

Assessing Phosphorus Sources with Synoptic Sampling in the
Surface Waters of a Mixed-Use, Montane Watershed

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ABSTRACT

Assessing Phosphorus Sources with Synoptic Sampling in the Surface Waters of a Mixed-Use, Montane Watershed

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Master of Science

Few elements in surface waters are monitored as closely as phosphorus (P) due to its role in the eutrophication and degradation of surface waters. Limiting P mobilization from source areas is, therefore, a central goal of water quality protection plans. But the work of locating sources in mixed-use watersheds is challenged by the spatial and temporal variability of critical source areas (CSAs) of P. Synoptic sampling is a proven method for capturing the spatial variation of water quality parameters in surface waters, though it's not often used to track temporal dynamics across the same study area. Phosphorus fractionation is an analytical method that divides the total P (TP) in water into fractions, which for this study included total dissolved P (TDP), particulate P (PP), dissolved reactive P (DRP), and dissolved organic P (DOP). The objective of this study was to demonstrate the utility of combining temporally repeated synoptic sampling with simple P fractionation as a unique strategy for locating and characterizing CSAs of P. Seven synoptic sampling campaigns were conducted over a two-year period (March 2015 – July 2016) in a rural, montane watershed in north central Utah, USA. In each campaign, we sampled 18 sites across three tributaries (Main Creek, Spring Creek, and Little Hobble Creek) during three distinct, annual hydrologic periods (rising flow, peak flow, and baseflow). Temporal repetition clearly identified the rising flow period as the period with greatest P loading in the watershed. Combining repeated synoptic sampling and P fractionation successfully identified CSAs of P and most probable transfer pathways. Specifically, stream segments along lower Spring Creek and Main Creek were associated with the greatest increases of PP loads during periods of rising flow and peak flow. In the same time periods, the greatest DOP loads stemmed from forested areas as well as areas in the lower watershed associated with winter grazing of cattle. The watershed exhibited a significant background concentration of DRP from groundwater-driven subsurface sources in the lower half of the watershed that persisted year-round. These assessments can be used to develop management practices that limit various P loads from these respective critical source areas. The characterization of CSAs could not have been made using only a traditional synoptic sampling approach. This study demonstrated that the combination of repeated synoptic sampling and P fractionation can be an effective technique for locating and characterizing critical P source areas in order to guide best management practices that improve surface water quality.

Keywords: water quality, critical source area, watershed, phosphorus, synoptic sampling, best management practice, hydrology, Wallsburg, Utah

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INTRODUCTION

Few elements in surface waters are monitored as closely as phosphorus (P). Phytoplankton growth accelerates when water bodies such as lakes, reservoirs, and estuaries, become loaded with P, which element is often a limiting nutrient for growth of aquatic organisms (Drever, 1997). Eutrophication degrades water quality directly due to toxic algal blooms, increased turbidity, shifts in aquatic species, and increased costs in water treatment (Foy, 2005). Ultimately, eutrophication cycles into the decomposition of algae and the severe depletion of dissolved oxygen, causing a loss of biodiversity at all trophic levels (Carpenter, et al., 1998).

Many environmental protection plans include goals to reduce annual P loads exported from watersheds in efforts to limit the eutrophication of downstream water bodies. Metrics such as the Total Maximum Daily Load (TMDL) are calculated to set P load limits from all sources within a watershed and include an added margin of safety. The success of an environmental protection plan in limiting P exports from a watershed depends on locating and correctly characterizing critical source areas associated with instream P loads.

Sources of P fall into two general categories: point sources and nonpoint sources. A point source of P comes from a “clearly identifiable point of discharge”, such as dissolved P in the effluent piped out of a wastewater treatment plant (Pierzynski, et al., 2005). On the contrary, nonpoint sources of P are trickier to assess and control, mainly because of the diffuse nature and often widespread area of the source, such as eroded streambank materials (Carpenter, et al., 1998). Relatedly, a critical source area (CSA) is often identified where a nonpoint source overlaps with a hydrologically active area, resulting in disproportionately high amounts of mobilized P (Pionke, et al., 2000).

Locating a CSA allows for additional investigation into characteristics of the P source, including: (1) dominant forms of P, (2) nature of the source (whether naturally occurring or anthropogenic), (3) possible pathways and processes through which the source mobilizes to nearby surface waters, and (4) quantitative estimates of P loading rates. These insights help prioritize the goals of environmental protection plans by informing decisions made to limit P mobility from CSAs.

However, locating and characterizing CSAs can be challenging in mixed-use watersheds with wide ranges of landscape characteristics. To locate and characterize CSAs in such a watershed requires one to understand the following: (1) the spatial distribution of P sources in the watershed; (2) temporal dynamics that affect source mobility; and (3) the chemical forms of P from those sources and associated transfer pathways and processes.

SYNOPTIC SAMPLING

Synoptic sampling is a proven strategy for capturing the spatial variation of water quality in surface waters across a study area or watershed that is not outfitted with numerous, automated monitoring stations (Banks and Palumbo-Roe, 2010, Grayson, et al., 1997). In its most basic form, synoptic sampling offers a summary of the flow rate and constituent concentration at a high density of sites across a study area at a single point in time and in a steady hydrologic state. Synoptic sampling has been most commonly used in baseflow conditions when streamflow is not influenced by recent flow events and constituent concentrations are potentially highest (Grayson, et al., 1997, Kimball, et al., 2002). The simple product of the flow rate and constituent concentration at a site provides an instantaneous load estimate.

After load estimates are calculated at all synoptic sampling sites, one gains a “spatially intensive snapshot” of constituent loading across the study area (Kimball, et al., 2002). Increases of instream constituent load readily reveal source areas. In this way, synoptic sampling is more effective in assessing constituent spatial loading patterns than either routine or event monitoring strategies (Eyre and Pepperell, 1999). Synoptic sampling has been applied in water quality studies, from sourcing heavy metal loads associated with acid mine drainage (Banks and Palumbo-Roe, 2010, Kimball, et al., 2002, Runkel, et al., 2013) to correlating land use changes with observed water quality parameters (Cox, et al., 2013, Eyre and Pepperell, 1999, Wayland, et al., 2003).

While useful for assessing water quality spatially, synoptic sampling is not commonly used as a strategy for capturing the temporal dynamics of instream P loads. The potential value of repeating synoptic sampling under different hydrologic conditions has been demonstrated. Wayland used temporally repeated synoptic sampling in baseflow conditions over two years in order to correlate certain water quality parameters with land use, but did not measure P (Wayland, et al., 2003). Banks used temporally repeated synoptic sampling to discriminate between point and nonpoint sources of zinc in a mining catchment. (Banks and Palumbo-Roe, 2010).

To forego repeated synoptic sampling may be acceptable if research is focused only on a single transfer pathway, as is the case with assessing subsurface transport of soluble metals associated with acid mine drainage, which can be assessed once in baseflow conditions. However, at the watershed scale and in a mixed landscape, a constituent such as P originates from numerous source areas, being mobilized through different pathways depending on annual hydrologic cycles and temporal changes in land use and cover (Harmel and Haggard, 2006,

Jordan, et al., 2012, Pionke, et al., 1999). For example, in a predominately snow-fed watershed, the spring snowmelt period may last for many weeks, during which P is mobilized through snowmelt pathways, such as runoff over frozen soils. Later in the dry season, P transfer may shift to primarily subsurface pathways or to irrigation induced erosion. For reasons like these, temporally repeated synoptic sampling is essential for locating and characterizing CSAs of P in a mixed-use watershed.

PHOSPHORUS FRACTIONATION OF WATER

When a CSA is located, classifying the forms of P helps further characterize the source. This is because certain forms of P are more likely to be mobilize to surface waters through certain processes and pathways. Knowing which forms of P dominate at different sites under different hydrologic conditions and land uses can in turn guide management strategies that limit those P exports.

In water quality monitoring, P is commonly reported as “Total P” (TP) because of the strong correlation in surface water bodies between mean TP concentration and chlorophyll *a*, an indicator of algal growth (Forsberg and Ryding, 1980, Prairie, et al., 1989, Smith, 1998). Total P represents P in all compounds and forms: both organic and inorganic P, both dissolved P and P associated with suspended particulates (Espinosa, et al., 1999, Haygarth, et al., 1997).

Total P in a water sample can be divided into general P fractions depending on a chosen combination of sample filtration and analytical method (Haygarth and Sharpley, 2000). These P fractions include: total dissolved P (TDP), dissolved reactive P (DRP), dissolved organic P (DOP), and particulate P (PP). Total dissolved P represents all P in solution, both inorganic and organic, since the samples are filtered prior to analysis. Particulate P (PP) can be derived by

subtracting TDP from TP, and represents P associated only with particulates suspended in the water. Dissolved reactive P is a fraction of TDP, consisting of inorganic phosphates which are almost completely bioavailable for algal growth (Lee, et al., 1980, Reynolds and Davies, 2001). Dissolved organic P (DOP) is another fraction of TDP. It is derived by subtracting DRP from TDP, and consists of the non-reactive, organic P fraction in solution.

By analyzing these general forms of P at each synoptic sampling site, one can gain meaningful insight into the nature of upstream CSAs. For example, an increased PP load between two sites would indicate an increase in suspended sediment load, as the PP fraction does not include any dissolved P forms. Particulate P originates from sediment sources associated with either local stream channel erosion or surface runoff between the two sites. Since the increase of PP must have been driven by flowing water, the detachment and mobilization of those particles would have been related to soil saturation and hydrologic conditions (Pierzynski, et al., 2005). If, for example, the increase in PP load occurred during baseflow conditions, it follows that PP was most likely mobilized through overland return flows associated with irrigation or from eroded streambank material, and not from a rain event.

With this sort of information, one could identify the stream segment between the two sites as being associated with a source area of sediment-bound P. This assessment, however, would be limited by a lack of data on PP transport during non-baseflow conditions. Thus, it is essential to repeat synoptic sampling with P fractionation under different hydrologic conditions. If the stream segment showed similar increases in PP loads under different hydrologic conditions, the stream segment and associated areas could be classified as a CSA. By locating and characterizing this CSA, a more effective investigation could be conducted in the future to

determine if the sediment was primarily originating from stream channels or from nearby fields, preparing the way for best management practices that limit PP transport and improve water quality.

OBJECTIVE

The objective of our study was to combine repeated synoptic sampling with phosphorus fractionation into a unique strategy for locating and characterizing critical source areas of P. We evaluated this strategy in a montane, mixed-use watershed, based the analysis of five P fractions in surface waters collected during seasonally repeated and annually replicated synoptic sampling campaigns.

METHODS

STUDY AREA

The Wallsburg watershed (184 km²) is a subwatershed of the Provo River Basin, located within the Wasatch Mountains of north central Utah, USA. This watershed drains into the Deer Creek Reservoir, a major municipal water that was classified as an impaired, eutrophic waterbody in the 1980's. Despite substantial water quality improvements in the Deer Creek Reservoir, there is an ongoing effort to further limit P inputs (WCD, 2012). To protect reservoir health, TMDLs were calculated by state officials, requiring that total P and total dissolved P concentrations of reservoir-feeding surface waters are limited to 0.05 mg/L and 0.025 mg/L, respectively.

The Wallsburg watershed was an ideal location for our study because: (1) it has historically contributed high annual P loads to the reservoir; (2) knowledge is limited concerning

the spatial and temporal variation of P sources within the watershed; (3) the land cover and use across the watershed is quite varied, providing an opportunity to connect P loads to sources, pathways, or processes; (4) the major tributaries are easily accessible for sampling purposes; and (5) periods of stable streamflow are commonly observed throughout a hydrologic year and is therefore conducive to synoptic sampling.

The watershed elevation ranges from 1306 m at the outlet to 2959 m above sea level. Land cover (Figure 1) includes woodland ecosystems of deciduous and coniferous tree species (e.g. *Populus tremuloides*, *Pseudotsuga menziesii*, *Acer grandidentatum*, etc.) (35.6 %), shrubland ecotones of primarily Gambel oak (*Quercus gambelii*) and sagebrush (*Artemisia tridentata*; 26 %), and semi-desert ecosystems of grasses and shrubs (30.8 %). The valley floor is covered by low intensity, irrigated agriculture of alfalfa (*Medicago sativa*), perennial grasses, and pasture (7.6 %). Some parts of the watershed are used for summer grazing and winter feeding of cattle and sheep. Toward the center of this agricultural landscape is the small town of Wallsburg, with a population of about 270 people.

HYDROLOGY

Three major, perennial tributaries exist in this watershed: Main Creek, Little Hobble Creek, and Spring Creek. The flow direction for these tributaries is generally northwest. Main Creek (~24 km long) reaches the length of the watershed before emptying into Deer Creek Reservoir. Little Hobble Creek (~11.7 km long) is joined by a minor tributary, Little Hobble Creek - Left Fork, and feeds into Main Creek 17.2 km from the headwaters of Main Creek. Spring Creek (~5.3 km) originates from a spring within the town of Wallsburg. The spring

discharges on average 70 L/s year-round, and runs parallel to Main Creek before the confluence of the two about 21.8 km from the headwaters of Main Creek.

Figure 2 shows an annual hydrograph of the Wallsburg watershed, with median monthly values based on 30 years of discharge measurements at the watershed outlet, from 1984 to 2014 (UAWQMS, 2017). The hydrograph shows the following: (1) discharge begins to rise between February and April due to snowmelt at low elevations, (2) peak discharge is usually observed around May, driven by snowmelt at all elevations, and (3) baseflow conditions prevail from July through October. Streamflow in the upper segments of Main Creek and Little Hobble Creek is dominated by snowmelt with some rain events before and after the summer months. Increases in discharge from the spring at Spring Creek are usually due to localized subsurface flows during snowmelt or rain events. During the baseflow conditions, groundwater contributions and subsurface flows become the dominant sources of streamflow.

