Quality Assessment Report for Water Quality Monitoring

July – September 2000

Submitted to the
Technical Oversight Committee

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Quality Assessment Report for Water Quality Monitoring
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This report is an assessment of the SFWMD laboratory and field sampling in Total Phosphorus (TP) monitoring primarily for the following projects/stations during the first quarter of 2000.

- Conservation Area Inflow and Outflows (CAMB)
  S5A, S6, S7, S8, S9, S11A, S31, S33, S140, S151, S333, G123
- Everglades National Park Inflow Monitoring (ENP)
  S18C, S332, S332D, S175, TAMBR105, US41-25
- Everglades Protection Area (EVPA)
  CA32, CA215, CA316, CA317, LOX6, S6D
- Non-Everglades Construction Project (NECP)
  G64, S142

The lists of qualified data (Table 3) also include information on stations other than those listed above or other projects since field QCs are collected for trips that include the samples for the stations of interest.

The South Florida Water Management District's Comprehensive Quality Assurance Plan (CQAP) requires analysis of laboratory quality control (QC) samples and the collection and analysis of field QC samples along with routine samples to assess the data quality. Included are the results from a split study with SFWMD and Florida Department of Environmental Protection (FDEP) laboratories for total phosphorus analysis to continually determine comparability of results.

Field Sampling Quality Assessment

Field QC measures consist of equipment blanks (EB), field blanks (FB), split samples (SS) and replicate samples (RS). Table 1 summarizes EB and FB recoveries for all projects and Table 2 summarizes field precision recoveries. Data not meeting the set criteria are flagged using FDEP data qualifier codes.

Table 1. Field and Equipment Blank Recoveries

Type of Blank	Project	# Blanks collected	% with value <0.004	% with value 0.004-0.008	# Blanks with value >0.008	Action Taken
FB	CAMB	63	97	3	0	N/A
	ENP	24	100	0	0	N/A
	EVPA	20	95	5	0	N/A
	NECP	5	100	0	0	N/A
EB	CAMB	106	90	10	0	N/A
	ENP	24	100	0	0	N/A
	EVPA	20	95	5	0	N/A
	NECP	7	100	0	0	N/A

Table 2. Field Precision Summary

Project Code	# of pairs	Mean % RPD	Comments
CAMB	53	8.0	Precision exceeded limits on the following sampling dates:9/19/00, 9/26/00. Affected field QC's and samples collected on those sites were flagged.
ENP	19	7.6	Precision criteria were met.
EVPA	23	11.7	One RS (8/28/00) was flagged for not meeting criteria.
NECP	5	9.0	Precision criteria were met.

Notes

1) All TP analyses were conducted by SFWMD laboratory.
2) Field precision acceptance criteria: <15%. This criteria is applied only if values >PQL.
3) FB and EB acceptance criteria: Must be </=2xMDL.
4) Associated samples are flagged when concentrations are low enough as compared to blank values for possibility of contamination.

Field sampling precision was excellent. A comprehensive list of flagged data for all trips that include samples for CAMB, ENP, EVPA and NECP during this quarter is presented in Table 3.

Table 3. List of Flagged Results

Project	Date Collected	Station	Type	Result	Flag Code	Comments
CAMB	7/11/00	S5A	Sample	0.122	Y	Improper preservation
	7/11/00	S8	Sample	0.306	J5	Questionable results
	7/13/00	G136	Sample	0.06	J5	Questionable results
	8/1/00	S9	Sample	0.024	Y	Improper preservation
	8/1/00	S9	Sample	0.02	Y	Improper preservation
	8/1/00	S9	SS	0.026	Y	Improper preservation
	8/8/00	S7	Sample	0.035	Y	Improper preservation
	8/8/00	S9	Sample	0.023	Y	Improper preservation
	8/10/00	S140	Sample	0.054	J3	Possible contamination
	8/15/00	S5A	Sample	0.115	Y	Improper preservation
	8/15/00	S7	Sample	0.035	Y	Improper preservation
	8/15/00	S9	Sample	0.013	Y	Improper preservation
	8/15/00	S5A	SS	0.115	Y	Improper preservation
	8/15/00	S7	SS	0.033	Y	Improper preservation
	8/15/00	S9	SS	0.013	Y	Improper preservation
	8/22/00	S7	Sample	0.025	Y	Improper preservation
	8/29/00	S5A	Sample	0.117	Y	Improper preservation
	8/29/00	S7	Sample	0.052	Y	Improper preservation
	8/29/00	S9	Sample	0.006	Y	Improper preservation
	8/29/00	S5A	SS	0.122	Y	Improper preservation
	9/5/00	S7	Sample	0.023	Y	Improper preservation
	9/5/00	S9	Sample	0.025	Y	Improper preservation
	9/6/00	S5A	Sample	0.074	Y	Improper preservation
	9/6/00	S5A	SS	0.073	Y	Improper preservation
	9/11/00	S6	Sample	0.066	Y	Improper preservation
	9/12/00	S7	Sample	0.074	Y	Improper preservation
	9/12/00	S9	Sample	0.018	Y	Improper preservation
	9/12/00	S9	SS	0.017	Y	Improper preservation
	9/14/00	G136	Sample	0.055	J3	Possible contamination
	9/19/00	S5A	Sample	0.145	Y	Improper preservation

