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Nitrogen, Phosphorus, and Suspended Solids Concentrations in Tributaries to the Great Bay Estuary Watershed in 2008

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Introduction

Nitrogen, phosphorus, and sediment loads to the Great Bay Estuary are a growing concern. In the 2006 State of the Estuaries report (NHEP, 2006), the New Hampshire Estuaries Project (now called the Piscataqua Region Estuaries Partnership or PREP) calculated the nitrogen load from tributaries to the Great Bay Estuary using data collected by the NH Department of Environmental Services. PREP needs to update this indicator for the 2009 State of the Estuaries report. 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 2008. The study design followed the tributary sampling design which was implemented by the New Hampshire Department of Environmental Services between 2001 and 2007 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. The samples were analyzed for total dissolved nitrogen (TDN), total nitrogen (TN), total phosphorus (TP), and total suspended solids (TSS). 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.

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, and TSS have been summarized in Tables 1 through 4. 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 December samples based on the recommendation from UNH staff.
- TN data for the two samples where TN was greater than TDN (02-WNC on 4/23/08 and 05-LMP on 12/17/08).

A number of the field duplicate samples for TP had relative percent difference values greater than the data quality objectives. However, the laboratory quality control tests do not indicate a

problem with the TP method. Therefore, the high variability in the field duplicates is likely indicative of natural variability in the river. The data were retained.

Results and Discussion

The quality assured results for TN, TP, TDN, and TSS concentrations for each station visit are shown in Table 5. Figures 2 through 5 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 the 2009 State of the Estuaries Report. The State of the Estuaries Report will be prepared by PREP by October 2009. 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 0.49 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 0.49 and 0.70 mg N/L.
- Most of the water samples had TP concentrations less than 0.06 mg P/L. However, there were sharp spikes in TP concentrations above this level at stations 02-GWR and 07-CCH.
- Suspended solids concentrations at all the stations followed the same pattern with a peak concentration in June 2008. The average TSS concentration was highest in the Oyster River and lowest in the Lamprey River.

References

NHEP. 2006. State of the Estuaries. New Hampshire Estuaries Project, University of New Hampshire, Durham, NH. 30 p. Published Online http://www.nhep.unh.edu/resources/soe_report.htm, Accessed December 24, 2008.

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 Dupes / 2 Failed DQO One failure had a RPD of 32%, which is still acceptable. The other failure had a RPD of 49% but this sample will be rejected because TN<TDN.
Precision-Lab	RPD < 15%	Lab Duplicates	12 Lab Replicates and 10 Lab Duplicates performed. 0 Failed DQO
Accuracy/Bias	RPD < 15% >85% and <115% recovery	Certified Reference Material Samples Laboratory Fortified Matrix Samples	36 CRM tests / 3 Failed DQO 59 LFM tests / 10 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 2008 (0.11-2.96 mg/L) matched the range from 2001-2007 (0.18-2.99).
Sensitivity	Not expected to be an issue for this project (see discussion below)	NA	Lowest detected concentration was 0.11 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 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 / 1 Failed DQO The failure had a RPD of 36%, which is still acceptable.
Precision-Lab	RPD < 15%	Lab Duplicates	11 Lab Dupes / 0 Failed DQO
Accuracy/Bias	RPD < 15% >85% and <115% recovery	Certified Reference Material Samples Laboratory Fortified Matrix Samples	10 CRM tests / 0 Failed DQO 86 LFM tests / 8 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	TDN concentrations were not measured in previous years. Two samples were flagged as problematic because the TDN was greater than the TN concentration. The laboratory reported that the TN value was wrong for these samples.
Sensitivity	Not expected to be an issue for this project (see discussion below)	NA	Lowest detected concentration was 0.17 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	9 Field Dupes / 4 Failed DQO The failures had RPDs ranging from 37 to 68%.
Precision-Lab	RPD < 15%	Lab Duplicates	8 Lab Dupes / 2 Failed DQO 6 Lab Reps / 0 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	42 CRM tests / 2 Failed DQO 78 LFM tests / 10 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 (5-322 ug/L) matched the range from 2001-2007 (8-350).
Sensitivity	Not expected to be an issue for this project (see discussion below)	NA	Lowest detected concentration was 5 ug/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 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 / 2 Failed DQO The failures had RPDs ranging from 32 to 64%.
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 2008 (0.9-8.3 mg/L) matched the range from 2001-2007 (<5-57).
Sensitivity	Not expected to be an issue for this project (see discussion below)	NA	Lowest detected concentration was 0.9 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)

