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Nitrogen, Phosphorus, and Suspended Solids Concentrations in Tributaries to the Great Bay Estuary Watershed in 2009

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A Final Report to

The Piscataqua Region Estuaries Partnership

Submitted by

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Introduction

Nitrogen, phosphorus, and sediment loads to the Great Bay Estuary are a growing concern. The Piscataqua Region Estuaries Partnership (PREP) calculates the nitrogen load from tributaries to the Great Bay Estuary for its State of the Estuaries reports. Therefore, the purpose of this study was to collect representative data on nitrogen, phosphorus, and suspended sediment concentrations in tributaries to the Great Bay Estuary in 2009. The study design followed the tributary sampling design which was implemented by the New Hampshire Department of Environmental Services between 2001 and 2007 and by the University of New Hampshire in 2008, so as to provide comparable data to the previous loading estimates.

Methods

Sampling and Analytical Methods

The field sampling and laboratory analysis methods have been documented in the approved Quality Assurance Project Plan (RFA #08113; NHEP, 2008).

Grab samples were collected from the head-of-tide stations on eight tributaries to the Great Bay Estuary (Figure 1) on a monthly frequency from March to December. In some cases, samples were not collected every month, so a second sample was collected in some months to ensure data completeness (10 samples from each tributary in a year). The samples were analyzed for total dissolved nitrogen (TDN), total nitrogen (TN), total phosphorus (TP), total suspended solids (TSS), ammonia (NH_4), and nitrate (NO_3). A total of ten field duplicate samples were collected for each parameter (one station per sampling date) for quality assurance.

The Water Quality Analysis Laboratory at the University of New Hampshire used USGS Method I-4650-03 (alkaline persulfate digestion) to determine TN and TP and high temperature catalytic oxidation (Merriam et al., 1996) to determine the TDN concentrations in samples. Suspended solids concentrations were calculated using APHA method 2540-D. Nitrate concentration was determined using EPA method 353.2 and ammonium using EPA method 350.1.

Physico-chemical parameters (water temperature, specific conductance, dissolved oxygen, and pH) were measured in the field using a YSI 556 meter.

Quality Assurance Audit

Several quality control tests were planned in the Quality Assurance Project Plan (NHEP, 2008). The results of quality control samples for TN, TP, TDN, TSS, NH_4, and NO_3 have been summarized in Tables 1 through 6. All of the data quality objectives for the study were substantially met. There were no major deviations from the planned methods.

During the quality assurance review of the data, the following results were rejected:

- All pH data from the 6/17/09 and 7/15/09 samples based on the recommendation of UNH staff.
- TN data for one sample where TN was greater than TDN (07-CCH on 10/21/09).

A number of the field and laboratory quality control samples for TP had relative percent difference values greater than the data quality objectives (Table 3). However, the UNH

laboratory confirmed the validity of the methods for TP. Most of the samples that were outside of quality control limits had low concentrations (<10x the method detection limit) which artificially inflate the relative percent different calculations. In future years, the data quality objective for TP should probably be raised from <15% to <20% to be consistent with EPA monitoring programs. The high variability in the field duplicates for TP is likely indicative of natural variability in the river. All of the TP results were retained.

Several of the results for ammonium were reported at the method detection limit (0.005 mg/L). The UNH laboratory confirmed that these results should be reported as 0.005 mg/L, not <0.005 mg/L.

Results and Discussion

The quality assured results for TN, TP, TDN, TSS, NH_4, and NO_3 concentrations for each station visit are shown in Table 7. Figures 2 through 7 show the monthly concentrations for each parameter at each station.

The purpose of this report is to publish the results from the PREP sampling program for tributaries to the Great Bay Estuary. A detailed accounting of total nitrogen loads to the estuary from all sources (e.g., wastewater treatment facilities, non-point sources, and atmospheric deposition) will be included in PREP's State of the Estuaries reports. In the meantime, the following are some general observations which can be made based on the data:

- The average concentrations of TN at each station ranged from 0.36 to 1.1 mg N/L. The maximum concentrations occurred in the Cocheco River (station 07-CCH). The rest of the stations had average TN concentrations between 0.36 and 0.68 mg N/L.
- The average concentrations of TP at each station ranged from 0.019 to 0.061 mg P/L. The maximum concentrations occurred in the Cocheco River (station 07-CCH) and the Winnicut River (02-WNC).
- The average concentrations of TDN at each station ranged from 0.28 to 1.05 mg/L. The maximum concentrations occurred in the Cocheco River (station 07-CCH) and these levels were significantly higher than the other stations monitored. The rest of the stations had average TDN concentrations between 0.28 and 0.42 mg/L.
- The average suspended solids concentrations ranged from 1.9 to 5.9 mg/L. The highest average concentration was in the Winnicut River (02-WNC) but the Oyster River also had a high peak level on 11/18/09.
- The average concentrations of nitrate at each station ranged from 0.09 to 0.90 mg/L. The maximum concentrations occurred in the Cocheco River (station 07-CCH) and were consistently higher than the other stations throughout the entire monitoring period. The remaining stations had average TN concentrations between 0.09 and 0.18 mg N/L.
- The average ammonium concentration ranged from 0.014 to 0.026 mg/L. The Winnicut River had the highest average concentration (02-WNC), however, the maximum concentration varied among the stations during the various sampling dates.

References

NHEP. 2008. Ambient River Monitoring of Tributaries to the Great Bay Estuary in 2008 - 2012. New Hampshire Estuaries Project, University of New Hampshire, Durham, NH. Published Online, http://www.prep.unh.edu/resources/qapps/ambient_river_monitoring-nhep-08.pdf . Accessed March 26, 2009.

