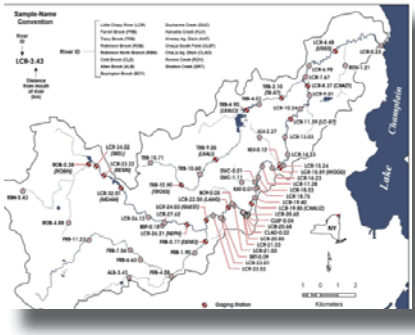
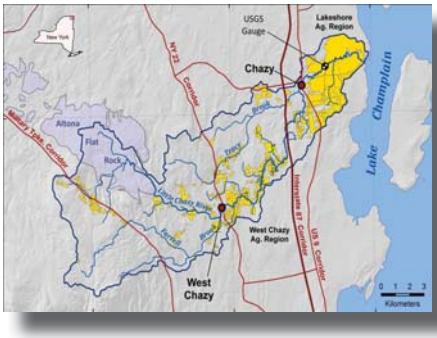
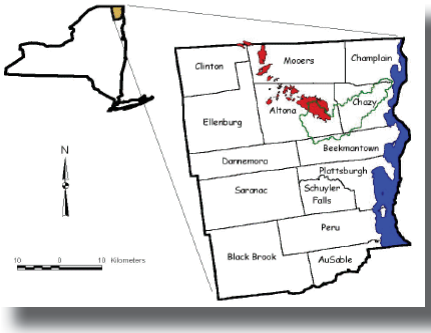
TECHNICAL REPORT NO. 68

Little Chazy River Nutrient Runoff Study







August 2012

Final Report

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NEIWPCC Job Code: 989-003-012
Project Code: LS-2010-045

Lake Champlain Basin Program

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Executive Summary:

We report the results of hydrologic conditions and nutrient (nitrate-N, total phosphorus and soluble reactive phosphorus) in the Little Chazy River for the period June 2011 to July 2012. These data are part of an ongoing project that began in January 2008 to assess source areas, transport and fate of nutrients in the watershed. The results confirm and refine the results of earlier investigations. Our objective is to continue water-quality sampling through December 2012 to obtain a continuous five-year record of monthly nutrient concentrations.

Project Introduction:

Lake Champlain is an oligotrophic to mesotrophic water body with low to moderate levels of phosphorus and nitrogen, the primary nutrients that control primary productivity and principal determinants for associated water quality issues. Major sources of nutrients in Lake Champlain include point sources such as municipal sewage treatment plants and non-point sources including urban runoff and agricultural inputs. Extensive dairy operations in the Lake Champlain basin produce large quantities of manure, which is applied back to soils and can potentially become a major source of nutrients to nearby surface waters. Consequently, reduction of nutrient inputs to Lake Champlain, which promotes healthy and diverse aquatic ecosystems and provides for sustainable human use and enjoyment of the lake, is listed as a priority in the Phosphorus Task Area of the LCBP Opportunities for Action.

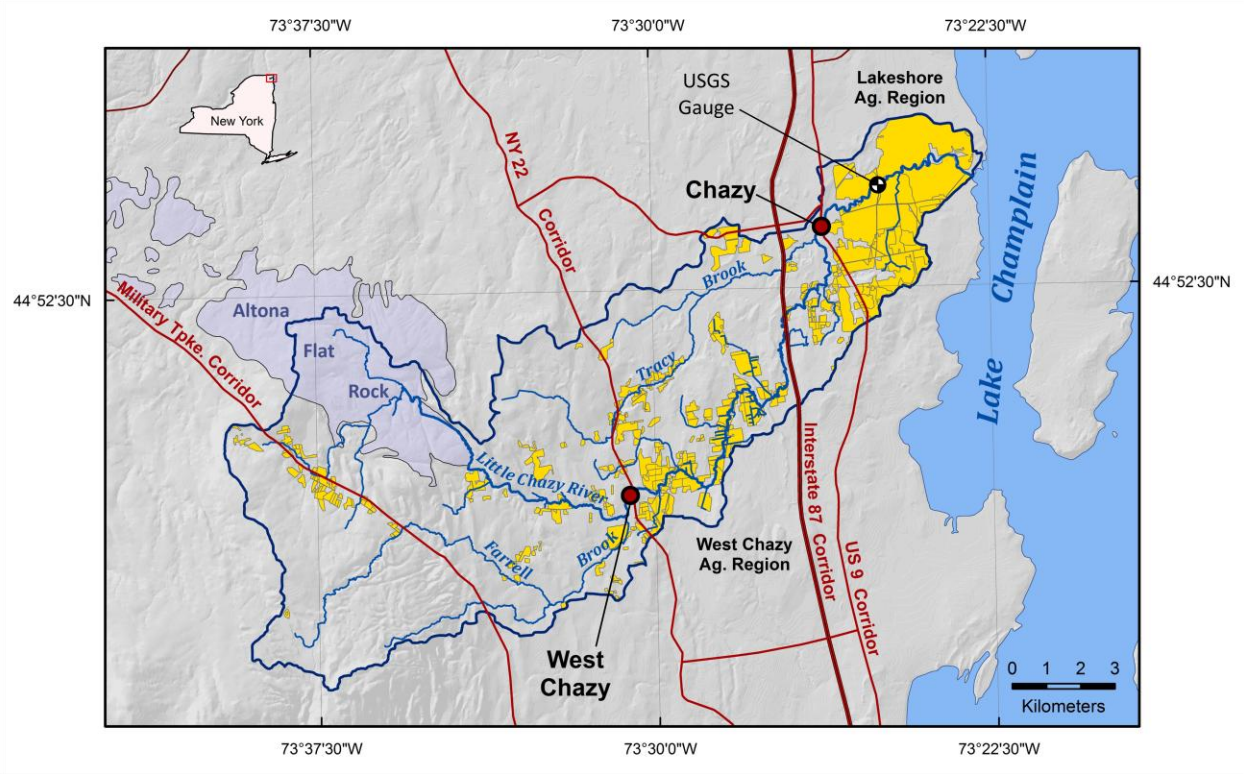

Figure 1. Map of northeastern New York, showing the distributions of agricultural land (yellow shading) and sandstone pavements or "Flat Rocks" (purple shading) in the Little Chazy River watershed. The Flat Rocks extent is from maps by Denny (1974). The figure is from Oetjen et al. (2012).

SUNY Plattsburgh and the William H. Miner Agricultural Institute (Miner Institute) have used a high-resolution synoptic water-sampling strategy to examine the spatial and downstream distribution of nutrient concentrations (i.e. nitrate-N, total phosphorus and soluble reactive phosphorus) in the Little Chazy River and its principal tributaries since January 2008 (Fig. 1). The Little Chazy River watershed is typical of medium-sized (basin area = 145 km^2), rural watersheds in the region, possessing a broad range of watershed issues and concerns reflected throughout the Champlain lowland. Agriculture accounts for approximately 17% of land cover in the watershed, compared to approximately 24% of land cover county-wide, most of which is concentrated near the lake shore east of Chazy village. The watershed was identified on the 1996 Lake Champlain Basin Waterbody Inventory/Priority Waterbodies List Report as a class C river with possible impaired fish survival (NYSDEC, 2001). Karim (1997) cited on-site septic problems, particularly in Chazy and West Chazy, and high levels of livestock and crop agriculture as water pollution concerns in the watershed. The Little Chazy River has the highest median nutrient concentrations and median unit nutrient load (nutrient load per unit area of watershed) of any New York tributary to Lake Champlain that is monitored as part of the Lake Champlain Long-term Water Quality and Biological Monitoring Program (Vermont DEC and New York DEC, 2009).

The scope of this study was limited to the maintenance of the hydrologic and monthly synoptic water quality databases for a one-year period, beginning on 01 June 2011 and ending on 31 July 2012. The original databases were created for a preliminary assessment of nonpoint source nutrient runoff in the Little Chazy River watershed that was funded by the NYSDEC and The Nature Conservancy (Franzi et al., 2009). Additional NYSDEC funds were made available to maintain minimal water-quality monitoring through December, 2010 and sampling continued to the start of this study. Our objective is to continue our monthly synoptic water sampling through December 2012 to achieve an uninterrupted five-year record of monthly nutrient concentrations and loadings.

Analytical Methods:

Stream Hydrology: SUNY Plattsburgh and Miner Institute monitored river height (stage), water temperature and logger temperature at 13 stream gaging stations (Fig. 1); four stations on Tracy Brook (TROSS, LKALI, LKALO and TB87), one station at the mouth of Farrell Brook (DENO) and eight stations on the main channel of the Little Chazy River below Miner Dam (MDAM, NEPH, GUEST, LANG, CHALIZ, WOOD, LC87 and CHAZY). All SUNY/Miner stations are equipped with Tru-Trac WT-HR water height (stage) dataloggers. Rating curves for each station were calibrated using the midsection method for determining discharge (Rantz et al., 1982a, 1982b). The stations operated during ice-free periods only and record lengths vary depending upon site conditions and datalogger maintenance needs.

Stream discharge records for the U.S. Geological Survey (USGS) gauging station near the river mouth east of Chazy (USGS) were obtained from the USGS website;

< http://waterdata.usgs.gov/ny/nwis/rt >

The USGS stream gage operates through the winter season and records are available from Water Year 1990 to present. Data since 1 October 2011 have not been approved but are available as provisional data. Stream discharge from 25 December 2011 to 6 March 2012 was affected by channel ice and records are not yet available. The USGS also provided stream gaging data, which were used to assess the accuracy of stream-gaging results by SUNY hydrological technicians.

