Use of Acoustic Doppler Current Profiler data to estimate sediment and total phosphorus loads to Lake Champlain from the Rock River

by

Elissa Schuett and William B. Bowden

Rubenstein School of Environment and Natural Resources
University of Vermont
Burlington, VT 05401

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Abstract

Estimations of total suspended sediment (TSS) and total phosphorus (TP) concentrations in the Rock River were made based on relationships to acoustic backscatter data from an Acoustic Doppler Current Profiler (ADCP) and on relationships to discharge. Linear models were used to calculate the estimated concentrations of TSS and TP by developing a rating curve from measured TSS and TP samples. The ADCP-based regressions explained a greater portion of the variance in the measurements than the discharge-based regressions. A comparison of TP loading based on a simple extrapolation of measured concentration data from grab samples similar to the approach used by the Vermont Department of Conservation (DEC) was nearly identical to an estimate of the TP loading based on the high-frequency ADCP data. This suggests the possibility that data from ADCPs may provide a reliable and more defensible estimate of TP load at a cost that might not be any greater than manual-based sampling – and that might be lower if integrated over time.

Introduction

Excessive phosphorus loading is widely viewed as one of the key water resource management issues affecting Lake Champlain, which defines the western border of Vermont. Phosphorus loading generally contributes to eutrophication of the lake and specifically may be responsible for algal blooms, especially of cyanobacteria that may at times create toxins that are of concern for human health. Excessive phosphorus loading from agricultural and urban land uses regularly tops the list of priority environmental concerns expressed by regional managers, policy makers, NGO's, researchers, and residents (State of the Lake and Ecosystems Indicators Report, LCBP 2012).

Transport of phosphorus is closely associated with transport of sediment; the relationship between total phosphorus and suspended sediment is often linear and significant. Thus, quantification of sediment loading can be used as a surrogate for quantification of phosphorus loading. This is important because sediment can be measured relatively easily (e.g., gravimetrically or acoustically) while total phosphorus requires manual digestion followed by spectrophotometric analysis. These latter processes are time consuming, expensive, and require the use of materials that are dangerous to use and dispose.

The long-term water-quality monitoring program for the Lake Champlain Basin is operated by the state of Vermont with support from the Lake Champlain Basin Program and in collaboration with the USGS. This program bases its estimates of phosphorus loading on intermittent grab sampling followed by manual analysis of total phosphorus as described above. Under the best of circumstances it is difficult to deploy sampling personnel during rapidly developing events. It is especially difficult when these events occur at night and over weekends and holidays. Equally important, due to the intermittent sampling it is not clear how non-linear dynamics such as hysteresis during events or season-specific sediment generation processes (e.g. ice floes, farming practices) affect the total loading of sediment and thus the loading of phosphorus.

Acoustic Doppler Current Profiling (ADCP) is widely used to measure water velocity and discharge and more recently has been used to measure suspended as well as bed-load transport of sediment (Elci et al., 2009, Wood and Teasdale, 2013). ADCP has the benefits of being non-destructive, autonomous, continuous, and relatively robust. Therefore, it is a potentially useful method to estimate sediment transport as well as discharge. However, the use of ADCP to estimate sediment load is not entirely proven and is likely to be site-specific.

The Rock River is an especially useful focus for this study because it typifies the intensive agricultural landscape that is known to contribute significant TP loading to Lake Champlain. It also has the benefit of having an ADCP that was installed in 2010 to measure discharge. The Rock River at the location of the ADCP gage is a small and hydrologically flashy stream, the type that poses the greatest challenge to characterize with traditional sampling techniques. It is not unusual for storm events to be over before personnel arrive to collect samples. Continuous monitoring in these circumstances would be particularly valuable. Furthermore, given the political and economic importance in Vermont placed on accurate estimates of phosphorus loading to Lake Champlain for the purposes of developing estimates of total maximum daily loads (TMDLs), it is imperative that we obtain accurate and defensible estimates of the TP loads.

The primary objective of this project was to calibrate the relationship between total suspended sediment (TSS) concentrations and estimates of particle transport based on data collected by ADCP. Our ultimate goal was to compare TP load estimates from the continuous proxy record to those from conventional estimates of TP load based on interpolation between intermittent manual samples to determine whether the conventional method introduces bias in estimates of event loads of sediment and TP. In addition, we wanted to evaluate whether the ADCP-based approach might provide advantages to the monitoring approach based on intermittent grab samples.

Project Objectives as Stated in the Grant Agreement

- Explore the relationship between suspended sediment concentration and estimates of particle transport based on data collected by acoustic Doppler current profiling (ADCP)

- Develop a relationship between estimates of total sediment and total phosphorus loading in the Rock River in conjunction with the manual sampling method currently being used by the VTDEC and a new method based on continuous measurements of TSS by ADCP.

- Examine the particle size distribution of TSS over storm events and over the season to determine how the ADCP data correlates with different particle size fractions.

- Measure the TP in the size fractions obtained during storms and over the season

- Assess the utility of ADCP derived TSS data to estimate TP concentrations and therefore TP loads

- Examine the fine-scale behavior of sediment loading during individual storm events to infer sources (from timing) and processes controlling sediment and phosphorus delivery to the stream

- Compare TP load estimates from the continuous proxy record to those from conventional estimates of TP load based on interpolation between intermittent manual samples to determine whether the conventional method introduces a bias in estimates of event loads of sediment and TP.

Methods

Field site and Equipment

In fall 2010, USGS established a stream gage on the Rock River in Highgate, Vermont (http://waterdata.usgs.gov/nwis/uv?04294140 . The gage drains an area of 11.3 square miles; the entire Rock River watershed is 52 square miles (Fig. 1). The watershed, including parts in Quebec, is composed primarily of agricultural land (41.4%) and forested land (40%), followed minimally by water/wetland (13.2%) and residential (5.4%) (Hegman et al., 1999), however these data are from 1993, more recent data is not available, but changes in land use, including conversion of forest land to agricultural use has been observed (SMRC 2006).

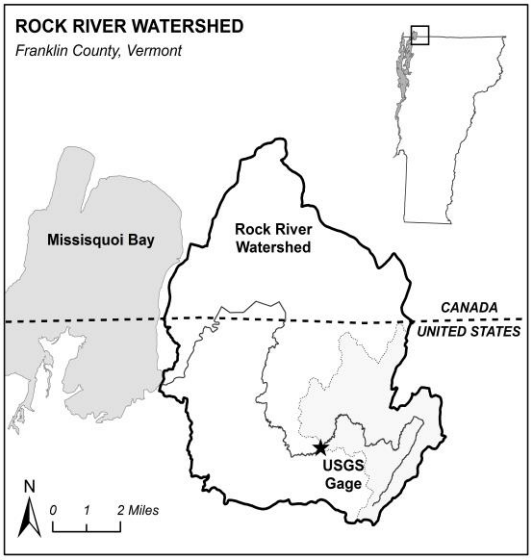

Figure 1 Rock River watershed

The shallow (0-20cm) soil within the Rock River watershed is composed of approximately 50-75% silt particles, 15-30% sand particles, and 15-25% clay particles (NRCS 2014).

Discharge at the gage was measured using a Sontek SL-3000 Acoustic Doppler Current Profiler (ADCP). The USGS programmed the ADCP to measure and store the average acoustic backscatter and velocity in 5 bins 0.67m each, beginning 0.5m from the sensor, over the entire acoustical beam length, across the river at the gage site (Fig. 2). Although data for 5 bins are available, only three were used in this analysis. During periods of low flow and when partially frozen, the fourth and fifth bins often had interference with the stream bottom or water surface. (See Fig. 3 and associated narrative in the Methods

section, below.) All ADCP data was processed by the USGS, but was still provisional at the time this work was done.

Sample collection and analysis

Samples were collected using an ISCO autosampler that was installed in the USGS well-house. The ISCO was set up to collect samples with a rise in stage over 1.5 feet in order to capture storm events. The tubing for sample collection was placed near the middle of the stream, 0.25m from the bottom. The ISCO and well-house are approximately 10 feet above the stream, requiring the ISCO to pull samples up 10 feet of tubing. Discrete samples were collected, filling two 1 Liter bottles to be used for nutrient and sediment analysis. During winter months, typically January and February) water in the tubing would freeze, preventing samples from being collected. Occasional manual samples were collected from the stream during the winter when open water was available.

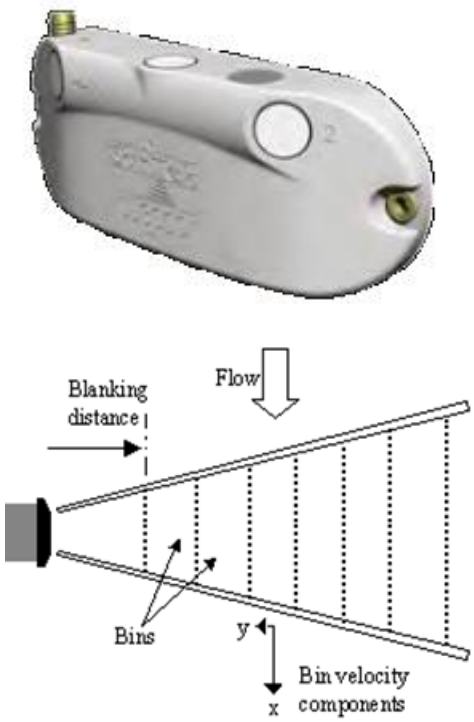

Figure 2 Image of the Sontek model SL-3000 ADCP and schematic of equally sized bins across the width of the river.

Sample and data analyses was done by the Bowden Watershed Research Laboratory (BWRL) in the Rubenstein Ecosystem Science Lab at the University of Vermont. Samples were filtered through weighed, ashed 47mm GF/F filters, recording the volume filtered. The filters were then dried at 60°C for 24 hours and weighed again to calculate total suspended sediment in mg/L. Loss on ignition (LOI or ash-free dry weight) was determined to quantify the organic matter present in the sediment samples by ashing the filters at 500°C for 2 hours and weighing the filters a third time. The material that remains on the filter is mineral content. The organic content (LOI) is calculated by subtracting the ashed filter (mineral) weight from the total dried filter weight.

Water from the second sample bottle was filtered through an ashed 25 mm GF/F filter and dried at 60°C for 24 hours. These filters were saved for later analysis of particulate phosphorus. The filtrate was frozen for later analysis of total dissolved phosphorus. Phosphorus was analyzed using the ascorbic acid molybdate blue method, creating a standard curve, and digesting the samples as appropriate. Particulate phosphorus samples are digested in an acidic environment, using hydrochloric acid and heated for two hours, and then reacted with the molybdate reagent and read on a spectrophotometer at 885 nm. The method detection limit for particulate phosphorus is 0.37 µg phosphorus and check standard concentrations of 1.5 µg and 15 µg phosphorus. The total dissolved phosphorus samples were digested in a persulfate solution and autoclaved prior to molybdate

reaction. The method detection limit for total dissolved phosphorus is 1.24 µg/L phosphorus and check standard concentration of 1.5 µg/L and 77.5 µg/L phosphorus. The methods are based on Arctic Long-Term Ecological program (LTER) methods, which can be traced back to USGS and EPA methods. Our specific protocols can be found in the Arctic LTER Streams protocol (http://ecosystems.mbl.edu/ARC/streams/Arctic%20LTER%20Streams%20Protocol%202013.pdf). Standard curves and standard check samples are used when determining phosphorus concentration. We did replicate analyses of each TDP sample and required that the replicates agree within 10%. Samples that did not pass this test were reanalyzed.

We also utilized data from samples that had been collected by the Friends of Northern Lake Champlain (FNLC). In collaboration with the VTDEC, this group collected regular samples during 2011-2013. Samples were collected by the FNLC once daily during a storm event and bi-weekly during the ice-free season when at baseflow, or when flow rates were below 30 cfs. These samples were analyzed for suspended sediment concentration and total phosphorus (EPA Standard Method 4500 PH accredited by New Hampshire Department of Environmental Services) by the La Rosa lab in the VTDEC. These methods are similar those used by the BWRL and described above. The number of storms sampled as well as the total number of samples obtained by the FNLC and BWRL are tabulated in Appendix A.

Particle Size

Particle size analysis was conducted on samples from nine storm events from May-September 2013. Samples were analyzed on a Mastersizer 3000 at the Lake Champlain Research Institute at SUNY Plattsburgh, which uses laser diffraction to measure particle sizes. The first set of samples from May 2013 did not have a high enough particle density to provide an accurate measurement. These samples were composited, with only moderate success. To address this problem of low particle density we began to collect two liters of water during each sampling event beginning in August 2013. One full liter was used for particle size analysis. To concentrate the sample, the liter was centrifuged down into a 50 mL conical tube. Each sample was centrifuged for 10 minutes at 2530 rpm. The remaining water was decanted, first by pouring and then by using a pipette to not disturb the sample. The 50ml tube was then refilled with the appropriate Rock River sample.

We used Stokes Law to estimate the efficiency with which we removed particles from suspension to the concentrated pellet at the bottom of the tube. We did this to ensure that our centrifuged sample was representative of the original particle size distribution. The settling velocity (V_t) is defined as:

$$V_t = \frac{gd^2(\rho_p - \rho_m)}{18\mu}$$

where

g= acceleration of gravity = 1.18*r*(rpm)^2, where r = centrifuge rotor radius in cm (20.4), and rpm is the rotation speed per minute (2530) at which the centrifuge was run = 1.18×10^{-5}*20.4*(2530)^2 = 1460 m/s^2

d = particle diameter (mm), clay particle size (0.001mm) was used as a reference

ρ_p = density of particle of clay, g/cm^3 = 2.837

ρ_m = density of medium, or density of water at 20°C, kg/m^3 = 998.2

μ = viscosity of medium, water at 20°C, kg/m.s = .001002

Using these values, we determined that a clay particle settles at 0.00015 m/s which means that a particle of clay will settle 8.9cm in ten minutes at 2530 rpm in a centrifuge. The centrifuge tubes that were used are 10cm long when filled to the top with water. A head space was left when centrifuging of approximately 1 cm and so all particles at least 0.001mm in diameter should have settled during centrifugation. The smallest particles of centrifuged or non-centrifuged samples we observed were in the range of 0.0015-0.0020 mm in diameter. Thus, we think that this procedure reasonably preserved the original particle size distribution of the samples.

Acoustic calculations

Post-processing of the ADCP signal includes compensation for physical characteristics like temperature as well as loss in signal strength with distance from the transducers due to beam spreading, absorption by the water, and attenuation by the sediment.