SAMPLING DATES

We conducted at least one sampling campaign per year during each of the three distinct, annual hydrologic periods (Table 1). We termed the first period “Rise”, which represents the rising limb of the annual hydrograph, spanning the months of February and March. The second period we termed “Peak”, or the period of peak snowmelt-driven streamflow, which historically comes in April or early May. The third period is “Base”, or the period of baseflow, which is historically observed from June through October, before snowfall begins again the winter.

The sampling dates we chose not only reflect changes in the annual hydrologic cycle, but also temporal changes to water use and land use. For instance, significant stream diversions occur between May and October as water is used for agricultural irrigation. Likewise, livestock

grazing and winter feeding areas change throughout the year, with cattle or sheep grazing different pastures and rangelands across the watershed. Given the potential for variation in climate or land use from year to year, we replicated our study in 2016, choosing sampling dates as close to the anniversaries of those in 2015. Sampling campaigns were not conducted within 24 hours of a rain event to avoid unfavorable, dynamic flow conditions.

SAMPLING SITES

The locations for water sampling used in this study were not randomly chosen, but were based on a water sampling plan created by the Utah Department of Water Quality (DWQ) for fecal coliform monitoring. Twenty-two sites were presented in the DWQ plan, but we immediately excluded three of these from our study due to restricted access. We accepted the remaining nineteen sites as sampling locations due to their relatively even spatial distribution along the longitudinal profiles of the three study tributaries, which allowed us to capture the spatial patterns of P loads potentially associated with surrounding landscape features.

Sampling locations along Main Creek bracketed the confluences with Spring Creek and Little Hobble Creek, which helped to account for P load contributions from those two tributaries. Most sites were located at a road-stream crossing to maximize accessibility. In steep, forested areas the terrain limited accessibility to locations closer to headwaters. For example, the uppermost site on Main Creek is MC-01, which occurs about 9 km downstream of the headwaters. Access to some sites in the lower watershed required permission from cooperative landowners. Except for MC-04, all sites had flowing water in the stream channel at some point in the hydrologic year. MC-04, which was planned midway between MC-03 and MC-05, never showed water during any of the seven sampling campaigns (due perhaps to an upstream

diversion), and was excluded from our analyses. The results of this study ultimately focus on the eighteen remaining sites shown in Figure 3.

SAMPLING PROCEDURE

To visit the 18 sites as quickly as possible, we used two teams, each responsible for approximately half the sites. One team visited the upstream half of the watershed, including all sites on Little Hobble Creek, sites 01 through 03 on Main Creek, and SC-01. The other team visited the sites in the downstream half of the watershed (MC-06 through 10, and SC-03 through 07). In this way, teams were able to sample all sites in approximately 2 hours, providing a temporal snapshot of P load across the watershed. Sampling always began at the same time in the mornings, with the first site being sampled around 09:00 (+/- 00:30) so as to minimize potential variation due to diel cycling (Cohen, et al., 2013, Hatch, et al., 1999).

At each sampling site, the exact location for streamflow measurements was chosen to maximize ideal flow conditions, which included avoiding sharp bends in the stream channel, excessively rocky sections, thick instream vegetation, and rapidly changing stream dimensions (Chang, 2006). Where possible, streamflow measurements were made in controlled hydraulic structures (e.g., culverts, pipes, concrete channels). Streamflow (L/s) was measured by velocity-area under the USGS Six-tenths Method using Hach FH950 Portable flow meters with electromagnetic velocimeters to measure flow velocity (Turnipseed and Sauer, 2010). This method of measuring streamflow is ideal in small, shallow streams (DeBarry, 2004). The range of stream channel widths was 50 - 400 cm and of stream depths was 10 - 50 cm. The number of cross sectional segments at each site was such that no segment accounted for more than 10% of the total streamflow.

Water samples were collected in acid-washed, 1 L plastic bottles, which were rinsed with stream water before collection. Samples were collected slightly upstream of where streamflow was measured to avoid sampling artificially suspended sediments. Here, a representative grab sample was collected by opening and closing the bottles manually at multiple points in the stream cross section. Samples were transported in coolers and stored at 4 °C until being analyzed within 24 hours of collection.

PHOSPHORUS FRACTIONATION AND DATA ANALYSIS

Phosphorus in samples was separated into three basic fractions for analysis: dissolved reactive P (DRP), total dissolved P (TDP), and total P (TP). Based on the results from these three fractions, two additional fractions were calculated (Table 2): particulate P (PP), and dissolved organic P (DOP).

Before analyzing TDP and DRP fractions, samples were filtered through cellulose acetate membranes of 0.45 µm pore size (Thermo Scientific Nalgene Syringe Filters 0.45 µm SFCA), which removed suspended particulates from samples before analysis. Before analyzing TP fractions, samples were prepared by microwave-assisted digestion with nitric acid. The Murphy and Riley ascorbic acid method was used to determine DRP concentrations, using a Thermo Scientific GENESYS spectrophotometer (Murphy and Riley, 1962). Total P and TDP concentrations were determined with a Thermo Scientific iCAP 7400 ICP-OES.

Concentrations of P lower than the instrument detection limits ($< 7 \mu\text{g/L}$) were reported as being 0.00 mg/L. Instantaneous P load values (mg/s) were calculated as the simple product of streamflow (L/s) and concentration (mg/L) at a given site. It should be noted that load was reported as the rate *mg/s* because measurements were an instantaneous load estimate at the time

of sampling, and should not have been extrapolated to greater units such as *kg/yr*, for example. However, loads reported as *mg/s* could easily be converted to *kg/yr* by multiplying by a factor of 31.536 in order to understand the reported rates in the context of annual P export.

The results for streamflow, P concentration, and P load for a given site were averaged between replicate years based on the hydrologic condition in which the samples were collected. For example, since the P concentrations were measured at the outlet during the ‘peak’ flow conditions in May 2015 and May 2016, these were averaged into one value to represent mean P concentrations in ‘peak’ flow conditions within the two-year study period. The bulk of data analysis and data visualization were performed with R 3.3.2 and the ggplot2 package (Team, 2017, Wickham, 2009).

ASSESSING CRITICAL SOURCE AREAS

To summarize our observations into meaningful assessments, we focused primarily on stream segments that exhibited the greatest relative increases in load. If a segment routinely exhibited relatively significant increases in P load during all hydrologic periods or if a segment exhibited significant increases in P load during a hydrologically active period, we deemed the stream segment and the associated watershed area as a CSA of P. We characterized the CSA based on P fraction data, hydrologic conditions, and land use in order to better connect the increases in P loads with source-driven or flow-driven pathways and processes.

RESULTS & DISCUSSION

The objective of our study was to combine repeated synoptic sampling with P fractionation into a unique strategy for locating critical source areas of P. In the first section below, the results and assessment are based on a traditional synoptic sampling approach that only evaluated TP during a single, baseflow sampling campaign. The assessment of CSAs based on this limited approach served as a baseline comparison for assessments that incorporated repeated synoptic sampling with and without P fractionation.

TRADITIONAL SYNOPTIC SAMPLING

The traditional synoptic sampling approach was limited to only TP concentrations and streamflow measured during a single synoptic sampling campaign on July 29, 2015. This campaign took place at baseflow, which is the most common condition for synoptic sampling studies (Kimball, 2002).

Field Results

Discharge (Figure 4, top left) at MC-10 (the watershed outlet) during the July baseflow conditions in 2015 was 90 L/s, about 40% less than the historic median for July. Streamflow measured at LHC-01 and MC-01 (the uppermost sites in the watershed) were also low compared to the historic means and were 21 L/s and 52 L/s, respectively. Five sites in the middle watershed showed dry streambed conditions, due to limited upstream sources and irrigation diversions. Discharge from SC-01 (at the spring source of Spring Creek) was similar to the historic average and was 77 L/s. The spatial distribution of discharge indicates that groundwater and subsurface flow contribute the major proportion of the total streamflow in the lower watershed during

baseflow, which is supported by the fact that no storm events or snowmelt influenced the baseflow sampling conditions.

Total P concentrations (Figure 4, top right) ranged from 0.018 to 0.268 mg/L throughout the watershed, with the highest concentration measured at LHC-01. Measurements could not, of course, be made at the dry sites. Concentrations increased the most between SC-03 and SC-04, and between MC-08 and MC-09.

Instantaneous load estimates for TP (Figure 4, bottom left) ranged from 0.00 mg/s at the dry sites to 5.54 mg/s at LHC-01. The greatest increases in TP load were measured between SC-03 and SC-04, and between MC-08 and MC-10, as visualized in a profile view of sampling locations along Main Creek (Figure 5).

Assessment and Discussion

Based only on the traditional synoptic sampling approach, the results showed sources of TP associated with the following areas (Table 3): (1) the subwatershed above LHC-01, (2) the spring at SC-01, (3) the segment of Spring Creek between SC-03 and SC-04, and (4) the segment of Main Creek between MC-08 and MC-10.

Because LHC-01 is the uppermost sampling location on this tributary, there are limits to what can be concluded about TP loads originating above LHC-01. The subwatershed upstream of LHC-01 is forested with no agricultural development, with some of the steepest terrain in the watershed ($20^{\circ} < \text{slope} < 60^{\circ}$). Overland flow was assumed not to be the transfer pathway for TP during baseflow conditions because there was no snowmelt and no rain event prior to sampling that could have supplied overland flow. With a single sampling campaign, it was difficult to know where TP loads came from within the forested area, or if loads came from subsurface or

instream sources. Areas with visual streambank erosion were observed above the sample location at the time of sampling. Although this subwatershed was identified as a source area, TP from this upstream area was not directly transferred to the watershed outlet during baseflow because the downstream sites (LHC-03 and LHC-04) were dry due to irrigation diversions.

The load measured at SC-01 was associated only with the spring, given the lack of localized overland flow or upstream sources. This means the TP load originated entirely from a subsurface source carried by groundwater.

The load increases along lower Spring Creek and lower Main Creek were partially flow-driven and partially source-driven. Given that baseflow conditions prevailed, increases in TP load around SC-04 and MC-09 were not associated with overland flow from rain, but were from either irrigation return flows, subsurface contributions, or instream processes. Given the proximity of these lower sites (< 1 km), increases in TP concentrations were not likely associated with rapid, instream biogeochemical cycling of P, such as P desorption from instream sediments, but were more likely from groundwater inputs (as was the case with SC-01) or from stream channel erosional processes. In short, we classified the aforementioned segments of Spring Creek and Main Creek as potential CSAs based on a traditional synoptic sampling approach, in which TP loads were dominated by either eroded stream channel sediments or groundwater inputs.

Despite identifying some potential CSAs of P in the watershed, a single synoptic sampling campaign conducted during baseflow and without P fractionation did limited our understanding of P sources in numerous ways. One limitation is the uncertainty of whether a potential CSA identified during the July 2015 baseflow conditions would be identified and characterized similarly in more active hydrologic conditions, when the risk is greater for P export to Deer Creek Reservoir. In other words, a single sampling campaign during baseflow did not

provide information to whether a source was predominately flow-driven or source-driven, or whether the source area was really ‘critical’ in the context of annual P export. Repeating synoptic sampling in various hydrologic conditions would address this concern.

Likewise, it was difficult to know whether the sampling campaign yielded a spatial snapshot that was representative of typical, baseflow loading patterns for this watershed. For example, does the relatively high load observed in the segment upstream of SC-04 occur regularly during baseflow or was it anomalous? Annual replication of synoptic sampling would address this limitation.

Irrigation diversions inhibited our ability to observe P transfer in the watershed and may have obscured important P source areas. For example, the relatively high load measured at LHC-01 vanished by the next downstream site, due to irrigation diversions and groundwater recharge removing the water completely from the main stream channel. In this way, this area of irrigated farmland appeared to act as a P sink, in the case that instream P precipitated or sorbed with soil particles after irrigation. However, could this area be a source of P during different hydrologic and land use conditions?

A final limitation of the traditional synoptic sampling approach used was the lack of information about the dominant P fractions associated with each site. Limiting the chemical analysis to only TP concentration prevented any distinctions as to whether samples contained significant amounts of PP, DOP, or DRP. Phosphorus fractionation has potential to improve the characterization of CSAs by adding information that links P sources to transfer pathways and processes.

REPEATED SYNOPTIC SAMPLING WITHOUT PHOSPHORUS FRACTIONATION

The assessment of CSAs based solely on a traditional synoptic sampling approach was limited. Presented here are the results and assessment achieved when the traditional synoptic sampling approach was temporally repeated with the goal of determining the temporal dynamics of P source areas. The assessment under this expanded approach was still limited to measuring streamflow and TP concentrations without further P fractionation. The TP load data were derived from two years of seasonally repeated and annually replicated synoptic sampling, with site values being the average of the values observed in 2015 and 2016, respective of hydrologic period.

Field Results

Streamflow patterns across the watershed fluctuated seasonally (Figure 6). At the watershed outlet (MC-10), average discharge ranged from 36 L/s for baseflow periods to 370 L/s during the peak snowmelt period. Average discharge at MC-10 during the 2015 and 2016 study period was less in each hydrologic period than the median historic discharge for the same periods. The range in average streamflow from baseflow to peak flow periods at the uppermost sites ranged from 18 - 95 L/s and 27 - 378 L/s for LHC-01 and MC-01, respectively. Discharge at SC-01 averaged 67 L/s year-round, contributing a significant proportion of flow to Main Creek during baseflow conditions, but a small proportion otherwise. Water diversions for agricultural were observed during the peak flow and baseflow campaigns. The streamflow patterns were similar between 2015 and 2016, but generally the magnitude of streamflow was slightly higher in 2016.

Over the study period, average TP concentrations (Figure 7) ranged from 0.000 - 0.41 mg/L in the upstream half of the watershed, and ranged from 0.022 - 0.204 mg/L in the downstream half. The average TP concentrations at MC-10, the watershed outlet, were 0.080, 0.053, and 0.042 mg-TP/L for the rise, peak, and baseflow periods, respectively. The average TP concentration at SC-01, a groundwater-fed location, was 0.036 mg/L year-round (0.032, 0.055, and 0.028 mg-TP/L for each hydrologic period, respectively). The greatest TP concentrations were observed at LHC-01 during peak and baseflow, and routinely for sites along the lower segments of Main Creek and Spring Creek. Sections within the lower reaches of Main Creek and Spring Creek tended to increase in TP concentration even as flow increased.

