HYDROLOGIC DYNAMICS CONTROL DISSOLVED ORGANIC MATTER EXPORT FROM WATERSHEDS: FIELDS-SCALE PROCESSES IN A SMALL, ARTIFICIALLY DRAINED AGRICULTURAL CATCHMENT, AND PATTERNS ACROSS ECOSYSTEMS

By

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Abstract

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Dissolved organic matter (DOM) is an important component of nutrient cycling and energy transfer within and between ecosystems. Understanding controls over the magnitude and quality of DOM that is transferred from soils to surface water is needed to better characterize the terrestrial-aquatic carbon flux and effects of terrestrial DOM on downstream ecosystems. A meta-analysis of the response of in-stream dissolved organic nitrogen concentration (DON) to high flow events indicates that DON typically increases with flow across a wide range of ecosystem types, likely as novel DOM sources in the landscape are mobilized and transported to streams and rivers. Mechanisms controlling DOM export, including dissolved organic carbon (DOC) and DON concentrations and the quality of DOM, were examined in a small agricultural catchment in eastern Washington State. In the soil column, DOC concentration declined and source of DOM shifted from humic-like and plant-derived to microbially-derived with depth through the profile. Across seasons and years, DOM exported via drain discharge during low flows resembled that found deep in the soil profile, and DOM exported during high flows suggests topsoil and litter sources contribute to export. A simple mixing model suggests that litter leachate can contribute over 50% of DOM during peak flow. Based on modeled contributions of litter, topsoil and subsoil DOM during storm events, DOC concentration is over-predicted, except for peak flows, suggesting removal via sorption and/or microbial decomposition in the soil column control DOC export on the timescale of events. Although the character of exported DOM shifts with flow conditions, laboratory incubations suggest bioavailability to the stream sediment microbial community is consistently low, with a maximum of 7% loss over 6 days, indicating exported DOM is likely transported beyond the immediate stream reach. An analysis of anticipated effects of climate change on the flow regime in the catchment projects the wettest years to become more variable, with non-linear effects on the magnitude of DOC export. Finally I explore how climate change assessments can be incorporated into nonpoint source nutrient management plans, despite current uncertainty about the magnitude and timeframe of climate effects on nutrient loading.

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GENERAL INTRODUCTION

Aquatic ecosystems receive energy and nutrient subsidies from terrestrial ecosystems in the form of dissolved organic matter (DOM), which fuels aquatic food webs [e.g. *Pace et al.*, 2004] and contributes to a significant flux of carbon dioxide from inland waters [*Raymond et al.*, 2013; *Regnier et al.*, 2013]. The quality of DOM can mediate its fate in inland waters [*Seitzinger et al.*, 2002; *Fellman et al.*, 2008], and land use and land cover changes have been correlated with changes in in-stream DOM concentration and quality [*Wilson and Xenopoulos*, 2009; *Petrone*, 2010; *Williams et al.*, 2010]. Understanding mechanisms that cause these changes is critical to manage the land to better protect water quality and predict how land-use and climate change will alter the delivery of terrestrial DOM to aquatic ecosystems and its fate there.

In terrestrial ecosystems, DOM is produced as litter and dead organic matter is leached and by roots and microbial activity. This DOM can be utilized by microbes, sorbed to soils, and re-released in altered forms. These production, retention, and alteration processes often result in characteristic patterns of DOM through soil profiles, in terms of both concentration and quality [*Kaiser and Kalbitz*, 2012]. As water flows over and through soils, it can mobilize distinct reservoirs of DOM and transport them to surface water. Because flow paths are dynamic and vary with catchment wetness, the concentration and quality of DOM delivered to surface water can vary dramatically over time [*Inamdar et al.*, 2013].

Annual DOM export from watersheds can be dominated by a few brief high flow events [*Raymond and Saiers*, 2010; *Yoon and Raymond*, 2012], during which the in-stream dissolved organic carbon (DOC) concentration often increases, and the quality of DOM can be much different from base flow conditions, [*Buffam et al.*, 2001; *Petrone et al.*, 2007; *Austnes et al.*, 2010]. Because high flow events have a disproportionate effect on the delivery of DOM to downstream ecosystems, and because their intensity and likelihood are expected to be altered by climate change [*Salathé et al.*, 2010; *Walsh et al.*, 2014], it is important to understand what controls DOM export from terrestrial systems during these periods.

DOM can be transported laterally through soil horizons to streams during very wet conditions, and it is often assumed that DOM within soil horizons remains unaltered during transport [e.g. *Seibert et al.*, 2009; *Winterdahl et al.*, 2011]. However, DOM is reactive, both biotically and abiotically, and it is possible that it could be altered and/or retained en route to surface water, particularly if it is transported vertically through deeper soil horizons with a strong affinity for DOM [*Dalzell et al.*, 2011]. Artificial subsurface drainage in agricultural catchments functions to enhance vertical transport of water through the soil column, potentially enhancing DOM export, but also providing an opportunity for DOM retention in deeper soil horizons prior to export. The balance between transport and removal rates will have implications for the quantity and quality of DOM exported from agricultural soils to surface water.

In the following chapters, I address gaps in our understanding of controls of DOM transport from terrestrial to aquatic ecosystems and implications for receiving streams using a meta-analysis, field and laboratory studies, and modeling exercises, focusing in particular on the role of hydrologic dynamics, which have been closely tied to the delivery of terrestrial DOM to surface water and its in-stream dynamics. Despite many individual studies, it was unclear whether the response of in-stream dissolved organic nitrogen (DON) concentrations to high flow events generally increased, similar to DOC, across different types of ecosystems, and, in the first chapter, I use a meta-analysis approach to address this. (This chapter has been previously published and retains formatting required by the publishing journal [*Martin and Harrison*, 2011].) Additionally, significant changes in in-stream DOC concentration and DOM quality have been correlated with agricultural land-use, but direct inputs of terrestrially-derived DOM are rarely measured, nor are mechanisms controlling the concentration and quality of these inputs. In the second and third chapters, I report results of a field study, based in a heavily agricultural area of eastern Washington State, coupled with laboratory experiments and modeling approaches, to characterize inter-annual, seasonal, and event-scale DOM export dynamics from tile drainage, and explore the importance of hydrologic dynamics and soil processing in controlling these patterns. In the final chapter I address the policy implications of this research, focusing on approaches that water quality managers can take to include climate change assessments in water quality management programs that target nonpoint source pollution, which includes nutrients and organic matter exported via tile drainage.

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CHAPTER ONE

Effect of high flow events on in-stream dissolved organic nitrogen concentration

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ATTRIBUTION

R.A. Martin (now R.A. Bellmore) contributed to the conceptual development of this manuscript, compiled the literature, conducted the meta-analysis and, and was the primary author of the text. J. A. Harrison also contributed to the conceptual development of the manuscript and edited the text.

1. Effect of high flow events on in-stream dissolved organic nitrogen concentration

1.1 ABSTRACT

Dissolved organic nitrogen (DON) can comprise a large and biologically important fraction of total dissolved N in surface water. Biotic and abiotic processes result in heterogeneous DON concentrations and bioavailability in soils, and as hydrologic connectivity expands and flow paths change in watersheds, novel sources of DON can be mobilized and transported to surface water. Although the relationship between in-stream DOC concentration and stream discharge has previously been examined in the literature, up to now there has not been a synthesis examining how DON concentrations, loads, and composition change during transitions from base flow to pulse flow conditions. I perform a meta-analysis to examine the effect of high flow on DON concentration ([DON]). The ratio of mean pulse flow [DON] to mean base flow [DON] (P:B) was calculated for individual events and averaged (geometric) within and then across sites to generate an overall effect size. For 47 sites (78 events), mean P:B was 1.58, which was significantly different from unity. This moderate increase in DON concentration contributed to over a more than 10-fold increase in the rate of DON yield from base flow to high flow. The response of [DON] to high flow was significant in catchments where individual storm events or snowmelt runoff events were responsible for elevated flows, whereas the response was not significant in catchments where high discharge resulted from a mixture of upstream snowmelt and rain events. Additionally, an examination of DOC:DON ratios during high flow indicates that multiple sources of DON may be mobilized during high flow. Finally, current models of annual DON export may be improved by including a positive relationship between discharge and DON.

1.2 INTRODUCTION

Terrestrial ecosystems export dissolved organic nitrogen (DON) to aquatic systems whether they are pristine or subject to anthropogenic N inputs (e.g. Hedin and others 1995, Currie and others 1996, van Kessel and others 2009). Consequently, DON can comprise a significant fraction of total dissolved nitrogen (N) in surface water (Perakis and Hedin 2002, Berman and Bronk 2003, Scott and others 2007) and total N exported to coastal ecosystems (Seitzinger and others 2010). Understanding both mechanisms controlling DON delivery from upland sources to surface water and DON is bioavailability is important for clarifying the role of DON in aquatic N cycling.

DON comprises a heterogeneous pool of N-containing, carbon-based compounds (Berman and Bronk 2003), and there is a growing body of evidence that a portion of the aquatic DON pool is highly bioavailable to both freshwater and marine microbial communities (Seitzinger and Sanders 1997, Seitzinger and others 2002, Wiegner and Seitzinger 2004, Petrone and others 2009), although it was historically assumed to be recalcitrant and of minor importance in stream ecosystem N cycling (Thurman 1985). DON can provide a critical source of N to biota (Brookshire and others 2005, Stepanauskas and others 2000a), and also has the potential to contribute to eutrophication (Seitzinger and Sanders 1997, Petrone 2010). In coastal ecosystems, high DON loading relative to inorganic N has been shown to promote harmful algal blooms (Hood and others 2006). Because DON in streams can be derived from autochthonous production or allochthonous inputs of dissolved organic matter (DOM), DON quantity and bioavailability in streams can vary seasonally and from reach to reach as a function of processes that control the production of DON and its delivery to streams (Kaplan and Bott 1989, Wiegner and others 2009, Aitkenhead-Peterson and others 2003).

Both over-land and sub-surface runoff deliver allochthonous DOM to surface water, and increases in runoff during snowmelt and storm events have been correlated with increases in surface water dissolved organic carbon (DOC) concentration (e.g. Hinton and others 1998, Buffam and others 2001, Raymond and Saiers 2010). However, the relationship between changes in discharge and DOC concentration does not necessarily reflect that of DON (e.g. Petrone and others 2006). Importantly, the C:N ratio of DOM varies widely among sources and through time (Seitzinger and others 2002, Petrone and others 2007, Williams and others 2001). DOC- and DON-rich sources of DOM may be mobilized at different times, resulting in dissimilar responses of DOC and DON during high flow events. Additionally, there is some evidence that DOC and DON release and transport dynamics in soils may differ from each other due to biotic control or different sorption-desorption dynamics (Kaiser and Zech 2000, Michalzik and Matzner 1999). Hence, there is reason to suspect that DOC and DON export from catchments might be decoupled.

A number of studies have reported [DON] over periods that include both base flow and pulse flow conditions, but results of these individual studies have not been synthesized to examine broad trends or patterns among ecosystems. Aquatic primary production exhibits pronounced seasonality (Paerl and others 2004), so an ability to predict nutrient and organic matter loading on short time-scales could be useful in efforts to anticipate or mitigate harmful impacts of seasonal DON pulses (Glibert and others 2010, Scott and others 2007). Current models describing watershed DON export have coarse temporal resolution and do not account for changes in concentration with discharge (e.g. Global NEWS, Harrison and others 2005, Aitkenhead-Peterson and others 2005, Clair and others 1996).

In this study, I use a meta-analysis to quantify the effect of high flow events on in-stream [DON] and evaluate the relationship between DON and DOC across a range of watershed sizes and ecosystem-types. I asked whether DON increases with discharge, consistent with mobilization of novel DON sources during high flow events, and to what extent [DON] and [DOC] are tightly coupled during pulse events. I also explored the modeling and management implications of the answers to these questions.

1.3 METHODS

1.3.1 Meta-analysis of DON concentration response to high flow events

I performed a meta-analysis to examine the effect of high flow events on [DON] relative to preceding base flow. I define a pulse event as a period of elevated stream discharge attributable to precipitation or snowmelt and the effect size as the ratio between pulse flow [DON] and base flow [DON] (hereafter referred to as P:B). I included studies in our meta-analysis only if they contained 3 or more [DON] measurements during a pulse period with sampling frequency equal to or greater than every other week during extended pulse events (i.e. snowmelt runoff). Information about [DON] data in relation to the timing of the pulse events was also required. While the majority of systems in our meta-analysis (32) were from published studies, I also included sources of high quality unpublished data (USGS, B. Pellerin; D. Sobota). Although additional studies have analyzed [DON] at sufficiently frequent intervals during high flow events, if [DON] data could not be associated with base flow or pulse flow given the information available (e.g. McHale et al. 2000), these studies were not included. I categorized pulses as storm, snowmelt, wet-season, or mixed snowmelt-wet season runoff (for large rivers that drain both types of catchments) based on information in the literature or from the provider of unpublished data. Additionally, I included several high flow events dominated by reservoir releases. Study sites range in size from small headwater streams to large rivers (watershed surface area range: 0.016 to 2.99×10^6 km^2, median 143 km^2). Watersheds were categorized according to major biome-type: alpine, desert shrub, Mediterranean forest/grassland, temperate forest/grassland, tropical forest/grassland, taiga/boreal forest, or tundra (Appendix 1.A), and the intensity of human impact in the dataset ranges from minimal in pristine forests to more severe in forests subject to substantial N deposition and in sites with intense agriculture. Sites were not further subdivided according to landcover-type for analyses due to limited sample size and mixed landcover present in many watersheds.

Because many studies only report one pulse event per site, or one site, traditional methods for meta-analyses that weight studies by sample size and variance could not be applied. Therefore, I used the geometric mean of P:B values for all sites to generate an overall effect size, and the geometric mean of different system types to estimate effect sizes for different pulse-types and biomes. If multiple high flow events were reported for a site, P:B for that site was calculated as the geometric mean of individual event P:B values. To determine whether there was a significant change in [DON] from base flow to pulse flow overall, or for different pulse-types or biomes, P:B values for sites were natural log-transformed, and 95% confidence intervals were calculated around the transformed means and then back-transformed. Confidence intervals that did not encompass 1 were interpreted as significantly different from unity. I also examined whether mean P:B values for sites were related to catchment area or the size of the event (max flow/mean base flow). Data were natural log-transformed to improve non-normality, and linear regressions were performed using R (version 2.11.1).

1.3.2 [DON] for base- and pulse- periods

The method for identifying average [DON] for base- and pulse periods varied according to the type and form of data presented in the study. In most studies, pulse events due to precipitation or snowmelt were identified by the authors. If the authors differentiated base- and pulse flow and calculated average (arithmetic, geometric, or flow-weighted) [DON] for the periods, these values were used in the meta-analysis. When the transition between base flow and pulse flow was not explicitly identified by the author, I defined the pulse period based and calculated flow-weighted average [DON] for the pulse period and the preceding base flow. I bounded the pulse events on the rising limb of the hydrograph where discharge reached double the preceding base flow and bounded the pulse event on the falling limb where discharge fell below double the original base flow (Figure 1.1). If discharge did not fall below this threshold, the end of the pulse event was set when a new steady base flow level had been established, when a successive event began, or at the inflection point on the falling limb of the hydrograph, in that order of priority. An event was determined to be "successive" if it followed a previous event during the same hydrologic period (i.e. within a single monsoon season [Brooks et al. 2007] or rainy season [Petrone et al. 2006]). The time between discharge peaks of successive events ranged from less than 1 day between storms (Brooks et al. 2007) to 37 days between snowmelt event peaks (Sebestyen et al. 2008).

If data were reported graphically, values for nutrient concentrations and discharge were estimated from figures using DataThief III (version 1.5) or Engauge Digitizer (version 4.1) or obtained from authors. I calculated flow-weighted mean [DON] for base flow and pulse flow if [DON] and discharge were available. Otherwise I calculated the arithmetic mean concentrations (Appendix 1.A). I assumed that [DON] was constant from mid-point to mid-point between sampling times (Figure 1.1), and the DON flux ([DON] multiplied by discharge) was integrated over the base flow or pulse flow period, then divided by the water flux during that period to estimate flow-weighted mean concentration. Mean DON flux during base flow and pulse flow was calculated by dividing the total flux during the period by the duration.

1.3.3 DOM quality

I surveyed the literature to find whether there are any patterns associated with the bioavailability of DON during base flow compared to pulse flow. Studies have assessed DON bioavailability in a variety of ways, and for this analysis, I considered studies that went beyond chemical analysis of DON to assess bioavailability, including in-stream DON additions and lab incubations to measure DON decomposition, mineralization, or incorporation into microbial biomass. Because of variability in methodology, it is difficult to quantitatively compare results among studies, but within-study comparisons between base flow and pulse flow are possible. Additionally, dissolved organic C:N variability was examined over the course of high flow events in studies where simultaneous [DOC] and [DON] data were available. Finally, I examined the data to determine whether [DOC] and [DON] peaked simultaneously or at different times during high flow events.

1.4 RESULTS

1.4.1 DON response to pulse events

Among sites included in the meta-analysis, mean base flow [DON] ranged from 0.011 to 0.723 mg N L^{-1} (geometric mean = 0.132, 95% CI = 0.103-0.170), and mean pulse [DON] ranged from 0.023 to 1.992 mg N L^{-1} (geometric mean = 0.205, 95% CI = 0.156-0.270, Figure 1.2, top). The mean [DON] was greater during pulse events than the previous base flow in 37 of

47 sites (78.7%), showed no response (± 5% change) to pulse flow in 4 sites (8.5%), and decreased in 6 sites (12.8%). The mean P:B for all sites was 1.58 (95% CI 1.32 – 1.90; Figure 1.3). When reservoir-dominated systems were removed, the mean increased slightly to 1.69 (95% CI 1.40 – 2.04). Because [DON] did not always remain elevated throughout a pulse event, the flow-weighted mean typically dampened the magnitude of the effect evident via a visual inspection of the data. When the maximum [DON] during the pulse event is compared to the mean base flow concentration, the average increase is 2.59-fold (95% CI 2.09 – 3.20).

The response of [DON] to pulse flow varied among event-type and ecosystem type. Of the 25 snowmelt catchments, [DON] increased in 20, showed no response in 3, and decreased in 2, and P:B for snowmelt systems was significantly greater than 1 (Table 1.1). The snowmelt catchment that showed the strongest decline was an alpine site with several lakes upstream (Williams and others 2001, Hood and others 2003). On average [DON] increased in all sites with storm events (14 total). Elevation of P:B for storm events was also significant (Table 1.1). Of the 3 rivers that drained mixed snowmelt- and rain-dominated catchments, [DON] showed no response to elevated discharge in 1 site and decreased in 2 sites. In snowmelt systems controlled by reservoir releases, [DON] increased in 2 of 5 sites and declined in 3 during high flow events. P:B for both mixed and reservoir-dominated systems was statistically indistinguishable from 1 (Table 1.1). Mean P:B values for catchments in Mediterranean, temperate, and taiga/boreal forest biomes were all significantly greater than 1. Alpine, desert shrub, tropical forest/grassland, and tundra were represented by only 1 site each, so confidence intervals could not be calculated for these ecosystems. However, the alpine site showed the largest decline in [DON] during high flow, whereas P:B values for the desert shrub site and tropical site were among the highest (Table 1.2).

In the previous analysis, the effect sizes of multiple events in individual sites were averaged for each site, but I also examined whether the relative response showed a pattern over several successive high flow events within a hydrologic season. If possible, events were binned according to whether they were the initial, second, third, or greater than third in a series of high flow events. The pulse order did not to appreciably affect mean P:B, and was significantly greater than 1 for all but the third pulse (Figure 1.3). Note that 8 of the 13 post-third events were from the San Pedro River, AZ (Brooks and others 2007).

I also examined whether effect size varied with catchment area or relative magnitude of the pulse-event. Studies have indicated that spatially variable melting or precipitation within a basin can result in asynchronous flushing and delivery of DOM to surface water, resulting in variable in-stream DOM concentrations (Boyer and others 2000). Larger catchments are more likely to experience heterogeneous inputs, which may diminish the apparent in-stream response. Across all study sites P:B was not significantly related to catchment area ($r^2 = 0.01$, df = 43, $p = 0.61$). However, within Mediterranean catchments, catchment size explained 33% of the variation in P:B (both catchment area and P:B ln-transformed), with P:B decreasing with increasing catchment size ($r^2 = 0.33$, df = 16, $p = 0.01$). There was no significant relationship between catchment size and P:B in temperate ($r^2 = 0.05$, df = 8, $p = 0.55$) or taiga/boreal biomes ($r^2 = 0.18$, df = 11, $p = 0.15$). The relative magnitude of the flow event may influence the response of DON concentration if, for example, certain size events are required to mobilize new sources of DON. However, I did not find that P:B values were related to the relative size (maximum flow/mean base flow) of the pulse event for sites ($r^2 = 0.01$, df = 34, $p = 0.48$) or within biomes; I did not have enough data to examine within-site relationships.

The mean DON yield during base flow and pulse flow ranged over 5 and 3 orders of magnitude, respectively, among sites for which yields could be calculated (Figure 1.2, bottom; Appendix B). The median increase in DON yield from base flow to pulse flow was 11.4-fold, just over an order of magnitude, with a maximum increase of 232-fold (mean = 14.2).

1.4.2 DOM Quality

For sites included in this meta-analysis, C:N of DOM generally varied considerably from base to pulse flow, and during pulse flow (average 4.0-fold variation in C:N during pulse flow) (Appendix 1.A). Additionally, [DOC] and [DON] peaked at different times during 37 of the 64 pulse events with this information available (DOC first in 15, DON first in 22). Only three studies (for five catchments total) were found to have directly compared DON bioavailability during pulse- and base flow conditions. Both of the snowmelt studies (2 catchments each) took place in forested ecosystems (boreal and temperate) with limited human impact (Stepanauskas and others 2000b, Kaushal and Lewis 2005). DON bioavailability was higher in 3 of 4 of these catchments during pulse flow than base flow and remained constant in another. In the single storm study, DON bioavailability declined by half from base flow to storm flow (Wiegner and others 2009).

1.5 DISCUSSION

1.5.1 DON response to high flow events across catchment types and events

DON represents a significant component of surface water N, but delivery mechanisms and in-stream production and cycling are still poorly understood. Here I examine how in-stream DON concentration responds to high flow events to expand our understanding of DON dynamics in relation to hydrologic variability. I found a significant increase in DON concentration from base flow to pulse flow, indicating that a novel source of DON is mobilized during pulse events.

Although, in general, [DON] increased with pulse flow (Table 1.1), there were some exceptions. Systems where P:B was <1 included reservoir-dominated systems, where low [DON] water from reservoirs may have diluted locally-sourced, terrestrially-derived DON. Other systems with P:B <1 included watersheds with a mixture of snowmelt and storm-derived pulses, suggesting that mixing of water masses originating from different sources may mute DON pulses in these basins.

DON concentration may change over a single event, or over a series of events, if the source of DON in the watershed is being depleted. Mean P:B did not decline over a series of events, when averaged across sites, although the significance varied (Figure 1.3). Although I did not quantitatively examine within-event dynamics, I observed that in some systems, DON was elevated throughout the pulse event; however, in many systems DON concentration decreased more rapidly than discharge. This observation is consistent with a ‘first-flush’ scenario, often seen for nitrate and DOC (i.e. Coats and Goldman 2001, Boyer and others 2000), where a DON reservoir is mobilized early during an event, but event water becomes progressively less enriched as the source of DON is depleted. If soil DON is a major contributor to surface water DON, these patterns can be explained by different timescales of production, diffusion, and desorption in soils. Desorption of DOM from soils is relatively fast, but slow diffusion from protected soil aggregates may not keep pace with desorption, resulting in declining soil and surface water concentrations during a runoff event (Worrall and others 2008). In contrast, DON production in soils between events may replenish the readily soluble reservoir and is likely to control concentrations over a series of events, as seen for DOC in some systems (Worrall and others 2008).

1.5.2 Uncertainty Associated with DON measurement

Uncertainty associated with [DON] can be considerable because of error associated with techniques used to measure TDN and because a subtraction method must be used to estimate [DON] (Keldjahl N – NH_4^+, or TDN – [NO_3^- + NH_4^+]). A review of techniques to estimate [DON] suggests that methods for generating TDN values are most likely to produce underestimates (Cornell and others 2003). However, since our analysis compares within-study patterns, a unidirectional bias should not affect results of this synthesis. More problematic is the compounded error associated with [DON] which results from indirect estimation. This makes estimating [DON] difficult when it is a small fraction of TDN; the standard deviation may increase dramatically above 25% once DON:TDN falls below 0.25 (Cornell and others 2003). 31 of 75 events included here report base flow DON:TDN below 0.25, with only 13 below this threshold during high flow events. The low DON:TDN ratios clearly present a problem for determining accurate [DON] and, therefore, estimates of DON fluxes; however, the focus of this study is on trends, rather than exact values, and repeated measurements of [DON] during base flow and pulse flow reduce the effects of low DON:TDN on our conclusions.

1.5.3 Sources of DON during high flow

For in-stream DON concentration to increase during high flow, additional DON must be mobilized within a catchment, and highly variable dissolved organic C:N ratios during high flow events (Appendix 1.A) suggest that multiple DON sources may contribute to surface water during pulse events. The hyporheic zone and riparian soils are near-stream sources of DON (Brookshire and others 2005, Wondzell and Swanson 1996) that may be rapidly mobilized as hydrologic connectivity between these sites and the stream increases and may explain the rapid increase in DOM concentration on the rising limb of the hydrograph observed in many systems (Boyer and others 1997). Wondzell and Swanson (1996) suggest that the turnover time of the DON-enriched water in the floodplain precludes it from being the dominant source of DON to the stream, at least initially, during storm events.

Upslope sources of DON may also contribute to elevated in-stream concentrations during high flow events. Organic-rich upper soil horizons may provide a source of DON if they become saturated and hydrologically connected to surface water over the course of a runoff event (Stieglitz and others 2003). DON concentration and lability have been found to be greatest near the soil surface (Qualls and Haines 1991, 1992, Michalzik and Matzner 1999, Yu and others 2002, Green and others 2008), a pattern attributed to both physical and biological processes. DON falls in precipitation, leaches from litter, and is excreted from root cells and microbes (Qualls and Haines 1991, Aitkenhead-Peterson and others 2003). As soil microbes use labile organic matter, more recalcitrant compounds are generated or left behind, and organic N can become bound in stable, slow-turnover material (Kiem and Kögel-Knabner 2003, Kalbitz and others 2003). These compounds, which are not rapidly recycled, can leach through the soil profile and bind to mineral soils (Michalzik and Matzner 1999). Consequently, flow paths through upper soil layers may deliver water enriched with DON to nearby streams compared to deeper flow paths (Hagedorn and others 2001, Balcarczyk and others 2009). Studies have reported that a significant portion of surface water can be derived from near-surface flow paths, rather than deeper groundwater during snowmelt runoff periods (e.g. Petrone and others 2007, Moravec and others 2010). Additionally, studies have found that during storm events, the relative contribution of deep sub-surface water declines while throughfall and shallow subsurface water contributions increase compared to base flow (Hornberger and others 1994, Hagedorn and others 2000, Inamdar and Mitchell 2007). These results suggest that hydrologic pulse events, including snowmelt runoff, storms, and rainy seasons that saturate the soil profile, may be important periods of DON delivery, both in terms of mass and lability, from uplands to surface water.

Although this meta-analysis can not distinguish sources of DON that contributed to observed patterns, responses in different ecosystem-types indicate that DOM from soils is likely an important contributor to surface water DON during high flow. Ecosystems that typically have large stores of soil organic matter – boreal and taiga forests, temperate forests, and grasslands (Anderson 1991) exhibited some of the largest responses during high flow. In contrast, the single alpine site, where soils are poorly developed, showed the greatest dilution of DON (Table 1.2). Despite trends based on ecosystem-type, base flow DON concentration was not significantly related to the relative or absolute increase in DON concentration during high flow ($r^2 = 0.06$, $p = 0.11$; $r^2 = 0.05$, $p = 0.15$). Further, temperate forests and pristine (non-wetland) sites, where terrestrial communities are likely to be N-limited (Vitousek and Howarth 1991), had lower DON concentrations compared to catchments with wetlands or agricultural activity (primarily Mediterranean catchments in this study). Wetland area has been previously correlated with in-stream DON concentrations (Pellerin and others 2004), as have anthropogenic inputs of N to catchments (Pellerin and others 2006, Brookshire and others 2007). The results presented in this meta-analysis are consistent with soils as a source of stream DOM. However, our observations that DOC and DON concentration frequently peaked at different times, suggests that future studies of DOM should consider potential mechanisms for DOC and DON decoupling, rather than bulk DOM transport alone. Additionally, the inconsistent relationship between in-stream

DON bioavailability and flow across studies indicates the need for identifying sources of DON throughout the year.

1.5.4 Modeling and management implications

In contrast to the many models predicting watershed TN and DIN export, there are few models of DON export from watersheds. The Global-NEWS DON sub-model uses runoff and watershed N-inputs to explain annual DON export from watersheds (Harrison and others 2005), and a regional neural network model uses basin size, slope, and precipitation to predict annual DON export from watersheds within a region (Clair and others 1994, 1996, Aitkenhead-Peterson and others 2005). Additionally, several regression models with single predictor variables, including percent cover by wetland, soil C:N, and atmospheric N deposition, have been generated (Pellerin and others 2004, Aitkenhead-Peterson and others 2005, Brookshire and others 2007). Although these models predict average annual DON export reasonably well, none incorporate the positive relationship between discharge and DON concentration that has been observed on intra-annual time scales (e.g. Petrone 2010). As a result, it would be difficult to accurately forecast seasonal export of DON or export under shifts in the hydrologic regime due to climate change, increased water use, or reservoir construction with these models. Both seasonal and interannual predictions of DON export are likely important for predicting the role of DON in coastal nutrient processing.

The ecosystem impact of increasing [DON] with flow observed for the majority of events in this study is likely magnified when total N export is considered. Pulse events can account for a large fraction of total annual runoff in a short period of time (e.g. Jordan and others 1997, Eyre and Pont 2003), and the fraction of annual DON flux exported during high flow events is correspondingly large (Petrone and others 2006). Although mean P:B for all sites was 1.58, the average rate of DON export increased by over an order of magnitude from base flow to high flow. Relatively small changes in concentration can translate into large changes in fluxes when discharge is high, so it is critical that DON dynamics are adequately characterized during high flow for accurate estimates of annual export. Additional studies of DON bioavailability during high flow events are necessary to better predict the fate of these large fluxes of DON.

Because DON export from land to surface water is affected by watershed hydrology and N dynamics, human alterations of the hydrologic and nitrogen cycles are likely causing changes in DON export patterns. Previous research suggests that alteration of hydrologic flow paths via tile drainage systems and stormwater runoff systems has increased annual DIN export by increasing annual runoff (Donner and others 2002), and impervious land cover in urban areas has been correlated with the fraction of annual NO_3^- exported during high flow events (Shields and others 2008). DON export could experience similarly strong effects. For example, falling water tables due to increased water consumption may result in less hydrologic flow through organic soil layers, and impervious surfaces may limit infiltration through soils, reducing the transport of soil-derived DON to surface water. Conversely, tile drains may shorten subsurface flow paths, decreasing the chance for DON to adsorb to soils thereby increasing export. Additionally, while there is evidence that N inputs to watersheds can influence DON export (Pellerin and others 2006, Brookshire and others 2007 Sobota and others 2009), further studies are needed in highly modified, N-enriched, urban and agricultural systems, particularly during high flow events, to identify the mechanisms and controls of DON export and DON bioavailability.

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1.8 TABLES

Table 1.1 Geometric mean of effect sizes for sites with similar event-types. Values in bold are significantly greater than 1.

Event-type	N (sites)	Mean effect size P:B (95% CI) (range)
Snowmelt	25	**1.54** (1.25– 1.90) (0.30 – 3.19)
Storm	15	**2.17** (1.54 – 3.07) (1.15 – 9.53)
Mixed	3	0.76 (0.30 – 1.95) (0.50 – 1.03)
Reservoir	5	0.92 (0.46 – 1.84) (0.42 – 1.72
Wet Season*	1	2.76

* Only one system of this type included in analysis, so no measures of variability are reported.

Table 1.2. Mean base flow and pulse flow [DON] and mean effect size for different ecosystem types. All are geometric means. Values in bold are significantly greater than 1.

Ecosystem	N (sites)	Base flow DON] (mg/L) (± 1 SE)	Pulse flow [DON] (mg/L) (± 1 SE)	Mean P:B (95% CI) (range)
Alpine*	1	0.114	0.029	0.30
Desert Shrub*	1	0.156	0.296	2.16
Mediterranean forest/grassland	20	0.153 (0.041)	0. 200 (0.097)	**1. 30** (1.02-1.64) (0.42 – 2.755)
Mediterranean forest/grassland without reservoir sites	15	0.151 (0.054)	0.220 (0.127)	**1.45** (1.13-1.87) (0.498 – 2.755)
Taiga/boreal forest	13	0.161 (0.032)	0. 293 (0.046)	**1.81** (1.43-2.28) (0.984 – 3.187)
Temperate forest/grassland	10	0.081 (0.026)	0.166 (0.082)	**2.22** (1.23-3.99) (0.799 – 9.530)
Tropical forest/grassland*	1	0.035	0.074	2.26
Tundra*	1	0.252	0.363	1.40

* Only one system of this type included in analysis, so no measures of variability are reported

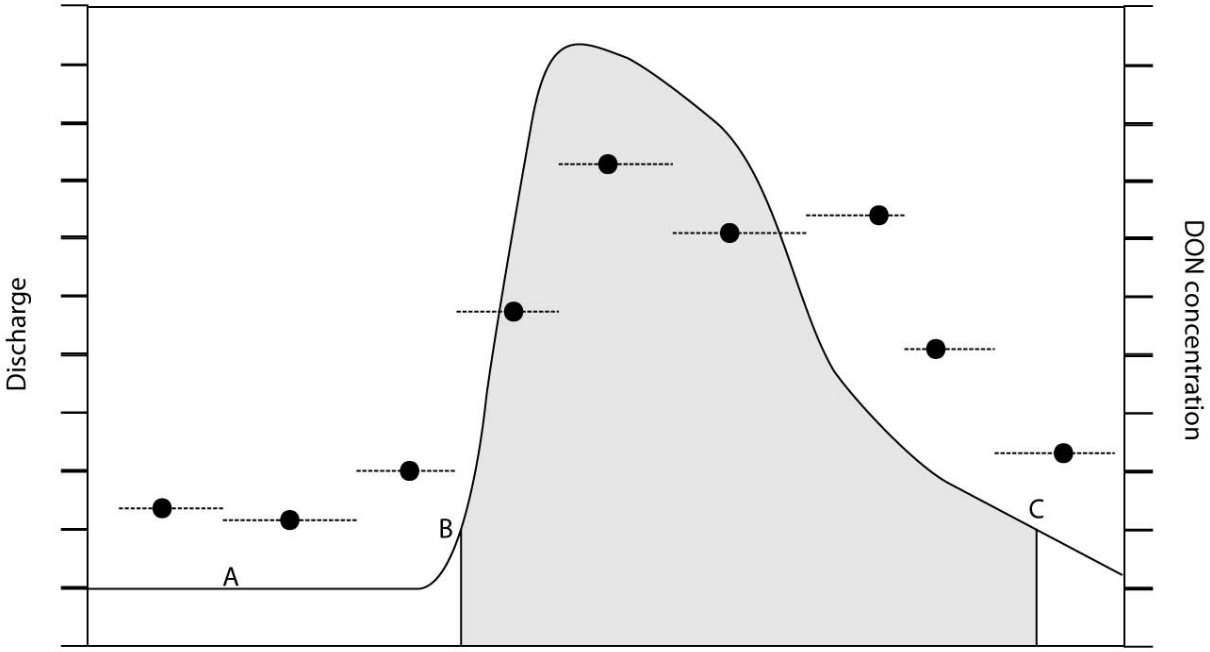
1.9 FIGURES

Figure 1.1 Representative hydrograph (-), discrete DON concentration data (•), and interpolated DON concentration (-----) from a hypothetical river, to illustrate the approach used for defining base flow, pulse flow, and for calculating flow-weighted mean concentrations in this study. Base flow (A) was defined as the period of steady flow prior to a pulse. The pulse (shaded area) was defined as starting when discharge more than doubled (point B) and was considered to end when base flow fell below double the previous base flow (C) (See Methods for exceptions). To determine loads, discharge was multiplied by the corresponding DON concentration for each time point with both concentration and discharge data, and concentrations were assumed to be constant from mid-point to mid-point between sampling events. The sum of discrete loads, integrated over the pulse period was then divided by total discharge over the same period to determine flow-weighted mean concentrations. A similar analysis using data from base flow periods was carried out to determine base flow flow-weighted mean concentrations for each study system.

Figure 1.2. Flow-weighted mean pulse flow versus base flow [DON] (top) and mean pulse flow versus base flow DON flux (bottom). The dotted lines represent a 1:1 ratio. Sites that reported multiple events have error bars (± 1 SE). Note the log scale on all axes.

Figure 1.3. P:B boxplots with median, quartiles, and ranges (whiskers) (○) for all sites ("All sites" – events within sites averaged) and for initial, second, third, and post-third events. Note that the sample size the "first" event includes more than one event per site if several

hydrologic periods were reported (e.g. multiple snowmelt years).The value above the box is n for each category. The dashed line is P:B = 1.