The complete corrected acoustic backscatter (ABS_{corr}) equation is, simplified from Urick (1975) and as described by Wood and Teasdale (2013):

$$ABS_{corr} = SNR_{value} + 20\log10\,(R\,) + 2\alpha_w R + 2\alpha_s R \qquad [1]$$

To reach this final ABS_{corr} value several steps are required. First, we used the raw signal-to-noise value (SNR_{value}) provided to us by the USGS for each of five bins to calculate the acoustic absorption by freshwater (α_w), which also requires using the acoustic frequency of the instrument and water temperature:

$$\alpha_w = [Bf^2/ f_t] \text{ x } 8.687 \qquad [2]$$

where

B = constant for viscosity mechanism in pure water, defined as 3.38×10^{-6}

f = acoustic frequency, kilocycles per second = 3000 for Rock River

f_t = temperature-dependent relaxation frequency (kHz) defined as $21.9 \times 10^{[6-(1520/T+273)]}$

T = water temperature in degrees C

The acoustic absorption by water was then used to calculate the corrected acoustic backscatter for each bin across the width of the river. The bin size for this study was 0.67m, with the first bin beginning at 0.5m from the instrument. The midpoint of the bin

is used in calculating the losses due to absorption. Equation [1] was used to calculate the water-corrected backscatter, excluding the final term for acoustic absorption by sediment.

The SNR_{value} was further corrected to determine the acoustic absorption by sediment. The calculation uses beam spreading across the width of the river and the acoustic absorption by water previously calculated. Sediment attenuation (α_s) is calculated by using the slope of the line from losses due to absorption by water across the width of the river, multiplied by -0.5. Then, sediment attenuation is multiplied by 2 times R, the slant distance along the acoustic beam to the measurement location incorporating the beam angle.

α_s = slope(bin 1-3 acoustic backscatter by water, beam distances of bin 1-3) x -0.5

Sediment-corrected backscatter is then calculated by using equation [1], multiplying α_s by 2R to determine the final term in the equation. Solving for the entire equation provides the value for sediment-corrected backscatter. When backscatter is low, the values in bins four and five of the corrected data are greater than the values in bins one through three, creating a negative slope, which is physically impossible. This happened frequently with this data, therefore, only the slope of the line for the first three bins was used throughout the analysis and the average of the first three bins is used in calculations used to estimate sediment and phosphorus concentrations.

Sediment-corrected backscatter is the value that was ultimately used in further analysis of the relationship to sediment and phosphorus. Figure 3 can be used to explain the process of normalizing the signal-to-noise ratio to sediment-corrected backscatter. Figure 3a was developed from data at a discharge of 33 ft^3/s under conditions when interference did not occur. Figure 3b was developed from data at a discharge of 12 ft^3/s under conditions in which interference did occur. There is a notable increase in SCB values in bins 4 and 5, which is not physically possible. We found that at the Rock River station, discharge values less than 20 ft^3/s typically resulted in interference in bins 4 and 5. Because 80% of data were at discharges less than 20 ft^3/s, bins 4 and 5 were not used in this analysis to reduce erroneous estimates of sediment and phosphorus.

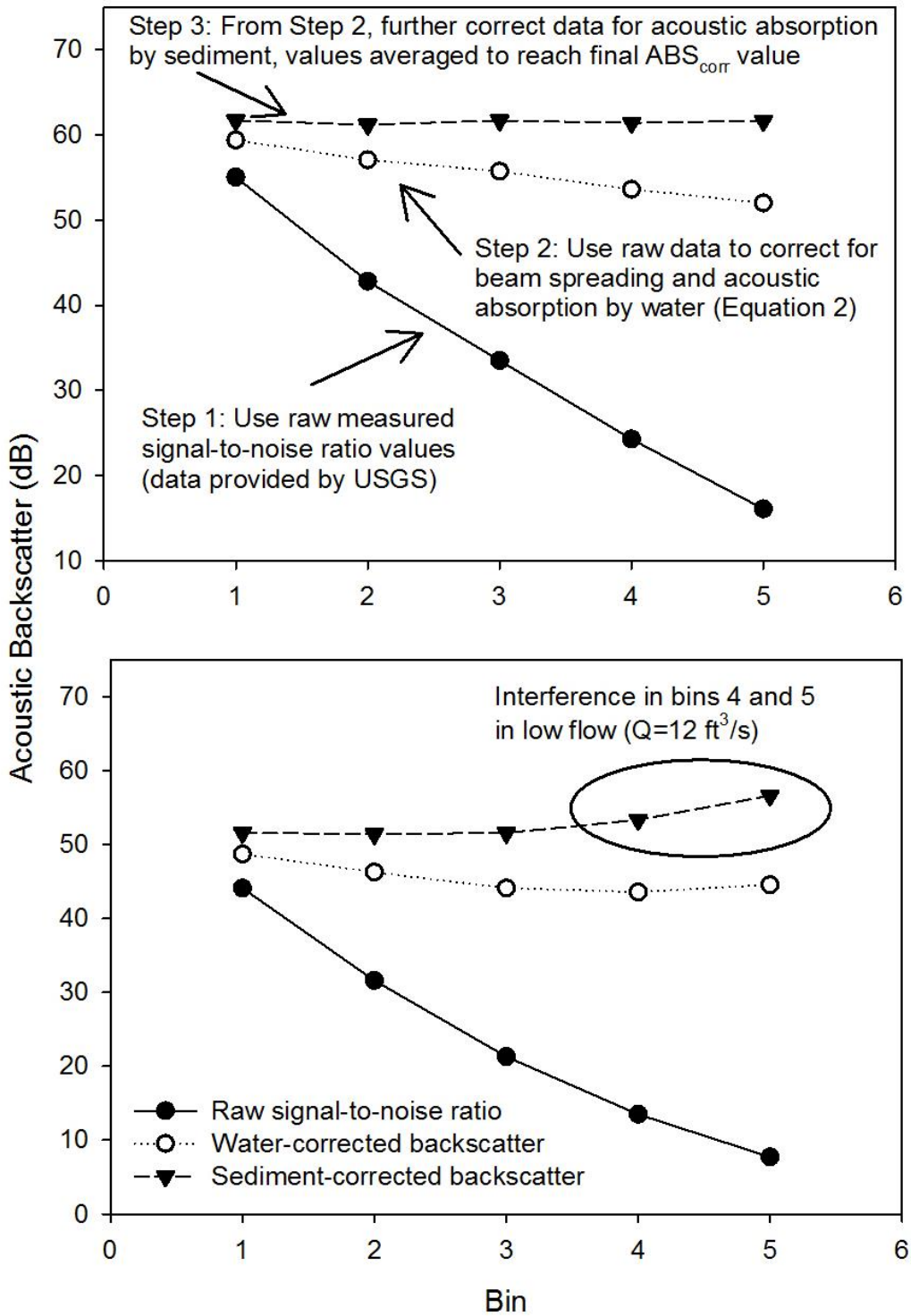

Figure 3a) Steps taken to correct raw signal-to-noise ratio to final ABS$_{corr}$ value. 3b) Interference at low flow resulting in values in bins 4 and 5 higher than values in bins 1-3, which is physically impossible.

Sediment and Phosphorus Rating Curves

The relationship between total suspended sediment (TSS) and ABS_{corr} was determined by using the log_{10} value of the measured TSS and the ABS_{corr} value at the time of sample collection to develop a linear regression rating curve. We evaluated the relationship between TSS and discharge in the same way. We also sub-divided the data by seasons and developed rating curves for each season that related log(TSS) to ABS_{corr} and to discharge. Seasons were defined as winter (January, February, and March), spring (April, May, and June), summer (July, August, and September) and fall (October, November, and December).

Rating curves for phosphorus were developed in a similar manner, to relate log(TP) to the ABS_{corr} and to discharge. Total dissolved phosphorus (TDP) and particulate phosphorus (PP) were measured values from lab analyses. Total phosphorus (TP) was calculated as the sum of TDP and PP. In the statistical analyses that follow we focused on TSS and TP. However, results of similar statistical analyses of the TDP and PP data are included in Appendix C. In these statistical analyses, seasons were separated, as for the sediment analysis.

Transformations of the data were evaluated, including log-log transforms and square root transforms (See Appendix D). These relationships did not explain any more of the variability than the log (dependent) variable versus independent variable relationship, and so we chose to use the simplest equations when estimating TSS and TP.

The linear rating curves that were developed for sediment and phosphorus were then used to predict the amount of each from the continuous discharge and ABS_{corr} values. The log(TSS) value was de-transformed to TSS, applying a nonparametric bias correction (Duan's factor). Duan's factor is calculated by averaging the residuals of the dependent variable from the regression model. TSS was calculated from log(TSS) by multiplying the log(TSS) value by the Duan factor and raising that to the 10 power.

Storm Events

Sample collection was more frequent during storm events than during baseflow; the ISCO was programmed to begin collection once stage was greater than 1.5 feet, collecting once every two hours until stage subsided or the ISCO was full (approximately 48 h). Analysis of storm events was done to identify non-linear transport of sediment and phosphorus (hysteresis) and to compare the transport dynamics among different storms.

Results and discussion

Particle size

The samples from the Rock River that were analyzed for particle size were predominantly composed of silt-sized particles (10 μm diameter), including samples collected during storm events (summarized in Appendix A). Samples were only available

during May-September of 2013, so we do not know if particle sizes differed during winter months, for example, during large snowmelt events. Given that we could not identify any notable differences in sample particle size by storm event or by season, we did not consider particle size further. Relationships between TSS and particle size were weak, as were ABS_{corr} and particle size.

Estimating TSS

Simple linear regression equations and scatter plots of the log(TSS) versus ABS_{corr} and versus discharge are shown by season in Table 1 and Figure 4. The regression for all seasons together was also calculated. Winter and fall had the strongest relationships to ABS_{corr}, but the regression for all seasons combined is sufficiently strong and was used to calculate sediment estimates. In all cases the regressions using ABS_{corr} explained more of the variance that the regressions using discharge. Inspection of Fig. 4b suggests that the relationship between log(TSS) and Discharge is non-linear despite the fact that a linear regression through the data is significant. For the sake of maintaining parallel presentation of the data, we have retained the log-linear form for Figs. 4a and 4b. However, we did explore other transformations of the data in Fig. 4b, including linear-linear and log-log relationships. These transformations did not improve either the r^2 or the root mean square error (RMSE) values compared to the linear fit. As we ultimately decided that a fit to the ABS_{corr} data was substantially better than any fit to the Discharge data, we decided not to pursue additional or more complicated fits to the data in Fig. 4b.

Table 1 Rating curves equations and r-squared values for log TSS vs discharge and log TSS vs ABS_{corr} by seasons. The probability of the slope being significantly different from zero ($p<0.05$) and of the regression equation being significant ($p<0.05$) is denoted by a *.

Variable	Slope	Intercept	r^2	Duan's correction	Number of samples
			Winter		
Discharge	0.006*	0.72	0.58*	1.37	20
ABS	0.055*	-2.40	0.72*	1.13	20
			Spring		
Discharge	0.002*	0.70	0.10*	1.42	115
ABS	0.046*	-1.96	0.55*	1.18	115
			Summer		
Discharge	0.002*	0.73	0.34*	1.24	79
ABS	0.031*	-0.95	0.56*	1.12	79
			Fall		
Discharge	0.006*	0.35	0.49*	1.22	134
ABS	0.052*	-2.35	0.77*	1.10	134
			All seasons		
Discharge	0.004*	0.59	0.30*	1.38	348
ABS	0.046*	-1.93	0.65*	1.16	348

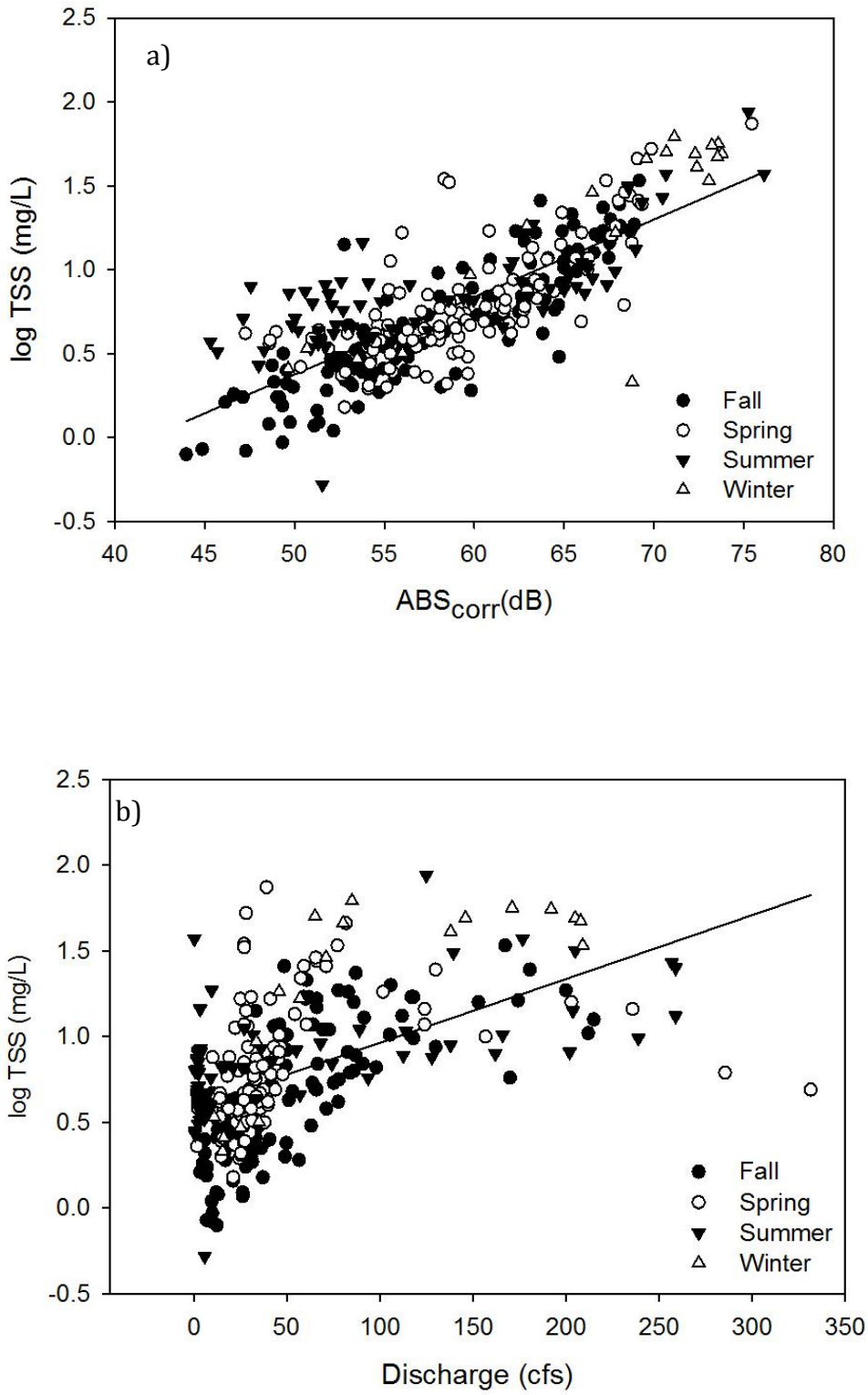

Figure 4 a) Log(TSS) versus ABS_{corr} and b) Log(TSS) versus Discharge by season. The line in Fig. 1a is for the All Seasons regression.