Instantaneous TP load estimates (Figure 8) ranged from 0.00 - 37.8 mg/s in the upstream half of the watershed, and ranged from 0.00 - 47.5 mg/s in the downstream half. The greatest loads in each sampling campaign were typically associated with the lower segments of Main Creek and Spring Creek. Dry sites were, of course, reported as having a TP load of 0.00 mg/s. Increases in streamflow drove increases in TP load, while some increases in TP load are also associated with increases in TP concentration. Overall, the greatest amount of TP load exiting the watershed was observed during the 'Rise' period of low elevation snowmelt. There were relatively high TP loads coming from forested areas (MC-01 and LHC-01) during the peak periods, but these loads rapidly diminished before reaching downstream sites. During rising and baseflow periods, relatively low loads of TP came from the same forested areas.

Figure 9 shows the temporal dynamics and relative contributions of instantaneous TP load estimates along the profile of Main Creek (note the vertical axis of each subplot is set to its own scale). The P loading patterns varied over the three hydrologic periods, and showed that certain stream segments were regularly associated with CSAs. For example, the average TP load

routinely increased between MC-07 and MC-10. More specifically, repeated increases were observed between MC-07 and MC-08, which segment contains the confluence with Spring Creek. On the contrary, some CSAs were only observed under particular hydrologic conditions. Site MC-01, for example, exhibited high TP loads only during the peak flow period.

Assessment and Discussion

Based on repeated synoptic sampling without P fractionation, the results indicated CSAs associated with the following areas (Table 3): (1) the subwatersheds upstream of MC-01 on Main Creek and LHC-01 on Little Hobble Creek, (2) segments of Spring Creek between SC-03 and SC-07, and (3) the lowest segments of Main Creek between MC-06 and MC-09.

When compared to other sites and to other flow conditions, relatively high loads were measured at sites MC-01 and LHC-01 during peak flow. This is an example of how repeated synoptic sampling informed the assessment of CSAs based on the temporal dynamics of a source and hydrologic conditions, because the subwatershed above MC-01 was not previously identified as a CSA through the traditional synoptic sampling method.

The subwatersheds above MC-01 and LHC-01 are forested with no agricultural development, and contain some of the steepest terrain in the watershed ($20^{\circ} < \text{slope} < 60^{\circ}$). The traditional synoptic sampling approach without P fractionation, limited our ability to interpret likely sources, source areas, and pathways upstream of these two sampling locations. Areas of erosion on steep slopes upstream of these two sites were visible. The TP loads at these upper sites is flow-driven by the annual cycle of high elevation snowmelt. This hydrologic condition could suggest that sources of TP at MC-01 and LHC-01 during peak flow could have stemmed

from stream channel sediments, eroded hillslope sediments, subsurface flows, or overland flows given the saturated soil conditions.

The segments of Spring Creek between SC-03 and SC-07 and the segments of Main Creek between MC-06 and MC-09 are surrounded by farmland, used for growing cover crops, such as hay and alfalfa, and for grazing livestock on gentle terrain (slope < 2°). The lowest segment between MC-09 and MC-10 is surrounded with riparian vegetation and contains a series of beaver dams. The greatest loads in this general area of the lower watershed were observed during rising and peak flow periods, suggesting the TP was predominantly mobilized through flow-driven pathways. However, TP concentrations also tended to increase in the lower watershed, suggesting source-driven pathways, too.

The stream segment between MC-07 and MC-08 contains the confluence with Spring Creek, and the greatest increases in TP concentration and load in this segment occurred in the rising flow period. During the sampling campaigns in rising flow period, winter cattle feeding was observed adjacent to lower Spring Creek and Main Creek. However, without knowing the composition of TP, it is difficult to say if the winter feeding of cattle adjacent to the streams influenced the TP loads through inputs of manure, livestock induced streambank erosion, or otherwise. Regardless, the contribution of Spring Creek to the TP load in Main Creek was routinely significant, especially during the rising flow period of low elevation snowmelt.

The saturated soil conditions in the lower watershed (downstream of MC-05 and SC-04) must be considered during the rising and peak flow periods. Converging surface water and groundwater flows creates one of the most dynamic and hydrologically active areas in the watershed. During periods of low elevation snowmelt followed by high elevation snowmelt, the

potential is high for substantial subsurface P inputs to the streams, an increased potential for overland flow, and increased risk for stream channel erosion.

Seasonally repeated and annually replicated synoptic sampling helped to overcome some of the limitations of traditional, single event synoptic sampling. Repeated synoptic sampling in different hydrologic conditions allowed for the confirmation or rejection of potential CSAs identified in the baseflow period. For example, SC-01 was a suspected CSA of TP during baseflow conditions, but did not contribute a major proportion of downstream load during rising and peak flow periods. On the contrary, some areas in lower Main Creek were suspected CSAs during the baseflow period and contributed the greatest loads during the rising and peak flow periods. These areas are CSAs in the context of annual P export. Other areas, such as lower Spring Creek between SC-04 and SC-07, were not identified during baseflow conditions as being critical contributors to TP loads, but synoptic sampling during rising and peak flow periods suggested the area was a CSA of TP.

Using a repeated synoptic sampling approach that included annual replication provided more representative spatial snapshots of P loading patterns. The assessment gained more confidence that the spatial variation observed in each of the hydrologic periods were representative of the respective period. This was true even if general streamflow rates were lower than expected based on historic data.

Irrigation diversions, as previously explained, proved problematic during the traditional synoptic sampling campaign conducted in baseflow conditions. Through a repeated synoptic sampling approach that included sampling in different hydrologic conditions, the influence of irrigation diversions on P transfer in the watershed was better understood. During baseflow conditions, the TP contributions of the upper watershed (areas between LHC-01 and LHC-04 and

between MC-01 and MC-06) were obscured due to the lack of streamflow caused by irrigation diversions and groundwater recharge. During the rising flow period when high elevation snowmelt had yet to begin and irrigation diversions were not yet in place, the TP load originating from the forested subwatersheds was relatively low and was not reduced as measured at downstream sites. During the peak flow period, with high elevation snowmelt occurring and with irrigation diversions in place, repeated synoptic sampling confirmed that TP loads from forested areas were significantly reduced as streams enter the agricultural areas. This scenario suggests that diversions for irrigation may have facilitated a potential sink rather than source of instream TP as water was applied to nearby farmland, where P could precipitate or sorb to soil particles after irrigation.

After using a repeated synoptic sampling approach without P fractionation, the challenge remained to distinguish sources and pathways of P. This was due to the lack of information about the dominant P fractions in the composition of TP measured. The TP analysis made no distinction as to whether samples contained significant amounts of PP, DOP, or DRP. Phosphorus fractionation has the potential to guide the assessment of CSAs by suggesting the nature of transfer pathways and processes responsible for mobilized P in the watershed.

REPEATED SYNOPTIC SAMPLING WITH PHOSPHORUS FRACTIONATION

An assessment based on seasonally and annually repeated synoptic sampling, but without P fractionation, greatly improved our understanding of the spatial variation and temporal dynamics of TP sources and CSAs in the Wallsburg watershed. However, that approach did not provide information on the chemical composition or dynamics of TP, and limited our ability to connect TP loads to specific sources or pathways.

The following results and assessment were based on the same hydrologic data described previously, but expands interpretations of the TP results by including P fractionation data. The data were derived from temporally repeated synoptic sampling in which water samples were analyzed for five P fractions: TP, PP, TDP, DRP, and DOP.

The map arrays (Figures 10 and 11) are arranged such that the hydrologic sampling period changes from left to right, and P fractions change from top to bottom. The fractions are arranged such that TP (top row) is comprised of the sum of the two rows beneath it (PP and TDP), and that TDP (third row) is comprised of the sum of the two rows beneath it (DRP and DOP). Likewise, the stacked bar charts (Figures 12 – 15) are arranged such that the DRP and DOP bars stack to equal TDP, and the total height of the stacked bars (DRP, DOP, and PP) equals TP.

Field Results

Spatial and temporal variations in streamflow across the watershed were described in the previous results section, as were TP concentrations and TP loads (Figures 6 – 8). Over the study period, average TDP concentrations (Figure 10, row 3) in the upstream half of the watershed ranged from 0.000 – 0.116 mg/L, and ranged from 0.016 – 0.070 mg/L in the downstream half. Average DRP concentrations (Figure 10, row 4) in the upstream half of the watershed ranged from 0.000 – 0.087 mg/L, and ranged from 0.012 to 0.045 mg/L in the downstream half. Average DOP concentrations (Figure 10, row 5) in the upstream half of the watershed ranged from 0.00 – 0.116 mg/L, and ranged from 0.000 – 0.030 mg/L in the downstream half. Average PP concentrations (Figure 10, row 2) ranged from 0.000 – 0.107 mg/L in the upstream half of the watershed, and ranged from 0.000 - 0.098 mg/L in the downstream half.

Over the study period, average instantaneous TDP loads (Figure 11, row 3) in the upstream half of the watershed ranged from 0.00 – 11.8 mg/s, and ranged from 0.00 – 17.0 mg/s in the downstream half. Average instantaneous DRP loads (Figure 11, row 4) in the upstream half of the watershed ranged from 0.00 – 2.15 mg/s, and ranged from 0.00 to 10.6 mg/s in the downstream half. Average instantaneous DOP loads (Figure 11, row 5) in the upstream half of the watershed ranged from 0.00 – 11.8 mg/s, and ranged from 0.00 – 7.95 mg/s in the downstream half. Average instantaneous PP loads (Figure 11, row 2) ranged from 0.00 – 9.78 mg/s in the upstream half of the watershed, and ranged from 0.00 – 19.3 mg/s in the downstream half.

The highest PP loads (relative to each hydrologic period) were observed at sites along the lower reaches of Main Creek and Spring Creek (Figures 11, 12 and 14). Additionally, relatively high PP loads were observed during peak flow at LHC-01 and MC-01, the uppermost sites in the watershed (Figures 11 and 12). In general, PP concentrations across the watershed were positively related to increases in streamflow. Figures 13 and 15 show that PP in the lower watershed comprised a range of proportions depending on the hydrologic periods.

Loads of DRP were essentially absent at the upper watershed sites. In each hydrologic period, significant DRP loads were first observed downstream of MC-06, with the greatest increases occurring between MC-07 and MC-08 and between SC-04 and SC-07 during the period of rising flow (Figures 12 and 14). By contrast, at the source of Spring Creek (SC-01), the DRP fraction routinely dominated about 90% of TP, with some localized inputs of DOP and PP during the peak flow period. Downstream of SC-01, the proportion of DRP decreases as DOP and PP increase.

The highest DOP load was observed exiting the forested areas at MC-01 during the period of peak flow, but irrigation diversions at the downstream sites prevented further transport. Significant increases in DOP loads were observed between MC-07 and MC-08 and between SC-06 and SC-07 during the period of rising flow (Figures 12 and 14). The percentage of DOP in the composition of TP was quite low at sites along Spring Creek except in the rising flow period (Figures 13 and 15). Dissolved organic P comprised the majority of the TP loads in the upper watershed, but generally less than 25% in the lower watershed.

Assessment and Discussion

Based on repeated synoptic sampling combined with P fractionation, the results indicated CSAs associated with the following (Table 3): (1) the subwatersheds upstream of MC-01 and LHC-01, (2) segments of Spring Creek between SC-04 and SC-07, (3) the generalized area of the lower half of the watershed in terms of DRP loads related to groundwater, and (4) the lower segments of Main Creek, particularly between MC-06 and MC-09. The CSAs listed here are similar to those identified in the previous assessment, given that both were based on repeated sampling. The addition of P fractionation data, however, allowed this assessment to include P sources and pathways associated with the P source areas.

The subwatersheds above MC-01 and LHC-01 were identified as CSAs of TP during the peak flow period. This flow period is characterized by high elevation snowmelt, saturated forest soils, and high stream volumes and velocities. Through P fractionation, we observed that TP at these uppermost sites was comprised of DOP (55%) and PP (45%), with near-zero DRP loads. The most likely sources of the relatively high DOP loads were organic P leached from forest soils and surface-level biological materials, such as plant detritus, interacting with overland flow.

The observed PP load likely originated from detached soil particles on steep, forest slopes, being mobilized by overland flow and from stream channel materials. Though specific areas upstream of these two sites cannot be identified, repeated synoptic sampling with P fractionation helped determine potential sources and pathways within these subwatersheds. A weakness of this study strategy was that the relative importance of these DOP and PP sources could not be properly assessed in the context of annual P export, in part because of the effect of downstream diversions.

Even without P fractionation, segments of Spring Creek between SC-04 and SC-07 were associated with CSAs during the rising and peak flow periods. Through P fractionation, it was observed how the composition of TP along the profile of Spring Creek shifted under different hydrologic and landscape conditions. At the spring source (SC-01), TP was comprised almost entirely of DRP during each sampling campaign during the study period. While the assessment did not prioritize SC-01 as a ‘critical’ source area because the percent contribution to downstream load was small, the DRP measured at SC-01 was evidence that groundwater discharge through springs and other subsurface pathways were supplying a nearly constant background load of DRP (approx. 60 kg/yr at SC-01). Other springs contribute flow to Main Creek in the lower part of the watershed, and similar DRP concentrations have been observed at those sites (data not shown). The DRP in groundwater-driven inflows is possibly derived from groundwater interactions with P-rich, unconsolidated sediments and geologic parent material. or from soluble soil P dissolving in subsurface flows. Very little DRP was detected in the upper half of the watershed on Main Creek and Little Hobble Creek, as streamflow in these areas mostly originates from surface sources and not from groundwater recharge.