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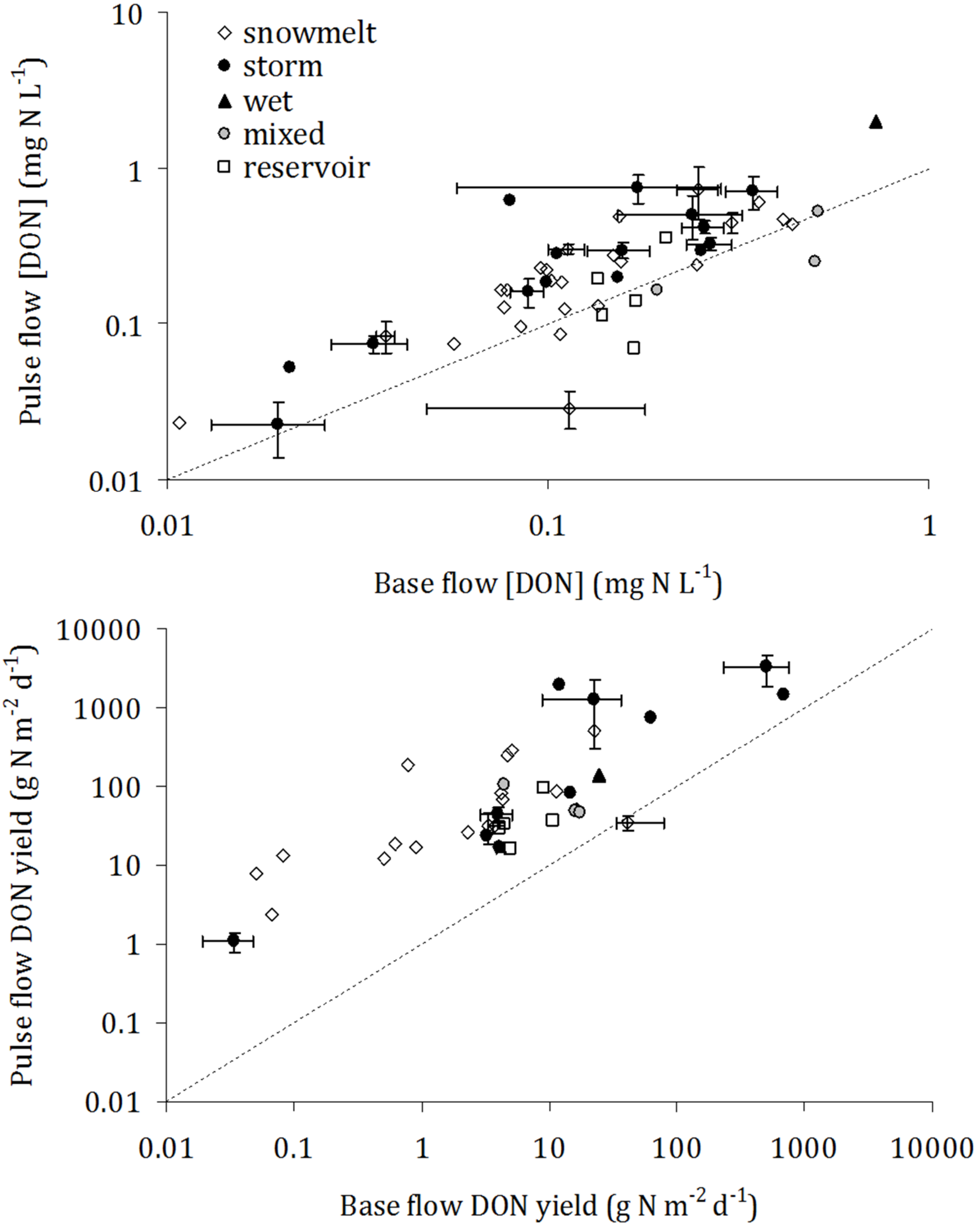

10
1
0.1
0.01
◇ snowmelt
● storm
▲ wet
● mixed
☐ reservoir
Pulse flow [DON] (mg N L^{-1})
0.01
0.1
1
Base flow [DON] (mg N L^{-1})
10000
1000
100
10
1
0.1
0.01
Pulse flow DON yield (g N m^{-2} d^{-1})
0.01
0.1
1
10
100
1000
10000
Base flow DON yield (g N m^{-2} d^{-1})

Figure 1.2. Flow-weighted mean pulse flow versus base flow [DON] (top) and mean pulse flow versus base flow DON flux (bottom). The dotted lines represent a 1:1 ratio. Sites that reported multiple events have error bars (± 1 SE). Note the log scale on all axes.

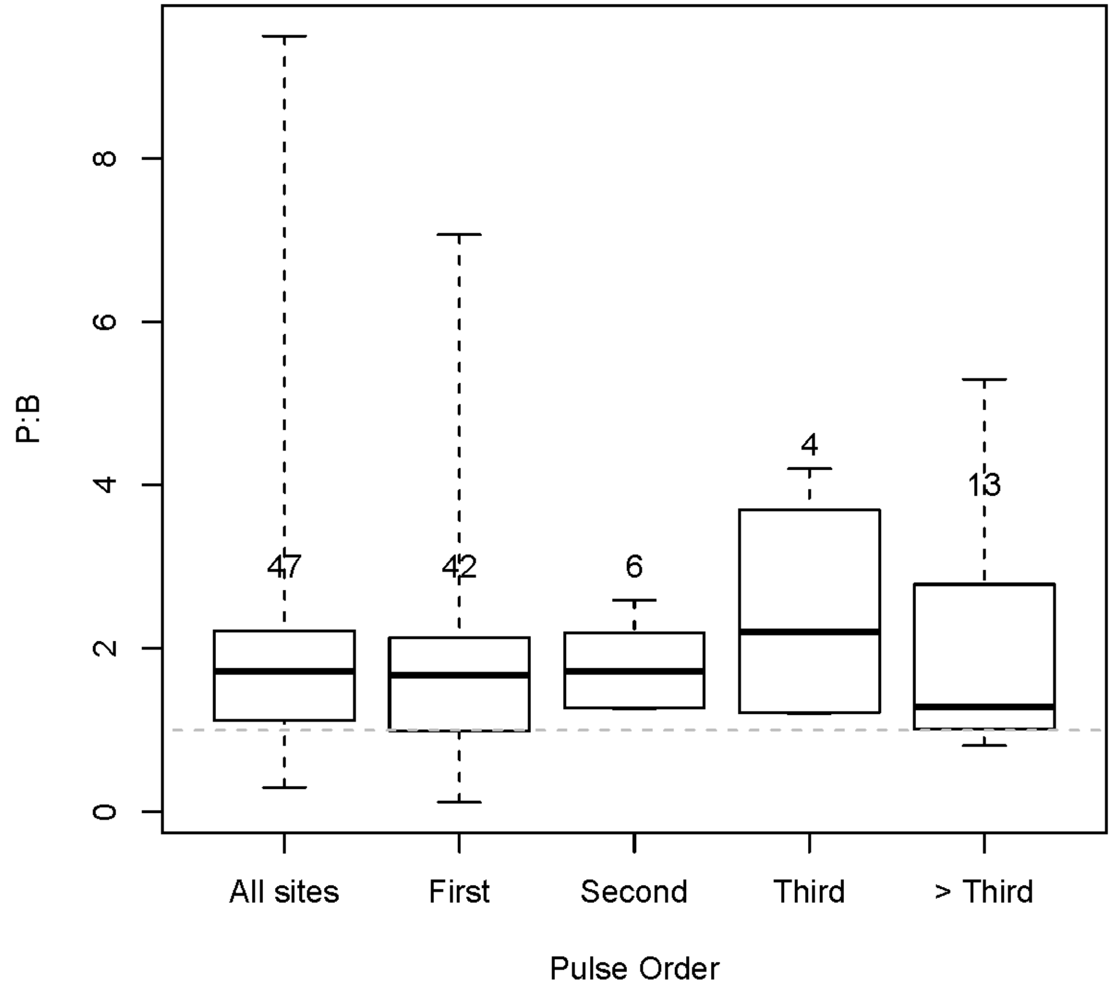

Figure 1.3. P:B boxplots with median, quartiles, and ranges (whiskers) (○) for all sites (“All sites” – events within sites averaged) and for initial, second, third, and post-third events. Note that the sample size the “first” event includes more than one event per site if several hydrologic periods were reported (e.g. multiple snowmelt years).The value above the box is n for each category. The dashed line is P:B = 1.

1.10 APPENDICES

Appendix 1.A

Source	Site	Number of events	Pulse-type	Biome	Mean [DON] calculation method
Brooks and others 2007	San Pedro River	11	storm	Desert shrub	flow-weighted mean; concentration and Q values available
Bernal and others 2005	Fuirosos River	Multiple*	storm	Mediterranean forest	Arithmetic mean; provided by the author
Buffam and others 2001	Paine Run	5	storm	Temperate forest	flow-weighted mean; author-provided mean and author-defined pulse period
Coats and Goldman 2001	Blackwood	1	snowmelt	Mediterranean forest	Flow-weighted mean; concentration and Q values extracted from figures
	Incline	1	snowmelt	Mediterranean forest	Flow-weighted mean; concentration and Q values extracted from figures
	Third Creek	1	snowmelt	Mediterranean forest	Flow-weighted mean; concentration and Q values extracted from figures
	Upper Truckee	1	snowmelt	Mediterranean forest	Flow-weighted mean; concentration and Q values extracted from figures
Hagedorn and others 2001	headwater catchment	1	storm	Temperate grassland/ forest	Flow-weighted mean; concentration and Q values extracted from figures

Holmes et al. 2011, CADIS-AON	Kolyma	1	snowmelt	Taiga/boreal forest	arithmetic mean; concentration values available; pulse period defined by the author
	Lena	2	snowmelt	Taiga/boreal forest	arithmetic mean; concentration values available; pulse period defined by the author
	Mackenzie	1	snowmelt	Taiga/boreal forest	arithmetic mean; concentration values available; pulse period defined by the author
	Ob	1	snowmelt	Taiga/boreal forest	arithmetic mean; concentration values available; pulse period defined by the author
	Yenisey	1	snowmelt	Taiga/boreal forest	arithmetic mean; concentration values available; pulse period defined by the author
	Yukon	2	snowmelt	Taiga/boreal forest	arithmetic mean; concentration values available; pulse period defined by the author
Inamdar and Mitchell 2007	S1	3	storm	Temperate forest	Flow-weighted mean; concentration and Q values extracted from figures
	S2	3	Storm	Temperate forest	Flow-weighted mean; concentration and Q values extracted from figures
	S3	1	storm	Temperate forest	Flow-weighted mean; concentration and Q values extracted from figures

	S5	1	Storm	Temperate forest	Flow-weighted mean; concentration and Q values extracted from figures
Kaushal and Lewis 2003	McCullough Gulch	1	snowmelt	Temperate forest	Flow-weighted mean; concentration and Q values extracted from figures
	Spruce Creek	1	snowmelt	Temperate forest/ grassland	Flow-weighted mean; concentration and Q values extracted from figures
Petrone and others 2006	High Permafrost	7	snowmelt and storm	Taiga/boreal forest	Flow-weighted mean; concentration and Q values available
	Medium permafrost	3	storm	Taiga/boreal forest	Flow-weighted mean; concentration and Q values available
	Low permafrost	1	storm	Taiga/boreal forest	Flow-weighted mean; concentration and Q values available
Petrone and others 2007	forest catchment	1	snowmelt	Taiga/boreal forest	Flow-weighted mean; concentration and Q values available
	wetland catchment	1	snowmelt	Taiga/boreal forest	Flow-weighted mean; concentration and Q values available
Sobota, D, unpub.	American River	1	snowmelt	Mediterranean forest/ grassland	Flow-weighted mean; concentration and Q values available

Bear River	1	snowmelt	Mediterranean forest/ grassland	Flow-weighted mean; concentration and Q values available
Cache Creek	1	snowmelt	Mediterranean forest/ grassland	Flow-weighted mean; concentration and Q values available
Calaveras River	1	snowmelt	Mediterranean forest/ grassland	Flow-weighted mean; concentration and Q values available
Feather River	1	reservoir	Mediterranean forest/ grassland	Flow-weighted mean; concentration and Q values available
Lower Sacramento River	1	mixed	Mediterranean forest/ grassland	Flow-weighted mean; concentration and Q values available
Lower San Joaquin River	1	mixed	Mediterranean forest/grassland	Flow-weighted mean; concentration and Q values available
Merced River	1	reservoir	Mediterranean forest/grassland	Flow-weighted mean; concentration and Q values available
Mokelumne River	1	reservoir	Mediterranean forest/grassland	Flow-weighted mean; concentration and Q values available
Salt/Mud Slough	1	wet	Mediterranean grassland/wetland	Flow-weighted mean; concentration and Q values available

	Stanislaus River	1	reservoir	Mediterranean forest/grassland	Flow-weighted mean; concentration and Q values available
	Tuolumne River	1	reservoir	Mediterranean forest/grassland	Flow-weighted mean; concentration and Q values available
	Upper Sacramento River	1	snowmelt	Mediterranean forest/grassland	Flow-weighted mean; concentration and Q values available
	Upper San Joaquin River	1	mixed	Mediterranean forest/grassland	Flow-weighted mean; concentration and Q values available
Sebestyen and others 2008	Pope Brook (W-9)	2	snowmelt	Temperate forest	Flow-weighted mean; concentration and Q values extracted from figures
Stepanauskas and others 2000	Lillån	1	snowmelt	Taiga/boreal forest	Flow-weighted mean; concentration and Q values extracted from figures
	Stridbäcken	1	snowmelt	Taiga/boreal forest	Flow-weighted mean; concentration and Q values extracted from figures
Townsend-Small and others 2011	Upper Kuparuk R.	3	snowmelt and storm	Tundra	Flow-weighted mean; concentration and Q values available
US Geological Survey, B. Pellerin, unpub.	Willow Slough	3	storm	Mediterranean forest/grassland	Flow-weighted mean; concentration and Q values available

Wiegner and others 2009	Wailuku R.	4	storm	Tropical forest/grassland	arithmetic mean; concentration provided by author, pulse period defined by author
Williams and others 2001, Hood and others 2003	North Boulder Creek, Green Lake 4 GL4	2	snowmelt	Alpine	Flow-weighted mean; concentration and Q values extracted from figures
Wondzell and Swanson 1996	McRae Creek	Multiple*	storm	Temperate forest	geometric mean; concentration provided by author, pulse period defined by author

*It was unclear from the publication exactly how many storm events were included in “storm” averages proved by the author

Q is discharge

Appendix 1.B

Source	Site	Mean base [DON] (mg/L) (± 1 SE)	Mean pulse [DON] (mg/L) (± 1 SE)	P:B* (± 1 SE)	Mean base flow yield (g N m^{-2} d^{-1}) (± 1 SE)	Mean pulse flow yield (g N m^{-2} d^{-1}) (± 1 SE)	Mean base DOM C:N	DOM C:N range during pulse events
Brooks and others 2007	San Pedro River	0.156 (0.029)	0.296 (0.034)	2.16 (0.61)	0.03 (0.01)	1.08 (0.29)	32.8	9.4-50.2
Bernal and others 2005	Fuirosos River	0.257	0.423	1.61	NA	NA	33	3.4-170.8
Buffam and others 2001	Paine Run	0.021	0.052	2.48	NA	NA	NA	NA
Coats and Goldman 2001	Blackwood	0.057	0.075	1.32	4.21	82.3	NA	NA
	Incline	0.075	0.165	2.20	0.51	12.0	NA	NA
	Third Creek	0.011	0.023	2.13	0.07	2.40	NA	NA
	Upper Truckee R.	0.077	0.127	1.66	4.35	68.4	NA	NA
Hagedorn and others 2001	headwater catchment	0.079	0.615	7.76	12.2	2000	28.2	6.7-25.0
Holmes et al. 2011, CADIS-AON	Kolyma	0.108	0.186	1.72	NA	NA	31.1	46.2-71.0
	Lena	0.248 (0.031)	0.740 (0.269)	2.81 (1.17)	NA	NA	39.5	21.6-50.4
	Mackenzie	0.156	0.252	1.61	NA	NA	42.8	42.1-51.9
	Ob	0.099	0.222	2.24	NA	NA	45.7	22.1-49.3
	Yenisey	0.095	0.228	2.40	NA	NA	49.8	27.7-72.0
	Yukon	0.112 (0.012)	0.303 (0.022)	2.71 (0.74)	NA	NA	25.0	38.4-41.2
Inamdar and Mitchell 2007	S1	0.171 (0.114)	0.749 (0.151)	9.53 (3.88)	22.8 (14.1)	1270 (960)	62.8	4.9-42.9

	S2	0.238 (0.086)	0.505 (0.157)	2.24 (0.89)	497 (261)	3320 (1420)	18.1	4.0-44.9
	S3	0.252	0.294	1.17	691	1450	10.5	8.3-10.9
	S5	0.106	0.280	2.65	61.9	761	58.6	10.2-47.2
Kaushal and Lewis 2003	McCullough Gulch	0.108	0.086	0.80	NA	NA	2.31	26.27
	Spruce Creek	0.085	0.096	1.13	NA	NA	3.71	31.29
Petrone and others 2006	High Permafrost	0.190 (0.032)	0.310 (0.028)	1.72 (0.6)	3.6 (1.1)	41.1 (8.3)	42.9	6.3-101.8
	Medium permafrost	0.088 (0.009)	0.160 (0.033)	1.74 (0.74	4.11 (0.28)	17.1 (2.1)	84.0	19.3-52.9
	Low permafrost	0.099	0.183	1.85	3.28	23.9	53.1	49.2-66.0
Petrone and others 2007	forest catchment	0.154	0.490	3.19	0.05	8.00	14.7	15.7-51.9
	wetland catchment	0.415	0.475	1.15	0.08	13.3	90.8	51.7-81.9
Sobota, D, unpub.	American River	0.078	0.163	2.08	11.5	88.5	23.9	6.0-31.5
	Bear River	0.102	0.188	1.84	0.79	183	21.8	18.8-53.0
	Cache Creek	0.135	0.129	0.95	0.62	18.8	51.3	5.0-99.2
	Calaveras River	0.358	0.602	1.68	5.08	291	14.7	17.8-19.9
	Feather River	0.138	0.112	0.81	10.9	37.2	24.0	18.0-24.1
	Lower Sacramento River	0.193	0.166	0.86	16.2	47.8	13.5	8.5-23.3
	Lower San Joaquin River	0.502	0.25	0.50	17.4	46.3	10.0	13.9-27.1
	Merced River	0.171	0.138	0.811	4.12	28.8	15.8	11.7-38.2
	Mokelumne River	0.135	0.192	1.42	4.41	33.7	21.0	7.5-25.9
	Salt/Mud Slough	0.723	1.99	2.76	24.5	140	13.7	2.6-10.4

	Stanislaus River	0.205	0.353	1.72	8.94	95.8	16.9	5.9-24.5
	Tuolumne River	0.168	0.070	0.42	4.96	16.1	13.9	22.4-84.6
	Upper Sacramento River	0.110	0.123	1.11	16.6	50.7	23.4	7.4-105.0
	Upper San Joaquin River	0.511	0.528	1.03	4.50	104	17.9	12.0-22.8
Sebestyen and others 2008	Pope Brook (W-9)	0.038 (0.002)	0.084 (0.019)	2.18 (0.94)	3.34 (1.10)	32.1 (13.5)	31.9	11.5-58.6
Stepanauskas and others 2000	Lillån	0.439	0.437	1.0	22.5	504	50.7	56.2-72.1
	Stridbäcken	0.245	0.241	0.98	4.74	252	54.9	38.5-57.7
Townsend-Small and others 2011	Upper Kuparuk R.	0.252 (0.050)	0.363 (0.092)	1.40 (0.66)	NA	NA	20.5	26.7-37.9
US Geological Survey, B. Pellerin, unpub.	Willow Slough	0.345 (0.053)	0.711 (0.169)	1.99 (1.02)	NA	NA	14.9	4.9-31.3
Wiegner and others 2009	Wailuku R.	0.035 (0.008)	0.074 (0.009)	2.26 (0.87)	NA	NA	NA	NA
Williams and others 2001, Hood and others 2003	North Boulder Creek, Green Lake 4 (GL4)	0.114 (0.066)	0.029 (0.008)	0.30 (1.81)	40.5 (37.5)	35.0 (7.3)	NA	NA
Wondzell and Swanson 1996	McRae Creek	0.020	0.023	1.15	NA	NA	NA	NA

[*] P:B is the geometric mean for sites with SE provided.

NA Adequate data not available

CHAPTER TWO

Hydrologic control of dissolved organic carbon and nitrogen and dissolved organic matter quality in a semi-arid artificially drained agricultural catchment

2. Hydrologic control of dissolved organic carbon and nitrogen and dissolved organic matter quality in a semi-arid artificially drained agricultural catchment

2.1 ABSTRACT

Agricultural practices have altered field- and watershed-scale dissolved organic matter (DOM) dynamics. However, mechanisms responsible for these changes are not clear, and field-scale processes are rarely directly linked to the magnitude and quality of DOM that is transported from agricultural soils to surface water. In a small (12 ha) agricultural catchment in eastern Washington State, I tested the hypothesis that hydrologic connectivity in the catchment is the dominant control over the concentration and quality of DOM exported to surface water via artificial subsurface drainage. Dissolved organic carbon (DOC) concentration, Fluorescence Index, Freshness Index, and the concentrations of humic-like PARAFAC components varied with depth through the soil profile. In drain discharge, these characteristics were significantly, positively correlated with drain flow across seasons and years, suggesting that DOM from shallow sources is consistently exported via subsurface drainage when the hydrologic connectivity in the catchment is greatest. Assuming changes in projected streamflow for the Palouse River (which contains the study catchment) under the A1B climate scenario apply to the study catchment, I project annual DOC loads to be more variable from year to year in the future, and the potential range of annual DOC export for wet years is expected to be much greater in the future. Results from this study highlight the variability in the magnitude and quality of DOM inputs from agricultural soil to surface water on daily and interannual timescales, pointing to the need for a more nuanced understanding of agricultural impacts on DOM dynamics in surface water.

2.2 INTRODUCTION

Terrestrial ecosystems export approximately as much carbon to inland waters as they store each year, and an estimated two-thirds of this exported carbon never reaches the coastal ocean, implying an important role for organic carbon mineralization in freshwater ecosystems [*Battin et al.*, 2009; *Regnier et al.*, 2013]. However, the flux of dissolved organic carbon (DOC) from soils to inland waters and its eventual fate there is not well characterized [*Battin et al.*, 2008]. Human activities, including agriculture, have modified dissolved organic matter (DOM) export in a variety of ways [*Stanley et al.*, 2012; *Regnier et al.*, 2013] that have led to changes in the timing and quality of DOM export, which is particularly important because both influence its biodegradability in inland waters [e.g. *Buffam et al.*, 2001; *Fellman et al.*, 2009]. Understanding mechanisms that control these dynamics is critical to better quantify and predict carbon processing in inland waters.

Agricultural practices influence both soil organic matter and hydrologic dynamics [e.g. *Boyer and Groffman*, 1996; *Dalzell et al.*, 2011; *Jacinthe et al.*, 2001; *McTiernan et al.*, 2001], leading to watershed-scale effects on streamwater DOC concentration ([DOC]) and DOM quality. Agricultural effects on in-stream [DOC] are highly variable across catchments, with agricultural area having been found to increase [*Oh et al.*, 2013], decrease [*Cronan et al.*, 1999] or have no discernable effect [*Wilson and Xenopoulos*, 2008] on [DOC]. The direction of change likely depends on the reference land-use (e.g. forested or wetland) [*Graeber et al.*, 2012]. In contrast to the inconsistent effects observed for concentration, the quality of in-stream DOM shifts predictably towards more reduced, lower molecular weight, potentially more labile compounds in agricultural catchments relative to natural land cover; however, mechanistic explanations for these changes are lacking [*Cronan et al.*, 1999; *Seitzinger et al.*, 2002; *Petrone et al.*, 2009; *Wilson and Xenopoulos*, 2009; *Williams et al.*, 2010].

Artificial subsurface drainage is an important field-scale modification associated with agricultural management. Subsurface drainage alters hydrologic flow paths, potentially influencing biogeochemical processing of DOM [*McTiernan et al.*, 2001; *Dalzell et al.*, 2011]. Subsurface drainage reduces water movement overland and laterally through shallow soil by enhancing vertical flow through the soil profile. Movement of DOM through the soil column may increase biotic or abiotic removal prior to export [e.g. *Qualls et al.*, 2002], and indeed, studies have found [DOC] in subsurface drain discharge to be lower than in receiving streams [*Warrner et al.*, 2009; *Vidon et al.*, 2012]. However, [DOC] has been observed to increase in subsurface drainage during stormflow [*Vidon et al.*, 2012]. This positive relationship between discharge and [DOC] during stormflow is also common in streams and has been attributed to enhanced hydrologic connectivity between streams and upland areas in catchments, resulting in the mobilization and lateral transport of DOM from organic-rich landscape patches (e.g. hyporheic zone, organic horizon, riparian soils) to surface water [e.g. *Boyer et al.*, 2000; *Xu et al.*, 2012]. However, this shift to lateral flow paths that bypass deeper soil horizons [e.g. *Bishop et al.*, 2004; *Seibert et al.*, 2009] cannot explain DOM dynamics in subsurface artificial drainage. An alternative explanation may be that the travel time of DOM from shallow soils through the subsoil is too rapid for significant removal or processing to occur, and studies have found that "quick-flow" or macropore flow can contribute substantially to subsurface drain flow during storm events, rapidly exporting near-surface materials to streamwater via artificial drainage [*Schilling and Helmers*, 2008].

In many agricultural systems I do not have a clear understanding of the dynamic balance between transport and removal mechanisms across hydrologic conditions, and the net effect on DOM loss from soils to streams, without which it will be difficult to predict how these systems might respond to future hydrologic changes or to adjust management strategies to improve water quality [*Ruark et al.*, 2009]. To understand the role of hydrologic conditions in controlling DOM export, I address the following questions: 1.) How do [DOC], [DON] and DOM quality vary in the landscape? 2.) What is the relationship between hydrologic conditions, DOM patterns in the landscape, and the export of terrestrial DOM via artificial subsurface drainage, in terms of concentration, load, and quality? and 3.) What are the implications for interannual variability in DOM export? I hypothesized that increasing hydrologic connectivity would result in the mobilization and export of shallower sources of DOM via drain flow, resulting in changes in the concentration and quality of exported DOM as drain discharge increased. I addressed these questions by monitoring hydrologic and dissolved organic matter dynamics at a dryland experimental farm in eastern Washington State, USA across three water years.

2.3 METHODS

2.3.1 Study site

Research was conducted during the 2011, 2012, and 2013 water years (Oct – Sep) at the experimental Cook Agronomy Farm, which is located in Whitman County in the Palouse region of eastern Washington State (Fig. 2.1). Precipitation averages 540 mm annually, with most coming as rain or snow during the winter and spring months (November through April). Soils are poorly drained Mollisols, part of the Palouse-Thatuna series [*USDA*, 1978] overlying Columbia River Basalt flows [*McDonald and Busacca*, 1992], and the area is characterized by rolling hills, with an average slope of 17% across the county [*NRCS*]. At the study site a restrictive argillic layer is intermittently present at approximately 1 m depth, resulting in complex sub-surface. During the sampling period, crops rotated among winter wheat, spring wheat, and garbanzo beans, and an alfalfa buffer strip was grown along the edge of the field (Fig. 2.1). The study site is located in the Missouri Flat Creek catchment; the 660 ha including and above the study site is 92% agricultural land cultivated similarly to the study catchment, 2% developed, and the remainder shrub, forested or other cover [*Schwarz,* 2013].

The southwest 12 ha section of the farm is artificially drained with a subsurface drain; the drain outlet discharges directly into Missouri Flat Creek. The hydrologic budget for the catchment suggests that nearly all lateral hydrologic losses (i.e. not to deep ground water) occur via the subsurface drain (E. Brooks, unpub.). Drain discharge is typically low in the summer, and previous research indicates that after approximately 150 mm of winter precipitation, the subsurface drain begins to respond to precipitation and melt events [*Keller et al.*, 2008]. Most subsurface drain discharge is derived from winter precipitation [*Moravec et al.*, 2010; *Donaldson*, 2013].

2.3.2 Field sampling

Wells and lysimeters were nested (~1 m apart from each other) at sampling sites across the artificially drained section of the farm (Fig. 2.1). Collectively these instruments are referred to as soil water samplers. In locations with an argillic layer present, a shallow well (SW) was installed above the argillic layer to sample shallow soil water, and a deep well (DW) was installed to sample permanent ground water. In locations with no argillic layer, one deep well was installed and screened from the bedrock to approximately 1 m depth. During the 2012-2013 water years, shallow lysimeters (SL) were installed at 0.5 m below the surface.

Wells and lysimeters were monitored approximately every other week during the summer and fall, if water was available, and approximately every week during the winter and spring for water table elevation (wells only), electrical conductivity at 25°C (EC), DOC, total dissolved nitrogen (TDN), nitrate+nitrite (NO_3^-), and ammonium (NH_4^+). Water table elevation was calculated from depth to water measured manually with an e-tape. EC was measured on unfiltered samples using an Orion Model 115 with Conductivity Cell 014016 probe, and samples for nutrients were filtered through pre-ashed GF/F Whatman filters (0.7μm) or 0.45 μm Millipore filters and stored frozen in high density polyethylene bottles until analysis. Comparisons of DOC concentrations between the 0.7 and 0.45 μm filters showed no significant difference.

During the 2011 water year, the drain was sampled manually on a weekly basis for water chemistry and discharge. In October 2011 a flume was installed below the drain outlet with a pressure sensor (INW, model PT12, Kirkland, WA) and temperature and conductivity probe (Campbell Scientific, CS547A-L, Logan, UT). Stage height, electrical conductivity, and temperature were measured every 15 minutes. Additionally, an autosampler (ISCO, Model 3700 or 6712, Lincoln, NE) was installed and set to collect drain discharge weekly and more frequently during high flow events.

For DOM and absorbance and fluorescence spectra, soil water and drain discharge samples were collected approximately monthly in pre-ashed amber glass bottles. These samples were filtered through GF/F Whatman filters, kept on ice and analyzed within 5 days of collection. Samples collected by the autosampler during high flow events were frozen prior to spectroscopic analyses; storage and freezing effects were minimal and are discussed below.

2.3.3 Laboratory analyses

Samples were analyzed for NO_3^- + nitrite (hereafter referred to as NO_3^-) and NH_4^+ according to the standard EPA methods (353.2 and 350.1, respectively) using a discrete nutrient analyzer (WestCo Smartchem). Initially, nitrite was measured separately from NO_3^- but found to be very low, so it was not measured separately for the majority of samples. DOC and TDN were analyzed on a Lachat TOC-TN analyzer (IL 550 TON-TN) equipped with electrochemical (ECD) NO and non-dispersive infrared absorption (NDIR) detectors. Dissolved organic nitrogen (DON) was calculated as the difference between TDN and total dissolved inorganic nitrogen (NO_3^- + NH_4^+).

Absorbance spectra for bulk DOM samples were analyzed using a J&M TIDAS spectrophotometer (World Precision Instruments, Sarasota, FL) at each unit wavelength from 200-700 nm. Fluorescence excitation-emission matrices (ex 240-450 nm every 10 nm by em 300-600 nm every 2 nm) were generated with a spectrofluorometer (Fluoromax-4, HORIBA Jobin Yvon, Edison, NJ). Appropriate corrections for the instrument (variable lamp intensity), water matrix (background), internal absorbance (Inner Filter Effect, as in *McKnight et al.*, 2001), and Raman signal were applied to fluorescence data to permit comparisons across sampling dates. All samples were kept at 20°C during measurements using a temperature controlled cuvette holder and recirculating cooling water bath.

Indices of DOM quality based on spectroscopic characteristics were then calculated. Fluorescence Index (FI), which has been used as an indicator of the relative contributions of plant-derived and microbially-derived compounds to the DOM pool [*McKnight et al.*, 2001], is calculated as the ratio between emission intensity at wavelengths 470 nm and 520 nm associated with excitation wavelength 370 nm. Values typically range between 1.2 and 1.8, with lower values corresponding to plant-derived material and higher values corresponding to microbially-derived material. A second index derived from fluorescence data, β/α (or Freshness Index), has been found to relate to the contribution of recently derived DOM, with β representing recently derived material and α more decomposed material. β/α is calculated as the emission intensity at 380 nm divided by max emission intensity between 420 and 435 nm associated with excitation wavelength 310 nm [*Parlanti et al.*, 2000]. Values typically range from 0.3 to 0.8 [e.g. *Graeber et al.*, 2012; *Wilson and Xenopoulos*, 2008b]. Specific UV Absorbance at 254 nm (SUVA) is a widely measured indicator of DOM aromaticity, with higher values indicating more aromatic material [*Weishaar et al.*, 2003]. SUVA is calculated as absorbance at 254 nm divided by [DOC] with units of L mg^{-1} m.

A number of samples collected from the subsurface drain, including those collected during high flow events, were filtered, stored in acid-washed HDPE bottles and frozen prior to absorbance and fluorescence analysis. Vidon et al. [2008] report no effects of freezing for samples with [DOC] <15 mg L^{-1} on SUVA or FI, and I assessed the effects of storage and freezing by comparing samples collected in July 2013 that were stored in pre-ashed amber glass vials and run immediately with samples that were stored in HDPE bottles and frozen for 8 months. I observed changes in fluorescence intensity of only a few percent across analyzed wavelengths and not in a consistent direction, except in the protein-like region (ex 250-290, em 300-350), which showed changes upwards of 100% between fresh and frozen samples. Consequently, I omit frozen samples when analyzing data from this region.

2.3.4 Bioassays

Drain discharge was collected 5 times during the 2012 water year to assess the bioavailability of DOC across a range of seasons and hydrologic conditions. Samples for bioassays were filtered (0.2 µm, Millipore) and stored on ice (up to 4 days) to limit microbial activity until analyses began. An inoculum was generated using a method similar to Petrone et al. [2009] with stream sediment collected just downstream of the drain outlet on the same day as the drain discharge. A slurry of sediment and deionized water (1:3) was shaken for 30 minutes then centrifuged for 20 min at 3000 rpm. The supernatant (5 mL per replicate) was filtered first through a 0.7 µm filter to remove protists, then through a 0.2 µm filter. The material collected on the 0.2 µm filter was then backwashed into deionized water and used as an inoculum, similar to Qualls and Haines [1992].

A total of 200 mL of filtered drain water was added to 8 acid-washed, autoclaved mason jars. The jars were incubated at 12°C (similar to springtime stream temperature). Each was subsampled (15 ml) immediately and after 1, 2, 3, 4, and 6 days. Samples were filtered through 0.2 µm filters, frozen, and later analyzed for DOC, DON, and NO_3^- as above. [DOC] values from the initial sampling time and the subsequent sampling time with minimum mean [DOC] were analyzed using a two-way ANOVA to test for effects of treatment (inoculated or not) and time.

2.3.5 Statistical analyses

Water chemistry and DOM quality indices for samples from individual soil water samplers were averaged across time, and averages for each sampler were used in analyses to test for differences among sampler types. One-way ANOVA with $\alpha = 0.05$ was used to compare mean EC, [DOC], [DON], and C:N among shallow lysimeters, shallow wells, and deep wells. EC, DON, and C:N were log-transformed to meet the assumption of normality. Because the quality of DOM collected via suction has been found to differ from naturally dissolved OM [*Zsolnay*, 2003], SUVA, FI, and β/α are compared among shallow wells, deep wells, and litter leachate, rather than shallow lysimters. Litter leachate was generated twice in the laboratory using sub-samples of litter collected in July following spring wheat harvest, so mean litter values were compared to shallow and deep well data using one-sample t-tests, with μ set as the mean litter value; the Bonferroni correction was applied to α (0.05/2 tests results in α = 0.025). Values for FI were log-transformed to meet the assumption of normality. All analyses were run using R [*R Core Team*, 2012].

Relationships between water table depth at the sampling location nearest the drain outlet (location 95, Fig. 2.1) and drain discharge, water chemistry and DOM quality indices were examined using linear regression, with all drain data log-transformed to improve the normality of residuals. Because wells were not screened across the entire range of water table fluctuations (e.g. deep wells only screened up to the argillic layer), for analyses I used water table elevation measurements from deep wells when the water table elevation was below the elevation of the argillic layer and from shallow wells when it rose above the argillic layer. Relationships between drain flow rate and drain water chemistry and DOM indices were examined using linear or polynomial regression (DON, C:N). All analyses were run using R [*R Core Team*, 2012].

Additionally, I applied a multiple regression approach to model drain discharge [DOC] with predictor variables including instantaneous discharge, cumulative discharge over the previous 2 and 30 days, EC, instantaneous drain discharge temperature, and average air temperature over the preceding week. To determine which variables to include in models, a stepwise approach (forward and backwards) was used, and the model with the lowest AIC value was selected (MASS package in R, [*Venables and Ripley*, 2002]). Partial correlation coefficients were calculated as the average r^2 contribution for all orderings among regressors [*Lindeman et al.*, 1980] (relaimpo package in R, [*Grömping*, 2006]). All data were examined together, and then data were analyzed by flow condition (baseflow, rising limb of high flow events, or falling limb) and season [winter (Dec-Feb), spring (Mar-May), summer (Jun-Aug), or fall (Sep-Nov)]. I consider winter and spring as the wet season and summer and fall as the dry season. These seasons are defined differently from summer and winter and high discharge and low discharge seasons from a study of seasonal nitrate dynamics at the study site [*Kelley et al.*, 2013].

Parallel factor analysis (PARAFAC) was applied to assess excitation-emission data [*Stedmon and Bro*, 2008]. This multivariate approach is similar to principal component analysis, but components correspond to known excitation-emission pairs, and component values for each sample are quantitatively comparable across the dataset. Ideally, PARAFAC model components represent individual fluorophores or groups of similar fluorophores [*Stedmon and Bro*, 2008]. Soil water (n=113) and drain discharge (n=159) samples were modeled separately, and corresponding components were identified.

2.3.6 Estimating annual and event DOC and DON fluxes

Annual subsurface drain DOC-C and DON-N fluxes [kg ha^{-1} y^{-1}] were estimated for water years 2001-2013 using LOADEST [*Runkel et al.*, 2004]. The model assumes a concentration-discharge relationship and was calibrated with synoptically measured discharge and [DOC] and [DON] data from 2011-2013 using the formulation

$$load = a_0 + a_1 * \ln(Q) + a_2 * \ln(Q^2) \quad (1)$$

where a_0, a_1, and a_2 are constants and Q is discharge. Prior to 2012, instantaneous drain discharge was measured manually, typically at least monthly (13-38 samples/year) [*Keller et al.*, 2008]; during 2012 and 2013 discharge was measured automatically every 15 minutes. For LOADEST estimates, daily discharge was linearly interpolated between sampling dates for years 2001-2011, while discharge was averaged hourly for years 2012-2013. Years 2008 and 2010 were removed because there were fewer than 12 discharge measurements, and 2002 was removed because sampling was biased toward high flow events that year. The fractions of DOC and DON exported during high flow events were estimated for water years 2012 and 2013. Flow was characterized as "event" from the onset of rapidly increasing discharge following a precipitation event until the relationship between the log of discharge and time

$$\ln(Q) = a*t + b \quad (2)$$

became linear [*Blume et al.*, 2007], which generally corresponded to a return in baseflow EC values.

2.3.7 DOC loads and quality under climate scenarios

The Palouse watershed, where this study site is located, is projected to experience increases in precipitation intensity and earlier onset of the wet season under future climate scenarios [*Salathé et al.*, 2010]. These changes could lead to an increasing number or magnitude of episodic export events and greater interannual variability in DOM export to surface water. I examined the potential effects of climate change via changes in runoff on DOC export and DOM quality, as defined by FI, under two climate scenarios (A1B and B1) by applying projected changes to the flow regime for the Palouse River to the artificially drained catchment. Greenhouse gas emissions under B1 are on the low end of future scenarios, and global surface temperatures are projected to rise 1-3 ^{o}C by 2100 [*IPCC*, 2007]. Greenhouse gas emissions under A1B are on the high end of future scenarios, although a mix of fossil fuels and alternative energy technology is developed; global surface temperatures are projected to rise 1.5-4.5 ^{o}C by 2100. Because major effects of climate change on the environment are often due to changes in extremes, rather than changes in the mean, I focus here on DOC export and DOM quality in the driest and wettest 10% of observed and projected years for each scenario and timeframe.