Merriam, J.L, W.H. McDowell, and W.S. Currie. 1996. A high-temperature catalytic oxidation technique for determining total dissolved nitrogen. *Soil Science Society of America Journal* 60: 1050-1055.

Table 1: Summary of Quality Control Samples for Total Nitrogen

Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Results
Precision-Overall	RPD < 30%	Field Duplicates	10 Field Duplicates / 0 Failed DQO.
Precision-Lab	RPD < 15%	Lab Duplicates	9 Lab Duplicates / Failed DQO 10 Lab Replicates / 3 Failed DQO Two of the failures were close to the DQO (<18%)
Accuracy/Bias	RPD < 15% >85% and <115% recovery	Certified Reference Material Samples Laboratory Fortified Matrix Samples	14 CRM tests / 1 Failed DQO 44 LFM tests / 13 Failed DQO All of the failures were close to the DQO or were for samples with low concentrations (<10xMDL)
Comparability	Measurements should follow standard methods that are repeatable	NA	The range of TN concentrations in 2009 (0.20-2.46 mg/L) matched the range from 2001-2008 (0.11-2.99 mg/L).
Sensitivity	Not expected to be an issue for this project (see discussion below)	NA	Lowest detected concentration was 0.20 mg/L.
Data Completeness	Valid data for 90% of planned samples (9 samples at each tributary)	Data Completeness Check	79 routine samples and 10 field duplicates were collected (99% of planned samples)

Table 2: Summary of Quality Control Samples for Total Dissolved Nitrogen

Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Results
Precision-Overall	RPD < 30%	Field Duplicates	10 Field Dupes / 0 Failed DQO
Precision-Lab	RPD < 15%	Lab Duplicates	7 Lab Dupes / 0 Failed DQO
Accuracy/Bias	RPD < 15% >85% and <115% recovery	Certified Reference Material Samples Laboratory Fortified Matrix Samples	13 CRM tests / 5 Failed DQO 120 LFM tests / 7 Failed DQO The failures were mostly close to the DQO or were for samples with low concentrations (<10xMDL)
Comparability	Measurements should follow standard methods that are repeatable	NA	The range of TDN concentrations in 2008 (0.17-2.57 mg/L) matched the range from 2009 (0.20-2.22).
Sensitivity	Not expected to be an issue for this project (see discussion below)	NA	Lowest detected concentration was 0.20 mg/L.
Data Completeness	Valid data for 90% of planned samples (9 samples at each tributary)	Data Completeness Check	80 routine samples and 10 field duplicates were collected (100% of planned samples)

Table 3: Summary of Quality Control Samples for Total Phosphorus

Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Results
Precision-Overall	RPD < 30%	Field Duplicates	10 Field Dupes / 2 Failed DQO All of the failures were close to the DQO or were for samples with low concentrations (<10xMDL)
Precision-Lab	RPD < 15%	Lab Duplicates	9 Lab Dupes / 4 Failed DQO All of the failures were close to the DQO or were for samples with low concentrations (<10xMDL) 12 Lab Reps / 8 Failed DQO All but 3 of the failures were <20% RPD or for samples with low concentrations (<10xMDL)
Accuracy/Bias	RPD < 15% >85% and <115% recovery	Certified Reference Material Samples Laboratory Fortified Matrix Samples	30 CRM tests / 3 Failed DQO 71 LFM tests / 22 Failed DQO All of the failures were close to the DQO or were for samples with low concentrations (<10xMDL)
Comparability	Measurements should follow standard methods that are repeatable	NA	The range of TP concentrations in 2008 (3 - 224 ug/L) matched the range from 2001-2007 (5-350).
Sensitivity	Not expected to be an issue for this project (see discussion below)	NA	Lowest detected concentration was 3 ug/L.
Data Completeness	Valid data for 90% of planned samples (9 samples at each tributary)	Data Completeness Check	80 routine samples and 10 field duplicates were collected (100% of planned samples)

Table 4: Summary of Quality Control Samples for Suspended Solids

Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Results
Precision-Overall	RPD < 30%	Field Duplicates	10 Field Dupes / 0 Failed DQO
Precision-Lab	RPD < 15%	Lab Duplicates	**NO DATA**
Accuracy/Bias	RPD < 15% >85% and <115% recovery	Certified Reference Material Samples Laboratory Fortified Matrix Samples	**NO DATA**
Comparability	Measurements should follow standard methods that are repeatable	NA	The range of TSS concentrations in 2009 (1-28 mg/L) matched the range from 2001-2007 (0.9-57).
Sensitivity	Not expected to be an issue for this project (see discussion below)	NA	Lowest detected concentration was 1 mg/L.
Data Completeness	Valid data for 90% of planned samples (9 samples at each tributary)	Data Completeness Check	77 routine samples and 10 field duplicates were collected (96% of planned samples)

The laboratory did not do any duplicates/replicates for TSS because they used the entire sample (or what was left after taking the aliquot for chemistry) to get a good TSS value. The laboratory did not have a CRM sample for TSS.

