North Carolina Department of Environment and Natural Resources
Division of Water Quality

Beverly Eaves Perdue
Governor

Coleen H. Sullins
Director

Dee Freeman
Secretary

DATE: December 7, 2009

TO: Participating Certified, Academic and Government Laboratories

FROM: The State of North Carolina Wastewater/Groundwater Laboratory Certification Program

SUBJECT: 2009 Chlorophyll *a* round robin results

Attached are the results for the third North Carolina Division of Water Quality (DWQ) Chlorophyll *a* round robin interlaboratory comparison study. The purpose of this study was to determine the analytical conditions and the level of interlaboratory agreement for the determination of chlorophyll *a* in surface water samples.

The Division of Water Quality would like to take this opportunity to thank the laboratories for their participation in the study. With one hundred percent cooperation, we were able to obtain a sizable data pool and generate meaningful results.

It is recommended that each laboratory in the study examine their results with respect to the data pool and the statistical graphs attached to the results report.

As a result of the success of this round robin and due to the fact that there are no commercially-prepared performance evaluation samples, the DWQ intends to use the round robin split sample approach to continue to assess laboratory performance in the coming years.

Contact us at (919) 733-3908 if you have any questions.

Sincerely,

Pat Donnelly
Certification Branch Manager
Laboratory Section

Attachment

Cc: Kent Wiggins
Jay Sauber
Dana Satterwhite
Ramon L. Cook
Pete Caldwell
Danielle Mir
Jennie Atkins
Gary Francies

DENR DWQ Laboratory Section NC Wastewater/Groundwater Laboratory Certification Branch
1623 Mail Service Center, Raleigh, North Carolina 27699-1623
Location: 4405 Reedy Creek Road, Raleigh, North Carolina 27607-6445
Phone: 919-733-3908 \ FAX: 919-733-6241
Internet: www.dwqlab.org

June 2009 NC DWQ Chlorophyll *a* Round Robin

Currently, 40 miles and 112,000 acres of surface waters in North Carolina are impaired due to chlorophyll *a*, a chemical parameter used to assess the phytoplankton population (2008 Draft NC Impaired Waters List). These impairments lead to the development of TMDLs and increased regulation, often at significant costs to both the state and the stakeholders in the watershed. It is important that the North Carolina Division of Water Quality (NC DWQ) understands the quality of the data used to make these decisions.

Because of the lack of performance evaluation samples for the parameter to test the entire chlorophyll *a* analysis, NC DWQ conducted a chlorophyll *a* round robin in August 2007 involving the state's certified laboratories as well as other academic and governmental laboratories. Seventeen laboratories in all analyzed eight surface water samples for chlorophyll *a* concentration. Analysis of the results indicated significant inconsistencies with the quality of the data. The division used the results of that round robin to work with laboratories to improve analyses.

The data presented within this report represent the third chlorophyll *a* round robin that was held in July 2009. Seventeen laboratories participated, each analyzing eight samples. All eight samples were collected from Triangle area waterbodies.

Experimental

Sampling

On July 15, 2009, NC DWQ staff collected eight grab samples from four area waterbodies. The locations are presented on page 2. Samples were placed in light protected carboys and transported on ice to NC DWQ's Environmental Sciences Section (ESS).

At ESS, each of the eight samples were split into seventeen 500 mL subsamples using a churn splitter to be sent to participating laboratories. Every sample was churned for two minutes prior to splitting and was continually churned during the split. Splitter faucet was purged prior to sample collection. The order in which the subsamples were split from the samples was randomized in an effort to control bias. Subsamples were put in amber HDPE bottles, then placed on ice and were either delivered to laboratories by NC DWQ staff (in-state laboratories) or shipped overnight (out-of-state laboratories).