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: Validated Laboratory Results at Tributary Stations

STATIONID	DATE	TOTAL NITROGEN (mg N/L)	DISSOLVED NITROGEN (mg N/L)	TOTAL PHOSPHORUS (mg P/L)	SUSPENDED SOLIDS (mg/L)
02-GWR	03/26/08	0.374	0.327	0.009	2.310
	04/23/08	0.245	0.194	0.016	1.720
	05/21/08	0.340	0.205	0.016	2.400
	06/18/08	0.688	0.195	0.020	4.570
	07/23/08	0.435	0.299	0.040	1.900
	08/20/08	0.602	0.413	0.322	1.970
	09/17/08	0.842	0.341	0.027	2.160
	10/22/08	0.654	0.358	0.060	2.940
	11/19/08	0.555	0.355	0.026	2.020
	12/17/08	0.273	0.290	0.010	1.650
02-WNC	03/26/08	0.428	0.385	0.006	1.370
	04/23/08		0.412	0.020	2.100
	05/21/08	0.579	0.408	0.026	2.380
	06/18/08	0.664	0.455	0.047	5.000
	07/23/08	0.796	0.454	0.043	2.140
	08/20/08	0.878	0.623	0.051	2.510
	09/17/08	0.781	0.657	0.040	2.580
	10/22/08	0.921	0.521	0.041	2.220
	11/19/08	0.683	0.555	0.023	1.510
	12/17/08	0.526	0.427	0.011	1.490
05-BLM	03/26/08	0.334	0.281	0.009	1.650
	04/23/08	0.231	0.168	0.014	1.890
	05/21/08	0.445	0.248	0.021	2.540
	06/18/08	0.410	0.285	0.022	4.110
	07/23/08	0.413	0.257	0.023	2.340
	08/20/08	0.699	0.313	0.045	2.690
	09/17/08	0.768	0.374	0.042	2.270
	10/22/08	0.632	0.329	0.013	2.530
	11/19/08	0.600	0.398	0.021	1.560
	12/17/08	0.401	0.344	<0.005	1.580

STATIONID	DATE	TOTAL NITROGEN (mg N/L)	DISSOLVED NITROGEN (mg N/L)	TOTAL PHOSPHORUS (mg P/L)	SUSPENDED SOLIDS (mg/L)
05-LMP	03/26/08	0.381	0.285	<0.005	1.920
	04/23/08	0.334	0.229	0.021	1.200
	05/21/08	0.385	0.265	0.020	1.530
	06/18/08	0.480	0.359	0.015	4.700
	07/23/08	0.597	0.403	0.027	2.160
	08/20/08	0.504	0.421	0.020	1.350
	09/17/08	0.540	0.389	0.033	1.490
	10/22/08	0.586	0.336	0.009	0.910
	11/19/08	0.573	0.420	0.015	1.160
	12/17/08		0.330	<0.005	1.320
05-OYS	03/26/08	0.379	0.345	0.011	2.460
	04/23/08	0.366	0.249	0.023	2.900
	05/21/08	0.336	0.265	0.016	2.470
	06/18/08	0.666	0.358	0.084	8.030
	07/23/08	0.957	0.601	0.068	5.000
	08/20/08	0.580	0.439	0.025	4.570
	09/17/08	0.707	0.431	0.035	3.900
	10/22/08	0.742	0.444	0.027	3.280
	11/19/08	0.630	0.482	0.034	3.010
	12/17/08	0.422	0.413	0.014	4.670
05-SFR	03/26/08	0.313	0.280	0.007	1.380
	04/23/08	0.320	0.208	0.019	2.290
	05/21/08	0.502	0.369	0.018	3.200
	06/18/08	0.601	0.428	0.031	5.050
	07/23/08	0.926	0.569	0.040	2.800
	08/20/08	0.656	0.314	<0.005	3.690
	09/17/08	0.855	0.353	0.014	1.940
	10/22/08	0.582	0.341	0.018	1.790
	11/19/08	0.578	0.314	0.012	2.930
	12/17/08	0.895	0.259	0.013	1.990

