Major urban areas in the basin, many of which are located along river valleys, include: Binghamton, N.Y. in the Upper Susquehanna Subbasin; Corning and Elmira, N.Y., in the Chemung Subbasin; Scranton and Wilkes-Barre, Pa., in the Middle Susquehanna Subbasin; Clearfield, Lock Haven, and Williamsport, Pa., in the West Branch Subbasin; Altoona and Lewisburg, Pa., in the Juniata Subbasin; and Harrisburg, Lancaster, Sunbury, and York, Pa., in the Lower Susquehanna Subbasin.

SAMPLE COLLECTION

2011 sampling efforts at the six long-term (Group A) sites included sampling during monthly base flow conditions, monthly flow-independent conditions, and seasonal storm conditions. This resulted in two samples collected per month: one with a set date near the twelfth of each month independent of flow and one based on targeting monthly base flow conditions. The mid-monthly samples were intended to be flow independent with the intention that the data would help to quantify long-term trends. Additionally, due to the linkage of high flow and nutrient and sediment loads, it was necessary to target storm events for additional sampling to adequately quantify loads. Long-term site sampling goals included targeting one storm per season with a second storm collected during the spring season. Spring storms were planned to collect samples before and after agricultural crops had been planted.

All storm samples were collected during the rising and falling limbs of the hydrograph with goals of three samples on each side and one sample as close to the peak as possible. The enhanced sites (Group B) targeted a mid-monthly flow independent sample and two storm samples per season. Storm samples were planned to have one sample on the rising limb and one on the falling limb of the hydrograph with the goal that one of the two be as close to the peak as possible. Due to the quick nature of the hydrograph on several of the smaller streams, sometimes the two storm samples per season were taken from two different storms with the goal of having samples as close to the peak of each storm as possible.

The goal of actual sample collection was to collect a sample representative of the entire water column. Due to variations in stream width and depth and subsequent lack of natural mixture of the stream, it was necessary to composite several individual samples across the water column into one representative sample. The number of individual verticals at each site varied from three to ten dependent upon the stream width. Based on USGS depth integrated sampling methodology at each vertical location, the sampler was lowered at a consistent rate from the top of the water surface to the stream bottom and back to insure water from the entire vertical column was represented (Myers, 2006). Instream water quality readings were taken at each vertical to insure accurate dissolved oxygen and temperature values.

All samples were processed onsite and included whole water samples analyzed for nitrogen and phosphorus species, TOC, TSS, and SS. For Group B sites, SS samples were only collected during storm events. Additionally, filtered samples were processed onsite to analyze for dissolved nitrogen (DN) and DP species. Several sites included additional parameters pertinent to the natural gas industry.

SAMPLE ANALYSIS

Samples were either hand-delivered or shipped directly to the appropriate laboratory for analysis on the day following collection. When storm events occurred over the weekend, samples collected were analyzed on the following Monday. Samples collected in Pennsylvania and at the Octoraro Creek site near Richardsmere, Md., were delivered to PADEP's Bureau of Laboratories in Harrisburg, Pa. Samples collected at New York sites were shipped to Columbia Analytical Services in Rochester, N.Y. Parameters for all samples at all sites included various nitrogen and phosphorus species, TOC, and TSS. Specific parameters, methodology, and detection limits are listed in Table 2.

Due to the high influence of stormflow on sediment concentrations, SS samples were collected during storm events at all sites with the goal of two samples for each event and one event per quarter. Of the two samples per storm, the more sediment laden sample was analyzed for both sediment concentration and sand/fine particle percentage. The additional sample was submitted for sediment concentration only. Sediment samples were shipped to the USGS sediment laboratory in Louisville, Ky., for analysis. Additional SS samples also were collected at all Group A sites as part of each sampling round. These samples were analyzed at the SRBC laboratory for sediment concentration alone.