Table 5: Summary of Quality Control Samples for Nitrate

Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Results
Precision-Overall	RPD < 30%	Field Duplicates	10 Field Dupes / 0 Failed DQO
Precision-Lab	RPD < 15%	Lab Duplicates	9 Lab Dupes / 0 Failed DQO
Accuracy/Bias	RPD < 15% >85% and <115% recovery	Certified Reference Material Samples Laboratory Fortified Matrix Samples	24 CRM tests / 6 Failed DQO 44 LFM tests / 6 Failed DQO All of the failures were close to the DQO or were for samples with low concentrations (<10xMDL)
Comparability	Measurements should follow standard methods that are repeatable	NA	NA (Not sampled in previous years)
Sensitivity	Not expected to be an issue for this project (see discussion below)	NA	Lowest detected concentration was 25 ug/L.
Data Completeness	Valid data for 90% of planned samples (9 samples at each tributary)	Data Completeness Check	80 routine samples and 10 field duplicates were collected (100% of planned samples)

Table 6: Summary of Quality Control Samples for Ammonium

Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Results
Precision-Overall	RPD < 30%	Field Duplicates	10 Field Dupes / 3 Failed DQO All of the failures were close to the DQO or were for samples with low concentrations (<10xMDL)
Precision-Lab	RPD < 15%	Lab Duplicates	8 Lab Dupes / 2 Failed DQO All of the failures were close to the DQO or were for samples with low concentrations (<10xMDL)
Accuracy/Bias	RPD < 15% >85% and <115% recovery	Certified Reference Material Samples Laboratory Fortified Matrix Samples	30 CRM tests / 0 Failed DQO 75 LFM tests / 13 Failed DQO All of the failures were close to the DQO or were for samples with low concentrations (<10xMDL)
Comparability	Measurements should follow standard methods that are repeatable	NA	NA (Not sampled in previous years)
Sensitivity	Not expected to be an issue for this project (see discussion below)	NA	Lowest detected concentration was 4.6 ug/L.
Data Completeness	Valid data for 90% of planned samples (9 samples at each tributary)	Data Completeness Check	80 routine samples and 10 field duplicates were collected (100% of planned samples)

Table 7: Validated Laboratory Results at Tributary Stations

STATIONID	DATE	TOTAL NITROGEN (mg/ NL)	DISSOLVED NITROGEN (mg N/L)	NITRATE (mg N/L)	AMMONIUM (mg N/L)	TOTAL PHOSPHORUS (mg P/L)	TOTAL SUSPENDED SOLIDS (mg/L)
02-GWR	03/25/09	0.334	0.293	0.130	0.063	0.025	1.99
	04/15/09	0.253	0.204	0.087	0.010	0.011	1.70
	05/20/09	0.361	0.272	0.130	0.015	0.016	2.63
	06/17/09	0.446	0.304	0.086	0.007	0.022	2.69
	08/19/09						2.11
	09/16/09	0.332	0.270	0.113	0.020	0.020	2.65
	10/07/09	0.421	0.311	0.060	0.005	0.058	
	10/21/09	0.486	0.368	0.089	0.027	0.106	3.00
	11/04/09	0.422	0.268	0.072	0.007	0.100	
	11/18/09	0.364	0.307	0.086	0.008	0.033	3.40
	12/16/09	0.293	0.230	0.095	0.014	0.019	1.30
02-WNC	03/25/09	0.464	0.434	0.280	0.009	0.009	2.30
	04/15/09	0.442	0.362	0.163	0.009	0.009	1.92
	05/20/09	0.584	0.311	0.185	0.023	0.041	2.85
	06/17/09	0.559	0.361	0.064	0.023	0.048	2.06
	07/15/09						2.57
	08/19/09						8.00
	09/16/09	0.579	0.481	0.201	0.041	0.045	3.53
	10/07/09	0.767	0.505	0.127	0.065	0.098	
	10/21/09	0.747	0.512	0.191	0.026	0.054	27.89
	11/04/09	1.626	0.384	0.041	0.018	0.224	
	11/18/09	0.466	0.440	0.077	0.018	0.033	6.32
	12/16/09	0.538	0.419	0.143	0.026	0.014	1.81
05-BLM	03/25/09	0.436	0.294	0.165	0.018	0.058	1.45
	04/15/09	0.294	0.218	0.072	0.015	0.014	1.68
	05/20/09	0.490	0.236	0.100	0.005	0.018	3.05
	06/17/09	0.448	0.258	0.025	0.018	0.025	3.36
	07/15/09						3.31
	08/19/09						2.92
	09/16/09	0.510	0.374	0.134	0.041	0.042	3.61
	10/07/09	0.374	0.326	0.055	0.036	0.023	
	10/21/09	0.398	0.333	0.078	0.014	0.026	3.00
	11/04/09	0.363	0.282	0.077	0.026	0.031	
	11/18/09	0.351	0.278	0.052	0.013	0.025	2.90
	12/16/09	0.478	0.327	0.103	0.030	0.025	2.26