Daily stream flow for the Palouse River [at Hooper, USGS ID 13351000, (the closest location to the study site with climate projections)] under historical conditions (water years 1916-2006) and climate change projected for the 2020's (30 years centered on 2025), 2040's (30 years centered on 2045), and 2080's (30 years centered on 2085) were downloaded from the Columbia Basin Climate Change Scenarios Project. For each future time period, daily flow is projected for 91 static climate water years using a suite of climate models (10 for A1B and 9 for B1); I selected stream flow output from Variable Infiltration Capacity (VIC) hydrologic model runs, which were driven by precipitation and temperature output from climate models that were bias corrected and downscaled using the hybrid delta approach [*Hamlet et al*., 2010]. Flow values for each day were averaged across the ensembles for use in analyses, resulting in 91 water years with daily flow for each future time period under both scenarios.

For the artificially drained catchment of this study, I estimate annual runoff, DOC flux, and average FI for each of the historical and projected water years to examine relative changes and trends, rather than absolute changes, due to the uncertainty associated with climate scenarios projections. To estimate runoff I apply relative projected changes in the Palouse River flow regime to the artificially drained catchment. I assume a positive linear relationship between flow and [DOC], with [DOC] tripling between the average minimum daily flow and average maximum daily flow across historical water years. Projected daily flow values are outside the historical range (0.96 to 1.98 times historical minimum and maximum, respectively), resulting in modeled [DOC] values that range from 0.99 to 13.77 times the applied low-flow value. This relative increase is within the range of [DOC] values observed in our study system across flow conditions (max [DOC]/min [DOC] = 22.8), and fewer than 1.5% of applied DOC values were above the value applied to the average maximum daily flow. Daily DOC loads were calculated by multiplying flow by the DOC value and summed within water years to calculate annual export. For FI, I assumed a negative linear relationship between FI and flow, with FI 1.65 and 1.45 at the same low and high flow values; the maximum applied FI value was 1.651, and the minimum value of FI was set at 1.23 (the lowest value observed in our system). Daily FI values were weighted by daily DOC load when averaging within a water year, resulting in an FI value representing the average FI for the total pool of DOC exported annually.

The wettest and driest 10% of years (n=9 each) were identified for the historical period and each scenario and timeframe. Because data were non-normal and variances appeared to be unequal (Bartlett's test was not applied because the data were non-normal), the Kruskal-Wallis test was applied to test whether mean ranks were different among groups; the Nemenyi post-hoc test was used to conduct multiple comparisons among groups.

2.4 RESULTS

2.4.1 Hydrologic dynamics

The drain flowed nearly year-round, but discharge was flashy, typically increasing by an order of magnitude in less than 48 hours in response to precipitation and melt events (Fig. 2.2). As the wet season progresses, the water table rises, reaching the surface in the lowest elevation wells (Fig. 2.3), leading to greater baseflow and intense high flow events. Drain discharge was log-linearly correlated with water table elevation at location 95, nearest the drain outlet (discharge log-transformed, $p < 0.001$, $r^2 = 0.63$, n=36, data not shown). High flow events contribute substantially to annual discharge, accounting for 48% and 25% of total annual flow in 2012 and 2013, respectively, while only occurring during 16 and 8% of the time (Table 2.1).

During mid-March of 2012, the drain experienced a clog that greatly reduced flow. Once the clog was manually removed, flow returned instantly. Samples taken during the clogged period (March 16-29) and for a week following were omitted from analyses of relationships between discharge and [DOC] and DOM quality.

2.4.2 Soil water EC and DOM

Because soil water samples were collected from samplers at uneven time intervals due to water availability, and soil water DOM chemistry did not show consistent patterns over time, values were averaged across time within samplers prior to examining how chemistry varied with depth. EC of soil water increased with depth through the soil profile (Fig. 2. 4, Table 2.2). Although spatial variability of EC at a given depth was high, mean EC in shallow lysimeters was significantly different from that in deep wells (Table 2.2). Higher EC with depth indicates longer residence time of soil water with depth, as EC reflects the extent of water-mineral reactions in the soil profile [*Bishop et al.*, 2004; *Keller et al.*, 2008].

Five PARAFAC components were identified for soil water DOM (Table 2.3). Components 1, 2, and 4 (C1, C2, C4) were identified as humic-like. All correlated with [DOC] ($r^2 = 0.82, 0.86, 0.76$, respectively), and together accounted for an average of 82% of measured fluorescence. Component 3 (C3) corresponds to tyrosine-like protein and showed no relationship with [DOC], accounting for an average of 12% of DOM fluorescence, but up to 68%. Component 5 (C5) comprised only a small fraction of DOM fluorescence (mean 6%), and was not correlated with any other component or [DOC]. C3, C4, and C5 are not analyzed further because of uncertainty around the protein-like region due to freezing (C3) and a lack of a match with components identified in drain water (C4, C5).

[DOC] and the humic-like components (C1, C2) decreased with depth, although not significantly for C1 and C2, while FI and β/α increased (Fig. 2.4, Table 2.2), indicating a shift towards a smaller DOM pool that is composed of a greater fraction of newly produced microbial products with depth, consistent with adsorption and/or removal of aromatic compounds and production of DOM via microbial activity. Neither [DON], C:N, nor SUVA showed a clear pattern with depth, and [DON] and C:N were highly variable over space and time (Fig. 2.4, Table 2.2).

2.4.3 Subsurface drain DOC and DON export dynamics

[DOC] in drain discharge exhibited a log-linear relationship with water table depth at location 95 ($p < 0.001$, $r^2 = 0.36$, $n = 33$), while [DON] was not significantly correlated with water table depth (data not shown). Similarly, [DOC] was linearly correlated weakly, although significantly, with instantaneous drain discharge ($r^2 = 0.35$, $p < 0.001$; Fig. 2.4). In contrast to [DOC], [DON] correlated less well with instantaneous drain discharge and displayed a unimodal relationship ($r^2 = 0.15$, $p < 0.001$; Fig. 2.4). Another 14% of the variability in [DOC] could be explained by including additional predictor variables: cumulative discharge over 2 and 30 days, water temperature of drain discharge, and average air temperature over the preceding week (model $r^2 = 0.49$, $p < 0.001$; Table 2.4). [DOC] was negatively correlated with the cumulative discharge variables and water temperature.

When drain samples are separated according flow conditions (whether they were taken during baseflow or rising or falling limb of high flow events), significant predictor variables for [DOC] and model performance change (Table 2.4). Instantaneous discharge is the most important predictor during the fall and winter, but EC is a much better predictor of [DOC] during the spring. During the summer, [DOC] was best predicted by the mean [DOC] value (i.e. no significant correlations). Regardless of season, instantaneous discharge was the best predictor of [DOC] during the rising limb of high flow events, whereas instantaneous discharge and 30-day cumulative discharge were nearly equally important predictors for [DOC] during falling limbs of high flow events. During baseflow periods, water temperature was the only significant predictor, although it explained very little of the variability ($r^2 = 0.08$, $p < 0.001$) (Table 2.4).

Estimated annual DOC-C and DON-N fluxes varied by nearly an order of magnitude from 2001-2013 (excluding 2002, 2008, and 2010), ranging from 1.0 to 8.6 kg C ha^{-1} (Fig. 2.5) and 0.23 to 1.8 kg N ha^{-1}, with median values 5.6 and 1.3 kg ha^{-1}, respectively. Interannual variability in annual discharge was the dominant control over both DOC and DON export, with annual runoff explaining nearly all of the interannual variability (DOC: $p < 0.001$, $r^2 = 0.98$, $n = 10$; DON: $p < 0.001$, $r^2 = 0.99$, $n = 10$). Annual flow-weighted (FW)-[DOC] and [DON] generally increased with annual drain flow (Fig. 2.6), but the intensity of high flow events within a year also affect FW-[DOC] and FW-[DON] because the highest concentrations are modeled to occur during the highest flows. For example, 2012 and 2013 water years were similar in terms of total runoff (110 and 126 mm, respectively), but 53% of DOC was exported during high flow events in 2012, compared to only 30% in 2013 (Table 2.1), resulting in higher flow-weighted [DOC] during 2012 than 2013 (5.82 vs 5.49 mg C L^{-1}).

2.4.4 Subsurface drain DOM quality

Four PARAFAC components were identified for DOM in drain discharge (Table 2.3). C1, C2 and C3 corresponded to those in the soil DOM model, and C4 exhibited tryptophan-like fluorescence (Table 2.3). Similar to soil water, C1 and C2 correlated well with drain water [DOC] ($r^2 = 0.74$ and 0.75, respectively), and accounted for the majority of DOM fluorescence, whereas the protein-like components were uncorrelated with [DOC] but together accounted for an average of 23% of DOM fluorescence (Table 2.3).

C1, C2 and β/α in drain discharge exhibited log-linear relationships with water table depth at location 95 [$p < 0.001$ for all relationships, $r^2 = 0.59$ (C1), 0.56 (C2), and 0.46 (β/ α), n=21], while C:N, FI and SUVA were not significantly correlated with water table depth (data not shown). FI and β/α showed strong, negative relationships with discharge (Fig. 2.4), suggesting that the contribution of recently produced microbial products to the DOM pool declines as discharge increases. In contrast to FI and β/α, SUVA and C:N showed no strong relationships with discharge (Fig. 2.4). The non-significant relationships between SUVA and C:N and either water table depth or discharge is consistent with the lack of any uni-directional pattern of SUVA or C:N in the soil profile (Fig. 2.7).

Measured bioavailability of DOM in drain discharge was low or undetectable across seasons and discharge conditions. No significant effects of treatment were detected, suggesting the uninoculated samples were not bacteria-free, so all replicates were combined for analysis. The period with the highest observed DOC loss (7.4%) was during Dec 2011, which had the lowest drain discharge and lowest SUVA value among time points when bioavailability was measured (Table 2.5), consistent with observations that lower aromaticity corresponds to greater bioavailability [e.g. *Warrner et al.*, 2009].

2.4.5 DOM export under future climate scenarios

During the driest 10% of potential water years, runoff and DOC export are projected to increase under both the B1 and A1B scenarios by 2080: runoff by 23% and 45%, respectively, and DOC export by 32% and 52%, respectively, although these changes are only significant for the A1B scenario (Fig. 2.8; Kruskal-Wallis test, $p < 0.05$; Nenemyi post-hoc test, n=9 for each group). During the wettest 10% of years, runoff and DOC export are also projected to increase by 2080, although not significantly, runoff by an average of 11% and 20% under the B1 and A1B scenarios respectively, and DOC export by 35% and 54%. Importantly, during the wettest years, the range of annual DOC export is projected to increase dramatically relative to historical conditions (Fig. 2.8). FI values are projected to decrease on average during the wettest years in the future, with mean values shifting from 1.48 historically to 1.46 and 1.44 by 2080 for the B1 and A1B scenarios (Fig. 2.8), although these shifts were not statistically significant. Similar to annual runoff and DOC export, the range and variance in average FI among the wettest years is projected to increase (Fig. 2.8).

2.5 DISCUSSION

DOM export via artificial subsurface drainage from this agricultural catchment is strongly linked to hydrologic dynamics, with a greater relative contribution and higher concentrations of more decomposed, plant-derived material and less fresh, microbially derived material exported at higher flows. DOM patterns in soil water support the hypothesis that DOM in surface soils is mobilized and rapidly transported to the subsurface drain during these high flow events, resulting in the subsurface drain functioning as a direct linkage between materials in surface soils and the receiving aquatic ecosystem during these periods. Because of the strong influence of total runoff and high flow events on the magnitude and quality of DOM that is exported to surface water, future changes in the hydrologic regime will have implications for the magnitude and quality of DOM that reaches surface water annually.

2.5.1 Subsurface drain DOM dynamics

Values for [DOC], [DON], and DOM characteristics in drain discharge generally fall within the range of measured values for catchment sources (Fig. 2.4). [DOC] and aspects of DOM quality that varied with depth in the soil profile are strongly correlated with discharge (Fig. 2.7). [DOC] and the amount of humic DOM (C1, C2) increase, while the freshness of (β/α) and the relative contribution of microbial material (FI) to DOM decrease with increasing drain discharge, strongly suggesting inputs of shallow DOM sources, which exhibited the highest values for [DOC], C1, and C2, and the lowest values of FI and β/α (Fig. 2.4). Other studies have reported similar patterns for DOM quality with respect to the depth of DOM sources; FI increased from throughfall to ground water in tropical and temperate forest systems [*Johnson et al.*, 2011; *Inamdar et al.*, 2012], and DOM aromaticity and degree of humification decreased, as indicated by the absorbance coefficient at 254 nm and humification index, and the contribution of microbially-derived and protein-like fluorescent components increased with depth in the temperate forest [*Inamdar et al.*, 2012]. While some studies have reported increased export of recalcitrant, aromatic DOM during high flow events [*Wiegner et al.*, 2009; *O'Donnell et al.*, 2010], similar to what was observed here, others have found opposite responses, reporting the mobilization of more labile DOM during high flow events [*Austnes et al.*, 2010]. Examining patterns in terrestrial sources and the extent of hydrologic connectivity during storm events more closely may provide insights into the cause of these disparate responses.

In contrast to [DOC] and fluorescence indices, [DON], C:N, and SUVA were poorly or uncorrelated with drain discharge (Fig. 2.4). Uncertainty around [DON] as a result of the subtraction method combined with the generally low contribution of DON to TN (average 11% across all samples) likely contributed to some variability in [DON] and C:N estimates, possibly masking patterns. However, C:N of DOM does not always exhibit patterns with soil depth [e.g. *Qualls and Haines*, 1992]. The lack of a relationship between SUVA and discharge is likely a result of a lack of a directional pattern with soil water depth; SUVA values were lowest for litter leachate, highest in shallow wells, and intermediate for DOM in deep wells.

The rapid mobilization and transport of topsoil DOM during high flow in this system is likely explained by macropore flow. This mechanism has been proposed to explain nitrate transport in this system [*Kelley et al.*, 2013], and water and solute transport in other artificially drained catchments in the Midwest, USA and Europe [*Stone and Wilson*, 2006; *Schilling and Helmers*, 2008; *Tiemeyer et al.*, 2008; *Cuadra and Vidon*, 2011]. In our study system, the soil column is nearly saturated during the wet season (Fig. 2.3) and a precipitation event can raise the water table quickly and fill macropores near the surface (e.g. from earthworms or root holes that remain undisturbed near the surface in this no-till system), which could result in topsoil DOM being transported quickly to the subsurface drain. Drain water EC data support this hypothesis; EC drops rapidly as discharge increases, reflecting inputs of precipitation water and/or shallow soil water, and quickly returns to baseflow values as discharge declines (Fig. 2.2).

Controls other than hydrologic mixing of available sources likely play a role in DOC export dynamics in this system, as water table depth and instantaneous discharge only explain 37% and 35% of [DOC] variability, respectively. A simple conceptual model of hydrologic transport of DOM in the catchment and export via subsurface drainage leads to predictions about DOC dynamics with respect to discharge. Assuming that (1) concentrations of DOM in source pools (i.e. top-soil and sub-soil) remain relatively constant and distinct over time and (2) catchment wetness increases hydrologic connectivity and drain discharge and, consequently, the contribution of shallow DOM sources, I would predict that [DOC] would strongly and linearly correlate with drain discharge. This relationship might be modified over time if source pools are depleted via flushing or modified by biological activity, if mobilized DOM is modified along flow paths to the subsurface drain, or if thresholds for various flow paths exist (e.g. tipping point where macropore flow begins to dominate discharge), resulting in a non-linear relationship between discharge and source-pool mobilization. Two- and 30-day cumulative discharge account for an additional 8% of [DOC] variability, suggesting short-term and seasonal hydrologic flushing can overwhelm DOC production or diffusion in this system. Other studies have also reported significant effects of flushing over similar time-scales [*Boyer et al.*, 2000; *Worrall et al.*, 2008; *Morel et al.*, 2009]. Additionally, water temperature was negatively correlated with [DOC] (Table 2.3), suggesting higher temperatures may enhance microbial decomposition of DOC relative to DOC production.

The importance of flow path, flushing, and microbial activity for regulating drain discharge [DOC] differ across seasons and flow conditions (Table 2.4). For example, during fall and winter, instantaneous discharge remains the most important predictor of [DOC]; but during the spring, EC is a better predictor, possibly because shallow soil water is translocated down through the bulk of the soil profile – not just macropores -- with successive precipitation events (e.g. Klaus et al. [2013], Donaldson [2013]) resulting in a change in the relationship between hydrologic connectivity, the mobilization of distinct DOM sources, and discharge. Additionally, flushing variables explain more variability during the falling limb of events than the rising limb, suggesting dilution of DOM sources as high flow events progress. In contrast to high flow events, during baseflow conditions water temperature is the only significant predictor of [DOC], suggesting microbial activity becomes more important than hydrologic dynamics during these periods.

2.5.2 Implications for watershed DOM dynamics

Interannual variability in total DOC and DON fluxes are due largely to variation in annual runoff, which has been observed at other artificially drained agricultural sites in the Midwest, where fluxes are similar (0.1-17.6 kg C ha^{-1} y^{-1}) [*Kovacic et al.*, 2000; *Ruark et al.*, 2009; *Dalzell et al.*, 2011] and across watersheds generally [*Harrison et al.*, 2005]. The DOC flux-runoff relationship for this site is very similar to what has been observed in agricultural watersheds in the U.S. at a range of scales, and for watersheds globally (Fig. 2.5), although this study isolates the DOC flux from soil, in contrast to the other values, which represent a mixture of terrestrial and autochthonous DOC in the stream. The terrestrial DOC flux to surface water is not often directly measured [e.g. *Worrall et al.*, 2012], although it is an important and poorly quantified flux in the context of watershed carbon budgets [*Regnier et al.*, 2013].

Assays suggested that the bioavailability of DOM exported from this system is low regardless of initial quality (Table 2.5). However, this was not unexpected, given that SUVA values were always above 1, possibly a critical threshold for rapid decomposition [*Warrner et al.*, 2009]. These results suggest that exported DOM may be transported beyond the local receiving stream before being metabolized, particularly because large loads of the least labile material (based on FI, β/α), are exported to the stream during cold high flow periods when in-stream metabolism is expected to be low [*Griffiths et al.*, 2012]. These results are consistent with the hypothesis that stream network DOM dynamics are dominated by episodic DOM inputs to headwater streams that are then transported downstream with minimal local processing [*Wilson et al.*, 2013].

Ultimately, the observed concentration and character of in-stream DOM results from a combination of many processes in both terrestrial and aquatic systems. In this study I show that sources of terrestrial DOM in the contributing landscape can be highly variable across space and time, in terms of both quality and concentration. For example the range of FI values in soil water (1.23-1.67) is similar to that observed in a cross-system analysis [*Jaffé et al.*, 2008], and both [DOC] and C:N ranged two orders of magnitude, from 0.91 to 36.0 mg C L^{-1} and 1.2-158, respectively. This spatio-temporal variability, in combination with dynamic hydrologic conditions in the catchment, results in a highly variable terrestrial source of DOM to Missouri Flat Creek (Fig. 2.4), despite the small size of and uniform land-use in the study catchment. These results suggest that attempts trace land-use effects with in-stream DOM concentration or quality should be done carefully, particularly during low-flow conditions when the rates of autochthonous production and processing are high relative to allocthonous inputs [*Ågren et al.*, 2014]. Additionally, the mechanisms by which land-use predominantly affect in-stream DOM may depend on season and flow conditions. For instance, during warm, low-flow conditions, the dominant effect of agricultural land-use on the bulk DOM pool may be to stimulate autochthonous DOM production via nutrient fertilization and increased light availability (as suggested by Wilson and Xenopoulos [2008b]). In contrast, during high flow conditions, direct hydrologic inputs of agriculturally-derived DOM may contribute substantially to the bulk DOM pool [*Royer and David*, 2005]. Additional research is required to clarify the importance of these different mechanisms across time and systems to better interpret and predict changes in DOM associated with land-use.

2.5.3 Future changes in DOM export magnitude and quality

Annual runoff in the study catchment is strongly affected by high flow events, and as climate change is anticipated to increase the frequency and intensity of precipitation events, it is likely to affect DOC export during extreme hydrologic years. I find that runoff and DOC export are projected to increase during both the wettest and driest years relative to historical conditions by 2080, with DOC export nearly doubling from the wettest historical year to the wettest projected year (A1B scenario). Another study modeled the effects of climate change under the A1B scenario on DOC export over a very similar timeframe (2061-2090) but in very different system types - small boreal wetland and forested catchments [*Oni et al.*, 2014]. They projected similar responses to increases in runoff when using the riparian flow-concentration integration model (RIM), which primarily explains variability in [DOC] via changes in riparian flow paths that mobilize distinct DOM pools [*Seibert et al.*, 2009]. Additionally, our results also suggest that the quality of DOM may subtly shift under future hydrologic conditions to more aromatic, plant-derived material, which has not been addressed in other models of DOM export under future climate conditions [e.g. *Oni et al.*, 2014]. Notably, even a quadrupling of DOC export would have a minimal effect on the soil carbon pool in this system; the highest estimated annual DOC flux reported here is only 8.6 kg C ha^{-1}, in comparison to an average of 260,000 kg C ha^{-1} stored in the top 150 cm of soil at this site [*Huggins and Uberuaga*, 2010], and an mean soil organic carbon accumulation rate of 71 kg C ha^{-1} y^{-1} in the top 20 cm for comparable types of systems in the region [*Brown and Huggins*, 2012]. These results suggest that the receiving aquatic system is likely to be much more sensitive than the terrestrial system to the effects of climate change on DOC fluxes.

Quantitative estimates are uncertain due to a combination of uncertainty about hydrologic projections, the assumption that the flow distribution for the artificially drained study catchment will be similarly affected by climate change, and the assumption that relationships between hydrologic conditions and the concentration and quality of exported DOM will remain stationary. While I did not find a strong effect of temperature on [DOC] in this study (Table 2.4), warmer temperatures overall, which are predicted for the area [*Salathé et al.*, 2010], may reduce DOM export. For example, Laudon et al. [2012] report a decrease of approximately 1 mg DOC-C L^{-1} for every 1°C increase in mean annual temperature (above 2°C) across systems. However, this effect may be negligible for winter high flow export. Additionally, high flow events are projected to occur earlier in the fall when temperatures are warmer, potentially resulting in more DOM being metabolized in the local stream rather than being exported downstream. In addition, land management changes, such as shifting to a crop-fallow rotation to ensure adequate soil water (which is common just west of the study area), could enhance soil moisture at the onset of the wet season following fallow years, priming the catchment for strong runoff responses to precipitation events during the winter. Additionally, farmers are already installing more subsurface drains in the area (*C. Kelley*, pers. communication), which could further enhance winter runoff. Nevertheless, in the absence of these other elements, increased frequency and severity of high flow events is likely to increase the delivery of DOM to and through the stream network.

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2.8 TABLES

Table 2.1. Percent of annual runoff and DOC and DON export that occurred during high flow events, and the percent of time that high flow events comprised during 2012 and 2013 water years.

Water Year	**2012**	**2013**
Flow	47.9	24.8
DOC export	52.5	30.4
DON export	54.0	28.6
Time	15.8	8.3

Table 2.2. EC, [DOC], [DON], and DOM characteristics of soil water collected from shallow lysimeters (SL), shallow wells (SW), deep wells (DW), and laboratory litter leachate (Litter). Data were averaged through time for each sampler, and these means were used to examine differences among sampler types. Means with different superscripts are significantly different from one another (one-way ANOVA, $\alpha = 0.05$ and Tukey's HSD, $\alpha = 0.0167$ for EC, DOC, DON, C:N; one-sample t-test with μ = litter leachate value with $\alpha = 0.025$ for FI, β/α and SUVA; two-sample t-test, $\alpha = 0.05$ for C1 and C2). EC, [DON], C:N, FI, C1, and C2 values were log-transformed to meet the assumption of normality.

	Source	n	mean (± sd)
EC*	SL	5	300.00 (233.11)^{a}
	SW	4	331.48 (51.49)^{ab}
	DW	7	577.17 (233.41)^{b}
DOC	SL	8	7.33 (1.41)^{ab}
	SW	4	11.10 (6.45)^{a}
	DW	7	5.11 (2.24)^{b}
DON	SL	8	1.25 (1.21)^{a}
	SW	4	1.04 (0.48)^{a}
	DW	7	0.87 (0.61)^{a}
C:N	SL	8	14.30(10.60)^{a}
	SW	4	24.72(25.99)^{a}
	DW	7	13.19(6.66)^{a}
FI	Litter	1	1.385 (na)^{a}
	SW	2	1.513 (0.029)^{b}
	DW	7	1.571 (0.039)^{b}
β/α	Litter	1	0.504 (na)^{a}
	SW	2	0.723 (0.053)^{ab}
	DW	7	0.725 (0.036)^{b}
SUVA	Litter	1	1.19 (na)^{a}
	SW	2	4.15 (1.35)^{ab}

	DW	7	2.46 (0.58)^{b}
C1	SW	2	1.86 (1.15)^{a}
	DW	7	0.81 (0.46)^{a}
C2	SW	2	1.48(0.88)^{a}
	DW	7	0.72(0.35)^{a}

*1-way ANOVA was borderline significant (p=0.051)

Table 2.3. PARAFAC components from models of subsurface drain and soil water samples. Components 1 – 3 were consistent between models.

Model	Component	Excitation (secondary) wavelength	Emission (secondary) wavelength	Mean (sd) percent of fluorescence for drain samples	Mean (sd) percent of fluorescence for soil samples	DOM characteristics
Drain, Soil	1	250	480	33.1 (10.3)	35.9 (8.4)	UV-C Humic-like (HMW, aromatic, fulvic acids)[1]
Drain, Soil	2	240 (320)	410 (400)	43.1 (12.1)	33.3 (7.9)	Humic-like (HMW, widespread)
Drain, Soil	3	270	300	13.2 (17.7)	6.3 (12.4)	Tyrosine-like[1]
Drain	4	280	330	7.6 (10.6)	--	Tryptophan-like[1]
Soil	4	240 (290)	350 (522)	--	12.5 (2.9)	UV-A Humic-like (LMW, widespread, indicates biogical activity) [1]
Soil	5	240	300-600	--	6.3 (11.2)	Humic-like, of terrestrial origin[2]

[1] As identified in Fellman et al. [2010]

[2] Similar to component 5 in Kothawala et al. [2014]

Table 2.4. Predictor variables for drain [DOC] for all data and for data collected during different seasons and flow conditions.

Data Subset	N	Model/ Adj R^2	Model p-value	Variables included in model[#]	r^{2*}	p-value
All	204	0.50/ 0.49	<0.001	(+) ***Instantaneous Q***	0.31	<0.001
				(-) **Water temperature**	0.07	<0.001
				(-) **2-day cumulative Q**	0.06	<0.001
				(-) **30-day cumulative Q**	0.03	<0.001
				(+) Air Temperature	0.03	0.055
Season						
Fall	30	0.53/ 0.49	<0.001	(+) ***Instantaneous Q***	0.31	0.007
				(-) *Water temperature*	0.22	0.071
Winter	101	0.55/ 0.52	<0.001	(+) ***Instantaneous Q***	0.26	<0.001
				(-) **2-day cumulative Q**	0.05	0.001
				(-) **30-day cumulative Q**	0.03	0.005
				(+) Air temperature	0.01	0.098
				(+) *EC*	0.20	0.155
Spring	57	0.52/ 0.49	<0.001	(-) ***EC***	0.30	<0.001
				(+) ***Instantaneous Q***	0.15	0.001
				(-) **30-day cumulative Q**	0.07	0.006
Summer	16	0.20/ 0.00	0.436	None		
Flow Conditions						
Baseflow	119	0.14/ 0.12	<0.001	(-) **Water Temperature**	0.08	0.004
				(+) Instantaneous Q	0.03	0.131
				(-) 2-day cumulative Q	0.03	0.165
Rising Limb	45	0.63/ 0.59	<0.001	(+) ***Instantaneous Q***	0.29	<0.001
				(+) ***EC***	0.18	0.038
				(-) **2-day cumulative Q**	0.08	<0.001
				(+) Air temperature	0.06	0.009
				(-) 30-day cumulative Q	0.03	0.086
Falling Limb	40	0.31/ 0.25	0.004	(-) ***30-day cumulative Q***	0.11	0.002
				(+) ***Instantaneous Q***	0.10	0.005
				(+) **Air temperature**	0.09	0.016

[#] Sign indicates direction of relationship with DOC. Variables in bold are significant predictors ($p < 0.05$); italicized variables explain at least 10% of the variability ($r^2 \geq 0.10$)

*Calculated as the average R^2 contribution all orderings among regressors.

Table 2.5. Maximum net DOC removal in drain discharge over 6 days in laboratory incubations. P values are for time effect in two-way ANOVA, with treatment and time as factors. Treatment was not significant, and percent loss is calculated with data from both treatments.

Sample Date	Drain discharge (L/d)	Initial				% DOC loss	time to max DOC loss (d)	p-value
		[DOC] (mg C/L)	C:N	FI	SUVA			
12/15/11	3460	1.06	3.2	1.58	1.13	7.4	1	0.015
2/7/12	24500	2.95	12.1	1.55	3.21	3.5	3	0.025
3/10/12	16800	2.23	NA	1.59	2.83	0.0	--	NS
5/21/12	84600	2.01	2.4	1.56	2.89	0.0	--	NS
9/16/12	6910	0.69	1.4	1.62	2.62	0.0	--	NS

2.9 FIGURES

Figure 2.1. Artificially drained catchment in Cook Agronomy Farm in eastern Washington, modified from Keller et al. [2008] (above). The grey dotted line outlines the 12 ha drainage area, the black dashed line approximates the buried subsurface drain, and contour lines are at 2.5 m intervals. Soil water sampling sites are numbered from lowest to highest surface elevation on the map. SL, shallow lysimeter; SW, shallow well; DW, deep well (see text).

Figure 2.2. Precipitation events (inverted triangles) drain discharge (black line) and EC of drain discharge (gray line) during 2012 and 2013 water years. Inverted triangles represent precipitation events with accumulation greater than 7.5 mm over two days. The arrows correspond to measurements of water table depth shown in Fig. 3. Daily precipitation data are from the Palouse Conservation Field Station, 5 miles west of the study site.

Figure 2.3. Soil surface elevation and representative water table elevations during the dry summer period (measured Jul 8, 2012) and wet winter period (measured Feb 12, 2013) along a transect of wells. Labeled black bars show the distance and depths of wells relative to the drain outlet, represented by the star.

Figure 2.4. [DOC], [DON], DOM quality indices, and EC in soil water (boxplots) and drain discharge (scatterplots). Soil water values include all samples collected in deep wells (DW), shallow wells (SW), and shallow lysimeters (SL) during 2012-2013 water years; numbers above boxplots are sample sizes. For DOM quality indices (right panels), values for litter leachate rather than shallow lysimeters are shown because DOM collected under suction has been found to be chemically distinct from naturally dissolved OM [*Zsolnay*, 2003]. No value is shown for litter leachate for the sum of humic components 1 and 2 because concentrations in lab-generated

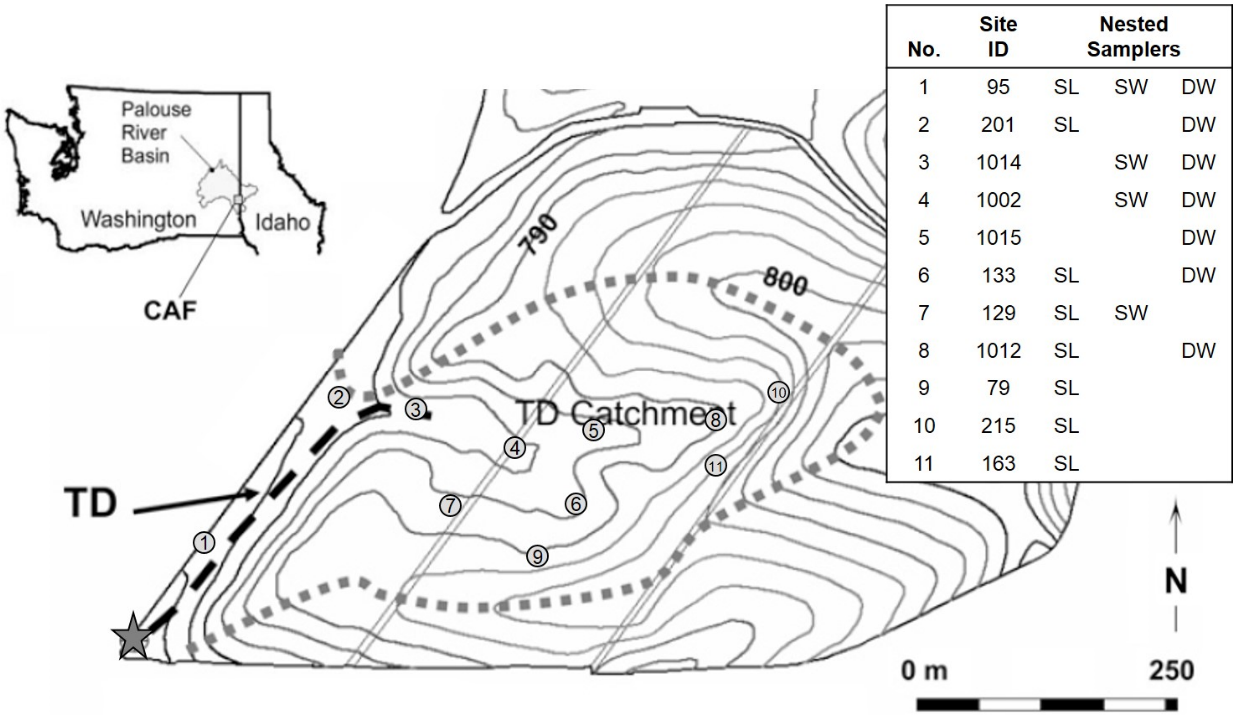
leachate are irrelevant to field values. Drain discharge samples are identified by flow conditions – baseflow (○), rising limb (△), or falling limb (▽) – and season – fall (brown), winter (blue), spring (green), and summer (red).

Figure 2.5. Relationship between annual DOC flux (“yield”) and runoff for multiple years at Cook Farm (this study), for agricultural catchments in the US ranging in size from 2.2 to 14500 km^2 [*Kronholm and Capel*, 2012]; two blackwater streams with extremely high DOC flux omitted), and for large coastal watersheds globally [*Harrison et al.*, 2005]. Dotted lines represent flow-weighted [DOC] of 4 and 6 mg C L^{-1}.

Figure 2.6. Relationship between flow-weighted [DOC] and [DON] and annual runoff from 2001-2013 (2002 removed because of biased sampling; 2008 and 2010 removed because there were fewer than 12 observations during these water years). For DOC, $r^2 = 0.89$, $p < 0.001$, n=10. For DON, $r^2 = 0.92$, $p < 0.001$, n=10.

Figure 2.7. Relationship between the fit (r^2) of linear models of drain solutes and DOM quality indices vs instantaneous discharge and variation of the solutes and DOM quality indices through the soil profile (depth variation index). The depth variation index was calculated as the absolute value of the difference between mean values of the shallowest and deepest samplers, divided by the range of observed values. Open circles indicate insignificant relationships between the DOM characteristic and drain discharge.

Figure 2.8. Distributions of annual runoff and annual DOC export relative to historical median (dasthed line) and DOC load-weighted FI for the driest and wettest 10% of years for the historical period (1916-2006) and future climate scenarios. Stars above boxplots indicate a significant difference from historical mean (Kruskal-Wallis test, $p < 0.05$, Nemenyi post-hoc comparison test, $p < 0.05$, n=9 for each group).



