

Analysis of Marsh Phosphorus Data from Loxahatchee National Wildlife Refuge

prepared for

U.S. Department of the Interior

by

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Monitoring of phosphorus concentrations at 14 stations in Loxahatchee National Wildlife Refuge (Figures 1-3) is required for determining compliance with the Everglades Settlement Agreement (USA et al., 1995). The Agreement establishes stage-dependent limits on the monthly geometric-mean concentration across all stations. Interim and long-term limits were derived using marsh data collected at the same stations between 1978 and 1983. Compliance with interim limits is expected to provide water quality similar to that present in 1978-1979. Under the terms of the proposed modified consent decree (USA et. al, 1995), compliance with interim limits is required by February 1, 1999 and compliance with long-term limits is required by December 31, 2006. Data collected between 1993 and 1998 (Figures 1 -5) provide a recent baseline, an opportunity to refine sampling procedures, and basis for characterizing spatial and temporal variability in marsh P concentrations. Periodic review of sampling procedures and results by the Everglades Technical Oversight Committee will help to ensure that the collected data are representative and appropriate for tracking compliance starting in February 1999.

In 1978-1983 (period of record used for deriving limits), samples were collected in a bucket dropped from a hovering helicopter. Current procedures involve collection from the ground, away from the helicopter wash, in laboratory-prepared sampling bottles, and with extreme care not to disturb the bottom sediments. It seems likely that risk of contamination was considerably higher with the historical procedure. The risk of contamination under current procedures is unknown, but is thought to increase as water depth decreases.

In 1993-1997, samples were not collected when the water depth at given station was less than ~20 cm. This criterion reflected concerns about potential contamination of samples collected in shallow waters. The protocol resulted in several missing values and possible reductions in the accuracy and precision of the monthly geometric means used for determining compliance. The number of sampled stations is plotted against stage for the 1978-1983 and 1993-1998 periods in Figure 6. Based upon the fact that the number of stations did not decrease appreciably at low stage in 1978-1983, it is unlikely that a minimum sampling depth criterion was invoked during that period. In 1993-1998, the decrease in the number of sampled stations at low stages is partially responsible for the relatively high standard errors of the marsh geometric means on the corresponding dates (Figures 4 & 5).

A special study was undertaken in 1997 to examine the relationship between water depth at each station and the reproducibility of the measured P concentrations. The study involved collection of triplicate samples at each station in 11 out of the 17 sampling rounds between August 1997 and December 1998. The basic premise was that if sampling at shallow depths introduced contamination, then the variability among replicate samples would be higher at shallower depths. Results described below indicate no significant relationship between water depth and variance among replicates for water depths between 10 and 140 cm. Sampling at depths down to 10 cm appears to be feasible without affecting the reproducibility of the results. Results of the study are also useful for evaluating the potential effects of replicate sampling on the precision of the spatial geometric mean.

The data used in this study were collected by South Florida Water Management District (SFWMD) under monitoring project "EVPA". Results are summarized in the following tables:

- 1 Total P Concentrations (ppb), September 1993 - December 1998
- 2 Water Depths (cm), September 1993 - December 1998
- 3 Data from Replicate Sampling Period, August 1997 - December 1998

Phosphorus concentrations reported in Table 1 are each derived from single samples reported in SFWMD's primary water quality database (replicates not used). Total water column depths were infrequently recorded in 1993-1995 (Table 2). The depth of sample collection was generally one half of the total water column depth at each location. Triplicate samples were collected in 11 out of the 17 months between August 1997 and December 1998 (Table 3). Concentrations reported in Table 3 are the geometric means of replicate samples (primary sample plus 1 or 2 duplicates).

Spatial variations in geometric mean P concentrations, frequency of concentrations exceeding 10 ppb, and water depth are shown in Figure 1, 2, and 3, respectively. These are based upon the 1993-1998 period. Bar charts of similar data are shown in Figures 7 and 8. Generally, concentrations are higher and depths are shallower in the northern portions of the Refuge, as compared with the interior and southern locations. The concentration pattern may reflect penetration of phosphorus loads from the S5A pumping station and/or effects of shallower water depths.

Figure 9 plots the water depth at each station against the average stage used for tracking compliance (gauges 7, 8C, & 9) for the intensive survey period (August 1997-December 1998). A regression of the mean water depth against stage (not shown) has a slope of 1.0 (when both depth and stage are expressed in feet). Thus, there is reasonable consistency, on the average, between the depth and stage measurements. Spatial variations in topography and water surface elevation are presumably responsible for the wide range of depths observed on any given date. Results indicate that depths generally exceed 20 cm at all stations when the average stage exceeds ~16.7 feet. The lowest stage (15.3 ft) was observed in June 1998, when three stations were sampled and the depth ranged from 12 to 20 cm. Compliance would not be determined under these extreme conditions, since stage was below the specified minimum stage of 15.41 ft (lower range of 1978-1983 data used for developing limit equations).

Figure 10 plots the geometric mean concentration and variability among replicates as a function of water depth for the August 1997-December 1998 period. Variability is expressed as a coefficient of variation (% variation around the geometric mean) and is computed as the standard deviation of natural-log-transformed concentrations. There is a slight negative correlation between concentration and depth ($r = -0.37$, $p < 0.01$). Three mechanisms may be involved:

1. Effects of location (shallower stations located in northern areas closest to S5A)
2. Actual increases in concentration occurring at shallow depths, attributed to diffusion of phosphorus from sediment porewaters, focusing / "alligator hole" effects; and/or lower water residence times in Refuge as a whole; and/or
3. Artifacts of the sampling process.

Even if sampling artifacts are present, it is unlikely that contamination effects are greater than those experienced in 1979-1983, when sampling methods were relatively crude (see above). The relative unimportance of sampling artifacts is supported by the absence of a significant correlation between water depth and variability among replicates ($r = 0.18$, $p > 0.10$). Similar conclusions are reached when the geometric mean and CV are plotted against stage (Figure 11). These results indicate that the precision of the sampling process is independent of water depth over the 10-140 cm range. Consistent sampling at depths down to 10 cm is recommended.

Impacts of spatial and sampling variability on the precision of the monthly geometric mean can be evaluated using the following model:

$$Y_{dsr} = \ln(\text{TP, ppb}) = \mu + \delta_d + \delta_{ds} + \delta_{dsr}$$

where,

Y_{dsr} = natural log of concentration on date d, at station s and in replicate r

μ = natural log of the long-term geometric mean for the marsh

δ_d = date effect (mean = 0, standard deviation = σ_d)

δ_{ds} = spatial effect (mean = 0, standard deviation = σ_s)

δ_{dsr} = replicate error (mean = 0, standard deviation = σ_r)

The model has been calibrated by applying a nested one-way analysis of variance (Snedecor & Cochran, 1989) to marsh data collected between August 1997 and December 1998 (excluding June 1998, when the stage was below the compliance test limit). Resulting parameter estimates are:

$$\text{Temporal: } \sigma_d = 0.20$$

$$\text{Spatial: } \sigma_s = 0.22$$

$$\text{Replicate: } \sigma_r = 0.18$$

For the present purposes, each of the variance terms is assumed to be random. In fact, a portion of the temporal variance is non-random or related to deterministic factors (stage-dependence, fixed seasonal effects, Figures 5 & 12). Similarly, a portion of the spatial variance is non-random (related to station location, Figures 1-2, 7 & 8). Additional analyses would be required to further partition these variance components. Because non-random components are ignored, results discussed below may over-estimate the standard errors of the marsh geometric means.

Variability among replicates (18%) represents the combined effects of variations in sampling and laboratory analyses. Results from the Everglades Round Robin (triplicate analyses performed on same sample) can be used to estimate analytical variations. In 13 samples with mean

concentrations between 5 and 25 ppb, the relative standard deviation among replicates ranged from 10% to 23% for major government and university labs participating in the study. Based upon these results, an appreciable portion of the variance among replicates in the Refuge study can be attributed to the analytical variations associated with measuring phosphorus levels in this low concentration range.