Table 3. List of Flagged Results (Con't)

Project	Date Collected	Station	Type	Result	Flag Code	Comments
	9/19/00	S6	Sample	0.088	Y	Improper preservation
	9/19/00	S7	Sample	0.08	Y	Improper preservation
	9/19/00	S8	Sample	0.093	Y	Improper preservation
	9/19/00	S9	Sample	0.016	Y	Improper preservation
	9/19/00	C123S	RS	0.036	J3	Failed field precision criteria
	9/19/00	S5A	SS	0.146	Y	Improper preservation
	9/19/00	S6	SS	0.085	Y	Improper preservation
	9/19/00	S8	SS	0.094	Y	Improper preservation
	9/26/00	S31	Sample	0.016	J3	Reversal OPO4>TPO4
	9/26/00	S5A	Sample	0.13	Y	Improper preservation
	9/26/00	S140	RS	0.06	J3	Failed field precision criteria
	9/26/00	S5A	SS	0.134	Y	Improper preservation
	9/26/00	S5AU	Sample	0.198	Y	Improper preservation
	9/27/00	S6	EB	-0.004	Y	Improper preservation
EVPA	8/28/00	WCA2	RS	0.093	J3	Failed field precision criteria

Field Audits

There was no field audit conducted during this quarter.

Laboratory Quality Control Assessment

Routine laboratory QC samples include QC checks, matrix spikes and precision checks. The charts presented on the following pages show recoveries from various levels of QC samples for the TP analysis at SFWMD laboratory. Statistical evaluation of precision and matrix spikes recoveries is also included. Portion of or an entire analytical run is generally rejected if QC recoveries are outside the set limits. Data is flagged accordingly if any deficiency is noted after the samples have exceeded the required holding times.

Except for QC5, recoveries for the QC samples are generally within $\pm$ 10% from the true value, which are acceptable. QC5, with a true value of 0.008 mg/L, is less than the practical quantitation limit. Although a wider performance range can be expected at this level, the recoveries are biased on the high end of the chart, 100-125%. Method improvement has been initiated and recoveries at this level have improved.

Organic check is a solution prepared from phytic acid, a stable form of organic phosphate. Recoveries for this check sample are between 98-101%, indicating that the digestion process was effective. The same material is used to do matrix spikes, the mean recovery for which was 102.2%.

The precision target for TP analysis during this period was 5.0% and as the report shows, mean %RPD was 0.84 and 0.52% for low and high level analyses, respectively. The maximum RPD during this period was 3.3%.

Laboratory Performance Assessment by External Agencies

The Disrict's laboratory passed the June 2000 Proficiency Testing for TP and other analytes, administered by a private vendor which is required for the National Environmental Laboratory Accreditation Program (NELAP). Laboratories are required to pass two out of three studies to maintain certification under this program. In preparation for this accreditation program, the laboratory has also: 1) submitted a new Laboratory Quality Manual to the Florida Department of Health, and 2) created a Laboratory Ethics Policy and trained all laboratory staff on the policy.

The laboratory also obtained ratings of 4 for TP in the March 2000 Round Robin Study with the US Geological Survey, in which 4 is the highest obtainable rating. The TP levels in this study were 1.29 and 0.119 mg/L. The District participates twice a year on the USGS round robin study. Results of the fall study (conducted October-November 2000) will be included in the next quarterly report. An analysis of the District laboratory's performance on these USGS RR studies from 1997-2000 is also included.

A report of an independent audit of the District's laboratory conducted by USGS' quality assurance team is also attached.