No.	Site ID	Nested Samplers		
1	95	SL	SW	DW
2	201	SL		DW
3	1014		SW	DW
4	1002		SW	DW
5	1015			DW
6	133	SL		DW
7	129	SL	SW	
8	1012	SL		DW
9	79	SL		
10	215	SL		
11	163	SL		

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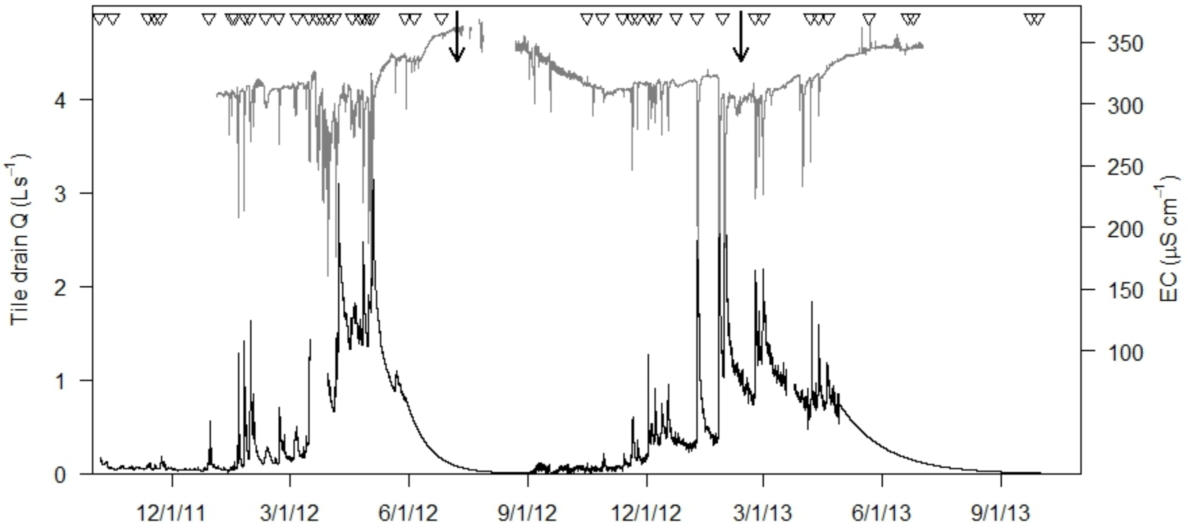

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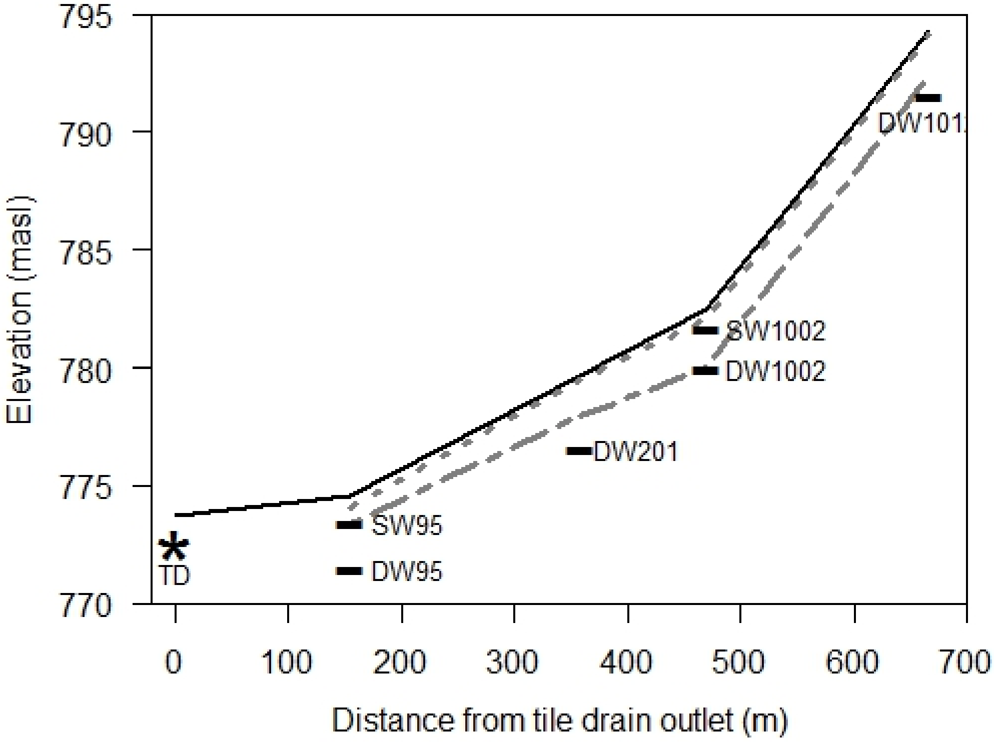

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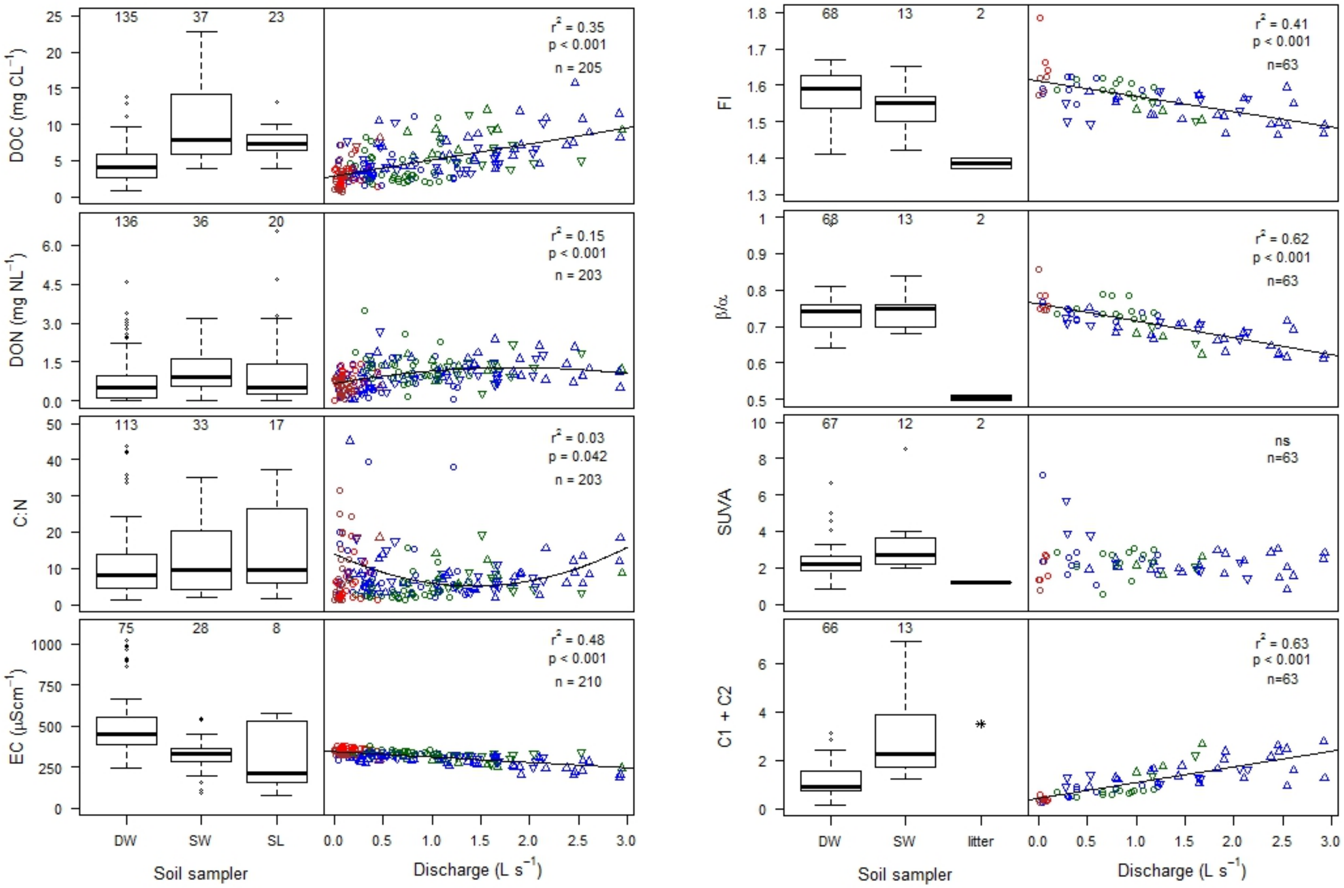

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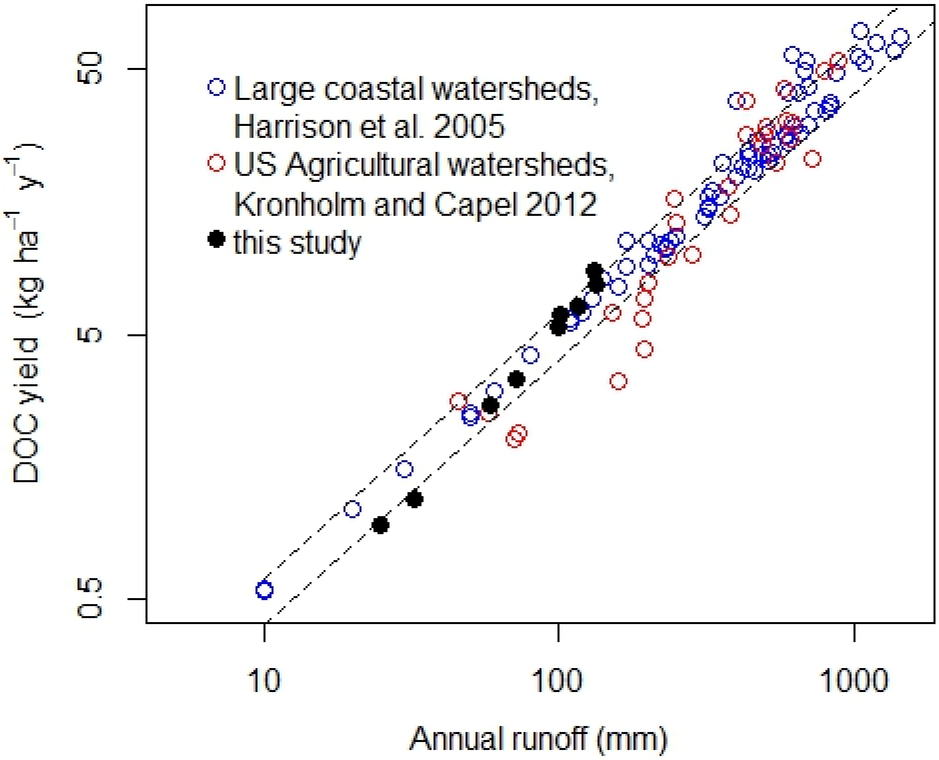

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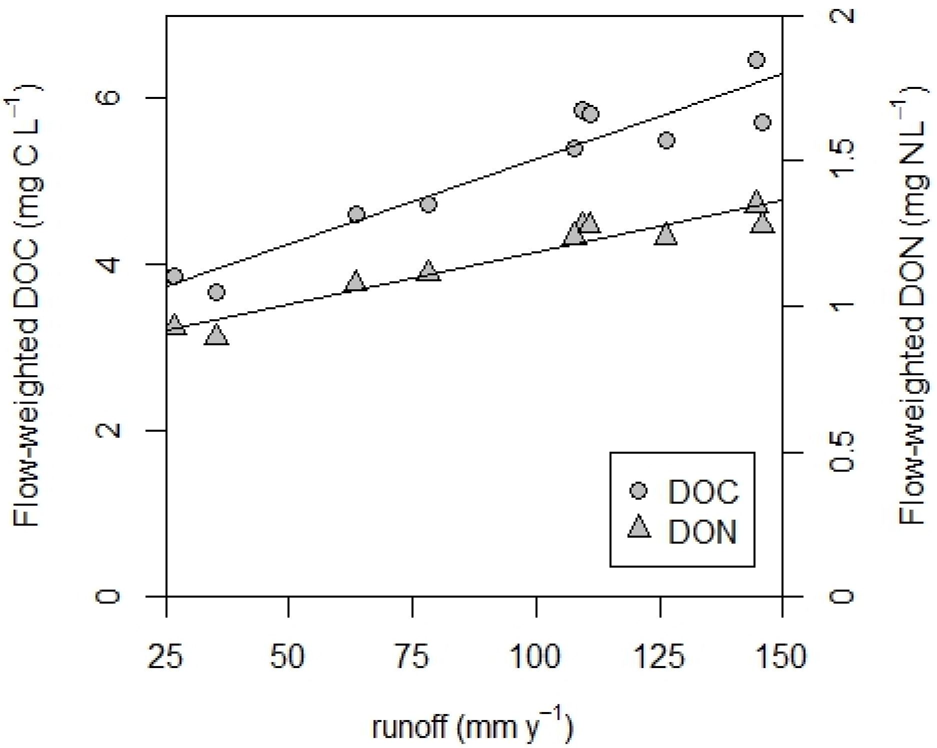

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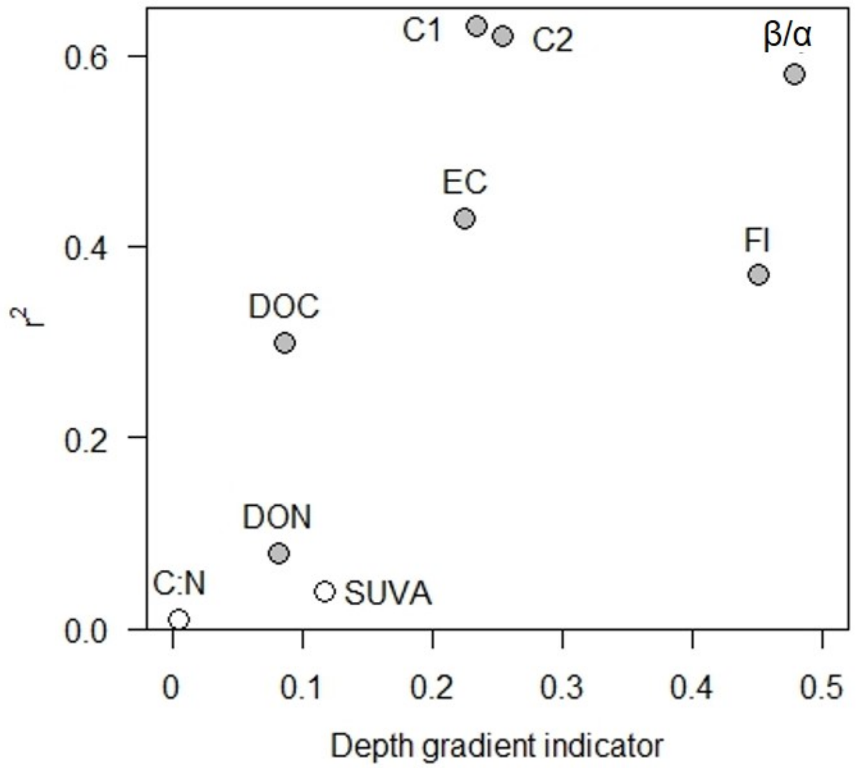

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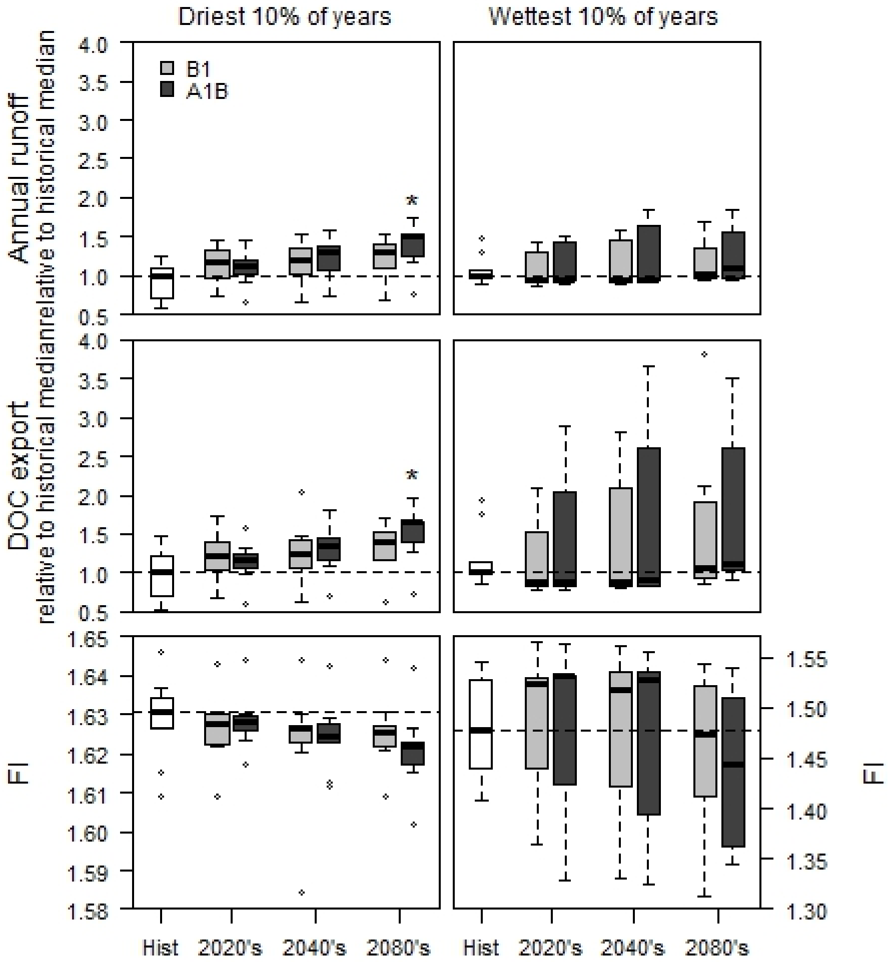

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CHAPTER THREE

DOM export from artificial subsurface drainage during storm events is controlled by source and processing along flow paths

3 DOM export from artificial subsurface drainage during storm events is controlled by source and processing along flow paths

3.1 ABSTRACT

Artificial subsurface drainage alters natural flow paths in many agricultural systems, potentially influencing the quantity and quality of dissolved organic matter (DOM) that is exported to surface water by exposing it to reactive mineral soil horizon prior to export. In this study I characterized sources of DOM, including litter, topsoil, and subsoil, to subsurface drain discharge during four storm events in a small agricultural catchment in eastern Washington State, and examine how these DOM sources can be modified by exposure to deeper soil horizons during transport to the drain using batch incubation experiments. Litter-derived DOM and DOM from topsoil, in addition to subsoil DOM, are required to explain DOM chemistry in subsurface drain discharge, with the largest inputs of litter-derived DOM during the highest flows. Laboratory incubations indicated that litter and topsoil dissolved organic carbon (DOC) can be rapidly removed and altered by deeper soil horizons, suggesting the potential for significant DOC retention during transport to the subsurface drain. End member mixing analysis predicted storm DOC dynamics well, suggesting that the dominant control over DOC export is hydrologic mobilization of available DOM sources. However, DOC concentrations were generally over-predicted, except at the highest discharges, resulting in a 30% over-estimate of observed DOC storm fluxes. Sensitivity analyses and estimates of DOC removal rates across flow conditions suggested that DOC removal in the soil column likely contributes to the discrepancy between modeled and measured DOC at low and medium discharges, but DOC removal has less of an effect at peak flows. This is consistent with a transition from flow paths through the soil matrix

to preferential flow paths at peak discharge. Even if all the difference between modeled and measured DOC fluxes can be attributed to retention in the soil column, and this rate is generally applicable to all storm events during the year, DOC retention during these periods is 1 to 2 orders of magnitude smaller than other estimates of carbon sequestration rates for similar systems.

3.2 INTRODUCTION

Hydrologic flow paths through catchments control surface water chemistry by mobilizing solutes and by mediating the role of reactive hotspots [*Ocampo et al.*, 2006; *Vidon et al.*, 2010]. Agricultural land is often artificially drained to improve moisture conditions for crops [*Sugg*, 2007], but subsurface drainage alters natural flow paths, routing soil water vertically through the soil profile and limiting lateral flow paths to surface water [*Jacinthe et al.*, 2001]. Effects of agricultural land-use on in-stream dissolved organic matter (DOM) dynamics have recently been documented, including changes in dissolved organic carbon concentration ([DOC]) [*Cronan et al.*, 1999; *Wilson and Xenopoulos*, 2008] and reduced complexity and aromaticity and increasing lability of in-stream DOM [*Seitzinger et al.*, 2002; *Wilson and Xenopoulos*, 2009; *Williams et al.*, 2010; *Lu et al.*, 2014]. Understanding how flow path affects the concentration and quality of DOM exported via subsurface drainage may clarify mechanisms that contribute to these observed changes.

Previous researchers have hypothesized that subsurface drainage should reduce [DOC] in water discharged to streams relative to natural catchments because DOM can be removed via sorption as it is transported through the mineral horizon en route to the drain [*Dalzell et al.*, 2011]. Sorption processes have been shown to control [DOC] through the soil horizon in a range of systems, with [DOC] typically decreasing with exposure to deeper soil horizons with greater sorption capacity [*Qualls et al.*, 2002; *Dittman et al.*, 2007]. Additionally, characteristic changes in DOM quality through the soil horizon – lower concentrations of aromatic, humic components, increasing relative contribution of hydrophilic DOM compounds, etc. [*Qualls and Haines*, 1991; *Fiedler and Kalbitz*, 2003; *Möller et al.*, 2005] can also be explained by a combination of preferential sorption and desorption [*Banaitis et al.*, 2006].

Sorption processes in the soils can control fluxes of DOM to surface water by retaining DOM prior to export [*Qualls et al.*, 2002; *O'Donnell et al.*, 2010]. Due to short residence times and/or diffusion-limited transport to sorption sites, DOM concentration may not be in equilibrium with the soil, which has implications for DOM export. In the field, locations with a higher degree of hydrologic connectivity with the surface have been associated with higher [DOC] relative to sites with lower hydrologic connectivity [*Asano et al.*, 2006]. Additionally, temporally variable [DOC] observed in the field has been modeled successfully by assuming a slow sorption rate [*Gjettermann et al.*, 2008], and disequilibrium conditions have even been documented at the scale of small cores [*Angley et al.*, 1992]. Together, these observations suggest disequilibrium conditions could be widespread.

The potential importance of DOM at non-equilibrium conditions is rarely accounted for in models of DOM export on the timescale of storm or snowmelt runoff events [e.g. *Boyer et al.*, 2000; *Seibert et al.*, 2009; *Inamdar et al.*, 2013]. This is due, in part, to the assumption that lateral flow paths dominate discharge during high flow events, and vertical transport of DOM to soil horizons with greater sorption capacity is limited. In systems with artificial subsurface drainage, however, the assumption that lateral flow paths are prominent is not valid, and, thus, DOM processing and removal through the soil column may strongly influence the concentration and quality of DOM that reaches subsurface drains and is then exported to surface water.

Understanding the extent of DOM removal along terrestrial flow paths during high flow events is important, not only because of effects on the concentration and quality of DOM that ultimately reaches surface water, but also because these brief periods can dominate annual DOM export from soils to streams [*Raymond and Saiers*, 2010; *Yoon and Raymond*, 2012; *Bellmore et al.,* in prep] and, thus, may be important but short-lived periods for DOC and dissolved organic nitrogen (DON) retention in subsoils.

In this study, I addressed the following questions: 1.) What DOM sources in the landscape contribute to subsurface drain discharge during storm events? 2.) How is DOM from shallow sources (litter and topsoil) altered following contact with deeper soil horizons, and how rapidly? and 3.) Does soil processing control the concentration and quality of DOM that is exported from artificial subsurface drainage on the timescale of a storm event? In a small agricultural catchment in eastern Washington, USA, I examined DOM dynamics in subsurface drain discharge during four winter storm events in the context of soil water and litter leachate samples to identify potential DOM sources. I applied end member mixing analysis (EMMA) to quantify the contributions of source water with distinct DOM characteristics over time during events, and used this model to predict [DOC] for drain discharge. Additionally, I used batch experiments, to measure potential DOC removal rates and examine changes in DOM quality after exposure to deeper soil horizons, and assess the plausibility that DOM retention controls [DOC] in drain discharge.

3.3 METHODS

3.3.1 Field site

I conducted research during January through July 2013 at the experimental Cook Agronomy Farm, which is located in Whitman County in the Palouse region of eastern Washington State (Fig. 3.1). Precipitation averages 540 mm annually, with most coming as rain and snow from October through May. Soils are poorly drained Mollisols, part of the Palouse-Thatuna series [USDA, 1978] overlying Columbia River Basalt flows [*McDonald and Busacca*, 1992], and the area is characterized by rolling hills, with an average slope of 17% across the county [NRCS Web Soil Survey]. A drain pipe buried at approximately 1.2 m depth drains the southwest 12 ha section of the farm (Fig 3.1). Previous research indicates that after approximately 150 mm of precipitation, the drain begins to respond to precipitation and melt events [*Keller et al.*, 2008]. During the sampling period, the catchment was planted with winter wheat, and an alfalfa buffer strip was grown along the edge of the field, overlying the subsurface drain line.

3.3.2 Precipitation and subsurface drain discharge

I obtained hourly precipitation data from the Palouse Conservation Field Station, located 9 km west of the study catchment, and calculated cumulative precipitation for rain events preceding and during intense drain flow events (up to 3 days prior to the peak discharge). A Parshall flume was installed at the drain outlet and equipped with a pressure sensor (INW, model PT12, Kirkland, WA) to measure drain discharge. I estimated cumulative storm flow for the period beginning with the onset of high drain flow following a precipitation event to the time when the log-linear relationship between discharge and time ($\ln(Q) = a*t+b$) returned to a linear relationship and thus corresponded to a return to baseflow conditions, as in Blume et al. [2007].

3.3.3 Sample collection

Drain discharge samples were collected manually prior to and after events, and during events with an autosampler (ISCO, Model 3700 or 6712, Lincoln, NE) programmed to sample drain discharge when stage height changed rapidly, resulting in 5 to 9 samples per event. Collection bottles in the autosampler were acid-washed, and all samples were retrieved within 7 days. Air temperatures were near freezing during the first three events in January and around 6°C during the fourth event in April, so decomposition in the field was likely minimal. Samples were filtered through pre-ashed 0.7 μm filters and stored frozen in acid-washed HDPE plastic bottles until analysis.

During the study period, in situ water quality data were collected by continuously diverting discharge at the drain outlet into a 19 L plastic bucket. A fluorometer designed to measure DOM fluorescence (FDOM) (Turner Designs, Cyclops 7, excitation 375 nm, emission 470 nm) was submerged in the water collection bucket and programmed to measure FDOM every 15 minutes, simultaneously with drain discharge. The bucket was lidded to keep water in the dark, and water volume was maintained at 17 L in the bucket, resulting in average water residence times ranging from 5 to 75 s during the study period. Additionally, a temperature-conductivity probe (Campbell Scientific, CS547A-L, Logan, UT) was installed in the stilling well in the flume to measure electrical conductivity (EC) simultaneously with discharge.

Water sources with distinct DOM signatures (end members), including subsoil, topsoil, and litter-derived DOM, that can contribute to drain discharge were characterized for the four storm events based on samples collected from 4 deep wells (screened from 1 to ~2.5 m below the surface), 2 shallow wells (screened from 0.1 to 1 m) (Fig. 3.1), and the average of an overland flow sample collected 1/26/13 and litter leachate generated in the laboratory (described below), respectively. Soil water was collected from the wells located in the study catchment multiple times during the study period, and I characterized end members for each event based on samples taken closest in time to the event. For event 1, deep soil water samples were taken 4 days prior to peak flow. In contrast, shallow soil water samples were not available until after event 1, so samples taken two days prior to event 2 were assigned to event 1. One set of end members was calculated for events 2 and 3: for subsoil and topsoil, the average of well samples from 2 days prior to event 2 and 1 day following event 3 were averaged. For event 4, deep and shallow well samples were taken 13 and 18 days prior to peak discharge, respectively. For all events, DOM associated with litter residue was defined by an average of an overland flow sample collected during event 2 and litter leachate generated in the laboratory. All water samples collected in the field were filtered through pre-ashed 0.7 μm filters and stored frozen in acid-washed HDPE plastic bottles until analysis.

3.3.4 Batch incubation experiments

I conducted batch experiments to examine how the shallower DOM sources would be affected by sorption and/or microbial processes in deeper soil horizons which they pass through en route to the subsurface drain during high flow events. Briefly, I combined DOM extracted from litter residue and topsoil with soil from topsoil and/or subsoil samples collected in the field, allowed them to incubate, and sacrificed samples over a 22 day period to quantify changes in [DOC], [DON], and fluorescence characteristics over time.

I collected soil and litter for batch incubations from 12 random locations along a 200 m transect in the drainage area that was parallel to and approximately 30 m upslope of the buried drain on July 10, 2013. I used an auger to core to 105 cm depth at each location, and soil from 90-105 cm was kept as the subsoil sample, and 0-15 cm depth for the topsoil. I collected the litter layer from a 30 cm X 30 cm area near each soil sampling location. I combined all samples from the subsoil to create a composite subsoil sample, all topsoil samples to create a composite topsoil sample, and all litter samples to create a composite litter sample. Field-moist soils were sieved through 2 mm mesh then stored refrigerated, while litter was stored at room temperature until the beginning of the experiment one week later.

I generated DOM from litter and topsoil by creating slurries and shaking them for 24 h at room temperature. I combined sieved field-moist soils and intact litter with a 0.005 M NaCl solution at ratios of 1:10 and 1:40 by weight, respectively, based on dry weight, which I determined by oven-drying four replicate subsamples of top- and subsoil each at 105°C for 24 h to estimate soil moisture content. Following NaCl extraction, I filtered slurries sequentially through 0.7 µm and then 0.2 µm filters to obtain DOM solutions.

For the incubations, I combined 40 mL of solution (DOM or blank) and four grams of soil (dry weight) in 60 mL acid-washed HDPE plastic bottles. Treatments included: litter and topsoil DOM solutions without soil, blank NaCl solution with topsoil and subsoil, litter DOM with topsoil and subsoil, and topsoil DOM with subsoil, for a total of 7 solution-soil combinations, each of which were incubated in warm (20°C) and cold (6°C) conditions. I did not adjust solution pH, which was 5.0 ± 0.2 for all DOM solutions. I kept incubation bottles in in the dark on shaker tables to enhance contact between the solution and soil.

I sacrificed three replicate incubation bottles for each solution-soil-temperature combination at 1.5, 9, 22, 45.5, 95, and 525 h after the beginning of the incubation. I centrifuged bottles for 20 min at 3000 rmp at 4°C and filtered the supernatant sequentially through 0.7 µm and then 0.2 μm filters, and kept the solution from each replicate for analysis of DOC, total dissolved nitrogen (TDN), nitrate (NO_3^-), and ammonium (NH_4^+). I composited equal parts of subsamples from each replicate for spectroscopic analyses, resulting in an n of 1 for each time point for each treatment combination. I kept samples on ice and analyzed them within 48 h.

I modeled [DOC] time series during the first 95 h of the experiment as in Gjettermann et al. [2007], assuming loss is a first order reaction and that the rate depends on the difference between the initial [DOC] in solution and [DOC] at equilibrium and that sorption/removal and desorption/production are equal:

$$DOC_i = DOC_{eq} + \left(DOC_0 - DOC_{eq}\right) * e^{(-k*t_i)} \quad [1]$$

where DOC_i is [DOC] at time i, DOC_{eq} is [DOC] at equilibrium, DOC_0 is the initial [DOC], k is the rate coefficient, and t_i is the time since the start of the incubation. DOC_i values are averages of triplicate samples ("bottle points") taken at each time point. I modeled times series using nonlinear least squares (nls) in R [*R Core Team*, 2014], with DOC_{eq} and k as estimated parameters.

3.3.5 Sample analysis

I analyzed samples for NO_3^- + nitrite (hereafter referred to as NO_3^-) and NH_4^+ according to the standard EPA methods (353.2 and 350.1, respectively) using a discrete nutrient analyzer (WestCo Smartchem). Nitrite concentrations have previously been measured separately from NO_3^- in drain discharge and soil water samples from this study site and were found to be very low, so nitrite was not measured separately here [*Bellmore et al.,* in prep]. DOC and TDN were analyzed on a Lachat TOC-TN analyzer (IL 550 TON-TN) equipped with electrochemical (ECD) NO and non-dispersive infrared absorption (NDIR) detectors. DON was calculated as the difference between TDN and total dissolved inorganic nitrogen (NO_3^- + NH_4^+).

Absorbance spectra for bulk DOM samples from the field and incubations were analyzed using a J&M TIDAS spectrophotometer (World Precision Instruments, Sarasota, FL) at each unit wavelength from 200-700 nm. Fluorescence excitation-emission matrices (ex 240-450 nm every 10 nm by em 300-600 nm every 2 nm) were generated with a spectrofluorometer (Fluoromax-4, HORIBA Jobin Yvon, Edison, NJ). Prior to analyses, samples were diluted with ultrapure water so a_{254} was less than 0.2. Appropriate corrections for the instrument (variable lamp intensity), water matrix (background), internal absorbance (Inner Filter Effect, as in *McKnight et al.*, 2001), and Raman signal were applied to fluorescence data to permit comparisons across sampling dates. All samples were kept at 20°C during measurements using a temperature controlled cuvette holder and recirculating cooling water bath.

Indices of DOM quality based on spectroscopic characteristics were then calculated. Fluorescence Index (FI), which has been used as an indicator of the relative contributions of plant-derived and microbially-derived compounds to the DOM pool [e.g. *Cory and McKnight*, 2005], is calculated as the ratio between emission intensity at wavelengths 470 nm and 520 nm associated with excitation wavelength 370 nm. Values typically range between 1.2 and 1.8, with lower values corresponding to plant-derived material and higher values corresponding to microbially-derived material. A second index derived from fluorescence data, β/α (or Freshness Index), has been found to relate to the contribution of recently derived DOM, with β representing recently derived material and α more decomposed material. β/α is calculated as the emission intensity at 380 nm divided by max emission intensity between 420 and 435 nm associated with excitation wavelength 310 nm [*Parlanti et al.*, 2000]. Values typically range from 0.3 to 0.8 [e.g. *Graeber et al.*, 2012; *Wilson and Xenopoulos*, 2008b]. Specific UV Absorbance at 254 nm (SUVA) is a widely measured indicator of DOM aromaticity, with higher values indicating more aromatic material [*Weishaar et al.*, 2003]. SUVA is calculated as absorbance at 254 nm divided by [DOC] with units of L mg^{-1} m. The effects of freezing and storing in HDPE bottles prior to spectroscopic analyses were found to be minimal and are discussed in Bellmore et al., [in prep].

I analyzed excitation emission samples with parallel factor analysis (PARAFAC) to identify groups of similarly fluorescing DOM molecules [*Stedmon and Bro*, 2008]. Drain discharge and soil water samples were analyzed with all samples collected at the study site during the 2011-2013 water years, as described in Bellmore et al., [in prep]. Samples from the batch incubation experiment were modeled separately. Corresponding components among models were identified with Tucker's congruence test.

3.3.6 DOM end member mixing analysis

I applied EMMA to estimate the contributions of subsoil water, topsoil water, and water associated with litter DOM to total drain flow during events and to predict [DOC] in drain discharge. This approach assumes the end member tracers are conservative and mix ideally. Potential violations of these assumptions and implications are discussed below. I apply EMMA to events 2 and 3, which occurred closest in time to field sampling of both deep and shallow wells, and during which the overland flow sample (assumed to be heavily influenced by litter-derived DOM) was collected. End members were defined by [NO_3^{-1}], FI and β/α (Table 3.1). [NO_3^{-1}], FI and β/α of tile drain samples from events 2 and 3 were normalized and analyzed using principal component analysis (PCA) in R, and residuals were examined with respect to observed values to determine the number of components needed to explain the data [*Hooper*, 2003]. Two components were required to eliminate structure in the residuals and together explained 98% of the variance.

Drain samples and end members were projected onto U-space (vector of normalized sample values times the eigenvector matrix) to visually examine the drain DOM dynamics in relation to end members. The contributions of end members to total drain flow at each sampling time were calculated as in [*Burns et al.*, 2001] using the following equations to solve for Q_s, Q_t, and Q_l at each sampling point:

$$Q_d = Q_s + Q_t + Q_l \quad [2]$$

$$Q_d U1_d = Q_s * U1_s + Q_t * U1_t + Q_l * U1_l \quad [3]$$

$$Q_d U2_d = Q_s * U2_s + Q_t * U2_t + Q_l * U2_l \quad [4]$$

where Q is drain flow, U1 is the first principal component, U2 is the second principal component, and subscripts d, s, t, and l correspond to the bulk drain sample, subsoil, topsoil and litter water, respectively. [DOC] was predicted for drain water samples as:

$$DOC_d = DOC_s * q_s + DOC_t * q_t + DOC_l * q_l \quad [5]$$

Where DOC is [DOC] of bulk discharge or end members and q is the fraction of flow attributed to each end member. Modeled [DOC] was compared to observed [DOC] during events 2 and 3 to assess model performance. Additionally, I estimated measured and modeled DOC fluxes and calculated DOC retention in the soil profile during the events by subtracting the observed DOC flux from modeled DOC flux, which assumes no DOC retention. To calculate fluxes, observed and predicted [DOC] were linearly interpolated between sampling time points, and [DOC] values were multiplied by observed drain discharge using 15-minute intervals.

The apparent DOC removal rate at each sampling time point during the events was calculated by solving the following system of equations for k, $DOC_{t\text{-}r}$, and $DOC_{l\text{-}r}$:

$$DOC_d = DOC_s * q_s + DOC_{t-r} * q_t + DOC_{l-r} * q_l \quad [6]$$

$$DOC_{t-r} = DOC_d + (DOC_t - DOC_d) * e^{(-k*t)} \quad [7]$$

$$DOC_{l-r} = DOC_d + (DOC_l - DOC_d) * e^{(-k*t)} \quad [8]$$

Where $DOC_{t\text{-}r}$ is the [DOC] in topsoil water after passing through the soil column, and $DOC_{l\text{-}r}$ is [DOC] in event water after passing through the soil column, and t an assumed residence time. A range of approximate residence times was estimated based on the drain discharge EC dynamics, which indicate that event water with low EC [*Kelley et al.,* in prep] begins to contribute to drain discharge almost immediately when discharge increases, and continues to contribute through much of the falling limb (Fig. 3.2). Therefore, I assume that the maximum residence time of event/newly mobilized shallow water in the subsoil is the time from the beginning of precipitation to the return of baseflow, which corresponds to 160 h for event 3 (which is longer than the corresponding time period for event 2), and I selected the time from peak precipitation intensity to peak discharge as a low-end approximate residence time (7 h for event 2, which is shorter than the corresponding period for event 3). This approach assumes DOC from litter and topsoil has the same residence time in the subsoil for events 2 and 3, and litter and topsoil DOC are equally reactive.

The sensitivity of modeled [DOC] to changes in end member characteristics was assessed by altering each of the end member characteristics singly, predicting flow contributions of each source and drain discharge [DOC], and comparing [DOC] to the original model results. FI, β/α, [NO_3^-] and [DOC] of end members were each increased and decreased by 5%. Additionally, the litter and topsoil end members' FI, β/α, and [DOC] values were altered to reflect changes observed in batch experiments after 95 hours, the time point closest to the longer approximate travel time (Table 3.2). For litter DOM, values were calculated by averaging across warm and cold litter DOM with topsoil treatments and litter DOM with subsoil treatments. For topsoil DOM, values were calculated by averaging across both worm and cold topsoil DOM with subsoil treatments. Additionally, the combined effects of retention on FI, β/α, and [DOC] of litter and topsoil end members, based on batch experiments, were considered simultaneously to predict drain discharge [DOC].

3.4 RESULTS

3.4.1 Event hydrology

Cumulative precipitation preceding events ranged from 5.0 to 8.7 mm, while cumulative area-weighted discharge during events ranged from 0.93 to 7.41 mm (Table 3.3), with peak discharge occurring from less than 7 (event 4) up to 31 h (event 1) after peak hourly precipitation intensity, which consistently corresponded to the time when approximately half of the precipitation volume had fallen. Drain discharge peaked at 2.92, 2.75, 3.36, and 1.84 L s^{-1} during events 1 through 4, respectively (Fig. 3.3).

3.4.2 Subsurface drain DOM dynamics

DOM dynamics responded consistently to increases in discharge across the four high flow events. [DOC] increased, and FDOM sensor values indicate that [DOC] peaked with discharge (Fig. 3.4a, b). Additionally, FDOM-discharge hysteresis loops are narrow, with similar FDOM to discharge relationships on the rising and falling limbs of the events, suggesting that [DOC] is diluted little on the falling limb of the hydrograph (Fig. 3.2). Similar to [DOC], C:N increased during high flow events, peaking with discharge (Fig. 3.4c, d). In contrast, [DON] increased at the onset of high flow events, but peaked before peak discharge and subsequently decreased (Fig. 3.4c, d). F_{max} of two humic-like PARAFAC components identified in drain discharge, C1 and C2, increased with discharge (Fig. 3.4g, h), while FI and β/α decreased with increasing discharge during each event (Fig. 3.4e, f). In contrast to the other quality indices, SUVA did not show a consistent pattern, but typically peaked prior to peak discharge (Figure 3.4g, h).

When drain discharge DOM is examined in the context of potential end members, the [DOC] and FI data show a shift from DOM associated with deep soil water to a mixture of shallow soil water and litter leachate DOM as discharge increases, then a return to deep soil water DOM as discharge declines back to baseflow (Fig. 3.5). Similarly, β/α and NO_3^- in drain discharge shift from values similar to deep soil water to shallow soil water and litter leachate DOM as discharge peaks (Fig. 3.5). The drain discharge samples fall within the β/α–NO_3^- mixing space of the end members, including uncertainty, but for a given FI value, the [DOC] value is generally too low for the drain discharge sample to fall within in the FI–[DOC] end member mixing space.