For a sampling program design consisting of n_s stations and n_r replicates per station, the standard error of the log mean on a given date (Y_d) can be estimated from:

$$SE(Y_d) = [\sigma_s^2/n_s + \sigma_r^2 / (n_s n_r)]^{1/2} = [0.0034 + 0.0023]^{1/2} = .076$$

The standard error of the log mean approximately equals the relative standard error (RSE) of the geometric mean expressed as a percent. With 14 stations and 1 replicate per station, the RSE is estimated at 7.6%. This represents the expected uncertainty in the geometric mean on any date when all 14 stations are sampled. Approximately 59% of the variance in the geometric mean $[(.0034 / (.0034 + .0023))]$ is attributed to spatial variability and 41%, to replicate variability. The following table demonstrates sensitivity of the RSE to alternative designs for the sampling program:

Number Of Stations	Number of Replicates			
	1	2	3	5
4	14.2%	12.7%	12.1%	11.7%
6	11.6%	10.4%	9.9%	9.5%
8	10.0%	9.0%	8.6%	8.3%
10	9.0%	8.0%	7.7%	7.4%
12	8.2%	7.3%	7.0%	6.7%
14	7.6%	6.8%	6.5%	6.2%

Replicate sampling would provide a modest increase in precision, but may not be appropriate because it was not performed during the period of model calibration (1978-1983). Effects of sampling and analytical error during that period are inherent in the regression models used for estimating the interim and long-term limits at a given stage. During the model calibration period, the relative standard errors of the marsh geometric means averaged 17%, as compared with 7.6% estimated above for recent data. It appears that recent refinements to sampling and/or analytical methodology have improved precision significantly.

Since a portion of the replicate variability is attributed to analytical error, continued refinements to laboratory procedures would also provide modest increases in precision. It does not appear that marsh sampling difficulties (down to a depth of 10 cm) are contributing significant variance to the overall process of tracking compliance in the Refuge. Therefore, collection of replicate samples in the future (beyond those normally required for QA/QC purposes) does not seem necessary or appropriate.

References

Snedecor, G.W. & W.G. Cochran, Statistical Methods, Eight Edition, Iowa State University Press, 1989.

United States of America, South Florida Water Management District, & Florida Department of Environmental Protection, "Joint Motion for Approval of Modifications to the Settlement Agreement Entered as a Consent Decree", U.S. District Court, Southern District of Florida, Case 88-186-CIV-HOEVELER, June 1995.

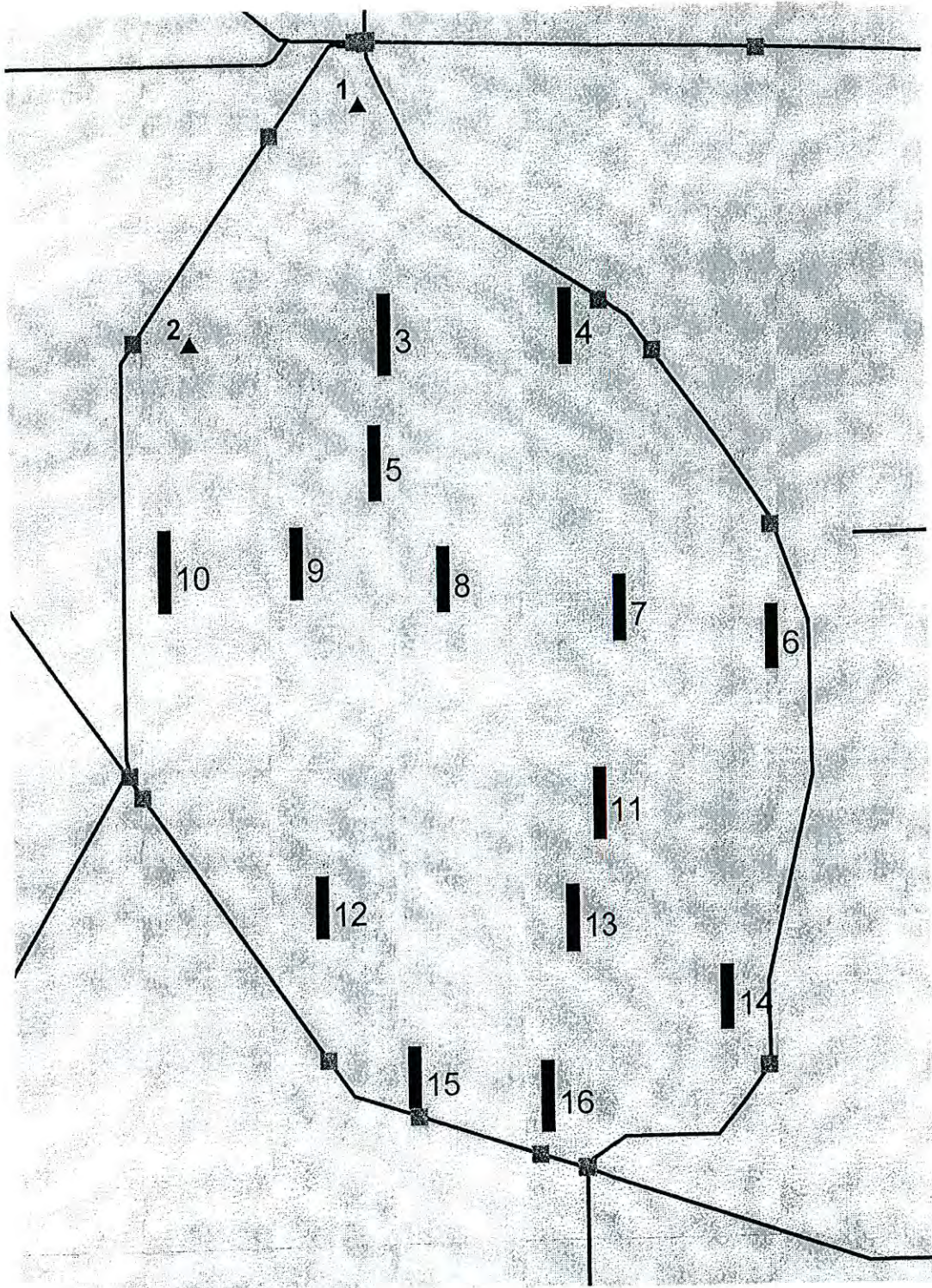
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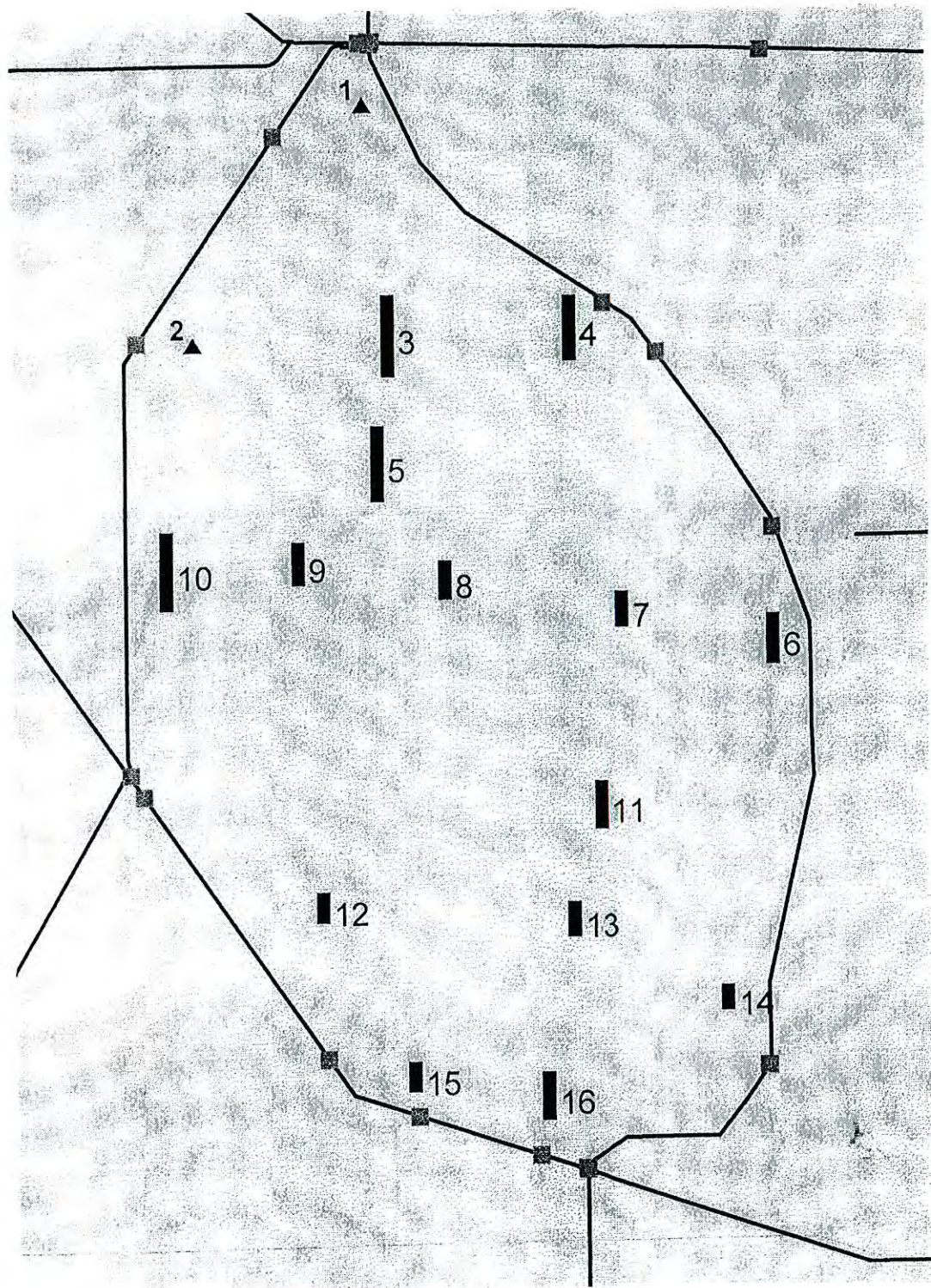
Figure 1