Table 2. Water Quality Parameters, Laboratory Methods, and Detection Limits

Parameter	Storet	Laboratory	Methodology	Detection Limit (mg/l)	References
Total Ammonia (TNH_3)	610	PADEP	Colorimetry	0.020	USEPA 350.1
		CAS*	Colorimetry	0.010	USEPA 350.1R
Dissolved Ammonia (DNH_3)	608	PADEP	Block Digest, Colorimetry	0.020	USEPA 350.1
		CAS*	Block Digest, Colorimetry	0.010	USEPA 350.1R
Total Nitrogen (TN)	600	PADEP	Persulfate Digestion for TN	0.040	Standard Methods #4500-N_{org}-D
Dissolved Nitrogen (DN)	602	PADEP	Persulfate Digestion	0.040	Standard Methods #4500-N_{org}-D
Total Organic Nitrogen (TON)	605	N/A	TN minus TNH_3 and TNOx	N/A	N/A
Dissolved Organic Nitrogen (DON)	607	N/A	DN minus DNH_3 and DNOx	N/A	N/A
Total Kjeldahl Nitrogen (TKN)	625	CAS*	Block Digest, Flow Injection	0.050	USEPA 351.2
Dissolved Kjeldahl Nitrogen (DKN)	623	CAS*	Block Digest, Flow Injection	0.050	USEPA 351.2
Total Nitrite plus Nitrate (TNOx)	630	PADEP	Cd-reduction, Colorimetry	0.010	USEPA 353.2
		CAS*	Colorimetric by LACHAT	0.002	USEPA 353.2
Dissolved Nitrite plus Nitrate (DNOx)	631	PADEP	Cd-reduction, Colorimetry	0.010	USEPA 353.2
		CAS*	Colorimetric by LACHAT	0.002	USEPA 353.2
Dissolved Orthophosphate (DOP)	671	PADEP	Colorimetry	0.010	USEPA 365.1
		CAS*	Colorimetric Determination	0.002	USEPA 365.1
Dissolved Phosphorus (DP)	666	PADEP	Block Digest, Colorimetry	0.010	USEPA 365.1
		CAS*	Colorimetric Determination	0.002	USEPA 365.1
Total Phosphorus (TP)	665	PADEP	Persulfate Digest, Colorimetry	0.010	USEPA 365.1
		CAS*	Colorimetric Determination	0.002	USEPA 365.1
Total Organic Carbon (TOC)	680	PADEP	Combustion/Oxidation	0.50	SM 5310D
		CAS*	Chemical Oxidation	0.05	GEN 415.1/9060
Total Suspended Solids (TSS)	530	PADEP	Gravimetric	5.0	USGS I-3765
		CAS*	Residue, non-filterable	1.1	SM2540D
Suspended Sediment Fines	70331	USGS	**		
Suspended Sediment (SS)	80154	SRBC	**		
		USGS	**		

* Columbia Analytical Services, Rochester, N.Y. (New York sites only)
** TWRI Book 3, Chapter C2 and Book 5, Chapter C1, Laboratory Theory and Methods for Sediment Analysis (Guy and others, 1969)

PRECIPITATION AND DISCHARGE

Precipitation data were obtained from long-term monitoring stations operated by the U.S. Department of Commerce. The data are published as Climatological Data–Pennsylvania, and as Climatological Data–New York by the National Oceanic and Atmospheric Administration at the National Climatic Data Center in Asheville, N.C. Monthly data from these online sources were compiled across the subbasins of the Susquehanna River Basin. Discharge values were obtained from the USGS gaging network system. All sites were collocated with USGS gages so that discharge amounts could be matched with each sample. Average daily discharge values for each site were used as input to the estimator model used to estimate nutrient and sediment loads and trends. Average monthly flow values were used to check for trends in discharge.

DATA ANALYSIS

Sample results were compiled into an existing database including all years of the program. These data were then listed on SRBC's web site as well as submitted to various partners for use with models and individual analyses. Specific analyses at SRBC include load and yield estimation, LTM comparisons, baseline comparisons, and trend estimation.

Loads and Yields

Loads and yields represent two methods for describing nutrient and SS amounts within a basin. Loads refer to the actual amount of the constituent being transported in the water column past a given point over a specific duration of time and are expressed in pounds. Yields compare the transported load with the acreage of the watershed and are expressed in lbs/acre. This allows for easy watershed comparisons. This project reports loads and yields for the constituents listed in Table 2 as computed by the Minimum Variance Unbiased Estimator (ESTIMATOR) described by Cohn and others (1989). This estimator relates the constituent concentration to water discharge, seasonal effects, and long-term trends, and computes the best-fit regression equation. Daily loads of the constituents were then calculated from the daily mean water discharge records. The loads were reported along with the estimates of accuracy. Average concentrations were calculated by taking the total load and dividing by the total amount of flow during the time period and were reported in mg/L.

Load and trend analyses were not completed at Group B sites. Summary statistics have been calculated for these sites, as well as the long-term sites for comparison. Summary statistics are listed in Appendix B and include minimum, maximum, median, mean, and standard deviation values taken from the 2011 dataset.