STATIONID	DATE	TOTAL NITROGEN (mg N/L)	DISSOLVED NITROGEN (mg N/L)	TOTAL PHOSPHORUS (mg P/L)	SUSPENDED SOLIDS (mg/L)
07-CCH	03/26/08	0.555	0.556	0.016	2.070
	04/23/08	0.597	0.498	0.027	2.600
	05/21/08	1.109	0.933	0.038	1.800
	06/18/08	1.119	1.158	0.071	4.960
	07/23/08	2.726	2.516	0.167	4.410
	08/20/08	1.172	0.610	0.039	2.440
	09/17/08	0.953	0.755	0.045	2.340
	10/22/08	1.162	0.666	0.041	1.890
	11/19/08	0.874	0.704	0.044	2.030
	12/17/08	0.631	0.611	0.017	2.070
09-EXT	03/26/08	0.319	0.287	<0.005	1.550
	04/23/08	0.354	0.272		2.000
	05/21/08	0.449	0.171	0.017	1.850
	06/18/08	0.758	0.408	0.034	4.900
	07/23/08	0.555	0.431	0.036	2.870
	08/20/08	0.652	0.474	0.056	2.090
	09/17/08	1.831	0.415	0.036	2.080
	10/22/08	0.624	0.408	0.019	1.620
	11/19/08	0.555	0.409	0.022	1.690
	12/17/08	0.429	0.325	0.018	1.670