2 0 2 Miles

Geometric Mean TP (ppb)
1994-1998
Range 6.7 - 9.0 ppb

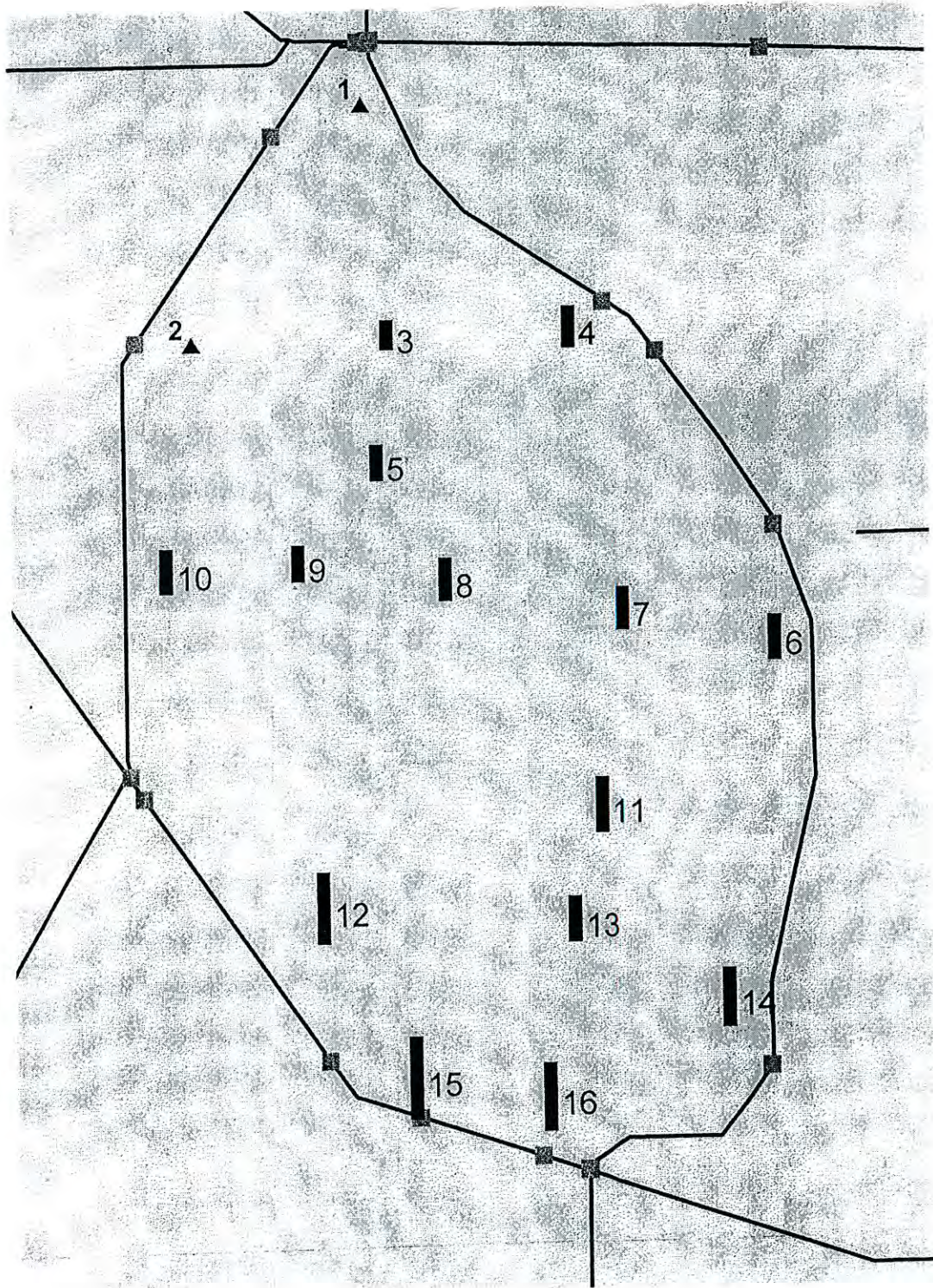
Figure 2



2 0 2 Miles

Frequency TP > 10 ppb
1994-1998
Range 8 - 31%

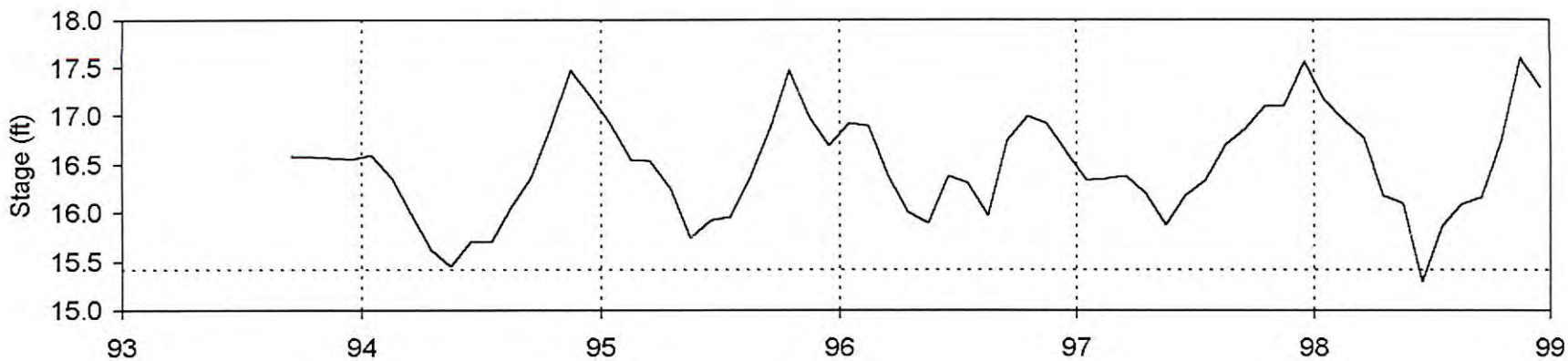
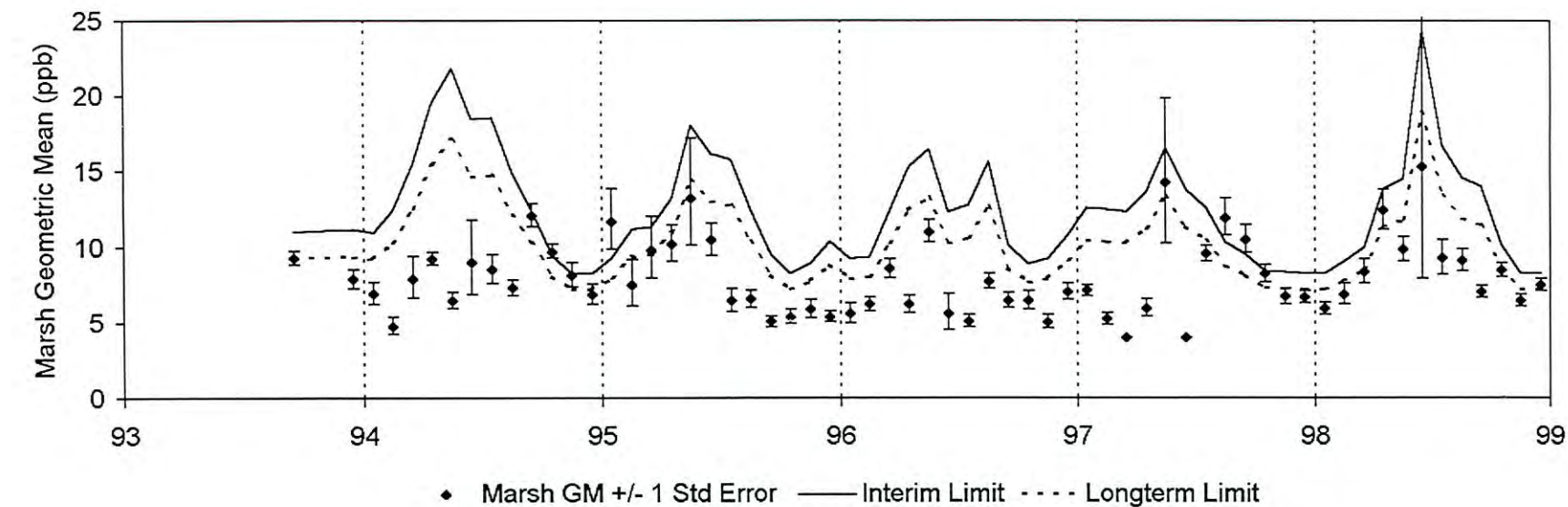
Figure 3