At the sites downstream of SC-01, the DRP-dominated load shifted into a mix of DOP, DRP, and PP. Significant increases in DOP and DRP occurred between SC-06 and SC-07 during the rising flow period of low elevation snowmelt. It was noted previously that the farmland adjacent to Spring Creek and Main Creek in this area was used for winter feeding of cattle, and the increase in DOP occurs in these stream segments. The DOP likely originated from manure accumulated at the soil surface during the winter. The increasing load of DRP in the lower segments of Spring Creek and Main Creek were likely due to inputs from groundwater inflows and areas with elevated soil P. Flow-driven increases in PP loads were observed between SC-04 and SC-07 during the rising and peak flow periods. During the rising hydrograph period, there was direct snowmelt runoff contributing to the low elevation Spring Creek flow. During the peak hydrograph period, snow had melted in the low elevation area and there was no overland flow directly into Spring Creek. These observations indicate that the flow driven increases in PP loads are due to streambank erosion. These areas were observed to be prone to streambank erosion, in part due to livestock activity in riparian areas as well as increased hydrologic activity and streamflow volumes.

The assessment of sources and pathways associated with areas between MC-06 and MC-09 was comparable to the assessment of Spring Creek CSAs given that landscape features and local runoff timing so similar. In general, TP loads increased significantly (especially during the rising flow period) between MC-07 and MC-08. This is the stream segment that contains the confluence with Spring Creek. In other words, Spring Creek was a routinely a significant source of TP into Main Creek. This observation was also true of each fraction, in that Spring Creek routinely supplied significant proportions of DRP, DOP, and PP to Main Creek.

As noted previously, DRP loads were not detected at sites along Main Creek until around MC-06. The increase of DRP loads around MC-06 corresponds with the general area of the watershed the experiences groundwater discharge, as evidence by the presence of springs.

The PP load in Main Creek at MC-08 was routinely dominated by PP loads coming from Spring Creek, despite streamflow velocities being generally lower in Spring Creek. During sampling campaigns, the water in lower Spring Creek was observed to have higher turbidity than the waters in Main Creek, even during baseflow conditions. The potential sources and pathways of the observed PP from Spring Creek were described previously.

An interesting observation was that PP concentrations, in each hydrologic period, tended to decrease between MC-09 and MC-10. This stream segment is more meandered, was surrounded with riparian vegetation, and contained a series of beaver dams. The streamflow velocity in this segment was significantly decreased by these factors, allowing PP to deposit into streambed sediments. In this way, this final stream segment seemed to act as a sink for PP, partially controlling the direct export of sediment-bound P into the Deer Creek Reservoir.

By combining repeated synoptic sampling with P fractionation, the assessment of CSAs in the Wallsburg watershed was most complete when compared to the assessment developed through a traditional synoptic sampling approach. With P fractionation, we were better able to distinguish critical sources and pathways of P under different land uses and hydrologic conditions. For example, the inputs of DOP from forested areas and from winter feeding areas was not clearly identified without P fractionation. Likewise, the input of DRP through groundwater discharge was an observation not previously noted.

APPLICATION

Only through P fractionation combined with repeated synoptic sampling was an assessment of CSAs in a mixed-use, montane watershed made more complete. This assessment strategy can better inform best management practices that may limit future P mobilization in the watershed. One might plan, for instance, might include reducing the impact of cattle. This could be done by relocating winter feeding areas further from the stream, or by restricting cattle access to streambank areas by installing fences. Relatedly, efforts at stream channel restoration and revegetation may reduce the transport of PP downstream. Another application of this study pertains to developing P export models and TMDL standards, in which one might account for the constant, background of bioavailable, DRP loads from groundwater.

OTHER CONSIDERATIONS

Repeated synoptic sampling with P fractionation may have limited use as a strategy for assessing CSAs in watersheds. Due to the intensive nature of synoptic sampling campaigns, for example, multiple teams or even multiple days may be required depending on the extent of the study area and on accessibility to the waterways. Depending on research goals and the number of sites, spatially intensive and temporally repeated campaigns can generate large numbers of samples resulting in potentially costly laboratory analysis. However, in a largely unmonitored watershed, the information gained through this strategy was, in our view, more valuable and immediately useful for assessing CSAs than that gained through long-term monitoring strategies with fewer sites.

The assessment strategy based on repeated synoptic sampling with P fractionation proved useful while maintaining simplicity. Adding various layers of complexity to this approach should be investigated further. For example, our study was based on sampling once in rising, peak, and

baseflow conditions, respectively, and then was replicated in a second year. Sampling multiple times throughout each period during a single year would provide a higher temporal resolution to the repeated synoptic sampling approach, and may present further insights into P dynamics. Likewise, our study specifically focused on streamflow and P fractions of the water chemistry. While this limited information proved useful in the assessment of CSAs, measuring for additional water quality parameters (i.e., electrical conductivity, pH, turbidity, etc.) may have allowed for deeper analysis into P dynamics across the watershed.

CONCLUSIONS

Traditional synoptic sampling provided a single, spatially intensive snapshot of TP loads across the Wallsburg watershed. This approach provided some information on the locations of critical P source areas, but it did not identify whether the CSAs were representative of the baseflow hydrologic period. Information was also limited in relation to the effects of irrigation diversions and to the composition of P sources and associated transfer pathways. Many of these limitations to traditional synoptic sampling were overcome by employing a seasonally repeated and annually replicated synoptic sampling strategy.

Repeated synoptic sampling throughout distinct hydrologic periods and replicated during a second year increased the confidence of capturing representative snapshots of water quality. This strategy confirmed whether a suspected CSA was really associated with a critical P source, and it showed whether relatively high P loads in the watershed coincided with hydrologic activity or with changes in landscape features. For example, the highest P loads exiting the Wallsburg watershed were observed during the annual rising flow period and did not coincide with the peak flow period. However, repeated synoptic sampling without P fractionation limited

the assessment of CSAs due to a lack of chemical information about the sources and associated pathways of P.

Repeated synoptic sampling combined with P fractionation proved to be a relatively simple and effective strategy to locating and characterizing CSAs in a mixed-use, montane watershed. Critical source areas of P in the Wallsburg watershed included: (1) the uppermost, forested subwatersheds which were dominated by DOP and PP during the peak flow period, (2) lower Spring Creek which exhibited the highest dissolved P and PP loads during low elevation snowmelt due to livestock impact and streambank erosion, (3) lower Main Creek which was influenced by Spring Creek as well as local streambank erosion and livestock impact, and (4) a generalized input of groundwater-related P. Through this assessment strategy, future efforts will be more effective by focusing on the identified CSAs and implementing best management practices in this mixed-use watershed.

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FIGURES

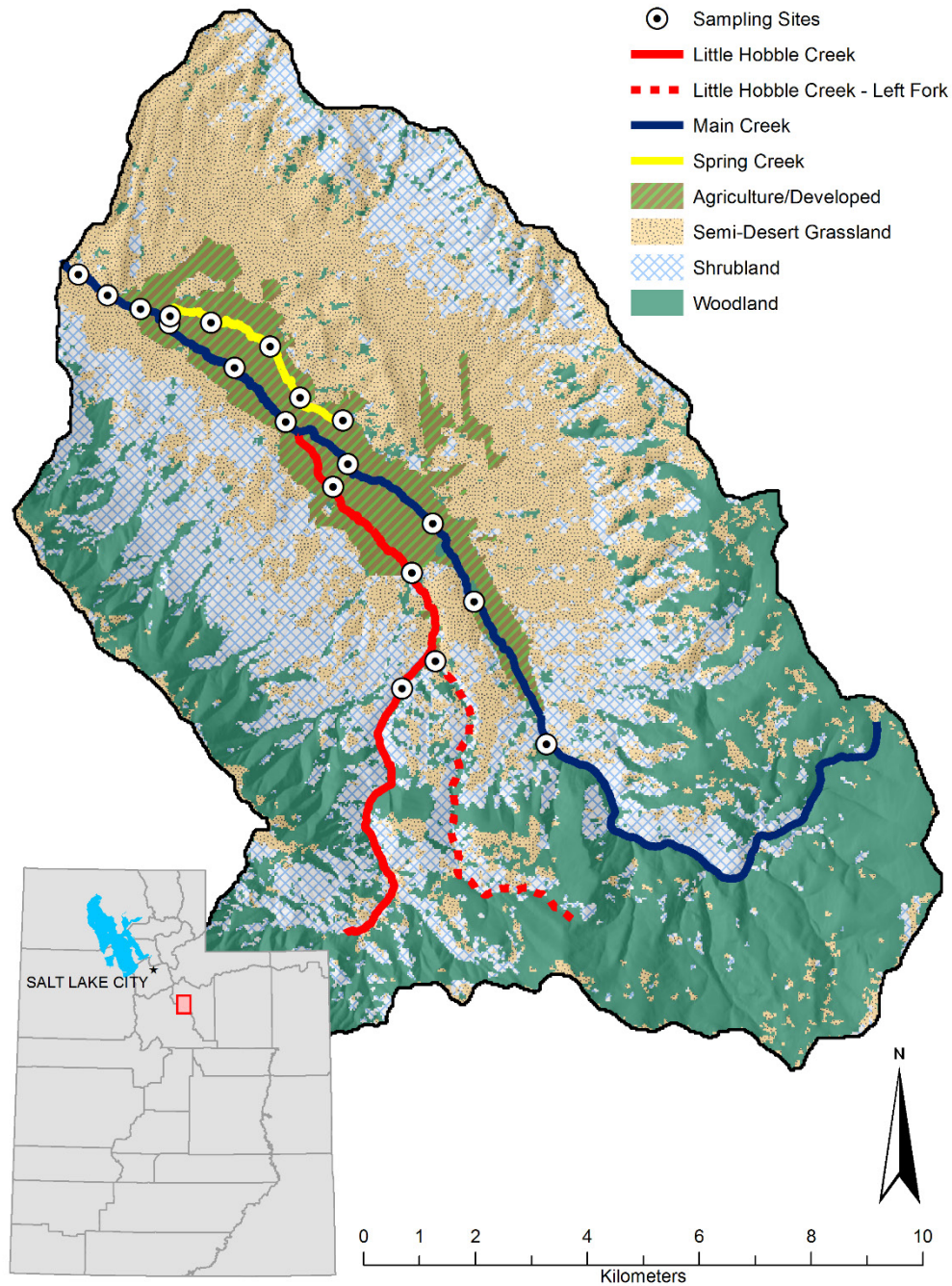


Figure 1. Map of the Wallsburg watershed including major land cover classes and the three perennial streams: Little Hobble Creek, Main Creek, and Spring Creek. Main Creek empties into the Deer Creek Reservoir (not shown) northwest of watershed. The inset figure shows the watershed extent (red box) within the state of Utah, USA, with Salt Lake City and the Great Salt Lake marked for reference. Data from USGS and Utah GIS Clearinghouse (UAGRC, 2017, USGS, 2011, USGS, 2016)

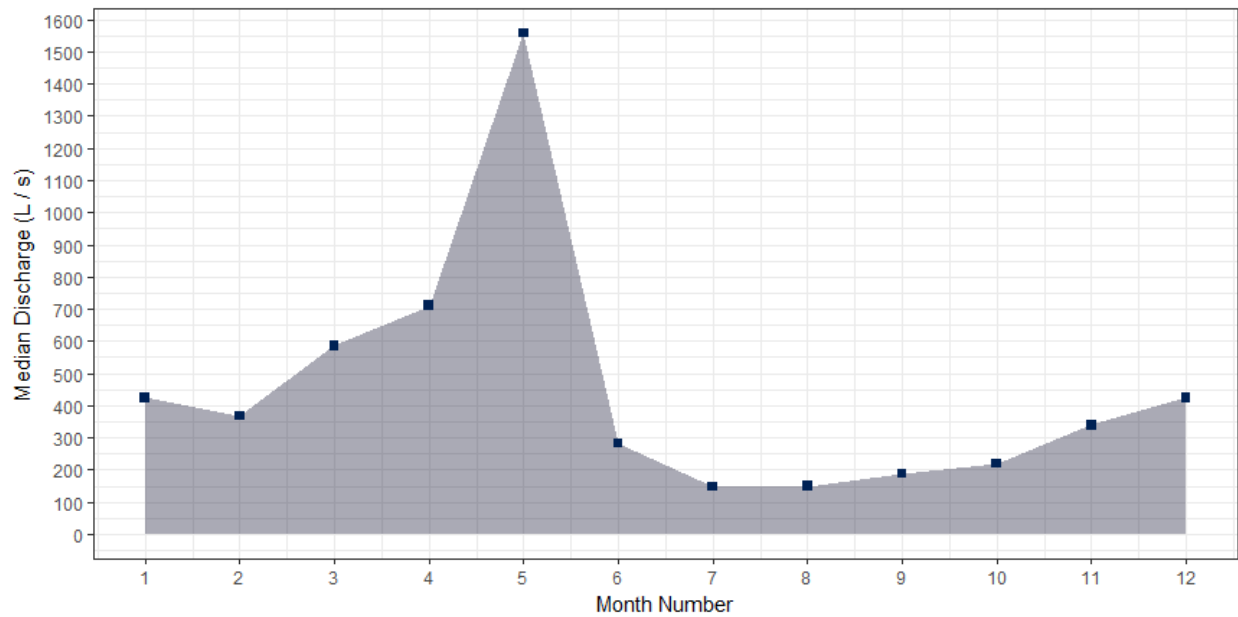


Figure 2. This annual hydrograph at the outlet of the Wallsburg Watershed shows the monthly median discharge into the Deer Creek Reservoir based on 30 years of historic flow data collected from 1984 to 2014 (UAWQMS, 2017). The month numbers represent January (1) to December (12). The hydrograph reflects the annual cycle of hydrologic conditions in the watershed: rising flow conditions during late winter (months 2 and 3) due to low elevation snowmelt, peak flow conditions around May (month 5) due to maximum snowmelt volumes, and groundwater-driven, baseflow conditions from summer into autumn (months 7 through 10). We chose to sample during these three distinct periods.