3.4.3 Batch incubations

Most DOC loss, including sorption and any decomposition, occurred in the first 24 to 48 h of the experiment. Removal rates for litter leachate ranged from 0.029 h^{-1} in the subsoil under cold temperatures to 0.085 h^{-1} in the topsoil treatment under cold temperatures (Table 3.4). Modeled removal rates for topsoil DOM in the subsoil were on the same order as that of litter DOM, although the rate coefficients were not statistically significant (Table 3.4). In treatments with no soil added, DOC loss was not detected during the first 12-24 h (data not shown), suggesting adsorption to bottle walls was not significant. Final [DOC] for the topsoil and subsoil slurries with blank solutions were similar to average values observed in the field during the January through April. Final [DOC] in topsoil (at 525 h) was 6.41 mg C L^{-1} (sd±0.80) and 9.70 mg C L^{-1} (sd±1.14) in the cold and warm treatments, respectively, compared to 8.57 mg C L^{-1} (sd±1.36) for all shallow soil water samples collected in the field. Cold subsoil equilibrium

[DOC] was 1.30 mg C L^{-1} (sd±0.16); warm was 2.15 mg C L^{-1} (sd±0.64) and average [DOC] for all deep soil water samples was 3.4 mg C L^{-1} (sd±1.36).

The quality of DOM also showed a marked shift during incubations (Table 3.5). Litter leachate DOM began with a FI of 1.40 and shifted close to 1.5 in both the topsoil and subsoil by 45 h, nearly reaching values observed for DOM released from topsoil and subsoil by the end of the experiment. Similarly, when exposed to subsoil, FI of DOM from topsoil also shifted from 1.46 to 1.53 and 1.56 in cold and warm treatments by 45 h, values closer to those observed for DOM released from the subsoil (Table 3.5). β/α values exhibited similar patterns during the incubation, with initial β/α increasing with the depth of the source, as well as exposure to deeper soil horizons. For example, litter leachate DOM had β/α of 0.51 and increased to 0.59 and 0.58 when exposed to topsoil and subsoil, respectively, after only 45 h. Topsoil DOM initially had β/α of 0.60, which and increased to 0.68 when exposed to subsoil after 45 h (Table 3.5).

Three PARAFAC components were identified in DOM in the batch incubation experiments (Table 3.6). C1 corresponds to UVC-humic-like material, C2 corresponds to high molecular weight humic-like material, and C3, which comprised most fluorescence of litter and subsoil DOM, corresponds to tryptophan-like DOM. The modeled fluorescence intensity (F_{max}) of C3 declined in treatments with topsoil (Table 3.5) but was produced when topsoil DOM was exposed to subsoil, consistent with greater C3 release by subsoil than topsoil in blank solution. In the topsoil DOM-subsoil treatment, C1 F_{max} decreased while C2 F_{max} increased, consistent with lower C1 F_{max} and higher C2 F_{max} end points for subsoil than topsoil in blank solution (Table 3.5). When litter DOM was combined with both topsoil and subsoil, C2 F_{max} initially decreased, but began to increase again after 21-45 h. In the litter DOM-topsoil treatment, C1 F_{max}

unexpectedly increased, while in the litter DOM-subsoil treatment, it initially decreased, then increased again after 9 and 45 h in the warm and cold treatments, respectively.

3.4.4 End member mixing analysis

Drain discharge samples from events 2 and 3 fall within the end member mixing space defined by the first two PCA components (Fig. 3.6). The mixing model indicates that baseflow is a mix of subsoil and topsoil water. As discharge increases, the contributions of topsoil water and event water with litter-derived DOM increase rapidly, with fraction of litter-influenced water peaking prior to peak discharge and the fraction of topsoil water peaking on the falling limb (Fig. 3.7). Additionally, modeled [DOC] dynamics capture observed dynamics well (Fig 3.7), with r^2 of 0.66 for a linear model of predicted versus observed [DOC] ($n = 21$, $m = 0.70$, $b= 4.63$); however, the model over-predicts [DOC] for nearly all of the sampling times except at peak flows (Fig. 3.7).

The sensitivity analysis indicates that the magnitude and dynamics of modeled [DOC] are not strongly affected by small changes in end member characteristics (Fig. 3.8, Table 3.2). Of these, modeled [DOC] is most strongly affected by changes in FI and β/α in topsoil and subsoil end members. However, the 5% changes would correspond to a large shift in these indices for this system; the percent differences between the highest and lowest end member FI and β/α values are only 15% and 28%, respectively, and CVs for field data are typically much lower than 5% (Table 3.1). In contrast, the modeled [DOC] is strongly affected by changes in litter and topsoil [DOC] values that reflect DOC loss in the batch experiments. Modeled [DOC] decreased most at peak flows (up to 40%) when litter-derived [DOC] was decreased, but modeled [DOC] decreased most during non-peak flows (up to 29%) when topsoil [DOC] was decreased (Fig. 3.8). When the potential effects of retention on FI, β/α and [DOC] of litter-derived DOM and topsoil DOM are considered simultaneously, modeled [DOC] decreases dramatically across all flow conditions relative to the original modeled values (Fig. 3.7).

The estimated DOC export in drain discharge during events 2 and 3 was 8.15 kg, which represents 70% of the potential export during these events based on predicted [DOC] values, assuming initial end member values. For this magnitude of removal to be realized within 160 h (residence time), the range of k values modeled for sampling points during events (excluding the samples at peak discharge) (Eq. 7-8) is 0.0012 to 0.049 h^{-1}, with a median of 0.020 h^{-1} (Fig. 3.9). When a residence time of only 7 h is assumed, k values are an order of magnitude greater, with a range of 0.0075 to 0.30 h^{-1}, and a median of 0.12 h^{-1}. The residence time is likely to decline with increasing discharge, resulting in a shallower relationship between k and discharge (Fig. 3.9).

3.5 DISCUSSION

3.5.1 Observed subsurface drain DOM dynamics and contributing DOM sources

Drain discharge DOM dynamics were similar during all the high flow events examined, with [DOC], FDOM, C1, C2, and C:N increasing, FI and β/α decreasing, and [DON] and SUVA increasing on the rising limb, but exhibiting more variability than the other parameters (Fig. 3.4). This pattern is consistent with relationships between [DOC] and DOM quality and discharge that have been observed in the system across seasons and years [*Bellmore et al.*, in prep]. Multiple studies have reported similarly strong shifts in DOM concentration and quality during storm events in small forested and wetland catchments, suggesting mobilization of novel DOM sources during these periods [e.g. *Buffam et al.*, 2001; *Hood et al.*, 2006; *Petrone et al.*, 2007; *Inamdar et al.*, 2012]. Additionally, some patterns in the DOM characteristics of end members observed here (e.g. decreasing FI, β/α, concentration of humic fluorescence with depth of source) have been reported in the field in systems very different from this one, including tropical and temperate forests [*Möller et al.*, 2005; *Johnson et al.*, 2011; *Inamdar et al.*, 2012], suggesting that processes that control these DOM patterns persist despite agriculture-related disturbances.

DOM in drain discharge generally fell within the mixing space of end members sampled in the field (Fig. 3.5). Notably, in all of the events, drain discharge chemistry measured during the highest discharges falls outside of the subsoil and topsoil water mixing space (Fig. 3.5), suggesting that some litter-derived DOM is bypassing processing in the soil column and reaching the subsurface drain. As the storm events progressed, DOM characteristics shifted rapidly towards values associated with litter leachate on the rising limb, and were more similar to values associated with shallow soil water on the falling limb on each hydrograph (Fig. 3.5). This pattern may be due to dilution of litter-derived DOM over the course of the event, resulting in a smaller contribution on the falling limbs, or as a result flow paths shifting toward shallow matric flow on the falling limb. The latter explanation is consistent with the progression of EC values in drain discharge during the events, which show lower values (corresponding to newer, shallower water) on the rising limb than the falling limb for a given discharge (Fig. 3.2). Additionally, the mixing model (which assumes no dilution) suggests that the fraction of flow derived from litter-influenced event water peaked at 56% and 52% during the rising limbs of events 2 and 3, respectively, while the contribution of topsoil water peaked at 56% and 74% on the falling limbs. Other studies have also reported larger inputs of surficial or event water on the rising limb than falling limb, particularly in response to intense precipitation events [*van Verseveld et al.*, 2008; *Inamdar et al.*, 2013]. These results highlight the potential for subsurface drainage to transport significant quantities of surface and near-surface sources of DOM and other solutes to surface water with minimal processing.

3.5.2 Relationship between results from batch experiment and field samples

In the batch experiment, [DOC] declined immediately and rapidly in treatments with soil added and apparent equilibrium conditions for [DOC] were usually reached within 45 hours, suggesting sorption was largely responsible for change in DOM, at least initially, although microbial processing cannot be ruled out as a contributing factor. Additionally, higher temperatures would be expected to enhance microbial decomposition, but loss coefficients (k) were not consistently higher for warm treatments than cold treatments (Table 3.4). Finally, [DOC] and DOM quality indices observed at the end of the experiment in treatments with soil added strongly resemble DOM samples taken in the field from the corresponding soil horizon (Table 3.5), and sorption is recognized as an important control of [DOC] and DOM quality patterns through soil horizons [*Banaitis et al.*, 2006; *Kaiser and Kalbitz*, 2012].

DOC loss rates estimated from batch experiments indicate the potential for a rapid decrease in [DOC] in the soil, and are on the same order of magnitude as those estimated for DOC at pH 5 by Gjettermann et al. [2007] in a similar experiment. However, batch experiments almost certainly enhance DOM delivery to sorption sites relative to field conditions, where sorption is probably diffusion-limited in larger pores. This may explain some of the disparity between laboratory and field conditions observed in previous studies. For example, sorption rates estimated for topsoil using batch experiments had to be reduced by two orders of magnitude in an application of the DAISY model to successfully replicate temporal variability of [DOC] observed in the field [*Gjettermann et al.*, 2008]. Similarly, values estimated here are 1 to 4 orders of magnitude greater than sorption coefficients for wetland and forest soils that were used to calibrate the INCA-C model [*Futter et al.*, 2007]. Additionally, pH differences may also contribute to disparities; Gjettermann et al. [2007] found that sorption rates declined by about an order of magnitude between pH 5 and pH 7 in the laboratory, possibly because the adsorption capacity of sesquioxides declines above pH 6.0 [*Kaiser et al.*, 1996]. While pH was not measured in the field during this study, values between 5.1 and 7.8 have been observed in drain discharge, with the lowest values measured at the highest flows [*Kelley*, 2011], which are the focus of this study. In batch experiments, pH was near 5, suggesting the batch pH conditions are likely similar to field conditions during high flow events, but if pH was closer to 7.8, sorption could be substantially reduced in the field.

3.5.3 Mixing model performance

The conservative mixing model replicated [DOC] dynamics well ($r^2 = 0.66$), with predicted [DOC] increasing with total discharge and the contributions of topsoil and litter-influenced event water during both events (Fig. 3.7). This result is consistent with the hypothesis that the primary control of [DOC] and DOM quality in export is the hydrologic mobilization and transport of DOM available in the landscape [*McGlynn and McDonnell*, 2003; *Laudon et al.*, 2011]. However, the model consistently over-predicts [DOC], except at the highest discharges.

This pattern could be a result of end members being poorly characterized due to spatio-temporal variability in the field, or failing to meet assumptions of conservative transport and ideal mixing. The sensitivity analysis suggests that the model is likely robust to some uncertainty associated with spatio-temporal variability of end members measured in the field and potential effects of retention on FI β/α of end members (Fig. 3.8, Table 3.2). Additionally, because FI and β/α are ratios, they only mix linearly if denominators are equal among sources. Based on average numerator and denominator values for the end members, the maximum error that would result from mixing ratios rather than components is 5.6% for FI and 8.5% for β/α (data not shown), which are similar to the values used in the sensitivity analysis, so error associated with the nonlinear mixing is likely to be small.

End members are assumed to be constant over time, so depletion of DOC or loss of nitrate due to denitrification is not be accounted for by the model. Previous research suggests that NO_3^- may be being removed from soil water via denitrification, but this appears to be occurring over the timescale of seasons [*Kelley et al.*, in prep], so denitrification is unlikely to substantially affect NO_3^- of end members on the timescale of events. A comparison of average [DOC] residuals prior to event 2 and following event 3 shows larger residuals after event 3 (mean over-prediction of 2.2 (1 sd ± 0.76) mg C L^{-1} for three samples prior to event 2 and 4.3 (1 sd ± 0.62) mg C L^{-1} for three samples after event 3), suggesting some depletion may be occurring (Fig. 3.7). However, a previous study found that cumulative discharge during the two days prior to sample collection explained only a small fraction (partial $r^2 = 0.08$) of [DOC] variability in drain discharge during the rising limbs of high flow events, and none of the variability during falling limbs or baseflow across two water years [*Bellmore et al.,* in prep], suggesting that [DOC] depletion over the timescale of a few days does not significantly affect concentrations in drain discharge.

While the above uncertainties associated with end member characterization and mixing may be contributing to some of the discrepancy between measured and modeled [DOC], none appear to be the overwhelming cause. In contrast, the sensitivity analysis suggest that DOC removal in the soil column during travel to the subsurface drain could explain much of the discrepancy. When the percent of DOC removal measured in batch experiments is applied to the concentrations of litter and topsoil end members, modeled [DOC] decreases dramatically, primarily during peak flow when litter [DOC] is decreased, and during baseflow when topsoil

[DOC] is decreased (Fig. 3.8). Combining the effects of soil retention on end member characteristics results in a dramatic decrease in modeled [DOC] across flow conditions, resulting in under-prediction at peak flows (Fig. 3.7). These results suggest that DOM retention in the soil column strongly controls DOM export during low to medium flows, but exerts less of an effect at high flows.

DOC loss coefficients required to explain the discrepancy between measured and modeled DOC at each time point are consistent with this hypothesis, with k values decreasing with increasing discharge (Fig. 3.9), which could reflect flow paths shifting from matrix flow to preferential flow paths as discharge increases, reducing contact between DOC and sorption/removal sites, although as discharge increases, mean travel time is also likely to be decreasing, resulting in a shallower relationship between k and discharge than if a constant travel time is assumed (Fig. 3.9). The highest estimated k values are similar to values derived from batch experiments (Table 3.4) and are likely unreasonable for field conditions. However, the lower values are on the order of the sorption rate estimated for subsoil in an application of the DAISY model in an agricultural setting [*Gjettermann et al.*, 2008], and similar to the highest calibrated sorption rates in an application of INCA-C in mixed forested-wetland catchments [*Futter et al.*, 2007], suggesting that these are not unreasonable removal rates for field conditions.

3.5.4 Spatially explicit sources of DOM

The results of the mixing model indicate that the contributions of shallower soil water and event water increase with discharge, which is consistent with increasing vertical hydrologic connectivity in the catchment with increasing discharge. However, this analysis does not distinguish contributions of horizontally spatially explicit sources of water and solutes, so this model would be less useful for constituents with more horizontal spatial heterogeneity than DOM. For example, previous research suggests that many of the wells are located in regions with longer mean residence times for soil water compared to water discharged from the subsurface drain, based on NO_3^-–nitrogen and NO_3^-–oxygen isotope data [*Kelley et al.,* in prep], and the longer residence times allows for more extensive NO_3^- processing, which likely explain [NO_3^-], NO_3^-–nitrogen and NO_3^-–oxygen isotope variability observed in the field (Table 3.1), we expect that DOM would reach an equilibrium with soil organic matter, and the longer residence times would not affect DOM characteristics to the same extent as NO_3^- isotope ratios. Consequently, DOM samples taken from these wells reflect equilibrium conditions for their respective soil horizons and are representative of vertical variability in the field generally.

3.5.5 Catchment-scale and management implications

Large runoff events can account for the majority of the annual DOC flux to surface water [e.g. *Raymond and Saiers*, 2010; *Yoon and Raymond*, 2012; *Bellmore et al.*, in review], and constraining estimates of the magnitude of sorption during these periods will clarify whether these are also disproportionately important periods for carbon retention and storage in the landscape. In our study, the observed DOC flux was 70% of the modeled DOC flux during events 2 and 3. Assuming this difference corresponds DOC retention in the soil column and that the 30% retention rate applies to all runoff events, DOC retention during events in 2012 and 2013 is estimate to be 1.4 and 0.9 kg C ha^{-1} y^{-1}, respectively, based on previous estimates of total annual DOC flux and the fraction of DOC exported during events [*Bellmore et al.,* in prep]. These values are 1 to 2 orders of magnitude lower than estimated annual carbon accumulation in the top 20 cm of soil alone in similar systems [*Brown and Huggins*, 2012], suggesting that DOC retention during events contributes minimally to carbon retention in this landscape, even though it may strongly affect the concentration of DOC in discharge. Jardine et al. [2006] also report a limited role for sorption during high flow events, due to a combination of short residence times of DOM in the subsoil and preferential flow that bypasses sorption sites. In contrast, in a catchment dominated by unsaturated vertical flow, nearly all of the DOC and DON passing through the mineral horizons was observed to be retained [*Qualls et al.*, 2002], suggesting both carbon retention and export rates may be affected by changes to the hydrologic regime that alter the extent to which systems are event-dominated.

Field data and modeling results from this study indicate that some DOM from shallow sources is transported to the subsurface drain relatively unmodified during high flow events, with the greatest contributions to drain DOM at the highest discharges. A lack of rapid DOM removal in the subsurface during periods with the highest discharge is consistent with the hypothesis that macropore flow is responsible for transporting shallow sources of DOM to depth on these short timescales [*Kelley et al.*, 2013]. No-till management at this site likely allows soil structure, including macropores, to remain intact near the surface, potentially enhancing the export of DOM and other solutes to surface water via subsurface drainage [*Kelley et al.*, 2013]. Other researchers have observed the rapid transport of surface-applied organic matter, including manure and pesticides [*Fenelon and Moore*, 1998; *Royer et al.*, 2007] to artificial subsurface drainage during very wet conditions, implying that DOM retention mechanisms in the soil column can be overwhelmed during these brief periods of rapid transport.

3.6 CONCLUSIONS

I examined [DOC] and DOM quality in DOM sources in the landscape (litter, topsoil, subsoil) that can contribute to subsurface drain discharge. [DOC] and DOM quality dynamics in drain discharge suggest that the dominant source of DOM shifts from subsoil-derived DOM at low flow to litter-derived DOM as discharge increases during high flow events, with the contribution of litter-derived DOM peaking with discharge. Laboratory batch incubation experiments indicate the potential for litter- and topsoil-derived DOM to be sorbed and/or degraded rapidly when exposed to deeper soil horizons, with equilibrium conditions being reached generally within 48 h. Results from EMMA suggest that retention strongly affects DOC export at low to medium flows, but has a limited effect at peak flows. This lack of retention in the subsoil during high flow events has implications for the delivery of topically-applied organically-bound nutrients and carbon-based agrochemicals chemicals to streams. Additionally, because high flow events dominate hydrologic and DOC fluxes to surface water in this catchment, DOC sorption in the subsoil may not be an important mechanism for carbon retention. Understanding the extent of DOM retention and the roles of sorption and microbial decomposition during high flow events is important for clarifying carbon retention mechanisms as well as understanding and predicting fluxes and quality of terrestrially-derived DOM to aquatic ecosystems.

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3.9 TABLES

Table 3.1. [DOC] and tracer characteristics for end members used in the mixing model. Values in parentheses are 1 standard deviation.

		DOC		FI		β/α		NO_3^-	
End Member	n	(mg C L^{-1}) ± 1 sd	CV (%)	± 1 sd	CV (%)	± 1 sd	CV (%)	(mg N L^{-1}) ± 1 sd	CV (%)
Litter	2	13.74*	NA	1.386 (0.037)	2.7	0.536 (0.037)	6.9	4.30*	NA
Topsoil	2	9.59 (1.34)	14.0	1.555 (0.007)	0.5	0.715 (0.021)	2.9	14.98 (6.97)	46.5
Subsoil	6	3.88 (1.44)	37.1	1.636 (0.030)	1.8	0.743 (0.028)	3.8	8.48 (4.80)	56.6

*n=1; concentration data from litter leachate not used.

Table 3.2 Changes applied to end member characteristics in sensitivity analysis, and corresponding changes in modeled [DOC]

Characteristic	End Member	End member change (%)	Mean change in [DOC] (%)
FI	Litter	+/- 5	4.5 / -3.5
	Topsoil	+/- 5	8.8 / -7.8
	Subsoil	+/- 5	7.5 / -9.0
β/α	Litter	+/- 5	2.2 / -2.0
	Topsoil	+/- 5	5.5 / -4.9
	Subsoil	+/- 5	4.9 / -6.2
NO_3^-	Litter	+/- 5	-0.3 / 0.3
	Topsoil	+/- 5	-1.5 / -1.9
	Subsoil	+/- 5	-1.0 / -1.0
DOC	Litter	+/- 5	1.7 / -1.7
	Topsoil	+/- 5	2.3 / -2.3
	Subsoil	+/- 5	1.0 / -1.0
	Based on change in batch experiments after 95 h		
FI	Litter	+7.5	6.1
	Topsoil	+1.0	0.7
β/α	Litter	+8.2	3.7
	Topsoil	-2.1	-2.1
DOC	Litter	-57	-19.9
	Topsoil	-35	-16.0

Table 3.3. Cumulative precipitation and discharge during events 1-4

Event	Cumulative Precipitation[1] (mm)	Cumulative Discharge[2] (mm)
1	8.38	3.93
2	10.06	2.93
3	13.41	7.41
4	11.46	0.93

[1] Palouse Conservation Field Station

[2] Cook Agronomy Farm subsurface drain flume

Table 3.4. Sorption rate coefficient estimates from the batch incubation experiment and significance level of the parameter in the model.

Treatment			n	k_f (h^{-1}) (±1 SE)	p
Soil	DOM	Temp			
topsoil	litter	Cold	5	0.085 (0.020)	0.024
		Warm	5	0.032 (0.004)	0.004
subsoil	litter	Cold	5	0.029 (0.006)	0.015
		Warm	6	0.050 (0.004)	<0.001
subsoil	topsoil	Cold	6	0.051 (0.035)	Ns
		Warm	6	0.025 (0.011)	Ns

Table 3.5. [DOC] and DOM quality indices in blank solution after 45 h exposure to topsoil or subsoil, and in litter leachate DOM and top soil leachate DOM initially and after 45 h exposure to topsoil or subsoil in the batch experiment.

DOM Source	Litter (initial)	Litter		Litter		Topsoil (initial)	Topsoil		Blank		Blank	
Soil Source	--	Topsoil		Subsoil		--	Subsoil		Topsoil		Subsoil	
Incubation temp (°C)	--	6	22	6	22	--	6	22	6	22	6	22
[DOC] (mg L^{-1}) (sd)	284.35 (27.82)	168.45 (8.33)	122.20 (6.32)	152.68 (20.7)	101.62 (6.34)	5.13 (0.48)	2.87 (0.15)	3.38 (0.43)	5.63 (1.01)	7.80 (0.53)	1.52 (0.33)	1.78 (0.05)
C:N	13.7	14.1	16.5	13.3	18.8	12.9	3.2	3.8	7.6	10.3	4.3	6.1
FI	1.40	1.48	1.47	1.48	1.51	1.46	1.53	1.56	1.50	1.49	1.54	1.57
β/α	0.51	0.59	0.59	0.58	0.58	0.60	0.65	0.68	0.66	0.64	0.69	0.66
SUVA$_{254}$	1.20	1.26	1.59	1.50	1.61	1.98	1.77	1.39	2.41	3.04	1.22	0.42
C1 F_{max} (%)*	5.11 (6.9)	6.31 (9.2)	6.63 (13.5)	3.17 (5.2)	5.26 (7.3)	0.44 (28.9)	0.37 (18.8)	0.39 (20.1)	0.45 (28.6)	0.45 (28.3)	0.30 (9.5)	0.45 (16.6)
C2 F_{max} (%)*	16.7 (22.6)	16.6 (24.1)	16.1 (32.6)	10.16 (16.5)	15.8 (22.0)	0.73 (47.7)	0.77 (38.5)	0.78 (40.6)	0.74 (46.8)	0.72 (45.8)	0.51 (16.5)	0.72 (26.9)
C3 F_{max} (%)*	52.0 (70.5)	45.8 (66.7)	26.5 (53.9)	48.08 (78.3)	50.7 (70.6)	0.36 (23.4)	0.85 (42.7)	0.76 (39.2)	0.39 (24.6)	0.41 (25.9)	2.30 (74.0)	1.53 (56.6)

*Percent of total fluorescence

Table 3.6. PARAFAC components identified for samples in the batch experiment.

Component	Excitation (nm)	Emission (nm)	Characteristics*
1	260 (380)	486	Humic-like; UVC
2	240 (320)	430	Humic-like (high molecular weight)
3	280	330	Tryptophan-like

*From Fellman et al. [2010]

3.10 FIGURES

Figure Captions

Figure 3.1. Map of Cook Agronomy Farm, near Pullman, WA. The grey dotted line indicates the catchment area that contributes to the subsurface drain; the black dashed line indicates the approximate location of the subsurface drain line; the star identifies the drain outlet. Numbered circles indicate the locations of wells. Contour lines have values in m above sea level with intervals of 2.5 m. Modified from Keller et al. [2008].

Figure 3.2. FDOM and EC in drain discharge with respect to flow during the four storm events, indicated by the number in the top left of each panel. The loops track the progression of FDOM and EC through time, with solid lines are corresponding to the rising limb. Note that the EC axis is reversed.

Figure 3.3. Precipitation (black bars) and discharge (blue line) associated with four storm events. Note scales on the x axes of the left and right panels are not identical.

Figure 3.4. [DOC] and DOM quality dynamics in subsurface drain discharge during three high flow events in 2013. Instantaneous discharge is the dotted gray line in all panels. Panels a and b show grab sample [DOC] (black circles) and continuous FDOM measurements (blue line). Panels c and d show [DON] (black) and C:N (blue); panels e and f show FI (black) and β/α (blue); panels g and h show the fluorescence intensities (F_{max}) of two humic-like components, C1 (black) and C2 (red) (Table 3.5) and SUVA (blue). The axis label color corresponds to the same colored points in the associated panels.

Figure 3.5. Drain discharge [DOC] and FI (left column) and NO_3^{-1} and β/α (right column) progression during events 1-4 (black to white from start to end of event) plotted with subsoil

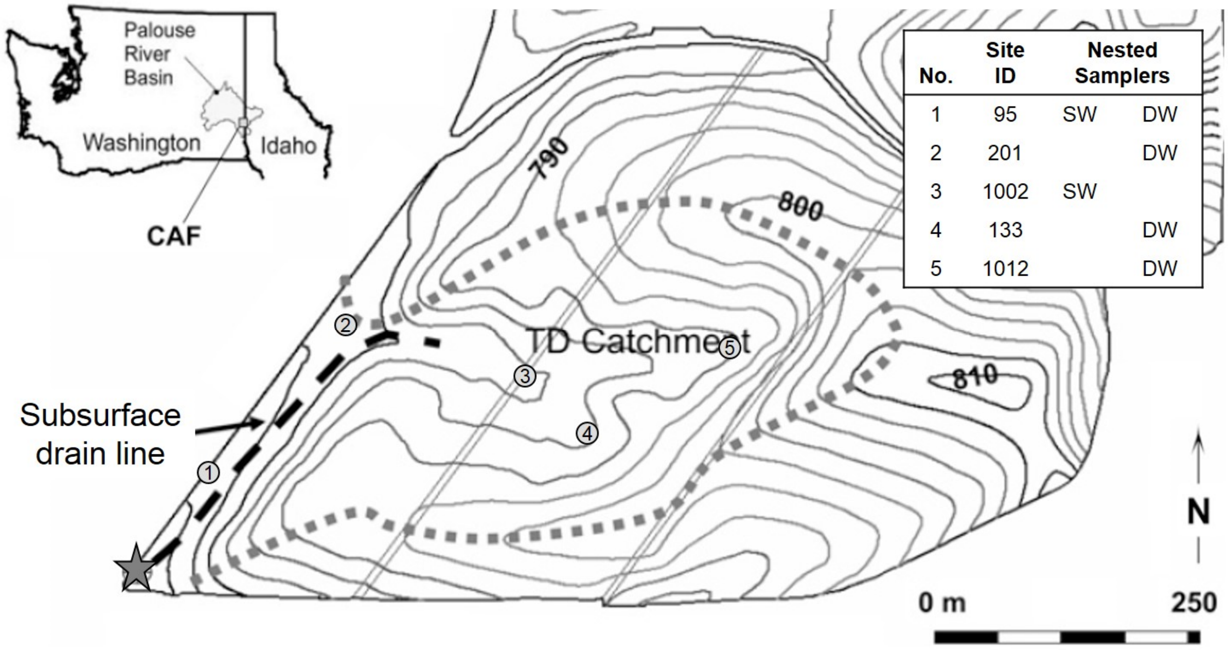
(red), topsoil (tan) and litter (green) DOM end members associated with the respective events. The sample associated with the highest discharge is circled. Error bars are ±1 standard deviation.

Figure 3.6. Drain discharge samples (black to white from start to end of event) and end members plotted in U-space, defined by drain discharge samples associated with events 2 and 3. The progression of drain samples during the event is from black to white, and the sample associated with the highest discharge is circled.

Figure 3.7. Results of the end member mixing model; the fraction of total flow attributed to litter-influenced event water, topsoil water, and subsoil water over time (based on initial end member characterization) with total drain flow overlain are shown in the top panel. Observed [DOC] and [DOC] modeled assuming conservative tracers and DOC, or assuming that retention alters fluorescence characteristics and DOC are shown in the bottom panel.

Figure 3.8. Sensitivity of modeled [DOC] to changes in end member characteristics; changes to end member values were made one at a time and used to predict drain [DOC]. Effects of changes to the litter end member are shown in the top row (green), topsoil (tan) in the middle row, and subsoil (red) in the bottom row. Observed [DOC] values are shown in black and the original model values are shown in blue. Upper bounds are filled circles, and lower bounds are open circles.

Figure 3.9. The relationship between k values estimated for each sampling point to account for the difference between modeled and observed [DOC], assuming a travel time of either 7 (gray dots and dashed line) or 160 hours (black circles and black dashed line), and instantaneous discharge associated with each sample during events 2 and 3 ($r^2 = 0.42$, $p = 0.01$, $n = 14$ for both relationships). The red line shows a hypothetical relationship between k and discharge assuming residence time increases with discharge.



No.	Site ID	Nested Samplers	
1	95	SW	DW
2	201		DW
3	1002	SW	
4	133		DW
5	1012		DW

Figure 3.1. Map of Cook Agronomy Farm, near Pullman, WA. The grey dotted line indicates the catchment area that contributes to the subsurface drain; the black dashed line indicates the approximate location of the subsurface drain line; the star identifies the drain outlet. Numbered circles indicate the locations of wells. Contour lines have values in m above sea level with intervals of 2.5 m. Modified from Keller et al. [2008].

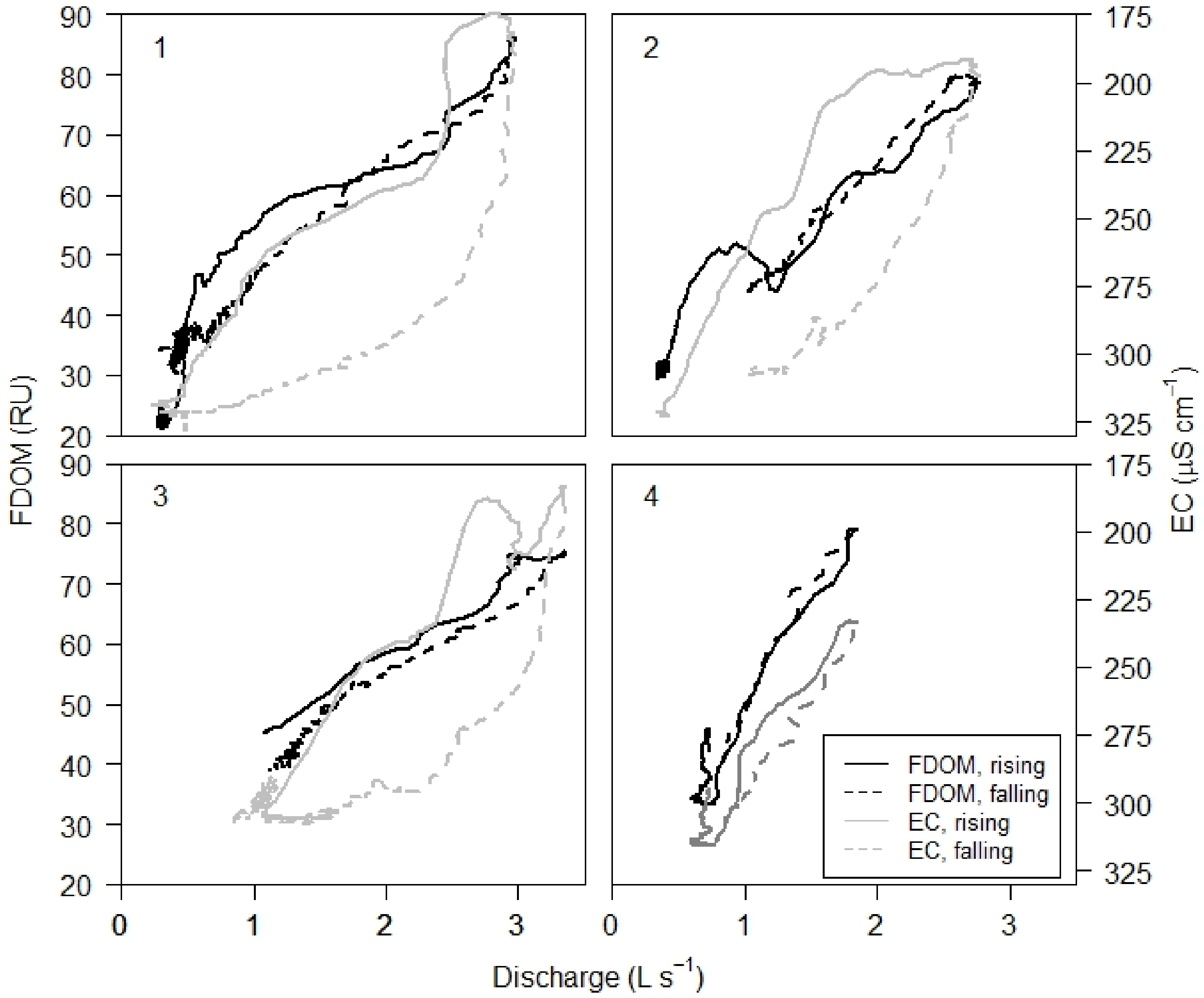


Figure 3.2. FDOM and EC in drain discharge with respect to flow during the four storm events, indicated by the number in the top left of each panel. The loops track the progression of FDOM and EC through time, with solid lines are corresponding to the rising limb. Note that the EC axis is reversed.

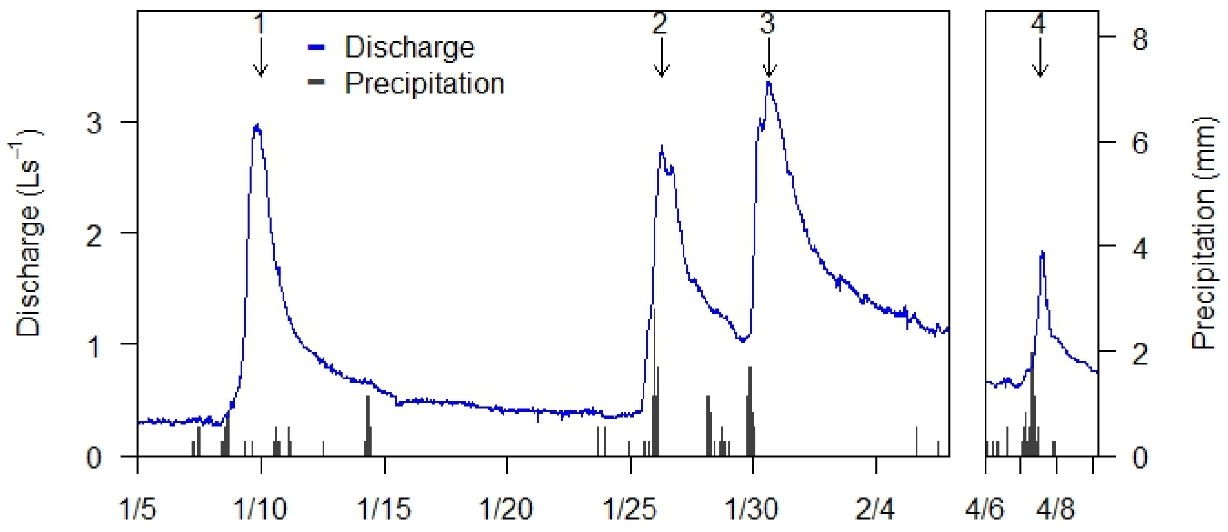
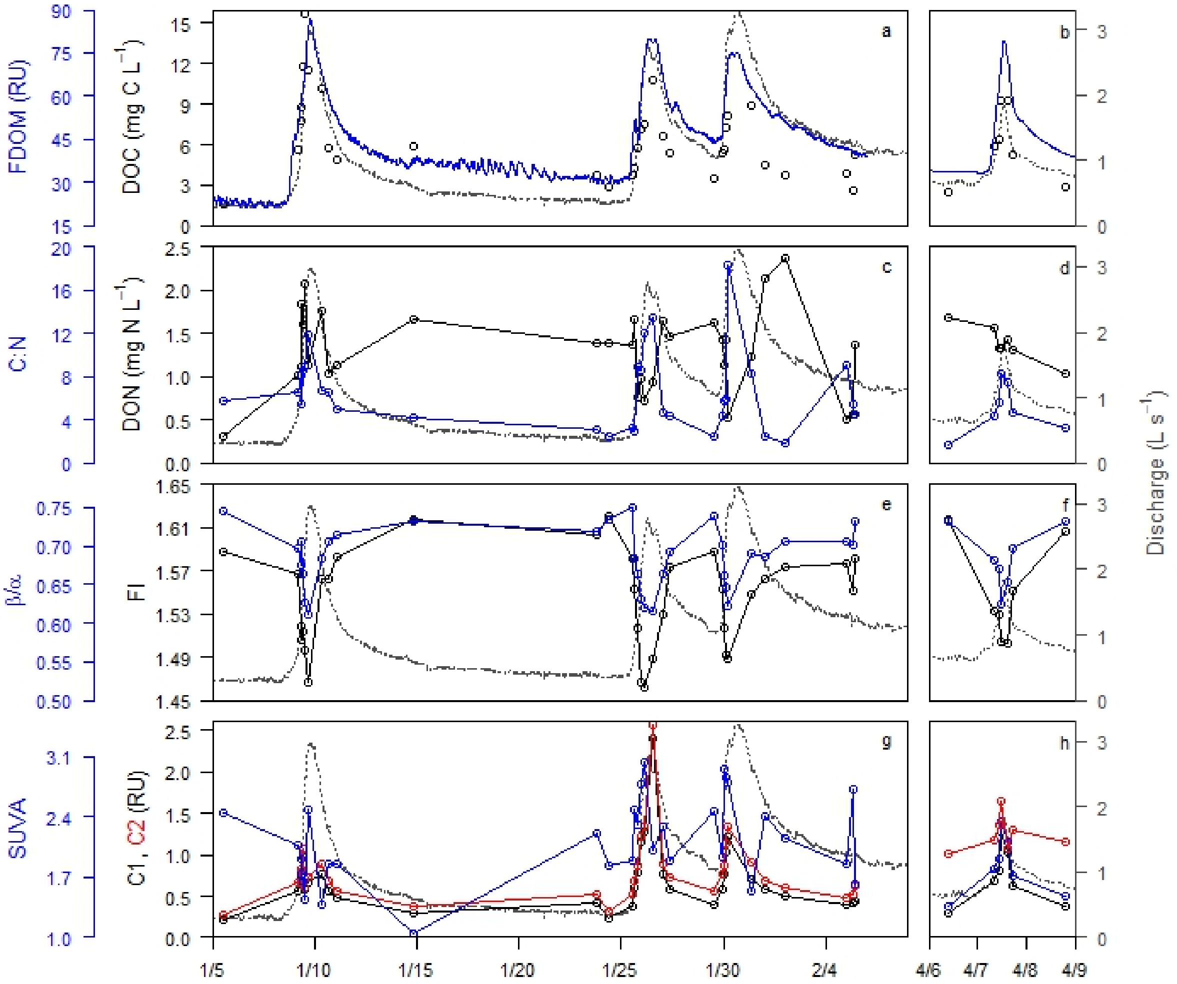


Figure 3.3. Precipitation and discharge associated with four storm events. Note scales on the x axes of the left and right panels are not identical.