2 0 2 Miles

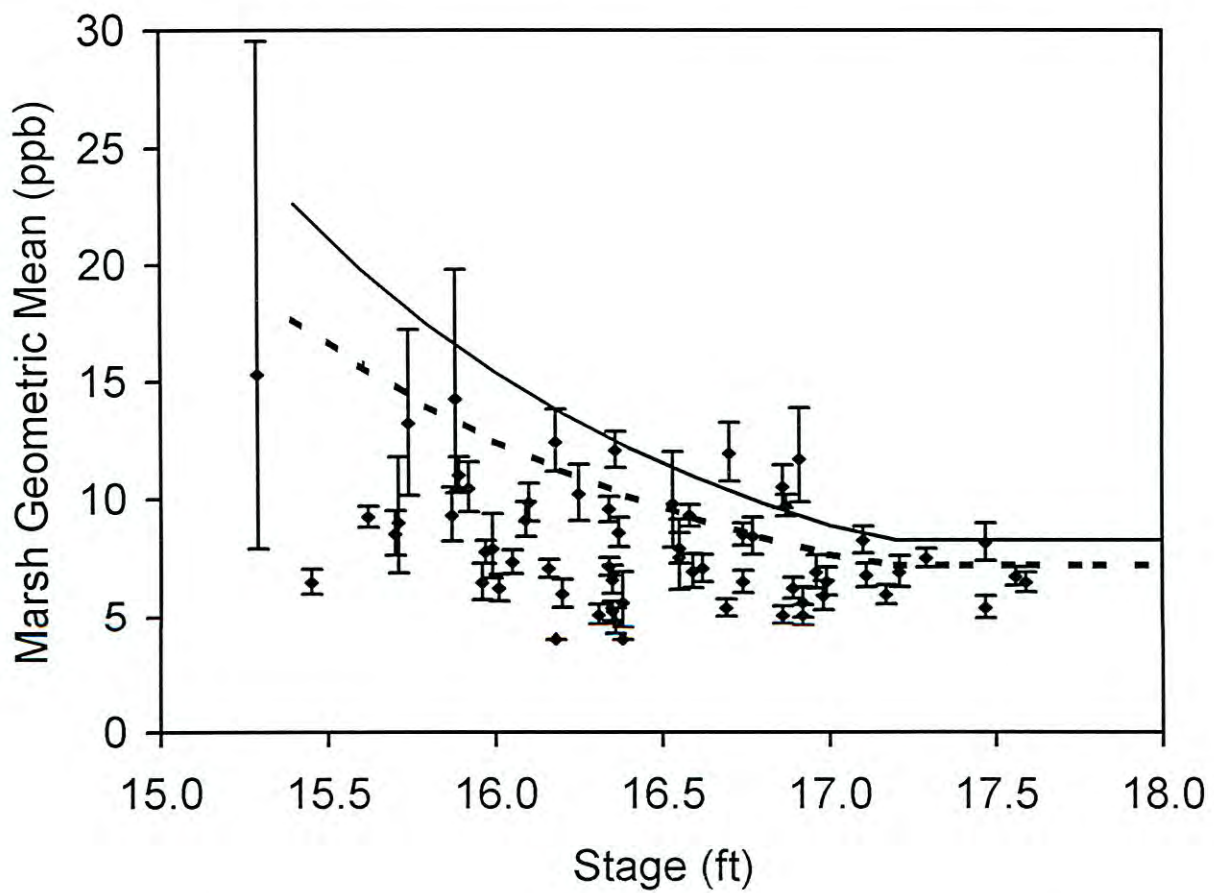
Mean Water Depth (cm)
1994-1998
Range 31 - 93 cm

Marsh Geometric Means & Stage vs. Time



Limits not applicable to June 1998 results because stage was below 15.42 ft.

