


Coupling of reactive riverine phosphorus and iron species during hot transport moments: impacts of land cover and seasonality

Braden D. Rosenberg · Andrew W. Schroth 

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Abstract Spring runoff often comprises the majority of annual discharge and riverine phosphorus (P) export due to sustained high flow, and the magnitude of spring runoff can be a strong predictor of receiving water summer harmful algal bloom severity. Yet the loading of reactive forms of P during this time period remains poorly-characterized in time, space and geochemical partitioning. Here, we explore the hypothesis that riverine dissolved and suspended sediment P loads during spring runoff have a particularly high proportion of potentially reactive species due to unique hydrologic pathways and P association with iron (Fe). The concentration, distribution and temporal dynamics of dissolved P (DP), dissolved and colloidal Fe, and redox sensitive suspended sediment P (RSP) and Fe during spring runoff and summer storms were compared in forested and agricultural catchments of the same watershed. The dominant carrier of RSP was Fe (oxy)hydroxides across land cover and season, but Fe (oxy)hydroxide particles and

colloids in agricultural catchments were strongly enriched in RSP and DP during spring runoff and summer storms, particularly at the onset of snowmelt. In 2014, 83% of DP and 74% of RSP were delivered to Missisquoi Bay during spring runoff. Suspended sediment was significantly more redox sensitive than typically input to limnological models, suggesting that the reactivity of this load may be systematically underestimated. Changes in the timing, provenance and severity of spring runoff associated with climate or land cover change will have dramatic impacts on total riverine P loads and their potential reactivity in receiving water ecosystems.

Keywords Iron · Phosphorus · Snowmelt · Spring runoff · High flow events · Seasonality · Suspended sediment · Nutrient loading · Eutrophication

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B. D. Rosenberg · A. W. Schroth (✉)
Department of Geology, University of Vermont, 180
Colchester Ave., Burlington, VT 05405, USA
e-mail: Andrew.Schroth@uvm.edu

Present Address:

B. D. Rosenberg
The Cadmus Group Inc., 100 5th Ave., Waltham, MA 02451,
USA

Introduction

High flow events are known to be important drivers of riverine loading of both dissolved and suspended sediment forms of nutrients and pollutants to receiving water bodies, as these events deliver much of the annual water budget in temperate climates (Barnett et al. 2005; Shanley et al. 2002). The increased erosion and river discharge associated with these events

contribute a disproportionately large amount of sediment, nutrients, and when present, contaminants to annual riverine loads (Richards et al. 2008; Su et al. 2011; Zhu et al. 2012). In addition, the activation of specific flowpaths during periods of increased flow may result in a biogeochemically distinct load compared to baseflow, in terms of the reactivity of suspended sediment as well as the concentration and size distribution of nutrients and metals (Bayard et al. 2005; Gburek and Sharpley 1998; Sebestyen et al. 2008). However, it is notoriously difficult to sample rivers that are, in many cases, inaccessible at high discharge and/or predict the magnitude and duration of these events, especially when bulk grab samples are needed to characterize suspended sediment.

The geochemistry of riverine loads is clearly impacted by season (Adhikari et al. 2010; Beaulieu et al. 2012; Dupas et al. 2015), particularly in systems where spring is characterized by high discharge and prolonged snowmelt. The spring runoff period, comprised of both snowmelt and frequent rain events, in catchments in northern forests delivers up to 75% of the annual water in less than 25% of the year (Gburek and Sharpley 1998; Shanley et al. 2002). The snowmelt period may also have a unique biogeochemistry, as materials that accumulate in and below the snowpack are flushed out of the system prior to extensive uptake, transformation, or sequestration by senescent local vegetation. Frozen/saturated soils promote surface and shallow subsurface flow during melting (Bayard et al. 2005; Sebestyen et al. 2009; Shanley and Chalmers 1999), so riverine geochemistry is disproportionately influenced by the land surface and upper soil horizons. Numerous studies have linked snowmelt to unique riverine geochemistry in terms of DOC (Dawson et al. 2008; Sebestyen et al. 2008), nitrogen (Pellerin et al. 2012; Sebestyen et al. 2009), phosphorus (Jamieson et al. 2003; Ontkian et al. 2005; Royer et al. 2006), and trace metals (Dahlqvist et al. 2007; Rember and Trefry 2004). While the spring runoff period is characterized by sustained high discharge and associated runoff/shallow subsurface flow, summer in temperate climates such as Vermont is characterized by baseflow conditions with intermittent storm events (Shanley et al. 2002). During this time, the activation of runoff/shallow subsurface flow paths is dependent on the duration and magnitude of specific storms and antecedent

conditions (e.g., soil moisture); unsaturated soils may not promote abundant runoff and associated mobilization of surface materials (Kollet and Maxwell 2006). As such, summer riverine geochemistry may be influenced more by deeper flow paths, riparian zones, and baseflow geochemical processes than pooling of material and processes within the upper soil profiles (Fisher et al. 2004; Lapworth et al. 2009).

Watershed loading of nutrients and contaminants is often partitioned into solute and sediment fluxes that differ in their fate and reactivity in the environment. As a nutrient, phosphorus (P) is considered readily bioavailable as dissolved orthophosphate (PO_4^{3-}). Excessive loading of dissolved P has been linked to eutrophication in rivers and receiving water bodies (Michalak et al. 2013; Yuan et al. 2013), and is derived from both point-sources (wastewater treatment, sewage and industrial effluent) and diffuse sources (e.g., agricultural runoff) (Van Drecht et al. 2009). Non-point sources and runoff are of particular interest to this study, as the export of DP is known to differ across land covers, particularly that of agricultural (Hansen et al. 2004; Jamieson et al. 2003; Walter et al. 2001) and forested (Edwards and Withers 2007; Meyer and Likens 1979) catchments. In addition, the tight cycling of metal species, particularly Fe and Mn, has been shown to be important in the cycling, transport, and fate of P in some systems (Baken et al. 2015a; Lijklema 1980). As Fe and Mn are ubiquitous components of natural soils, the export of metals from river systems is well studied (e.g., Pokrovsky et al. 2006; Schroth et al. 2011; Stolpe et al. 2013), but the interaction of different Fe and Mn size fractions with P during high flow events and across land covers has not been explored. This is critical, as recent studies found that redox cycling of Fe has a strong control on P mobility at the surface–groundwater interface in some environments (Baken et al. 2015b; van der Grift et al. 2014), suggesting the transport and fate of P may be closely related to the size distribution and speciation of Fe.

Given extensive erosion during high flow events, a relatively high fraction of many constituents are associated with suspended sediment (Dhillon and Inamdar 2013; Walling et al. 2008). Sediment mobilized from the land surface and stream bed during high flow events is an important control on downstream water quality through the delivery of nutrients and

contaminants associated with suspended sediment (Walter et al. 2001; Withers and Jarvie 2008). The dramatic differences in biogeochemical reactivity of sediment from different source environments is well documented in soils and sediment literature (e.g., Abdala et al. 2015; Hansen et al. 2004), but is rarely considered in watershed studies of suspended sediment, nor when estimating loads. Of particular interest are Fe/Mn (oxy)hydroxides, which are very effective scavengers of oxyanions such as phosphate as a result of surface charge and surface area (Delgado and Scalenghe 2008; van der Grift et al. 2014). These metal (oxy)hydroxides develop within the soil and river system depending on redox conditions and pH (Baken et al. 2015a; van der Grift et al. 2014) and are highly susceptible to reductive dissolution in suboxic to anoxic environments (Baken et al. 2015b; Lovley et al. 2004). Dissolution results in the release of adsorbed P, making Fe/Mn (oxy)hydroxides a dominant internal P source to receiving waters that reach an/hypoxic sediment water interface conditions (Smith et al. 2011; Schroth et al. 2015; Giles et al. 2016). More recalcitrant forms of sediment also exist, but are less likely a dominant source of nutrients, as dissolution occurs much more slowly in most natural systems and stability may not be impacted by redox dynamics (e.g., apatite-derived P). While high flows increase sediment loads, the biogeochemical nature and ramifications of that sediment for receiving waters may differ across land covers, particularly between agricultural and forested environments (Owens and Walling 2002; Walling et al. 2008).

In this study, our objective is to examine the reactivity and form of P and Fe in high flow events associated with spring runoff in comparison to high flow events during the summer after vegetation across the landscape becomes active. We analyze the behavior and association of different fractions of P and Fe during these hot transport moments in agricultural and forested catchments to examine land cover impacts on high flow event geochemistry in the Lake Champlain Basin, and how this changes or is similar within and across the seasons. To our knowledge, we are the first study to examine the relationship between reactive P and Fe species in the context of ‘redox sensitivity’, which is critical to understanding the potential impact of spring runoff and summer storm hot moments on eutrophication issues that plague the receiving water body, Lake Champlain.