*Note: Field duplicate samples not included

Figure 1: Sampling locations in the Great Bay Estuary Watershed

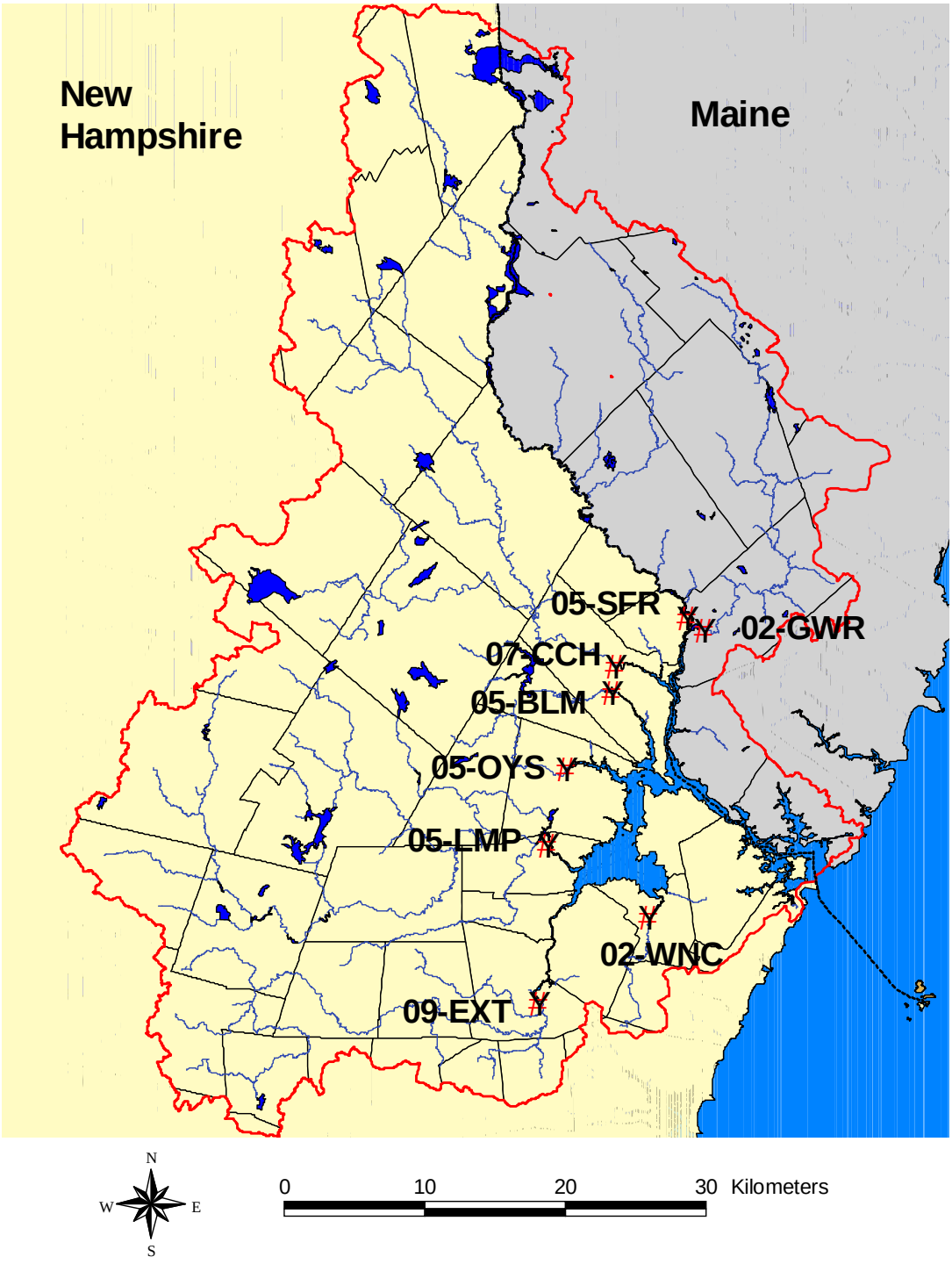

Figure 2: Total Nitrogen