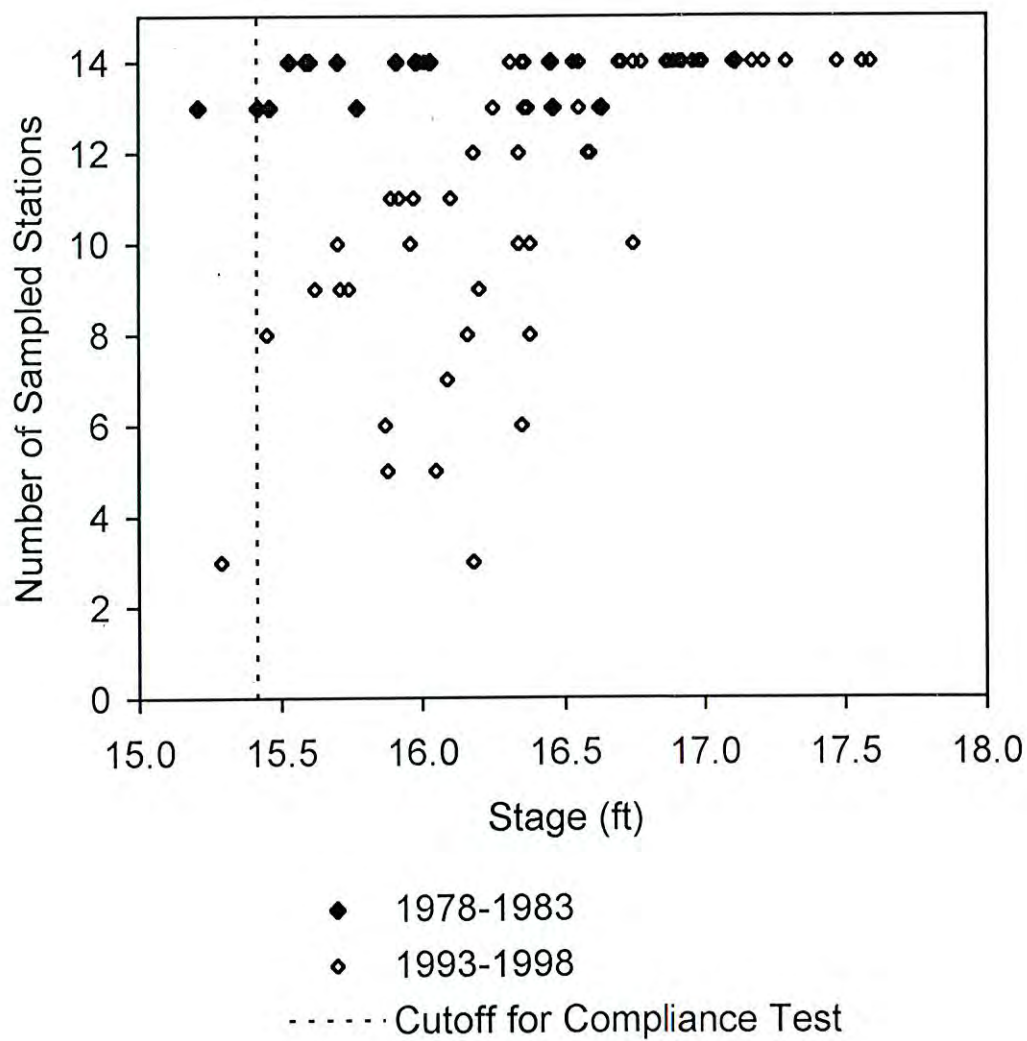
Marsh Geometric Means vs. Stage



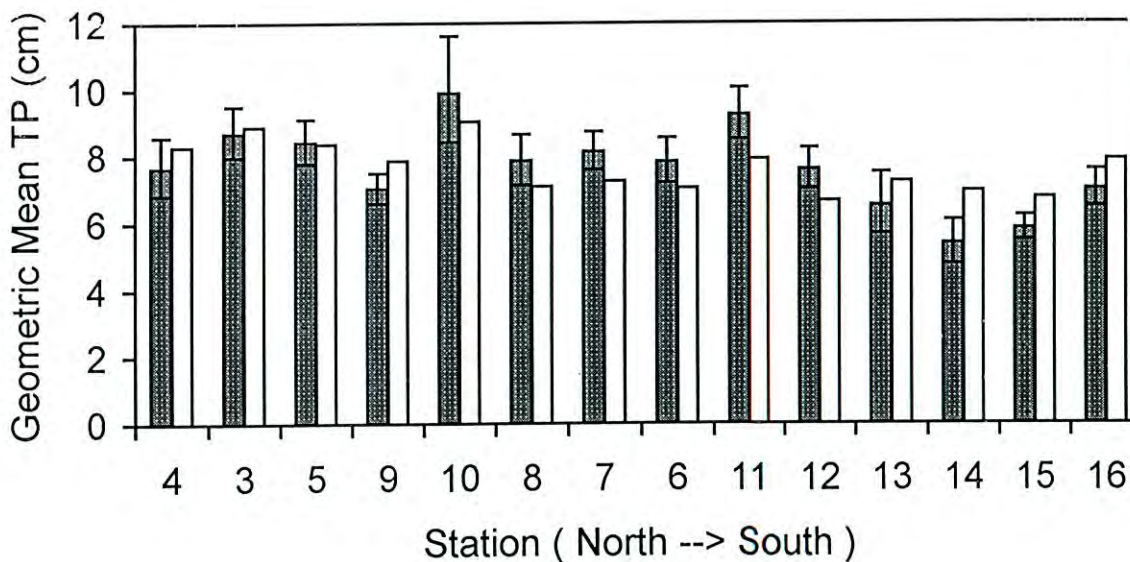
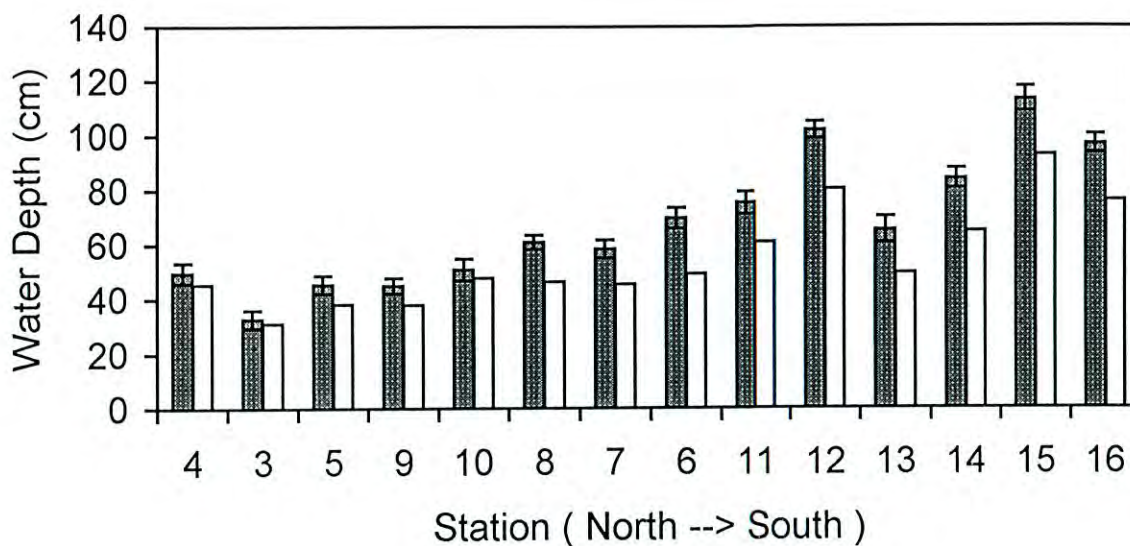
◆ Marsh — Interim Limit - - - Longterm Limit

Means +/- 1 Standard Error
September 1993 - December 1998

Number of Sampled Stations vs. Stage



Spatial Variations in Water Depth & Phosphorus



■ Complete Dates □ All Dates

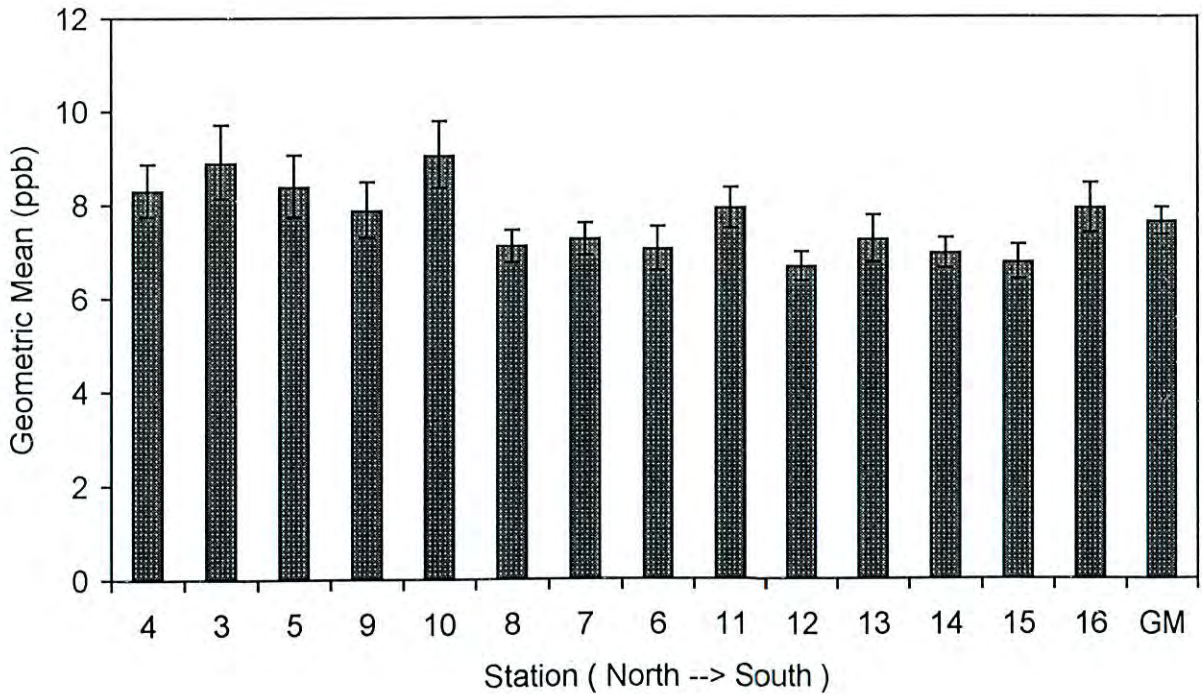
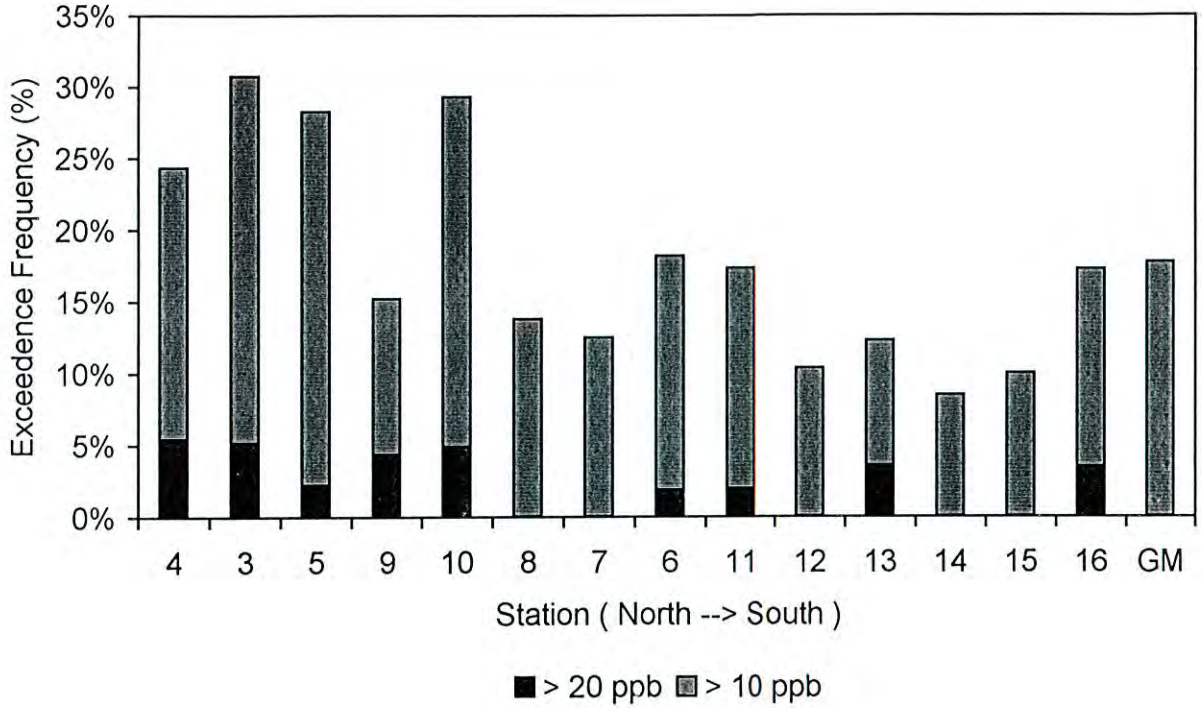
Means +/- 1 Standard Error

