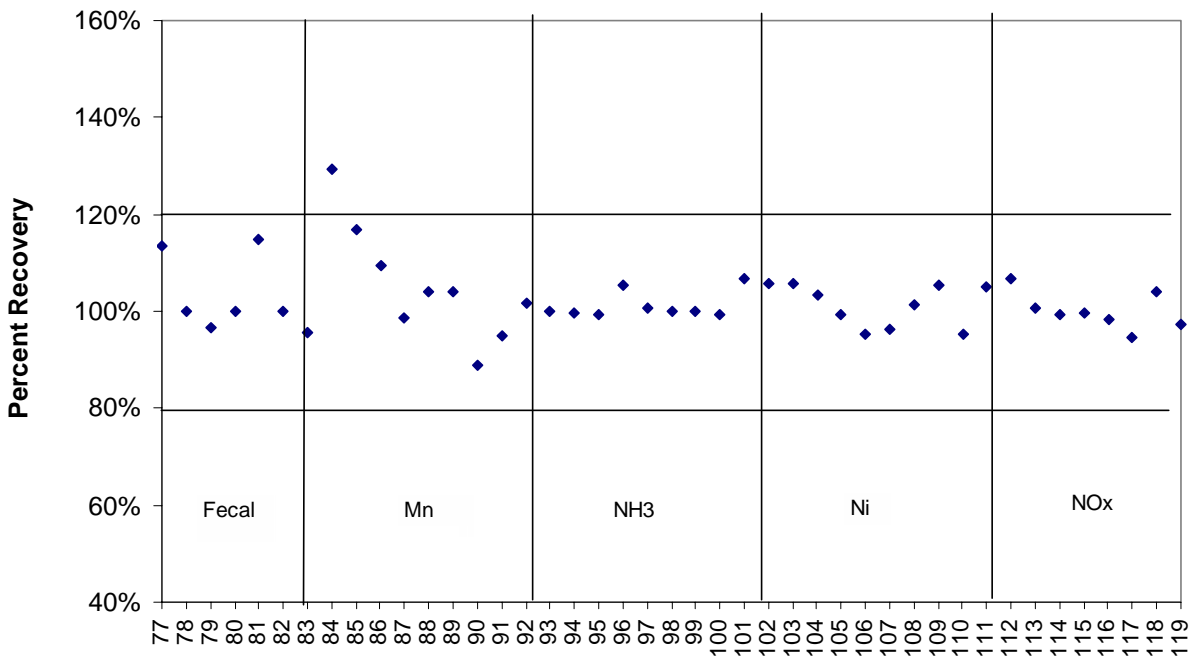


Figure 28G. Scatter plot of reported percent recoveries for performance evaluation samples in 2006. See Table 28F to reference sample ID numbers with sample descriptions and results.