Split Study

To continually assess comparability of results, the District splits field samples on a quarterly basis with the Florida Department of Environmental Protection's laboratory. The samples are collected from the Loxahatchee National Refuge site (EVPA Project). This split study is conducted quarterly. The result of the split study is presented in Table 4 below:

Table 4. Results of quarterly split analysis study between SFWMD and FDEP laboratories

Station	Sampling Date	Type	SFWMD		FDEP		Difference	%RPD	Comments
			Field #	TP mg/L	Field #	TP mg/L	(SFWMD-FDEP)		
LOX6	9/11/00	EB	P5765-1	<0.004	P5823-1	<0.004	0.000	0.0	
LOX6	9/11/00	Sample	P5765-2	0.007	P5823-2	0.008	-0.001	13.3	<PQL
LOX4	9/11/00	Sample	P5765-12	0.015	P5823-4	0.018	-0.003	18.2	
S6D	9/11/00	FB	P5766-4	<0.004	P5823-5	<0.004	0.000	0.0	
LOX16	9/11/00	Sample	P5766-7	0.010	P5823-6	0.011	-0.001	9.5	<PQL
LOX11	9/11/00	Sample	P5766-10	0.011	P5823-7	0.015	-0.004	30.8	<PQL
						Mean	-0.002	12.0	

Both laboratories obtained acceptable blank (EB and FB) results. FDEP recovered higher P for LOX6, LOX4, LOX16 and LOX11 than the SFWMD laboratory but three samples of these pairs had concentrations <PQL.

USGS
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Branch of Quality Systems

Laboratory Review of

South Florida Water Management District

West Palm Beach, Florida

November 17, 2000

On November 8th and 9th, 2000 Brooke Connor and Bill d'Angelo of the U.S. Geological Survey performed an on-site review of the South Florida Water Management District (SFWMD) located in West Palm Beach, Florida. The review was requested through the U.S. Geological Survey laboratory in Ocala, Florida. The SFWMD is not seeking USGS approval at this time but rather is seeking an outside review of their operations. SFWMD has participated in the USGS standard reference sample (SRS) program at least since 1994. The results of the SRS are attached in this report.

SFWMD supervisory chemist David Struve and quality assurance officer Delia Ivanoff indicated that the three areas of interest for the review were in nutrients, classical analyses, and metals. Each of these areas was visited in the laboratory, and several analysts were interviewed. The following findings are based upon a thorough review of the quality documents provided by the laboratory prior to the review, and by the information obtained during the interviews.

Laboratory Strong Points

- The quality system, method performance and documentation are excellent. The laboratory is preparing for NELAC certification and therefore has an organized and complete quality system.
- Quality control parameters are up-to-date, verified, and in use by the analysts. We found numerous instances of control limits posted on analytical instruments that were up-to-date. These data matched the published data, which means there is a system of checks and balances. The analysts were aware of the documents, the limits, and the update frequencies. This assured us that communication is excellent at the laboratory.
- The laboratory was clean and well kept. Binders were organized and labeled appropriately. Bottles and refrigerator storage spaces were color-coded. Laboratory notebooks were complete and available. The staff was cheerful and cooperative.
- Internal audits are performed and records are easily accessible.
- Laboratory managers are educated, informed, and part of the process. Analysts understood their procedures and discussed method issues freely with us.

Suggestions for Improvement

(1) Temperature tolerance limits on refrigerators are listed as 4°C ±1°. This will be nearly impossible to adhere to given the refrigerators are opened throughout the day and contents are continually shifted. Delia suggested that they could plot 3 standard deviations of the existing refrigerator temperature readings to determine tolerances. We agree with this and further suggest that a corrective action be set such that only extreme temperature deviations for a defined time period would invalidate samples or require service to the unit.

(2) The practical quantitation limit (PQL) is said to be 4 times the MDL. However, the PQL is not used as the reporting limit. SFWMD uses the MDL for the reporting limit. Additionally, SFWMD determines the MDL from 7 replicate analyses performed on the same day, instrument, run, and at two or three different concentrations. This single step approach will result in MDLs that are impossibly low because only a few measures of the total method variability are captured in this manner. In these cases, the analysts suggest a better (higher concentration) MDL to use as the reporting limit.

There are several problems with this approach. First is that the reporting limit is in some cases statistically determined, and in others it is based on analyst judgment. Since the MDL is a statistical determination that implies a level of confidence about false negatives, it is not good practice to interchange this term with either (1) the reporting level, or (2) a statically determined MDL.