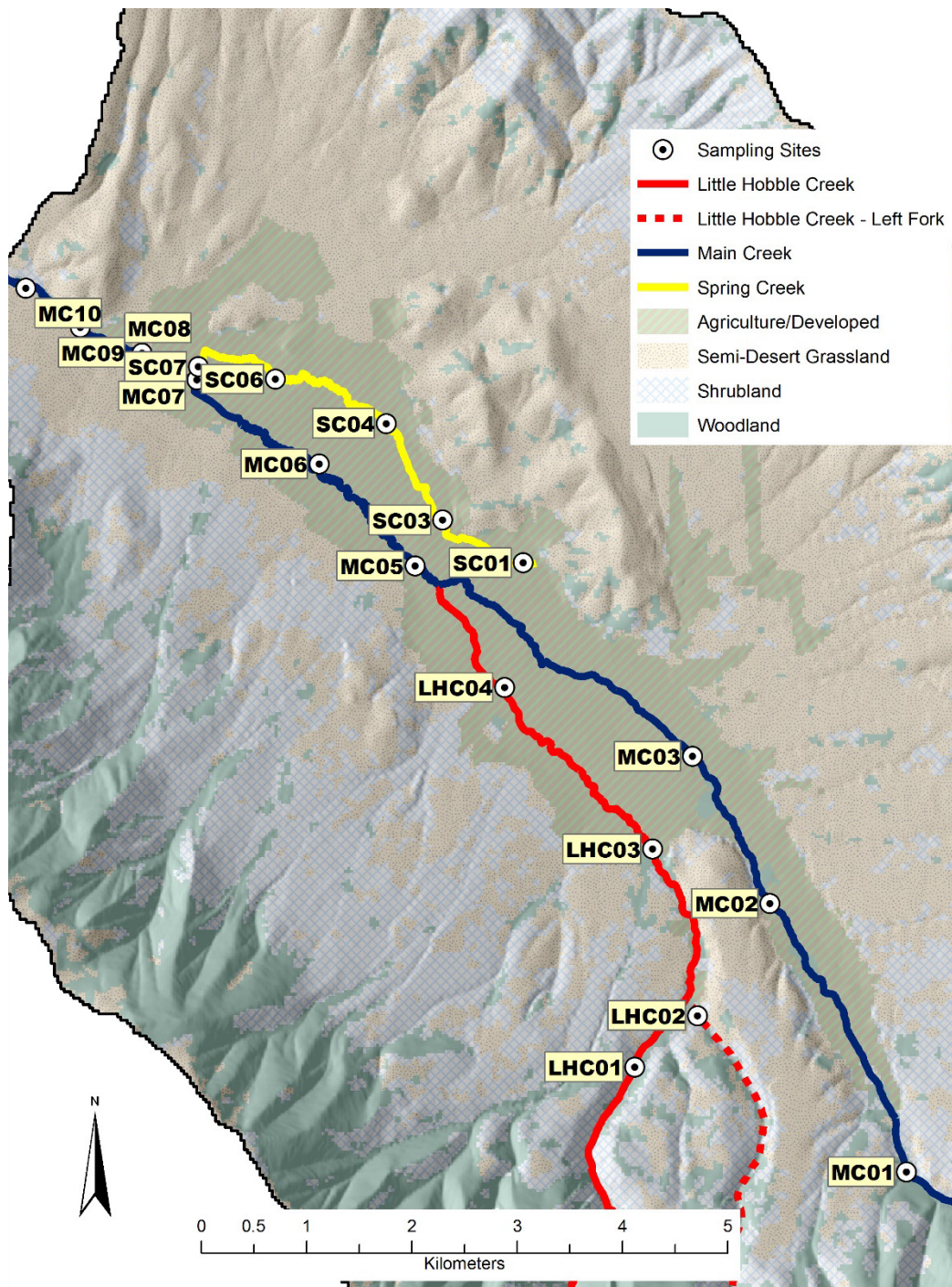


Figure 3. Synoptic sampling sites along the three major tributaries in the Wallsburg watershed. Prefixes of site names are abbreviated tributary names: MC = Main Creek; LHC = Little Hobble Creek; SC = Spring Creek. LHC02 is actually on the left fork of Little Hobble Creek.

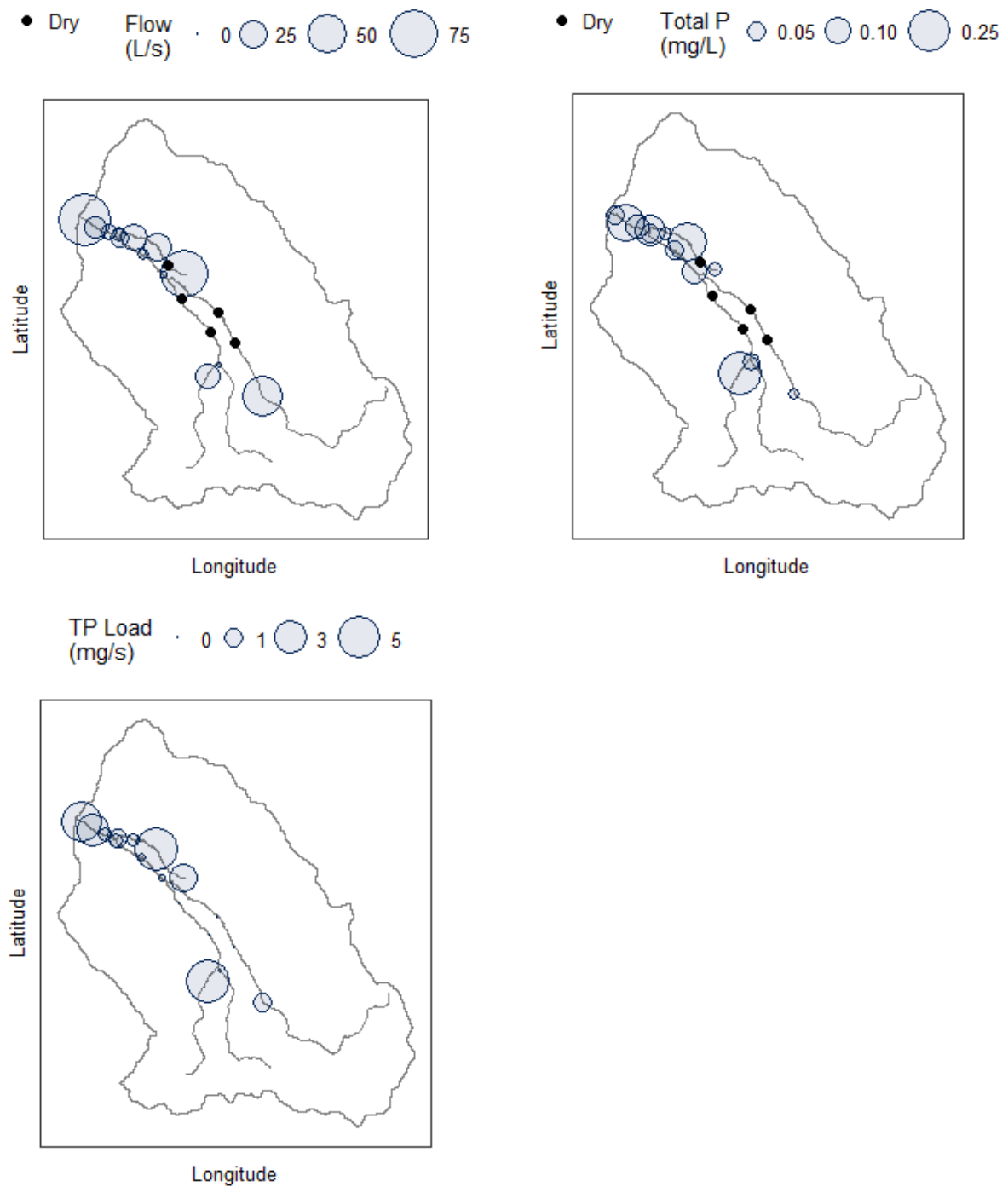


Figure 4. Spatial variation of streamflow (top, left), total phosphorus (TP) concentrations (top, right), and TP loads (bottom, left) from a traditional synoptic sampling approach. Measurements were obtained from a single sampling campaign during baseflow conditions in July 2015. The larger the area of a circle at a sampling site, the greater the value of the parameter at that site. Sites without flowing water in the streambed were marked as “dry”, indicated by a black dot.

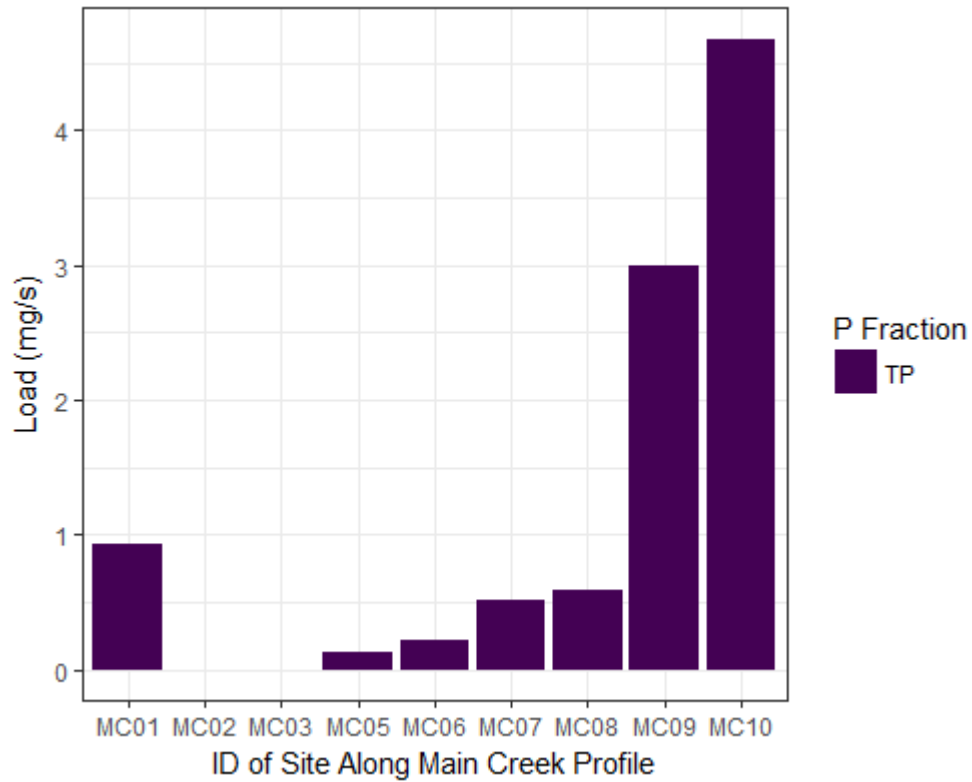


Figure 5. Total phosphorus (TP) loads at each site along the profile of Main Creek (MC) as calculated from the July 2015 sampling campaign. MC01 was the uppermost site on Main Creek, and MC10 was at the watershed outlet. The greatest contributions to instream TP load originated between sites MC08 and MC10, suggesting a TP source area associated with the stream or land between those sites.

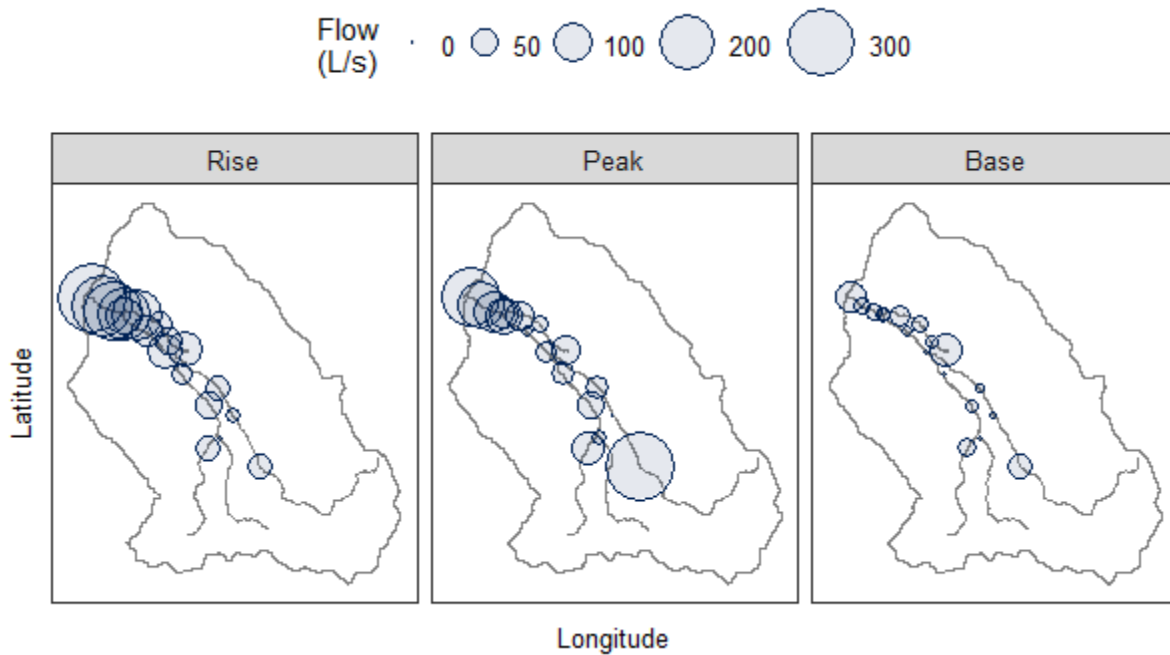


Figure 6. Seasonally repeated and annually replicated streamflow observed in three distinct flow periods for each of 18 synoptic sampling sites, averaged over 2015 and 2016 measurements. “Rise” refers to a period of low elevation snowmelt in late winter in which streamflow is beginning to rise. “Peak” refers to the period of high elevation snowmelt and spring runoff, and corresponds to the timing of the historic peak in streamflow. “Base” refers to the period of groundwater-driven streamflow observed in the dry season of summer. The larger the area of the circle at a site, the greater the streamflow. The temporal variability of streamflow is readily observed.