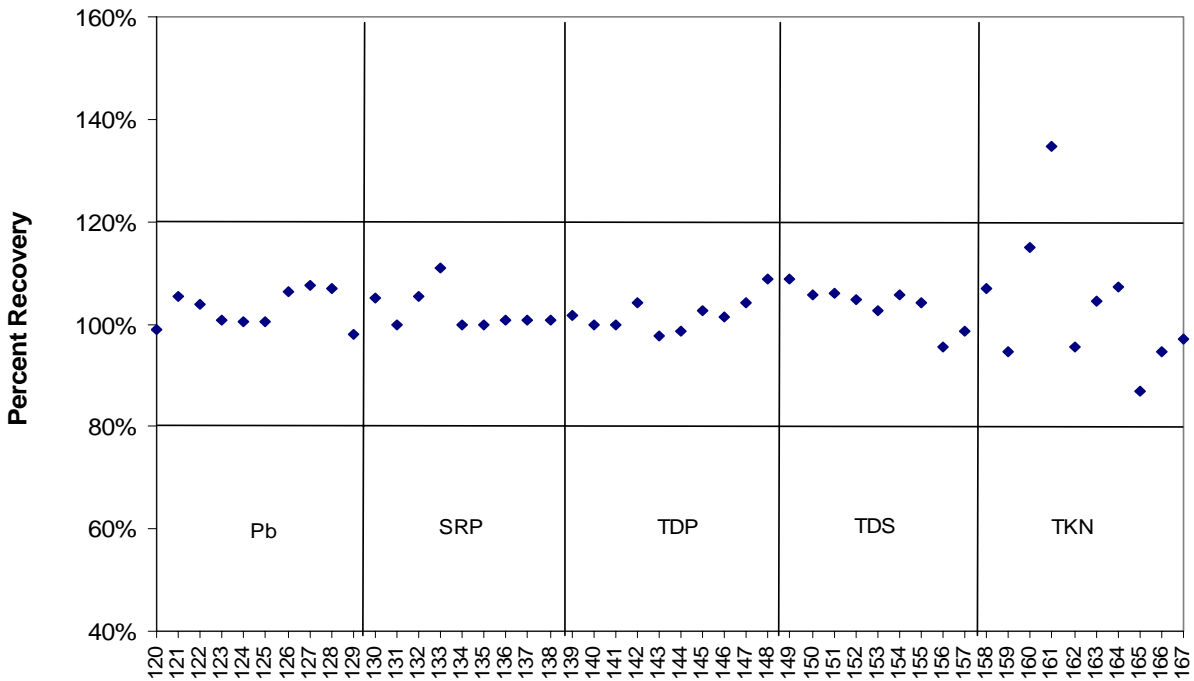


Figure 28H. Scatter plot of reported percent recoveries for performance evaluation samples in 2006. See Table 28F to reference sample ID numbers with sample descriptions and results.

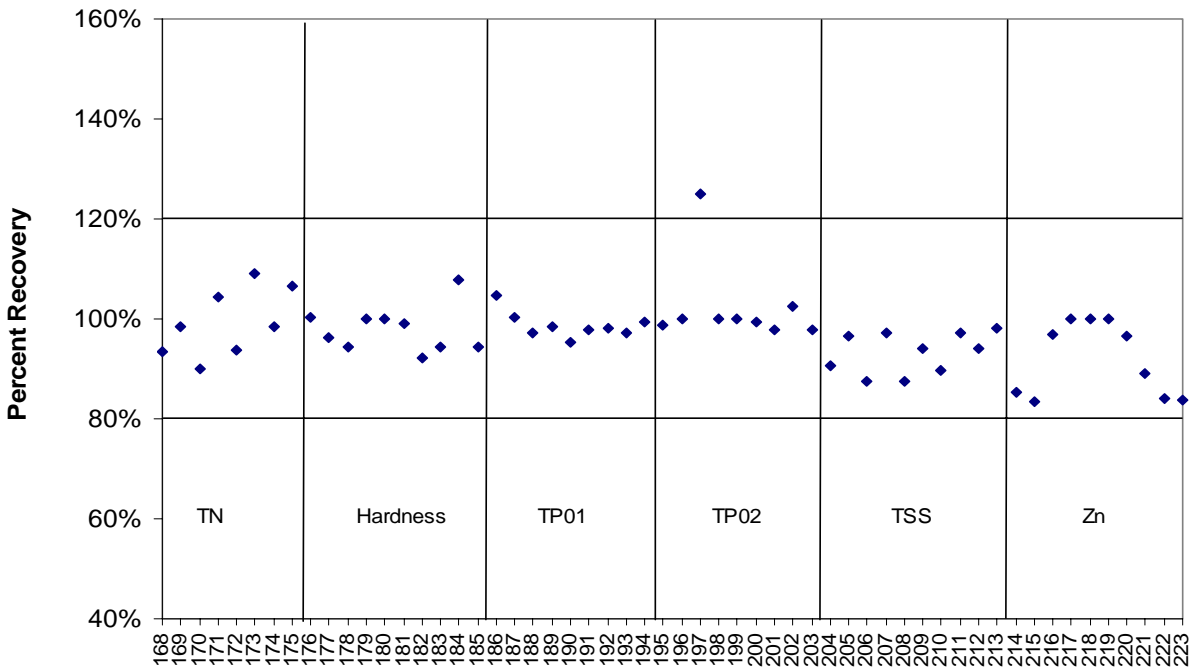


Figure 28I. Scatter plot of reported percent recoveries for performance evaluation samples in 2006. See Table 28F to reference sample ID numbers with sample descriptions and results.

Almost all of the performance evaluation standards were acceptable for all months. Definitions of the chemical parameters are in, Table 28B. TKN had one failure (5/24/06). Alkalinity, chloride, hardness, pH, TDS, and TSS are pre-made standards and are the only standards that do not require dilution. The remaining standards were diluted before they were submitted to the lab.