STATIONID	DATE	TOTAL NITROGEN (mg N/L)	DISSOLVED NITROGEN (mg N/L)	NITRATE (mg N/L)	AMMONIUM (mg N/L)	TOTAL PHOSPHORUS (mg P/L)	TOTAL SUSPENDED SOLIDS (mg/L)
05-LMP	03/25/09	0.195	0.279	0.143	0.006	0.013	2.67
	04/15/09	0.259	0.211	0.166	0.012	0.011	1.14
	05/20/09	0.340	0.283	0.159	0.017	0.013	1.28
	06/17/09	0.378	0.311	0.068	0.020	0.023	2.97
	07/15/09						1.26
	09/16/09		0.372	0.150	0.017	0.029	1.94
	10/07/09	0.385	0.357	0.114	0.041	0.019	
	10/21/09	0.363	0.276	0.074	0.016	0.019	1.85
	11/04/09	0.324	0.252	0.043	0.017	0.026	
	11/18/09	0.518	0.304	0.052	0.012	0.024	2.44
	12/16/09	0.444	0.282	0.116	0.029	0.014	1.50
05-OYS	03/25/09	0.310	0.333	0.210	0.010	0.005	2.25
	04/15/09	0.299	0.255	0.168	0.006	0.012	2.75
	05/20/09	0.457	0.334	0.194	0.018	0.023	3.07
	06/17/09	0.515	0.391	0.128	0.020	0.037	5.69
	07/15/09						3.55
	08/19/09						2.57
	09/16/09	0.487	0.398	0.199	0.009	0.035	3.51
	10/07/09	0.520	0.462	0.241	0.033	0.068	
	10/21/09	0.552	0.412	0.211	0.014	0.030	2.65
	11/04/09	0.485	0.375	0.134	0.028	0.040	
	11/18/09	0.636	0.434	0.151	0.038	0.057	27.57
	12/16/09	0.428	0.371	0.180	0.023	0.016	1.90
05-SFR	03/25/09	0.254	0.252	0.127	0.017	0.003	2.00
	04/15/09	0.253	0.224	0.111	0.010	0.015	1.22
	05/20/09	0.375	0.289	0.158	0.013	0.019	1.99
	06/17/09	0.302	0.227	0.062	0.009	0.016	2.29
	08/19/09						3.31
	09/16/09	0.513	0.446	0.298	0.005	0.022	1.96
	10/07/09	0.447	0.427	0.220	0.013	0.022	
	10/21/09	0.384	0.314	0.126	0.011	0.068	1.78
	11/04/09	0.328	0.274	0.122	0.025	0.048	
	11/18/09	0.352	0.312	0.086	0.014	0.021	1.70
	12/16/09	0.280	0.244	0.099	0.018	0.017	1.01

STATIONID	DATE	TOTAL NITROGEN (mg N/L)	DISSOLVED NITROGEN (mg N/L)	NITRATE (mg N/L)	AMMONIUM (mg N/L)	TOTAL PHOSPHORUS (mg P/L)	TOTAL SUSPENDED SOLIDS (mg/L)
07-CCH	03/25/09	0.671	0.657	0.600	0.028	0.025	2.30
	04/15/09	0.633	0.584	0.496	0.028	0.023	4.21
	05/20/09	1.254	1.159	1.150	0.043	0.044	2.45
	06/17/09	0.573	0.504	0.337	0.019	0.040	4.34
	07/15/09						2.97
	08/19/09						1.94
	09/16/09	2.266	2.213	2.048	0.014	0.112	2.03
	10/07/09	2.461	2.193	1.914	0.023	0.125	
	10/21/09		1.048	0.854	0.016	0.100	4.29
	11/04/09	0.905	0.851	0.766	0.019	0.069	
	11/18/09	0.609	0.598	0.425	0.024	0.037	3.18
	12/16/09	0.721	0.643	0.375	0.029	0.030	1.95
09-EXT	03/25/09	0.311	0.281	0.139	0.008	0.005	1.15
	04/15/09	0.276	0.213	0.112	0.008	0.021	2.37
	05/20/09	0.483	0.283	0.153	0.023	0.032	1.89
	06/17/09	0.472	0.343	0.083	0.020	0.036	2.15
	07/15/09						1.52
	08/19/09						1.88
	09/16/09	0.426	0.339	0.069	0.013	0.028	1.90
	10/07/09	0.422	0.366	0.102	0.024	0.028	
	10/21/09	0.497	0.340	0.075	0.013	0.064	2.69
	11/04/09	0.467	0.310	0.039	0.021	0.026	
	11/18/09	0.395	0.361	0.048	0.011	0.026	2.16
	12/16/09	0.374	0.338	0.091	0.023	0.018	1.70