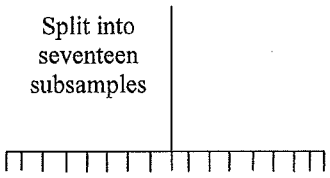
Analysis

Participating laboratories were asked to analyze the eight samples according to their Standard Operating Procedures for chlorophyll *a* analysis. Each was also asked to complete a questionnaire concerning the analysis. The answers to the questionnaire will remain on file for confidential purposes. Analyses of the data are presented graphically on pages 10 and 11.

Ellerbe Creek (Falls of the Neuse Reservoir)- By boat, DWQ monitoring station
36.06800, -78.79500

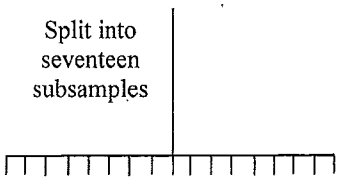
Sample CRR 319

Split into seventeen subsamples



Sample CRR 791

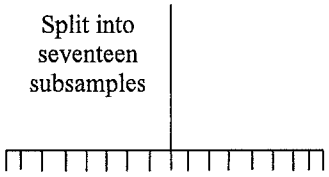
Split into seventeen subsamples



Bass Lake - Dock
35.64246, -78.80538

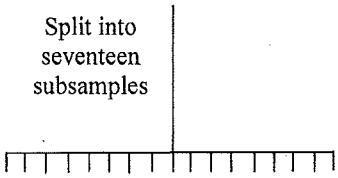
Sample CRR 442

Split into seventeen subsamples



Sample CRR 054

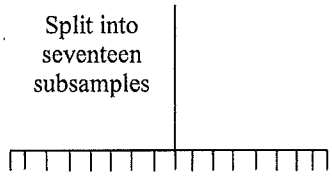
Split into seventeen subsamples



Lake Wheeler – Lake Wheeler Park Boat Dock
35.69326, -78.70078

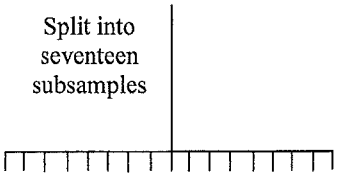
Sample CRR 106

Split into seventeen subsamples



Sample CRR 149

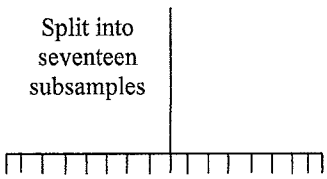
Split into seventeen subsamples



Raleigh Area Pond
35.79725, -78.68619

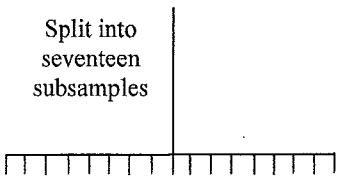
Sample CRR 288

Split into seventeen subsamples



Sample CRR 834

Split into seventeen subsamples



Participating Laboratories

The laboratories were referred to by ID throughout the round robin.