Methods

Field sites and sampling design

Sampling locations, located in northern Vermont within the Missisquoi River watershed, drain into Lake Champlain at Missisquoi Bay (Fig. 1). The Missisquoi River watershed can be partitioned into regions of low and high elevation. The lowlands contain the majority of the Champlain Valley agricultural land, and higher elevations are primarily montane-forested catchments of the northern Green Mountains (Fig. 1). Throughout the lower elevations, much of the agriculture is concentrated near the river within floodplains. Individual monitoring locations were chosen to utilize pre-existing structure including gages and ISCO auto-samplers from USGS and NSF’s Vermont Experimental Program to Stimulate Competitive Research (EPSCoR). Two sampling locations are located on the Missisquoi River: the outlet at Swanton (OUT) and the uplands at North Troy (FOR); and two sites, located on tributaries in the sub-watersheds of Hungerford Brook (AGR) and Wade Brook (FOR), were selected as representative of agricultural and forested catchments that dominate the majority of the Lake Champlain Basin in the lowlands of the Champlain Valley and the Green Mountains respectively (Fig. 1). The sample location OUT provides an integrated biogeochemical and hydrologic signal of the entire watershed export and representative of what is delivered to Missisquoi Bay. Samples from Missisquoi River in North Troy and Wade Brook are grouped as FOR for discussion purposes to increase data available for that forested land cover, as both catchments have very similar land covers. Due to the level of consistency in concentrations between the two forested sites, they are aggregated as a single FOR site in all figures and load calculations for this report.

Our sampling program targeted high-flow events from the onset of snowmelt, during both temperature-driven melt and rain-on-snow events, to the end of the summer in 2014. Meteorological data and resulting forecasts of rising hydrographs at multiple sites helped design sampling strategies for days following above-freezing nights, and during or immediately after precipitation events (Fig. 2). Sampling in mid to late afternoon helped capture peak discharge typical of a

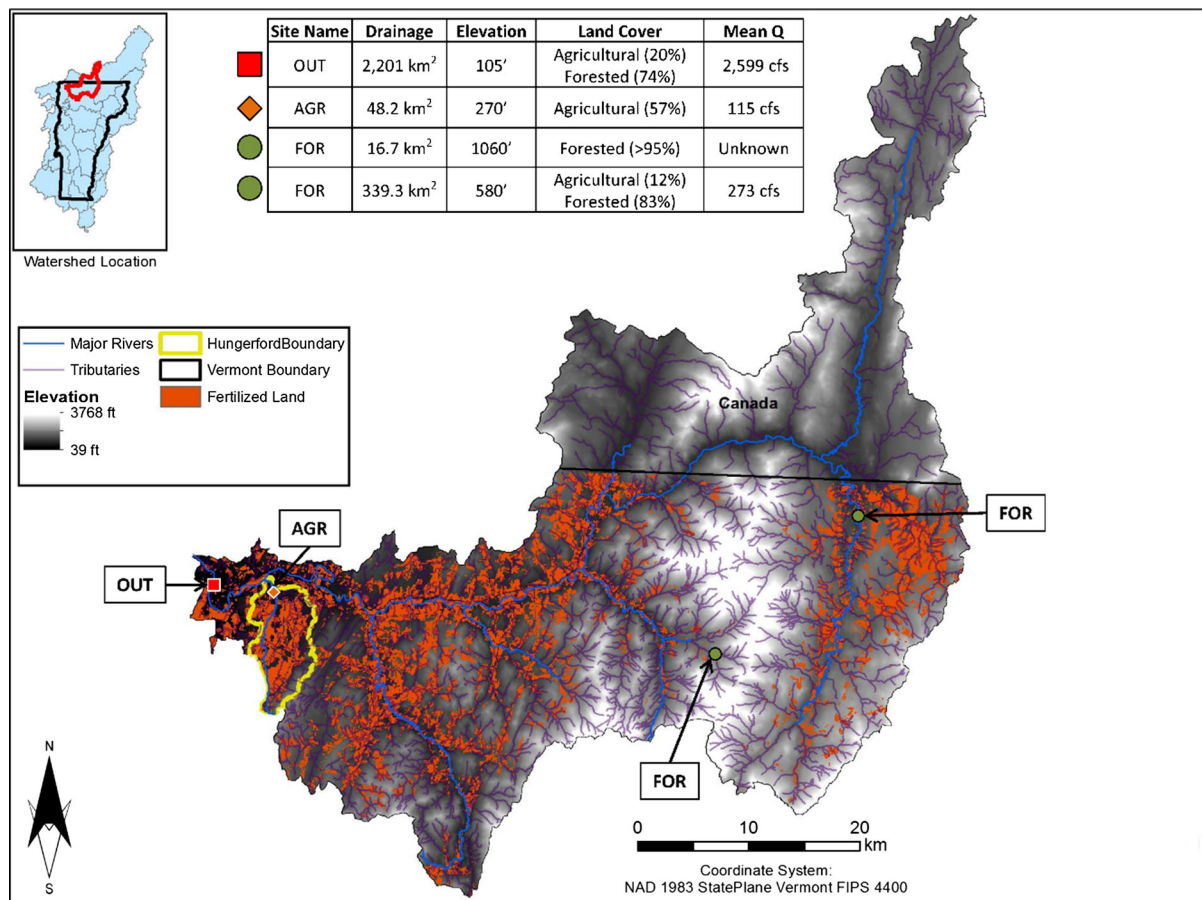


Fig. 1 Site locations and agricultural land within the Misisquoi Basin in Vermont. Major rivers and tributaries are shown for reference. Agricultural land was defined as either cultivated

crops or pasture/hay. The Hungerford Brook sub-catchment is highlighted for reference. (Color figure online)

snowmelt-driven hydrograph. The spring runoff period was defined as the onset of melt (3/28/2014) to the end of sustained high discharge and the growth of vegetation (5/2/2014). Following spring runoff, weekly to bi-weekly baseflow samples were collected, with targeted storm event sampling from May to September. Metals samples were collected in 250 mL acid-washed bottles from stream channel center using an acid-washed bucket sampling rig composed of a cleaned bucket and rope system suspended over culverts or bridges. Suspended sediment and SRP samples were collected in a 20 L acid-washed carboy using the same sampling rig, with care taken not to disturb channel bottom sediment.

Sample preparation and analysis

Sample splits for metals analysis were filtered in a laminar flow hood with 0.45 µm PES disposable filters and 0.02 µm Anotop[®] Plus nonsterile PES filters within 24 h of sampling and stored in 15 mL bottles soaked in trace metal grade HCl and rinsed with distilled de-ionized water following the method in Shiller (2003). After filtration, sample for trace metal (TM) analysis was acidified to 0.1% HNO₃ using Optima[®] ultra-pure concentrated nitric acid (Shiller 2003). Remaining unfiltered sample was also acidified to 0.1%. The acidified and filtered samples were analyzed by ICP-MS at Woods Hole Oceanographic

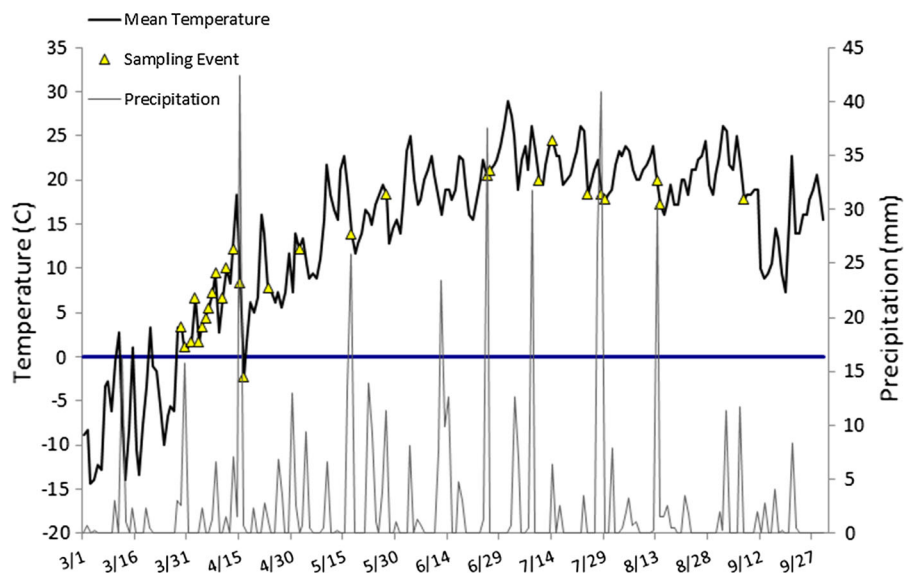


Fig. 2 Weather history from Burlington, VT within the Champlain Valley. Mean daily temperature and precipitation are shown with sampling events. No similar weather history was

available near our sampling locations, but the Burlington Airport weather is a good approximation for the Champlain Valley

Institution's plasma facility. A spike of Sc and In was used to calculate Fe and Mn concentrations for the <0.45 and <0.02 μm fractions (truly dissolved = <0.02 μm ; colloidal = 0.02 – 0.45 μm) (Shiller 2003). Because 0.02 μm filters leach P, only the <0.45 μm fraction for P was used, consistent with (Shiller 2003)'s observation. Filter contamination was checked using full process filtered blanks and was always less than 10% of the lowest concentration counts for each analyte measured. The international geostandard SLRS-4 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to validate daily ICP-MS runs, with material measured once for every 10 uncharacterized samples. Standard concentrations were used to calculate ICP-MS error for each analysis day, with triplicate SLRS-4 measurements all within 10%. Thus, any colloidal value $<10\%$ of the measured total <0.45 μm fraction was considered insignificant, and removed from analysis. River samples were analyzed for SRP following filtration through a 0.45 μm PES filter within 24 h. Concentrations were measured using the spectrophotometric molybdenum blue method (Murphy and Riley 1962) following EPA Method 365.1. In addition, the <0.45 μm fraction was analyzed on the ICP-MS as explained above. Concentrations determined by SRP and ICP-MS were combined to increase sample count.