*Note: Field duplicate samples not included

Figure 1: Sampling locations in the Great Bay Estuary Watershed

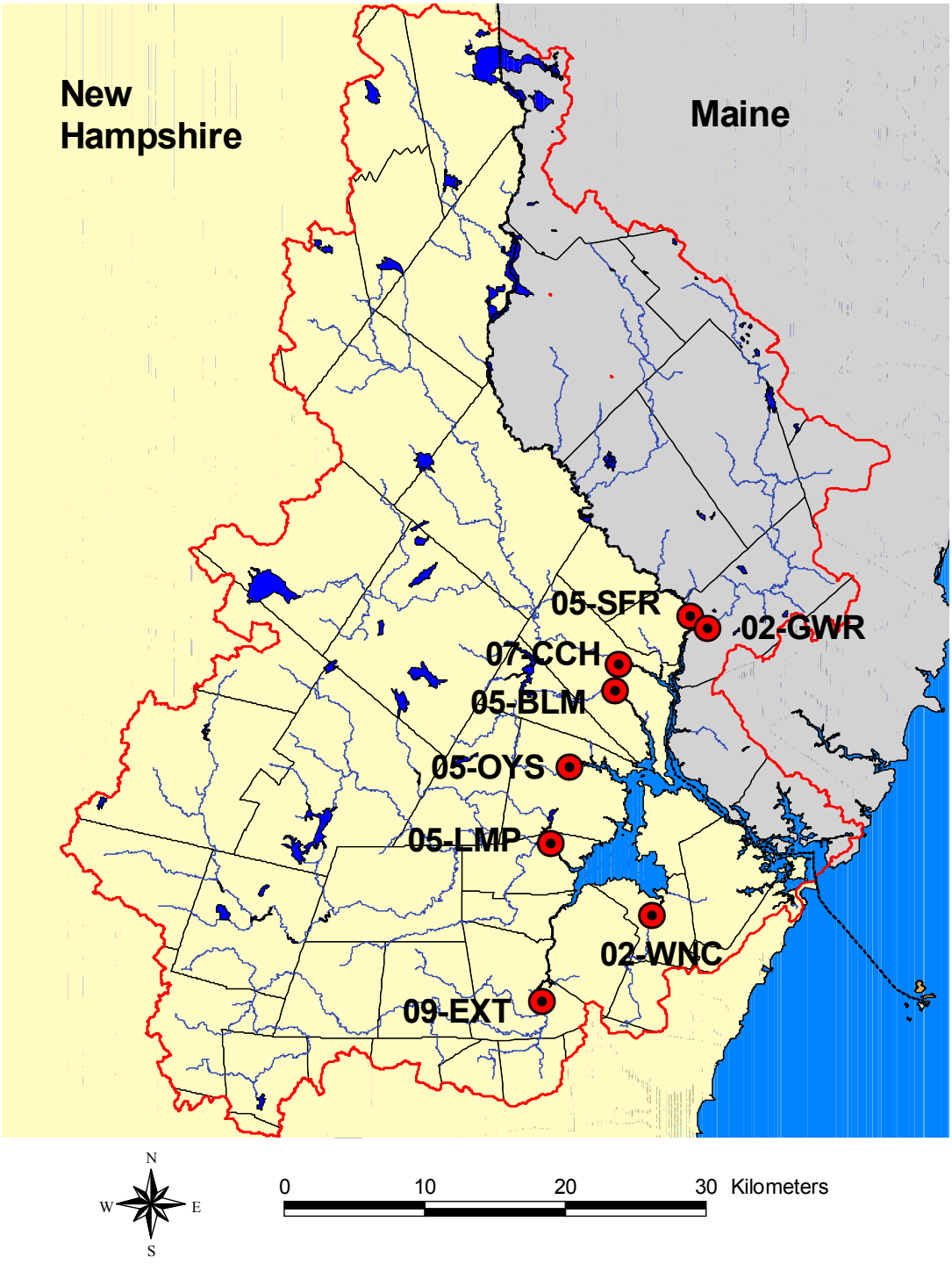

Figure 2: Total Nitrogen Concentrations (in mg N/L) at Tributary Stations