All Dates = September 1993 - December 1998

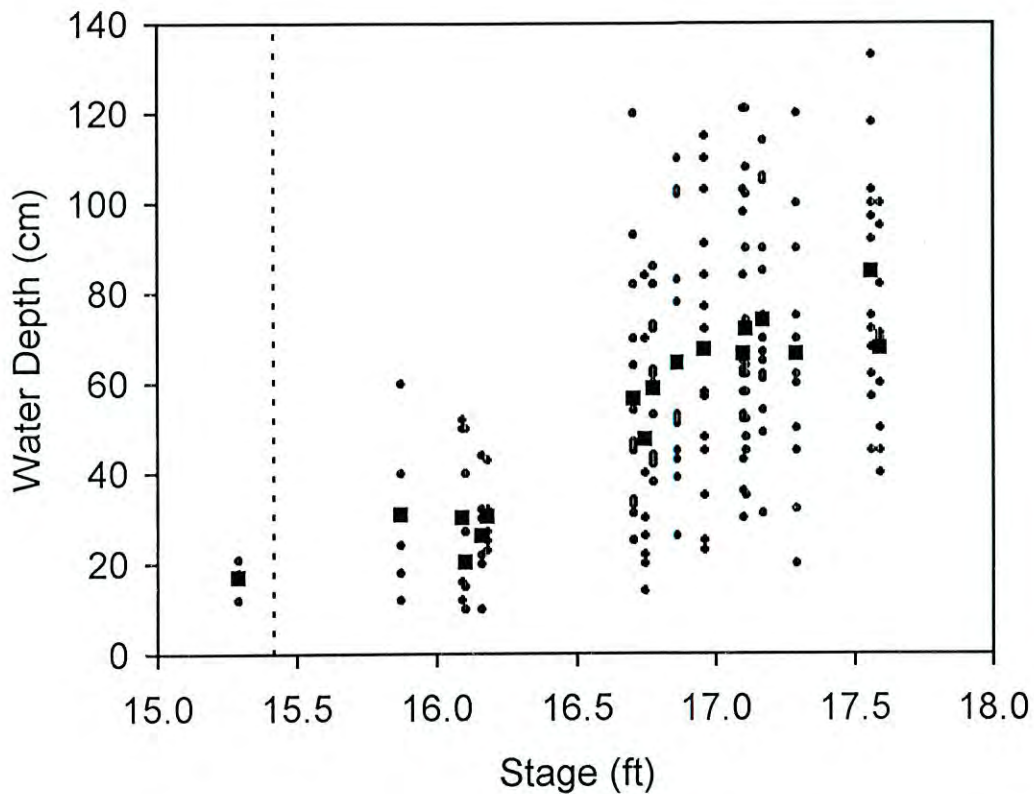
Complete Dates = 10 months between August 1997 & December 1998 when each station was sampled.

Spatial Variations in Phosphorus

September 1993 - December 1998



Water Depth vs. Stage



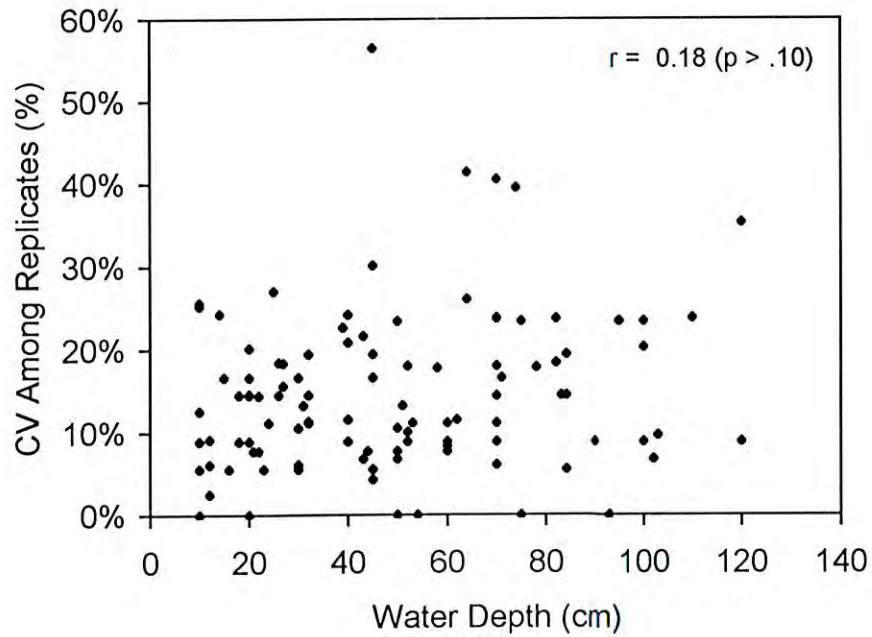
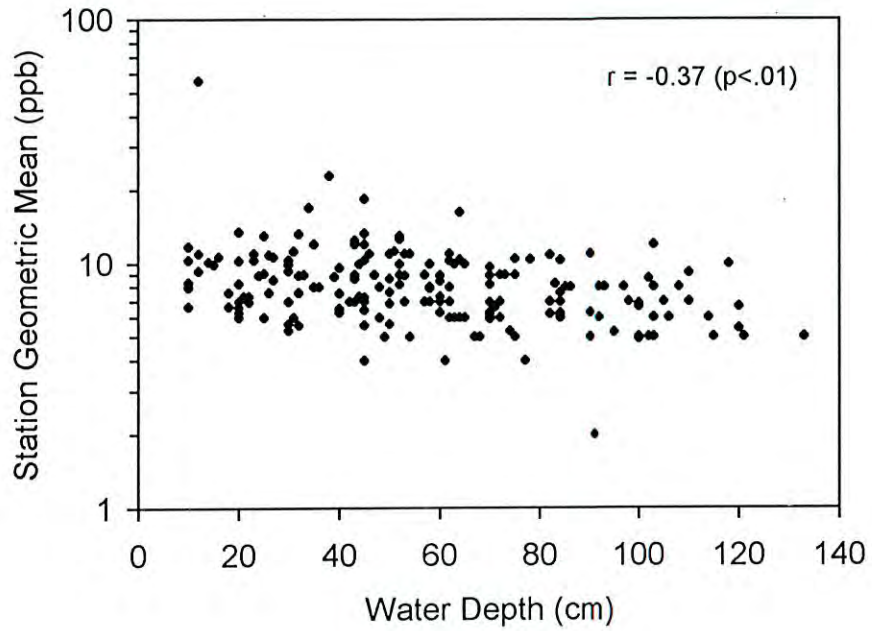
• Station ■ Mean - - - - - Cutoff for Compliance Test