To extract suspended sediment, known sample volumes were poured into Nalgene[®] vacuum filtration rigs containing pre-weighted 0.45 μm PES filters and connected to a fume hood vacuum system. Additional sample was added in 250 mL aliquots until the filtration rate dropped drastically, indicating the filter was clogged. Following filtration, the filtrate was discarded and the filters were air-dried in the fume hood for a minimum of 48 h. Dry weight was then measured to determine the sediment mass and suspended sediment concentration (in mg/L). When possible sediment extractions were optimized for a target mass of 0.1 – 0.2 g dry sediment for each analysis; it was not possible to extract this amount of sediment during some sampling events, particularly during the summer.

Following collection of suspended sediment, two preparations targeted different geochemical pools of particulate P, Fe, and Mn: (1) ascorbic acid extraction following Anschutz et al. (2000) (referred to subsequently as the 'redox sensitive' pool); and (2) Aqua Regia digestion following EPA Method 3050B, which targets all non-silicate bound P, providing a measure of total P. Both methods were modified for use on sediment-laden filters rather than loose material to ensure full contact of extraction/digestion solution with the filters. For the extraction, multiple filters with sediment totaling 0.1 – 0.2 g were placed in 15 mL

acid-washed tubes with 10 mL of extracted solution and placed in a shaker for 24 h. The ascorbic acid extraction targets easily reduced metal (oxy)hydroxides within sediment by simulating anoxic conditions that may occur at the lake bottom or within a saturated soil, and consistent method used in studies to quantify redox-driven internal loading of P from sediments in the receiving water body, Missisquoi Bay (e.g., Giles et al. 2016; Smith et al. 2011). The forced reductive dissolution of metal (oxy)hydroxides also releases adsorbed P. For the Aqua Regia (AR) acid digestion method, whole filters with sediment were folded and placed within digestion tubes, along with filter blanks to ensure no leaching of TM or P. NIST standards for phosphorus were used as positive control to develop a method error for each run. Solutions from both the extraction and digestion procedures were analyzed with an ICP-OES.

Calculation of spring runoff and annual loads

Annual and seasonal loads of geochemical constituents were estimated using the USGS EGRET package (Hirsch and De Cicco 2015). This recently developed R-script employs a weighted regression on time, discharge, and season using approved daily USGS discharge measurements and user-provided sample concentrations. We used our data and the EGRET script to model daily TSS and DP loads. Using these daily TSS estimates and the suspended sediment time series data, we determined the daily reducible and digestible P loads by assigning the suspended sediment P concentrations for individual days to that day's TSS load. For the load calculations, we used 7 months of constituent data, and an approved USGS discharge record of 10 months (with two months of ice cover). The EGRET package utilizes historical records, supplementing the high-resolution data collected for this study. A historical record including approximately 20 years of TSS and phosphorus data was also used, providing additional data points for modeling low TSS conditions. Accurately determining the contribution of high-flow and high-TSS events to annual loads without introducing high-event bias may be a limitation of EGRET (Hirsch et al. 2010). To assign values of suspended sediment P concentration to days that were not sampled, we averaged adjacent sampling days.

Results

Spring runoff period

The 2014 Vermont spring runoff period was characterized by sustained high discharge supplied by a near-average (65-year record) high-elevation snowpack that melted rapidly (UVM-EcoInfo 2015). A large percentage of the total study (March–September) water budget was exported from the system during this spring runoff period, accounting for 59% at OUT, 71% at AGR, and 60% at FOR (Fig. 3). In 2014, snowmelt in northern Vermont began around 3/28/14 at low elevations, identified by flowing rivers and active USGS gages. This was also a time when temperatures remained above freezing for extended periods (Fig. 2) and a thick snowpack remained throughout the watershed. Snowmelt at higher elevations did not begin until 4/7–4/10 (UVM-EcoInfo 2015), although safety concerns prevented sampling until 4/11 (Fig. 3c). Samples were collected at periods of temperature-driven melt when river levels were high compared to baseflow (Fig. 3). In addition, a number of large rain-on-snow events were captured at all sites, including a 10-year flood on 4/15 (Fig. 3).

Suspended sediment

During the 2014 spring runoff, total suspended sediment (TSS) concentrations were generally high with peak values associated with rain-on-snow events (Fig. 3). At all sites, the TSS loads were high throughout snowmelt, driven by consistently high (and positively correlated with) discharge ($p < 0.05$); TSS dropped rapidly as conditions trended toward baseflow (Fig. 3). Redox sensitive P concentrations varied across sites with a mean concentration of 0.11, 0.03, and 0.05 mg/L for AGR, FOR, and OUT respectively. Digestible P was also variable with mean values of 0.27, 0.12, and 0.15 mg/L for AGR, FOR, and OUT, respectively. Redox sensitive and digestible Fe concentrations were much higher than P at all sites with mean reducible Fe values of 0.90, 0.63, and 0.58 mg/L for AGR, FOR, and OUT, respectively. The concentrations of both redox sensitive and digestible Mn were low and very similar across streams draining different land covers. There was a strong positive and statistically significant relationship between RSP and reducible Fe across all sites during spring runoff (AGR:

$R^2 = 0.802$, $r = 0.896$; FOR: $R^2 = 0.989$, $r = 0.974$; OUT: $R^2 = 0.875$, $r = 0.936$; $p < 0.001$ for spring samples only) (Fig. 5). The relationship also exists for summer samples, but there were insufficient data points from summer storms to analyze the relationship.

Dissolved and colloidal constituents

Mean DP concentrations during the spring runoff period were 103, 5.6, and 20.8 $\mu\text{g/L}$ for AGR, FOR,

and OUT, respectively. At all sites, DP concentrations were highest within 1–2 days of the onset of snowmelt and decreased over time, with minimum values occurring near the end of the defined spring runoff period (Figs. 4a–c). Maximum DP concentrations at AGR were nearly two orders of magnitude greater than at FOR. Mean truly dissolved and colloidal Fe concentrations were similar across land covers (10–20 and 55–60 $\mu\text{g/L}$ respectively) and did not display the same degree of variability as DP values. The same was

Fig. 3 Discharge for each of the gaged sites during the 2014 sampling period. Sampling events are marked along the discharge plot. The inset shows the TSS to discharge relationship at each site. The spring runoff period is shown in grey. Average TSS values for spring runoff and summer are shown above the inset plot