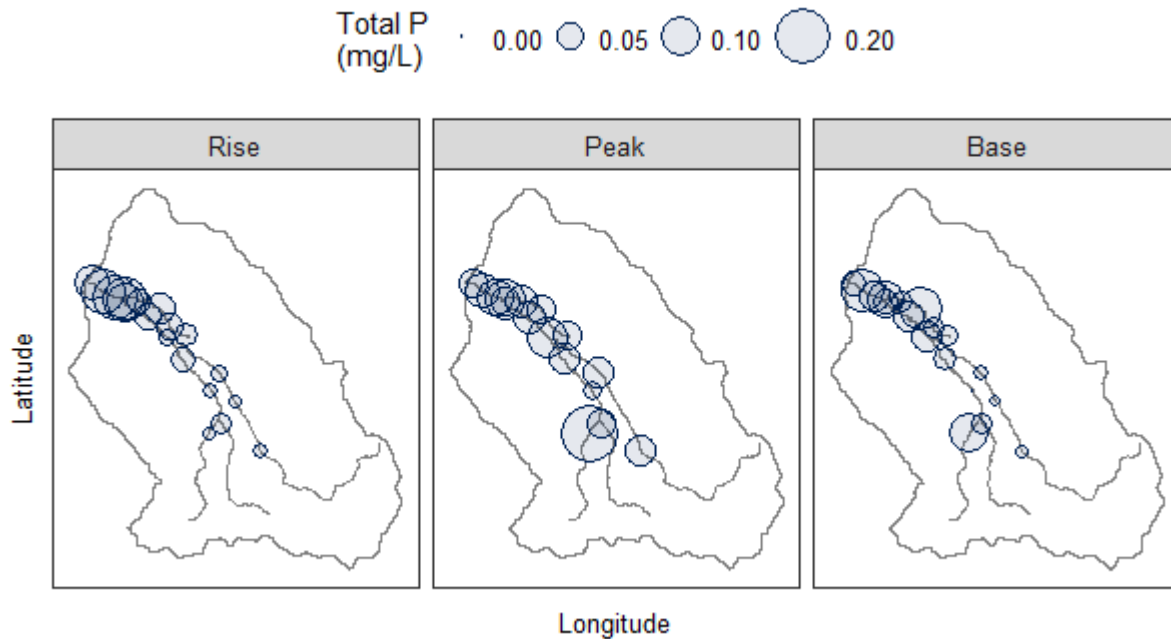


Figure 7. Average total phosphorus (TP) concentrations observed in three flow periods at 18 synoptic sampling sites. “Rise” refers to a period of low elevation snowmelt in late winter in which streamflow is beginning to rise. “Peak” refers to the period of high elevation snowmelt and spring runoff, which generally corresponds to peak streamflow. “Base” refers to the period of groundwater-driven streamflow observed in the dry season of summer. Total P concentrations are averages from seasonally repeated sampling campaigns in 2015 and 2016. Concentrations in the upstream half were highest during peak snowmelt, but generally, high TP concentrations were observed in the downstream half of the watershed.

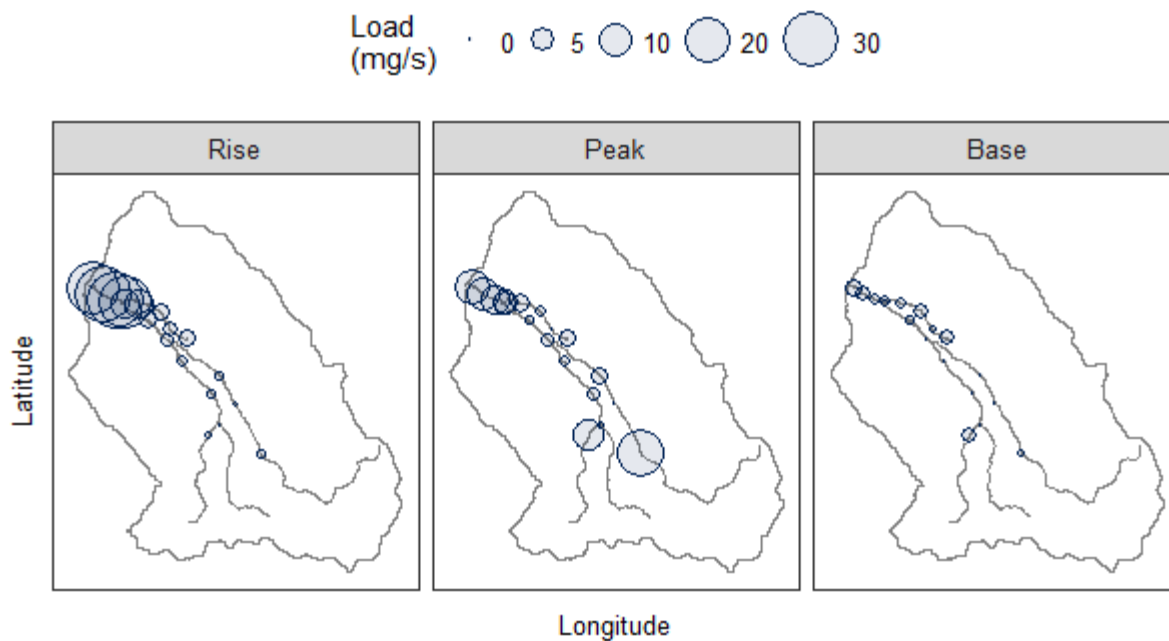


Figure 8. Average total phosphorus (TP) loads calculated in the three flow periods for each of 18 synoptic sampling sites. “Rise” refers to a period of low elevation snowmelt in late winter in which streamflow is beginning to rise. “Peak” refers to the period of high elevation snowmelt and spring runoff, which generally corresponds to peak streamflow. “Base” refers to the period of groundwater-driven streamflow observed in the dry season of summer. Total P load averages at each site were based on the 2015 and 2016 calculations. The spatial patterns suggest that loads were often flow-driven, with the lower segments of the watershed exhibiting the highest loads during the period of rising flow due to low elevation snowmelt.

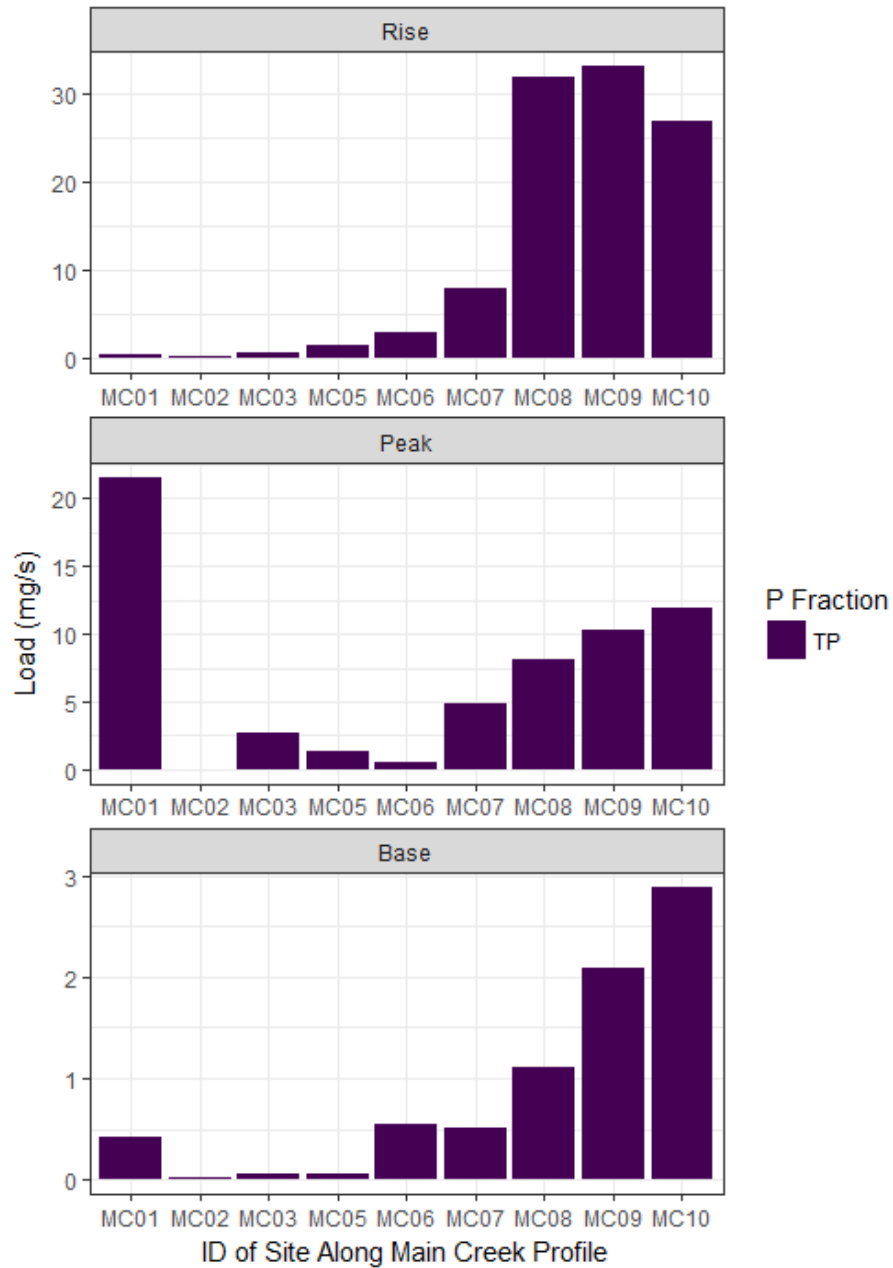


Figure 9. Average total phosphorus (TP) loads at each site along the profile of Main Creek (MC) for individual hydrologic periods during which the 2015 and 2016 sampling campaigns took place. “Rise” refers to a period of low elevation snowmelt in late winter in which streamflow is beginning to rise. “Peak” refers to the period of high elevation snowmelt and spring runoff, which generally corresponds to peak streamflow. “Base” refers to the period of groundwater-driven streamflow observed in the dry season of summer. MC01 is the uppermost site on Main Creek, and MC10 is at the watershed outlet.

Note: y-axis scales are not equal in range. This is intentional to better visualize patterns in TP loads.

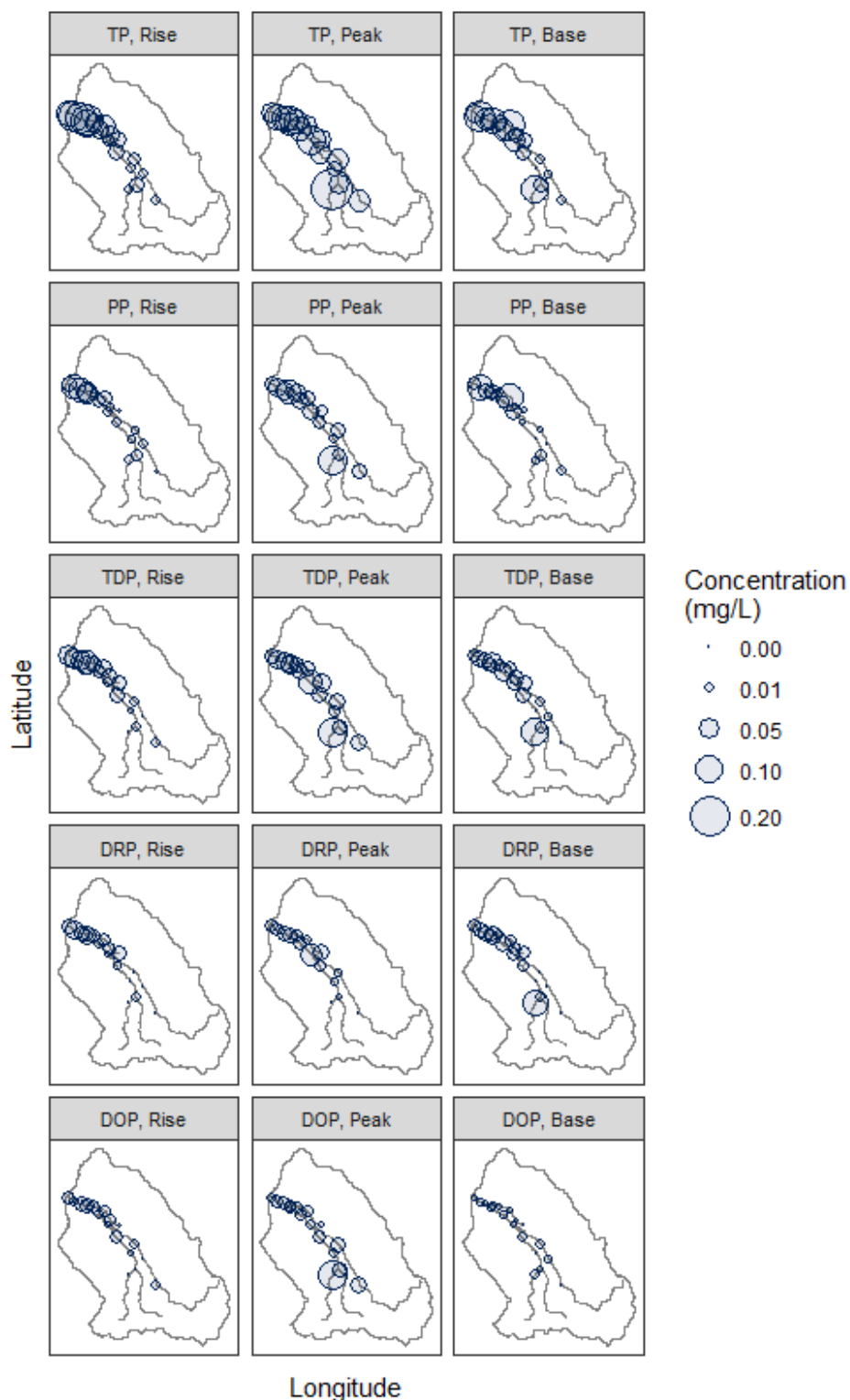


Figure 10. Concentrations of total phosphorus (TP), particulate phosphorus (PP), total dissolved phosphorus (TDP), dissolved reactive phosphorus (DRP), and dissolved organic phosphorus (DOP) at 18 synoptic sampling locations and rising flow, peak flow, and baseflow conditions averaged over 2015 and 2016.