Water Quality Sampling: Synoptic sampling involves the collection of closely spaced water samples in a short time period (generally less than four hours) to provide a snapshot of nutrient (nitrate-N, total phosphorus and soluble reactive phosphorus) concentrations and loadings throughout the watershed (Fig. 2). Sample spacing along the mainstream, tributaries and other inflows varies with accessibility and land use. Channel distance between samples varies from more than 5 km in forested upland regions to a few hundred meters in villages or agricultural lands where anthropogenic inputs such as ditches and drains are more common.

A high-resolution temporal sampling strategy was used to evaluate the temporal distribution of nutrient concentrations at the USGS gauging station during the Tropical Storm Irene event (Aug–Sep 2011). Sampling interval varied from 3-4 hours during the initial phases of the rainfall events to >24 hours during periods of prolonged baseflow.

Water Quality Analysis: Water samples were collected in acid-washed, 500 ml polyethylene bottles within a period of approximately four hours to minimize temporal variations in nutrient concentrations. At the end of the collection period, samples were transported to the lab in coolers within a period of one hour and immediately split into two fractions; one which was filtered through a 0.47 um membrane filter to remove particulates and the other left unfiltered. Filtered subsamples were analyzed for nitrate using a Dionex Ion Chromatograph with conductimetric detection and colorimetrically for soluble-reactive phosphorus (primarily phosphate) using a UV-Vis spectrophotometer with the ascorbic acid method (APHA, 1998). For total phosphorus, unfiltered water samples were digested using potassium persulfate in sulfuric acid on a block digester (APHA, 1998), followed by analysis for soluble-reactive phosphorus.

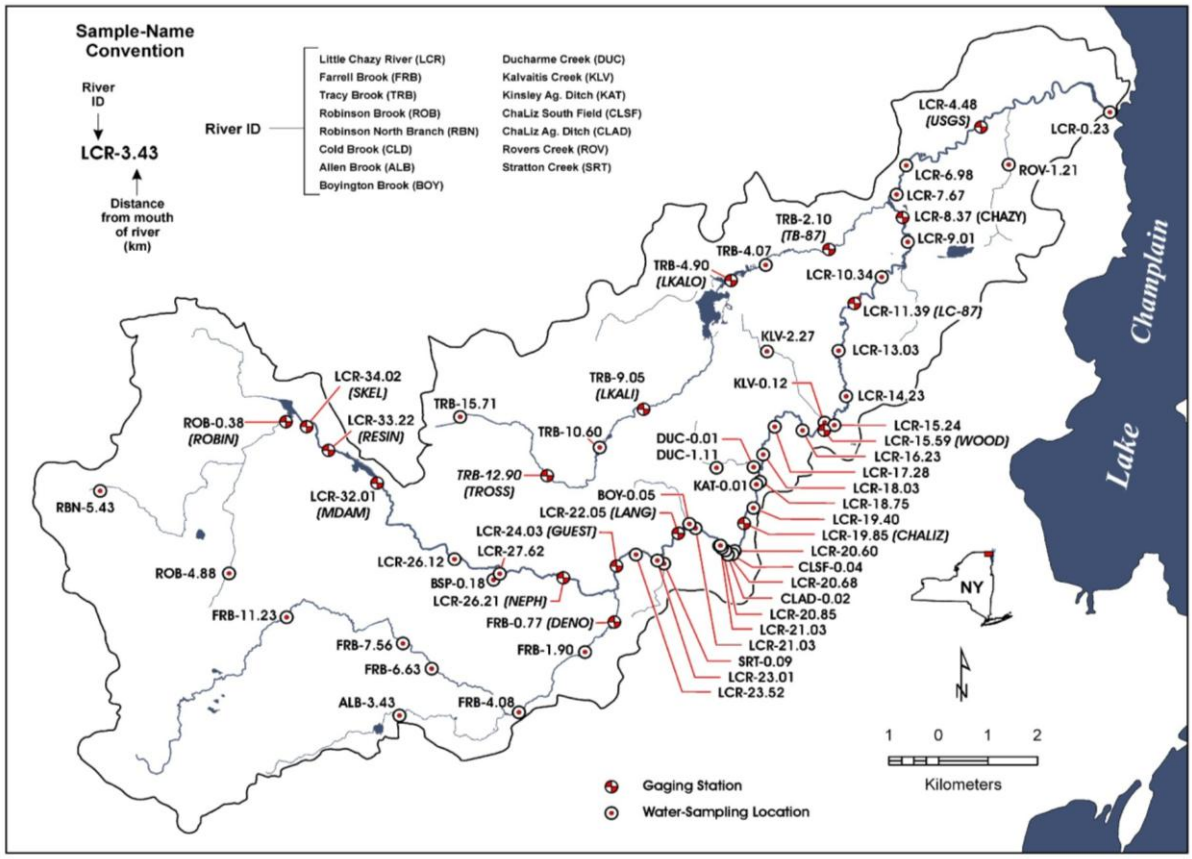

Figure 2. Locations for stream gaging stations and water-quality sampling stations used in this study.

Quality Assurance Tasks Completed

Standard quality assurance protocols as specified in the QAPP for the analytes measured in this project (nitrate-N, SRP and TP) for the period June, 2011 through July 2012 included:; documented procedures in sample collection and custody to minimize contamination or misidentification, repeated updating of instrument standards throughout each run, use of external QCCS samples (measured every 10-15 samples) to validate standards and verify accuracy, consistent analysis of duplicate samples for analysis of precision, matrix spikes (accuracy) and use of field blanks to document potential contamination. Quality assurance and quality control data are available in Excel spreadsheet files in Appendix A1 of this report.

Accuracy is assessed and kept under control through continual analysis of QCCS check samples purchased from a separate vendor with specified concentrations. QCCS check samples are analyzed continuously throughout each run, and are specified to be within +/- 20% of the true value through the QAPP. Shewhart control charts are typically used to analyze trends in instrument performance; with QCCS samples typically run every 15 samples.

Shewhart Control Charts: Figure 3 depicts a Shewhart Control chart for the length of the study for the three chemical analyses routinely measured (nitrate-N, total phosphorus and soluble reactive phosphorus). Over the course of the study, 307 QCCS check samples were analyzed, with only four falling slightly outside of the specified boundaries of +/- 20%. All four of the suspect analyses were for

total phosphorus, which involves laborious sample preparation procedures including filtration, digestion, neutralization and dilutions. For the three "suspect analytes" in the early part of the study, corrective actions were taken through retraining of laboratory staff. For the latter event, no actions were taken since all of the other analyses for that data run were within QC limits. Overall averages (+/- S.D.) for analysis of QC Check Samples (% of certified "true value") were:

SRP	101.2%	+/-	6.5%
TP	103.0%	+/-	7.6%
NO3	100.5%	+/-	1.7%

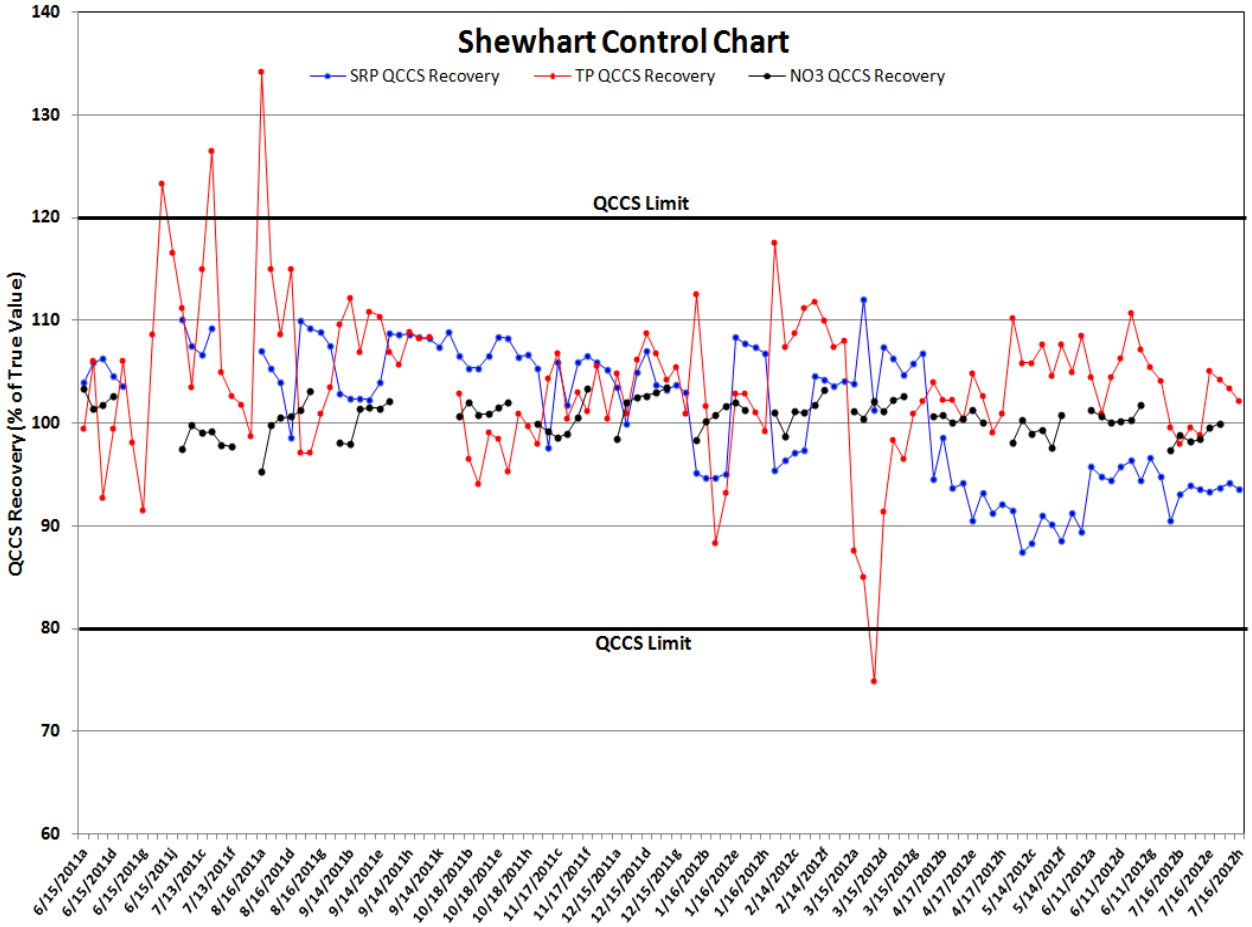

Figure 3. Shewhart control charts illustrating accuracy for nitrate, total phosphorus, and soluble reactive phosphorus for the length of the project. QCCS limits are established at +/- 20%.