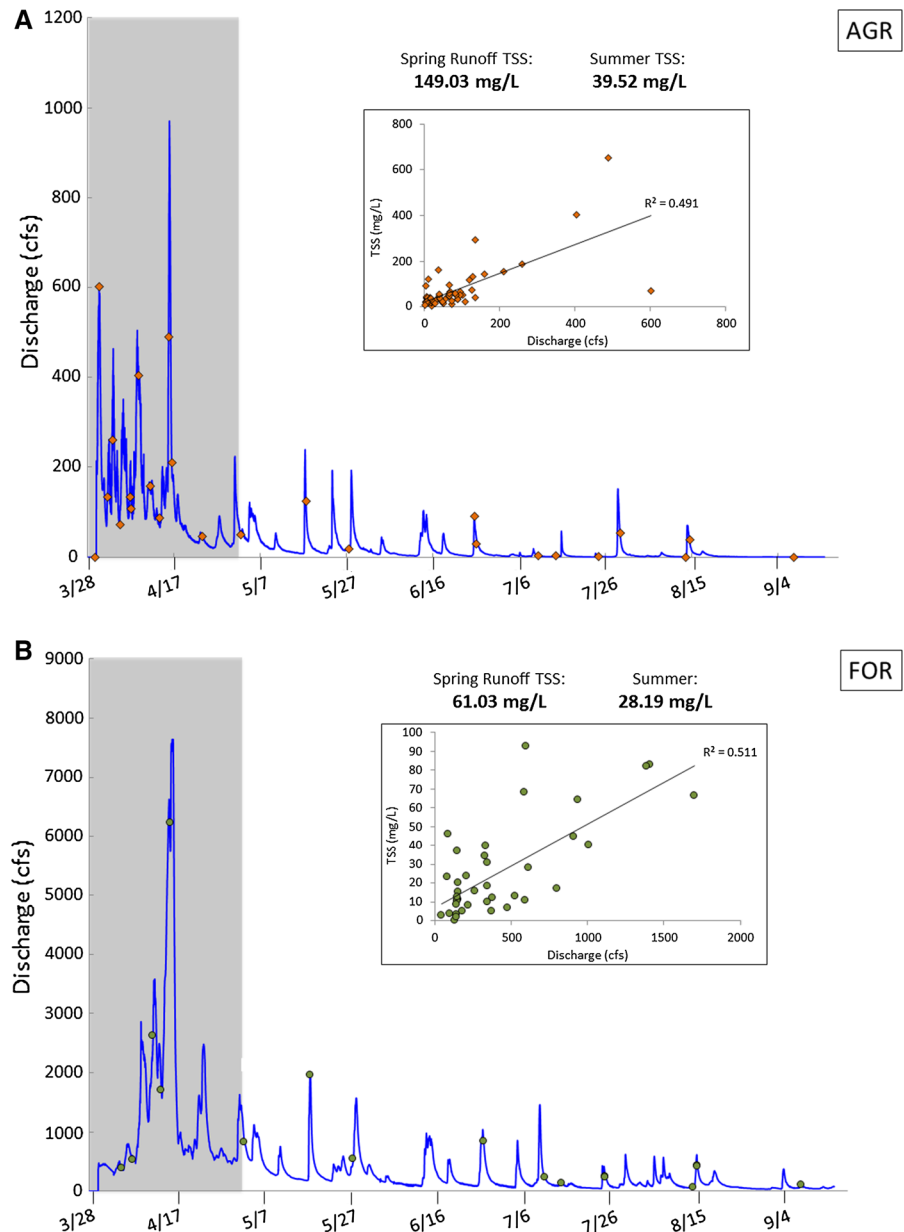
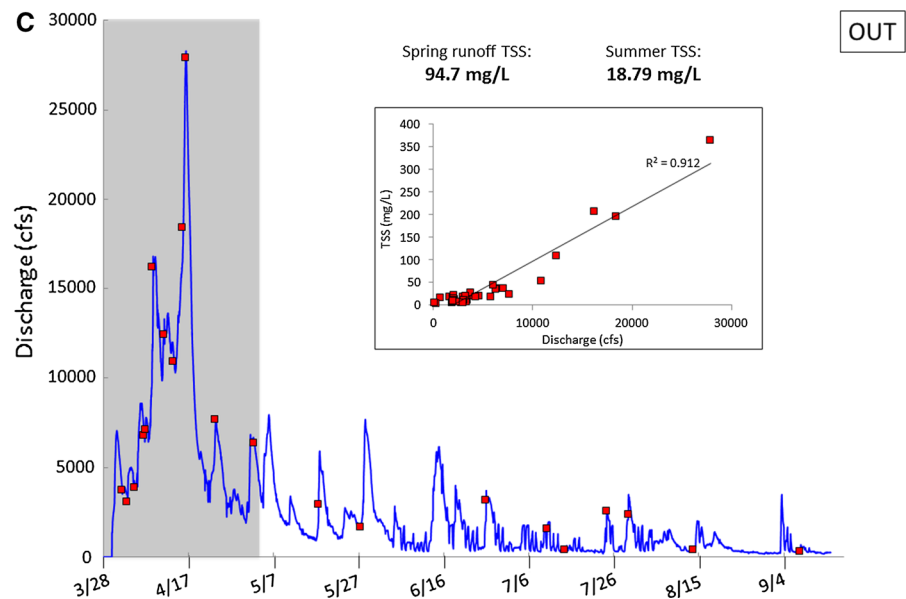


Fig. 3 continued

true for truly dissolved Mn, which had mean values of 37.3, 10.1, and 19.9 $\mu\text{g/L}$ for AGR, FOR, and OUT respectively. Colloidal Mn values were generally low with the exception of two very high concentrations occurring during a large rain-on-snow event at OUT (Fig. 4c). Peak truly dissolved Fe and Mn concentrations occurred at all sites approximately one week into snowmelt and decreased rapidly over time (Fig. 4). Colloidal Fe concentrations varied with discharge at OUT and AGR, but decreased over time at FOR (Fig. 4). The same trends exist in colloidal Mn with the exception of AGR, where colloidal Mn values are generally insignificant. Across all sites, the majority of Fe is colloidal and the majority of Mn is truly dissolved.

Post-snowmelt period

The end of the spring runoff period marks the hydrological transition from sustained high discharge and associated runoff/shallow subsurface flow to groundwater-fed baseflow conditions with intermittent storms. From May to September, samples were collected weekly to bi-weekly during baseflow conditions with targeted sampling during storm events. Characterization of suspended sediment was only possible during storm events, as baseflow did not result in sufficiently high TSS concentrations. The lack of summer storm suspended sediment samples

was due in part to a dry summer with minimal storm activity. Suspended sediment extractions were not possible on the small amount of suspended sediment available at baseflow and even moderate flow conditions.

Suspended sediment

From May to September, TSS concentrations were generally low, peaking only during intermittent storm events (Fig. 3). (Low summer sediment loads were especially noticeable at the FOR forested site, where water ran clear even during larger storm events.) Therefore, characterization of suspended sediment in the forested catchments during the summer was conducted on limited samples from FOR. Summer storm RSP concentrations were high at AGR relative to the other sites, with mean concentrations of 0.06, 0.01, and 0.01 mg/L for AGR, FOR, and OUT respectively; digestible P was also high at AGR and relatively low at the other sites with mean values of 0.14, 0.04, and 0.03 mg/L for AGR, FOR, and OUT respectively. The concentrations of redox sensitive and digestible Fe were much higher than P at all sites and similar across sites with mean reducible Fe concentrations of 0.47, 0.26, and 0.24 mg/L and mean digestible Fe values of 1.7, 1.1, and 1.0 mg/L for AGR, FOR, and OUT respectively. The concentrations of both redox sensitive and digestible Mn were

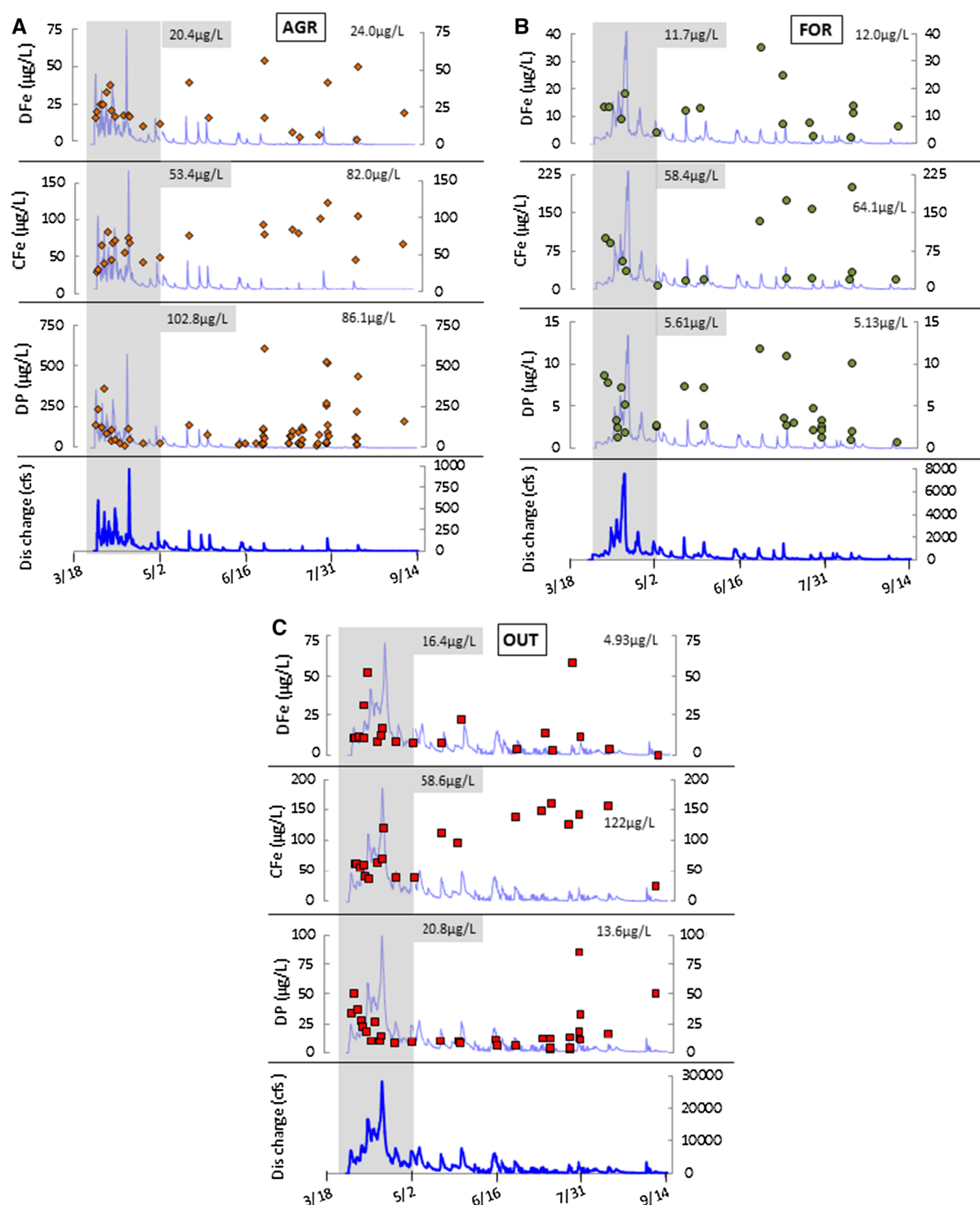


Fig. 4 Soluble P and TM concentrations over time at each site. Dissolved P values in the summer include both ICP-MS DP and SRP. Mean concentrations for each constituent during spring runoff are shown in *grey boxes*, and summer concentrations are