The

log(LOI) versus ABS_{corr} and discharge are shown by season in Table 2. The LOI values are equivalent to the organic content of the particles. The LOI relationships are not as strong as the relationship with log(TSS), particularly in the spring and summer seasons and so the LOI data was not used further in this analysis. Regressions using ABS_{corr} explained more of the variance than the regressions using discharge in each season except winter.

Table 2 Rating curves equations and r-squared values for log LOI vs discharge and log LOI vs ABS_{corr} by seasons. The probability of the slope being significantly different from zero ($p<0.05$) and of the regression equation being significant ($p<0.05$) is denoted by a *.

Variable	Slope	Intercept	r^2	Number of samples
		Winter		
Discharge	0.010*	-0.17	0.74*	20
ABS	0.080*	-4.50	0.61*	20
		Spring		
Discharge	-0.001*	0.04	<0.01*	109
ABS	0.05*	-2.17	0.10*	109
		Summer		
Discharge	0.004*	0.12	0.20*	79
ABS	0.051*	-2.67	0.40*	79
		Fall		
Discharge	0.006*	0.26	0.49*	134
ABS	0.055*	-2.61	0.78*	134
		All seasons		
Discharge	0.004*	0.14	0.16*	342
ABS	0.049*	-2.50	0.28*	342

The data collected by the Friends of Northern Lake Champlain (FNLC) was analyzed using an identical approach to the way we analyzed the ISCO samples we collected (Table 3). The general trends in the FNLC data are similar to those that we observed in the ISCO data and lead to similar conclusions. Notably, the ABS_{corr}-based regressions explained more of the variance in the FNLC data than the discharge-based regressions.

Table 3 Rating curves equations from Friends of Northern Lake Champlain samples and r-squared values for log TSS vs discharge and log TSS vs ABS_{corr} by seasons. The probability of the slope being significantly different from zero ($p<0.05$) and of the regression equation being significant ($p<0.05$) is denoted by a *.

Variable	Slope	Intercept	r^2	Number of samples
		Winter		
Discharge	0.006*	1.31	0.46*	21
ABS	0.062*	-2.04	0.63*	39
		Spring		
Discharge	0.002*	1.59	0.10	23
ABS	0.041*	-0.69	0.53*	23
		Summer		
Discharge	0.006*	1.58	0.53*	13
ABS	0.022*	0.61	0.26	12
		Fall		
Discharge	0.008*	0.95	0.55*	33
ABS	0.058*	-1.86	0.75*	33
		All seasons		
Discharge	0.005*	1.33	0.30*	90
ABS	0.050*	-1.27	0.55*	107

We compared the TSS concentrations (mg/L) estimated from the manual grab samples collected by the FNLC to the TSS concentrations estimate from the ISCO samples collected by the Bowden Watershed Research Lab (BWRL). Because these two sets of samples were collected in different years, the only meaningful comparison we can make is to test whether the mean concentrations in samples collected by the two groups (or methods) differed. To obviate concerns about the normality and other statistical characteristics of the two data sets, we used a non-parametric Mann-Whitney test to make this comparison. We found that the TSS concentrations in the samples collected by FNLC were significantly larger than the TSS concentrations in the samples collected by the BWRL ($p<0.05$).

The difference in total mass of TSS in these two sample sets may be attributable to differences in the way the samples were obtained. In this study as ISCO autosampler was used, which was positioned about 10 feet above the river water surface. Thus, it is possible that during sampling, larger sand-sized particles may have been left behind while smaller silt and clay particles were drawn all the way to the sampler. In this slow-moving river, it is unlikely that large particles would remain in suspension very long. Nevertheless, we cannot disprove that a self-sorting process may have affected the mass of larger suspended sediment particles collected. Even if a self-sorting bias did exist for the sediment mass, it may have had a lesser effect on the estimated total mass of phosphorus collected if most of the phosphorus was associated with the smaller silt and clay particles instead of the sand.

The FNLC data will not be used in further data analyses because it is clear that these samples were significantly different from the samples analyzed for this project by the BWRL and the FNLC group only sampled once or twice during a storm while the BWRL data as based on many samples during each storm.

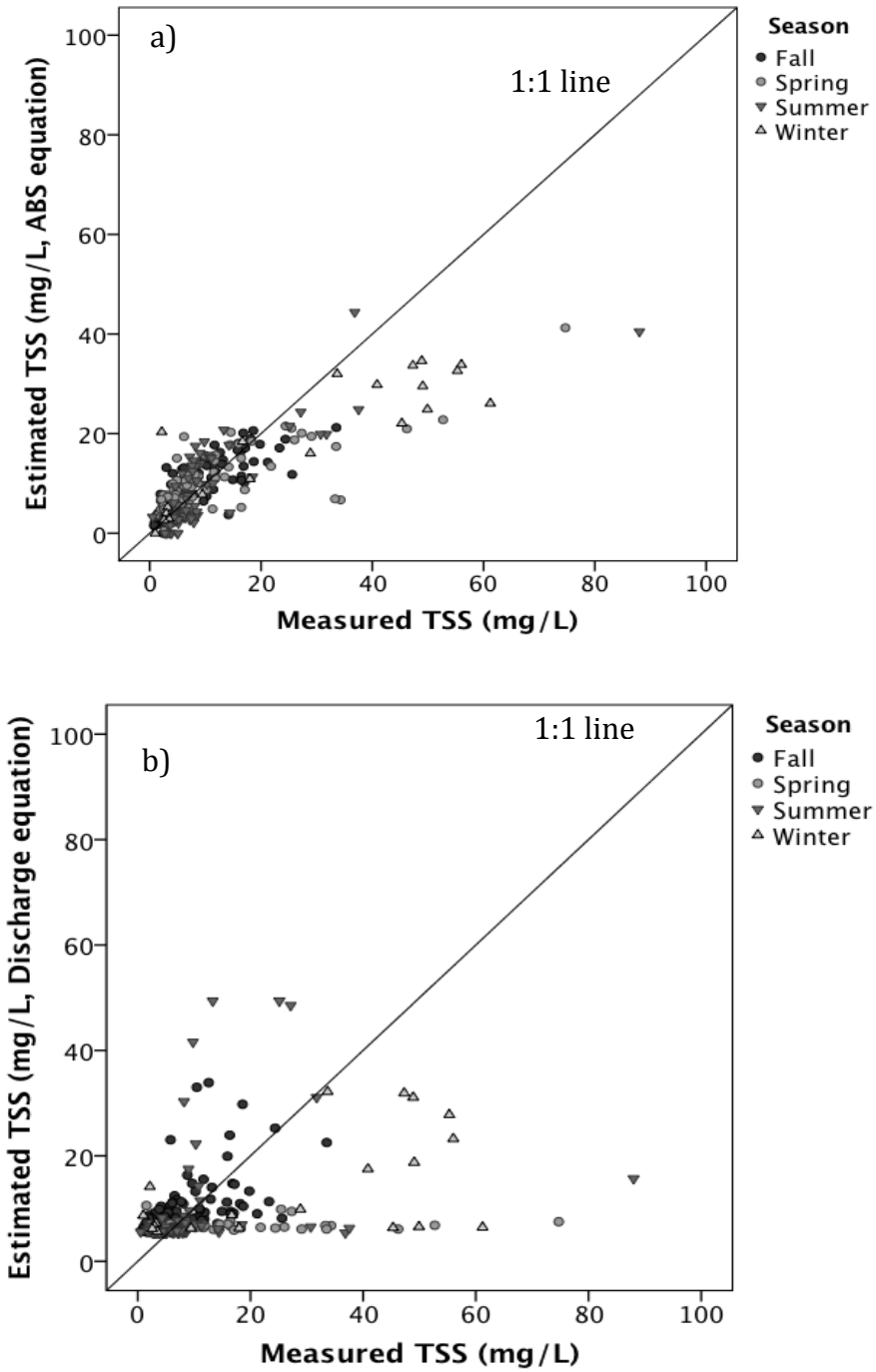

Figure 5 Estimated log TSS versus Measured log TSS using a) ABS_{corr} equation and b) discharge equation for estimations

A rating curve for *estimated* total suspended sediment was developed using all of the TSS samples collected by the BWRL for this project as the dependent variable with either ABS_{corr} or discharge as the dependent variable. To evaluate the utility of these rating curves we used them to estimate the expected TSS based on the ABS_{corr} and discharge values at the same time that manual samples were taken. We then plotted the estimated versus the measured values with 1:1 lines (Figure 5). The ABS_{corr} equation tended to underestimate the measured TSS at higher concentrations. However, overall the ABS_{corr} equation better estimated the measured TSS value than did the discharge equation. Regression analysis was also used for the estimated TSS versus measured TSS (Table 4).

Table 4 Regression analysis of TSS estimated (Q) v. TSS measured and TSS estimated (ABS) v. TSS measured. All analysis were significant ($p<0.05$) as indicated by *.

Variable	Slope	Intercept	r^2
TSS estimated (Q)	0.21	6.60	0.15*
TSS estimated (ABS)	0.52	4.04	0.70*

It should be noted that this is not a true *validation* of the general utility of these rating curves because the data used to create the rating curves was also used to perform the evaluation. However, these rating curves are still useful as a way to predict the expected TSS concentration at times that TSS was not measured manually during this study, which was most of the time.

The rating curves for discharge and ABS_{corr} based on samples taken during all seasons were used to estimate sediment values for the entire sampling period (October 2011-September 2013). Estimated and measured values of TSS (and TP, see below) are shown in Figs. B.1-B.8 in Appendix B. Relationships for seasonal data were not pursued further as the "all seasons" relationship provided reasonable estimates.

Estimating Phosphorus Concentration

We developed rating curves for total dissolved phosphorus (TDP), particulate phosphorus (PP), and total phosphorus (TP = TDP + PP) concentrations versus ABS_{corr}, and discharge following a similar approach to the one described for TSS above (Table 5, Figure 6, and Appendix C). We used seasonal relationships for this analysis because the seasonal equations explained more of the variation in the data. There is no *a priori* reason to expect that total dissolved phosphorus should be related ABS_{corr}, which is based on particle characteristics in the water. However, for the sake of completeness we provide the relationships of total dissolved phosphorus and particulate phosphorus to ABS_{corr} and discharge, in Appendix C. For the purposes of this report we use the total

phosphorus data (dissolved plus particulate) as the best measure of the amount of phosphorus moving in the river. The non-linear nature of the data in Fig. 6b is noted. However, as for the log(TSS) data in Fig. 4b, we found the other transformations of the data did not yield improved explanations (higher r^2) or better predictions (lower RSME) of the TP data.

Table 5 Rating curve equations and r-squared values for log total phosphorus versus discharge and log total phosphorus versus ABS_{corr}. The probability of the slope being significantly different from zero ($p<0.05$) and of the regression equation being significant ($p<0.05$) is denoted by a *.

Variable	**Slope**	**Intercept**	**r^2**	**Duan's correction**	**Number of samples**
		Winter			
Discharge	0.004*	2.17	0.65*	1.14	23
ABS	0.045*	-0.38	0.84*	1.05	23
		Spring			
Discharge	0.002*	2.06	0.14*	1.19	104
ABS	0.034*	0.11	0.55*	1.09	104
		Summer			
Discharge	0.003*	2.23	0.59*	1.10	72
ABS	0.028*	0.73	0.67*	1.07	72
		Fall			
Discharge	0.004*	2.08	0.40*	1.13	118
ABS	0.035*	0.28	0.58*	1.10	118
		All seasons			
Discharge	0.003*	2.11	0.39*	1.17	317
ABS	0.033*	0.34	0.55*	1.12	317

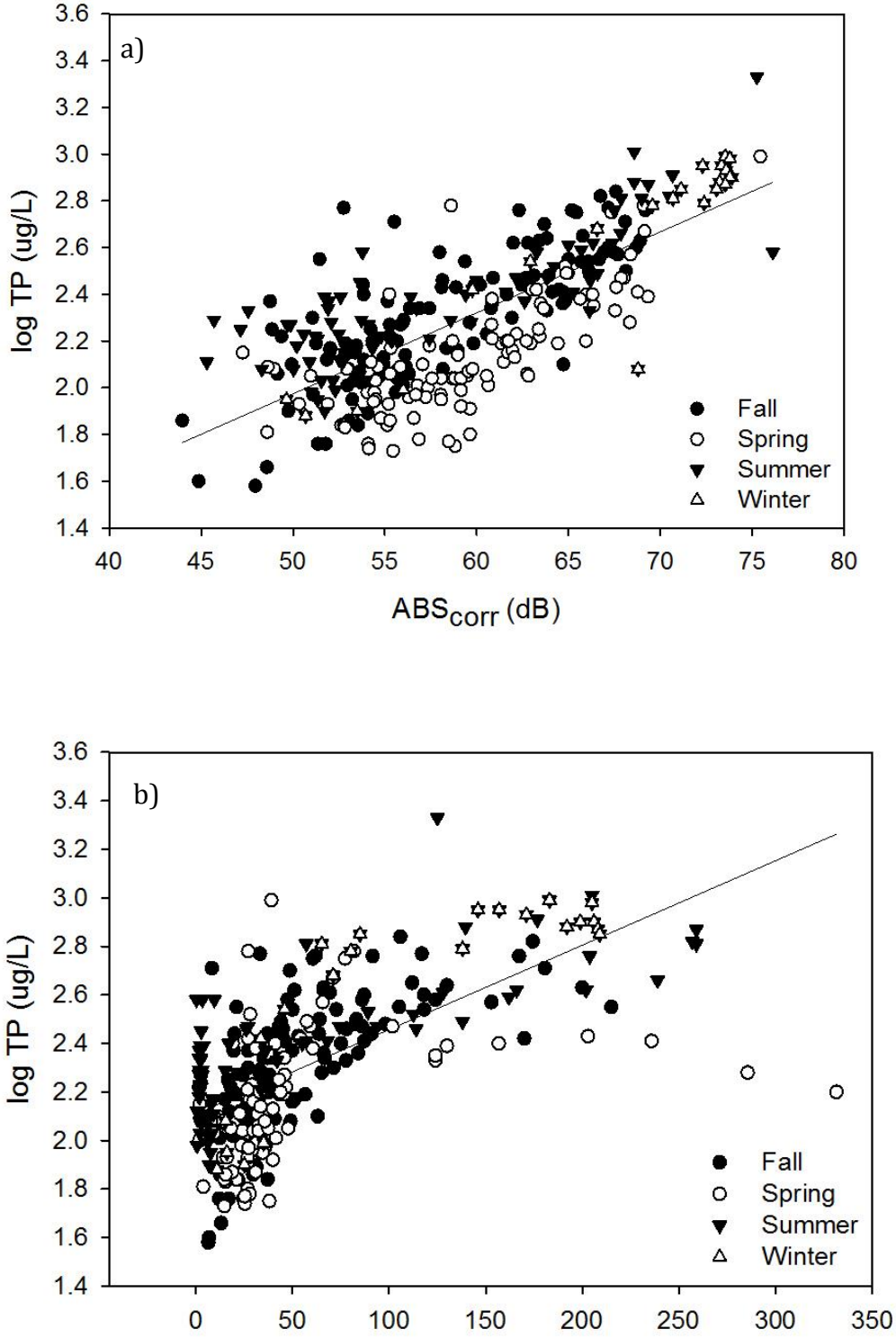

Figure 6 a) Log(TP) versus ABS_{corr} and b) Log(TP) versus Discharge by season. The line is Fig. 3a is the "all seasons" regression.