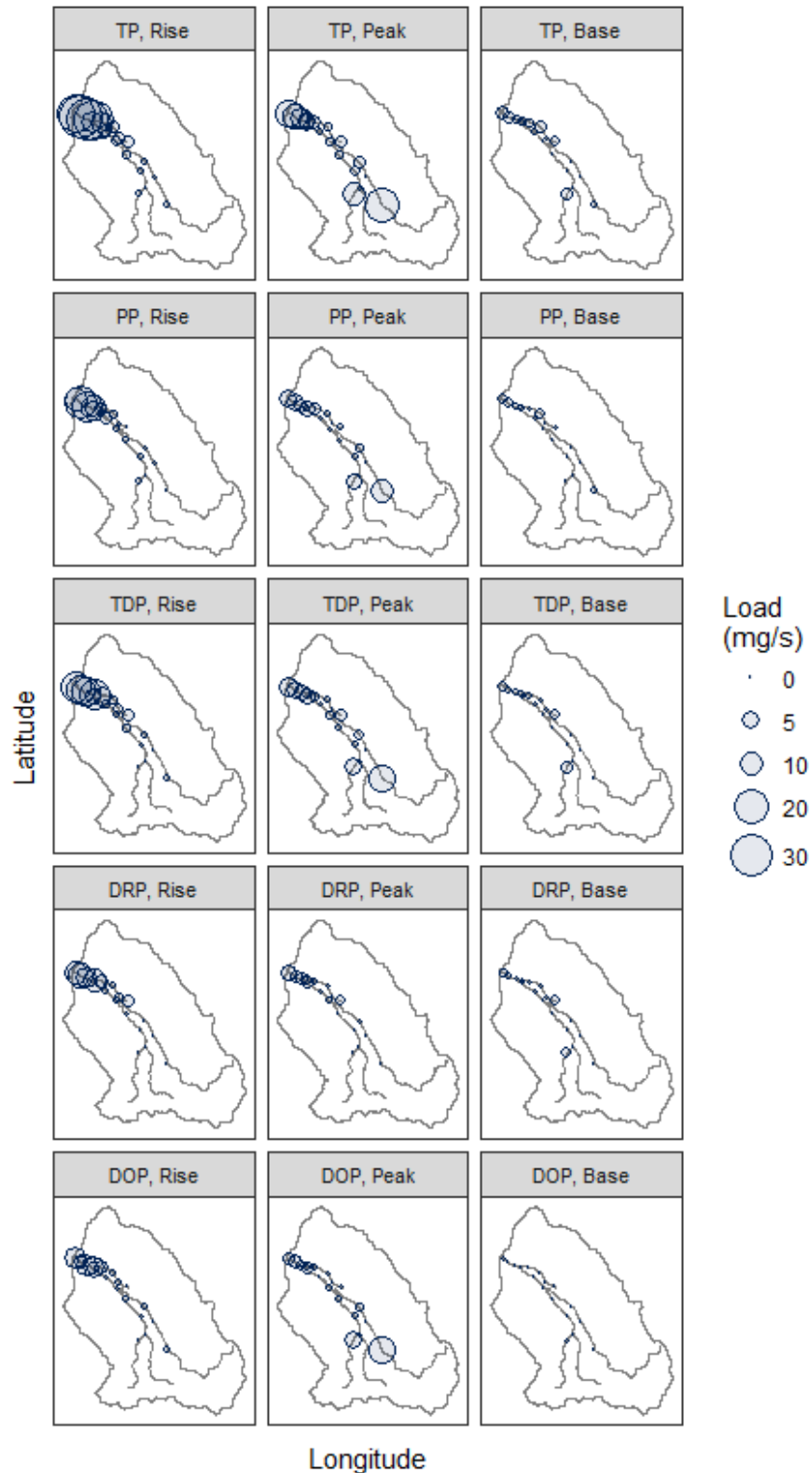


Figure 11. Loads of total phosphorus (TP), particulate phosphorus (PP), total dissolved phosphorus (TDP), dissolved reactive phosphorus (DRP), and dissolved organic phosphorus (DOP) at 18 synoptic sampling locations and rising flow, peak flow, and baseflow conditions averaged over 2015 and 2016.

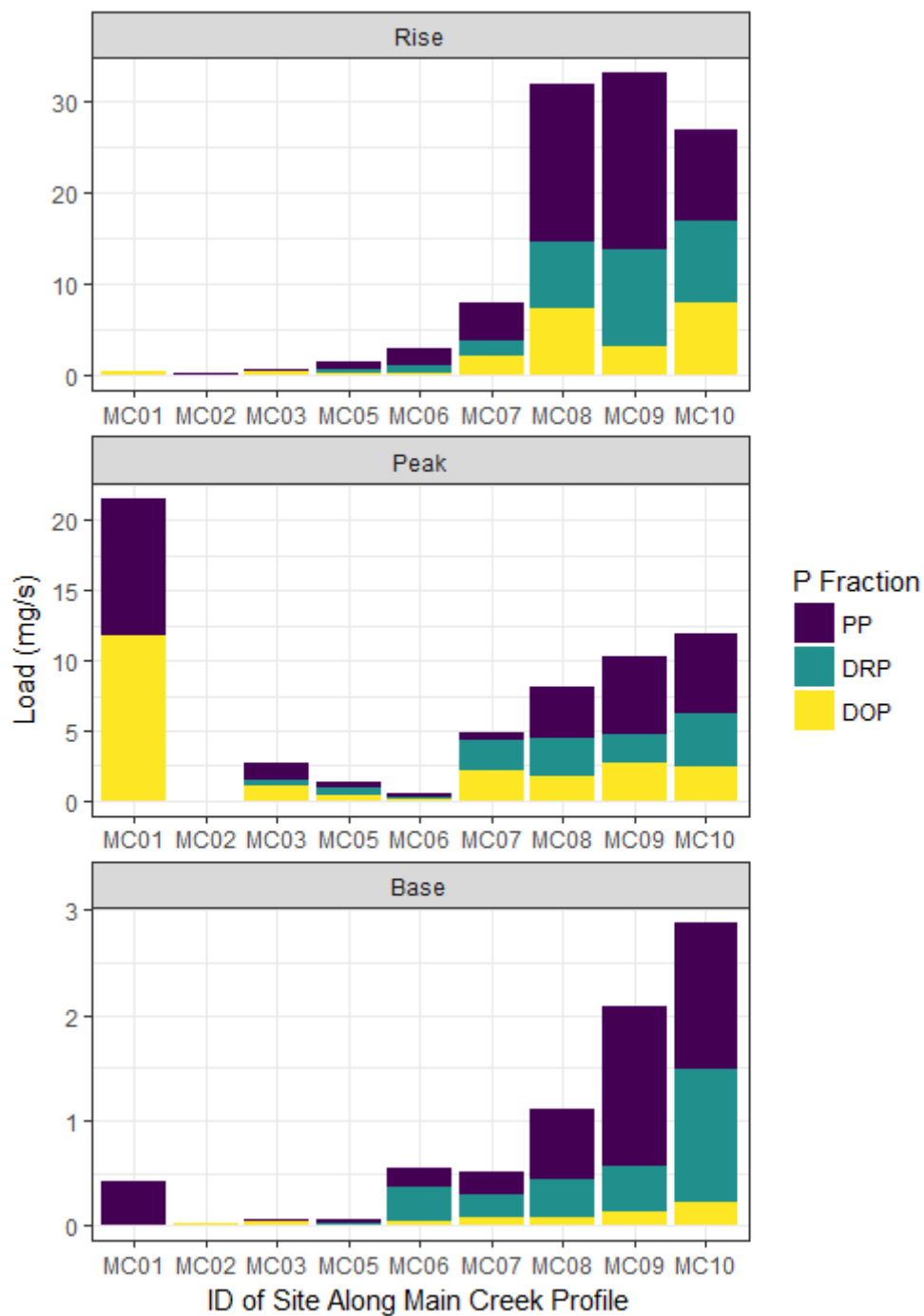


Figure 12. Three P fractions of TP along the profile of Main Creek (MC) for each hydrologic period, each set to its own scale in order to compare patterns in load increase. The height of DOP and DRP equals TDP, and the full height equals TP.

Note: y-axis scales are not equal in range. This is intentional to better visualize patterns in TP loads.

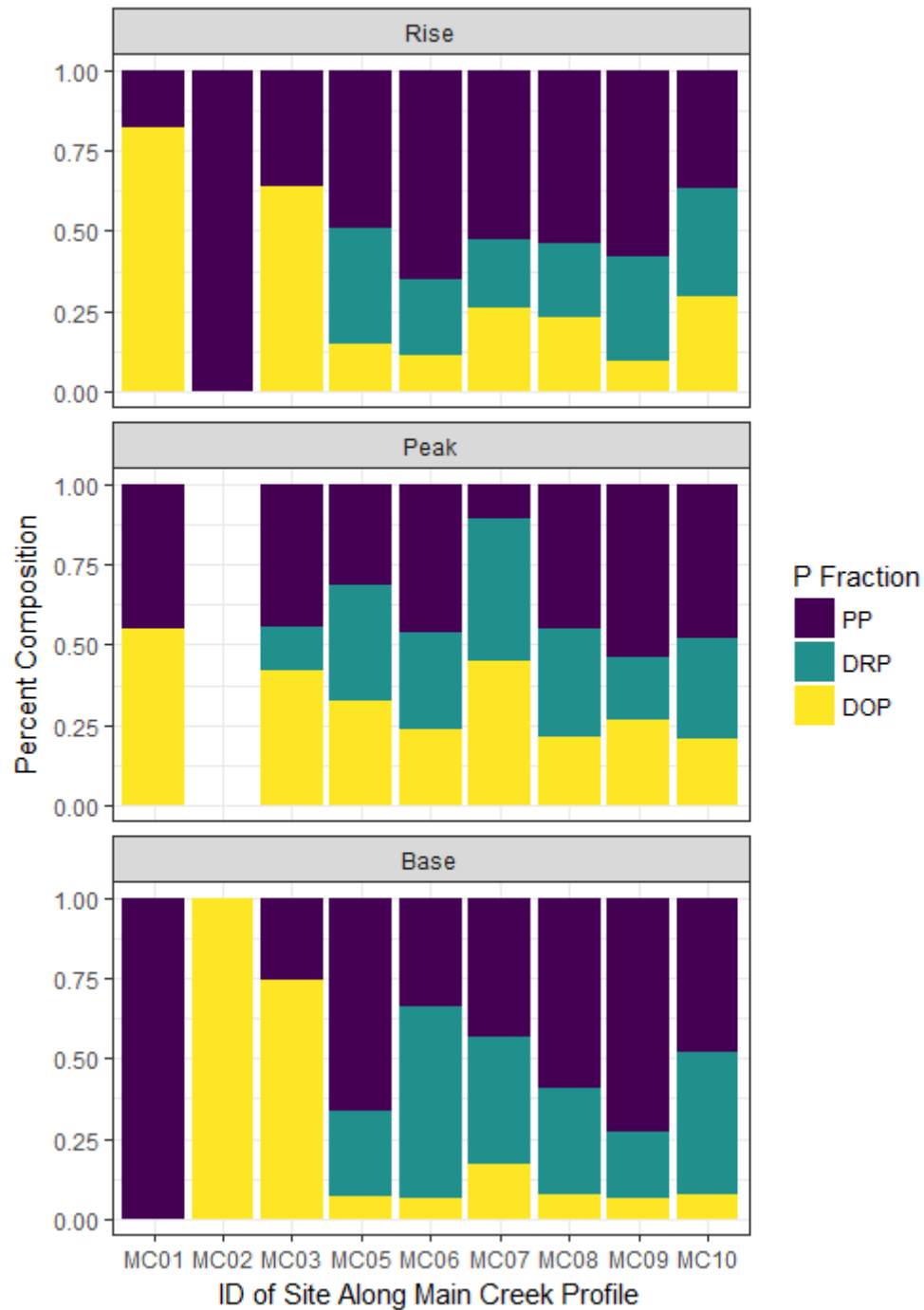


Figure 13. The composition of TP as three P fractions, along the profile of Main Creek (MC) for each hydrologic period. The height of DOP with DRP equals the percent TDP.