Long-term Mean Ratios

Due to the relationship between stream discharge and nutrient and SS loading, it can be difficult to determine whether the changes observed were related to land use, nutrient availability, or simply fluctuations in water discharge. Although the relationship is not always linear at higher flows than lower flows, in general, increases in flows coincide with increases in constituent loads (Ott and others, 1991; Takita, 1996, 1998). In an attempt to determine annual changes from previous years, 2011 nutrient and SS loads, yields and concentrations were compared to LTMs. LTM load and discharge ratios were calculated for a variety of time frames, including annual, seasonal, and monthly, by dividing the 2011 value by the LTM for the same time frame and reported as a percentage or ratio. It was thought that identifying sites where the percentage of LTM for a constituent, termed the load ratio, was different than the corresponding percentage of LTM for discharge, termed the water-discharge ratio or discharge ratio, would suggest areas where improvements or degradations may have occurred for that particular constituent. At odds with this conclusion is that individual high flow events tend to produce higher loads, especially for TP and SS, than would be predicted by a simple comparison with the LTM. Thus, the presence or absence of significant storm events during a time period tends to be the major contributing factor towards the resultant loads.

Baseline Comparisons

As a means to determine whether the annual fluctuations of nutrient and SS loads were due to water discharge, Ott and others (1991) used the relationship between annual loads and annual water discharge. This was accomplished by plotting the annual yields against the water-discharge ratio for a given year to calculate a baseline regression line. Data from the initial five-year study (1985-89) were used to provide a best-fit linear regression trend line to be used as the baseline relationship between annual yields and water discharge. It was hypothesized that as future yields and water-discharge ratios were plotted against the baseline, any significant deviation from the baseline would indicate that some change in the annual yield had occurred, and that further evaluations to determine the reason for the change were warranted.

Due to the size of the current dataset, the opportunity exists for there to be non-linear changes in the yield versus water discharge plot as more years are added. Therefore, this report included comparisons to baselines created from different time frames including the initial five-year period of the dataset for each station, the first half of the entire dataset, the second half of the entire dataset, and the entire dataset. Although the tendency was for increasing loads to be associated with increasing flows, this relationship was not strictly linear, especially when dealing with TP and SS.

All comparisons include an associated R^2 value representing the strength of the correlation between the two parameters in the regression. The closer the R^2 is to a value of one, the better the regression line is for accurately using one variable (flow) to predict the other with an R^2 of one meaning that there is perfect correlation between the two variables. For example, R^2 values for TN tend to be close to one as the relationship between TN and flow is very consistent through various ranges of flows. R^2 values for TP and SS tend to vary more, especially towards higher flows. Thus, when regression graphs include high flow events, the resulting correlation tends to be less perfect indicated by a low R^2 value. This is an indication that single high flow events, and not necessarily a high flow year, are the highest contributors to loads in TP and SS and that these contributions do not necessarily follow a strictly linear increase. As has been evident in the last few years, the high loads that have occurred at Towanda and Danville can be linked directly to high flow events, specifically Hurricane Ivan in 2004, Tropical Storm Ernesto in 2006, and by the combination of a synoptic type storm event and Tropical Storm Nicole in 2010 (Maddox et al., 1979). Several significant high flow events occurred in 2011 including a very wet spring and high summer flows resulting from Hurricane Irene and Tropical Storm Lee. Seasonal baselines also were calculated for the initial five years of data at each site.

Figure 2 shows the baseline regression line developed for TN at Marietta using the first half of the dataset where each hollow circle represents an individual year during the first half of the dataset. Each hollow circle was plotted using an individual year's yield and the same year's discharge ratio. The discharge ratio was calculated by dividing the year's annual flow by the 12-year average flow for the baseline years used. A regression line was drawn through these data points and the equation of the trend line was used to calculate a baseline prediction for the 2011 yield given the 2011 discharge ratio. The baseline prediction for 2011 TN yield is shown as a black diamond on the graph at 15.44 lbs/ac. The actual 2011 yield at the same discharge ratio, 11.72 lbs/ac, is shown as the black circle. Since the actual 2011 yield was lower than the prediction made by the first 12 years of data, the comparison implies that improvements may have occurred.

Figure 3 shows the baseline regression lines that were developed using the initial five years at Marietta, the first 12 years at Marietta, and the most recent 12 years at Marietta. Using multiple regression lines developed from different time periods within that dataset also can show whether changes occurred. The larger vertical oval in the graph shows the relevant comparisons to be made; at a discharge ratio of 2.20, the initial five-year baseline predicts the 2011 yield to be 20.73 lbs/ac, while the actual 2011 yield was 11.72 lbs/ac (shown in the bottom of the oval). This suggests a more dramatic reduction than the comparison to the regression from the most recent 12 years, which predicted the 2011 TN yield to be 13.94 lbs/ac shown within the smaller oval. Additional support for improvements can be seen when comparing the entire baseline regression lines to each other. As more recent years were added to the baseline, the entire regression line lowered. This implied that the more recent 12-year dataset included lower yield values as compared to the initial 12-year dataset. Thus, a regression line that predicts lower yields for the same water discharge ratio directly implies improved water quality between the two timeframes.