The estimated phosphorus concentrations were plotted against the measured phosphorus in each season, in an approach similar to that described for TSS above (Figure 7). As for TSS we found that estimated TP was lower than measured TP at higher values of measured TP. The estimated TP based on the ABS_{corr} values was more accurate than the estimate based on discharge.

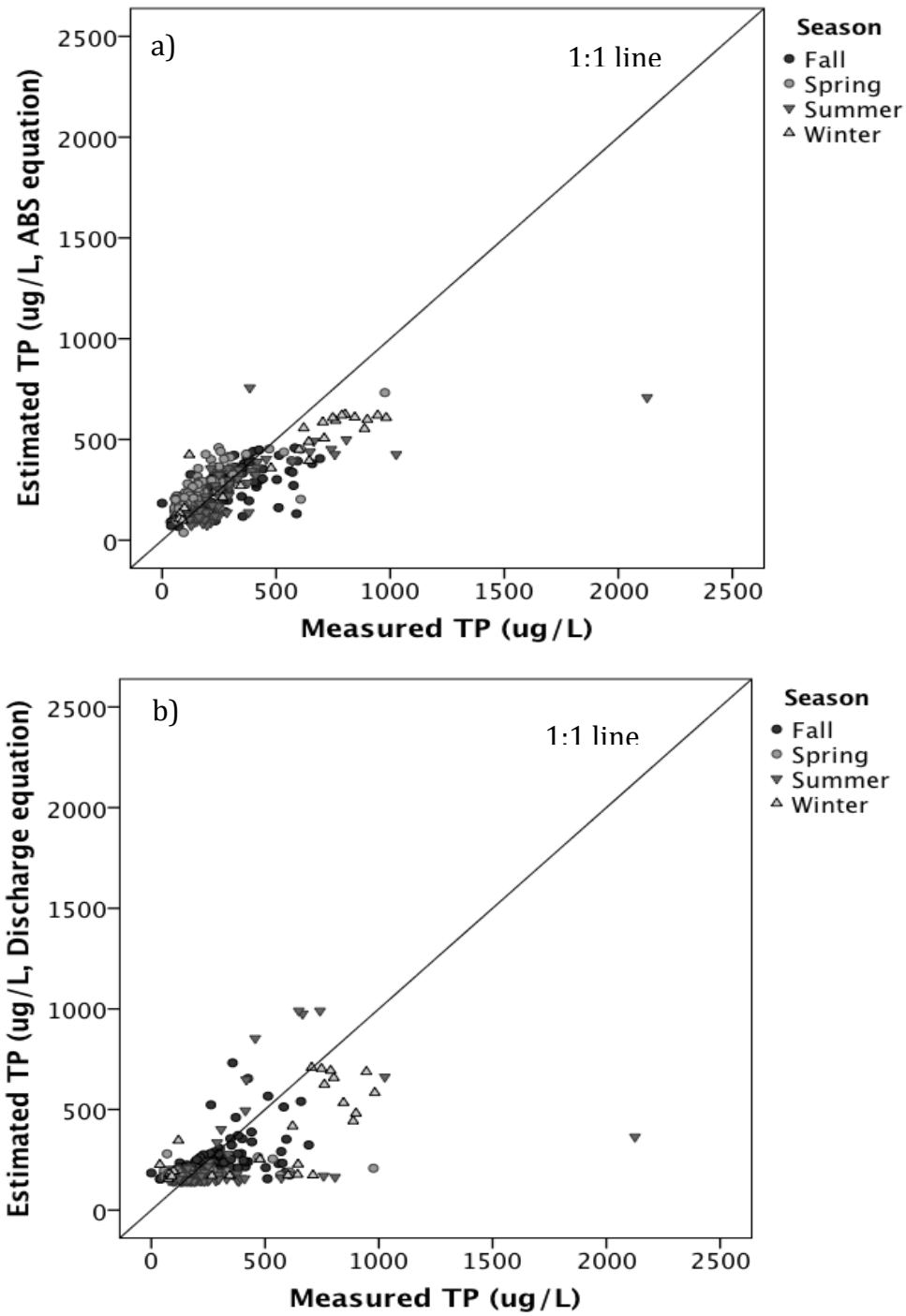

Figure 7 Estimated total phosphorus versus measured phosphorus using a) ABS_{corr} equation and b) discharge equation for estimations

As explained above for TSS, the rating curves for discharge and ABS_{corr} based on samples taken during all seasons were used to estimate TP values for the entire sampling period (October 2011-September 2013), plotted in Figure 7 with 1:1 lines. Regression analysis of estimated TP versus measured TP is shown in Table 6.

Table 6 Regression analysis of TP estimated (Q) v. TP measured and TP estimated (ABS) v. TP measured. All analysis were significant (p<0.05) as indicated by *.

Variable	Slope	Intercept	r^2
TP estimated (Q)	0.36	134.00	0.34*
TP estimated (ABS)	0.63	93.95	0.67*

Estimated and measured values of TP (as well as TSS, TDP and PP) are shown in Figs. B.1-B.8 in Appendix B. Typically the estimates of TP based on ABS_{corr} tended to follow changes in the measured values of TP better than the estimates of TP based on discharge.

Storm Events

Previously (Bowden et al. 2012) we noted that hysteresis complicates the analysis of sediment and phosphorus transport. A single storm from each season was plotted to look more closely at patterns of sediment and phosphorus throughout the rising and falling limbs of the event. Precipitation data for South Hero, Vermont was downloaded from the Climate Data Online database from NOAA. Storms selected were from 24-28 March 2013 (Winter, Figure 8), 16-22 April 2013 (Spring, Figure 9), 9-13 September 2013 (Summer, Figure 10), and 1-8 October 2012 (Fall, Figure 11). The winter storm of March 2013 was due snowmelt as temperatures rose rather than from direct precipitation.

Measured sediment and phosphorus concentrations can change significantly during the course of a storm event (Figures 8a, 9a, 10a, 11a). Furthermore, we often observed more complicated patterns in which ABS_{corr} and discharge followed more intricate – but not random – patterns, suggesting the possibility that sediment and TP concentrations during storm events might be more dynamic than we have previously imagined. The values of TSS and TP calculated based on the ABS_{corr} data followed the measured values fairly well, although the peak calculated was often lower than the peak measured value. This difference can also be seen in the measured versus calculated TSS and TP plots (Figures 4 and 7).

Often, the ABS_{corr} values increased slightly ahead of discharge on the rising limb of the storm (Figure 8b, 9b, 10b, 11b). The precipitation data that is available is daily data, so it cannot be determined how closely the change in ABS_{corr} or discharge relates to the timing of the precipitation. We suspect that the ABS_{corr} values follow precipitation closely, possibly due to rain erosion from stream banks, with a lag in the increase in discharge.

Different values of sediment or phosphorus at the same discharge value on the ascending and descending limb of the hydrograph sometimes create a hysteresis loop (Figure 8c, 9c, 10c, 11c). Hysteresis complicates analysis of sediment and phosphorus loading during individual storms. However, because we were able to analyze numerous storm events over the course of a season we were able to build significant relationships between the ABS_{corr} data and the sediment and phosphorus concentrations

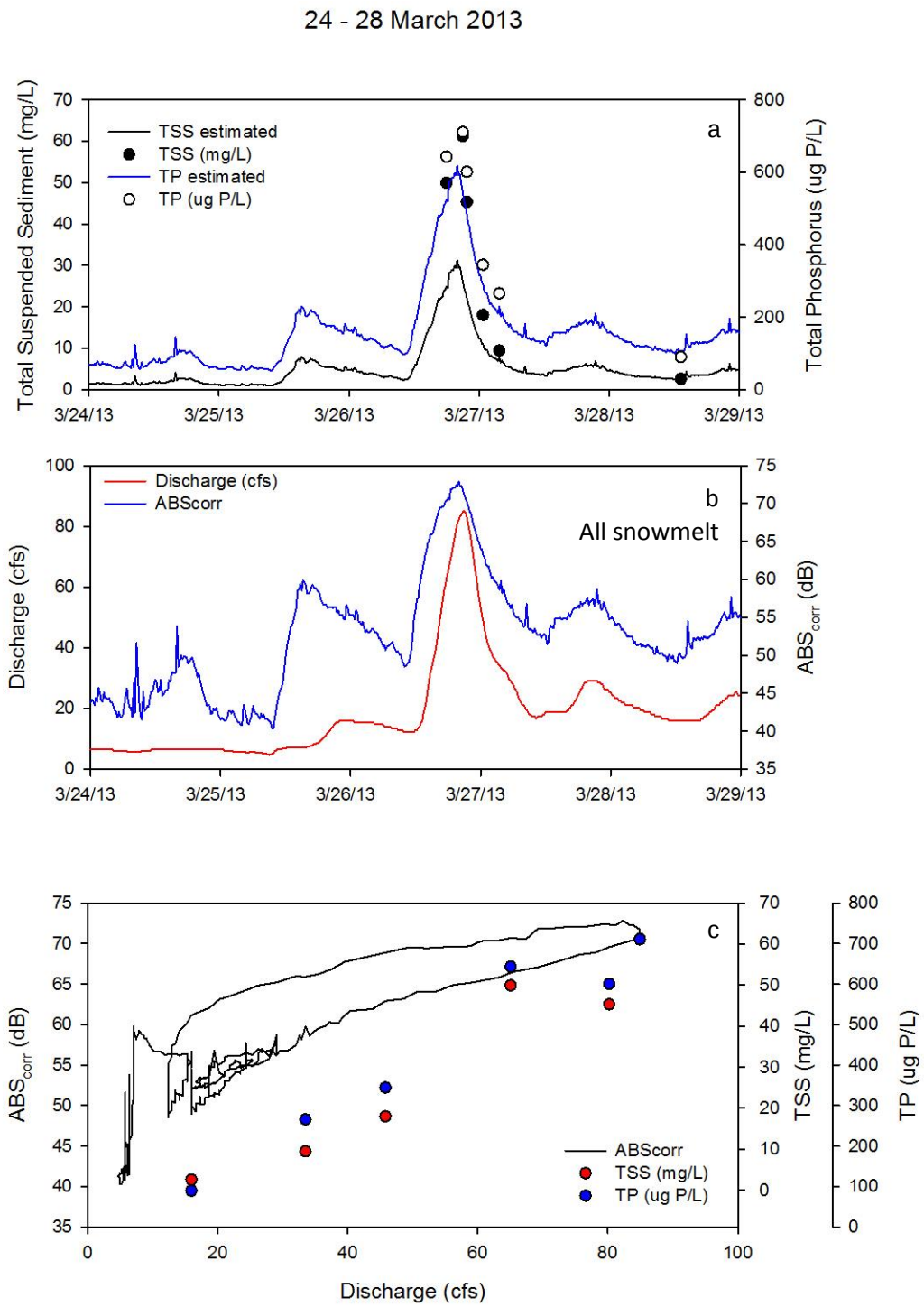

Figure 8 Increased discharge event due to snowmelt, 24-28 March 2013: a) Samples for sediment and phosphorus were collected during the peak and falling limb of the event, and followed a similar pattern of the estimated TSS and TP values; b) the discharge and ABS_{corr} hydrograph; c) ABS_{corr} versus discharge, creating a hysteresis loop due to different ABS_{corr} values at the same discharge value on the rising and falling limb of the event.

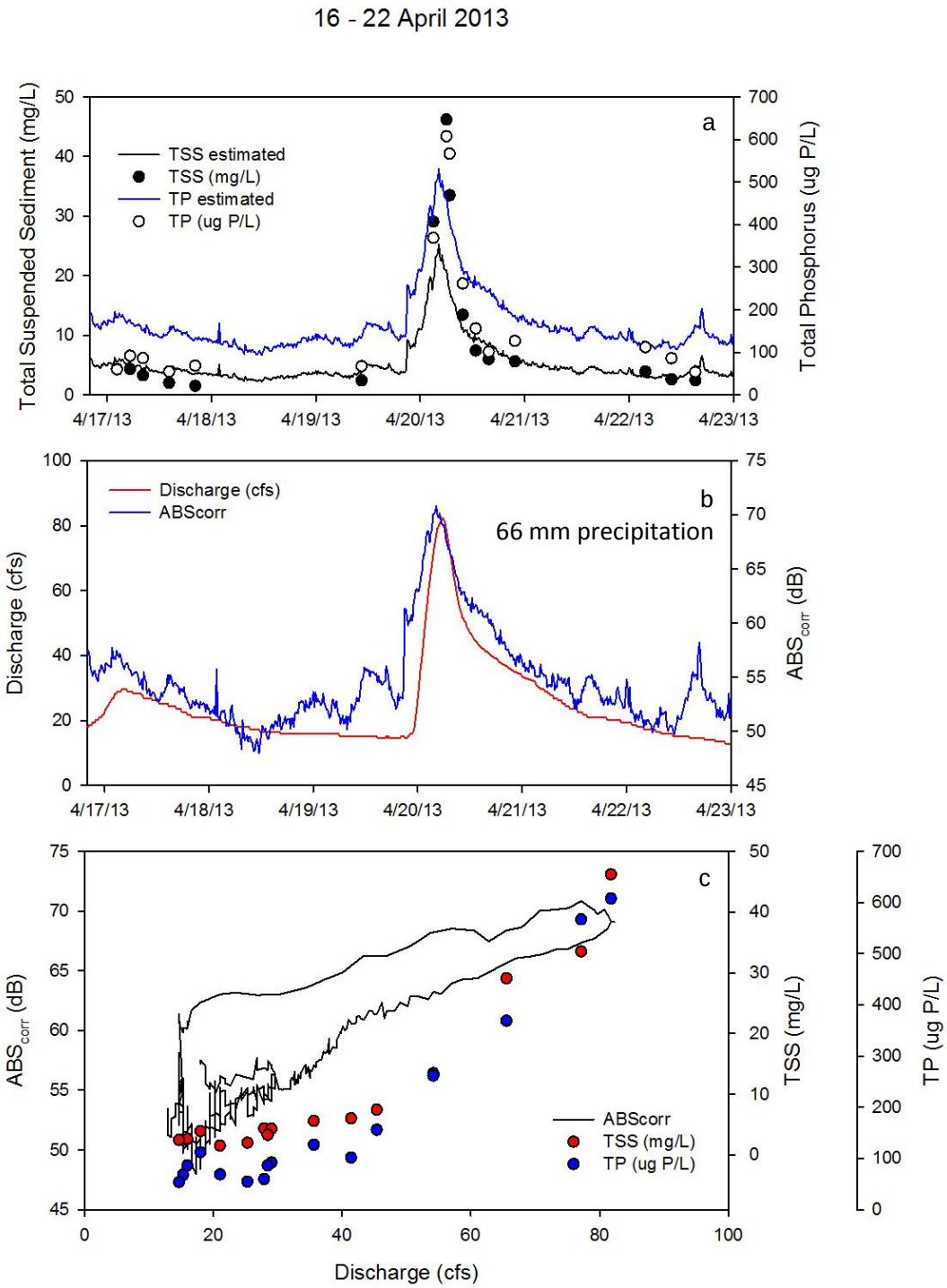

Figure 9 Increased discharge event due to snowmelt, 16-22 April 2013: a) Samples for sediment and phosphorus were collected during the peak and falling limb of the event, and followed a similar pattern of the estimated TSS and TP values; b) the discharge and ABS_{corr} hydrograph; c) ABS_{corr} versus discharge, creating a hysteresis loop due to different ABS_{corr} values at the same discharge value on the rising and falling limb of the event.