Concentrations at Tributary Stations

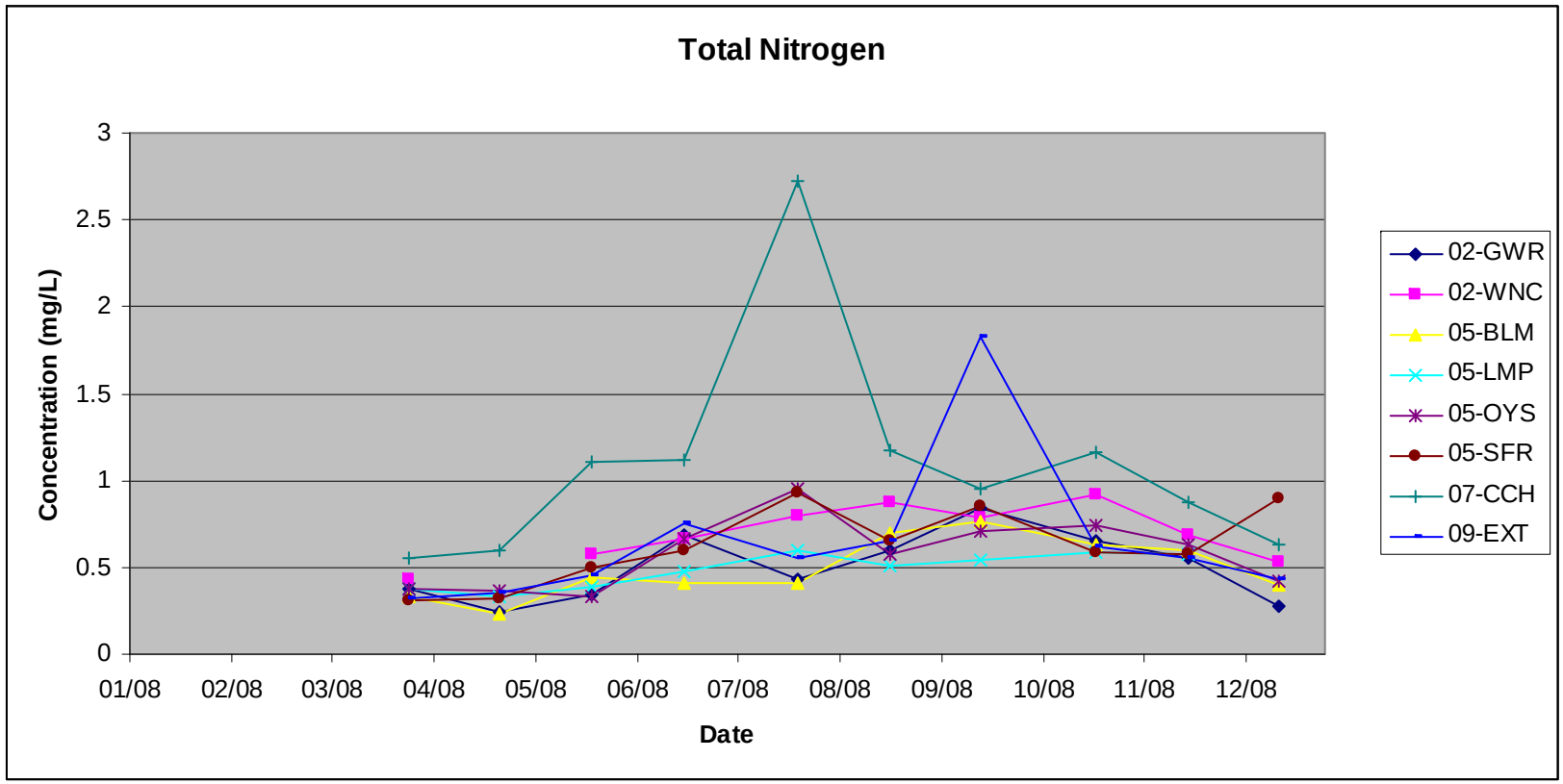

Figure 3: Total Phosphorus Concentrations at Tributary Stations

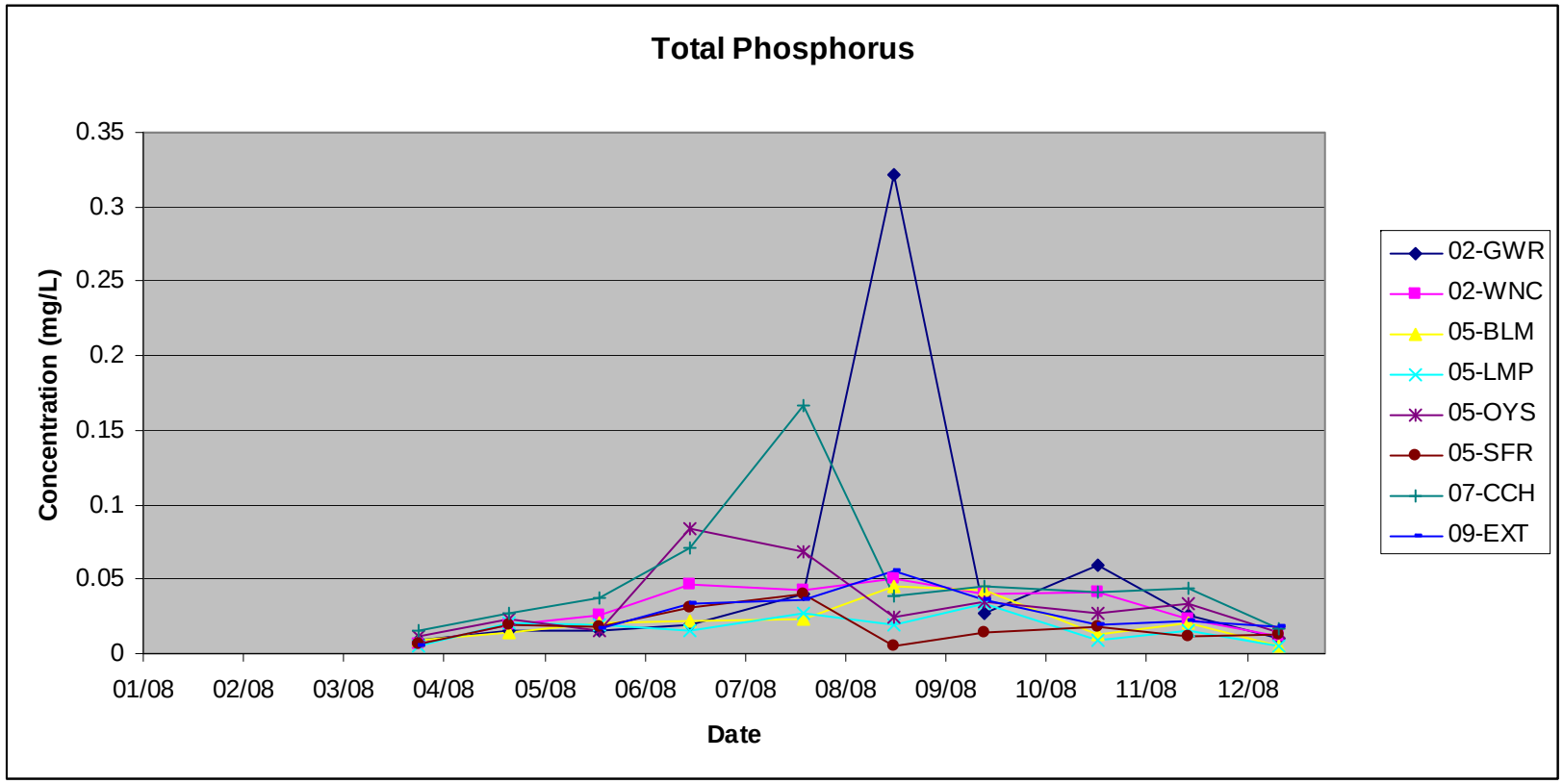