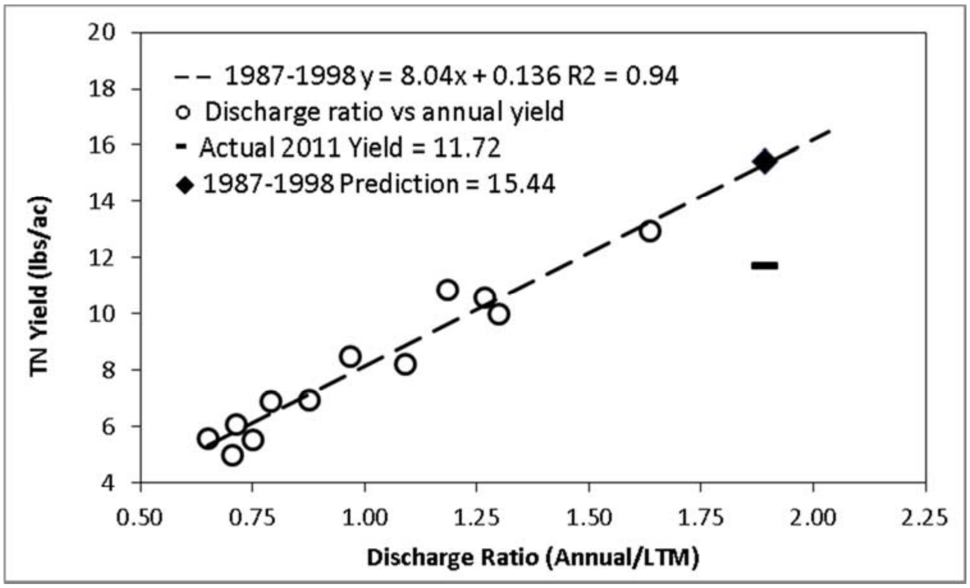

Figure 2. First Half Baseline Regression Line, 2011 TN Yield Prediction, and Actual 2011 Yield for TN at Marietta

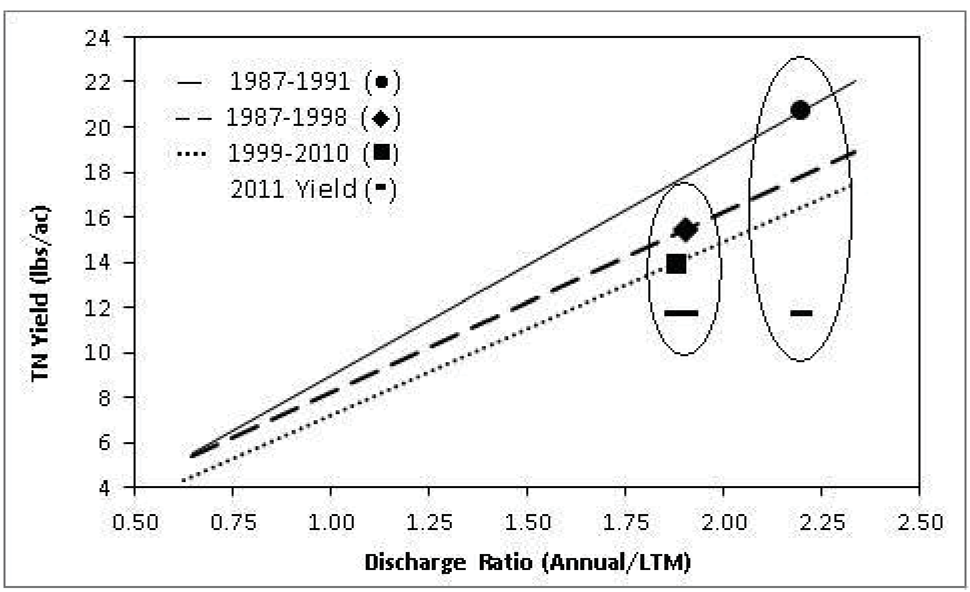

Figure 3. Initial, First Half, and Second Half Baseline Regression Lines, Yield Predictions, and Actual 2011 Yields for TN at Marietta