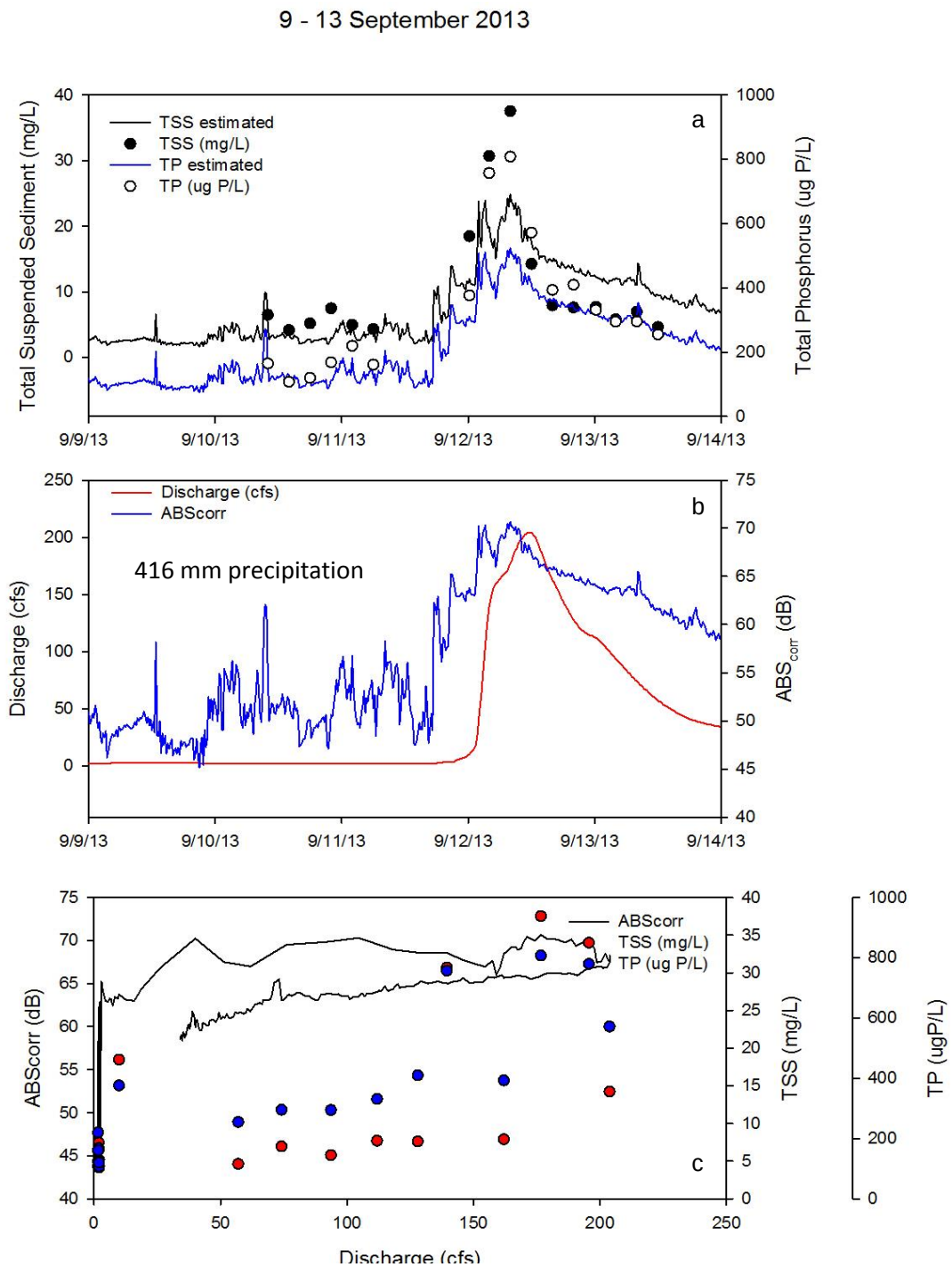

Figure 10 Increased discharge event due to snowmelt, 9-13 September 2013: a) Samples for sediment and phosphorus were collected during the peak and falling limb of the event, and followed a similar pattern of the estimated TSS and TP values; b) the discharge and ABS_{corr} hydrograph; c) ABS_{corr} versus discharge, creating a hysteresis loop due to different ABS_{corr} values at the same discharge value on the rising and falling limb of the event.

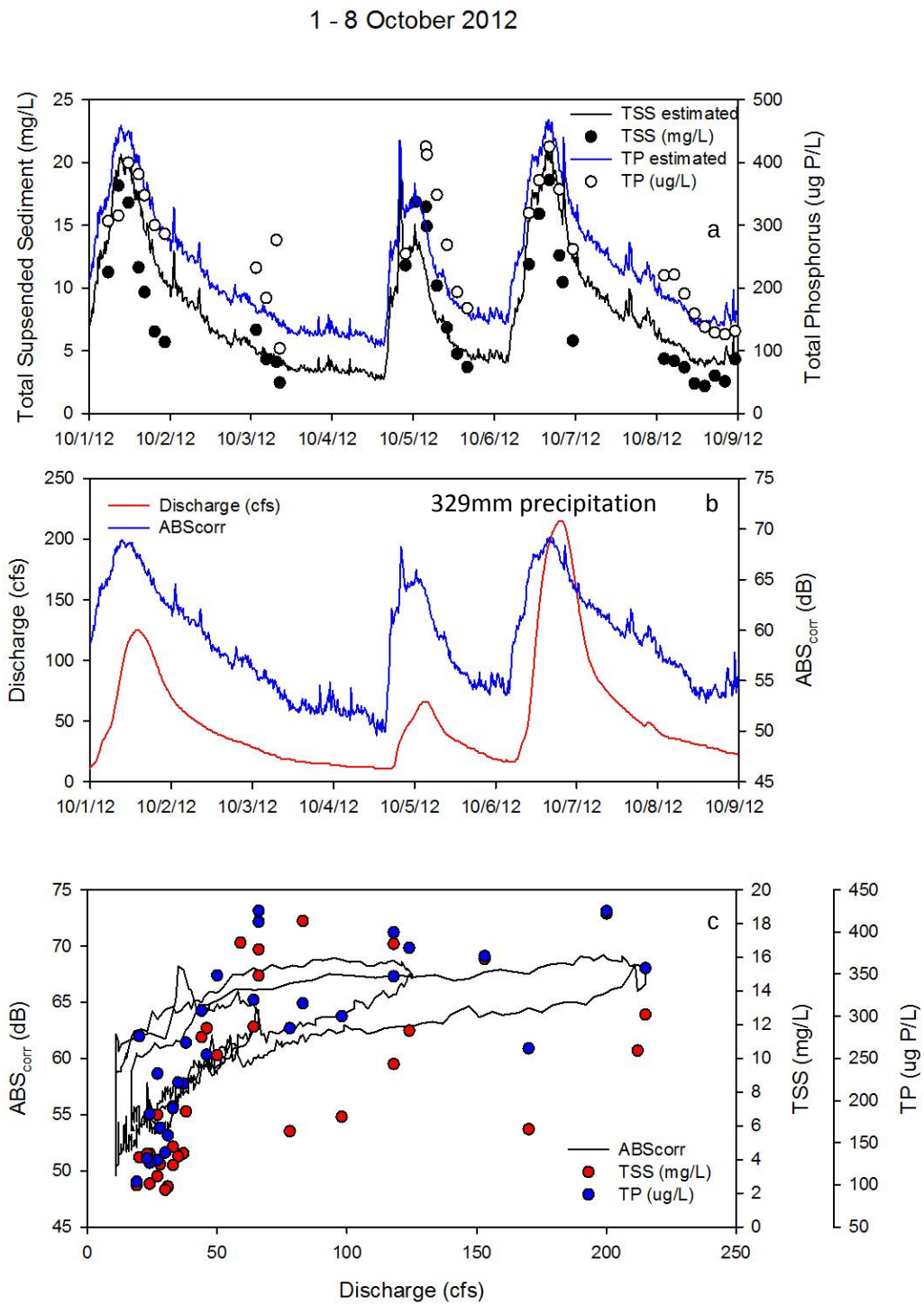

Figure 11 Increased discharge event due to snowmelt, 1 – 8 October 2013: a) Samples for sediment and phosphorus were collected during the peak and falling limb of the event, and followed a similar pattern of the estimated TSS and TP values; b) the discharge and ABS_{corr} hydrograph; c) ABS_{corr} versus discharge, creating a hysteresis loop due to different ABS_{corr} values at the same discharge value on the rising and falling limb of the event.

Discussion

ADCP instruments are being used more frequently to measure discharge in streams and have been shown to provide useful information about suspended sediment concentrations. We extended this application to estimate TP concentrations, which are typically strongly related to TSS in our rivers. We first developed rating curves from manually collected samples to estimate the amount of sediment. In our sediment analysis, we also measure loss on ignition, which provides information about the amount of organic matter present. The rating curves for loss on ignition data were more variable, especially in spring and summer, when more organic matter may be present in these streams after snowmelt and during agricultural management operations in these watersheds.

We found that the ABS_{corr} data from the ADCP provided better estimates of TSS and TP than could be produced from a relationship based on discharge. These estimates should still be used with caution as a large portion of the variability in the data was unexplained in the regression model. But we observed that estimates of TSS and TP based on ABS_{corr} more closely resembled the pattern of changes in measured TSS and TP than those based on discharge. Previously, we might have interpreted the variation in these TSS and TP samples as some combination of sampling and analytical error when in fact, they may indicate real and important patterns in TSS and TP that are only partially related to discharge. For example, bank failures upstream might cause a temporary increase in TSS and TP without any appreciable difference in discharge. This type of random variation in concentration would not be evident from infrequent, manual, grab sampling.

The linear regression model we developed to estimate total phosphorus based on ABS_{corr} explained over half of the variability in the seasonal TP data, with slopes that were significantly different from zero ($p<0.05$ for all seasons). Estimates of total phosphorus load could be obtained in either of two ways. First, we could estimate TP indirectly using the estimate of TSS and a separate estimate of the relationship between TP and TSS. However, both of these relationships are inherently uncertain and so multiplying them multiplies the uncertainty. Alternatively, we could estimate TP directly using the relationship between TP and ABS_{corr}. We used the latter approach in this analysis.

The state of Vermont used discharge and manual samples from the same time period as this analysis to estimate TP load, using the FLUX model, method 6. Their estimate of the phosphorus load during the experiment period was 6,359 kg TP, with a confidence interval of 4,911-8,234 kg. Our estimated TP load using the discharge-based regression equation for TP concentration multiplied by the recorded discharge was 6,493 kg, which is remarkably close to the load estimated from the FLUX model. Using the regression between TP concentration and ABS_{corr} and calculating in a similar manner, we calculate a load of 5,200 kg of TP over the experiment period, which falls within the confidence interval of the FLUX model estimate. Statistically we cannot distinguish among these calculated values. Furthermore, the load estimate based on ABScorr data may be artificially low due the bias observed at high values of measured TP (Fig. 7a).

The estimates of TP loading based on the FLUX model, discharge, and the ADCP ABS_{corr} data are similar. Although we cannot easily estimate a confidence limit around the ABS_{corr} regression estimate, it is unlikely that this value is significantly different from the other estimates presented in this report. Tentatively, therefore, we conclude that it may be possible to estimate the TP load from ADCP data without having to deploy field teams or automated samplers to take manual samples which then have to be analyzed by costly and laborious analytical procedures. Clearly, there is a cost to install and maintain ADCPs and some field sampling would seem prudent to verify that ADCP-derived estimates of TP concentrations are reasonable. However, we think these early results are encouraging. Specifically, data from ADCPs may provide a reliable and defensible estimate of TP load at a cost that might not be any greater than manual-based sampling – and that might be lower if integrated over time. As an added benefit, the ADCP-based estimates of TSS and TP concentrations may reveal short-term dynamics in these water quality variables that have been missed by intermittent grab sampling and that could be important in understanding how these rivers behave during rapidly change discharge events.

Acknowledgements

This project was supported by funding from the Vermont Department of Environmental Conservation and by funding from USGS Section 103.b funds made available to the Vermont Water Resources and Lake Studies Center. We thank Joshua Benes and Elizabeth Elmstrom for assisting with sample collection and analysis, SUNY-Plattsburgh for use of the Mastersizer 3000 for particle size analysis, Laura Medalie for assistance with calculations of acoustic backscatter, and Dr. Jamie Shanley as liaison with USGS. The conclusions expressed in this report are those of the authors and should not be attributed to either the Vermont Department of Conservation or the USGS.

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Appendix A: Storm and Baseflow Samples

Grab samples were collected by the Friends of Northern Lake Champlain during the same sampling period for this study (Fall 2011 – Fall 2013), during storm events and at baseflow. Samples were only collected once per day, but some storms have multiple samples if the storm extended over several days.

Season	Number of Storms	Storm event samples	Baseflow samples	Total Samples
Winter	4	17	22	39
Spring	5	12	14	26
Summer	1	5	8	13
Fall	11	24	9	33
Total	21	58	35	93

Samples collected using an ISCO autosampler were able to capture more samples during a single storm event. A discharge threshold of about 25 ft^3/s was used to trigger the ISCO sampler to begin to collect samples for a storm event. The FNLC and BWRL data sets represent a similar number of storms, but many more samples were collected during each individual storm by the ISCO sampler used in the this (BWRL) study, representing more complete characterization of each storm hydrograph.