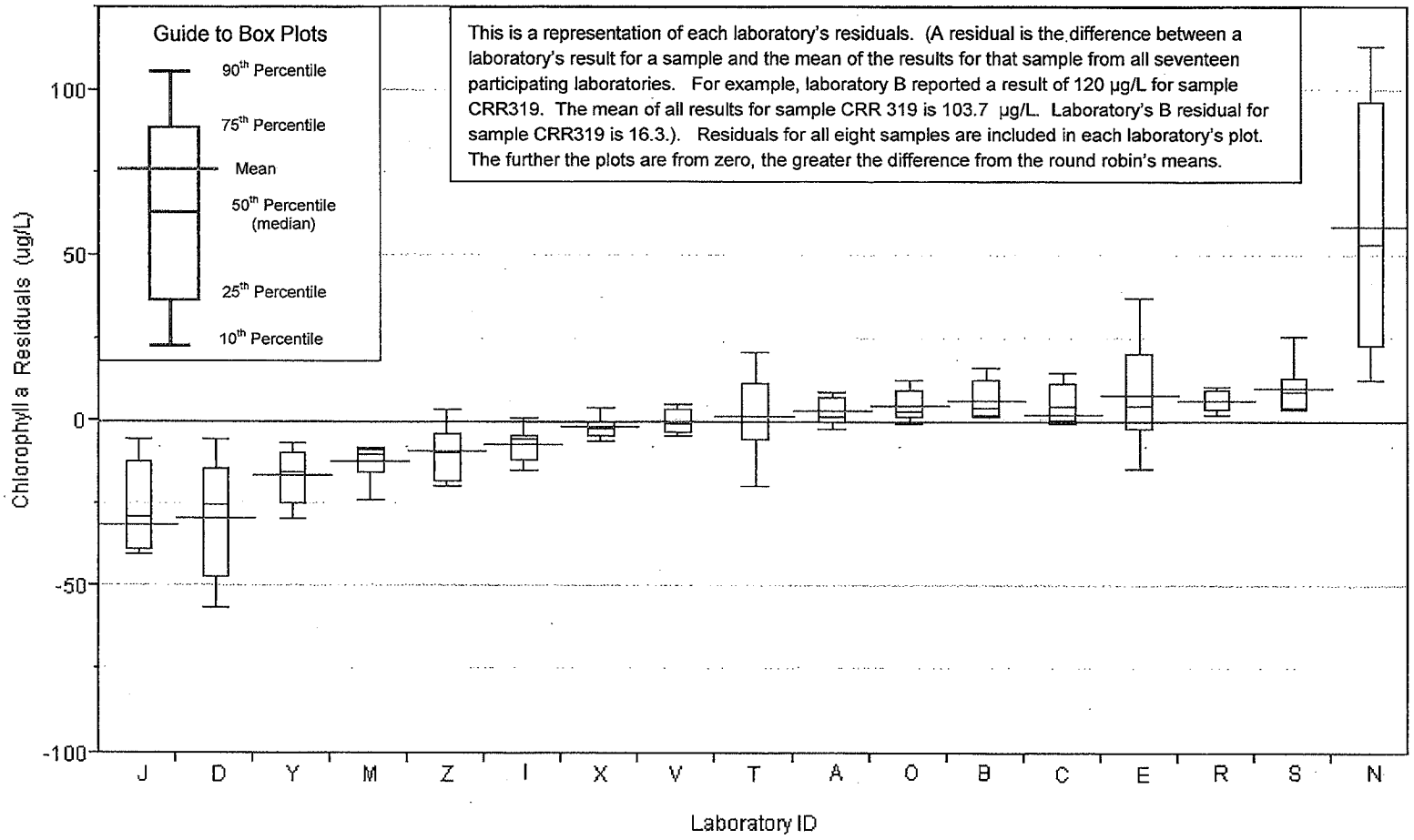
Charlotte-Mecklenburg Utilities Division – Hal Marshall Laboratory
Columbia Analytical
City of Durham Water and Wastewater Laboratory
NC DWQ Laboratory
East Carolina University Department of Biology
Environment 1
EPA Science and Ecosystems Support Division
Florida Department of Environmental Protection
Meritech
NCSU Center for Applied Aquatic Ecology
NOAA Center for Coastal Fisheries and Habitat Research
Research and Analytical
Tennessee Department of Health
Tritest
UNC Institute for Marine Sciences
UNCW Center for Marine Sciences
USGS