An MDL as a reporting limit, by definition, will result in up to 50 percent false positives. Accurate quantitation is difficult to attain at these low concentrations, and in almost all cases, we noted that results were extrapolated below the lowest calibration standard in order to report this low. It is not good laboratory practice to extrapolate beyond the range of the calibration curve. That is why a PQL is used. The initial assessment that the PQL is 4 times the MDL is a good one. Reporting at roughly 2 times the MDL will decrease the likelihood of a false positive to less than 1 percent.

All laboratory quality control samples are in the upper to mid-range of the calibration curve. There is no validation of the calibration accuracy or of recoveries at the low end of the calibration curve.

One suggestion is to collect MDL data over time, with much greater that 7 replicates, and to use spikes much closer in concentration to the predicted MDL. These lower concentration spikes will show greater variability, and running them on different calibration curves with different analysts or different instruments will include more of the normal variability routine samples would observe. The MDL will be much more realistic if calculated in this manner. (It might be a good idea to reference the Open-File Report on long term MDLs here.)

(3) It was noted that standard reference materials are not in use for internal QC. It is suggested that the laboratory implement the use of real matrix reference materials in appropriate analyses. The USGS standard reference materials are an excellent tool for low concentration analyses. EPA round robin samples can also be used as well as commercially available materials. Internal laboratory control limits can be applied to these samples as they currently are to continuing calibration checks.

(4) The QC limits on the QC sheets need dates. The date the limit should be implemented and the date that the limit should be taken out of service would be very useful.

(5) All runs should be terminated with a continuing calibration verification standard, whether the run is 30 minutes long or 3 days. There must be some assurance that calibration was in control while samples were being analyzed for all analytes.

(6) We discussed the feasibility of two separate analyses for high and low concentration analyses. The benefit of reporting data for a single analyte under two different methods is that the reporting level will be true, the quality control parameters will have been analyzed under identical calibration criteria as the samples, and the curves can be focused on a narrower analytical range.
This practice is seen in many laboratories and requires the correct analysis to be either initially requested or a rerun if a sample exceeds the limits of the first analysis (be it high or low originally).

Detailed Findings - Metals

- Aluminum - Wrong method reference on worksheet.
- ICP – For metals, low end of standard curve is not checked with intermediate standards or QC check standards.
- ICP standards include all parameters and are not separated based on interferences.
- For Ca, K and Na the range of acceptable values on the worksheets do not match those in the CompQAP.
- Some ICP stock solutions were labeled with date received, but not date opened.

General QA issues

- It is very confusing trying to decipher the QA samples on the run sheets. Numbers are assign to duplicates spikes and continuing calibration samples sequentially and do not reflect what kind of QA sample they are.
- Continuing blanks are not run.
- Standard Reference Samples should be run with other QA samples.

- Spikes for Nutrients and Ion Chromatography are at too high a level (50% of calibration range). Spikes should be at a lower level (10 – 25% of calibration range). Spikes need to be run at a low enough level to keep the sample within the calibration curve, but high enough that it can be easily distinguished from sample variation.

Classical Parameters

- Turbidity – Low standard is lower than MDL. (0.08 vs. MDL of 0.1)
- Color – Low standard needs to be closer to MDL.
- IC – Low standard needs to be closer to MDL.

In general, with the exception of nutrients, the lower part of the calibration curve is not checked and results for low samples are extrapolated from the low standard back to the MDL. There is no daily check of the MDL. Although, for the most part, the values for these parameters are in the mid to upper range of the calibration curve, there is no validation of low samples or of values for field and equipment blanks.

Summary

The South Florida Water Management District Laboratory is well run, thoroughly documented, organized and clean. It was a pleasure to review this excellent laboratory, and to exchange useful information. If we can be of further assistance, please do not hesitate to call.

Brooke Connor, Chemist, Branch of Quality Systems
LeRoy Schroder, Chief, Branch of Quality Systems
Bill d'Angelo, Quality Control Officer, Ocala Laboratory

Glossary

Equipment blank (EB). Analyte-free water that is processed on-site through all sampling equipment used in routine sample processing. EB values are indicative of effectiveness of decontamination process.

Field blank (FB). Analyte free water that is poured directly into the sample container on site during routine collection, preserved and kept open until sample collection is completed for the routine sample at that site. FB values are indicative of environmental contamination on site.

Split sample (SS). A second aliquot of the same sample obtained from the same sampling device. Results for SS are compared with routine sample results; agreement between these two results is mostly an indication of laboratory precision.