Matrix Spike Recovery: Accuracy was also assessed through matrix spike recovery (%R) in which water sample unknowns were repeatedly spiked with a known standard to account for the effects of the sample matrix on accurate sample characterization. Calculations for matrix spike recovery are based on the formula below and are presented in Fig. 4 for nitrate, total phosphorus and soluble reactive phosphorus, respectively.

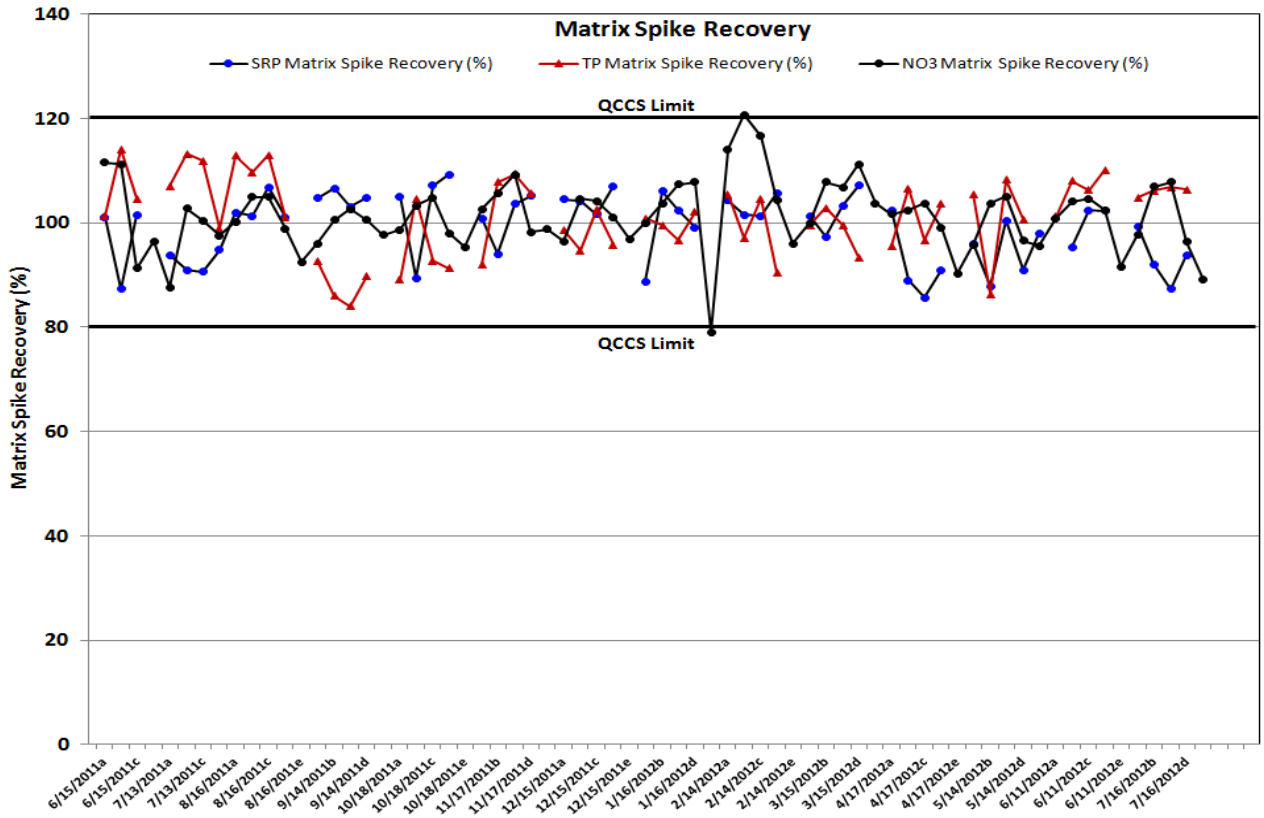

Figure 4. Matrix spike recovery analysis of nitrate, total phosphorus and soluble reactive phosphorus throughout the course of the project.

Recovey (%R) is calculated as follows:

$$\%R = [(Cs-Cu)/CA] * 100$$

Where: CS = measured concentration of spiked sample, mg/L
CU = measured concentration of unspiked sample, mg/L
CA = actual concentration of spike added, mg/L

And: CA ={[(Vu*Cu) + (Vstd * Cstd)]/(Vu+Vstd)} - CU

Where: Vu = Volume of unspiked sample, ml
Vstd = Volume of known standard added as spike, ml
Cstd = Concentration of known standard added as spike, mg/L

Matrix spike recovery was within the specified QAPP limits (80-120%) on all but two of 178 matrix spike determinations for nitrate. The two exceptions were only marginally outside the acceptable limits, and within the same run multiple acceptable determinations were completed, so no corrective actions were necessary. In one of the exceptions, the matrix spike concentration was actually smaller than the sample concentration, making the relative recovery difficult to determine. Normally, matrix spikes should be performed with a low volume of a much higher concentration to approximately double the

spiked sample mass. However, when the unspiked sample mass is not known in advance, this can be exceedingly difficult to predict.

Replicate Samples: Precision was measured as relative standard deviation (RSD) of duplicate samples for the three analytes (Table 1) over the entire sample period. For nitrate, four exceptions were encountered (highlighted in bold). In all four cases, sample concentrations were exceedingly low, making small variations in sample reproducibility appear much larger on a relative scale. For total P, ten exceptions were encountered, most likely due to the combination of extensive sample preparation (digestion, neutralization, dilution, etc.) and low analyte concentrations (note ug/L concentrations). For soluble reactive P, seventeen exceptions were encountered, however for ten of these sample concentrations were less than 5.0 ug/L, again causing large values for deviations measured on a relative scale.

It should also be noted that measurements of the QC check sample also measure analytical precision and almost all were within the specified QC limits (Fig. 3). This suggests that much of reductions in precision encountered in measuring samples are due to the added effects of sample collection and preservation, which add to the inherent lack of analytical precision.

Table 1. Results of analyses of duplicate samples. Relative standard deviation values greater than 20% are indicated by boldface font.