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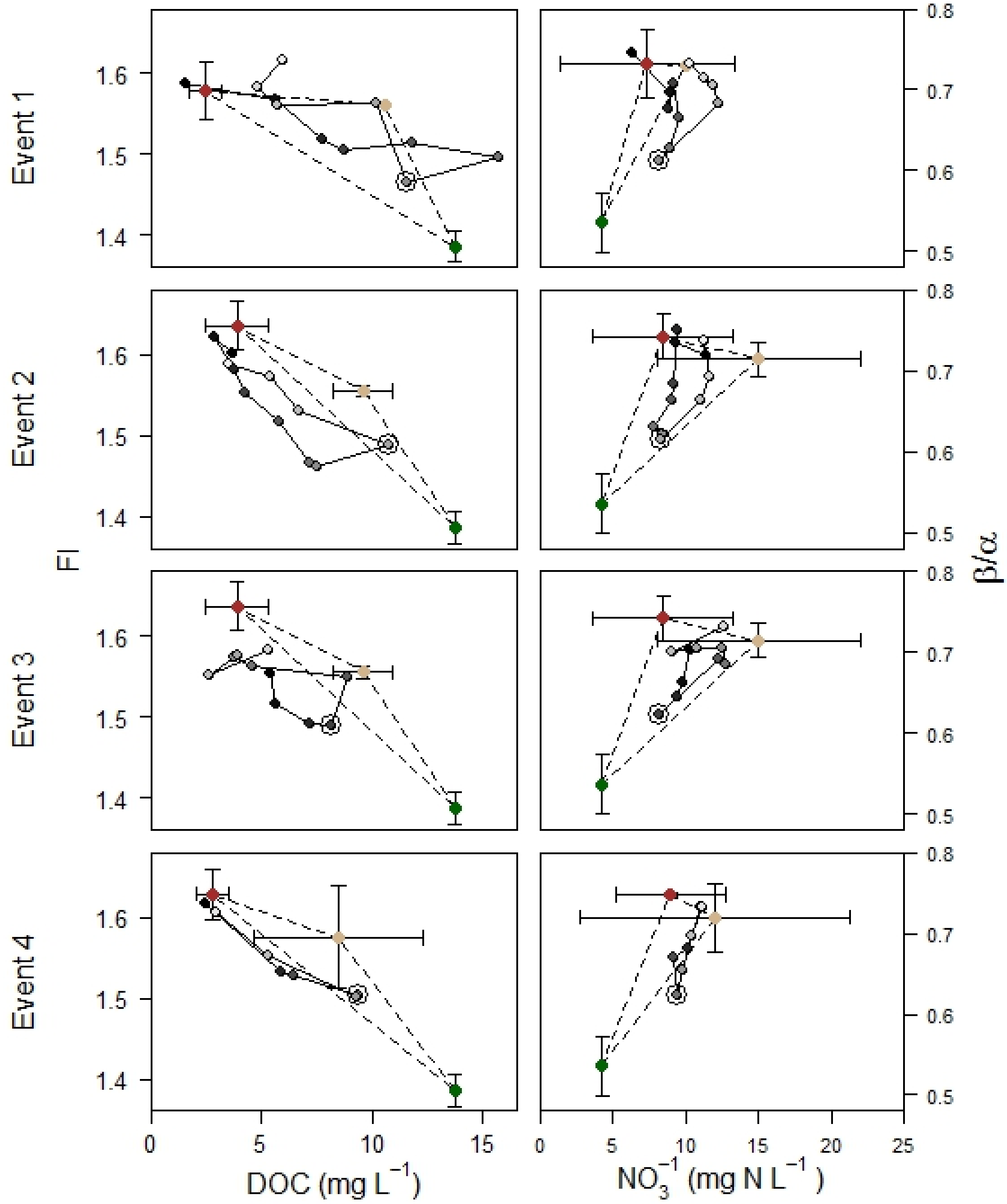

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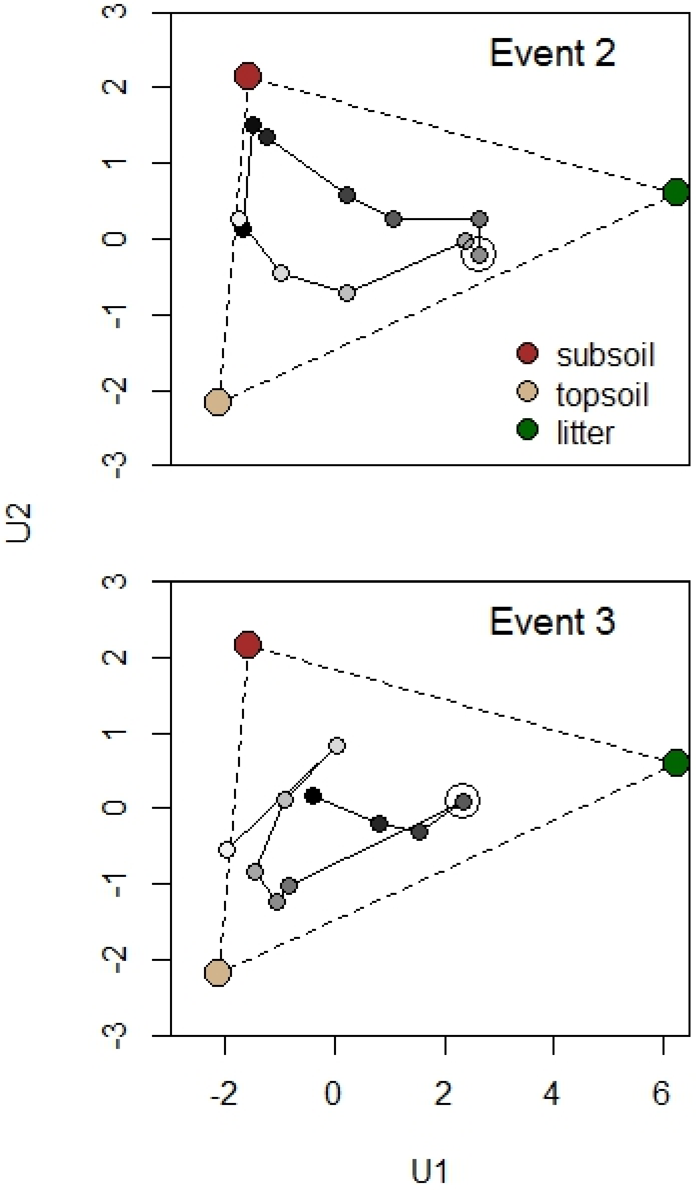
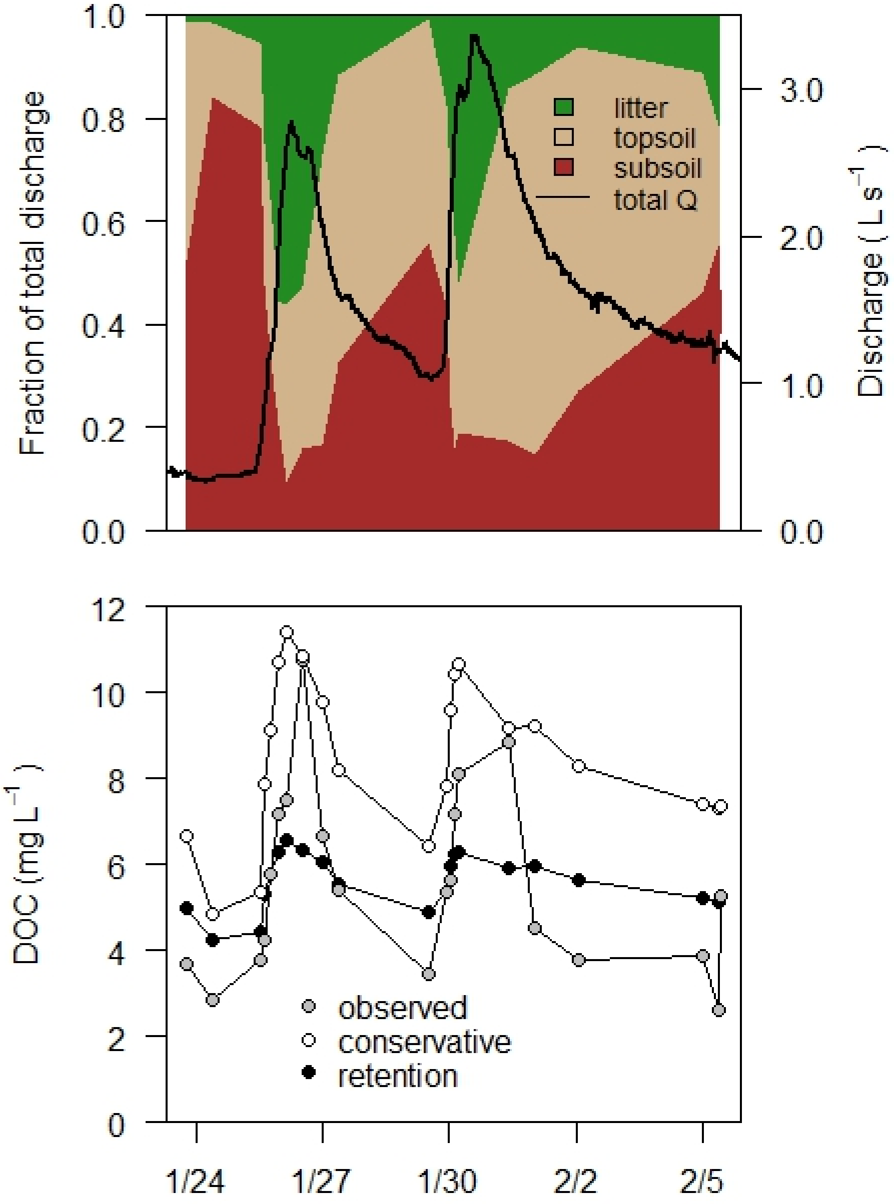


Figure 3.6. Drain discharge samples (black to white from start to end of event) and end members plotted in U-space, defined by drain discharge samples associated with events 2 and 3. The progression of drain samples during the event is from black to white, and the sample associated with the highest discharge is circled.



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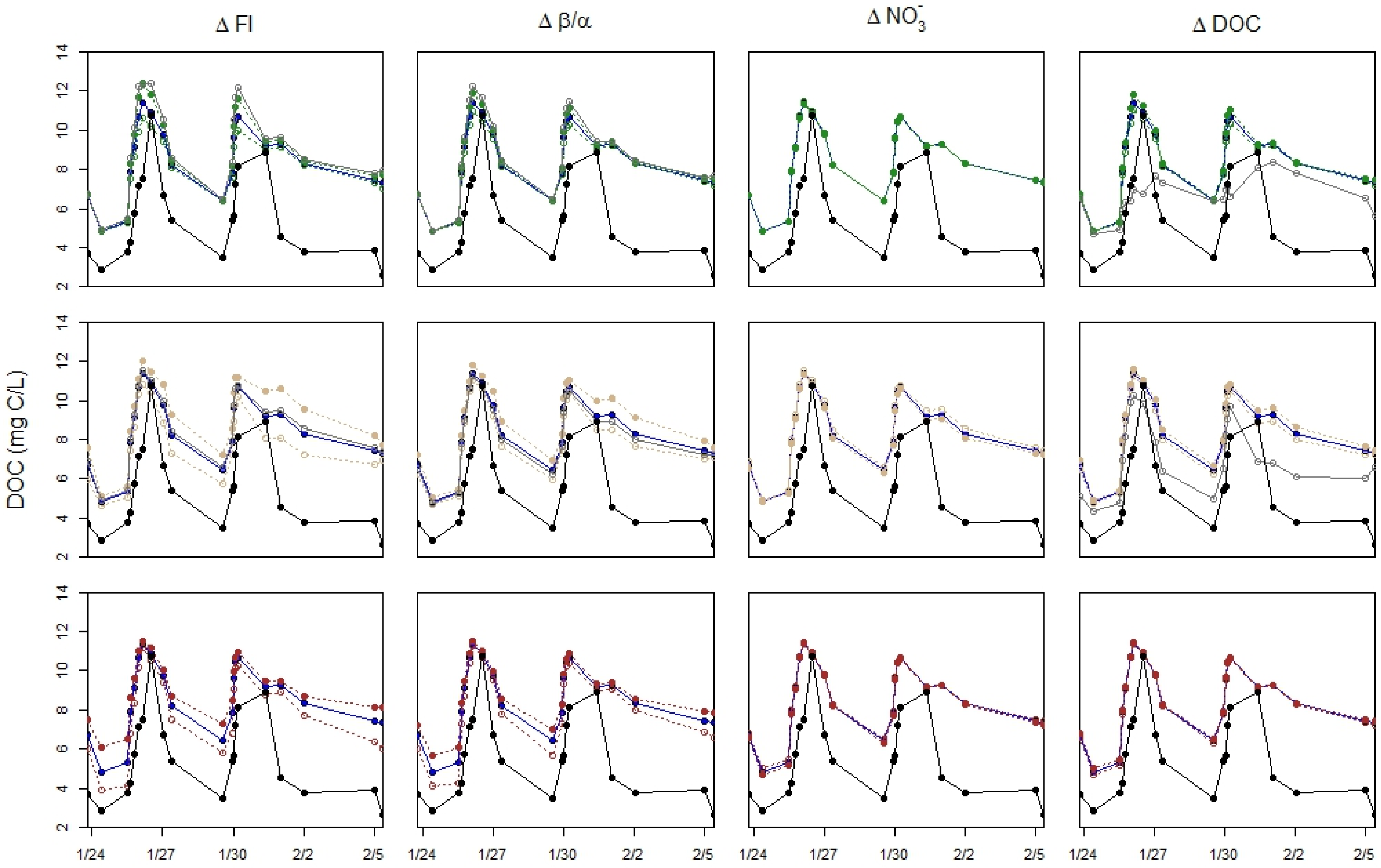
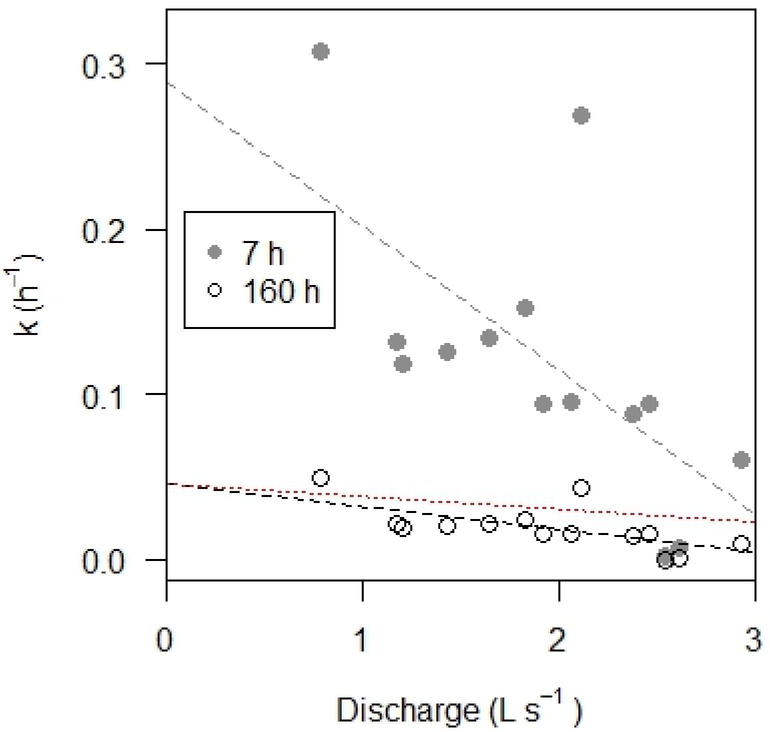


Figure 3.8. Sensitivity of modeled [DOC] to changes in end member characteristics; changes to end member values (Table 3.6) were made one at a time and used to predict drain [DOC]. Effects of increasing or decreasing values by 5% to the litter end

member are shown in the top row (green), topsoil in the middle row (tan), and subsoil in the bottom row (red). Effects of changing FI, β/α and [DOC] to reflect changes observed in litter and topsoil DOM in batch experiments after 95 hours are shown in gray. Observed [DOC] values are shown in black and the original model values are shown in blue. Upper bounds are filled circles, and lower bounds are open circles.



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3.11 APPENDICES

Appendix C. Artificial subsurface drain discharge samples, water years 2012-2013.

Ch*	DateTime	Water Year	Season	Flow	DOC (mg C/L)	DOC sd	DOC n	TN (mg N/L)	TN sd	TN n
2, 3	12/8/2010 12:00	2011	Winter	NA	3.537	NA	1	3.805	NA	1
2, 3	1/14/2011 12:00	2011	Winter	NA	7.551	0.253	2	20.580	1.651	2
2, 3	1/21/2011 12:00	2011	Winter	NA	7.702	NA	1	18.879	NA	1
2, 3	1/28/2011 12:00	2011	Winter	NA	5.560	NA	1	20.663	NA	1
2, 3	2/4/2011 12:00	2011	Winter	NA	4.510	0.585	2	18.511	0.719	2
2, 3	2/11/2011 12:00	2011	Winter	NA	7.005	NA	1	17.824	NA	1
2, 3	3/4/2011 12:00	2011	Spring	NA	6.015	1.110	2	21.649	NA	1
2, 3	3/25/2011 12:00	2011	Spring	NA	6.290	NA	1	19.498	NA	1
2, 3	4/1/2011 12:00	2011	Spring	NA	6.701	NA	1	18.246	NA	1
2, 3	4/4/2011 12:00	2011	Spring	NA	3.298	NA	1	15.012	NA	1
2, 3	4/15/2011 12:00	2011	Spring	NA	5.601	NA	1	17.289	NA	1
2, 3	4/22/2011 12:00	2011	Spring	NA	4.830	NA	1	16.960	NA	1
2, 3	4/29/2011 12:00	2011	Spring	NA	4.880	NA	1	16.773	NA	1
2, 3	5/11/2011 12:00	2011	Spring	NA	1.744	0.317	2	11.444	0.954	2
2, 3	5/13/2011 12:00	2011	Spring	NA	2.537	0.165	2	14.776	0.068	2
2, 3	5/27/2011 12:00	2011	Spring	NA	3.013	NA	1	13.580	NA	1
2, 3	6/3/2011 12:00	2011	Summer	NA	2.198	NA	1	13.577	NA	1
2, 3	6/19/2011 12:00	2011	Summer	NA	1.638	NA	1	14.085	NA	1
2, 3	6/23/2011 12:00	2011	Summer	NA	1.870	NA	1	13.776	NA	1
2, 3	6/29/2011 12:00	2011	Summer	NA	1.814	NA	1	13.872	NA	1
2, 3	7/25/2011 12:00	2011	Summer	NA	1.701	0.368	2	13.570	0.623	2
2, 3	10/1/2011 12:00	2012	Fall	baseflow	2.144	0.129	3	7.998	0.063	3
2, 3	12/15/2011 12:00	2012	Winter	baseflow	1.064	0.133	3	4.646	0.052	3
2, 3	1/8/2012 22:19	2012	Winter	baseflow	5.012	NA	1	9.424	NA	1
2, 3	1/9/2012 12:00	2012	Winter	baseflow	1.413	NA	1	5.039	NA	1
2, 3	1/10/2012 0:00	2012	Winter	baseflow	7.128	NA	1	13.712	NA	1
2, 3	1/14/2012 20:24	2012	Winter	baseflow	2.657	NA	1	7.617	NA	1
2, 3	1/15/2012 12:00	2012	Winter	baseflow	1.332	0.109	3	4.682	0.006	3
2, 3	1/19/2012 1:27	2012	Winter	baseflow	2.953	NA	1	5.174	NA	1
2, 3	1/19/2012 11:27	2012	Winter	baseflow	2.921	NA	1	4.569	NA	1
2, 3	1/19/2012 18:59	2012	Winter	rising limb	2.945	NA	1	5.726	NA	1
2, 3	1/19/2012 20:24	2012	Winter	rising limb	3.482	NA	1	8.301	NA	1
2, 3	1/20/2012 1:29	2012	Winter	falling limb	2.817	NA	1	8.029	NA	1
2, 3	1/20/2012 10:41	2012	Winter	falling limb	7.715	NA	1	5.495	NA	1

Ch*	DateTime	Water Year	Season	Flow	DOC (mg C/L)	DOC sd	DOC n	TN (mg N/L)	TN sd	TN n
2, 3	1/21/2012 1:11	2012	Winter	rising limb	2.592	NA	1	6.552	NA	1
2, 3	1/21/2012 6:59	2012	Winter	rising limb	3.062	NA	1	7.656	NA	1
2, 3	1/21/2012 12:33	2012	Winter	falling limb	3.688	0.888	2	10.259	0.194	2
2, 3	1/21/2012 18:44	2012	Winter	falling limb	2.950	NA	1	8.895	NA	1
2, 3	1/22/2012 23:42	2012	Winter	baseflow	2.618	0.348	2	6.166	0.675	2
2, 3	1/24/2012 23:25	2012	Winter	rising limb	3.503	1.605	2	7.303	0.674	2
2, 3	1/26/2012 19:37	2012	Winter	falling limb	10.260	NA	1	11.910	NA	1
2, 3	1/29/2012 22:53	2012	Winter	rising limb	3.923	NA	1	6.752	NA	1
2, 3	1/30/2012 1:11	2012	Winter	rising limb	7.350	0.113	2	9.332	1.148	2
2, 3	1/30/2012 4:30	2012	Winter	rising limb	8.280	0.008	2	11.626	0.438	2
2, 3	1/30/2012 22:35	2012	Winter	falling limb	8.074	0.865	2	13.989	0.710	2
2, 3	1/31/2012 20:27	2012	Winter	falling limb	6.849	0.223	2	13.723	0.069	2
2, 3	2/3/2012 12:00	2012	Winter	falling limb	2.946	0.061	3	13.601	0.424	3
2, 3	2/14/2012 9:30	2012	Winter	baseflow	3.792	NA	1	11.202	NA	1
2, 3	2/14/2012 9:50	2012	Winter	baseflow	4.006	NA	1	13.168	NA	1
2, 3	2/15/2012 12:00	2012	Winter	baseflow	2.170	NA	1	12.485	NA	1
2, 3	2/21/2012 10:00	2012	Winter	rising limb	10.491	2.040	2	12.643	1.981	2
2, 3	2/22/2012 12:00	2012	Winter	falling limb	4.095	0.582	3	14.222	0.103	3
2, 3	2/23/2012 17:25	2012	Winter	falling limb	5.222	0.780	2	12.605	0.821	2
2, 3	2/25/2012 8:35	2012	Winter	falling limb	4.251	0.208	2	12.101	0.394	2
2, 3	2/25/2012 12:44	2012	Winter	falling limb	4.739	0.677	2	12.324	0.201	2
2, 3	3/2/2012 12:00	2012	Spring	baseflow	2.691	NA	1	9.987	NA	1
2, 3	3/3/2012 12:50	2012	Spring	baseflow	4.538	1.036	2	11.353	0.937	2
2, 3	3/9/2012 12:00	2012	Spring	baseflow	2.227	0.049	3	12.828	0.146	3
2, 3	3/11/2012 12:55	2012	Spring	baseflow	4.308	0.718	2	13.336	0.017	2
2, 3	3/13/2012 13:14	2012	Spring	baseflow	5.575	NA	1	14.539	NA	1
2, 3	3/13/2012 13:44	2012	Spring	baseflow	7.613	NA	1	15.056	NA	1
2, 3	3/14/2012 12:49	2012	Spring	baseflow	6.480	NA	1	15.936	NA	1
2, 3	3/15/2012 2:11	2012	Spring	baseflow	8.196	NA	1	15.647	NA	1
2, 3	3/15/2012 15:01	2012	Spring	rising limb	8.982	NA	1	16.658	NA	1
2, 3	3/15/2012 21:11	2012	Spring	rising limb	8.244	NA	1	15.188	NA	1
2, 3	3/16/2012 10:08	2012	Spring	rising limb	7.977	0.421	2	16.503	0.612	2
2, 3	3/17/2012 17:21	2012	Spring	NA	5.064	0.835	3	17.388	0.753	3
2, 3	3/23/2012 12:00	2012	Spring	NA	5.431	NA	1	19.408	NA	1
2, 3	3/29/2012 11:05	2012	Spring	NA	8.738	1.031	2	17.311	0.618	2
2, 3	3/29/2012 12:00	2012	Spring	NA	5.329	0.001	2	18.265	0.231	2
2, 3	3/30/2012 17:17	2012	Spring	NA	10.182	NA	1	14.875	NA	1
2, 3	4/1/2012 20:25	2012	Spring	NA	10.702	NA	1	18.335	NA	1

Ch*	DateTime	Water Year	Season	Flow	DOC (mg C/L)	DOC sd	DOC n	TN (mg N/L)	TN sd	TN n
2, 3	4/4/2012 12:00	2012	Spring	NA	5.500	0.023	2	18.840	0.026	2
2, 3	4/6/2012 12:00	2012	Spring	baseflow	7.242	NA	1	19.458	NA	1
2, 3	4/11/2012 12:06	2012	Spring	falling limb	7.149	NA	1	18.880	NA	1
2, 3	4/13/2012 17:00	2012	Spring	falling limb	6.535	NA	1	17.312	NA	1
2, 3	4/15/2012 16:07	2012	Spring	falling limb	11.329	NA	1	14.331	NA	1
2, 3	4/23/2012 12:00	2012	Spring	falling limb	4.385	NA	1	14.371	NA	1
2, 3	5/2/2012 18:40	2012	Spring	falling limb	5.009	NA	1	16.635	NA	1
2, 3	5/3/2012 7:00	2012	Spring	falling limb	4.585	NA	1	15.565	NA	1
2, 3	5/3/2012 18:00	2012	Spring	rising limb	9.211	NA	1	10.854	NA	1
2, 3	5/8/2012 6:33	2012	Spring	falling limb	6.725	NA	1	14.163	NA	1
2, 3	5/21/2012 12:00	2012	Spring	baseflow	2.010	0.087	3	12.857	0.927	3
2, 3	5/30/2012 12:00	2012	Spring	baseflow	2.251	NA	1	12.436	NA	1
2, 3	6/8/2012 12:00	2012	Summer	baseflow	1.334	NA	1	10.926	NA	1
2, 3	6/11/2012 22:01	2012	Summer	baseflow	3.936	NA	1	10.865	NA	1
2, 3	6/14/2012 12:31	2012	Summer	baseflow	7.156	NA	1	9.680	NA	1
2, 3	6/22/2012 10:48	2012	Summer	baseflow	9.162	NA	1	10.382	NA	1
2, 3	6/24/2012 10:56	2012	Summer	baseflow	6.082	NA	1	10.981	NA	1
2, 3	6/30/2012 20:16	2012	Summer	baseflow	3.852	NA	1	11.729	NA	1
2, 3	7/7/2012 1:23	2012	Summer	baseflow	2.917	NA	1	11.574	NA	1
2, 3	7/10/2012 14:35	2012	Summer	baseflow	1.640	NA	1	8.920	NA	1
2, 3	7/25/2012 12:30	2012	Summer	baseflow	2.901	NA	1	9.498	NA	1
2, 3	8/17/2012 2:00	2012	Summer	baseflow	3.875	0.049	2	7.385	0.120	2
2, 3	8/30/2012 13:20	2012	Summer	baseflow	3.729	0.272	2	7.142	0.262	2
2, 3	9/3/2012 15:21	2012	Fall	baseflow	2.446	0.309	2	8.870	0.147	2
2, 3	9/10/2012 15:31	2012	Fall	baseflow	3.528	0.449	2	7.574	0.035	2
2, 3	9/16/2012 12:00	2012	Fall	baseflow	0.687	0.174	3	6.245	1.491	3
2, 3	9/17/2012 8:45	2012	Fall	baseflow	1.445	0.262	2	7.740	0.141	2
2, 3	9/23/2012 12:00	2012	Fall	baseflow	4.431	0.026	2	6.213	0.048	2
2, 3	9/26/2012 12:00	2012	Fall	baseflow	1.050	NA	1	7.024	NA	1
2, 3	9/29/2012 12:00	2012	Fall	baseflow	1.452	NA	1	7.164	NA	1
2, 3	10/2/2012 12:00	2013	Fall	baseflow	1.217	NA	1	6.711	NA	1
2, 3	10/5/2012 12:00	2013	Fall	baseflow	1.067	NA	1	6.338	NA	1
2, 3	10/8/2012 12:00	2013	Fall	baseflow	0.951	NA	1	6.288	NA	1
2, 3	10/11/2012 12:00	2013	Fall	baseflow	3.515	NA	1	5.515	NA	1
2, 3	10/12/2012 12:10	2013	Fall	baseflow	3.113	0.565	2	6.179	0.268	2
2, 3	10/14/2012 12:00	2013	Fall	baseflow	1.008	NA	1	5.317	NA	1
2, 3	10/23/2012 12:00	2013	Fall	baseflow	0.845	0.105	3	5.011	0.687	3
2, 3	10/23/2012 12:00	2013	Fall	baseflow	1.129	NA	1	5.717	NA	1

Ch*	DateTime	Water Year	Season	Flow	DOC (mg C/L)	DOC sd	DOC n	TN (mg N/L)	TN sd	TN n
2, 3	10/24/2012 10:00	2013	Fall	baseflow	1.700	0.354	2	5.760	0.198	2
2, 3	10/27/2012 10:00	2013	Fall	baseflow	5.179	0.108	2	5.019	0.045	2
2, 3	10/30/2012 14:30	2013	Fall	baseflow	3.250	0.641	2	5.258	0.287	2
2, 3	11/2/2012 10:00	2013	Fall	baseflow	2.771	0.231	2	5.071	0.028	2
2, 3	11/5/2012 10:00	2013	Fall	baseflow	2.846	0.691	2	5.008	0.031	2
2, 3	11/8/2012 10:00	2013	Fall	baseflow	2.676	0.030	2	5.224	0.168	2
2, 3	11/12/2012 20:32	2013	Fall	baseflow	7.067	NA	1	6.475	NA	1
2, 3	11/14/2012 10:00	2013	Fall	baseflow	2.745	0.615	2	5.375	0.120	2
2, 3	11/17/2012 10:00	2013	Fall	baseflow	2.747	0.269	2	4.974	0.002	2
2, 3	11/20/2012 10:00	2013	Fall	rising limb	8.126	0.607	2	7.628	0.309	2
2, 3	11/21/2012 20:32	2013	Fall	falling limb	6.959	NA	1	6.334	NA	1
2, 3	11/28/2012 16:33	2013	Fall	baseflow	3.578	0.465	2	6.643	0.158	2
2, 3	11/29/2012 6:35	2013	Fall	baseflow	3.940	0.504	2	6.488	0.025	2
2, 3	11/30/2012 10:00	2013	Fall	baseflow	5.879	NA	1	4.959	NA	1
2, 3	12/3/2012 12:00	2013	Winter	baseflow	2.579	0.059	3	8.496	0.224	3
2, 3	12/12/2012 12:50	2013	Winter	rising limb	6.943	0.663	2	9.166	0.070	2
2, 3	12/17/2012 13:38	2013	Winter	rising limb	4.170	0.255	2	9.445	0.191	2
2, 3	12/18/2012 15:14	2013	Winter	falling limb	4.797	0.057	2	9.847	0.100	2
2, 3	12/21/2012 12:00	2013	Winter	baseflow	3.537	NA	1	8.483	NA	1
2, 3	12/22/2012 12:00	2013	Winter	baseflow	2.523	NA	1	8.768	NA	1
2, 3	12/23/2012 12:00	2013	Winter	baseflow	2.915	NA	1	8.750	NA	1
2, 3	12/24/2012 12:00	2013	Winter	baseflow	3.274	NA	1	9.693	NA	1
2, 3	12/26/2012 12:00	2013	Winter	baseflow	2.557	NA	1	8.526	NA	1
2, 3	12/28/2012 12:00	2013	Winter	baseflow	3.996	NA	1	7.537	NA	1
2, 3	1/5/2013 12:00	2013	Winter	baseflow	1.557	0.062	3	6.692	0.767	3
3	1/5/2013 15:05	2013	Winter	baseflow	4.669	NA	1	9.376	NA	1
3	1/9/2013 5:31	2013	Winter	rising limb	5.599	NA	1	9.939	NA	1
3	1/9/2013 8:01	2013	Winter	rising limb	7.718	NA	1	9.936	NA	1
3	1/9/2013 9:27	2013	Winter	rising limb	8.712	NA	1	11.072	NA	1
3	1/9/2013 10:58	2013	Winter	rising limb	11.793	NA	1	11.160	NA	1
3	1/9/2013 13:15	2013	Winter	rising limb	15.689	NA	1	11.006	NA	1
3	1/9/2013 16:54	2013	Winter	rising limb	11.519	NA	1	9.287	NA	1
3	1/10/2013 8:24	2013	Winter	falling limb	10.194	NA	1	14.064	NA	1
3	1/10/2013 16:07	2013	Winter	falling limb	5.718	NA	1	12.972	NA	1
3	1/11/2013 2:24	2013	Winter	falling limb	4.811	1.373	2	12.364	0.587	2
3	1/11/2013 13:20	2013	Winter	falling limb	4.144	NA	1	11.796	NA	1
3	1/12/2013 6:42	2013	Winter	baseflow	3.711	NA	1	11.881	NA	1
3	1/14/2013 19:45	2013	Winter	baseflow	5.913	NA	1	12.004	NA	1

Ch^*	DateTime	Water Year	Season	Flow	DOC (mg C/L)	DOC sd	DOC n	TN (mg N/L)	TN sd	TN n
3	1/17/2013 0:00	2013	Winter	baseflow	1.485	0.062	3	6.692	0.767	3
3	1/23/2013 19:04	2013	Winter	baseflow	3.699	NA	1	12.768	NA	1
3	1/24/2013 0:00	2013	Winter	baseflow	2.517	NA	1	9.750	NA	1
3	1/24/2013 9:30	2013	Winter	baseflow	2.880	NA	1	10.710	NA	1
3	1/25/2013 12:16	2013	Winter	rising limb	3.790	NA	1	10.830	NA	1
3	1/25/2013 15:02	2013	Winter	rising limb	4.250	NA	1	10.890	NA	1
3	1/25/2013 18:31	2013	Winter	rising limb	5.770	NA	1	9.780	NA	1
3	1/25/2013 23:38	2013	Winter	rising limb	7.170	NA	1	8.750	NA	1
3	1/26/2013 3:01	2013	Winter	rising limb	7.490	NA	1	9.150	NA	1
3	1/26/2013 12:24	2013	Winter	rising limb	10.770	NA	1	9.200	NA	1
3	1/27/2013 0:32	2013	Winter	falling limb	6.690	NA	1	12.670	NA	1
3	1/27/2013 8:43	2013	Winter	falling limb	5.409	NA	1	13.066	NA	1
3	1/29/2013 12:45	2013	Winter	baseflow	3.638	NA	1	12.491	NA	1
3	1/29/2013 22:55	2013	Winter	rising limb	5.369	NA	1	11.754	NA	1
3	1/30/2013 0:23	2013	Winter	rising limb	5.636	NA	1	10.971	NA	1
3	1/30/2013 2:32	2013	Winter	rising limb	7.200	NA	1	10.860	NA	1
3	1/30/2013 5:32	2013	Winter	rising limb	8.130	NA	1	8.710	NA	1
3	1/31/2013 9:23	2013	Winter	rising limb	8.876	NA	1	13.543	NA	1
3	1/31/2013 12:00	2013	Winter	rising limb	4.810	NA	1	14.023	NA	1
3	2/1/2013 0:50	2013	Winter	rising limb	4.548	NA	1	14.868	NA	1
3	2/2/2013 0:54	2013	Winter	rising limb	3.790	NA	1	14.920	NA	1
3	2/4/2013 17:53	2013	Winter	baseflow	3.884	NA	1	11.295	NA	1
3	2/5/2013 8:45	2013	Winter	baseflow	2.625	0.032	2	9.654	0.308	2
3	2/5/2013 9:53	2013	Winter	baseflow	5.274	NA	1	14.005	NA	1
3	2/5/2013 9:57	2013	Winter	baseflow	2.477	NA	1	9.747	NA	1
3	2/12/2013 12:00	2013	Winter	baseflow	3.090	NA	1	13.180	NA	1
2, 3	2/19/2013 10:07	2013	Winter	baseflow	11.118	NA	1	12.069	NA	1
2, 3	2/20/2013 3:10	2013	Winter	baseflow	2.518	0.067	2	10.419	0.296	2
2, 3	2/20/2013 12:56	2013	Winter	baseflow	4.589	NA	1	11.884	NA	1
2, 3	2/22/2013 17:18	2013	Winter	rising limb	3.581	NA	1	12.984	NA	1
2, 3	2/22/2013 18:08	2013	Winter	rising limb	5.537	NA	1	11.159	NA	1
2, 3	2/22/2013 20:24	2013	Winter	rising limb	5.032	NA	1	10.893	NA	1
2, 3	2/22/2013 22:19	2013	Winter	rising limb	6.636	NA	1	9.947	NA	1
2, 3	2/23/2013 8:25	2013	Winter	falling limb	4.630	NA	1	11.788	NA	1
2, 3	2/23/2013 17:47	2013	Winter	falling limb	6.003	NA	1	11.545	NA	1
2, 3	2/24/2013 0:31	2013	Winter	falling limb	4.549	NA	1	11.587	NA	1
2, 3	2/25/2013 9:18	2013	Winter	falling limb	3.837	NA	1	12.844	NA	1
2, 3	2/25/2013 12:10	2013	Winter	falling limb	3.293	NA	1	12.894	NA	1