presented on the *right side* of each figure. The hydrograph shown in the background is for reference. Please see bottom discharge plot for values

low across all land covers. Since suspended sediment could not be extracted during periods with very low TSS concentrations, the biogeochemical nature of suspended sediment during baseflow conditions is unknown; however, this also makes baseflow essentially irrelevant to sediment-bound nutrient budgets.

Dissolved and colloidal species

Mean DP concentrations during the late spring and summer period were 86.1, 4.8, and 13.6 $\mu\text{g/L}$ for AGR, FOR, and OUT, respectively (Fig. 4). At all sites, DP concentrations were highest during storm events and at least one order of magnitude lower at baseflow (Fig. 4). At AGR, the concentration of DP increased rapidly during storm events, with peak concentrations preceding the peak discharge during some storm events (Fig. 4a). Maximum DP concentrations at AGR were nearly two orders of magnitude greater than at FOR. The mean truly dissolved Fe concentrations were 24.0, 12.0, and 4.93 $\mu\text{g/L}$ and mean colloidal Fe concentrations were 82.0, 122, and 64.1 $\mu\text{g/L}$ for AGR, FOR, and OUT, respectively (Fig. 4). Across all sites, truly dissolved Mn had a mean concentration of 74.1, 14.4, and 35.7 $\mu\text{g/L}$ for AGR, FOR, and OUT, with very low or insignificant colloidal Mn concentrations. Truly dissolved Fe concentrations increased over time, while truly dissolved Mn concentrations were more variable (Fig. 4). Colloidal Fe and Mn concentrations varied with discharge at all sites with the exception of AGR, where colloidal Mn values were generally insignificant (Fig. 4a–c). Across all sites, the majority of Fe

was colloidal and the majority of Mn was truly dissolved during spring runoff, summer storms, and baseflow conditions. No discernable pattern appears between concentrations of soluble-phase Fe and Mn at baseflow and discharge (Fig. 4). Few relationships between P and metals are evident in the dissolved and colloidal phases. There were no statistically significant relationships (at $p = 0.05$) between DP and colloidal or truly dissolved Fe in the agricultural system, but a strong positive correlation between DP and colloidal Fe at the forested sites ($n = 5$, $R^2 = 0.904$, $r = 0.951$, $p = 0.013$) (Table 1).

Discussion

Spring runoff and summer storms as hot transport moments of reactive Fe and P species in suspended sediment

Since it has been suggested that the magnitude of P loading during spring runoff drives the severity of algal blooms in many lakes (Michalak et al. 2013; Stumpf et al. 2012) and that sediment redox chemistry drives the onset and propagation of summer algal blooms in Lake Champlain (Pearce et al. 2013; Smith et al. 2011), (Giles et al. 2016), characterization of metal and P redox sensitivity in riverine suspended sediment loads is critical to describe the potential mobilization of these constituents in receiving waters. Suspended sediment concentrations at all sites confirm that the spring runoff period is a ‘hot transport moment’ of sediment (Fig. 3) when extensive high

Table 1 R^2 values for statistically significant correlations (p-test; $p < 0.05$) between DP and soluble metals

	Truly dissolved Fe	Colloidal Fe	Truly dissolved Mn	Colloidal Mn
Spring runoff (2014)				
Dissolved P				
AGR	–	–	–	–
OUT	–	–	–	–
FOR	0.2195	0.9041	–	–
All sites	0.2014	–	–	–
Summer (2013 and 2014)				
Dissolved P				
AGR	0.7211	–	–	–
OUT	0.4145	–	–	–
FOR	0.705	0.5929	–	–
All sites	0.6228	–	–	–

These data are also presented in Fig. 4

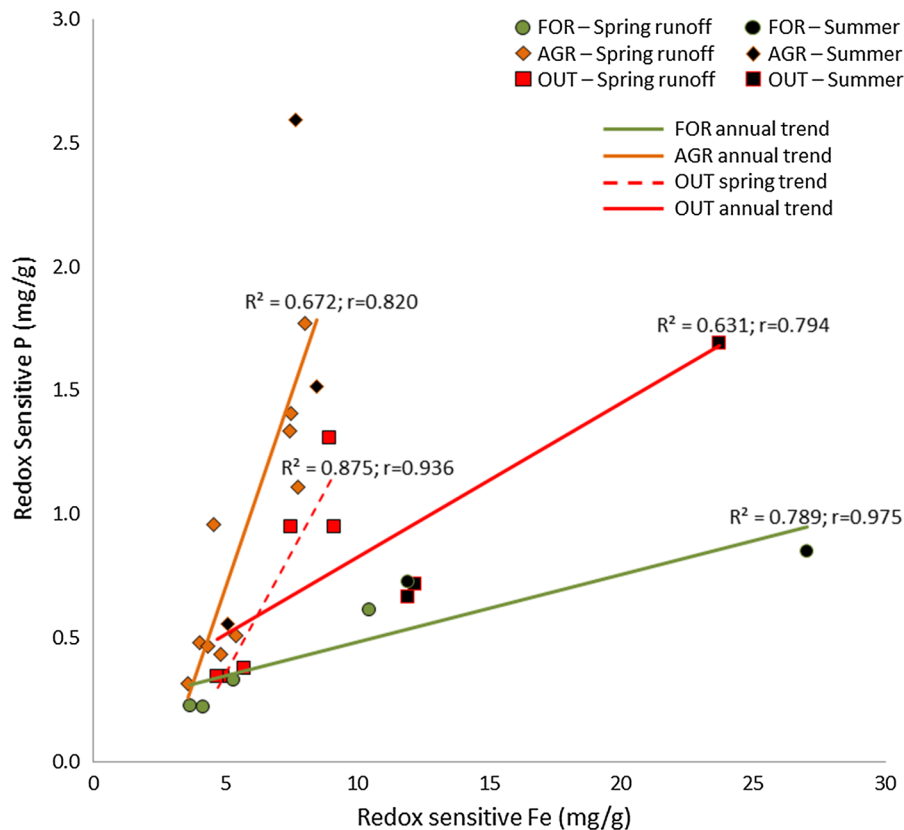


Fig. 5 Redox sensitive P versus redox sensitive Fe at all sites. Colored samples were collected during spring runoff. Samples in black were collected during summer storms. Annual trends are presented with *solid lines*. The trend for spring runoff at OUT is shown in a *hashed line*. There was no statistically

significant difference between spring runoff and annual trends for AGR or FOR. Slopes for the various trend lines are presented in the discussion. All relationships are statistically significant (*p*-test; *p* < 0.05). Both R-square and Pearson's correlation coefficient values are shown in figure. (Color figure online)

flow-driven erosion produces relatively high sustained suspended sediment loads. This is not surprising, as variably frozen and saturated soils are common throughout the lowland portion of the watershed, which isolates water at and within the soil surface and upper horizons that are actively melting, thereby promoting erosion (Fig. 3) (Gao et al. 2004; Groffman et al. 2001). Particularly high suspended sediment concentrations at AGR are likely a result of easily eroded and abundant bare agricultural soils coupled with streambank and riverbed erosion (Fig. 3a) (Langendoen et al. 2012). Relatively high concentration of redox sensitive and digestible P in suspended sediment at AGR during the 2014 spring runoff suggests that higher P concentrations in soils of manure-amended fields (Hansen et al. 2004; Walter et al. 2001), and their enrichment in labile P (Huang et al. 2011;

Jamieson et al. 2003) manifests in suspended sediment loads that bear a particularly high concentration of RSP. Conversely, spring runoff suspended sediment loads from the forested catchments had relatively low TSS, RSP and ARP concentrations due to root network and soil O-horizon anchoring of mineral soil and stream banks that suppresses erosion coupled with lack of P amendment in the watershed (Fig. 3c). This confirms that land cover exerts not only an important control on the concentration of sediment in spring runoff, but also its composition and its redox sensitivity.