		Nitrate-N (mg/L)				TP (µg/L)				SRP (µg/L)			
Sample Date	Sample ID	1	2	AVG	RSD %	1.0	2.0	AVG	RSD %	1.0	2.0	AVG	RSD %
15-Jun-11	LCR-15.24	0.37	0.37	0.37	0.6	41.6	52.3	46.9	16.2	9.8	7.2	8.5	**21.8**
15-Jun-11	LCR-32.01	0.00	0.00	0.00	**51.0**	23.5	38.2	30.8	**33.8**	4.9	3.9	4.4	15.7
15-Jun-11	CLAD-0.01	0.05	0.03	0.04	**31.3**	52.3	42.2	47.3	15.0	4.2	3.3	3.7	18.4
13-Jul-11	LCR-4.48	0.14	0.16	0.15	9.0	71.3	72.6	71.9	1.3	22.8	22.4	22.6	1.0
13-Jul-11	LCR-15.24	0.38	0.39	0.39	1.2	32.4	44.1	38.2	**21.6**	0.7	2.7	1.7	**84.9**
13-Jul-11	LCR-24.3	0.24	0.24	0.24	0.6	22.6	37.6	30.1	**35.2**	2.0	1.7	1.8	12.9
13-Jul-11	CLAD-0.01	0.04	0.02	0.03	**42.5**	71.3	67.4	69.3	4.0	0.7	1.3	1.0	**47.1**
16-Aug-11	LCR-4.48	0.14	0.15	0.14	2.4	51.1	49.1	50.1	2.7	24.4	24.7	24.5	1.0
16-Aug-11	LCR-15.24	0.17	0.17	0.17	0.9	26.5	23.3	24.9	9.2	7.0	6.0	6.5	10.9
16-Aug-11	LCR-24.03	0.20	0.20	0.20	1.5	25.9	28.4	27.1	6.7	5.7	4.0	4.8	**24.4**
16-Aug-11	CLAD-0.01	0.00	0.00	0.00	**56.4**	25.2	29.7	27.5	11.6	0.3	0.3	0.3	0.0
14-Sep-11	LCR-4.48	0.37	0.37	0.37	1.0	48.2	51.5	49.8	4.7	11.8	11.5	11.6	1.3
14-Sep-11	LCR-15.24	0.42	0.44	0.43	2.7	42.2	55.4	48.8	19.1	4.2	6.3	5.2	**27.4**
14-Sep-11	LCR-24.03	0.20	0.20	0.20	1.4	63.1	37.0	50.1	**37.0**	2.0	2.3	2.1	10.6
14-Sep-11	CLAD-0.01	0.19	0.19	0.19	0.7	54.1	71.3	62.7	19.4	1.3	1.3	1.3	0.0
18-Oct-11	LCR-4.48	0.33	0.33	0.33	0.4	28.5	27.3	27.9	3.2	10.8	11.8	11.3	6.1
18-Oct-11	LCR-15.24	0.29	0.29	0.29	0.4	19.0	14.0	16.5	**21.8**	9.8	8.8	9.3	7.4
18-Oct-11	LCR-24.03	0.06	0.06	0.06	1.0	12.7	11.4	12.1	7.4	12.4	10.8	11.6	10.0
18-Oct-11	CLAD-0.01	0.15	0.15	0.15	3.2	15.9	18.4	17.1	10.5	4.6	5.6	5.1	13.7
15-Nov-11	LCR-4.48	0.17	0.18	0.17	2.9	18.7	20.6	19.6	7.0	8.4	7.5	7.9	8.7
15-Nov-11	LCR-15.24	0.21	0.21	0.21	0.6	12.2	15.4	13.8	16.4	9.7	10.4	10.1	4.6
15-Nov-11	LCR-24.03	0.07	0.07	0.07	0.1	7.7	9.7	8.7	15.7	1.6	2.3	1.9	**23.6**
15-Nov-11	CLAD-0.01	0.03	0.03	0.03	1.2	14.8	13.5	14.2	6.4	4.2	5.8	5.0	**22.8**
14-Dec-11	LCR-4.48	0.41	0.41	0.41	0.6	16.4	18.3	17.4	8.0	2.2	2.5	2.4	9.4
14-Dec-11	LCR-15.24	0.46	0.46	0.46	0.3	5.2	8.5	6.9	**33.7**	2.5	3.2	2.9	15.7
14-Dec-11	LCR-24.03	0.24	0.25	0.24	2.9	8.5	7.2	7.9	11.8	2.2	2.9	2.5	17.7
14-Dec-11	CLAD-0.01	0.13	0.14	0.13	0.6	7.2	9.2	8.2	17.0	4.5	5.1	4.8	9.4
16-Jan-12	LCR-4.48	0.40	0.41	0.41	1.0	9.8	11.0	10.4	8.3	6.7	7.4	7.1	6.8
16-Jan-12	LCR-15.24	0.50	0.51	0.50	0.7	6.7	6.7	6.7	0.0	5.4	5.4	5.4	0.0
16-Jan-12	LCR-24.03	0.36	0.35	0.35	0.5	12.2	10.4	11.3	11.5	0.9	2.0	1.5	**53.1**
16-Jan-12	AGIN-5	4.00	4.01	4.00	0.1	9.8	8.6	9.2	9.4	3.9	2.4	3.1	**33.5**
14-Feb-12	LCR-4.48	0.44	0.44	0.44	0.6	19.8	22.4	21.1	8.6	7.8	5.4	6.6	**26.4**
14-Feb-12	LCR-15.24	0.45	0.43	0.44	2.8	12.1	16.0	14.1	19.3	3.8	1.5	2.6	**61.1**
14-Feb-12	LCR-24.03	0.32	0.32	0.32	0.3	12.8	10.9	11.8	11.5	2.0	1.6	1.8	12.9
14-Feb-12	CLAD-0.01	0.03	0.03	0.03	0.9	9.6	11.5	10.5	12.9	3.4	3.8	3.6	7.3
15-Mar-12	LCR-4.48	0.30	0.30	0.30	0.0	19.3	24.4	21.8	16.6	12.3	14.9	13.6	13.5
15-Mar-12	LCR-15.24	0.30	0.30	0.30	1.6	13.5	16.1	14.8	12.3	9.7	8.4	9.0	10.1
15-Mar-12	LCR-24.03	0.21	0.24	0.23	8.6	16.1	18.0	17.0	8.0	2.6	3.9	3.2	**28.3**
15-Mar-12	CLAD-0.01	0.28	0.28	0.28	1.7	147.0	141.9	144.5	2.5	42.3	44.6	43.4	3.7
17-Apr-12	LCR-4.48	0.12	0.11	0.11	9.7	18.9	22.8	20.8	13.3	8.51	9.16	8.8	5.2
17-Apr-12	LCR-15.24	0.17	0.17	0.17	0.6	12.4	14.3	13.3	10.3	5.24	4.58	4.9	9.4
17-Apr-12	LCR-24.03	0.19	0.20	0.19	6.4	11.1	9.1	10.1	13.7	4.58	5.24	4.9	9.4
17-Apr-12	CLAD-0.01	0.01	0.01	0.01	14.2	20.2	18.9	19.5	4.7	10.15	11.45	10.8	8.6

Table 1 continued. Results of analyses of duplicate samples.

		Nitrate-N (mg/L)				TP (μg/L)				SRP (μg/L)			
Sample Date	Sample ID	1	2	AVG	RSD %	1.0	2.0	AVG	RSD %	1.0	2.0	AVG	RSD %
14-May-12	LCR-4.48	0.23	0.23	0.23	1.8	26.2	27.5	26.9	3.4	8.1	8.79	8.5	5.4
14-May-12	LCR-15.24	0.28	0.28	0.28	0.1	15.4	17.9	16.6	10.9	2.3	2.93	2.6	17.7
14-May-12	LCR-24.03	0.12	0.12	0.12	0.4	23.7	18.6	21.1	17.1	1.3	1.63	1.5	15.7
14-May-12	CLAD-0.01	0.06	0.07	0.07	4.1	15.4	16.6	16.0	5.7	1.0	1.95	1.5	**47.1**
11-Jun-12	LCR-4.48	0.20	0.20	0.20	0.0	39.2	40.5	39.9	2.3	22.0	21.0	21.5	3.2
11-Jun-12	LCR-15.24	0.37	0.38	0.38	1.1	26.1	22.9	24.5	9.4	10.8	9.8	10.3	6.7
11-Jun-12	LCR-24.03	0.27	0.28	0.27	0.7	12.4	17.0	14.7	**22.0**	5.2	5.6	5.4	4.3
11-Jun-12	CLAD-0.01	0.02	0.02	0.02	0.3	17.6	15.7	16.7	8.3	1.3	2.3	1.8	**38.6**
16-Jul-12	LCR-4.48	0.13	0.13	0.13	1.8	61.2	55.0	58.1	7.5	38.6	39.5	39.0	1.7
16-Jul-12	LCR-15.24	0.21	0.21	0.21	1.4	27.2	21.0	24.1	18.1	13.9	12.3	13.1	8.5
16-Jul-12	LCR-24.03	0.18	0.18	0.18	0.4	18.5	21.6	20.1	10.9	6.3	4.7	5.5	20.2
16-Jul-12	CLAD-0.01	0.00	0.01	0.01	15.8	12.4	15.4	13.9	15.7	0.6	1.3	0.9	**47.1**

Deliverables Completed:

Quarterly Reports: Quarterly Reports were submitted on 5 May 2011, 8 August 2011, 27 January 2012, 1 May 2012 and 18 July 2012.

Hydrologic Datasets: Tropical Storm (TS) Irene had two effects on the stream gage network in the Little Chazy River; damage to the dataloggers and alteration of the rating relationship. Nearly all of the SUNY Plattsburgh and Miner Institute (SUNY/Miner) gages were submerged for varying durations during the event and did not record the runoff peak. The peak was recorded at the US Geological Survey gage at Stetson Road, where the event discharge was approximately 52 m^3/s (1840 ft^3/s), which was more than double the discharge of the spring runoff events in April 2011. Water height dataloggers for three SUNY/Miner gages (WOOD, NEPH and GUEST) were disabled by the flood and later replaced and the datalogger and containment structure at MDAM was lost without a trace. The MDAM station was later rebuilt. The gage near the mouth of Tracy Brook (TB87) was impacted by beaver activity, which could not be remediated, and the TROSS station was buried by alluvium and relocated. Rating curves for these stations are not available. Some data from the damaged or lost loggers were not recovered. Remarkably, most of the stream gage dataloggers resumed recording data once the flood water subsided.

Storm-related channel changes at the control sections of many SUNY/Miner gaging stations proved to be a far more vexing and pervasive problem. For example, post-TS Irene stream gaging data for the CHAZY gage plot consistently above the pre-TS Irene rating curve (Fig. 5), indicating the threshold was raised by deposition, a condition later confirmed by field observation. Most of the SUNY/Miner gaging station rating curves required reconstruction following the storm. For most stations, post-TS Irene stream gaging efforts produced too few data points over too small a range of discharge magnitude to produce reliable rating curves.

Despite the problems with calibration of the SUNY/Miner gages, all of the hydrologic data collected as part of this study are compiled as Excel spreadsheet files in Appendix B that accompanies this report.

Appendix B1 contains the results of stream gaging efforts during the study period and rating curves for all SUNY/Miner gages along the main channel of the Little Chazy River and the gage at the mouth of Farrell Brook (DENO).

Stream gaging results collected by SUNY/Miner field technicians at the USGS gaging station are also presented in Appendix B1 with USGS stream gaging data that were collected by USGS Hydrologic Technician Kenneth Planty from October 2010 through July 2012. The USGS station at this location has a bedrock control and thus was not affected by the storm-related channel changes that plagued many of the SUNY/Miner gages. The USGS rating curve depicted in the file was derived from the USGS and SUNY/Miner stream gaging data but was neither commissioned nor approved by the U.S. Geological Survey. The rating curve in this file should only be used to assess the accuracy of the stream gaging data collected by SUNY/Miner hydrologic technicians. All of the stream discharge data from the USGS gage that are cited in this report are from officially sanctioned USGS sources. At the time of this report (6 August 2012) data after 1 October 2011 have not been officially approved by the USGS and are considered to be provisional.