Ch*	DateTime	Water Year	Season	Flow	DOC (mg C/L)	DOC sd	DOC n	TN (mg N/L)	TN sd	TN n
2, 3	2/25/2013 14:59	2013	Winter	falling limb	4.156	NA	1	11.307	NA	1
2, 3	2/25/2013 15:19	2013	Winter	falling limb	6.503	NA	1	9.625	NA	1
2, 3	2/26/2013 0:59	2013	Winter	falling limb	6.719	NA	1	12.201	NA	1
2, 3	2/26/2013 12:03	2013	Winter	falling limb	3.235	NA	1	12.504	NA	1
2, 3	2/26/2013 15:14	2013	Winter	baseflow	3.182	NA	1	12.708	NA	1
2, 3	2/28/2013 22:08	2013	Winter	rising limb	10.875	NA	1	9.972	NA	1
2, 3	3/1/2013 19:11	2013	Spring	falling limb	3.837	NA	1	13.318	NA	1
2, 3	3/3/2013 20:30	2013	Spring	baseflow	5.006	NA	1	12.570	NA	1
2, 3	3/8/2013 10:00	2013	Spring	baseflow	2.670	NA	1	13.618	NA	1
2, 3	3/9/2013 10:41	2013	Spring	baseflow	10.891	NA	1	13.167	NA	1
2, 3	3/11/2013 12:00	2013	Spring	baseflow	2.125	0.159	2	9.487	0.467	2
2, 3	3/16/2013 10:49	2013	Spring	baseflow	3.430	NA	1	13.132	NA	1
2, 3	3/21/2013 11:30	2013	Spring	baseflow	2.630	NA	1	12.317	NA	1
2, 3	3/25/2013 16:25	2013	Spring	baseflow	5.070	NA	1	12.699	NA	1
2, 3	4/1/2013 10:24	2013	Spring	baseflow	3.111	NA	1	12.175	NA	1
2, 3	4/5/2013 10:45	2013	Spring	baseflow	5.182	NA	1	11.273	NA	1
2, 3	4/5/2013 22:28	2013	Spring	baseflow	2.574	NA	1	10.632	NA	1
2, 3	4/6/2013 9:17	2013	Spring	baseflow	2.443	NA	1	12.775	NA	1
2, 3	4/7/2013 8:05	2013	Spring	rising limb	5.865	NA	1	11.769	NA	1
2, 3	4/7/2013 10:14	2013	Spring	rising limb	6.420	NA	1	10.580	NA	1
2, 3	4/7/2013 11:30	2013	Spring	rising limb	9.320	NA	1	10.840	NA	1
2, 3	4/7/2013 14:24	2013	Spring	falling limb	9.262	NA	1	11.223	NA	1
2, 3	4/7/2013 17:09	2013	Spring	falling limb	5.255	NA	1	11.673	NA	1
2, 3	4/8/2013 18:56	2013	Spring	baseflow	2.920	NA	1	12.200	NA	1
2, 3	4/12/2013 22:04	2013	Spring	rising limb	9.338	NA	1	11.749	NA	1
2, 3	4/13/2013 1:50	2013	Spring	rising limb	11.978	NA	1	11.162	NA	1
2, 3	4/13/2013 11:12	2013	Spring	falling limb	4.684	NA	1	12.025	NA	1
2, 3	4/15/2013 16:51	2013	Spring	baseflow	5.442	NA	1	12.275	NA	1
2, 3	4/19/2013 11:46	2013	Spring	baseflow	5.808	NA	1	12.184	NA	1
2, 3	4/21/2013 21:08	2013	Spring	baseflow	3.038	NA	1	12.866	NA	1
2, 3	4/24/2013 15:40	2013	Spring	baseflow	2.163	0.078	2	13.026	0.066	2
2, 3	4/25/2013 14:45	2013	Spring	baseflow	2.172	0.040	2	13.129	0.014	2
2, 3	4/26/2013 10:45	2013	Spring	baseflow	2.075	0.019	2	13.184	0.013	2
2, 3	4/28/2013 6:30	2013	Spring	baseflow	3.000	NA	1	13.918	NA	1
2, 3	4/28/2013 12:19	2013	Spring	baseflow	1.909	NA	1	7.098	NA	1
2, 3	4/30/2013 4:51	2013	Spring	baseflow	2.801	NA	1	12.633	NA	1
2, 3	5/7/2013 4:57	2013	Spring	baseflow	2.240	NA	1	14.658	NA	1
2, 3	5/14/2013 5:06	2013	Spring	baseflow	2.943	NA	1	14.585	NA	1

Ch*	DateTime	Water Year	Season	Flow	DOC (mg C/L)	DOC sd	DOC n	TN (mg N/L)	TN sd	TN n
2, 3	5/21/2013 2:03	2013	Spring	baseflow	5.354	NA	1	14.052	NA	1
2, 3	5/22/2013 0:00	2013	Spring	baseflow	1.717	0.078	2	13.310	0.107	2
2, 3	5/23/2013 20:09	2013	Spring	baseflow	2.132	NA	1	14.379	NA	1
2, 3	5/28/2013 13:21	2013	Spring	baseflow	2.413	NA	1	14.812	NA	1
2, 3	6/3/2013 13:00	2013	Summer	baseflow	2.203	NA	1	14.981	NA	1
2, 3	6/10/2013 12:34	2013	Summer	baseflow	6.366	NA	1	14.177	NA	1
2, 3	6/15/2013 20:23	2013	Summer	baseflow	3.900	NA	1	9.870	NA	1
2, 3	6/16/2013 15:21	2013	Summer	baseflow	2.305	NA	1	15.069	NA	1
2, 3	6/29/2013 7:37	2013	Summer	baseflow	3.539	NA	1	13.359	NA	1
2, 3	7/11/2013 12:00	2013	Summer	baseflow	1.530	0.205	3	11.359	0.196	3
2, 3	7/13/2013 8:45	2013	Summer	baseflow	2.529	NA	1	12.859	NA	1
2, 3	7/20/2013 16:11	2013	Summer	baseflow	2.161	NA	1	12.736	NA	1
2, 3	7/27/2013 15:56	2013	Summer	baseflow	1.746	NA	1	10.817	NA	1
2, 3	9/30/2013 15:10	2013	Fall	baseflow	0.970	0.091	3	7.447	0.614	3

*Data incorporated into chapter 2 or both 2 and 3.

DateTime	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n	DON (mg N/L)	DON sd	C:N
12/8/2010 12:00	3.187	NA	1	0.009	NA	1	0.609	NA	6.77
1/14/2011 12:00	18.629	0.110	2	0.065	0.011	2	1.886	1.655	4.67
1/21/2011 12:00	18.570	NA	1	0.036	NA	1	0.272	NA	33.01
1/28/2011 12:00	18.710	NA	1	0.012	NA	1	1.941	NA	3.34
2/4/2011 12:00	17.359	0.482	2	0.052	0.002	2	1.100	0.866	4.79
2/11/2011 12:00	16.476	NA	1	0.051	NA	1	1.297	NA	6.30
3/4/2011 12:00	21.242	NA	1	0.069	0.020	3	0.338	NA	20.79
3/25/2011 12:00	17.886	NA	1	0.017	NA	1	1.595	NA	4.60
4/1/2011 12:00	17.186	NA	1	0.031	NA	1	1.029	NA	7.60
4/4/2011 12:00	19.640	0.439	2	0.189	0.020	3	NA	NA	NA
4/15/2011 12:00	15.289	NA	1	0.013	NA	1	1.987	NA	3.29
4/22/2011 12:00	15.651	NA	1	0.014	NA	1	1.295	NA	4.35
4/29/2011 12:00	14.944	NA	1	0.011	NA	1	1.818	NA	3.13
5/11/2011 12:00	15.011	0.173	2	0.009	0.005	2	NA	NA	NA
5/13/2011 12:00	14.064	NA	1	0.006	NA	1	0.707	NA	4.19
5/27/2011 12:00	12.841	NA	1	0.025	NA	1	0.714	NA	4.92
6/3/2011 12:00	13.659	NA	1	0.019	NA	1	NA	NA	NA
6/19/2011 12:00	14.106	NA	1	0.005	NA	1	NA	NA	NA
6/23/2011 12:00	14.256	NA	1	0.012	NA	1	NA	NA	NA
6/29/2011 12:00	14.231	NA	1	0.006	NA	1	NA	NA	NA
7/25/2011 12:00	12.322	0.030	2	0.005	0.000	2	1.243	0.624	1.60
10/1/2011 12:00	7.076	0.223	3	0.010	0.009	3	0.913	0.232	2.74
12/15/2011 12:00	4.245	0.036	2	0.011	0.003	3	0.390	0.063	3.18
1/8/2012 22:19	8.353	NA	1	0.007	NA	1	1.063	NA	5.50
1/9/2012 12:00	5.067	NA	1	0.006	NA	1	NA	NA	NA
1/10/2012 0:00	12.376	NA	1	0.016	NA	1	1.320	NA	6.30
1/14/2012 20:24	6.613	NA	1	0.005	NA	1	0.999	NA	3.10
1/15/2012 12:00	4.687	0.090	3	0.010	0.002	3	NA	0.090	NA
1/19/2012 1:27	4.948	NA	1	0.021	NA	1	0.205	NA	16.80
1/19/2012 11:27	4.393	NA	1	0.005	NA	1	0.171	NA	19.97
1/19/2012 18:59	5.625	NA	1	0.025	NA	1	0.076	NA	45.16
1/19/2012 20:24	7.226	NA	1	0.011	NA	1	1.063	NA	3.82
1/20/2012 1:29	7.842	NA	1	0.005	NA	1	0.182	NA	18.08
1/20/2012 10:41	4.487	NA	1	0.011	NA	1	0.997	NA	9.03
1/21/2012 1:11	6.504	NA	1	0.012	NA	1	0.036	NA	83.74
1/21/2012 6:59	7.224	NA	1	0.012	NA	1	0.420	NA	8.50
1/21/2012 12:33	8.594	0.256	2	0.005	0.000	2	1.659	0.322	2.59
1/21/2012 18:44	7.825	NA	1	0.005	NA	1	1.065	NA	3.23

DateTime	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n	DON (mg N/L)	DON sd	C:N
1/22/2012 23:42	5.954	0.887	2	0.005	0.000	2	0.207	1.115	14.78
1/24/2012 23:25	6.393	0.535	2	0.059	0.055	2	0.850	0.862	4.81
1/26/2012 19:37	11.153	NA	1	0.068	NA	1	0.690	NA	17.36
1/29/2012 22:53	6.211	NA	1	0.005	NA	1	0.536	NA	8.54
1/30/2012 1:11	7.443	0.120	2	0.023	0.005	2	1.865	1.154	4.60
1/30/2012 4:30	9.998	0.156	2	0.016	0.002	2	1.612	0.465	5.99
1/30/2012 22:35	12.882	0.261	2	0.014	0.001	2	1.094	0.757	8.61
1/31/2012 20:27	11.041	0.393	2	0.010	0.008	2	2.671	0.399	2.99
2/3/2012 12:00	13.255	0.427	3	0.061	0.028	2	0.285	0.602	12.06
2/14/2012 9:30	11.319	NA	1	0.005	NA	1	NA	NA	NA
2/14/2012 9:50	11.770	NA	1	0.005	NA	1	1.393	NA	3.36
2/15/2012 12:00	12.123	NA	1	0.012	NA	1	0.350	NA	7.24
2/21/2012 10:00	11.648	1.512	2	0.029	0.010	2	0.966	2.492	12.67
2/22/2012 12:00	13.881	0.137	3	0.023	0.003	3	0.318	0.171	15.05
2/23/2012 17:25	11.833	0.037	2	0.016	0.015	2	0.756	0.822	8.06
2/25/2012 8:35	11.566	1.219	2	0.013	0.001	2	0.523	1.281	9.49
2/25/2012 12:44	10.590	1.101	2	0.019	0.005	2	1.714	1.119	3.22
3/2/2012 12:00	10.948	NA	1	0.037	NA	1	NA	NA	NA
3/3/2012 12:50	10.576	0.046	2	0.019	0.020	2	0.757	0.938	6.99
3/9/2012 12:00	13.105	0.421	3	0.011	0.002	3	NA	0.446	NA
3/11/2012 12:55	11.454	0.026	2	0.010	0.007	2	1.871	0.032	2.69
3/13/2012 13:14	12.977	NA	1	0.005	NA	1	1.556	NA	4.18
3/13/2012 13:44	13.527	NA	1	0.100	NA	1	1.430	NA	6.21
3/14/2012 12:49	12.445	NA	1	0.033	NA	1	3.458	NA	2.19
3/15/2012 2:11	14.036	NA	1	0.013	NA	1	1.597	NA	5.99
3/15/2012 15:01	14.836	NA	1	0.030	NA	1	1.793	NA	5.85
3/15/2012 21:11	13.916	NA	1	0.037	NA	1	1.236	NA	7.78
3/16/2012 10:08	14.397	0.250	2	0.025	0.016	2	2.082	0.662	4.47
3/17/2012 17:21	15.220	1.640	3	0.011	0.007	3	2.156	1.805	2.74
3/23/2012 12:00	17.722	NA	1	0.057	NA	1	1.629	NA	3.89
3/29/2012 11:05	15.449	0.014	2	0.017	0.017	2	1.845	0.619	5.53
3/29/2012 12:00	17.729	0.009	2	0.015	0.001	2	0.522	0.231	11.92
3/30/2012 17:17	13.206	NA	1	0.130	NA	1	1.540	NA	7.72
4/1/2012 20:25	13.098	NA	1	0.164	NA	1	5.073	NA	2.46
4/4/2012 12:00	18.492	NA	1	0.014	0.659	2	0.334	NA	19.22
4/6/2012 12:00	17.136	NA	1	0.034	NA	1	2.287	NA	3.69
4/11/2012 12:06	16.665	NA	1	0.043	NA	1	2.172	NA	3.84
4/13/2012 17:00	16.474	NA	1	0.158	NA	1	0.680	NA	11.21

DateTime	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n	DON (mg N/L)	DON sd	C:N
4/15/2012 16:07	12.754	NA	1	0.102	NA	1	1.475	NA	8.96
4/23/2012 12:00	14.083	NA	1	0.021	NA	1	0.267	NA	19.14
5/2/2012 18:40	14.768	NA	1	0.029	NA	1	1.839	NA	3.18
5/3/2012 7:00	14.239	NA	1	0.032	NA	1	1.295	NA	4.13
5/3/2012 18:00	9.538	NA	1	0.088	NA	1	1.229	NA	8.75
5/8/2012 6:33	12.945	NA	1	0.025	NA	1	1.193	NA	6.58
5/21/2012 12:00	11.885	0.831	3	0.005	0.000	3	0.967	1.245	2.42
5/30/2012 12:00	12.263	NA	1	0.005	NA	1	0.168	NA	15.66
6/8/2012 12:00	9.811	NA	1	0.005	NA	1	1.110	NA	1.40
6/11/2012 22:01	10.269	NA	1	0.075	NA	1	0.521	NA	8.81
6/14/2012 12:31	8.857	NA	1	0.109	NA	1	0.714	NA	11.69
6/22/2012 10:48	9.570	NA	1	0.086	NA	1	0.726	NA	14.72
6/24/2012 10:56	10.555	NA	1	0.051	NA	1	0.375	NA	18.93
6/30/2012 20:16	11.100	NA	1	0.036	NA	1	0.593	NA	7.58
7/7/2012 1:23	10.397	NA	1	0.005	NA	1	1.172	NA	2.90
7/10/2012 14:35	8.074	NA	1	0.024	NA	1	0.822	NA	2.33
7/25/2012 12:30	8.900	NA	1	0.013	NA	1	0.585	NA	5.78
8/17/2012 2:00	6.632	0.007	2	0.023	0.019	2	0.730	0.122	6.19
8/30/2012 13:20	7.114	0.027	2	0.007	0.002	2	0.021	0.264	208.73
9/3/2012 15:21	8.054	0.013	2	0.019	0.008	2	0.797	0.148	3.58
9/10/2012 15:31	6.779	0.041	2	0.024	0.019	2	0.771	0.057	5.34
9/16/2012 12:00	5.679	1.348	3	0.005	0.000	3	0.561	2.010	1.43
9/17/2012 8:45	7.158	0.229	2	0.005	0.000	2	0.577	0.270	2.92
9/23/2012 12:00	5.438	0.029	2	0.038	0.038	2	0.737	0.068	7.02
9/26/2012 12:00	6.016	NA	1	0.005	NA	1	1.002	NA	1.22
9/29/2012 12:00	6.331	NA	1	0.005	NA	1	0.828	NA	2.04
10/2/2012 12:00	5.780	NA	1	0.015	NA	1	0.916	NA	1.55
10/5/2012 12:00	5.426	NA	1	0.005	NA	1	0.907	NA	1.37
10/8/2012 12:00	5.445	NA	1	0.005	NA	1	0.838	NA	1.32
10/11/2012 12:00	4.767	NA	1	0.005	NA	1	0.743	NA	5.52
10/12/2012 12:10	5.807	0.395	2	0.005	0.000	2	0.367	0.477	9.90
10/14/2012 12:00	4.513	NA	1	0.005	NA	1	0.799	NA	1.47
10/23/2012 12:00	4.587	0.616	3	0.005	0.000	3	0.419	0.923	2.35
10/23/2012 12:00	4.958	NA	1	0.018	NA	1	0.741	NA	1.78
10/24/2012 10:00	5.297	0.124	2	0.006	0.002	2	0.457	0.234	4.34
10/27/2012 10:00	4.765	0.001	2	0.013	0.000	2	0.241	0.045	25.09
10/30/2012 14:30	5.019	0.190	2	0.049	0.062	2	0.190	0.350	19.96
11/2/2012 10:00	4.804	0.051	2	0.005	0.000	2	0.261	0.058	12.37

DateTime	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n	DON (mg N/L)	DON sd	C:N
11/5/2012 10:00	4.897	0.049	2	0.006	0.001	2	0.105	0.058	31.66
11/8/2012 10:00	5.056	0.029	2	0.008	0.004	2	0.160	0.170	19.45
11/12/2012 20:32	5.929	NA	1	0.005	NA	1	0.542	NA	15.22
11/14/2012 10:00	4.890	0.133	2	0.008	0.004	2	0.477	0.179	6.71
11/17/2012 10:00	4.932	0.288	2	0.008	0.005	2	0.033	0.288	95.68
11/20/2012 10:00	7.107	0.113	2	0.008	0.002	2	0.513	0.329	18.48
11/21/2012 20:32	5.893	NA	1	0.005	NA	1	0.436	NA	18.62
11/28/2012 16:33	6.293	0.271	2	0.010	0.002	2	0.340	0.314	12.29
11/29/2012 6:35	5.972	0.168	2	0.010	0.000	2	0.506	0.170	9.08
11/30/2012 10:00	4.673	NA	1	0.005	NA	1	0.281	NA	24.38
12/3/2012 12:00	8.059	0.094	2	0.007	0.002	3	0.429	0.243	7.01
12/12/2012 12:50	8.554	0.239	2	0.020	0.021	2	0.592	0.250	13.68
12/17/2012 13:38	8.555	0.047	2	0.082	0.053	2	0.809	0.204	6.02
12/18/2012 15:14	8.975	0.053	2	0.005	0.000	2	0.867	0.114	6.45
12/21/2012 12:00	7.989	NA	1	0.024	NA	1	0.471	NA	8.77
12/22/2012 12:00	8.197	NA	1	0.041	NA	1	0.530	NA	5.55
12/23/2012 12:00	8.319	NA	1	0.029	NA	1	0.402	NA	8.46
12/24/2012 12:00	8.966	NA	1	0.059	NA	1	0.668	NA	5.72
12/26/2012 12:00	7.990	NA	1	0.022	NA	1	0.514	NA	5.80
12/28/2012 12:00	7.413	NA	1	0.005	NA	1	0.118	NA	39.43
1/5/2013 12:00	6.391	0.974	2	0.004	0.001	3	0.297	1.240	5.83
1/5/2013 15:05	8.250	NA	1	0.026	NA	1	1.101	NA	4.95
1/9/2013 5:31	8.922	NA	1	0.012	NA	1	1.005	NA	6.50
1/9/2013 8:01	8.818	NA	1	0.010	NA	1	1.108	NA	8.13
1/9/2013 9:27	9.204	NA	1	0.024	NA	1	1.844	NA	5.51
1/9/2013 10:58	9.518	NA	1	0.029	NA	1	1.613	NA	8.53
1/9/2013 13:15	8.927	NA	1	0.013	NA	1	2.066	NA	8.86
1/9/2013 16:54	8.136	NA	1	0.025	NA	1	1.126	NA	11.94
1/10/2013 8:24	12.285	NA	1	0.006	NA	1	1.774	NA	6.71
1/10/2013 16:07	11.924	NA	1	0.020	NA	1	1.027	NA	6.49
1/11/2013 2:24	11.219	0.395	2	0.005	0.000	2	1.140	0.707	4.92
1/11/2013 13:20	10.969	NA	1	0.005	NA	1	0.822	NA	5.88
1/12/2013 6:42	10.976	NA	1	0.005	NA	1	0.900	NA	4.81
1/14/2013 19:45	10.330	NA	1	0.005	NA	1	1.669	NA	4.13
1/17/2013 0:00	6.391	0.974	2	0.004	0.001	3	0.297	1.240	5.83
1/23/2013 19:04	11.365	NA	1	0.009	NA	1	1.393	NA	3.10
1/24/2013 0:00	9.240	NA	1	0.023	NA	1	0.486	NA	6.04
1/24/2013 9:30	9.327	NA	1	0.005	NA	1	1.378	NA	2.44

DateTime	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n	DON (mg N/L)	DON sd	C:N
1/25/2013 12:16	9.434	NA	1	0.022	NA	1	1.374	NA	3.22
1/25/2013 15:02	9.224	NA	1	0.005	NA	1	1.661	NA	2.99
1/25/2013 18:31	8.999	NA	1	0.026	NA	1	0.755	NA	8.92
1/25/2013 23:38	7.756	NA	1	0.020	NA	1	0.974	NA	8.59
1/26/2013 3:01	8.382	NA	1	0.042	NA	1	0.726	NA	12.04
1/26/2013 12:24	8.259	NA	1	0.005	NA	1	0.936	NA	13.42
1/27/2013 0:32	10.976	NA	1	0.049	NA	1	1.645	NA	4.74
1/27/2013 8:43	11.592	NA	1	0.006	NA	1	1.468	NA	4.30
1/29/2013 12:45	11.260	NA	1	0.005	NA	1	1.226	NA	3.46
1/29/2013 22:55	10.323	NA	1	0.009	NA	1	1.422	NA	4.40
1/30/2013 0:23	9.830	NA	1	0.014	NA	1	1.127	NA	5.83
1/30/2013 2:32	9.375	NA	1	0.068	NA	1	1.417	NA	5.93
1/30/2013 5:32	8.162	NA	1	0.033	NA	1	0.515	NA	18.41
1/31/2013 9:23	12.289	NA	1	0.012	NA	1	1.242	NA	8.34
1/31/2013 12:00	13.038	NA	1	0.027	NA	1	0.959	NA	5.85
2/1/2013 0:50	12.729	NA	1	0.005	NA	1	2.134	NA	2.49
2/2/2013 0:54	12.531	NA	1	0.008	NA	1	2.381	NA	1.86
2/4/2013 17:53	10.766	NA	1	0.028	NA	1	0.501	NA	9.05
2/5/2013 8:45	9.085	0.102	2	0.006	0.000	2	0.563	0.324	5.44
2/5/2013 9:53	12.602	NA	1	0.031	NA	1	1.372	NA	4.49
2/5/2013 9:57	9.665	NA	1	0.005	NA	1	0.076	NA	38.08
2/12/2013 12:00	11.370	NA	1	0.109	NA	1	1.701	NA	2.12
2/19/2013 10:07	11.178	NA	1	0.039	NA	1	0.852	NA	15.23
2/20/2013 3:10	9.471	0.199	2	0.008	0.004	2	0.940	0.357	3.13
2/20/2013 12:56	11.178	NA	1	0.031	NA	1	0.674	NA	7.94
2/22/2013 17:18	11.873	NA	1	0.045	NA	1	1.066	NA	3.92
2/22/2013 18:08	10.221	NA	1	0.018	NA	1	0.920	NA	7.02
2/22/2013 20:24	9.487	NA	1	0.002	NA	1	1.404	NA	4.18
2/22/2013 22:19	8.896	NA	1	0.027	NA	1	1.025	NA	7.56
2/23/2013 8:25	10.671	NA	1	0.004	NA	1	1.112	NA	4.86
2/23/2013 17:47	10.570	NA	1	0.010	NA	1	0.965	NA	7.26
2/24/2013 0:31	10.967	NA	1	0.006	NA	1	0.614	NA	8.65
2/25/2013 9:18	11.640	NA	1	0.011	NA	1	1.193	NA	3.75
2/25/2013 12:10	11.706	NA	1	0.050	NA	1	1.138	NA	3.38
2/25/2013 14:59	10.419	NA	1	0.001	NA	1	0.886	NA	5.47
2/25/2013 15:19	8.903	NA	1	0.028	NA	1	0.694	NA	10.93
2/26/2013 0:59	11.180	NA	1	0.032	NA	1	0.989	NA	7.93
2/26/2013 12:03	11.650	NA	1	0.022	NA	1	0.832	NA	4.54

DateTime	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n	DON (mg N/L)	DON sd	C:N
2/26/2013 15:14	11.381	NA	1	0.016	NA	1	1.312	NA	2.83
2/28/2013 22:08	9.138	NA	1	0.012	NA	1	0.823	NA	15.42
3/1/2013 19:11	12.379	NA	1	0.015	NA	1	0.924	NA	4.85
3/3/2013 20:30	11.621	NA	1	0.007	NA	1	0.942	NA	6.20
3/8/2013 10:00	12.096	NA	1	0.023	NA	1	1.499	NA	2.08
3/9/2013 10:41	12.081	NA	1	0.005	NA	1	1.081	NA	11.76
3/11/2013 12:00	8.745	0.186	2	0.003	0.002	2	0.739	0.503	3.36
3/16/2013 10:49	11.788	NA	1	0.008	NA	1	1.337	NA	2.99
3/21/2013 11:30	10.789	NA	1	0.027	NA	1	1.501	NA	2.04
3/25/2013 16:25	11.673	NA	1	0.009	NA	1	1.017	NA	5.82
4/1/2013 10:24	11.483	NA	1	0.047	NA	1	0.645	NA	5.63
4/5/2013 10:45	10.265	NA	1	0.032	NA	1	0.976	NA	6.20
4/5/2013 22:28	9.753	NA	1	0.011	NA	1	0.868	NA	3.46
4/6/2013 9:17	11.078	NA	1	0.006	NA	1	1.690	NA	1.69
4/7/2013 8:05	10.173	NA	1	0.029	NA	1	1.567	NA	4.37
4/7/2013 10:14	9.214	NA	1	0.031	NA	1	1.335	NA	5.61
4/7/2013 11:30	9.428	NA	1	0.085	NA	1	1.327	NA	8.20
4/7/2013 14:24	9.775	NA	1	0.015	NA	1	1.433	NA	7.54
4/7/2013 17:09	10.354	NA	1	0.009	NA	1	1.309	NA	4.68
4/8/2013 18:56	11.152	NA	1	0.009	NA	1	1.039	NA	3.28
4/12/2013 22:04	10.935	NA	1	0.041	NA	1	0.774	NA	14.08
4/13/2013 1:50	9.945	NA	1	0.076	NA	1	1.140	NA	12.25
4/13/2013 11:12	10.996	NA	1	0.021	NA	1	1.008	NA	5.42
4/15/2013 16:51	11.555	NA	1	0.025	NA	1	0.695	NA	9.13
4/19/2013 11:46	11.214	NA	1	0.014	NA	1	0.957	NA	7.08
4/21/2013 21:08	11.505	NA	1	0.002	NA	1	1.359	NA	2.61
4/24/2013 15:40	12.081	0.110	2	0.005	0.004	2	0.940	0.128	2.68
4/25/2013 14:45	12.133	0.163	2	0.004	0.000	2	0.992	0.163	2.56
4/26/2013 10:45	12.028	0.236	2	0.019	0.019	2	1.137	0.237	2.13
4/28/2013 6:30	12.543	NA	1	0.005	NA	1	1.370	NA	2.55
4/28/2013 12:19	6.481	NA	1	0.032	NA	1	0.585	NA	3.80
4/30/2013 4:51	9.985	NA	1	0.052	NA	1	2.596	NA	1.26
5/7/2013 4:57	13.215	NA	1	0.005	NA	1	1.438	NA	1.82
5/14/2013 5:06	13.202	NA	1	0.005	NA	1	1.378	NA	2.49
5/21/2013 2:03	12.807	NA	1	0.005	NA	1	1.239	NA	5.04
5/22/2013 0:00	12.412	0.088	2	0.013	0.022	2	0.885	0.140	2.26
5/23/2013 20:09	13.075	NA	1	0.005	NA	1	1.299	NA	1.91
5/28/2013 13:21	13.651	NA	1	0.005	NA	1	1.156	NA	2.44

DateTime	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n	DON (mg N/L)	DON sd	C:N
6/3/2013 13:00	13.538	NA	1	0.005	NA	1	1.438	NA	1.79
6/10/2013 12:34	12.985	NA	1	0.005	NA	1	1.187	NA	6.26
6/15/2013 20:23	8.862	NA	1	0.171	NA	1	0.837	NA	5.44
6/16/2013 15:21	13.705	NA	1	0.005	NA	1	1.359	NA	1.98
6/29/2013 7:37	12.300	NA	1	0.005	NA	1	1.054	NA	3.92
7/11/2013 12:00	11.731	0.407	3	0.046	0.002	3	NA	0.260	NA
7/13/2013 8:45	11.721	NA	1	0.005	NA	1	1.134	NA	2.60
7/20/2013 16:11	11.373	NA	1	0.005	NA	1	1.358	NA	1.86
7/27/2013 15:56	10.004	NA	1	0.005	NA	1	0.808	NA	2.52
9/30/2013 15:10	6.618	0.560	3	0.005	0.000	3	0.824	0.831	1.37

DateTime	Fluorescence Index (FI)	Freshness Index (β:α)	SUVA (a254 nm)	C1	C2	C3	C4
12/8/2010 12:00	NA	NA	NA	NA	NA	NA	NA
1/14/2011 12:00	1.467	0.648	2.622	1.075	1.259	0.000	0.113
1/21/2011 12:00	NA	NA	NA	NA	NA	NA	NA
1/28/2011 12:00	NA	NA	NA	NA	NA	NA	NA
2/4/2011 12:00	1.608	0.743	1.042	0.238	0.331	0.000	0.027
2/11/2011 12:00	NA	NA	NA	NA	NA	NA	NA
3/4/2011 12:00	1.537	0.706	2.344	0.754	1.001	0.000	0.087
3/25/2011 12:00	NA	NA	NA	NA	NA	NA	NA
4/1/2011 12:00	NA	NA	NA	NA	NA	NA	NA
4/4/2011 12:00	1.540	0.697	3.305	0.635	0.805	0.000	0.049
4/15/2011 12:00	NA	NA	NA	NA	NA	NA	NA
4/22/2011 12:00	NA	NA	NA	NA	NA	NA	NA
4/29/2011 12:00	NA	NA	NA	NA	NA	NA	NA
5/11/2011 12:00	NA	NA	NA	NA	NA	NA	NA
5/13/2011 12:00	1.558	0.714	2.011	0.373	0.463	0.000	0.035
5/27/2011 12:00	NA	NA	NA	NA	NA	NA	NA
6/3/2011 12:00	NA	NA	NA	NA	NA	NA	NA
6/19/2011 12:00	NA	NA	NA	NA	NA	NA	NA
6/23/2011 12:00	NA	NA	NA	NA	NA	NA	NA
6/29/2011 12:00	NA	NA	NA	NA	NA	NA	NA
7/25/2011 12:00	1.603	0.818	1.156	0.129	0.227	0.000	0.180
10/1/2011 12:00	1.619	0.786	0.762	0.097	0.149	0.000	0.042
12/15/2011 12:00	1.575	0.765	2.350	0.096	0.144	0.964	0.051
1/8/2012 22:19	NA	NA	NA	NA	NA	NA	NA
1/9/2012 12:00	NA	NA	NA	NA	NA	NA	NA
1/10/2012 0:00	NA	NA	NA	NA	NA	NA	NA
1/14/2012 20:24	NA	NA	NA	NA	NA	NA	NA
1/15/2012 12:00	1.589	0.757	7.095	0.104	0.147	0.084	0.021
1/19/2012 1:27	NA	NA	NA	NA	NA	NA	NA
1/19/2012 11:27	NA	NA	NA	NA	NA	NA	NA
1/19/2012 18:59	NA	NA	NA	NA	NA	NA	NA
1/19/2012 20:24	NA	NA	NA	NA	NA	NA	NA
1/20/2012 1:29	NA	NA	NA	NA	NA	NA	NA
1/20/2012 10:41	NA	NA	NA	NA	NA	NA	NA
1/21/2012 1:11	NA	NA	NA	NA	NA	NA	NA
1/21/2012 6:59	NA	NA	NA	NA	NA	NA	NA
1/21/2012 12:33	NA	NA	NA	NA	NA	NA	NA
1/21/2012 18:44	NA	NA	NA	NA	NA	NA	NA
1/22/2012 23:42	NA	NA	NA	NA	NA	NA	NA

DateTime	Fluorescence Index (FI)	Freshness Index (β:α)	SUVA (a254 nm)	C1	C2	C3	C4
1/24/2012 23:25	NA	NA	NA	NA	NA	NA	NA
1/26/2012 19:37	NA	NA	NA	NA	NA	NA	NA
1/29/2012 22:53	NA	NA	NA	NA	NA	NA	NA
1/30/2012 1:11	NA	NA	NA	NA	NA	NA	NA
1/30/2012 4:30	NA	NA	NA	NA	NA	NA	NA
1/30/2012 22:35	NA	NA	NA	NA	NA	NA	NA
1/31/2012 20:27	NA	NA	NA	NA	NA	NA	NA
2/3/2012 12:00	1.551	0.724	5.669	0.403	0.514	0.117	0.111
2/14/2012 9:30	NA	NA	NA	NA	NA	NA	NA
2/14/2012 9:50	NA	NA	NA	NA	NA	NA	NA
2/15/2012 12:00	NA	NA	NA	NA	NA	NA	NA
2/21/2012 10:00	NA	NA	NA	NA	NA	NA	NA
2/22/2012 12:00	1.494	0.704	3.767	0.594	0.790	0.267	0.272
2/23/2012 17:25	1.500	0.708	3.878	0.556	0.732	0.136	0.226
2/25/2012 8:35	NA	NA	NA	NA	NA	NA	NA
2/25/2012 12:44	NA	NA	NA	NA	NA	NA	NA
3/2/2012 12:00	NA	NA	NA	NA	NA	NA	NA
3/3/2012 12:50	NA	NA	NA	NA	NA	NA	NA
3/9/2012 12:00	1.586	0.734	2.829	0.311	0.398	0.126	0.054
3/11/2012 12:55	NA	NA	NA	NA	NA	NA	NA
3/13/2012 13:14	NA	NA	NA	NA	NA	NA	NA
3/13/2012 13:44	NA	NA	NA	NA	NA	NA	NA
3/14/2012 12:49	NA	NA	NA	NA	NA	NA	NA
3/15/2012 2:11	NA	NA	NA	NA	NA	NA	NA
3/15/2012 15:01	NA	NA	NA	NA	NA	NA	NA
3/15/2012 21:11	NA	NA	NA	NA	NA	NA	NA
3/16/2012 10:08	NA	NA	NA	NA	NA	NA	NA
3/17/2012 17:21	NA	NA	NA	NA	NA	NA	NA
3/23/2012 12:00	NA	NA	NA	NA	NA	NA	NA
3/29/2012 11:05	NA	NA	NA	NA	NA	NA	NA
3/29/2012 12:00	1.484	0.663	5.151	0.441	0.521	0.076	0.107
3/30/2012 17:17	NA	NA	NA	NA	NA	NA	NA
4/1/2012 20:25	NA	NA	NA	NA	NA	NA	NA
4/4/2012 12:00	NA	NA	NA	NA	NA	NA	NA
4/6/2012 12:00	NA	NA	NA	NA	NA	NA	NA
4/11/2012 12:06	NA	NA	NA	NA	NA	NA	NA
4/13/2012 17:00	NA	NA	NA	NA	NA	NA	NA
4/15/2012 16:07	NA	NA	NA	NA	NA	NA	NA
4/23/2012 12:00	NA	NA	NA	NA	NA	NA	NA

DateTime	Fluorescence Index (FI)	Freshness Index (β:α)	SUVA (a254 nm)	C1	C2	C3	C4
5/2/2012 18:40	NA	NA	NA	NA	NA	NA	NA
5/3/2012 7:00	NA	NA	NA	NA	NA	NA	NA
5/3/2012 18:00	NA	NA	NA	NA	NA	NA	NA
5/8/2012 6:33	NA	NA	NA	NA	NA	NA	NA
5/21/2012 12:00	1.564	0.718	3.085	0.323	0.428	0.243	0.096
5/30/2012 12:00	NA	NA	NA	NA	NA	NA	NA
6/8/2012 12:00	NA	NA	NA	NA	NA	NA	NA
6/11/2012 22:01	NA	NA	NA	NA	NA	NA	NA
6/14/2012 12:31	NA	NA	NA	NA	NA	NA	NA
6/22/2012 10:48	NA	NA	NA	NA	NA	NA	NA
6/24/2012 10:56	NA	NA	NA	NA	NA	NA	NA
6/30/2012 20:16	NA	NA	NA	NA	NA	NA	NA
7/7/2012 1:23	NA	NA	NA	NA	NA	NA	NA
7/10/2012 14:35	1.662	0.783	2.707	0.162	0.247	0.042	0.092
7/25/2012 12:30	NA	NA	NA	NA	NA	NA	NA
8/17/2012 2:00	1.784	0.748	1.352	0.193	0.384	0.566	0.162
8/30/2012 13:20	NA	NA	NA	NA	NA	NA	NA
9/3/2012 15:21	NA	NA	NA	NA	NA	NA	NA
9/10/2012 15:31	NA	NA	NA	NA	NA	NA	NA
9/16/2012 12:00	1.621	0.745	2.619	0.124	0.179	0.153	0.033
9/17/2012 8:45	NA	NA	NA	NA	NA	NA	NA
9/23/2012 12:00	NA	NA	NA	NA	NA	NA	NA
9/26/2012 12:00	NA	NA	NA	NA	NA	NA	NA
9/29/2012 12:00	NA	NA	NA	NA	NA	NA	NA
10/2/2012 12:00	NA	NA	NA	NA	NA	NA	NA
10/5/2012 12:00	NA	NA	NA	NA	NA	NA	NA
10/8/2012 12:00	NA	NA	NA	NA	NA	NA	NA
10/11/2012 12:00	NA	NA	NA	NA	NA	NA	NA
10/12/2012 12:10	NA	NA	NA	NA	NA	NA	NA
10/14/2012 12:00	NA	NA	NA	NA	NA	NA	NA
10/23/2012 12:00	1.583	0.744	2.366	0.129	0.181	0.030	0.052
10/23/2012 12:00	NA	NA	NA	NA	NA	NA	NA
10/24/2012 10:00	NA	NA	NA	NA	NA	NA	NA
10/27/2012 10:00	NA	NA	NA	NA	NA	NA	NA
10/30/2012 14:30	NA	NA	NA	NA	NA	NA	NA
11/2/2012 10:00	NA	NA	NA	NA	NA	NA	NA
11/5/2012 10:00	NA	NA	NA	NA	NA	NA	NA
11/8/2012 10:00	NA	NA	NA	NA	NA	NA	NA
11/12/2012 20:32	NA	NA	NA	NA	NA	NA	NA