Replicate sample (RS). A second sample collected from the same source as the routine sample, using the same sampling equipment. RS data are compared with routine sample to evaluate sampling precision.

Precision. The agreement or closeness between two or more results and is an indication that the measurement system is operating consistently and is a quantifiable indication of variations introduced by the analytical system over a given time period.

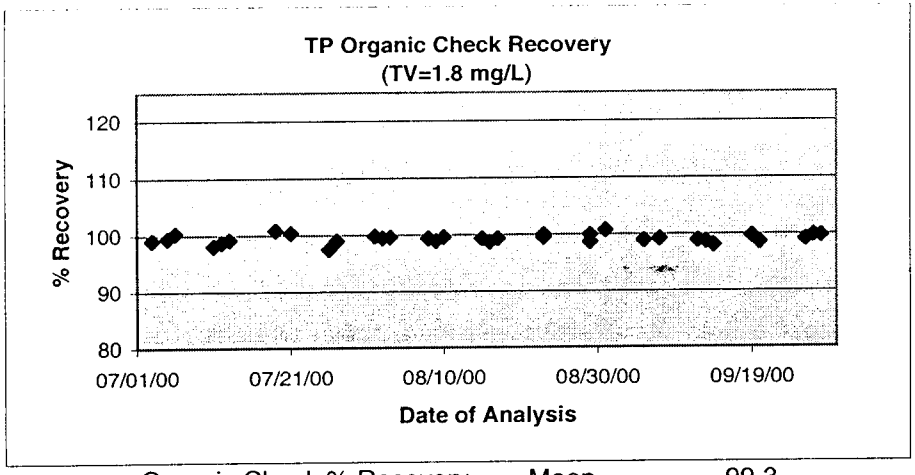
Accuracy. The agreement between the actual obtained result and the expected result. QC check samples having a known or "true" value are used to test for the accuracy of a measurement system.

Method Detection Limit (MDL). The smallest concentration of an analyte of interest that can be measured and reported with 99 percent confidence that the concentration is greater than zero. The MDLs are determined from the analysis of a sample in a given matrix, using accepted sampling and analytical preparation procedures, containing the analyte at a specified level. The MDL is determined by the protocol defined in section 40 CFR Part 136, Appendix B as established by the EPA.

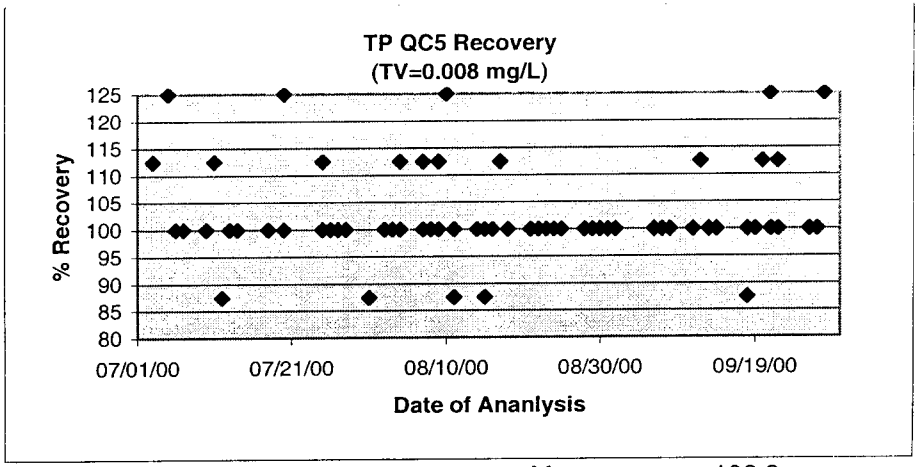
Practical Quantitation Limit (PQL). The smallest concentration of an analyte of interest that can be quantitatively reported with a specific degree of confidence. Generally, the PQL is 12 times the standard deviation that is derived from the procedure used to determine the MDL, or can be assumed to be 4 times the MDL.

Relative Standard Deviation (RSD). A measure of precision, used when comparing more than two results. It is calculated as: %RSD=[Std. Deviation ÷ Mean] * 100

Relative Percent Difference (RPD). A measure of precision, used when comparing two values. It is calculated as: %RPD=Absolute[Value 1 – Value 2] ÷ Mean *100.