Fecal coliform standards were acceptable. The performance acceptance limits for fecal coliform, supplied by ERA, are much wider than for the other parameters, (+/- 50%). The coliform standards are shipped directly to the laboratory from ERA.

SRP and TDP performance evaluation samples were mixed to low concentrations, approximately 10-20 times the minimum detection limit. *Standard Methods* (2005) recommends that performance evaluation samples be mixed to a minimum concentration of 5 times the minimum detection limit. Because of the low concentrations, the acceptance limit for SRP and TDP were widened from the recommended 80-120% range to 70-130% recovery. All SRP samples were acceptable in both the 70-130% and 80-120% range.

Conductivity had one failure in April with (78% recovery). None of the data were flagged.

The cBOD had five performance evaluation sample failures. The data were not flagged due the low levels and the inherent variability in the test.

Magnesium had one performance evaluation sample failure in April (129% recovery). The data were not flagged.

Total Kjeldahl Nitrogen analysis had one failure in May (135% recovery). All of the May data were flagged.

Total Phosphorus had one failure in May with (125% recovery). Two levels were submitted in May the other one was acceptable. The sample was the low level standard, therefore none of the data were flagged.

Analysis of Blanks

Equipment blanks were done for lake water and stormwater sampling equipment. Results from equipment blanks for 2006 yielded "non-detects" for all parameters.

The 2006 results from the "bottle/field blanks" which were carried in the field unopened yielded "non-detects" for all parameters.

Reagent blanks run by IRI laboratories during batch analyses resulted in no detectable levels for all parameters analyzed.

Recovery of Known Additions and Internally Supplied Standard Solutions

All of the recovery values for spike samples (known additions) reported by IRI, were within acceptance limits. All of the reported recoveries for internally supplied standards of known concentration were within acceptance limits.

FINAL ASSESSMENT OF DATA USABILITY

The 2006 data designated as “questionable usability” may still meet the data quality needs of some analyses. Users of these data should assess if the data quality indicators discussed in this document meet their needs. Much of the data designated as questionably usable are categorized as such because of a missed performance evaluation standard. Table 28G lists the overall completeness, representative, comparability and precision determined for the 2006 data by parameter. All additional parameters not analyzed by IRI and collected in the field (dissolved oxygen, temperature, conductivity, pH, and Secchi transparency) were deemed to be fully usable. These measurements followed standard methods and protocols for collection and equipment calibration.

The parameters listed on Table 28G as questionably usable, are only questionable for the months that they failed their monthly performance standards. No parameters in 2006 failed performance standards the entire year. It was determined there was only one performance standard had a failure in 2006, TKN for the month of May. A failure of one of the 221 blind monthly performance samples submitted gives an accuracy rate of 99.5%. When reviewing the monthly performance samples the “rule of sensibility” must be applied. The percent recovery must be viewed in relation to the values (low or high), stability of the test in question, and multiple of the reporting limit (2X) used to qualify the data.

Table 28G. Summary of 2006 data usability by parameter. '+' denotes that acceptance criteria were met, 'O' denotes that some of the data were of questionable usability, '-' denotes that data were not within acceptable range.

Parameter	Completeness (<5% missing data)	Representativeness (data representative of natural samples)	Comparability (splits, past years data)	Precision (lab field dups, performance samples)
Alkalinity	+	+	+	+
Ammonia	+	+	+	+
BOD 5 day	+	+	+	+
Cadmium	+	+	+	+
Chloride	+	+	+	+
Chlorophyll-a	+	+	+	+
Copper	+	+	+	+
Fecal Coliform	+	+	+	+
Hardness	+	+	+	+
Lead	+	+	+	+
Manganese	+	+	+	+
Nickel	+	+	+	+
Nitrate+Nitrite	+	+	+	+
pH	+	+	+	+
Silica	+	+	+	+
Soluble Aluminum	+	+	+	+
Soluble Reactive Phosphorus	+	+	+	+
Total Aluminum	+	+	+	+
Total Dissolved Phosphorus	+	+	+	+
Total Dissolved Solids	+	+	+	+
Total Kjeldahl Nitrogen	+	+	+	O
Total Nitrogen	+	+	+	+
Total Phosphorus	+	+	+	+
Total Suspended Solids	+	+	+	+
Zinc	+	+	+	+