Appendix B2 contains pre-TS Irene hydrographs (01 June to 28 August 2011 for most stations) at the SUNY/Miner stream gages on main channel between Chazy and Miner Dam at Altona Flat Rock. Post-TS Irene ratings are not reliable at the present time so post-storm hydrographs are not available.

Stage records for all SUNY/Miner gages for the entire term of the project (June 2001 to July 2012) are included in Appendix B3. Data for the USGS gage are available from the USGS website.

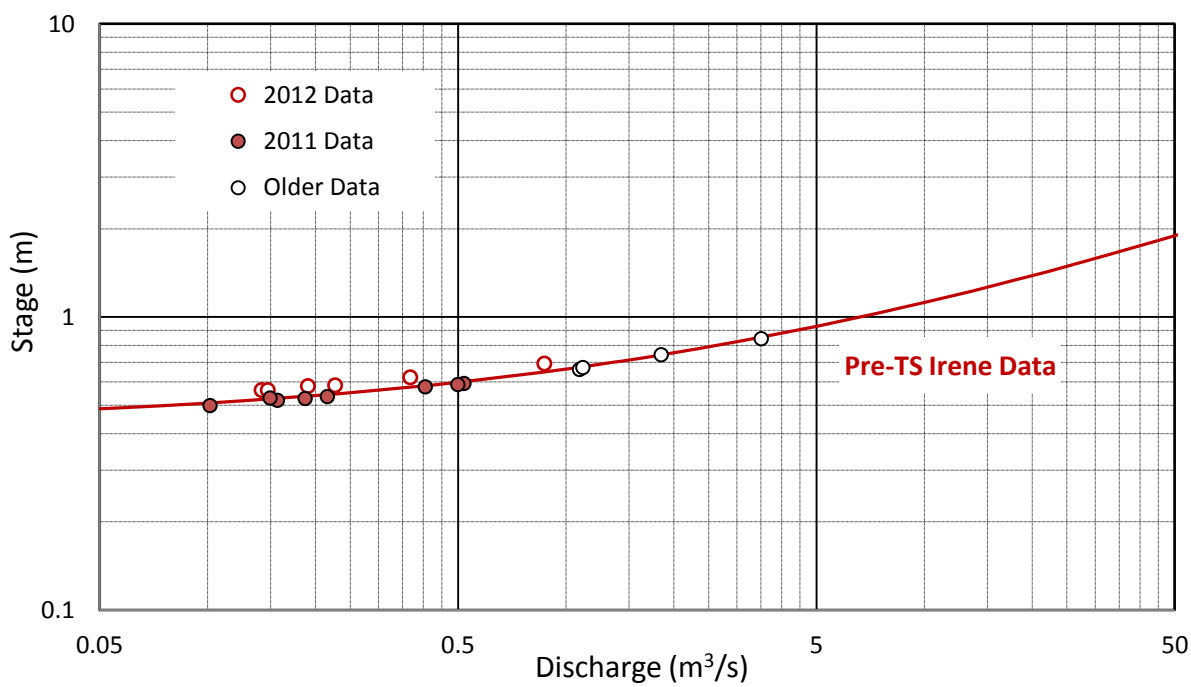

Figure 5. Rating curve for the CHAZY gage showing the effect of channel changes at the gage control caused by TS Irene. In this case, gravel deposition at the control shifted the 2012 data points above the pre-Irene rating curve for the station.

Water Quality Datasets: The project QAPP was approved on 15 June 2011 and monthly synoptic water-sample suites for nutrient concentrations (nitrate-N, total phosphorus and soluble reactive phosphorus) were collected between June 2011 and July 2012. Each sample suite consisted of 250 ml samples that were collected at approximately 60-65 sites throughout the watershed (Fig. 2), depending upon site accessibility, weather or hydrologic conditions at the time of sampling. Quality Assurance and Quality Control information and water quality datasets for nitrate-N and phosphorus may be found as Excel spreadsheets in Appendix A, which accompanies this report.

Field Notebooks: Field notebooks are available as Adobe portable document files (pdf) in Appendix C.

Conclusions:

Temporal Variability of Streamflow: The mean daily discharges for the Little Chazy River at the USGS gaging station near Chazy are shown for entire duration of the SUNY Plattsburgh and Miner Institute nutrient runoff study (January 2008 to August 2012) in Fig. 6. The record also indicates the coverage of USGS approved and provisional stream discharge data, the duration of the current study and the winter 2011-12 data gap that coincides with the development of channel ice at the USGS gage site.

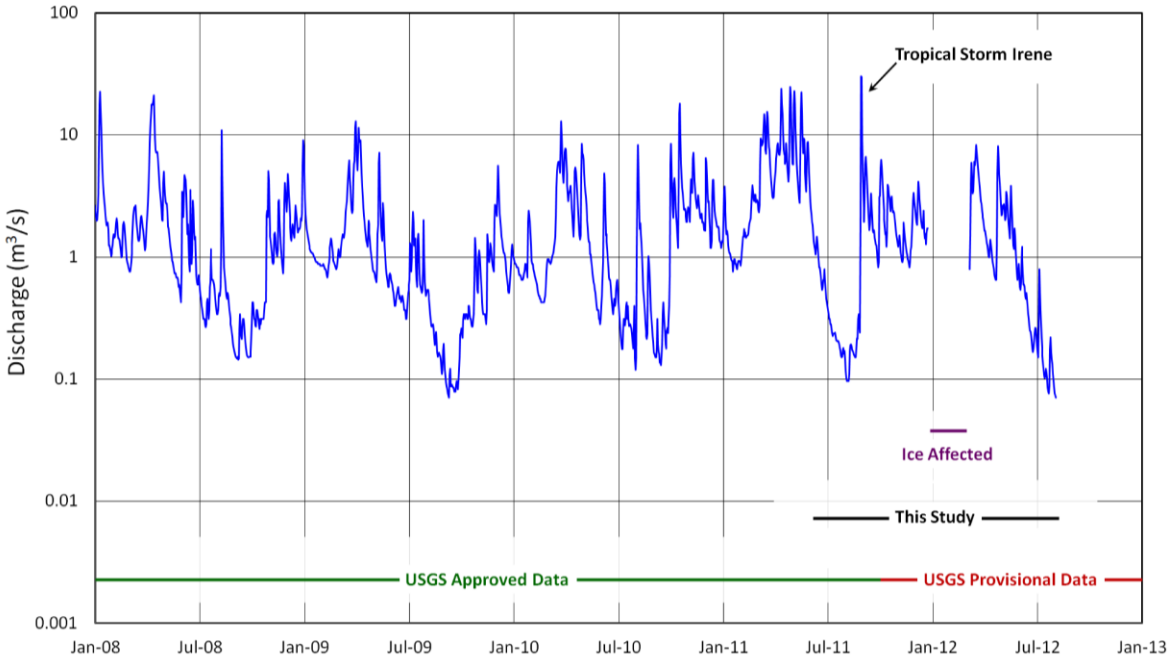

Figure 6. Mean daily discharge for the US Geological Survey gage on Stetson Road in Chazy from January 2008 to August 2012. The horizontal lines indicate the data that have been approved by the USGS or remain provisional, the time covered by this study (Jun 2011 to Jul 2008) and an ice affected interval this past winter (25 Dec 2011 to 06 March 2012) for which no discharge estimates are currently available.

Longitudinal Variability of Streamflow: The high resolution stream-gage network proposed for this study was intended to refine the longitudinal variability of stream discharge in the Little Chazy River first observed by Lehman et al (2006) and to further assess the effect of variable discharge on nutrient transport through the watershed. Channel changes resulting from TS Irene runoff altered the stage-discharge relations at most gages and made it impossible to obtain reliable post-storm discharge estimates.

Lehman et al. (2006) identified two influent zones along the main channel of the river; at Altona Flat Rock, which probably contributed to the demise of Miner's hydroelectric dam and power project (Franzi and Adams, 1999), and at another Miner hydroelectric dam in the village of Chazy (Fig. 7). They also observed that downstream patterns of stream discharge change with hydrologic regime from baseflow to surface runoff events. Much of the stream discharge during baseflow conditions is generated in a 6 km reach where the river descends from Altona Flat Rock into the Champlain Lowland. The river gains little additional discharge as it traverses the agricultural regions below West Chazy and becomes influent at the impoundment just south of the village of Chazy. The point along the river at which the transition to influent conditions occurs migrates upstream as baseflow discharge decreases. Longitudinal variability of daily average stream discharge along the main channel was estimated for three sample days in the summer of 2011 (15 June, 13 July and 16 August) using pre-storm rating curves (Fig. 8). The 2011 discharge profiles are similar to earlier observations and provide at least some degree of corroboration the observations of Lehman et al (2006) but fall short of providing high-resolution discharge and nutrient loading for the post-storm study period.