Y = Total Water Depth at Sampling Station

X = Average Stage at Gauges 7, 8-C, & 9

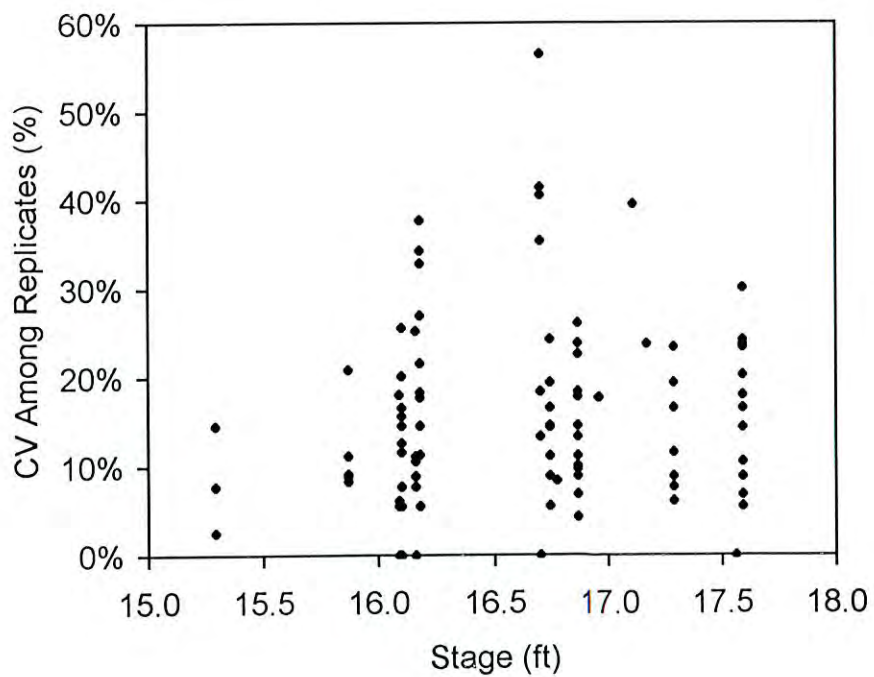
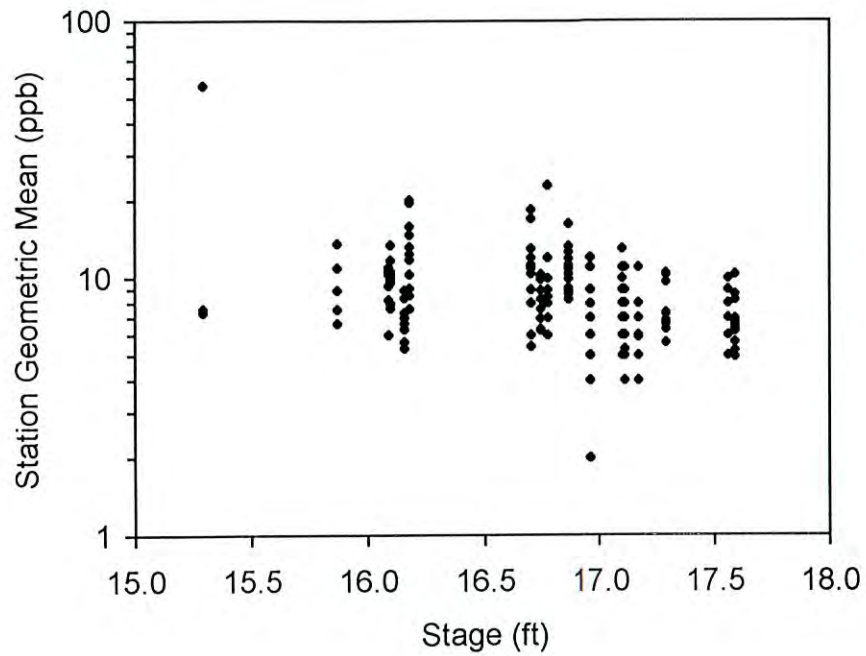
August 1997-December 1998