Season	Number of Storms	Storm event samples	Baseflow samples	Total
Winter	2	19	5	24
Spring	9	82	33	115
Summer	4	28	51	79
Fall	10	106	36	142
Total	25	235	125	360

Appendix B: Seasonal TSS and TDP, PP, and TP Estimate Figures

All estimates were created from the described equations. These figures show mean daily estimates as related to the actual discharge and ABS_{corr} values. Measured TSS, TDP, PP, and TP values are also mean daily values. The y-axis was always set at zero, despite ABS_{corr} or estimated values being below zero because it is not physically possible for those values to be negative. The ABS_{corr} value was most often negative in winter, when the river was frozen over, or during summer low flows because the beam spreading created a negative slope across the bins.

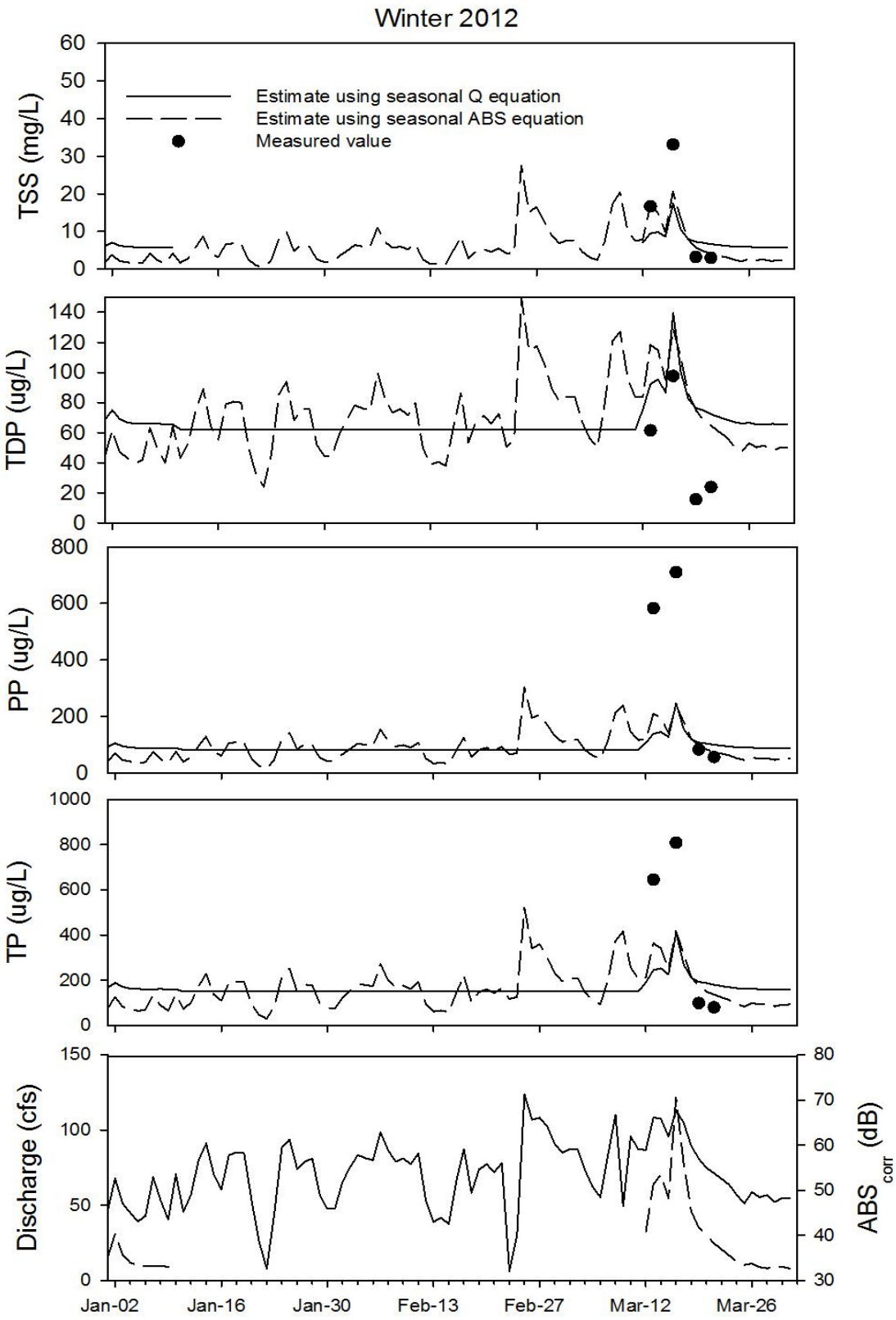


Figure B.1 Winter 2012 estimates of TSS, TDP, PP, and TP using ABS_{corr} and discharge equations

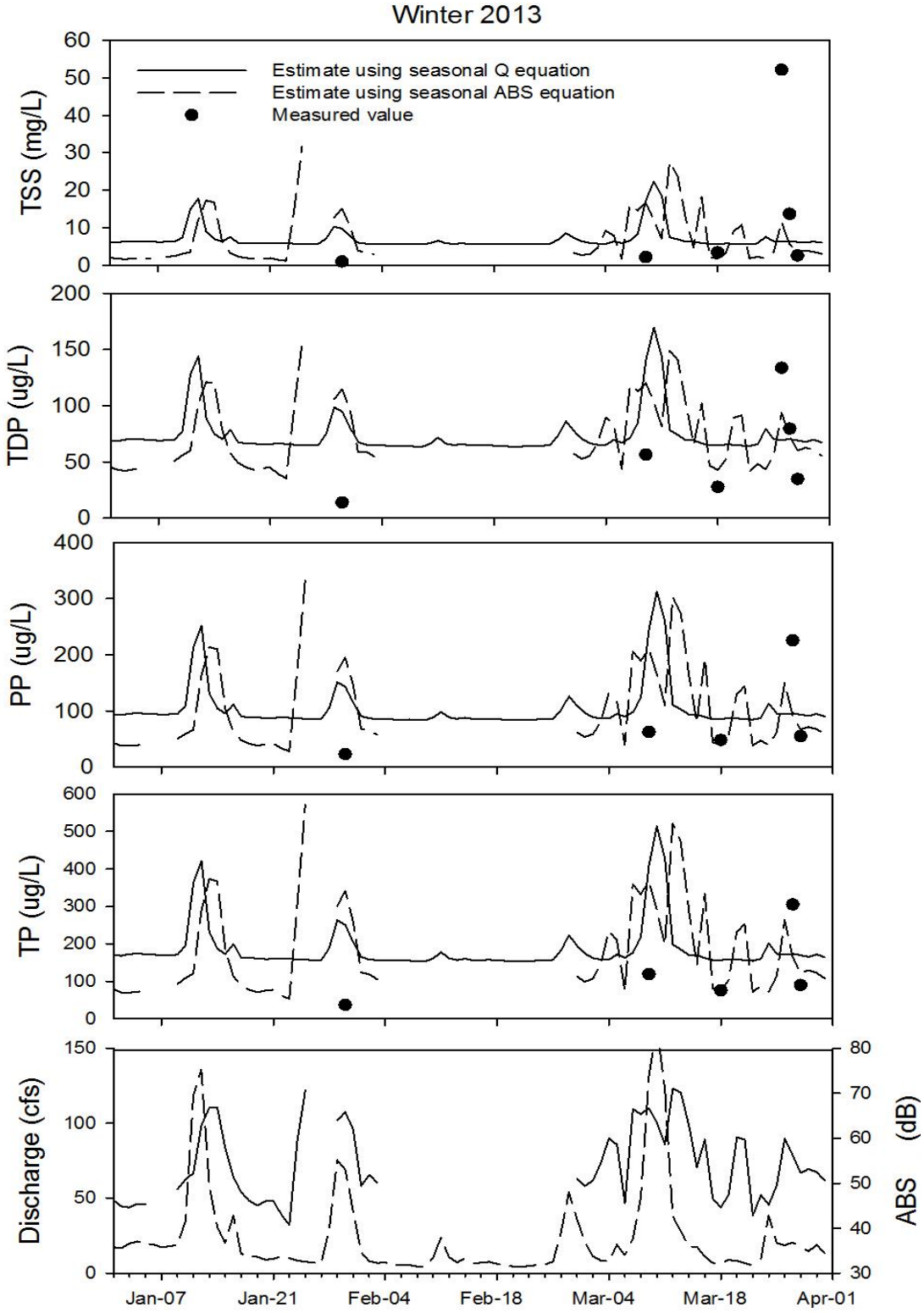


Figure B.2 Winter 2013 estimates of TSS, TDP, PP, and TP using ABS_{corr} and discharge equations

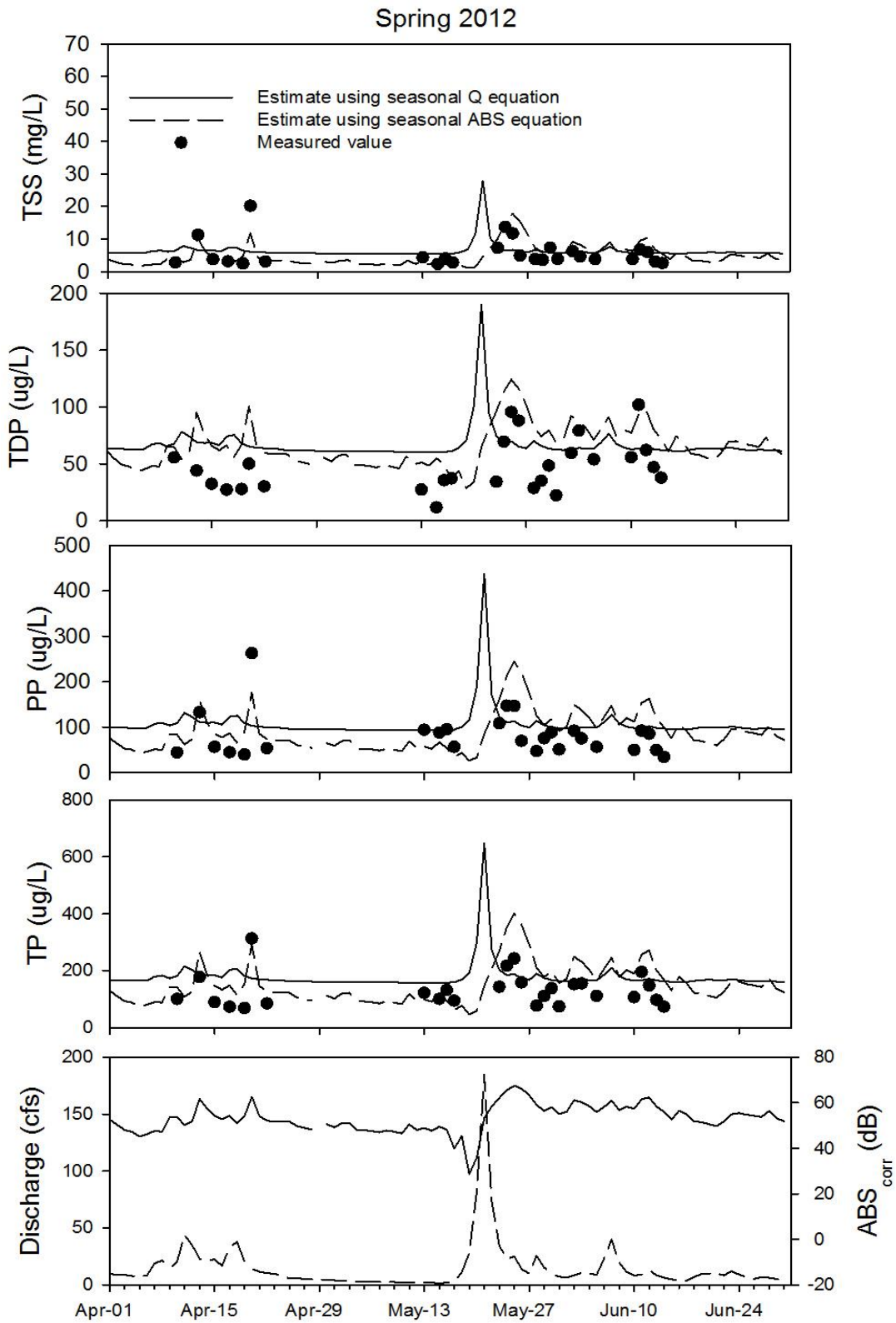


Figure B.3 Spring 2012 estimates of TSS, TDP, PP, and TP using ABScorr and discharge equations

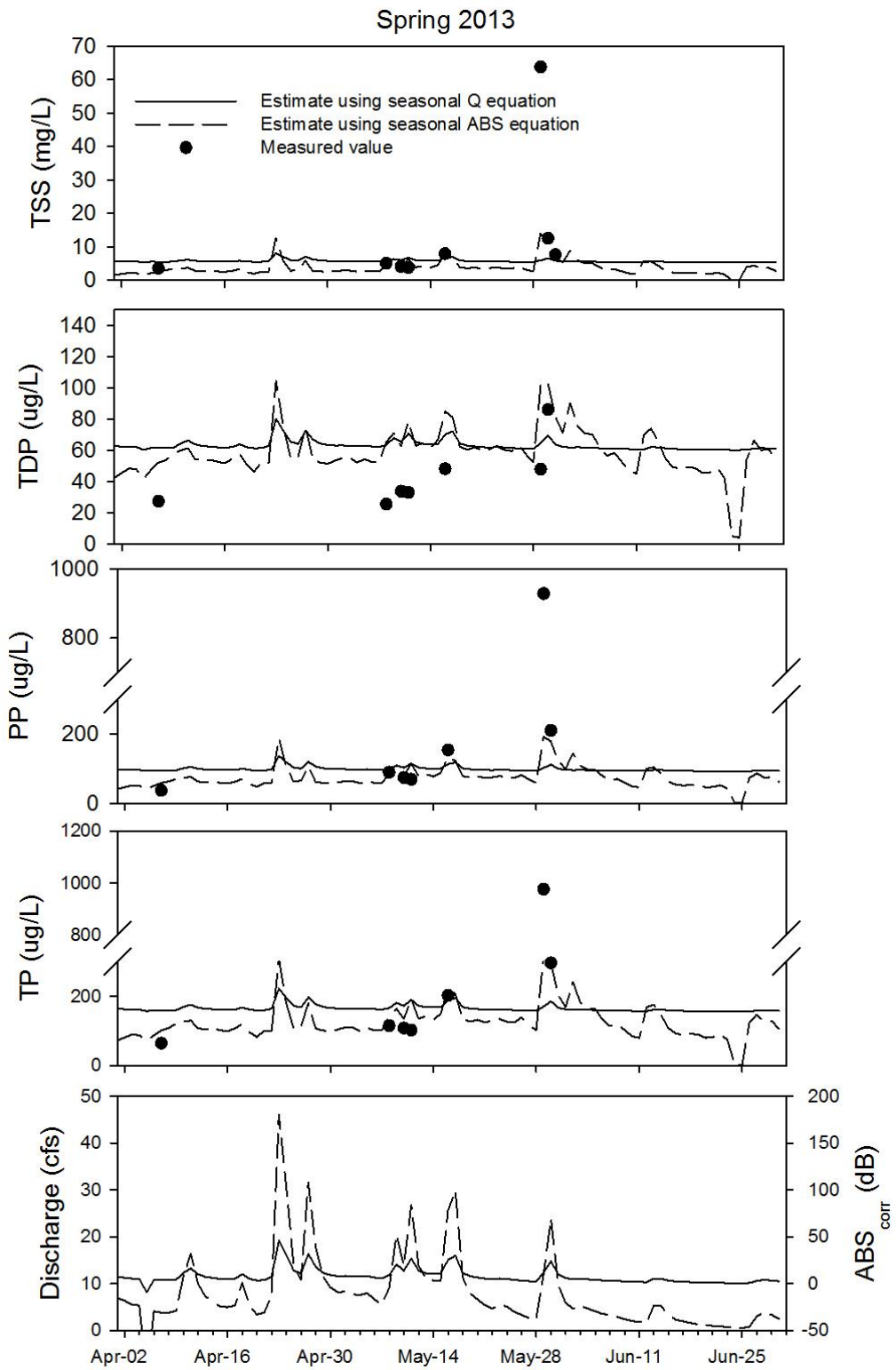


Figure B.4 Spring 2013 estimates of TSS, TDP, PP, and TP using ABS_{corr} and discharge equations