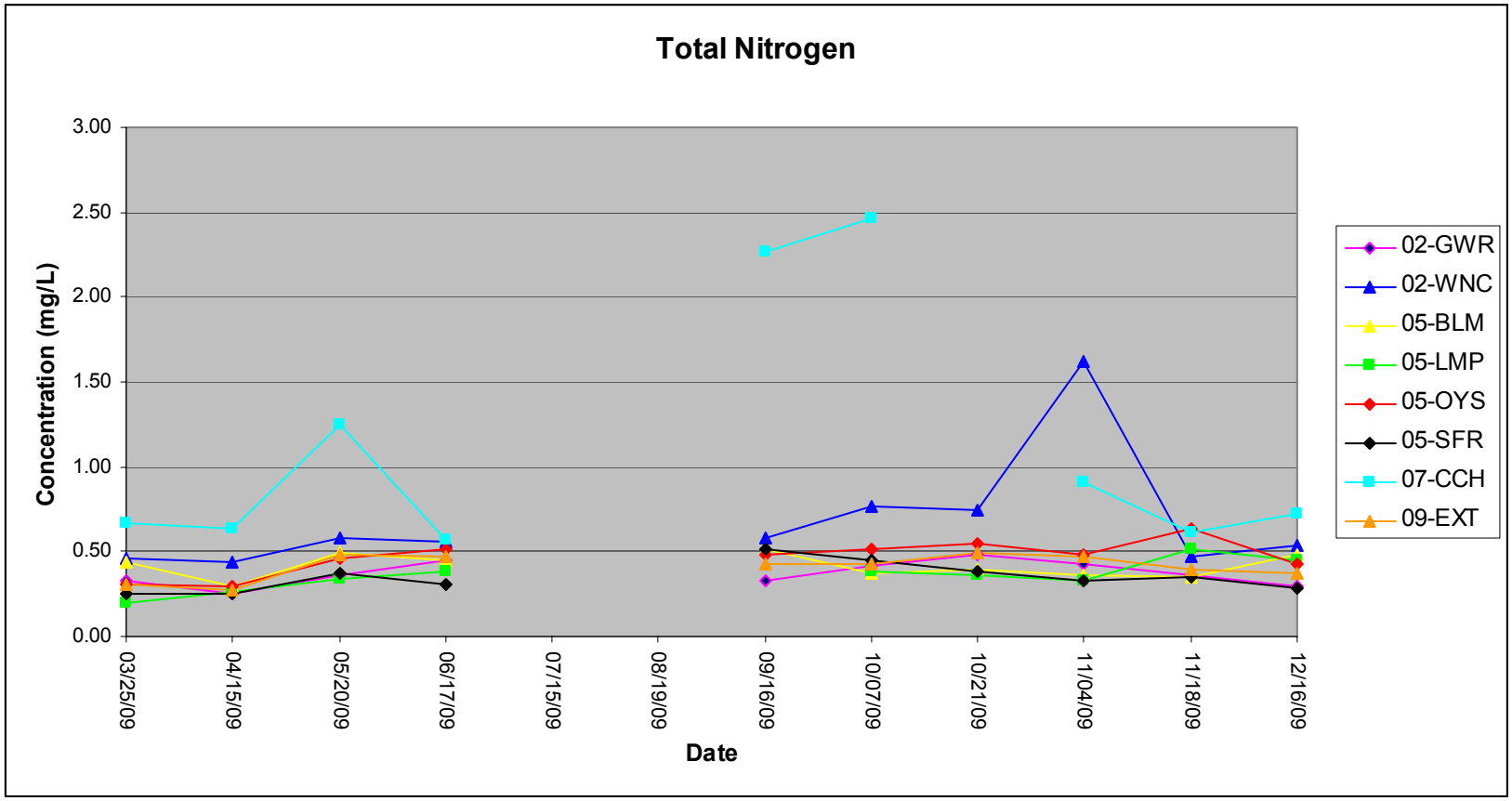

Figure 3: Total Phosphorus in Concentrations (mg P/L) at Tributary Stations

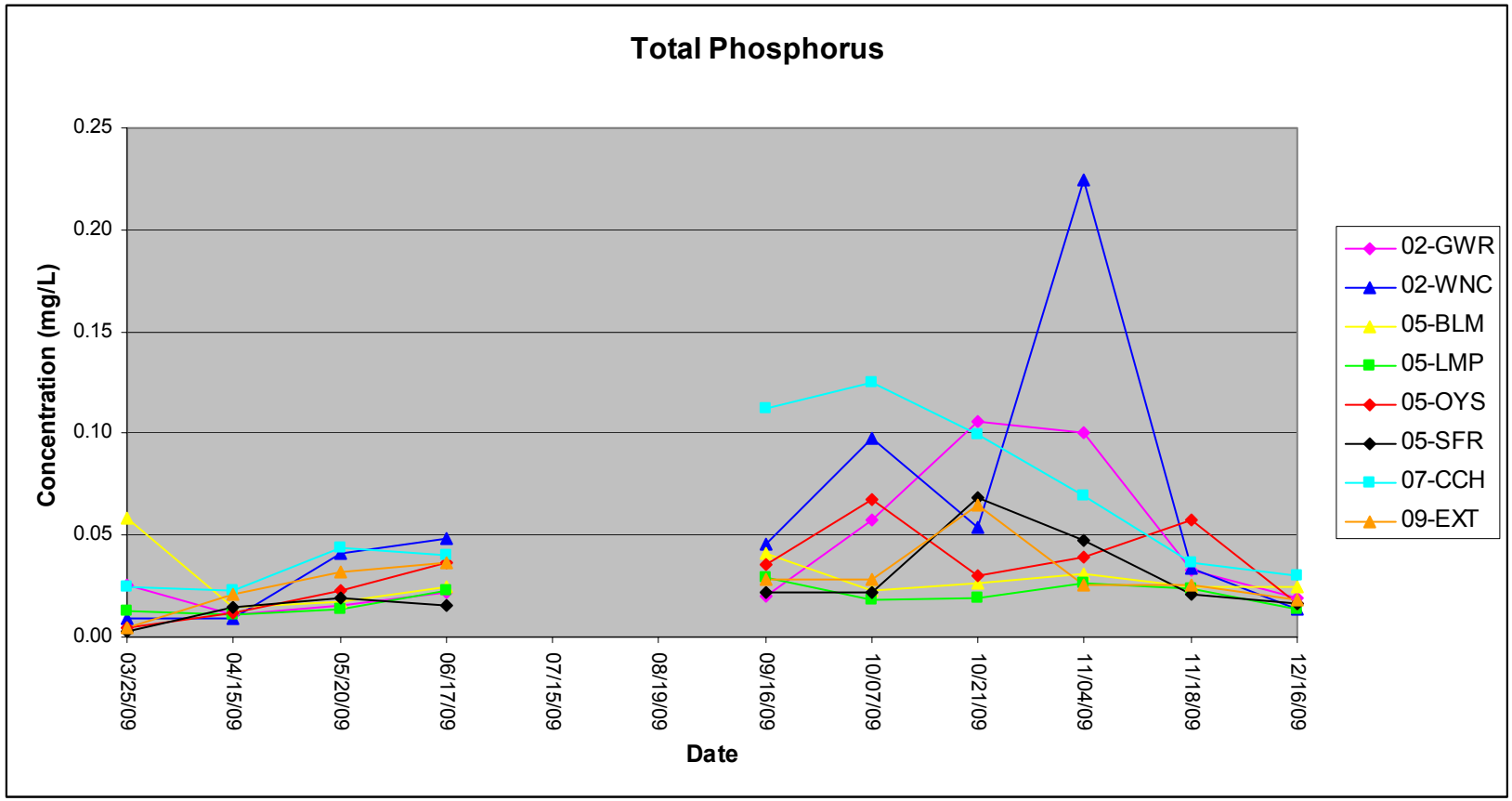

Figure 4: Total Dissolved Nitrogen Concentrations (in mg N/L) at Tributary Stations