We interpret the spatial and temporal differences ratios of RSP:ARP and RFe:ARFe as representing changing redox sensitivity of suspended sediment P and Fe loads throughout the spring runoff period, as an extractable P fraction of ~30% in agricultural runoff

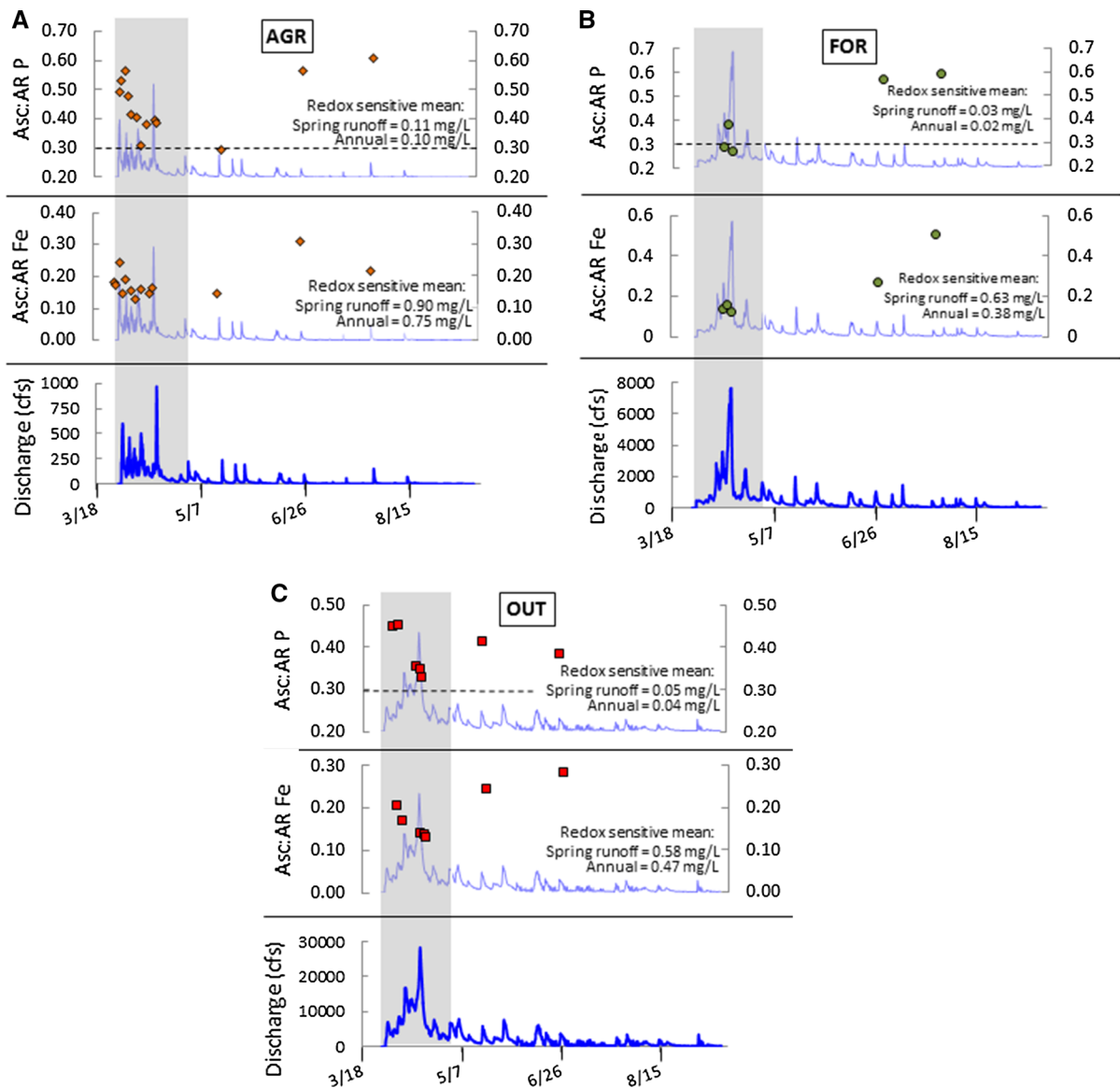


Fig. 6 Asc:AR ratio for P, Fe, and Mn over time at each gaged site. The *hashed line* represents a literature-supported 30% particulate P bioavailability (Sharpley et al. 1992; Poirier et al. 2012). Mean concentrations for the redox sensitive fraction are

shown in each plot for comparison. The hydrograph shown in the background is for reference. Please see bottom discharge plot for values

has been considered potentially bioavailable in many studies (Dupas et al. 2015; Poirier et al. 2012; Sharpley et al. 1992). Yet during the entire time series of spring runoff, all suspended sediment samples bore over 30% of total particulate P that was redox sensitive (Fig. 6). This demonstrates that this is not only a hot moment of P loading due to high concentrations of sediment P, but also particularly reactive sediment and many models may underestimate the potential role that these

sediment loads may play in redox-driven internal loading of P upon deposition in receiving waters. The systematic decrease in RSP and RFe relative to AR fractions that occurs over the course of time, and independent of discharge at AGR and OUT, suggests that a the large scale depletion particularly redox sensitive sediment occurs over the duration of spring runoff. Thus, the early stage of snowmelt is a crucial hot moment of sediment export because the most

redox sensitive pools of Fe and P that accumulated in frozen soils and streambanks of the winter landscape were flushed into Lake Champlain. Furthermore, the similarity in temporal trends of these ratios in AGR and OUT suspended sediment composition highlights the geochemical similarities between stream water draining the agricultural catchment and that of the entire Missisquoi Basin outlet early in snowmelt, reflecting the disproportionate influence of lowland agricultural fields on the suspended sediment P geochemistry and loading in the Missisquoi River during spring runoff. Since the Hungerford Brook sub-catchment (AGR) is characteristic of the Lake Champlain lowland region (Fig. 1), it follows that RSP exported from agricultural land during spring runoff will elevate the potential redox sensitivity sediment deposited in the Lake during spring, with potential to promote internal P loading when waters warm.

Summer storms

During summer storms, increased anchoring of vegetation and decreased flows suppressed TSS concentrations and related RSP and TP concentrations at all sites relative to those of the spring runoff period, further highlighting the importance of spring runoff as a hot moment for reactive P delivery to Lake Champlain (Figs. 3, 6). In general, the composition of river water in this region during summer has been shown to be characteristic of deeper flowpaths, except under storm conditions when groundwater tables become high and surface soils become saturated promoting an increase in the relative proportion of surface runoff to stream discharge (Gburek and Folmar 1999). Elevated TSS, RSP and ARP concentrations observed during summer storm events at AGR were likely due to some component of increased in-stream, land surface, and streambank erosion due to this change in flowpaths (Figs. 3, 6) (Langendoen et al. 2012), coupled with intermittent manure amendment and cut and till schedules (Hansen et al. 2000; Panuska et al. 2008). Streambank erosion in the agricultural lowlands has been identified as a major source of P export in the Champlain Valley, especially in regions with long-term P amendment resulting in pools of legacy soil P in easily erodible soils (Langendoen et al. 2012). Relatively low storm event TSS, RSP and ARP concentrations in FOR are again due to abundant root networks, continuous understory anchoring, coupled

with lack of P amendment continue to suppress loading of RSP from the forested systems. This is important in the context of Lake Champlain Basin management, as efforts to reduce P loading from forested catchments within the Basin may have minimal effect on reactive P species delivery to receiving waters. Reduction targets for forested catchments may also be difficult to achieve due to the low existing concentrations in loads exported from these catchments, even during storms and spring runoff.

Interestingly, we also observe a shift in the redox sensitivity of suspended summer storm sediment loads relative to those at the end of spring runoff, where the ratio of RS to AR phases in summer storm event suspended sediment increases dramatically after basin-wide green up and prolonged baseflow conditions (Fig. 6). With the caveat that this trend is based on limited observations due to low storm frequency and TSS concentrations during our summer sampling, this trend is noteworthy and makes sense in the context of what we know about riparian hydrology and biogeochemistry. This pool of particularly redox sensitive sediment must have developed basin-wide during preceding baseflow conditions when anoxic Fe(II) rich groundwater likely interacted with oxic surface water in riparian interfaces (Baken et al. 2015a), causing the precipitation of relatively P-rich Fe (oxy)hydroxides that are flushed during high-flow events (Fig. 6). Indeed, the development of such Fe deposits often manifests as discontinuous orange flocs along riverbeds and banks where strong redox gradients are common under baseflow conditions (Lapworth et al. 2009; van der Grift et al. 2014). These abundant redox sensitive suspended sediment phases can scavenge available soil/hyporheic water P (Baken et al. 2015a; van der Grift et al. 2014) across land covers. Furthermore, the progressive increase in the redox sensitivity following prolonged periods of baseflow suggests that antecedent conditions (sustained baseflow), which promote riparian redox gradients and facilitate Fe (oxy)hydroxide generation, may have a dramatic effect on high flow event suspended sediment redox sensitivity during summer storms. Thus, while the relatively low concentration of suspended sediment and P indicate that summer storms of 2014 were less of a hot moment for cumulative loading than the spring runoff period, suspended sediment selective extraction ratios

indicate that sediment P and Fe of summer storm loads can be particularly ‘redox sensitive’. This could significantly impact internal loading in the lake since these storms are occurring in a season when algal bloom/thermal stratification dynamics are prone to quickly promote internal release of redox sensitive P at the sediment–water interface of Missisquoi Bay (Giles et al. 2016).