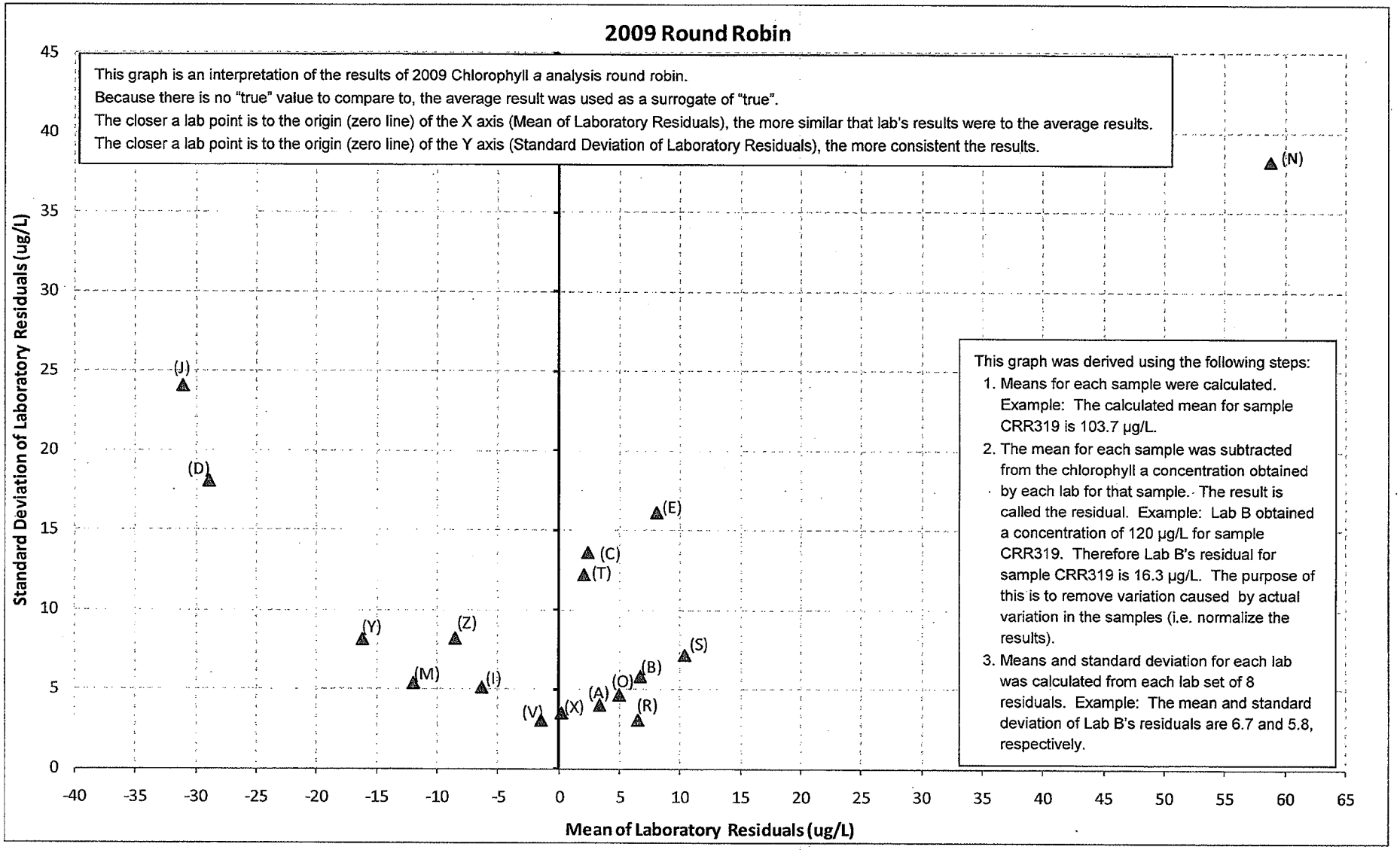
NC DWQ appreciates the time and cooperation of each participating laboratory.