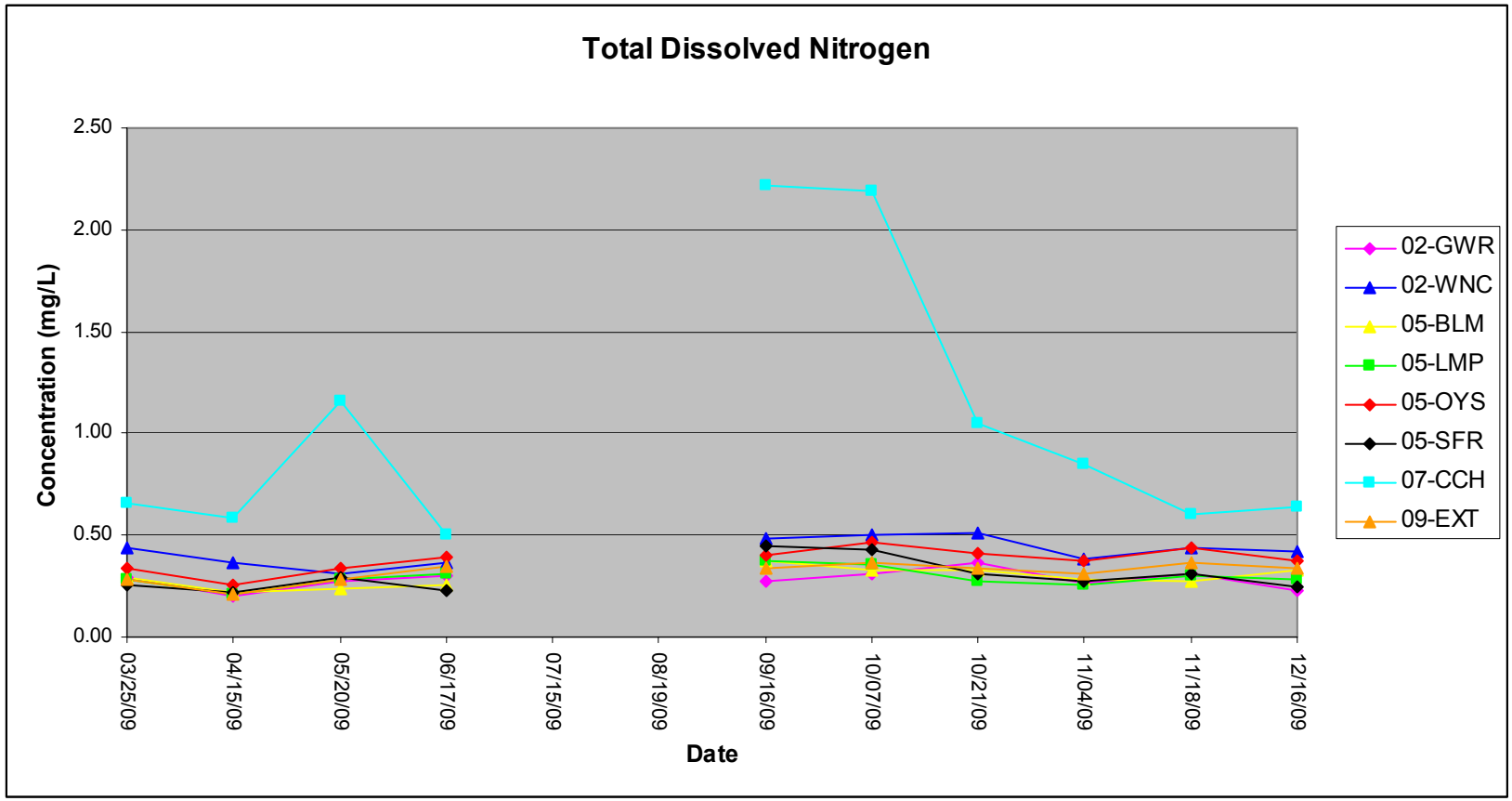

Figure 5: Suspended Solids Concentrations (in mg/L) at Tributary Stations

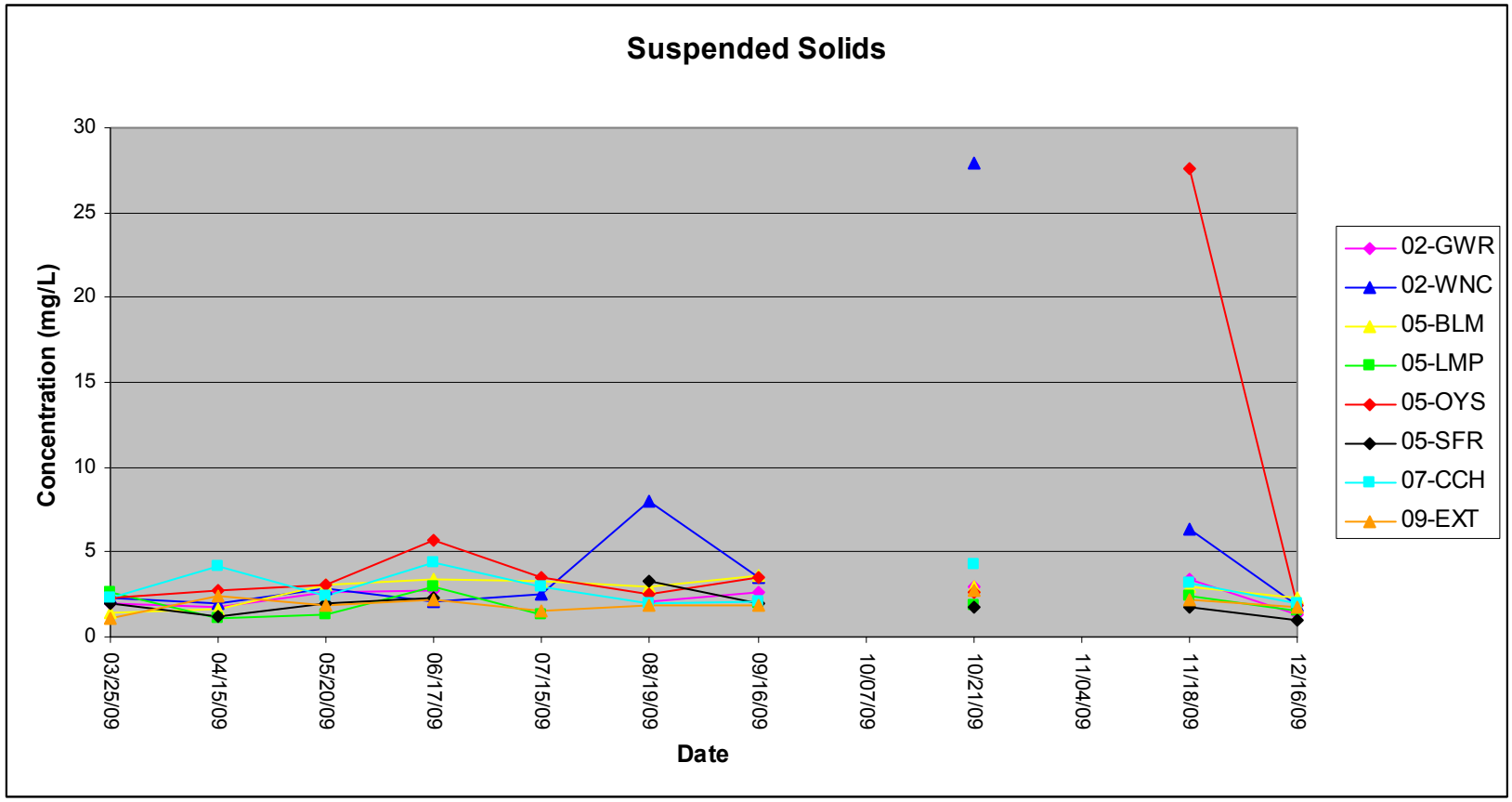