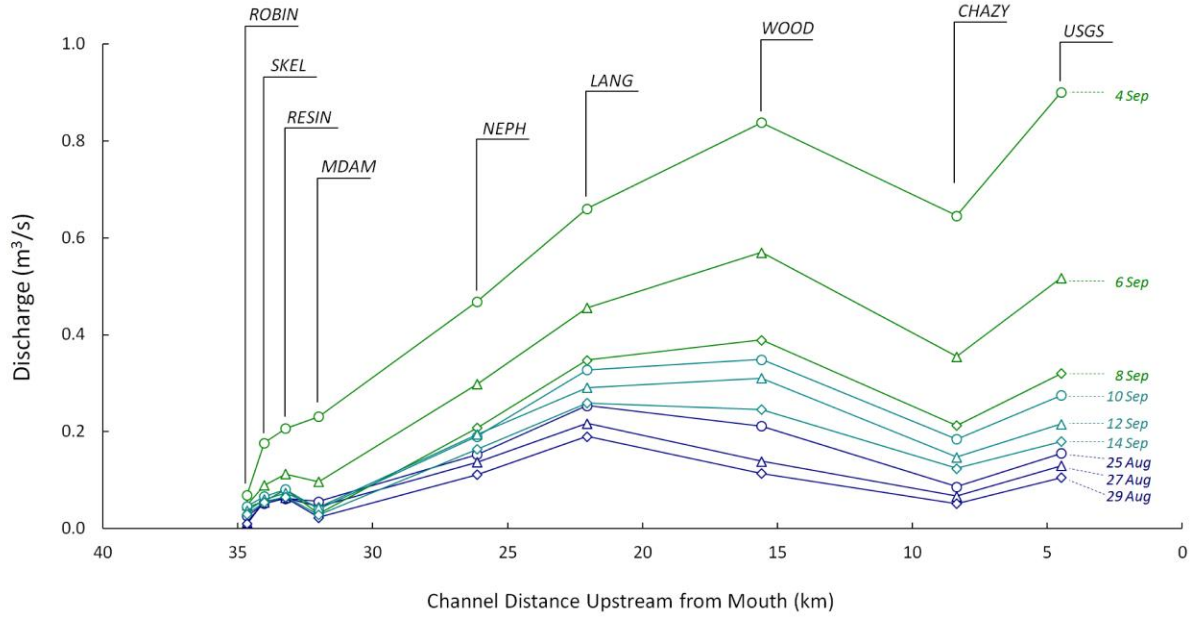

Figure 7. Longitudinal variability of daily average discharge along the main channel of the Little Chazy River for nine days immediately preceding, during and after a runoff event from 25 August to 14 September 2005 (from Lehman et al., 2006). The gage network in 2005 included three stations on Altona Flat Rock but did not include the LC87, CHALIZ and GUEST gages in the Champlain Valley, which were built later.

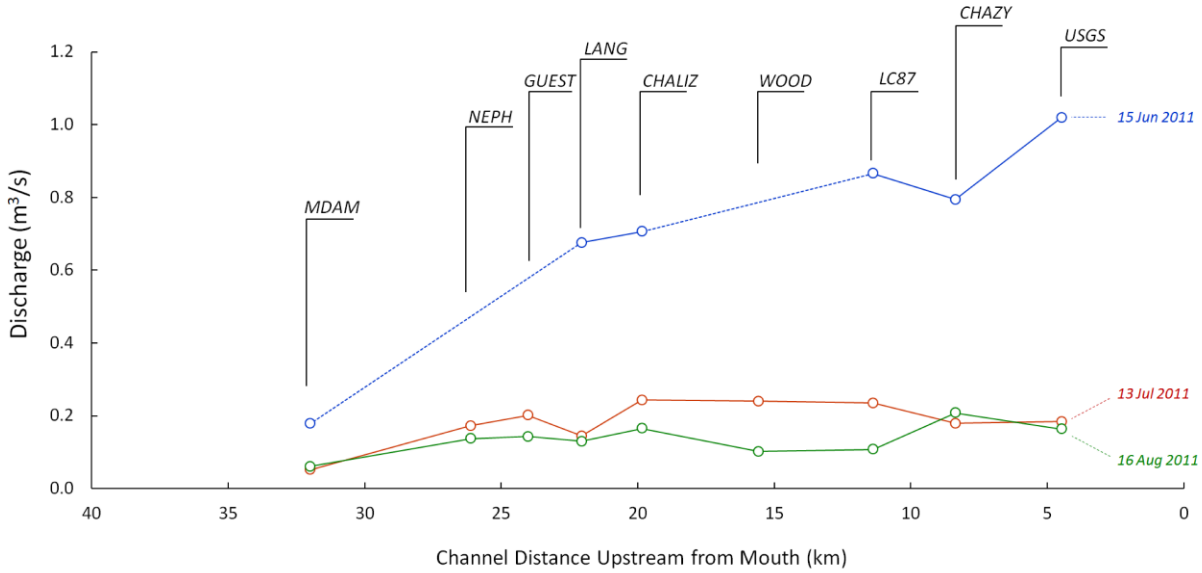

Figure 8. Longitudinal variability of daily average discharge along the main channel of the Little Chazy River for three sample dates in summer 2011 (this study). The gages at NEPH, GUEST and WOOD were not operating at the time of the June 2011 sampling.

<u>Longitudinal Variability of Nutrient Concentrations:</u> Nutrient concentrations and loads are greatest in the main channel of the Little Chazy River in the agricultural regions between the villages of West Chazy and Chazy (West Chazy agricultural region on Fig. 1) and between Chazy and Lake Champlain

(Lakeshore agricultural region on Fig. 1). Little Chazy River nutrient levels are not significantly affected by contributions from its principal tributaries Farrell Brook and Tracy Brook (Appendix A2), neither of which have extensive agricultural land use in their basins.

The greatest increases in nitrate-N concentration (Fig. 9) occur in agricultural areas and rise less steeply or fall in reaches that flow through the I-87 and US 9 highway corridor or residential areas. A pronounced drop in nitrate-N occurs in the village of Chazy where the river is impounded behind two small dams. Dilution and sequestration may account for the drop in nitrate-N in these impoundments. Stream water nitrate-N rises abruptly in the Lakeshore agricultural area east (downstream) of Chazy. Median nitrate-N concentrations in the Champlain lowland agricultural areas for the period of this study fall consistently near the 25th percentile for the entire database.

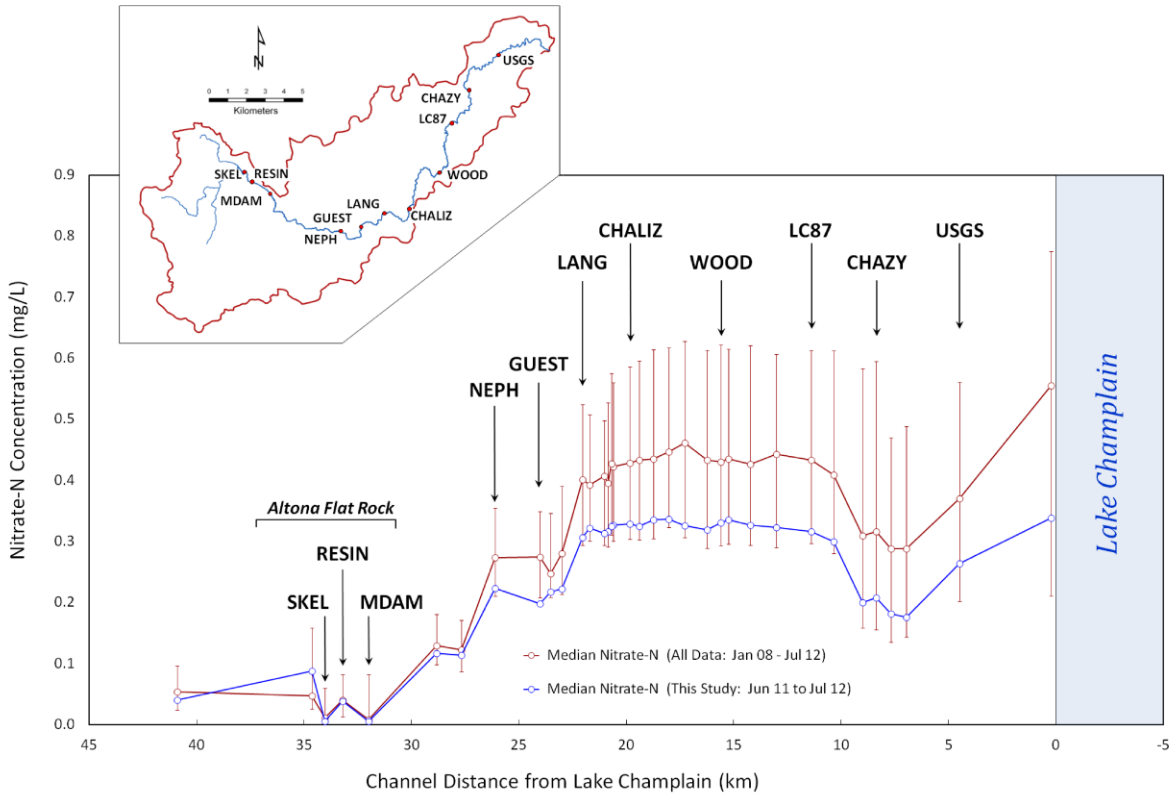

Figure 9. Comparison of the longitudinal variability of median monthly nitrate-N concentrations along the main channel of the Little Chazy River from this study (blue) to the variability observed in the entire database (red), January 2008 to present. The error bars for the entire database represent the 25th and 75th percentiles of the sample population. The sample population (N) for the entire database is 57 observations for all stations except for sites on Altona Flat Rock (N = 43-44), where access is limited during the winter months and Military Turnpike (channel distance = 41 km) (N = 56), where two small headwater stream concentrations are averaged. The sample population for this study is 14 for all stations except the Altona Flat Rock stations (N = 11-12).

Total phosphorus concentrations (Fig. 10) increase steadily from West Chazy (GUEST) to Chazy. The greatest increases and variability in phosphorus concentration occurs in agricultural areas but phosphorus concentrations do not show the same magnitude of decrease as nitrate-N in the village of Chazy impoundments. Phosphorus concentrations more than double in the reach between Chazy and Lake Champlain. Trends for soluble reactive phosphorus are similar to the trends for total phosphorus (Appendix B1). Total phosphorus concentrations in the Champlain lowland agricultural areas for the period of this study were generally well below the median for the entire database.