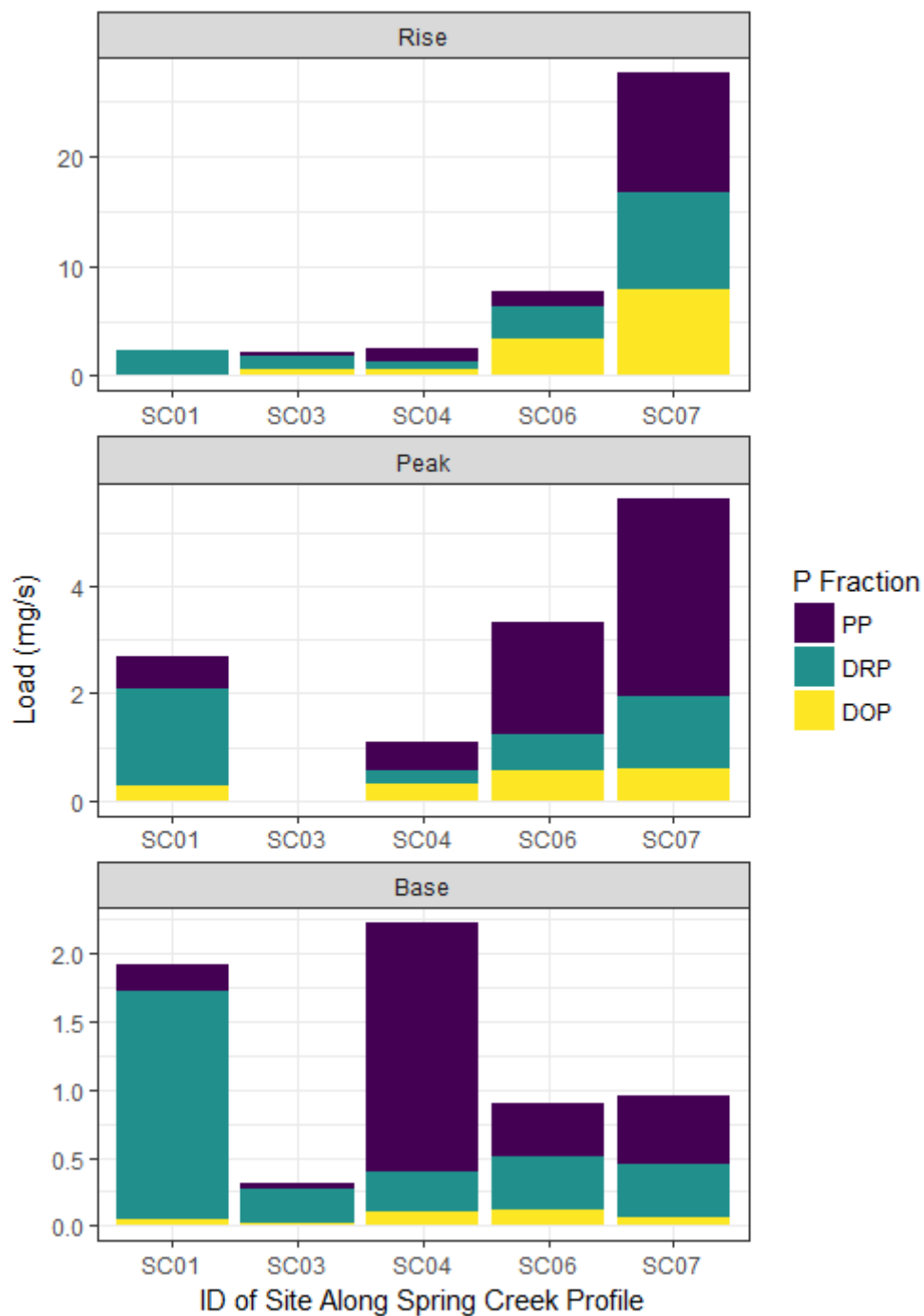


Figure 14. Three P fractions of TP along the profile of Spring Creek (SC) for each hydrologic period, each set to its own scale so as to compare patterns in load increase. The height of DOP and DRP equals TDP, and the full height equals TP.

Note: y-axis scales are not equal in range. This is intentional to better visualize patterns in TP loads.

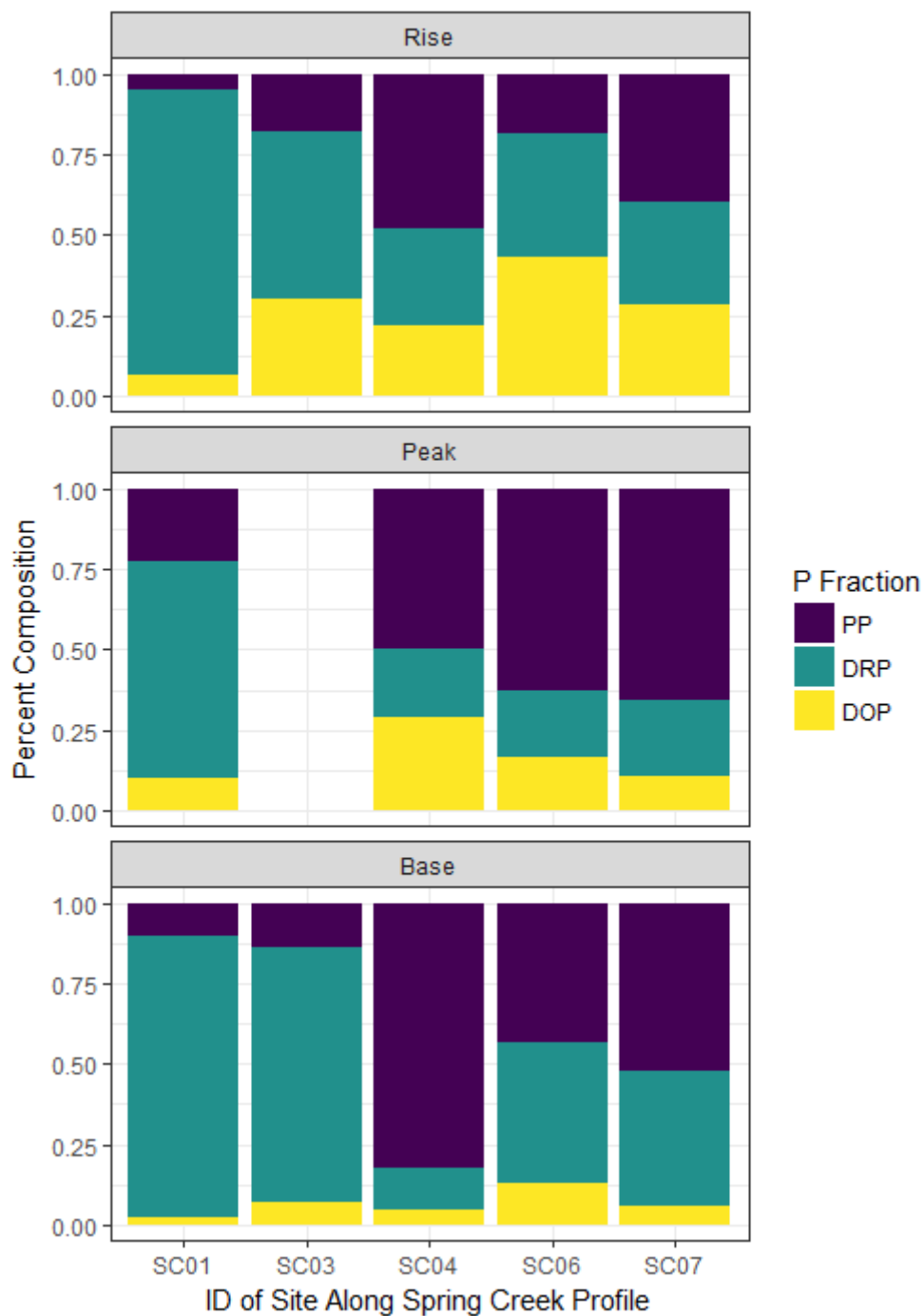


Figure 15. The composition of TP as three P fractions, along the profile of Spring Creek (SC) for each hydrologic period. The height of DOP and DRP equals the percent TDP.

TABLES

Table 1. Summary of general hydrologic conditions in the Wallsburg watershed during which sampling took place, and the actual dates of sampling during 2015 and 2016.

Hydrologic Period	General Hydrologic Conditions	Sampling Date 2015	Sampling Date 2016
Rise	low elevation snowmelt; gradual rising limb of annual hydrograph	March 12	February 20
Peak	full snowmelt and spring rain; highest flows and erosion potentials; some irrigation diversions in place	May 06	May 03
Base	minimal rain, if any; total baseflow conditions; groundwater inputs become a major proportion of streamflow; widespread irrigation diversions;	July 23	July 28
Base	some precipitation (as rain or early snow); near baseflow conditions	November 06	-

Table 2. Summary of phosphorus fractionation scheme.

P Fraction	Abbrev.	Filtered	Determination	Significance
Total	TP	No	Microwave-assisted digestion and ICP-OES	Total P load to downstream waters
Particulate	PP	No	= TP - TDP	Indicative of sediment sources and erosion
Total Dissolved	TDP	Yes	Direct ICP-OES on filtrate	Total dissolved P load to downstream waters
Dissolved Reactive	DRP	Yes	Direct colorimetry on filtrate	Most bioavailable P to algae
Dissolved Organic	DOP	Yes	= TDP - DRP	Indicative of P in plant tissue, manure, and other biologic inputs

Table 3. Summary of critical source areas of phosphorus based on three assessment strategies. Site names are listed as sites along Main Creek (MC), Spring Creek (SC) and Little Hobble Creek (LHC). Phosphorus (P) fractions listed are total P (TP), particulate P (PP), dissolved reactive P (DRP), and dissolved organic P (DOP).

Assessment Strategy	Description of Critical Source Areas
Traditional Synoptic Sampling During Baseflow	Unclear TP sources from forested subwatershed above LHC-01
	Subsurface TP source transferred through groundwater discharge at the spring at SC-01
	Subsurface TP from groundwater or sediment-bound P from stream channel erosion in segments between SC-03 and SC-04 and between MC-08 and MC-10
Repeated Synoptic Sampling without P Fractionation	Unclear TP sources from either stream channel sediments, eroded hillslope sediments, subsurface flows, or overland flows in the forested subwatersheds upstream of MC-01 and LHC-01, mostly during the peak flow period
	Potential TP sources related to cattle activity (manure or streambank erosion) in segments between SC-03 and SC-07 during the rising flow period. TP from stream channel erosion and subsurface sources likely during rising and peak flow periods.
	Sources of TP in the segments between MC-06 and MC-09 stemmed in part from Spring Creek. Also showed sources of TP associated with flow-driven stream channel erosion. TP sources associated with overlay flow likely during rising flow period.
Repeated Synoptic Sampling with P Fractionation	Sources of PP from erosion on steep slopes and stream channels during peak flow period in the forested subwatersheds upstream of MC-01 and LHC-01. Also, sources of DOP from organic materials near the surface of forest soils.
	Segments between SC-03 and SC-07 showed some sources of DRP from groundwater inflows year-round. Sources of PP were associated with livestock-induced streambank erosion and general flow-driven stream channel erosion. Sources of DOP were associated with manure in winter feeding areas during the rising flow period.
	DRP was identified in the generalized area of the lower watershed, stemming from groundwater inflows, and potentially from subsurface flows in areas of high soil P content.
	Segments between MC-06 and MC-09 showed similar P sources to critical source areas on Spring Creek. PP and DOP on the Main Creek increased in part due to P inputs from Spring Creek, but also experienced PP from overland flow and stream channel erosion during the rising and peak flow periods, as well as DOP associated with cattle during the rising flow period. Inputs of DRP were associated with groundwater-driven inflows.

APPENDIX

SAMPLING LOCATIONS

Site ID	Latitude	Longitude
MC-01	40.33435162	-111.37944236
MC-02	40.35728625	-111.39483444
MC-03	40.36984173	-111.40358072
MC-04 (Discarded)	40.37931736	-111.42154966
MC-05	40.38603544	-111.43470598
MC-06	40.39472365	-111.44550919
MC-07	40.40185587	-111.45926740
MC-08	40.40413263	-111.46540180
MC-09	40.40630804	-111.47236134
MC10	40.40964399	-111.47848216
LHC-01	40.34323148	-111.40988804
LHC-02	40.34765063	-111.40288004
LHC-03	40.36188729	-111.40798506
LHC-04	40.37566981	-111.42463011
SC-01	40.38636154	-111.42263026
SC-03	40.38997124	-111.43168295
SC-04	40.39821153	-111.43803567
SC-06	40.40197245	-111.45049584
SC-07	40.40300304	-111.45909890

DISSOLVED REACTIVE PHOSPHORUS ANALYSIS

1. Make the molybdate-based reagent (referred to here as Reagent A)
 - a. Dissolve 12 g of ammonium molybdate in 250 ml of distilled water, and dissolve 0.2908 g of antimony potassium tartrate in 100 ml of distilled water.
 - b. Make 1000 ml of 5 N H₂SO₄ by adding 141 ml of concentrated H₂SO₄ to water and bringing to a volume of 1 liter.
 - c. Add these three solutions together and bring to a volume of 2000 ml with distilled water, then storing Reagent A in a Pyrex bottle in a dark, cool place.
2. Make the active, combined reagent solution just prior to analysis.
 - a. Dissolve 0.528 g of ascorbic acid into 100 mL of Reagent A.
 - i. The combine reagent must be made prior to each analysis.
3. Samples should be at room temperature for analysis.
4. Filter 10.0 mL of representative water sample through 0.45 µm syringe filters into acid-washed test tubes.
5. Add 1.0 mL of combined reagent to each test tube.
6. Add silicone stoppers, and invert until mixed.
7. Wait 10-15 minutes for light blue color to develop.
 - a. Do not wait more than 30 minutes to analyze once reagent is added.
8. Invert samples again prior to measuring.
9. Measure absorbance on a spectrophotometer, such as a Thermo Scientific GENESYS, at 880 nm wavelength.
10. Calculate DRP concentration based on a calibration curve developed using the same equipment and analytical environment.

TOTAL DISSOLVED PHOSPHORUS ANALYSIS

1. Filter about 10 mL of sample through a 0.45 µm syringe filters into acid-washed test tubes of an autosampler rack.
2. Analyze the filtrate directly on an inductively coupled plasma spectrophotometer, such as the Thermo Scientific iCAP 7400 ICP-OES.
3. Concentrations will represent all dissolved phosphorus in sample.

TOTAL PHOSPHORUS ANALYSIS

1. Collect 45 mL of a representative sample from the sample bottle.
 - a. Sediments and other suspended material may have settled in the bottle.
 - b. Shake adequately before extracting a sample, or shake while extracting a sample for even collection of suspended sediments.
2. Digest the sample using a microwave system, such as the Milestone Ethos.
 - a. Add the 45 mL of sample to a Teflon microwave tube.
 - b. In a fume hood, add 5 mL of concentrated nitric acid to the sample.
 - c. Seal the tube according to the equipment being used.
 - d. Microwave for one hour, during which time the sample reaches and maintains 170°C for 20 minutes.
3. Once cooled and transferred to an autosampler rack, run the samples on an inductively coupled plasma spectrophotometer, such as the Thermo Scientific iCAP 7400 ICP-OES.
4. Multiply the concentrations obtained through the ICP by the dilution factor (in this case, 1.11)

DATA PREPARATION, ANALYSIS, AND PLOTTING

The data and results of this thesis study were prepared and organized using Microsoft Excel 2016 and the R programming language through RStudio desktop software. The data and R code used for creating the figures in this paper can be found on GitHub, at the following URL:

<https://github.com/austinwpearce/thesis>.