Figure 6: Nitrate Concentrations (in mg N/L) at Tributary Stations

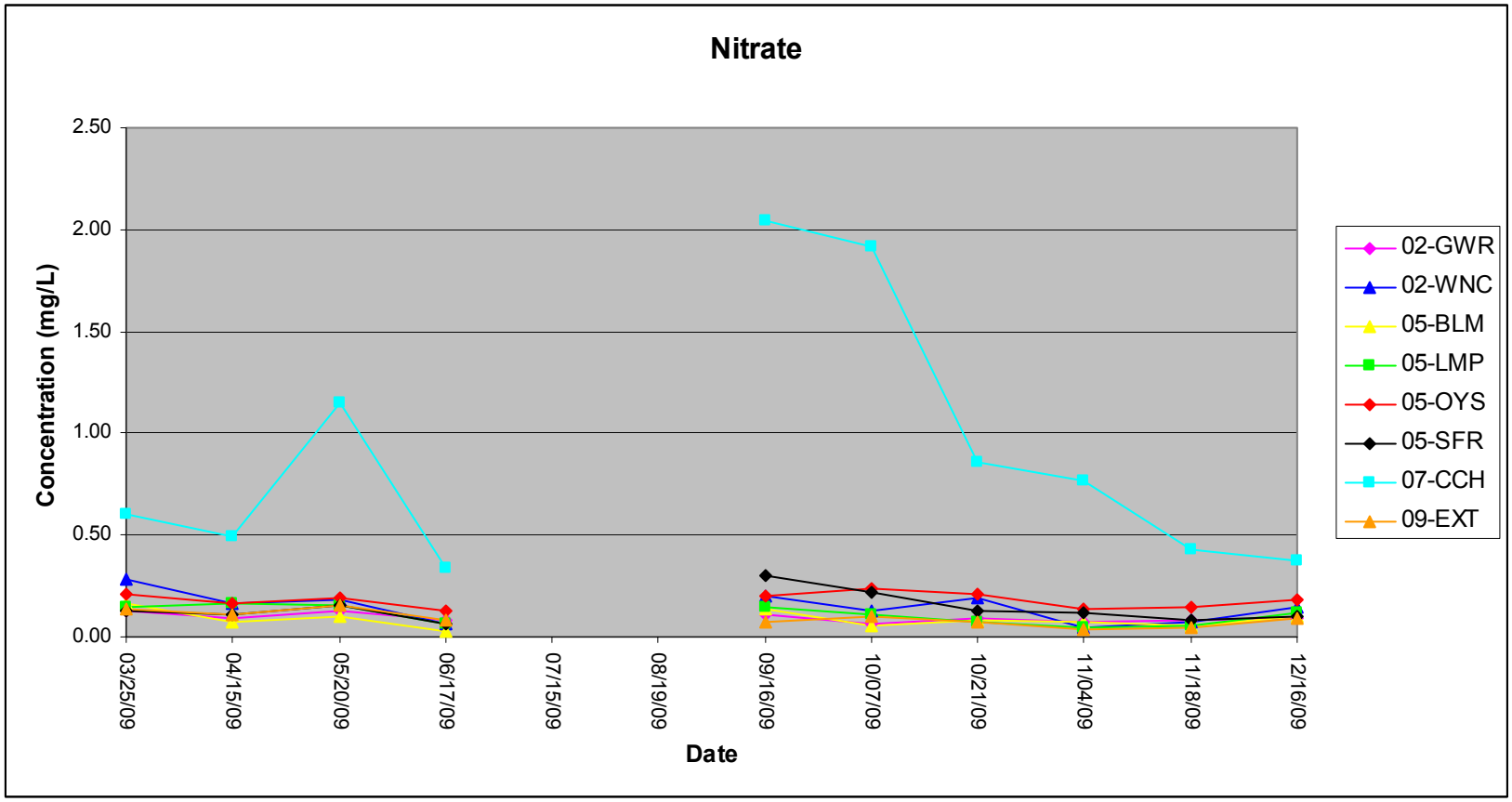

Figure 7: Ammonium Concentrations (in mg N/L) at Tributary Stations