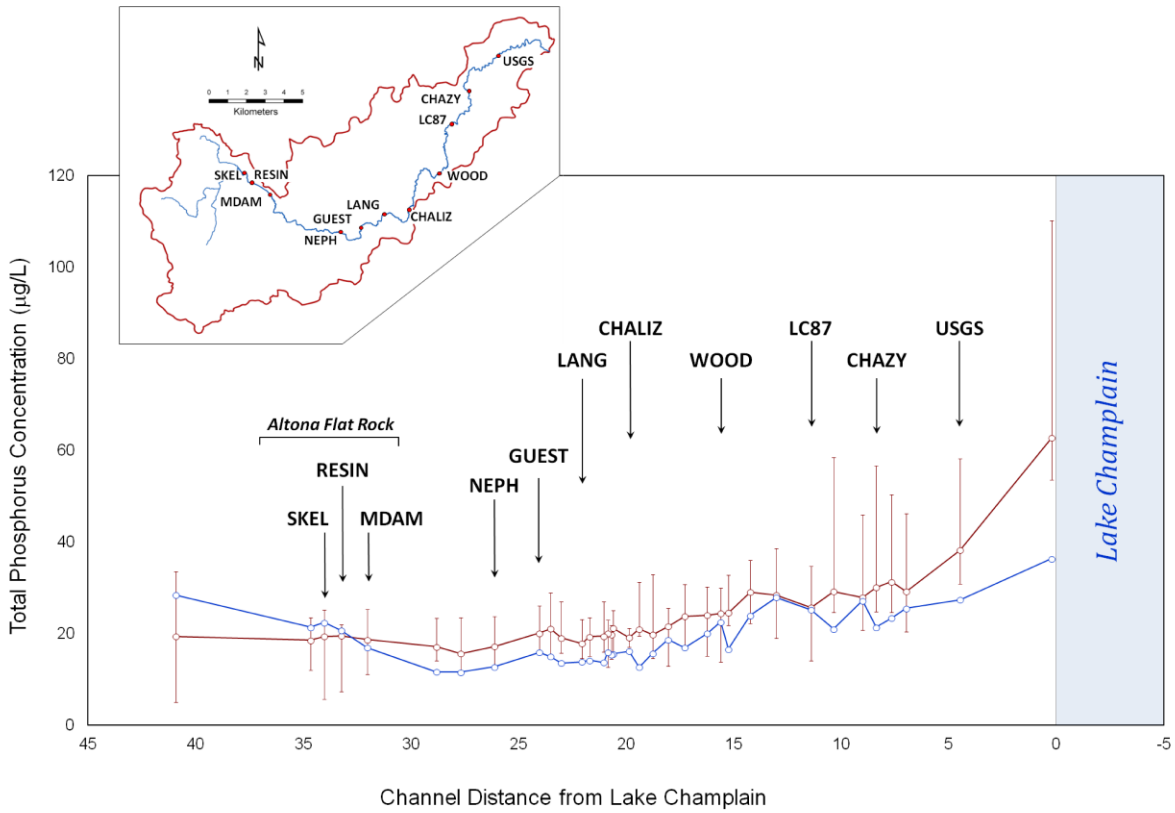

Figure 10. Comparison of the longitudinal variability of median monthly total phosphorus concentrations along the main channel of the Little Chazy River from this study (blue) to the variability observed in the entire database (red), January 2008 to present. The error bars for the entire database represent the 25th and 75th percentiles of the sample. The sample population (N) for the entire database is 57 observations for all stations except for sites on Altona Flat Rock (N = 43-44), where access is limited during the winter months and Military Turnpike (channel distance = 41 km) (N = 56), where two small headwater stream concentrations are averaged. The sample population for this study is 14 for all stations except the Altona Flat Rock stations (N = 11-12).

Longitudinal variability of nitrate-N, total phosphorus and soluble reactive phosphorus concentrations reflect primarily agricultural influences and are punctuated by abrupt increases related to runoff from tile drains or drainage ditches from crop fields. The downstream drop in nitrate-N concentration through the I-87 corridor to the village of Chazy probably reflects the combined effects of decreased agricultural input, dilution by less-impacted ground or surface water, sequestration by aquatic plants and denitrification or ammonification. Pronounced increases in all nutrients downstream from Chazy are believed to be related to agricultural inputs.

Temporal Variability of Nutrient Concentrations: Nutrient loads (kg/d) were determined for the USGS gaging station on the Little Chazy River at Stetson Road in Chazy for each monthly sample day since January 2008. Loads are the product of nutrient concentration and stream discharge. Nutrient concentrations were obtained from Franzi et al. (2009, unpublished data and this study) and daily average stream discharge data were obtained from the U. S. Geological Survey website. Nitrate-N (Fig. 11) and total phosphorus (Fig. 12) loads to Lake Champlain show a first-order seasonal variability that closely follows seasonal streamflow hydrology. Secondary variations include high loads associated with large runoff events (e.g. January 2008 and May 2011) and low loads associated with unusually dry summer conditions (e.g. April and July 2012) and or mid-winter (January and February) low flow conditions.

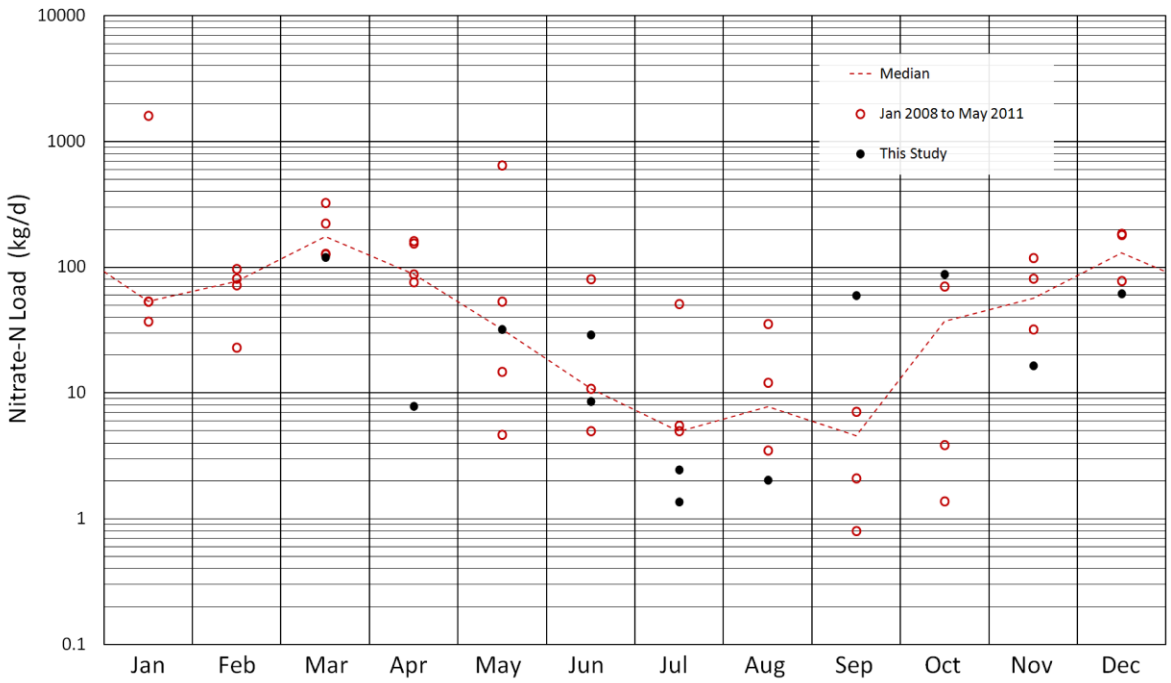

Figure 11. Monthly nitrate-N loads at the U.S. Geological Survey stream gage on Stetson Road in Chazy. Streamflow was affected by channel ice in January and February 2011 so stream discharge and nitrate-N load estimates are not available at the present time.

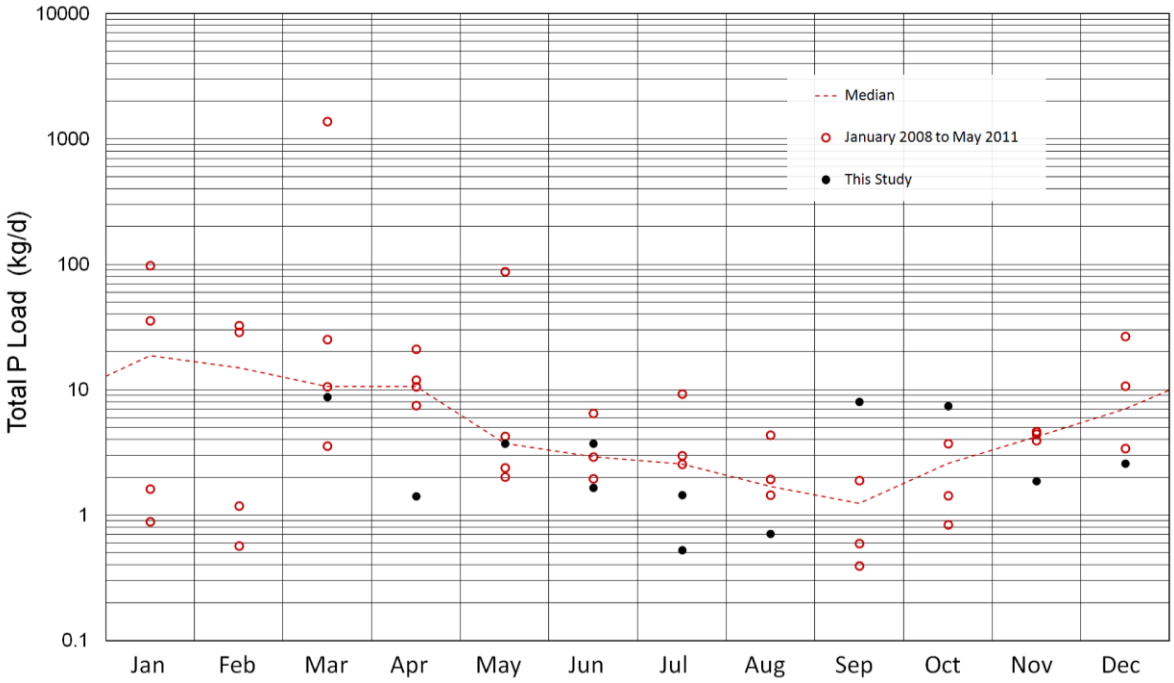

Figure 12. Monthly total phosphorus loads at the U.S. Geological Survey stream gage on Stetson Road in Chazy. Streamflow was affected by channel ice in January and February 2011 so stream discharge and nitrate-N load estimates are not available at the present time.