Station Geometric Means & Replicate Variability vs. Depth

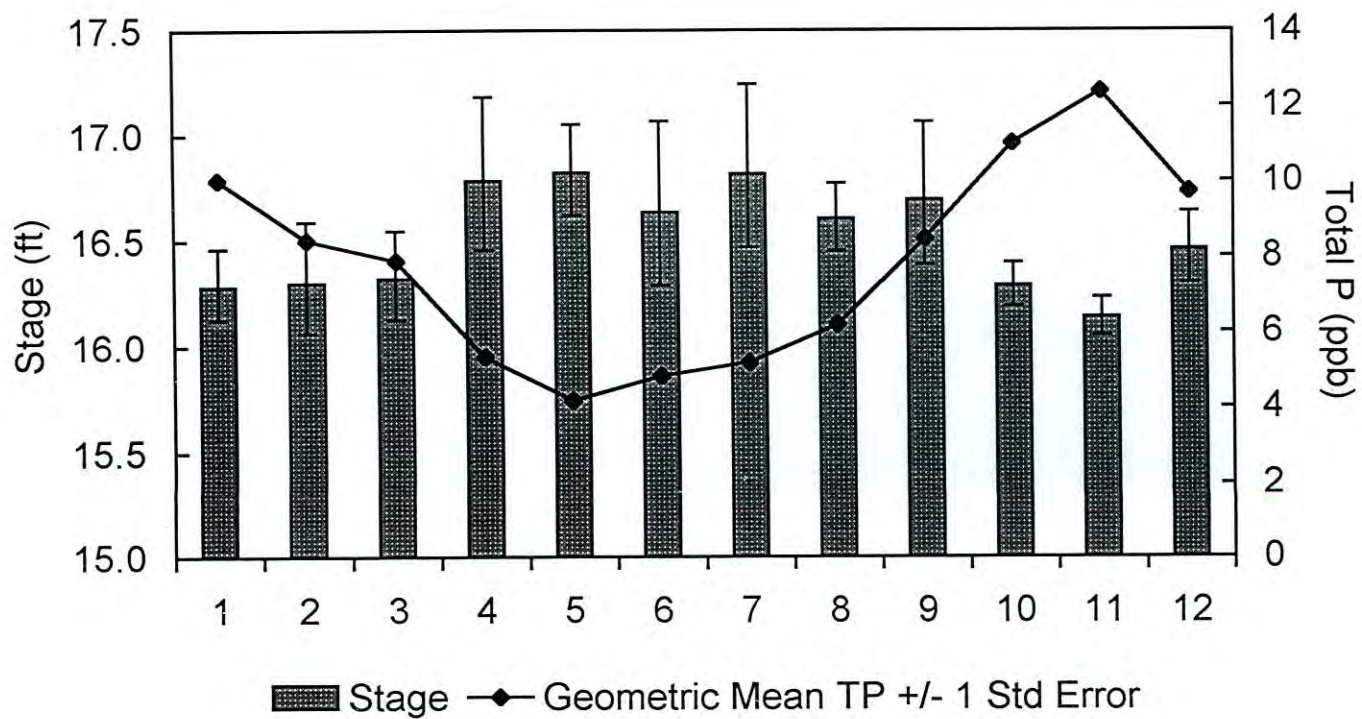


August 1997 - December 1998

Station Geometric Means & Replicate Variability vs. Stage



Seasonal Variations in Phosphorus & Stage



September 1993 - December 1998

Table 1

Total P Concentrations (ppb), September 1993 - December 1998															
	<u>LOX3</u>	<u>LOX4</u>	<u>LOX5</u>	<u>LOX6</u>	<u>LOX7</u>	<u>LOX8</u>	<u>LOX9</u>	<u>LOX10</u>	<u>LOX11</u>	<u>LOX12</u>	<u>LOX13</u>	<u>LOX14</u>	<u>LOX15</u>	<u>LOX16</u>	<u>GeoMn</u>
9309			10	9	8	8	14	10	9	7	10	9	9	10	9.29
9312	8	6	15	5	11	6	9	7		8	8	6	10	8	7.89
9401	11	11	11		6	7	9	7		5	5	5	4	7	6.93
9402	4	15	4	4	13	4	4	4	4	4	4	4	4	4	4.78
9403	18	8	11	4	6	5	4	43	7	4	8	9	7	8	7.90
9404				11	11	10			8	9	7	9	9	10	9.25
9405				7		9			7	4	6	7	6	7	6.48
9406			12	4	4	5	34		20		20	6	5		9.01
9407	20			7	10	6			7	7	7	10	10	7	8.52
9408									7		9	7	6	8	7.33
9409	11		15	11	9	14	10	11	9	18	16	15	12	10	12.09
9410	10	10	14	11	8	8	10	10	11	8	10	11	7	10	9.72
9411	7	6	10	8	7	7	10	10	10	6	4	9	20	8	8.15
9412	8	6	8	5	5	6	5	7	8	5	7	7	20	7	6.90
9501	40	7	10	6	8	8	10	20	10	5	7	20	20	30	11.70
9502	10	6	80	5	6	10	10	6	5	7	5	4	6	5	7.51
9503	50	6	20	8	10	20	20	20	8	6	5	4	4	5	9.78
9504		10	7	9	6	6	20	10	10	8	20	9	10	20	10.21
9505				20	10	10			20	5	10	8	10	78	13.24
9506			10	20	9	8	20		10	9	8	8	10	10	10.47
9507			13	6	6	8			6	5	4	4	7	10	6.46
9508	8	5	5	4	9	11	4	12	6	7	7	7	6	6	6.57
9509	7	5	6	10	7	4	4	5	4	4	4	5	4	5	5.08
9510	4	7	4	4	6	5	12	5	7	4	5	8	4	5	5.40
9511	4	8	5	4	4	4	4	5	8	7	7	9	14	6	5.89
9512	6	8	6	6	5	6	5	9	4	4	4	5	4	6	5.40
9601	4	23	5	4	5	5	5	6	6	6	6	5	4	5	5.60
9602	6	7	6	7	7	7	8	9	8	4	7	6	4	4	6.23
9603	11	15	8	7	5	8	7	8		9	9	9	10	9	8.58
9604	9	11	10	4	4	5	7	9	7	5	5	6	5	5	6.22
9605		14		12	8	8		13	13	11	11	12	8	14	11.04
9606	9	21	4	5	4	4	4	4							5.60
9607	7	7	4	4	9	4	4	8	4	7	4	5	4	4	5.10
9608	8		7		8	7	7		8	5	8	12	8	9	7.75
9609	8	8	5	5	7	6	7	10	6	6	10	5	4	7	6.49
9610	8	10	7	10	10	7	7	9	6	4	5	4	4	5	6.49
9611	4	4	4	4	4	4	6	9	6	5	4	10	7	4	5.07
9612	6	8	6		8	8	7	16	6	6	8	5	6	6	7.05
9701			8	9	8	7	8	9	8	7	6	6	5	6	7.14
9702									5	4	5	5	6	7	5.25
9703				4	4	4		4	4	4	4	4	4	4	4.00
9704				4	5	9			7	7	5	8	4	7	5.99
9705				44						16		10	6	14	14.27
9706				4	4	4									4.00
9707				8	10	12	10		12	8	8	8	9	12	9.56
9708	13	9	13	11	11	12	9	17	16	8	35	9	8	11	11.94
9709	13	13	7	11	10	12	9	14	22	13	9	7	7	8	10.50
9710	7	11	8	10	8	10	9	13	10	8	7	6	5	7	8.25
9711	8	7	9	7	6	7	8	8	11	8	4	5	5	5	6.76
9712	7	5	7	8	9	7	7	6	8	10	6	5	5	6	6.71
9801	6	4	11	7	6	5	5	5	8	6	5	5	6	7	5.95
9802	11	6	12	6	9	9	6	12	7	7	4	4	5	5	6.89
9803	12	10	7	7	8	6	7	23	9	8	6	7	7	9	8.40
9804	17		17	14	18	10	25		9	7	9	10	12	11	12.43
9805			8	8	10	11	7		12	11	12	9	7	17	9.84
9806										7	57		9		15.28
9807						15				8	10	6	9	10	9.30
9808				6	11	9				11		10	8	10	9.11
9809				6	6	6			7	9		7	8	8	7.05
9810			8	9	9	6	9			9	10	8	7	11	8.49
9811	9	10	5	6	5	5	5	7	6	6	6	8	6	9	6.46
9812	8	8	9	8	11	8	7	7	10	6	6	6	6	7	7.51
GeoMn	8.88	8.29	8.34	7.00	7.24	7.08	7.77	9.02	7.88	6.65	7.19	6.91	6.72	7.86	7.59

Table 2

Water Depths (cm), September 1993 - December 1998

	<u>LOX3</u>	<u>LOX4</u>	<u>LOX5</u>	<u>LOX6</u>	<u>LOX7</u>	<u>LOX8</u>	<u>LOX9</u>	<u>LOX10</u>	<u>LOX11</u>	<u>LOX12</u>	<u>LOX13</u>	<u>LOX14</u>	<u>LOX15</u>	<u>LOX16</u>	<u>Mean</u>
9309															
9312															
9401															
9402															
9403															
9404															
9405															
9406			10	26	21	29	14		36		26	39	84		32
9407	18			20	21	26			36	38	32	36	64	58	35
9408		34		31	31	36	23	23	43	56	43	50	73	61	42
9409	33	47	30	41	42	43	42	28	38	71	41	82	110	81	52
9410	43	67	50	51	52	51	51	51	49	80	34	59	110	77	59
9411															
9412															
9501															
9502															
9503	24	43	22	47	37	40	30	30	50	70	50	50	70		43
9504															
9505															
9506			30	40	30	40	30								34
9507			20	30	40	40			40	60	30	50	70	50	43
9508	35	20	25	40	35	35	25	25	40	60	40	50	70	50	39
9509	40	40	60	60	50	60	40	50	25	75	25	75	100	75	55
9510	47	80	90	90	80	72	62	70	95	115	80	100	125	147	90
9511	25	40	40	50	40	35	30	30	93	115	80	88	125	93	63
9512	38	55	37		60	52	50	95	82	105	65	82	128	125	75
9601	30	50	50	60	60	70	50	40	70	100	80	100	130	120	72
9602	33	48	60	75	71	52	48	47	80	100	68	80	110	93	69
9603	20	30	20	50	40	40	30	20	61	97	53	85	90	80	51
9604	15	32	21	47	41	40	23	200	62	62	50	47	72	51	55
9605		20		32	35	30		20	48	70	37	48	85	63	44
9606	27	41	47	42	45	52	30	28							39
9607	30	48	40	48	65	48	33	32	63	75	43	50	89	50	51
9608	22	23	48	28	31	48	23		48	58	38	34	61	50	39
9609	30	40	37	60	60	53	55	42	76	103	58	77	115	78	63
9610	31	62	57	69	59	54	65	54	82	111	67	83	125	83	72
9611	45	51	34	65	60	53	37	47	73	105	51	85	120	100	66
9612	23	40	28	52	45	50	35	30	73	87	50	73	103	79	55
9701			21		38	42	30	28	68	83	50	68	110	75	56
9702									62	81	52	64	107	73	73
9703				53	37	23		32	65	87	53	69	94	80	59
9704				38	30	32			57	87	48	65	108	81	61
9705				25						63		54	83	62	57
9706				40	33	37			73		49	58	83	56	54
9707				42	43	41	24		62	81	49	55	74	62	53
9708	25	47	31	54	46	45	33	34	64	93	45	70	120	82	56
9709	26	51	39	78	52	52	43	45	64	103	53	83	110	102	64
9710	30	53	36	58	62	63	43	52	65	103	62	84	121	98	66
9711	35	58	52	74	64	62	48	58	90	108	45	90	121	102	72
9712	45	68	57	92	75	72	62	72	97	118	92	100	133	103	85
9801	31	61	62	70	65	67	54	49	85	106	75	90	114	105	74
9802	23	25	35	72	58	57	48	45	84	110	77	91	115	103	67
9803	43	44	43	53	60	62	42	38	73	86	63	60	82	72	59
9804									25	32	27	23	32	43	30
9805			10	10	10	27	10		10	40	15	20	50	20	20
9806										21	12		18		17
9807										40	12	18	60	24	31
9808				20	16	12				50		30	52	30	30
9809			10	20	30	30			10	32		20	44	22	24
9810			22	20	30	40	26			84	14	70	84	84	47
9811	50	45	50	70	40	70	45	70	60	100	71	82	95	100	68
9812	20	45	50	75	62	60	32	45	70	90	70	90	120	100	66
Mean	31	45	38	49	46	46	38	48	61	80	49	65	93	76	54