Phosphorus association with Fe and Mn in suspended sediment during high flow events

The strong positive correlations between the concentrations of RSP and Fe in suspended sediment at all sites suggests that Fe (oxy)hydroxides serve as a critical sorption surface and transport vector for RSP in spring runoff suspended sediment (Fig. 5). This is not surprising, as Fe (oxy)hydroxides are known to be highly effective scavengers of oxyanions such as P in typical oxic mildly acidic-neutral freshwater systems (Baken et al. 2015b; van der Grift et al. 2014). Yet the slope of correlation between RSP and Fe differs dramatically by land cover due to a wide range in RSP concentrations across landscapes and a relatively similar range in RSFe (Fig. 5). This reflects varying amounts of RSP associated with Fe (oxy)hydroxides in each system’s spring runoff suspended sediment load, which is driven by land cover effects on Fe(oxy)hydroxide enrichment in sorbed P (Fig. 5). In AGR there are high but variable RSP concentrations with less variable reducible Fe concentrations, producing a relatively high slope (slope = 0.262) compared to the forested catchment (slope = 0.059) (Fig. 5). During spring runoff, the relationship between RSP and Fe at OUT appears similar to AGR, again reflecting a disproportionate influence of lowland agricultural regions on the redox sensitivity of P in suspended sediment loads (slope = 0.195) (Fig. 5). This suggests that a similar fraction of reducible Fe exists in the suspended sediment from both forested and agricultural sub-catchments, but the dramatic difference in P concentrations associated with reducible Fe phases reflects the abundance of P in suspended sediment sources in agricultural soils and stream bank sediments having a history of P amendment. These trends confirm that during spring runoff: (1) Fe (oxy)hydroxides are the dominant carrier of RSP across forested and agricultural catchments; and (2) reducible Fe mineral phases in sediments from agricultural fields

are relatively rich in RSP, which ultimately elevates the RSP loading to the Lake from the entire Missisquoi River Basin. The lack of a significant correlation between RSP and Mn (oxy)hydroxides ($p \gg 0.05$) at any site is interesting in the context of internal P loading studies on Missisquoi Bay lake sediments, where Mn (oxy)hydroxide reduction near the sediment water interface has been demonstrated to be the best indicator of initial P release from sediment and initiation of harmful algal blooms (Pearce et al. 2013; Smith et al. 2011; Giles et al. 2016), which warrants future mechanistic study.

Similar to suspended sediment loads during spring runoff, the strong positive correlation ($p < 0.001$) between RSP and Fe at each site suggests that these iron phases remain the dominant carrier of RSP across seasons (Fig. 5). While the small sample size for summer storm suspended sediment prevents statistically sound regression analysis for summer samples alone, their addition does not change the slope of the relationship between RSP and Fe at AGR or FOR in spring runoff, indicating a relatively consistent relationship and perhaps provenance across seasons. However, the addition of summer storm suspended sediment samples resulted in a significant change to the relationship between RSP and Fe at OUT (spring alone slope = 0.195 vs. all samples 0.062) to one more similar to that of FOR. These data may suggest that the proportional provenance of suspended sediment loads in the Missisquoi Basin during high flow events changes during the seasons, with less of a disproportionately high impact of the agricultural lowlands during the summer relative to the spring. Alternatively, in the larger Missisquoi River system represented at OUT, it is possible that some internal process depletes the amount of RSP in storm event suspended sediments (e.g., biological cycling, desorption, or redox dynamics) as water temperatures warm and the riverine/riparian ecosystem becomes more active. Yet this analysis conclusively demonstrates that Fe (oxy)hydroxides are the dominant carrier of particulate RSP during all seasons, and a systematic variation across season and land cover exists in the concentration of RSP associated with Fe (oxy)hydroxides in suspended sediment loads, with the more RSP concentrated on Fe phases in the spring runoff load from the agricultural Champlain Valley lowlands. As such, we can conclude that spring sediment P loads may exert disproportionate impact on receiving water

quality, not only due to higher sediment concentrations, but because the suspended sediment loads bear particularly P-rich redox sensitive Fe (oxy)hydroxides sourced in the agricultural lowlands of the watershed.

Spring runoff and summer storms as hot transport moments of reactive Fe and P dissolved and colloidal species

Previous studies have identified a large spring flush of various dissolved and colloidal constituents including metals (Dahlqvist et al. 2007; Rember and Trefry 2004), DOC (Dawson et al. 2008), and dissolved macronutrients (Jamieson et al. 2003; Sebestyen et al. 2009; Yuan et al. 2013), highlighting the importance of this event as a hot transport moment for many solutes. Indeed, dissolved phosphorus (DP) concentrations were relatively high during the onset of spring runoff across landscapes, confirming a ubiquitous hot transport moment as the spring thaw began. In line with expectations and similar to RSP, the highest DP concentrations were in systems with agricultural land cover that had histories of P amendments (Abdala et al. 2015; Hansen et al. 2004). Lower concentrations observed in the forested catchments are predictable since they have not received P amendment and relatively tight cycling of minimal available DP derived from weathering and recycling has been demonstrated elsewhere (House 2003; Stelzer et al. 2003). As was the case with RSP in suspended sediment loads, the relatively high mean DP concentration at OUT during spring runoff further demonstrates that spring runoff river water entering Lake Champlain is relatively enriched in labile P (in both dissolved and particulate fractions) derived from the agricultural lowland of its catchment. However, similar temporal changes in dissolved P concentrations occurred across all our study sites, where DP decreases over time independent of discharge, suggesting a basin-wide flushing of DP early in snowmelt, similar to observed RSP dynamics (Figs. 4, 6).

Unlike DP and truly dissolved Fe/Mn, colloidal metals exported from the lowland agricultural systems are coupled to discharge and do not change as a function of time during the spring runoff. This may indicate the rapid in situ development of colloids in soils, streams or wetlands (Kerr et al. 2008; Soto-Varela et al. 2015). Interestingly, there was a systematic decrease in colloidal Fe concentration in forested

catchments over time and independent of discharge (Fig. 4b), which is consistent with other studies from pristine forested catchments where a strong initial snowmelt flush has been observed (e.g., (Dahlqvist et al. 2007)). It is likely that different processes control the development and flushing of colloidal material in the watershed lowland regions relative to the mountains during spring runoff. Also similar to suspended sediment data, similar ranges in dissolved and colloidal metals across land covers indicates that while current and historical manure amendment of soils appears to be the main driver of elevated riverine P (both suspended sediment and soluble reactive forms), it does not appear to affect the concentration and distribution of colloidal and ‘truly’ dissolved Fe and Mn across these catchments. It is also important to note that across sites there is ample reactive and redox sensitive colloidal Fe (oxy)hydroxides in river loads to carry sorbed P species.

Summer storms

Lower summer DP concentrations across all sites (compared to spring runoff) suggests less dissolved P is exported from the entire landscape as biological uptake increases in the warmer months. However, similar to the snowmelt period, DP storm event concentrations at AGR were high relative to other land covers, which is expected in manure-amended systems, particularly during storms, when pathways enriched in labile amended P are activated (Royer et al. 2006; Walter et al. 2001). Given continued manure application during the summer, the maximum concentration of DP in river water derived from agricultural runoff during summer storms appears similar in magnitude to early spring storm runoff concentrations. Consistent with trends during spring runoff, water exported from forested catchments during summer storms had very low DP concentrations, in terms of both mean and maximum values, characteristic of these relatively pristine environments (Meyer and Likens 1979; Owens and Walling 2002; Stelzer et al. 2003). Similar DP concentrations during summer storms and spring runoff at OUT suggest that the impact of P amendment on DP loads during high flow events is consistent across seasons. This indicates an important seasonal impact on high flow event P loads where summer storms still export large

amounts of amendment-derived DP in runoff and shallow subsurface flow from agricultural fields. However, anchoring of sediment by crops and understory vegetation reduces the export of labile particulate RSP during the summer in comparison to spring runoff. While spring runoff DP dynamics were independent of discharge (Fig. 4), summer DP is strongly coupled to discharge ($p < 0.05$), suggesting flow-derived mobilization and export of the most concentrated DP loads during summer storms (Fig. 4). The high-frequency ISCO-derived DP dataset captures rapidly increasing concentrations during increased discharge associated with substantial rain events, confirming the typical relationship between flow and DP export in agricultural runoff during intermittent storm events, highly dependent on flow and fertilizer application timing (Hively et al. 2005; Panuska et al. 2008; Zhu et al. 2012). The increase in DP during storm events is evidence of the flushing of surface and shallow subsurface flow paths during these high-flow events, with ample DP replenished in these pathways by manure application between storms.