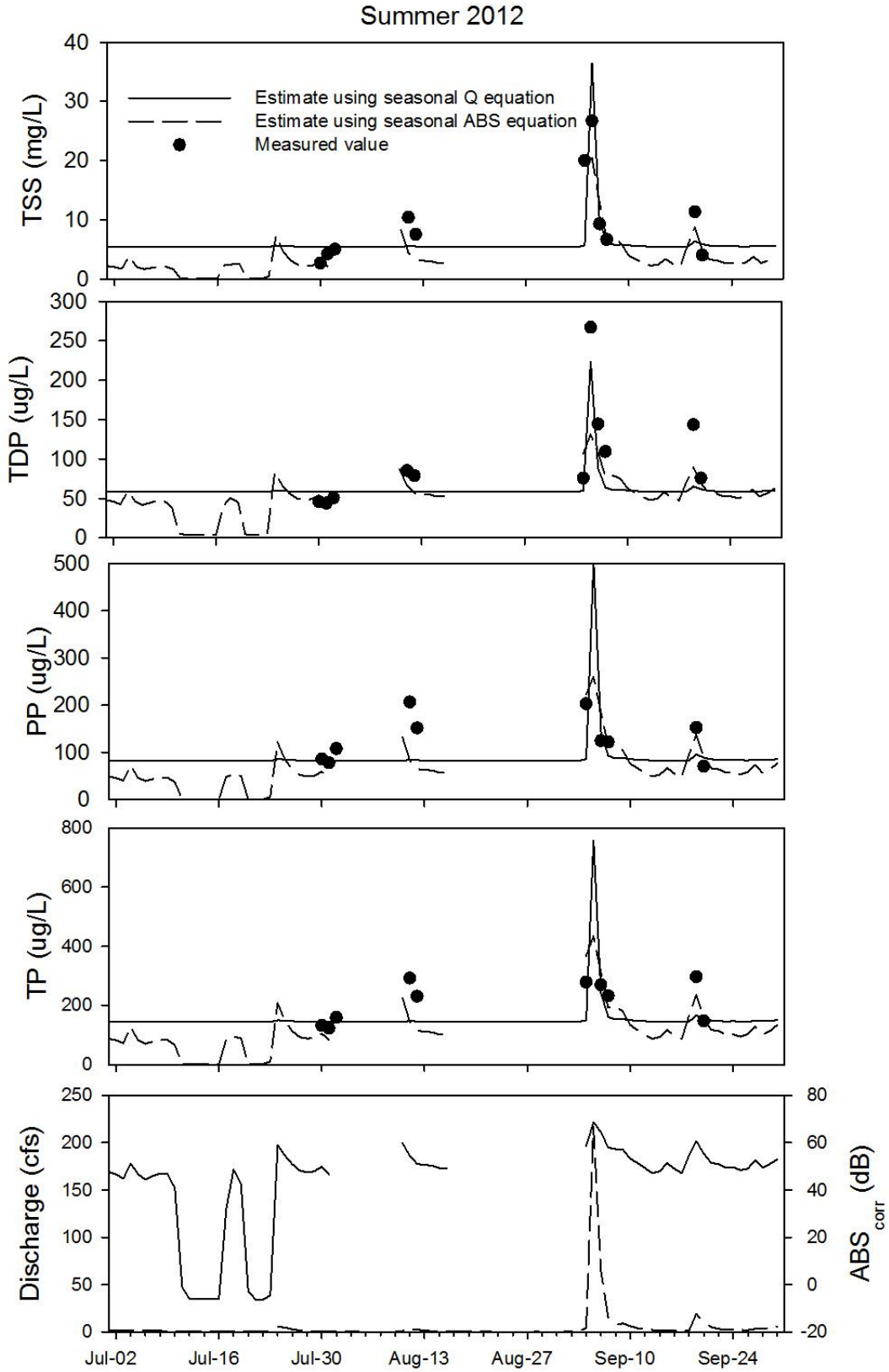


Figure B.5 Summer 2012 estimates of TSS, TDP, PP, and TP using ABS_{corr} and discharge equations

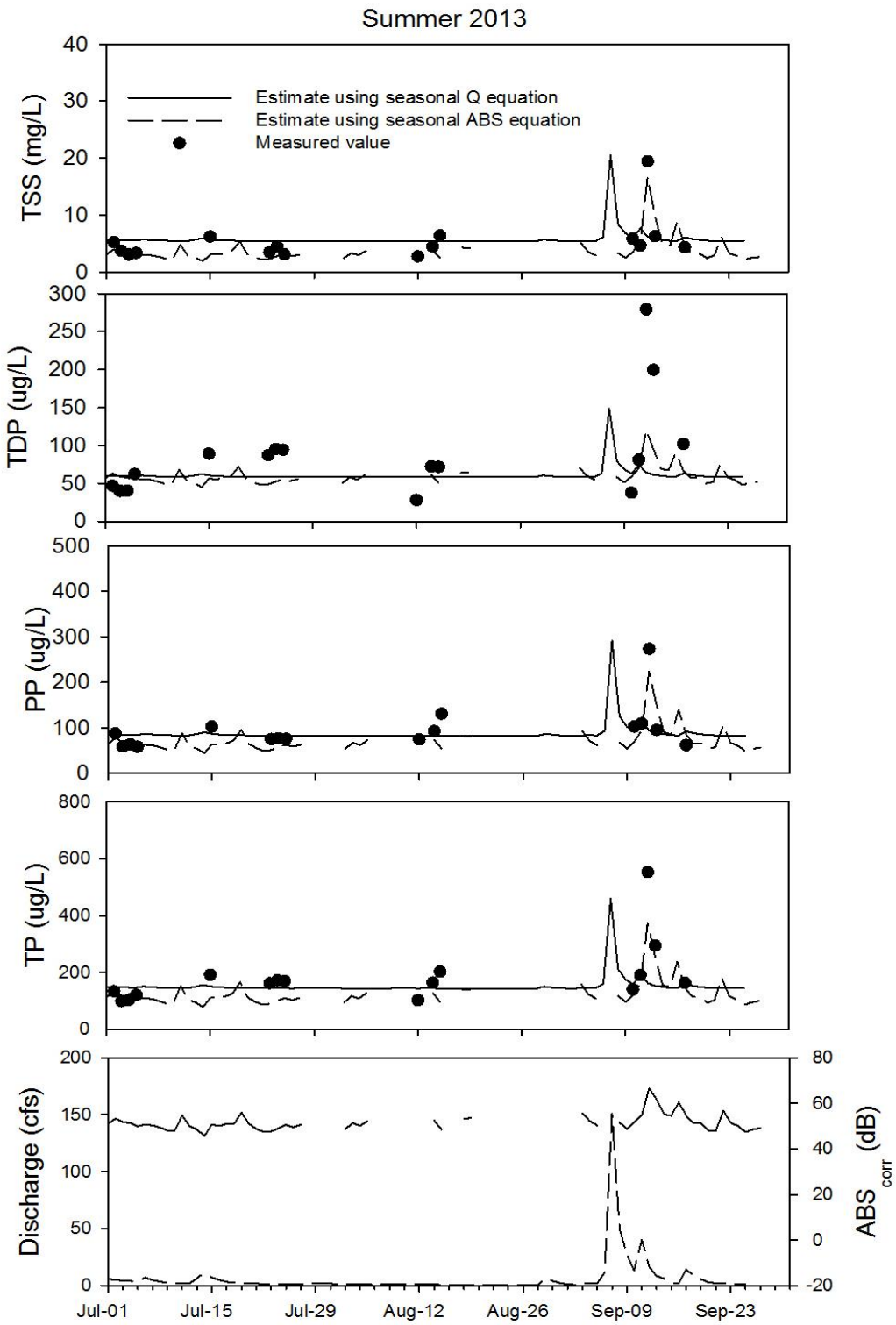


Figure B.6 Ssummer 2013 estimates of TSS, TDP, PP, and TP using ABS_{corr} and discharge equations

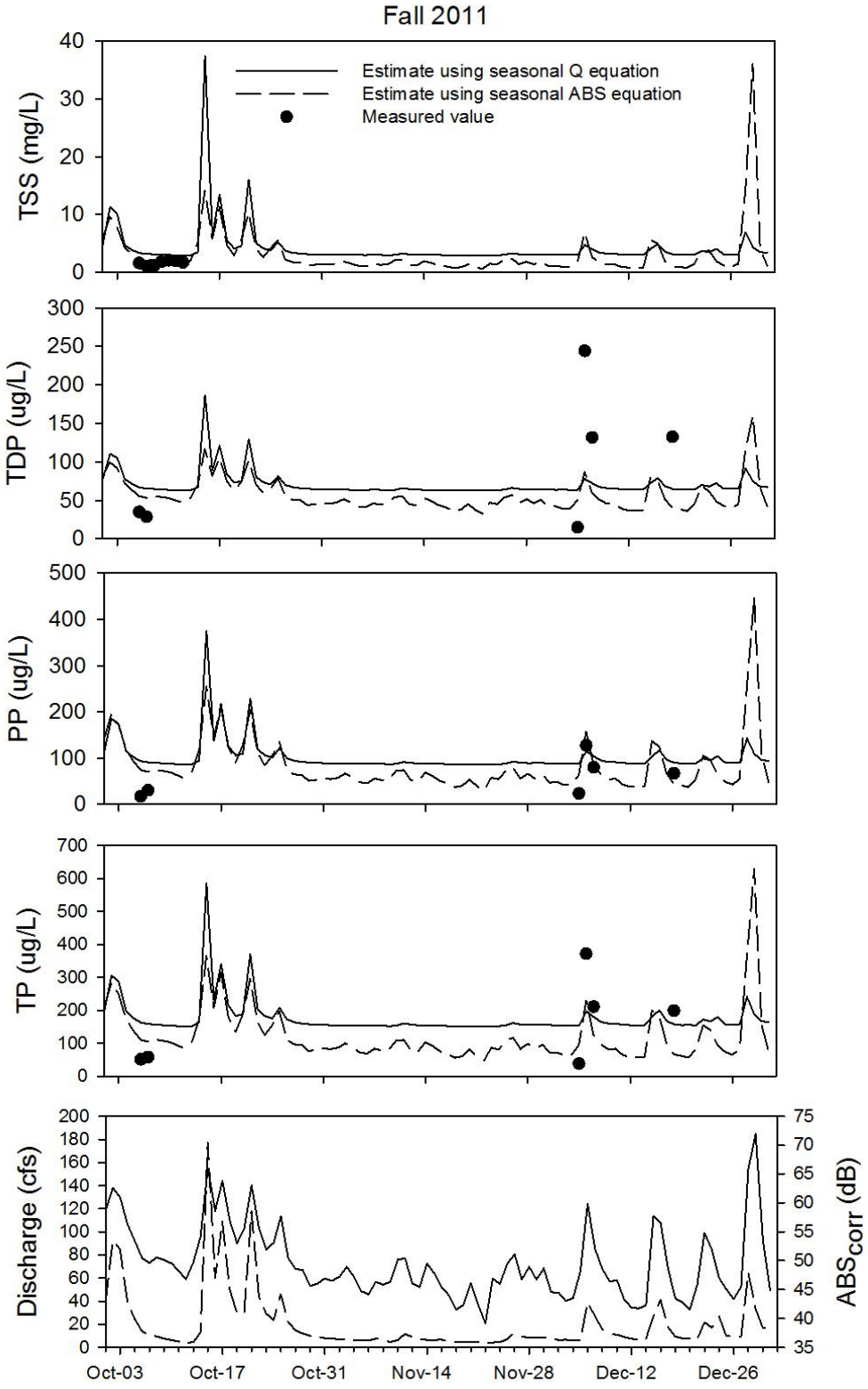


Figure B.7 Fall 2011 estimates of TSS, TDP, PP, and TP using ABS_{corr} and discharge equations