Figure 4: Total Dissolved Nitrogen Concentrations at Tributary Stations

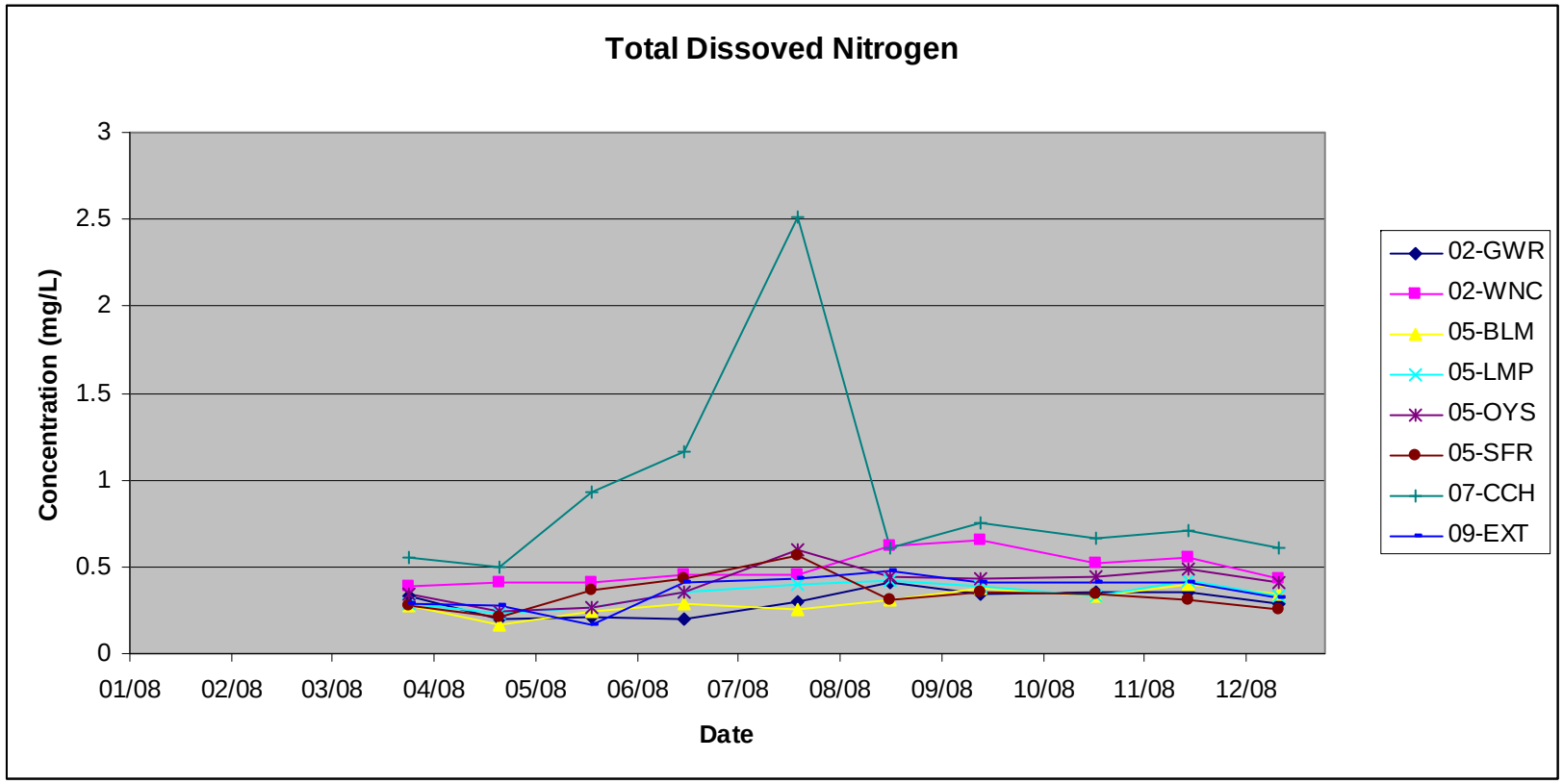

Figure 5: Suspended Solids Concentrations at Tributary Stations