June 2009 Chlorophyll *a* Round Robin Results

Laboratory ID	Falls Lake		Bass Lake		Lake Wheeler		Raleigh Area Pond	
	CRR319 (µg/L)	CRR791 (µg/L)	CRR442 (µg/L)	CRR054 (µg/L)	CRR106 (µg/L)	CRR149 (µg/L)	CRR288 (µg/L)	CRR834 (µg/L)
Z	86.1	95.1	48.4	47.6	18.4	19.8	96.1	N/A
X	99.6	108.8	49.5	49.8	29.2	28.2	90.2	91.3
Y	74.9	88.1	40.8	35.3	22.3	21.1	78.0	68.3
C	107.0	129.3	55.5	57.6	41.4	28.9	63.4	94.2
R	110.9	125.2	56.5	57.3	32.3	31.3	99.6	97.3
V	100.0	120.0	50.0	51.0	28.0	26.0	93.0	92.0
J	70.1	31.9	18.9	27.2	7.0	23.9	83.4	47.2
O	110.0	125.0	55.0	51.0	30.0	31.0	96.0	100.0
S	113.0	140.0	56.0	60.0	33.6	33.5	106.0	99.2
I	91.0	99.8	45.4	46.4	24.3	25.2	87.2	88.3
D	55.0	58.0	32.0	32.0	16.0	24.0	52.0	58.0
M	93.4	98.4	40.0	43.4	20.7	20.0	68.8	77.9
E	128.9	151.7	54.4	54.7	35.3	35.4	78.2	84.1
T	98.0	95.5	65.3	53.9	35.9	29.5	88.6	108.0
A	113.0	121.0	53.4	52.1	26.7	29.3	94.8	94.8
N	192.0	227.8	113.9	96.1	49.8	57.0	192.0	99.7
B	120.0	129.0	54.0	53.0	31.0	32.0	100.0	93.0

Note: N/A = Sample was lost during shipment


Guide to Box Plots
90th Percentile
75th Percentile
Mean
50th Percentile (median)
25th Percentile
10th Percentile
This is a representation of each laboratory's residuals. (A residual is the difference between a laboratory's result for a sample and the mean of the results for that sample from all seventeen participating laboratories. For example, laboratory B reported a result of 120 µg/L for sample CRR319. The mean of all results for sample CRR 319 is 103.7 µg/L. Laboratory's B residual for sample CRR319 is 16.3.). Residuals for all eight samples are included in each laboratory's plot. The further the plots are from zero, the greater the difference from the round robin's means.
Chlorophyll a Residuals (ug/L)
100
50
0
-50
-100
J
D
Y
M
Z
I
X
V
T
A
O
B
C
E
R
S
N
Laboratory ID


2009 Round Robin
This graph is an interpretation of the results of 2009 Chlorophyll a analysis round robin.
Because there is no "true" value to compare to, the average result was used as a surrogate of "true".
The closer a lab point is to the origin (zero line) of the X axis (Mean of Laboratory Residuals), the more similar that lab's results were to the average results.
The closer a lab point is to the origin (zero line) of the Y axis (Standard Deviation of Laboratory Residuals), the more consistent the results.
Standard Deviation of Laboratory Residuals (ug/L)
Mean of Laboratory Residuals (ug/L)
45
40
35
30
25
20
15
10
5
0
-40
-35
-30
-25
-20
-15
-10
-5
0
5
10
15
20
25
30
35
40
45
50
55
60
65
(J)
(D)
(Y)
(Z)
(M)
(I)
(V)
(X)
(A)
(O)
(B)
(R)
(C)
(T)
(E)
(S)
(N)
This graph was derived using the following steps:
1. Means for each sample were calculated. Example: The calculated mean for sample CRR319 is 103.7 µg/L.
2. The mean for each sample was subtracted from the chlorophyll a concentration obtained by each lab for that sample. The result is called the residual. Example: Lab B obtained a concentration of 120 µg/L for sample CRR319. Therefore Lab B's residual for sample CRR319 is 16.3 µg/L. The purpose of this is to remove variation caused by actual variation in the samples (i.e. normalize the results).
3. Means and standard deviation for each lab was calculated from each lab set of 8 residuals. Example: The mean and standard deviation of Lab B's residuals are 6.7 and 5.8, respectively.