Nutrient Runoff during the Tropical Storm Irene Event: Tropical Storm Irene deposited 102 mm of rainfall in the watershed and produced an estimated 5.16 hm^3 of stormflow runoff with a peak flow of approximately 52 m^3/s (1,840 ft^3/s) (Fig. 13). The discussion of event-related nutrient runoff closely flows that of Oetjen et al. (2012), who presented these data at the Northeastern Geological Society of America meeting in March 2012.

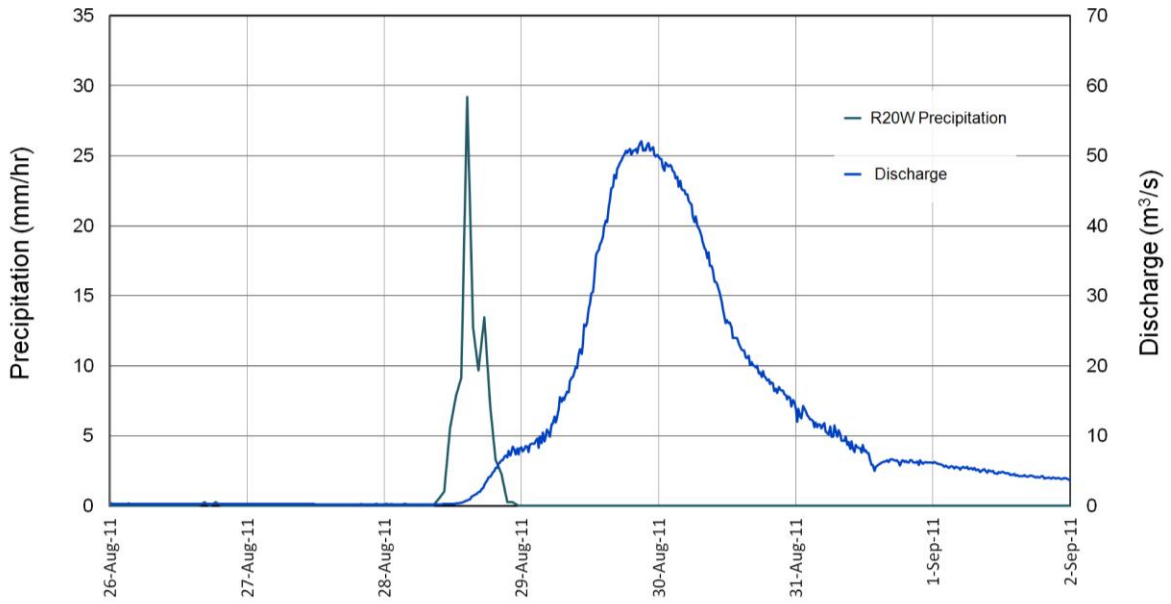

Figure 13. Precipitation and stream discharge for the Tropical Storm Irene runoff event. The precipitation data are from a rain gage operated by the Miner Institute at plot-study site R20W (courtesy of S. Kramer). Unit value stream discharge data are from the U.S. Geological Survey web site. Original figure from Oetjen et al. (2012).

Nutrient concentrations peaked on the rising limb of the runoff hydrograph during times of intense rainfall (Figs. 13 & 14). The highest concentrations were most likely due to initial surface water runoff (overland flow) during active rainfall, which removed large quantities of particulate and soluble material that accumulated on the soil surface between runoff-producing rainfall events. Nutrients present in the soil due to nitrification and mineralization may also have been flushed through shallow subsurface runoff pathways at the beginning of rainfall events.

Peak total phosphorus and soluble reactive phosphorus concentrations precede peak nitrate-N concentration several hours. The lags reflect differences in runoff pathways and nutrient mobility may explain this observation. Overland runoff pathways should contain both soluble and particulate nutrients, thus nutrient concentrations generally rise as the first overland flow reaches the stream channel. Total phosphorus and soluble reactive phosphorus tend to remain in the soil as particulates or by adsorption on to mineral surfaces. By contrast, the more soluble constituents (chloride, sulfate and nitrate-N) are mobile and travel through the soil with percolating ground water.

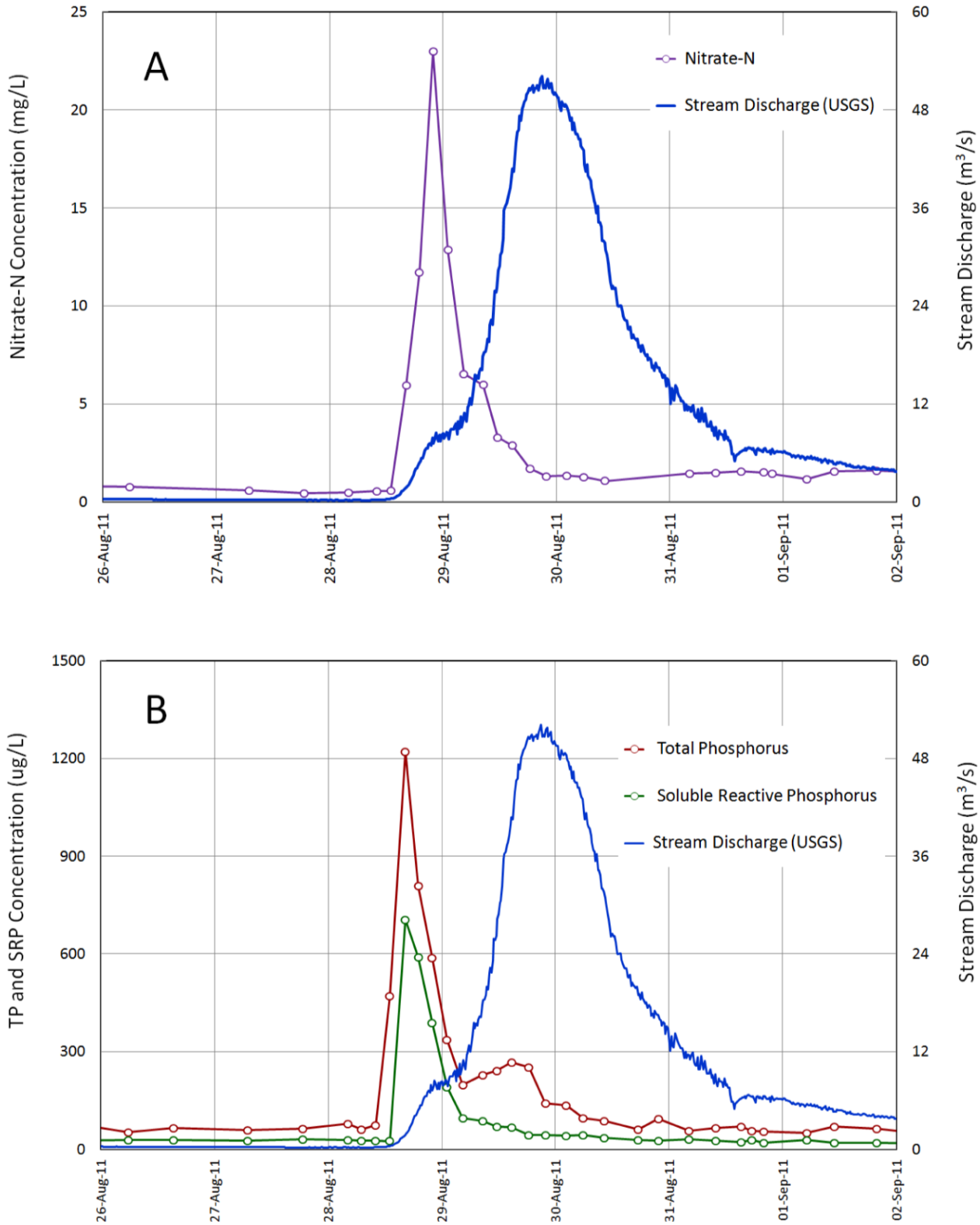

Figure 14. Nitrate-N (A), total phosphorus and soluble reactive phosphorus (B) concentrations during the TS Irene runoff event at the U.S. Geological Survey stream gage on Stetson Road in Chazy. Original figure from Oetjen et al. (2012).

Acknowledgements:

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We offer special thanks to Ken Planty (USGS) for supplying his stream gaging results for the USGS gage at Stetson Road in Chazy. We also thank the many SUNY Plattsburgh students who participated in this study over the past nearly five years, especially Brian Huber, Ethan Sullivan, Karl Oetjen, Tiara Zimmermann, Rebecca Kranitz, David Senderoff and Travis Lilly.

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