Organic Check % Recovery	Mean	99.3
	Min	97.5
	Max	100.8



QC5 % Recovery	Mean	102.3
	Min	87.5
	Max	125

TP Precision Data 7/1/00-9/30/00 Acceptance Limit = <5.0%			
Low Level (0-0.2)		High Level (0.2-2)	
Max	3.3	Max	2.1
Mean	0.84	Mean	0.52
SD	0.71	SD	0.43
n	250	n	55

TP Spike Recovery Data 7/1/00-9/30/00 Acceptable Limit = 90-110%			
	Min	84.1	
	Max	110	
	Mean	102.2	
	Std Dev	3.02	
	3xSD	9.07	
	LCL	93.13	
	UCL	111.27	
	# of Obs	320	

Appendix A

South Florida Water Management District

Laboratory 113

Standard Reference Sample Summary Data 1997-2000

Reviewer: Brooke Connor

Date compiled:10/2/2000

Ratings are based on the following scale:

Z-value	Rating
0.00 through 0.50	4 - excellent
0.51 through 1.00	3 - good
1.01 through 1.50	2 - satisfactory
1.51 through 2.00	1 - questionable
greater than 2.00	0 - poor
DNP - did not participate	NR - not rated

RV	Reported value
MPV	Statistically determined Most Probable Value.
F-sigma	F-pseudosigma (nonparametric)
(##)	The values in parentheses represent "less-than" values.
Z-value	(RV-MPV)/F-sigma
+	MPV in bar chart (bars represent RV)

Analyte	SRS	DATE	RV	MPV	F-sigma	Z-value	Method	Rating
P total as P	N68	Oct-00	0.808	0.827	0.03	-0.533		3
P total as P	N67	Oct-00	0.278	0.279	0.01	-0.096		4
P total as P	N66	Mar-00	0.856	0.856	0.04	0.000		4
P total as P	N65	Mar-00	0.118	0.119	0.011	-0.091		4
P total as P	N64	Oct-99	0.871	0.883	0.041	-0.293	Colorimetric	4
P total as P	N63	Oct-99	0.16	0.158	0.01	0.200		4
P total	N58	Jul-98	0.765	0.766	0.03	-0.030	Color: phosp	4
P total	N57	Jul-98	0.193	0.202	0.013	-0.690	Other	3
P total as P	M146	Jul-98	0.004	insuff data				NR
P total	N56	Feb-98	0.712	0.714	0.034	-0.040	Color: phosp	4
P total	N55	Feb-98	0.593	0.601	0.032	-0.250	Color: phosp	4
P total as P	M144	Feb-98		0.03	0.011			DNP
P total	N54	Aug-97	1.75	1.78	0.09	-0.330	Color: phosp	4
P total	N53	Aug-97	2.22	2.32	0.11	-0.910	Color: phosp	3
P total	M142	Aug-97	0.016	0.02	0.011	-0.310	Color: phosp	4
P total	N52	Jan-97	1.6	1.6	0.06	0.000	Color: phosp	4
P total	N51	Jan-97	0.034	0.04	0.01	-0.600	Color: phosp	3
P total	M140	Jan-97	0.028	0.032	0.009	-0.450	Color: phosp	4
P total	N50	Aug-96	0.893	0.903	0.039	-0.260	Color: phosp	4
P total	N49	Aug-96	0.168	0.167	0.013	0.080	Color: phosp	4
P total	M138	Apr-96	0.226	0.24	0.017	-0.800	Color: phosp	3
P total	N48	Feb-96	0.775	0.794	0.041	-0.460	Color: phosp	4
P total	N47	Feb-96	0.216	0.223	0.013	-0.540	Color: phosp	3
P total	M136	Feb-96	0.857	0.885	0.033	-0.850	Color: phosp	3
P total	N46	Jul-95	1.228	1.23	0.06	-0.030	Color: phosp	4
P total	N45	Jul-95	0.124	0.139	0.012	-1.250	Color: phosp	2
P total	M134	Jul-95	0.004	0.01	0.016	-0.380	Color: phosp	4
P total	N44	Jan-95	0.931	0.92	0.031	0.350	Color: phosp	4
P total	N43	Jan-95	0.126	0.131	0.013	-0.380	Color: phosp	4
P total	M132	Jan-95	0.01	0.026	0.008	-2.000	Color: phosp	1
P total	M130	Aug-94	0.012	0.085	0.104	-0.700	Color: phosp	3
P total	N42n	Jan-94	1.14	1.15	0.05	-0.200	Color: phosp	4