Increasing colloidal Fe concentrations in storms following the end of the spring runoff is also consistent with previous work suggesting that colloidal material at the hyporheic or riparian interface and wetlands where anoxic groundwater rich in Fe(II) and oxic surface water mix under baseflow (Pokrovsky and Schott 2002; Pokrovsky et al. 2006; Stolpe et al. 2013) is flushed from these Fe (oxy)hydroxide floc-rich interfaces during storm events (Kerr et al. 2008; Lapworth et al. 2009; Soto-Varela et al. 2015). Our data suggest that the processes controlling the development and flushing of colloidal Fe (oxy)hydroxides during summer are similar between pristine forested environments and the more developed lowlands of the Missisquoi Basin, but may be fundamentally different from those occurring during spring runoff. Data also suggest that summer storm loads are more concentrated in Fe (oxy)hydroxide colloids relative to high spring flows, presumably due to different provenance and antecedent conditions (sustained spring high flow/flushing vs. prolonged periods of baseflow between storm events in summer) that promote relative enrichment of summer storms in Fe (oxy)hydroxide colloids relative to spring runoff.

Phosphorus association with Fe and Mn dissolved and colloidal species during high flow events

Colloidal Fe (oxy)hydroxides are well-established redox sensitive transport vectors for an array of nutrients and pollutants as a result of high surface area and charge at typical freshwater pH ranges (Dahlqvist et al. 2007; Stolpe et al. 2013), and as highly effective scavengers of dissolved inorganic P similar to particle-sized metal (oxy)hydroxides. Generally, the dominant partitioning of Fe in colloidal fraction with intermittent events with relatively high concentrations of ‘truly dissolved’ Fe is in line with expectations, as is majority of Mn occurring ‘truly dissolved’ fraction (e.g., Dahlqvist et al. 2007; Pokrovsky et al. 2006; Stolpe et al. 2013), and indicates that soluble phase size partitioning of Mn and Fe does not vary systematically among our sites. Since abundant, Fe-rich organic ($<0.02 \mu\text{m}$) and mineral ($0.45\text{--}0.02 \mu\text{m}$) colloidal phases were present during spring runoff (Fig. 4), we explored the relationship with these various fractions and DP ($<0.45 \mu\text{m}$) to better understand when and where these constituents may be following similar pathways and when soluble P transport may be driven by the flushing of metal colloids formed in soil, riparian or hyporheic environments. The significant relationship between DP and colloidal Fe in FOR suggests that these colloids may be important carriers of soluble P in non-P amended systems, or to a ‘natural’ soil P saturation level, but it is unclear to what degree these highly reactive metal colloids transport amended P in agricultural systems during spring runoff. The lack of relationship between DP and colloidal Fe in AGR waters is inconsistent with the strong association of these elements in suspended sediment of spring runoff. This may indicate that P from manure amendment is flushed from the agricultural system as dissolved orthophosphate not associated with metal carriers when there is excess DP relative to available colloidal Fe (oxy)hydroxides. As Fe colloids are known to be strong sorbents of dissolved organic matter at circum-neutral pH (Pokrovsky et al. 2006; Stolpe et al. 2013), it is possible that colloid-sized Fe (oxy)hydroxides are coated with manure-derived OM, decreasing available binding sites for DP. Fe (oxy)hydroxide colloidal phases are clearly important for riverine transport of P, but more detailed study of colloidal speciation in

forested and manure-amended catchments is clearly warranted.

The general size partitioning of Fe and Mn during summer storms and baseflow remains consistent with spring runoff, and with previously discussed studies, supporting the interpretation that Fe and Mn size distributions are controlled by watershed conditions that are not altered by the agricultural practices in these catchments. The consistent coupling of colloidal Fe and DP at FOR further suggests that Fe(oxy)hydroxides are an important transport vector for soluble P from the forested catchments across seasons (Table 1). Surprisingly, the strong relationship between DP and truly dissolved Fe in summer samples collected from the agricultural system (Table 1) suggests these constituents share similar source environments and geochemical pathways during the summer; a relationship not evident during spring runoff (Table 1). Additionally, while high concentrations of truly dissolved Mn and DP in Lake Champlain are often coupled, reflecting the reductive dissolution of Fe/Mn minerals at the sediment water interface (Schroth et al. 2015; Giles et al. 2016), this relationship is not evident in our riverine data as a whole or partitioned by land use. This suggests that DP fluctuations during high flow events across the region are not likely driven by reductive dissolution of secondary Fe/Mn minerals.

Implications for Lake Champlain Basin water quality and eutrophication

Seasonal data from OUT allow us to quantitatively model the loading of reactive P species delivered to Lake Champlain from the Missisquoi River over the course of the 2014 hydrologic year to estimate seasonal loading of fractions of P that are most likely to contribute to algal blooms and eutrophication. Annual nutrient loads are traditionally generated for TP and DP, which fail to account for the variable reactivity and bioavailability of P within suspended sediment. To our knowledge, we are the first study to incorporate the redox sensitivity of solid phase P (TP) to model load estimates. Output clearly demonstrates the degree to which the spring was a dominant hot moment for reactive P delivery to the Lake, contributing 74 and 82% to annual RSP and DP loads respectively. Overall, this highlights how critical the spring runoff period is when estimating annual loads

of immediately and potentially bioavailable P to Lake Champlain, reflecting the unique biogeochemical and hydrologic nature of this time period. Spring runoff will be responsible for the majority of the annual reactive P load to some varying degree during typical hydrologic years in this and other similar systems, although there is certain to be significant variability in the relative contribution of individual seasons based on inter-annual variability in weather. These model results further highlight the importance of spring runoff loading of reactive P species to understanding and managing eutrophication, and emphasize the importance of projecting fluxes of species that are most reactive in ecosystems and receiving waters.

Our findings demonstrate that the reactivity of high flow event P loads varies significantly in time and space across the Lake Champlain Basin, and that significant seasonal changes in high flow event load geochemistry are driven in part by antecedent conditions and land cover that have important implications for water quality and eutrophication across the Lake Champlain Basin. Periods of prolonged baseflow conditions (sustained cold frozen soils or dry summertime periods) promote the development of abundant redox sensitive iron and sorbed P that can be ‘flushed’ during the following storm event or the onset of snowmelt, and these events are hot moments of loading of reactive species to Lake Champlain. Whereas prolonged or closely successive high flow events appear to deplete the pool of labile redox sensitive sediment, making Fe and P suspended sediment loads progressively less redox sensitive, with similar behavior of DP. The Fe (oxy)hydroxides present in both the suspended sediment and colloidal loads of high flow events are important carriers of redox sensitive P across the landscape, illustrating the strong coupling of Fe–P behavior during high flow events that dominate the annual load of both constituents across seasons and land covers that is delivered to the Lake. In general, the remarkably high P concentrations associated with redox sensitive Fe phases, particularly during the onset of spring when discharge and TSS concentrations are high, suggests that there may be systematic underestimation of the redox sensitivity of spring runoff and summer storm event-derived suspended sediment, particularly from P amended catchments. The high RSP concentrations in suspended sediment early in snowmelt relative to the summer reflect the increased influence of lowland

agricultural sub-catchments during spring, when the more inert montane catchments are disconnected from the rest of the watershed due to snow and ice. This lowland suspended sediment appears more conducive to the reductive release of P from lake sediment that promotes algal blooms and degrades water quality when compared to the significantly less redox sensitive sediment exported from the relatively pristine forested catchments that cover 70% of Vermont. Best management practices should focus on suppressing the release of this reactive lowland pool, particularly in catchments feeding shallow eutrophic bays where internal loading is a dominant P source. Targeted best management practices that reduce the buildup of reactive pools during winter (e.g., limiting late fall manure application) coupled with those that reduce erosion of P rich agricultural soils in the spring (e.g. cover crops, bank stabilization, buffer strips) should be priorities in the agricultural portion of the Lake Champlain Basin. A similar dynamic impacts DP loads during spring runoff, as DP pools in agricultural soils are depleted and water derived from forested catchments increases as the snowmelt progresses to higher elevations. DP pools are then intermittently replenished due to manure application, and flushed during subsequent summer storm events. Summer manure application schedules or injection practices that suppress the release of dissolved P during storms should be a priority to limit the impact of summer storms on algal blooms in receiving waters. In general, sustained high flow and erosion, low ecosystem productivity, large pools of available labile P, and particularly reactive suspended sediment make the spring runoff period disproportionately important to the annual load of these constituents to Lake Champlain. Anthropocene changes in the severity, timing and provenance of spring runoff and summer storms will likely have dramatic impact on not only the flux and temporal distribution of P loading, but also the timing and magnitude of the delivery of riverine particles and colloids with the most potential to impact summertime harmful algal bloom development. This should be taken into account when developing future P targets and best management practices for Lake Champlain and its watershed.

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