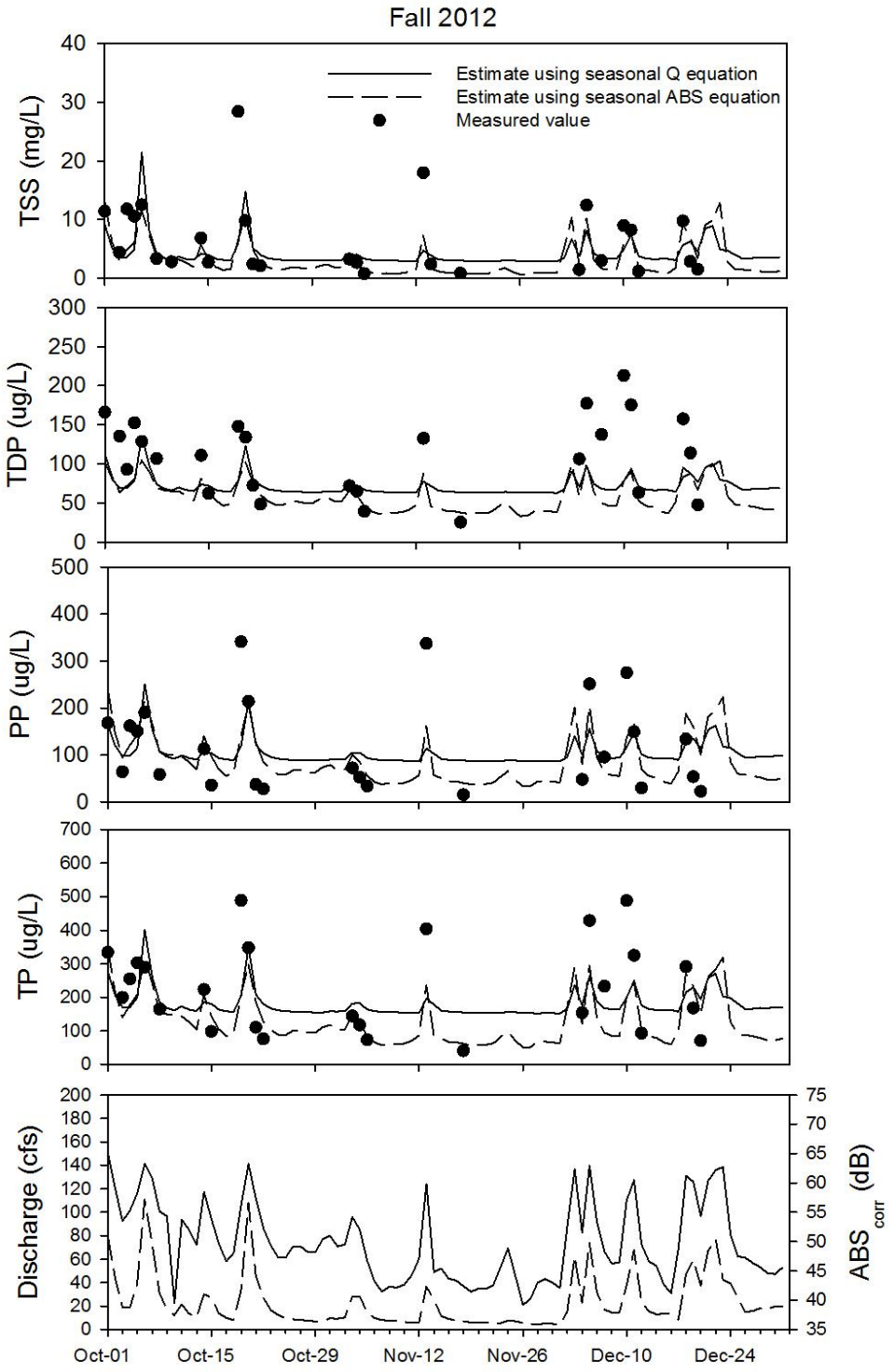


Figure B.8 Fall 2012 estimates of TSS, TDP, PP, and TP using ABS_{corr} and discharge equations

Appendix C: Total Dissolved and Particulate Phosphorus results

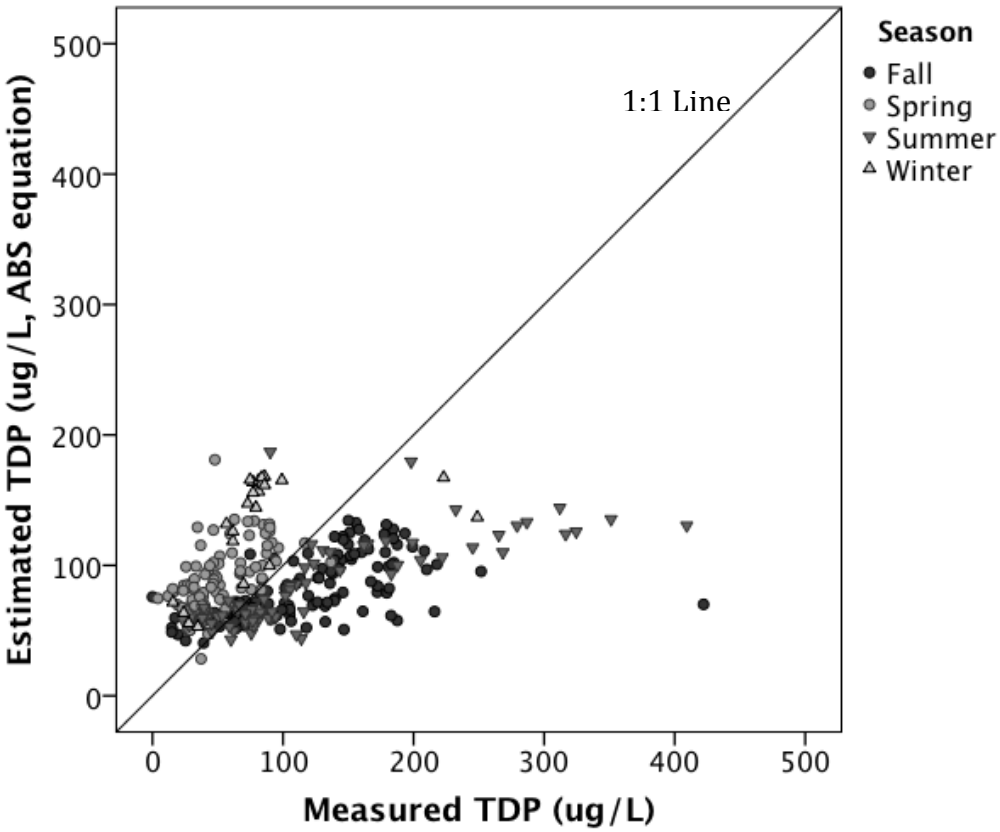
Samples were analyzed for total dissolved phosphorus (TDP) and particulate phosphorus (PP); these two concentrations were summed for total phosphorus. Data was analyzed using linear regression for TDP and PP, in the same manner as for TSS and TP. The TDP and PP regressions were not used in estimating phosphorus loads. All regressions were significant, however, ABS_{corr} did not always explain more variability than discharge for either TDP or PP, as was the case for TSS and TP.

Table C.1 Rating curve equations and r-squared values for Discharge v. log dissolved phosphorus and ABS_{corr} v. log dissolved phosphorus. The probability of the slope being significantly different from zero ($p<0.05$) and of the regression equation being significant ($p<0.05$) is denoted by a *.

Variable	**Slope**	**Intercept**	**r^2**	**Duan's correction**	**Number of samples**
		Winter			
Discharge	0.002*	1.62	0.33*	1.15	23
ABS	0.024*	0.20	0.54*	1.10	23
		Spring			
Discharge	0.002*	1.55	0.20*	1.11	104
ABS	0.022*	0.31	0.28*	1.09	104
		Summer			
Discharge	0.003*	1.83	0.67*	1.07	71
ABS	0.030*	0.25	0.62*	1.09	71
		Fall			
Discharge	0.003*	1.85	0.25*	1.13	121
ABS	0.028*	0.40	0.44*	1.10	121
		All seasons			
Discharge	0.003*	1.73	0.25*	1.31	319
ABS	0.021*	0.65	0.21*	1.20	319

Table C.2 Rating curve equations and r-squared values for Discharge v. log particulate phosphorus and ABS_{corr} v. log particulate phosphorus. The probability of the slope being significantly different from zero ($p<0.05$) and of the regression equation being significant ($p<0.05$) is denoted by a *.

Variable	Slope	Intercept	r^2	Duan's correction	Number of samples
		Winter			
Discharge	0.005*	2.01	0.65*	1.19	23
ABS	0.050*	-0.82	0.81*	1.07	23
		Spring			
Discharge	0.002*	1.91	0.06*	1.35	114
ABS	0.038*	-0.29	0.44*	1.18	114
		Summer			
Discharge	0.002*	1.99	0.36*	1.20	72
ABS	0.025*	0.67	0.47*	1.14	72
		Fall			
Discharge	0.06*	1.63	0.45*	1.22	137
ABS	0.030*	0.20	0.43*	1.36	137
		All seasons			
Discharge	0.004*	1.83	0.31*	1.19	346
ABS	0.034*	0.00	0.49*	1.31	346



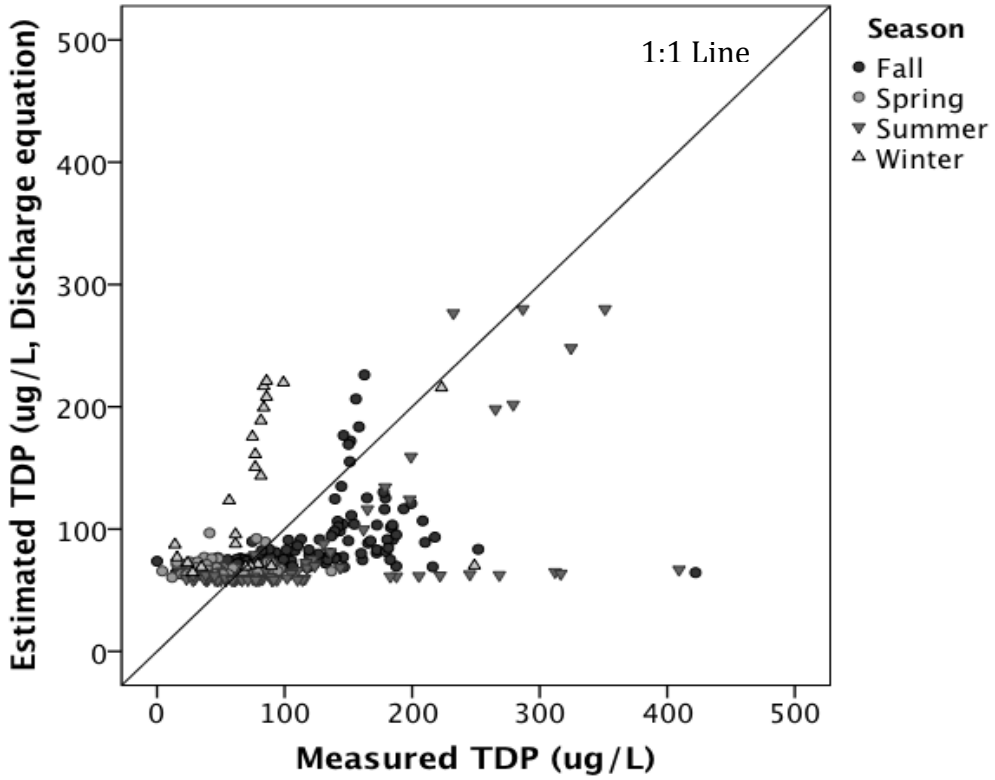


Figure C.1 Estimated TDP versus Measured TDP using ABS_{corr} and discharge estimate equations

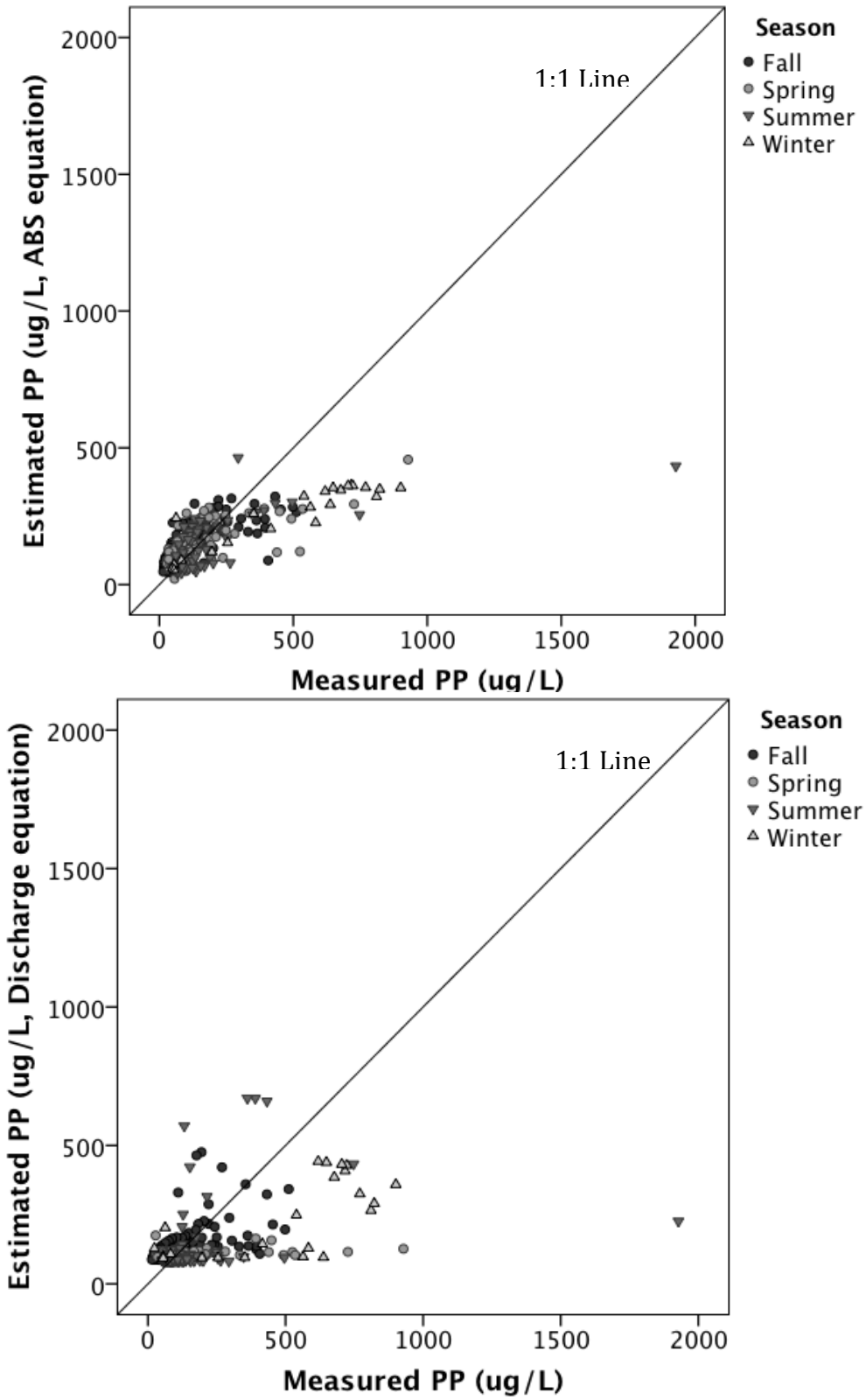


Figure C.2 Estimated Particulate Phosphorus versus Measured Particulate Phosphorus using ABS_{cor} and discharge estimating equations

Table D.1 Regression analysis of TSS v. Discharge or ABS_{corr}, transformed using log or square root transformation. All relationships were significant ($p<0.05$) as indicated by *.

	Regression analysis	Slope	Intercept	r^2
Discharge	log TSS v. log Q	0.323	0.316	0.211*
	sqrt TSS v. log Q	0.064	0.38	0.32*
	sqrt TSS v. sqrt Q	0.22	1.34	0.30*
ABS_{corr}	log TSS v. log ABS	6.16	-10.11	0.63*
	sqrt TSS v. log ABS	0.70	-4.61	0.64*
	sqrt TSS v. sqrt ABS	2.46	-16.12	0.58*

Table D.2 Regression analysis of various transformation TP and Q or ABS

	Regression analysis	Slope	Intercept	r^2
Discharge	log TP v. log Q	0.27	1.90	0.25*
	sqrt TP v. log Q	0.05	1.94	0.40*
	sqrt TP v. sqrt Q	1.04	8.21	0.42*
ABS_{corr}	log TP v. log ABS	4.42	-5.53	0.52*
	sqrt TP v. log ABS	0.50	-1.59	0.54*
	sqrt TP v. sqrt ABS	9.46	-57.72	0.54*