DateTime	Fluorescence Index (FI)	Freshness Index (β:α)	SUVA (a254 nm)	C1	C2	C3	C4
11/14/2012 10:00	NA	NA	NA	NA	NA	NA	NA
11/17/2012 10:00	NA	NA	NA	NA	NA	NA	NA
11/20/2012 10:00	NA	NA	NA	NA	NA	NA	NA
11/21/2012 20:32	NA	NA	NA	NA	NA	NA	NA
11/28/2012 16:33	NA	NA	NA	NA	NA	NA	NA
11/29/2012 6:35	NA	NA	NA	NA	NA	NA	NA
11/30/2012 10:00	NA	NA	NA	NA	NA	NA	NA
12/3/2012 12:00	1.546	0.717	2.850	0.353	0.449	0.226	0.103
12/12/2012 12:50	NA	NA	NA	NA	NA	NA	NA
12/17/2012 13:38	NA	NA	NA	NA	NA	NA	NA
12/18/2012 15:14	NA	NA	NA	NA	NA	NA	NA
12/21/2012 12:00	NA	NA	NA	NA	NA	NA	NA
12/22/2012 12:00	NA	NA	NA	NA	NA	NA	NA
12/23/2012 12:00	NA	NA	NA	NA	NA	NA	NA
12/24/2012 12:00	NA	NA	NA	NA	NA	NA	NA
12/26/2012 12:00	NA	NA	NA	NA	NA	NA	NA
12/28/2012 12:00	NA	NA	NA	NA	NA	NA	NA
1/5/2013 12:00	1.587	0.746	2.565	0.206	0.283	0.227	0.069
1/5/2013 15:05	1.622	0.750	1.613	0.225	0.324	0.055	0.073
1/9/2013 5:31	1.567	0.697	2.070	0.553	0.657	0.051	0.081
1/9/2013 8:01	1.518	0.676	1.907	0.731	0.833	0.092	0.118
1/9/2013 9:27	1.506	0.707	1.742	0.832	0.946	0.043	0.090
1/9/2013 10:58	1.514	0.665	1.661	0.974	1.069	0.053	0.114
1/9/2013 13:15	1.497	0.627	1.443	1.156	1.208	0.040	0.112
1/9/2013 16:54	1.466	0.612	2.481	1.324	1.457	0.094	0.202
1/10/2013 8:24	1.563	0.684	1.394	0.758	0.882	0.051	0.081
1/10/2013 16:07	1.562	0.706	1.845	0.568	0.677	0.044	0.088
1/11/2013 2:24	1.583	0.715	1.864	0.473	0.571	0.033	0.059
1/11/2013 13:20	NA	NA	NA	NA	NA	NA	NA
1/12/2013 6:42	NA	NA	NA	NA	NA	NA	NA
1/14/2013 19:45	1.617	0.733	1.037	0.304	0.386	0.015	0.038
1/17/2013 0:00	NA	NA	NA	NA	NA	NA	NA
1/23/2013 19:04	1.603	0.719	2.206	0.413	0.514	0.019	0.042
1/24/2013 0:00	NA	NA	NA	NA	NA	NA	NA
1/24/2013 9:30	1.621	0.735	2.090	0.225	0.309	0.055	0.049
1/25/2013 12:16	1.582	0.750	1.897	0.382	0.522	0.046	0.073
1/25/2013 15:02	1.553	0.683	2.480	0.595	0.687	0.034	0.068
1/25/2013 18:31	1.517	0.665	2.305	0.777	0.875	0.033	0.099
1/25/2013 23:38	1.467	0.631	2.777	1.162	1.212	0.055	0.126

DateTime	Fluorescence Index (FI)	Freshness Index (β:α)	SUVA (a254 nm)	C1	C2	C3	C4
1/26/2013 3:01	1.462	0.621	3.025	1.271	1.337	0.028	0.114
1/26/2013 12:24	1.489	0.616	2.015	1.197	1.279	0.085	0.116
1/27/2013 0:32	1.530	0.665	2.286	0.769	0.883	0.007	0.072
1/27/2013 8:43	1.574	0.693	1.895	0.590	0.720	0.037	0.087
1/29/2013 12:45	1.588	0.738	2.474	0.405	0.557	0.020	0.074
1/29/2013 22:55	1.553	0.702	1.933	0.588	0.772	0.009	0.092
1/30/2013 0:23	1.517	0.662	2.945	0.771	0.870	0.030	0.091
1/30/2013 2:32	1.492	0.646	2.863	1.032	1.131	0.067	0.128
1/30/2013 5:32	1.489	0.622	2.802	0.609	0.667	0.012	0.068
1/31/2013 9:23	1.549	0.691	1.537	0.695	0.908	0.053	0.144
1/31/2013 12:00	1.594	0.714	0.786	0.425	0.512	0.013	0.043
2/1/2013 0:50	1.563	0.685	2.397	0.585	0.687	0.033	0.063
2/2/2013 0:54	1.574	0.705	2.140	0.490	0.596	0.021	0.056
2/4/2013 17:53	NA	NA	NA	NA	NA	NA	NA
2/5/2013 8:45	1.551	0.701	2.722	0.423	0.514	0.045	0.052
2/5/2013 9:53	1.582	0.732	1.612	0.440	0.619	0.110	0.115
2/5/2013 9:57	NA	NA	NA	NA	NA	NA	NA
2/12/2013 12:00	NA	NA	NA	NA	NA	NA	NA
2/19/2013 10:07	NA	NA	NA	NA	NA	NA	NA
2/20/2013 3:10	1.562	0.713	2.269	0.348	0.435	0.204	0.054
2/20/2013 12:56	NA	NA	NA	NA	NA	NA	NA
2/22/2013 17:18	NA	NA	NA	NA	NA	NA	NA
2/22/2013 18:08	NA	NA	NA	NA	NA	NA	NA
2/22/2013 20:24	NA	NA	NA	NA	NA	NA	NA
2/22/2013 22:19	NA	NA	NA	NA	NA	NA	NA
2/23/2013 8:25	NA	NA	NA	NA	NA	NA	NA
2/23/2013 17:47	NA	NA	NA	NA	NA	NA	NA
2/24/2013 0:31	NA	NA	NA	NA	NA	NA	NA
2/25/2013 9:18	NA	NA	NA	NA	NA	NA	NA
2/25/2013 12:10	NA	NA	NA	NA	NA	NA	NA
2/25/2013 14:59	NA	NA	NA	NA	NA	NA	NA
2/25/2013 15:19	NA	NA	NA	NA	NA	NA	NA
2/26/2013 0:59	NA	NA	NA	NA	NA	NA	NA
2/26/2013 12:03	NA	NA	NA	NA	NA	NA	NA
2/26/2013 15:14	NA	NA	NA	NA	NA	NA	NA
2/28/2013 22:08	NA	NA	NA	NA	NA	NA	NA
3/1/2013 19:11	NA	NA	NA	NA	NA	NA	NA
3/3/2013 20:30	NA	NA	NA	NA	NA	NA	NA
3/8/2013 10:00	1.594	0.738	2.985	0.353	0.474	0.038	0.066

DateTime	Fluorescence Index (FI)	Freshness Index (β:α)	SUVA (a254 nm)	C1	C2	C3	C4
3/9/2013 10:41	NA	NA	NA	NA	NA	NA	NA
3/11/2013 12:00	1.567	0.725	2.678	0.319	0.421	1.506	0.080
3/16/2013 10:49	NA	NA	NA	NA	NA	NA	NA
3/21/2013 11:30	1.615	0.728	2.293	0.335	0.417	0.021	0.041
3/25/2013 16:25	1.603	0.742	1.252	0.298	0.384	0.023	0.050
4/1/2013 10:24	NA	NA	NA	NA	NA	NA	NA
4/5/2013 10:45	NA	NA	NA	NA	NA	NA	NA
4/5/2013 22:28	NA	NA	NA	NA	NA	NA	NA
4/6/2013 9:17	1.618	0.733	0.521	0.291	0.383	0.011	0.042
4/7/2013 8:05	1.532	0.681	2.125	0.687	0.832	0.028	0.103
4/7/2013 10:14	1.529	0.671	1.604	0.804	0.948	0.012	0.145
4/7/2013 11:30	1.504	0.624	2.609	1.274	1.399	0.016	0.131
4/7/2013 14:24	1.502	0.654	2.028	1.041	1.159	0.011	0.111
4/7/2013 17:09	1.552	0.697	2.249	0.622	0.737	0.029	0.087
4/8/2013 18:56	1.606	0.733	2.099	0.375	0.498	0.018	0.072
4/12/2013 22:04	NA	NA	NA	NA	NA	NA	NA
4/13/2013 1:50	NA	NA	NA	NA	NA	NA	NA
4/13/2013 11:12	NA	NA	NA	NA	NA	NA	NA
4/15/2013 16:51	NA	NA	NA	NA	NA	NA	NA
4/19/2013 11:46	NA	NA	NA	NA	NA	NA	NA
4/21/2013 21:08	NA	NA	NA	NA	NA	NA	NA
4/24/2013 15:40	1.577	0.784	2.821	0.275	0.342	0.544	0.750
4/25/2013 14:45	1.582	0.786	2.705	0.271	0.338	0.613	0.768
4/26/2013 10:45	1.587	0.790	2.769	0.264	0.331	0.941	0.808
4/28/2013 6:30	NA	NA	NA	NA	NA	NA	NA
4/28/2013 12:19	NA	NA	NA	NA	NA	NA	NA
4/30/2013 4:51	NA	NA	NA	NA	NA	NA	NA
5/7/2013 4:57	NA	NA	NA	NA	NA	NA	NA
5/14/2013 5:06	NA	NA	NA	NA	NA	NA	NA
5/21/2013 2:03	NA	NA	NA	NA	NA	NA	NA
5/22/2013 0:00	1.615	0.747	2.039	0.211	0.289	0.009	0.027
5/23/2013 20:09	NA	NA	NA	NA	NA	NA	NA
5/28/2013 13:21	NA	NA	NA	NA	NA	NA	NA
6/3/2013 13:00	NA	NA	NA	NA	NA	NA	NA
6/10/2013 12:34	NA	NA	NA	NA	NA	NA	NA
6/15/2013 20:23	NA	NA	NA	NA	NA	NA	NA
6/16/2013 15:21	NA	NA	NA	NA	NA	NA	NA
6/29/2013 7:37	NA	NA	NA	NA	NA	NA	NA
7/11/2013 12:00	1.641	0.754	1.572	0.148	0.214	0.001	0.019

DateTime	Fluorescence Index (FI)	Freshness Index (β:α)	SUVA (a254 nm)	C1	C2	C3	C4
7/13/2013 8:45	NA	NA	NA	NA	NA	NA	NA
7/20/2013 16:11	NA	NA	NA	NA	NA	NA	NA
7/27/2013 15:56	NA	NA	NA	NA	NA	NA	NA
9/30/2013 15:10	1.573	0.857	1.317	0.152	0.215	0.065	0.846

DateTime	water T (°C)	EC (µS/cm)	Q (L/s)	Cumulative water year discharge (mm)	Cumulative 2 day discharge (mm)	Cumulative 30 day discharge (mm)	Air T (°C)	Air T (°C) weekly average
12/8/2010 12:00	NA	NA	NA	NA	NA	NA	NA	NA
1/14/2011 12:00	NA	293.00	2.224	NA	NA	NA	NA	NA
1/21/2011 12:00	NA	293.23	0.308	NA	NA	NA	NA	NA
1/28/2011 12:00	NA	288.00	0.182	NA	NA	NA	NA	NA
2/4/2011 12:00	NA	305.69	0.080	NA	NA	NA	NA	NA
2/11/2011 12:00	NA	295.72	0.125	NA	NA	NA	NA	NA
3/4/2011 12:00	NA	303.20	0.455	NA	NA	NA	NA	NA
3/25/2011 12:00	NA	263.32	0.192	NA	NA	NA	NA	NA
4/1/2011 12:00	NA	NA	NA	NA	NA	NA	NA	NA
4/4/2011 12:00	1.00	NA	0.222	NA	NA	NA	NA	NA
4/15/2011 12:00	NA	NA	NA	NA	NA	NA	NA	NA
4/22/2011 12:00	NA	NA	0.063	NA	NA	NA	NA	NA
4/29/2011 12:00	NA	NA	0.500	NA	NA	NA	NA	NA
5/11/2011 12:00	7.49	299.60	0.003	NA	NA	NA	NA	NA
5/13/2011 12:00	9.27	229.00	NA	NA	NA	NA	NA	NA
5/27/2011 12:00	NA	NA	0.020	NA	NA	NA	NA	NA
6/3/2011 12:00	NA	NA	0.018	NA	NA	NA	NA	NA
6/19/2011 12:00	NA	NA	NA	NA	NA	NA	NA	NA
6/23/2011 12:00	NA	NA	0.011	NA	NA	NA	NA	NA
6/29/2011 12:00	NA	NA	NA	NA	NA	NA	NA	NA
7/25/2011 12:00	NA	NA	NA	NA	NA	NA	NA	NA
10/1/2011 12:00	NA	306.50	0.017	0.048	NA	NA	73.1	52.2
12/15/2011 12:00	2.54	275.50	0.040	4.257	0.069	1.340	28.9	26.8
1/8/2012 22:19	5.61	308.00	0.043	5.642	0.071	1.585	35.8	36.5
1/9/2012 12:00	5.68	307.00	0.059	5.662	0.069	1.586	41.5	36.3
1/10/2012 0:00	5.68	307.00	0.049	5.681	0.071	1.586	37.2	36.6
1/14/2012 20:24	5.44	306.00	0.058	5.840	0.068	1.575	28.0	29.8
1/15/2012 12:00	5.34	308.00	0.048	5.866	0.075	1.581	26.7	29.0
1/19/2012 1:27	5.28	307.00	0.054	6.030	0.098	1.617	24.9	26.0
1/19/2012 11:27	5.35	306.00	0.056	6.048	0.096	1.619	32.1	26.4
1/19/2012 18:59	5.22	293.00	0.161	6.064	0.090	1.622	29.3	26.7
1/19/2012 20:24	5.21	271.00	0.281	6.076	0.099	1.631	19.5	26.7
1/20/2012 1:29	5.27	286.00	0.230	6.122	0.134	1.667	21.2	26.5
1/20/2012 10:41	5.27	304.00	0.135	6.172	0.169	1.703	33.9	26.7
1/21/2012 1:11	5.28	296.00	0.198	6.233	0.204	1.745	37.4	26.9
1/21/2012 6:59	5.24	289.00	0.275	6.283	0.243	1.787	40.0	27.1
1/21/2012 12:33	4.95	288.00	0.645	6.448	0.398	1.946	33.9	27.1

DateTime	water T (°C)	EC (μS/cm)	Q (L/s)	Cumulative water year discharge (mm)	Cumulative 2 day discharge (mm)	Cumulative 30 day discharge (mm)	Air T (°C)	Air T (°C) weekly average
1/21/2012 18:44	5.11	301.00	0.386	6.539	0.476	2.029	33.3	27.0
1/22/2012 23:42	5.18	310.00	0.132	6.738	0.513	2.195	31.8	28.1
1/24/2012 23:25	5.10	264.00	0.321	6.881	0.144	2.277	36.3	29.5
1/26/2012 19:37	4.75	307.00	0.624	7.905	1.038	3.235	28.6	32.3
1/29/2012 22:53	4.97	310.00	0.201	8.524	0.283	3.389	36.5	31.8
1/30/2012 1:11	4.86	297.00	0.446	8.547	0.288	3.394	37.0	31.9
1/30/2012 4:30	4.56	274.00	1.373	8.657	0.372	3.481	37.6	32.0
1/30/2012 22:35	3.35	295.00	1.106	9.408	1.013	4.157	33.5	32.9
1/31/2012 20:27	4.28	306.00	0.473	9.844	1.335	4.534	35.4	33.7
2/3/2012 12:00	4.50	315.00	0.283	10.827	0.767	5.372	36.5	33.4
2/14/2012 9:30	4.59	310.00	0.192	12.500	0.375	6.639	33.1	35.9
2/14/2012 9:50	4.59	310.00	0.193	12.502	0.375	6.640	33.1	35.9
2/15/2012 12:00	4.62	310.00	0.150	12.654	0.304	6.746	31.7	35.2
2/21/2012 10:00	4.45	278.00	0.457	13.262	0.208	6.593	41.8	32.9
2/22/2012 12:00	4.74	306.00	0.533	13.760	0.608	6.975	43.5	35.0
2/23/2012 17:25	4.65	313.00	0.296	14.117	0.711	7.256	35.1	35.8
2/25/2012 8:35	4.72	314.00	0.369	14.473	0.452	6.857	29.8	35.7
2/25/2012 12:44	4.72	314.00	0.360	14.524	0.458	6.799	32.8	35.5
3/2/2012 12:00	4.75	315.00	0.153	15.364	0.235	5.304	35.8	28.6
3/3/2012 12:50	4.73	316.00	0.162	15.485	0.228	4.937	42.3	28.4
3/9/2012 12:00	4.63	316.00	0.194	16.929	0.328	5.367	61.6	37.9
3/11/2012 12:55	4.67	314.00	0.218	17.222	0.289	5.459	37.2	39.6
3/13/2012 13:14	4.57	298.00	0.372	17.599	0.375	5.442	37.8	38.9
3/13/2012 13:44	4.56	298.00	0.383	17.605	0.377	5.444	37.8	38.9
3/14/2012 12:49	4.67	314.00	0.313	17.858	0.481	5.502	39.0	39.5
3/15/2012 2:11	4.68	317.00	0.323	17.997	0.521	5.545	38.8	39.9
3/15/2012 15:01	4.88	288.00	0.753	18.190	0.566	5.655	48.3	40.1
3/15/2012 21:11	4.56	278.00	1.090	18.384	0.688	5.812	43.9	40.1
3/16/2012 10:08	4.40	279.00	1.396	18.915	1.084	6.271	38.4	39.7
3/17/2012 17:21	4.78	321.00	0.181	19.142	0.887	6.363	40.9	38.3
3/23/2012 12:00	4.10	277.00	0.094	19.651	0.171	5.890	36.9	34.5
3/29/2012 11:05	5.19	231.00	0.090	20.011	0.115	5.019	45.7	39.8
3/29/2012 12:00	5.31	285.00	0.337	20.022	0.124	5.024	46.6	39.9
3/30/2012 17:17	5.82	221.00	0.913	20.549	0.578	5.391	40.3	41.8
4/1/2012 20:25	5.21	274.00	0.731	21.961	1.323	6.556	34.5	41.8
4/4/2012 12:00	5.33	291.00	0.910	23.449	1.110	7.432	32.9	41.4
4/6/2012 12:00	5.01	283.00	1.081	25.007	1.558	8.407	32.9	38.2

DateTime	water T (°C)	EC (µS/cm)	Q (L/s)	Cumulative water year discharge (mm)	Cumulative 2 day discharge (mm)	Cumulative 30 day discharge (mm)	Air T (°C)	Air T (°C) weekly average
4/11/2012 12:06	5.76	308.00	1.832	32.697	3.066	15.325	60.2	43.3
4/13/2012 17:00	6.06	306.00	1.632	35.648	2.654	17.746	51.8	47.3
4/15/2012 16:07	6.23	314.00	1.384	37.950	2.355	18.979	53.3	48.5
4/23/2012 12:00	7.39	300.00	1.518	47.682	2.375	27.966	76.3	52.2
5/2/2012 18:40	8.32	322.00	2.537	59.880	2.955	37.387	46.6	45.6
5/3/2012 7:00	8.26	318.00	2.046	60.789	3.116	38.009	43.1	44.6
5/3/2012 18:00	8.48	233.00	2.949	61.569	3.248	38.545	46.1	44.6
5/8/2012 6:33	8.11	319.00	1.634	69.122	2.751	41.655	52.3	44.6
5/21/2012 12:00	9.08	337.00	0.979	80.967	1.440	35.660	66.3	58.3
5/30/2012 12:00	9.40	335.00	0.750	87.329	1.236	30.800	59.3	51.6
6/8/2012 12:00	9.99	334.00	0.445	91.460	0.741	20.853	52.4	52.6
6/11/2012 22:01	9.90	341.00	0.365	92.543	0.608	18.464	53.5	49.0
6/14/2012 12:31	9.90	346.00	0.314	93.236	0.523	16.834	64.1	53.1
6/22/2012 10:48	10.33	356.00	0.198	94.801	0.330	12.244	70.3	59.6
6/24/2012 10:56	10.46	357.00	0.176	95.095	0.294	11.037	61.2	59.1
6/30/2012 20:16	10.89	359.00	0.122	95.835	0.203	7.744	59.5	59.5
7/7/2012 1:23	11.22	362.00	0.085	96.333	0.141	5.401	54.5	61.3
7/10/2012 14:35	11.80	358.00	0.069	96.547	0.115	4.395	84.0	67.2
7/25/2012 12:30	15.42	364.00	0.030	97.088	0.048	1.849	81.0	65.6
8/17/2012 2:00	NA	NA	0.011	97.427	0.018	0.551	48.2	70.7
8/30/2012 13:20	13.95	343.00	0.006	97.515	0.010	0.301	76.9	62.2
9/3/2012 15:21	13.98	341.00	0.017	97.549	0.022	0.267	77.1	60.5
9/10/2012 15:31	13.59	337.00	0.069	97.862	0.123	0.488	64.7	63.1
9/16/2012 12:00	13.45	335.00	0.080	98.167	0.094	0.737	75.6	58.7
9/17/2012 8:45	13.38	329.00	0.041	98.221	0.114	0.783	66.4	58.5
9/23/2012 12:00	13.39	325.00	0.041	98.296	0.043	0.822	64.6	63.4
9/26/2012 12:00	13.31	324.00	0.080	98.430	0.101	0.938	70.2	60.8
9/29/2012 12:00	13.27	322.00	0.046	98.591	0.106	1.082	73.8	58.6
10/2/2012 12:00	12.99	322.00	0.032	0.060	0.090	1.218	67.1	48.1
10/5/2012 12:00	12.74	322.00	0.056	0.155	0.069	1.279	56.3	48.1
10/8/2012 12:00	12.48	321.00	0.085	0.305	0.108	1.331	65.3	47.5
10/11/2012 12:00	12.36	319.00	0.089	0.473	0.113	1.320	69.2	48.4
10/12/2012 12:10	12.21	318.00	0.076	0.538	0.122	1.333	62.7	50.4
10/14/2012 12:00	12.18	317.00	0.046	0.627	0.090	1.297	62.9	52.8
10/23/2012 12:00	11.43	313.00	0.055	1.029	0.096	1.415	38.1	42.9
10/23/2012 12:00	11.43	313.00	0.055	1.029	0.096	1.415	38.1	42.9
10/24/2012 10:00	11.27	313.00	0.056	1.067	0.090	1.423	38.2	42.0

DateTime	water T (°C)	EC (µS/cm)	Q (L/s)	Cumulative water year discharge (mm)	Cumulative 2 day discharge (mm)	Cumulative 30 day discharge (mm)	Air T (°C)	Air T (°C) weekly average
10/27/2012 10:00	10.96	314.00	0.061	1.187	0.081	1.388	41.1	36.1
10/30/2012 14:30	10.81	307.00	0.084	1.467	0.201	1.492	54.9	41.6
11/2/2012 10:00	10.68	309.00	0.073	1.628	0.108	1.545	52.1	47.9
11/5/2012 10:00	10.67	309.00	0.059	1.772	0.089	1.580	61.6	50.8
11/8/2012 10:00	10.47	312.00	0.087	1.929	0.110	1.572	35.5	48.5
11/12/2012 20:32	10.01	311.00	0.067	2.176	0.099	1.571	33.2	35.8
11/14/2012 10:00	10.04	311.00	0.145	2.356	0.202	1.695	38.6	32.1
11/17/2012 10:00	9.50	311.00	0.103	2.627	0.170	1.836	46.5	35.3
11/20/2012 10:00	9.26	284.00	0.464	3.020	0.312	2.090	46.1	40.2
11/21/2012 20:32	9.13	318.00	0.231	3.458	0.576	2.458	35.0	41.4
11/28/2012 16:33	8.72	317.00	0.153	4.423	0.230	3.027	39.6	36.1
11/29/2012 6:35	8.66	317.00	0.149	4.487	0.226	3.043	41.2	36.5
11/30/2012 10:00	8.58	316.00	0.170	4.627	0.237	3.107	46.7	37.9
12/3/2012 12:00	8.38	316.00	0.387	5.605	0.830	3.918	46.5	41.0
12/12/2012 12:50	7.93	297.00	0.493	8.727	0.594	6.567	34.7	31.6
12/17/2012 13:38	7.34	298.00	0.712	10.794	0.723	8.154	36.5	32.0
12/18/2012 15:14	7.24	314.00	0.585	11.395	0.964	8.672	27.8	31.3
12/21/2012 12:00	7.09	319.00	0.374	12.389	0.649	9.010	37.1	31.3
12/22/2012 12:00	7.03	319.00	0.372	12.677	0.585	9.117	38.7	32.4
12/23/2012 12:00	6.96	316.00	0.400	12.942	0.553	9.256	35.2	32.8
12/24/2012 12:00	6.88	315.00	0.344	13.236	0.559	9.383	30.7	32.4
12/26/2012 12:00	6.75	315.00	0.360	13.811	0.576	9.642	33.9	32.6
12/28/2012 12:00	6.64	316.00	0.349	14.335	0.524	9.935	29.0	30.9
1/5/2013 12:00	6.27	319.00	0.309	16.282	0.466	9.654	29.8	21.2
1/5/2013 15:05	6.26	318.00	0.292	16.313	0.465	9.648	20.4	21.3
1/9/2013 5:31	5.96	287.00	0.812	17.299	0.603	9.245	38.7	27.3
1/9/2013 8:01	5.84	261.00	1.157	17.381	0.656	9.299	38.2	27.6
1/9/2013 9:27	5.70	252.00	1.470	17.435	0.698	9.340	38.2	27.7
1/9/2013 10:58	5.49	241.00	1.902	17.520	0.767	9.409	37.1	27.8
1/9/2013 13:15	5.18	212.00	2.470	17.704	0.923	9.565	41.1	28.1
1/9/2013 16:54	4.11	177.00	2.925	18.015	1.200	9.838	37.6	28.4
1/10/2013 8:24	4.97	292.00	2.140	19.394	2.427	11.038	27.1	30.0
1/10/2013 16:07	5.26	304.00	1.664	19.864	2.812	11.415	26.2	30.2
1/11/2013 2:24	5.44	311.00	1.244	20.352	3.129	11.774	19.6	30.6
1/11/2013 13:20	5.55	315.00	1.044	20.760	3.056	12.024	22.2	30.0
1/12/2013 6:42	5.62	319.00	0.890	21.301	2.033	12.177	18.6	29.1
1/14/2013 19:45	5.69	322.00	0.590	22.739	1.077	12.572	21.8	25.3

DateTime	water T (°C)	EC (µS/cm)	Q (L/s)	Cumulative water year discharge (mm)	Cumulative 2 day discharge (mm)	Cumulative 30 day discharge (mm)	Air T (°C)	Air T (°C) weekly average
1/17/2013 0:00	5.66	322.00	0.485	23.608	0.788	12.524	26.1	21.8
1/23/2013 19:04	5.52	322.00	0.395	25.868	0.616	12.559	34.3	26.6
1/24/2013 0:00	5.52	322.00	0.350	25.927	0.612	12.564	27.0	26.6
1/24/2013 9:30	5.51	322.00	0.338	26.034	0.600	12.555	32.2	26.8
1/25/2013 12:16	5.45	309.00	0.519	26.367	0.587	12.553	38.5	28.2
1/25/2013 15:02	5.31	281.00	0.789	26.426	0.609	12.580	37.0	28.3
1/25/2013 18:31	5.09	248.00	1.184	26.543	0.682	12.658	37.1	28.4
1/25/2013 23:38	4.20	197.00	1.918	26.783	0.862	12.844	35.8	28.6
1/26/2013 3:01	3.76	194.00	2.457	27.042	1.081	13.065	32.7	28.8
1/26/2013 12:24	3.69	220.00	2.543	27.844	1.779	13.768	37.5	29.2
1/27/2013 0:32	4.20	269.00	2.063	28.808	2.595	14.599	30.0	29.5
1/27/2013 8:43	4.54	293.00	1.638	29.286	2.973	14.990	30.1	29.8
1/29/2013 12:45	4.86	307.00	1.059	31.544	2.038	16.675	33.8	32.1
1/29/2013 22:55	4.74	278.00	1.432	31.902	1.897	16.928	34.6	32.8
1/30/2013 0:23	4.48	248.00	1.832	31.984	1.909	16.995	34.7	32.8
1/30/2013 2:32	4.19	234.00	2.381	32.143	1.965	17.131	35.0	32.9
1/30/2013 5:32	3.39	195.00	2.929	32.418	2.108	17.374	34.7	33.0
1/31/2013 9:23	4.08	273.00	2.615	35.187	3.764	19.872	39.0	34.1
1/31/2013 12:00	4.13	277.00	2.550	35.417	3.898	20.076	43.9	34.3
2/1/2013 0:50	4.37	296.00	2.107	36.376	4.360	20.911	37.3	34.5
2/2/2013 0:54	4.52	303.00	1.651	37.820	3.417	22.115	33.4	34.6
2/4/2013 17:53	4.71	307.00	1.266	40.893	2.187	24.553	38.6	36.8
2/5/2013 8:45	4.75	306.00	1.221	41.512	2.075	25.021	38.0	37.3
2/5/2013 9:53	4.75	306.00	1.215	41.552	2.069	25.052	40.1	37.4
2/5/2013 9:57	4.75	306.00	1.215	41.552	2.069	25.052	40.1	37.4
2/12/2013 12:00	4.88	299.00	1.032	47.654	1.616	25.599	41.8	32.8
2/19/2013 10:07	5.04	307.00	0.813	52.642	1.360	27.829	35.0	36.9
2/20/2013 3:10	5.03	306.00	0.795	53.102	1.342	28.061	30.3	36.0
2/20/2013 12:56	5.04	306.00	0.829	53.356	1.321	28.188	36.0	35.5
2/22/2013 17:18	4.96	288.00	1.077	54.752	1.276	28.907	32.5	33.7
2/22/2013 18:08	4.94	284.00	1.110	54.779	1.284	28.924	33.8	33.7
2/22/2013 20:24	4.79	261.00	1.441	54.874	1.322	28.991	37.4	33.7
2/22/2013 22:19	4.63	242.00	1.845	54.982	1.379	29.075	35.5	33.7
2/23/2013 8:25	4.55	275.00	1.684	55.623	1.773	29.603	30.4	33.2
2/23/2013 17:47	4.19	237.00	2.035	56.196	2.103	30.065	33.6	32.6
2/24/2013 0:31	4.49	280.00	1.648	56.603	2.329	30.390	28.2	32.4
2/25/2013 9:18	4.77	304.00	1.354	58.160	2.483	30.570	35.0	32.0

DateTime	water T (°C)	EC (µS/cm)	Q (L/s)	Cumulative water year discharge (mm)	Cumulative 2 day discharge (mm)	Cumulative 30 day discharge (mm)	Air T (°C)	Air T (°C) weekly average
2/25/2013 12:10	4.77	304.00	1.400	58.288	2.461	30.465	38.3	32.0
2/25/2013 14:59	4.60	272.00	1.667	58.426	2.430	30.375	38.8	32.0
2/25/2013 15:19	4.58	272.00	1.677	58.454	2.424	30.361	38.2	32.0
2/26/2013 0:59	4.58	291.00	1.478	58.955	2.339	30.130	29.5	32.0
2/26/2013 12:03	4.72	304.00	1.289	59.444	2.290	29.976	36.6	31.8
2/26/2013 15:14	4.70	301.00	1.339	59.573	2.278	29.950	37.8	31.9
2/28/2013 22:08	4.04	231.00	2.166	62.006	2.125	30.137	37.4	33.3
3/1/2013 19:11	4.45	291.00	1.806	63.379	2.623	29.569	41.1	34.6
3/3/2013 20:30	4.70	309.00	1.378	66.008	2.556	28.436	29.6	37.1
3/8/2013 10:00	4.89	310.00	1.181	70.643	1.942	28.164	43.1	38.0
3/9/2013 10:41	4.94	311.00	1.054	71.483	1.861	28.165	40.5	36.7
3/11/2013 12:00	4.98	312.00	1.075	73.305	1.710	28.113	45.3	37.1
3/16/2013 10:49	5.25	315.00	1.024	77.291	1.554	28.151	44.2	44.2
3/21/2013 11:30	5.48	316.00	0.834	79.160	1.547	28.309	35.8	39.9
3/25/2013 16:25	5.53	317.00	0.954	79.353	1.527	28.310	48.6	34.7
4/1/2013 10:24	5.81	321.00	0.752	83.749	1.290	27.408	57.9	47.5
4/5/2013 10:45	6.20	309.00	0.699	86.136	1.199	25.320	49.6	50.4
4/5/2013 22:28	6.25	314.00	0.611	86.388	1.158	25.115	45.3	50.4
4/6/2013 9:17	6.30	315.00	0.652	86.618	1.095	24.821	47.6	50.5
4/7/2013 8:05	6.36	279.00	1.007	87.139	1.064	23.834	42.3	49.8
4/7/2013 10:14	6.36	263.00	1.278	87.215	1.096	23.792	47.8	49.6
4/7/2013 11:30	6.37	241.00	1.677	87.276	1.128	23.779	48.8	49.5
4/7/2013 14:24	6.57	255.00	1.611	87.448	1.229	23.778	49.7	49.2
4/7/2013 17:09	6.49	283.00	1.165	87.571	1.291	23.745	37.9	48.8
4/8/2013 18:56	6.54	309.00	0.793	88.357	1.534	23.121	39.7	46.9
4/12/2013 22:04	6.73	314.00	1.040	90.907	1.203	21.325	40.0	42.1
4/13/2013 1:50	6.64	253.00	1.571	91.068	1.278	21.332	39.5	42.0
4/13/2013 11:12	6.70	302.00	1.263	91.497	1.493	21.383	40.1	41.5
4/15/2013 16:51	6.74	321.00	0.809	93.128	1.411	21.020	44.6	39.8
4/19/2013 11:46	6.67	308.00	1.062	95.372	1.219	20.083	46.3	38.1
4/21/2013 21:08	6.65	321.00	0.812	97.246	1.525	20.086	36.6	40.0
4/24/2013 15:40	6.70	326.00	0.929	99.007	1.294	19.677	59.0	42.0
4/25/2013 14:45	6.74	327.00	0.754	99.634	1.280	19.623	65.0	43.4
4/26/2013 10:45	6.76	328.00	0.658	100.068	1.199	19.498	64.4	44.5
4/28/2013 6:30	6.87	330.00	0.611	101.081	1.101	19.337	45.9	47.3
4/28/2013 12:19	6.89	331.00	0.714	101.204	1.103	19.312	55.2	47.5
4/30/2013 4:51	7.01	332.00	0.721	102.195	1.151	19.230	27.3	49.1

DateTime	water T (°C)	EC (μS/cm)	Q (L/s)	Cumulative water year discharge (mm)	Cumulative 2 day discharge (mm)	Cumulative 30 day discharge (mm)	Air T (°C)	Air T (°C) weekly average
5/7/2013 4:57	7.43	337.00	0.590	105.786	0.953	18.738	47.8	53.1
5/14/2013 5:06	8.43	339.00	0.482	108.726	0.779	16.628	43.6	65.7
5/21/2013 2:03	9.15	341.00	0.395	111.085	0.639	14.410	56.0	52.9
5/22/2013 0:00	9.19	341.00	0.385	111.366	0.622	14.043	38.1	53.2
5/23/2013 20:09	9.29	359.00	0.365	111.906	0.590	13.407	45.9	50.2
5/28/2013 13:21	9.34	343.00	0.319	113.171	0.515	11.942	59.9	47.1
6/3/2013 13:00	9.48	346.00	0.268	114.548	0.434	10.040	66.9	52.0
6/10/2013 12:34	9.98	347.00	0.219	115.880	0.355	8.212	68.8	62.2
6/15/2013 20:23	10.42	346.00	0.188	116.730	0.304	7.045	57.6	56.6
6/16/2013 15:21	10.49	348.00	0.184	116.846	0.297	6.886	83.0	56.9
6/29/2013 7:37	11.21	345.00	0.128	118.380	0.206	4.779	76.0	61.8
7/11/2013 12:00	12.53	346.00	0.090	119.411	0.145	3.364	75.0	66.0
7/13/2013 8:45	12.61	345.00	0.085	119.539	0.138	3.188	61.4	65.3
7/20/2013 16:11	13.09	348.00	0.069	119.980	0.112	2.584	88.8	68.3
7/27/2013 15:56	13.43	344.00	0.056	120.323	0.091	2.112	83.9	71.0
9/30/2013 15:10	13.19	329.00	0.009	121.625	0.014	0.325	54.1	48.0

DateTime	Average water table height (m)	Maximum water table height (m)	water table height at location 95 (m)	water table depth good?
12/8/2010 12:00	NA	NA	NA	NA
1/14/2011 12:00	NA	NA	NA	NA
1/21/2011 12:00	NA	NA	NA	NA
1/28/2011 12:00	NA	NA	NA	NA
2/4/2011 12:00	NA	NA	NA	NA
2/11/2011 12:00	NA	NA	NA	NA
3/4/2011 12:00	NA	NA	NA	NA
3/25/2011 12:00	NA	NA	NA	NA
4/1/2011 12:00	NA	NA	NA	NA
4/4/2011 12:00	NA	NA	NA	NA
4/15/2011 12:00	NA	NA	NA	NA
4/22/2011 12:00	NA	NA	NA	NA
4/29/2011 12:00	NA	NA	NA	NA
5/11/2011 12:00	NA	NA	NA	NA
5/13/2011 12:00	NA	NA	NA	NA
5/27/2011 12:00	NA	NA	NA	NA
6/3/2011 12:00	NA	NA	NA	NA
6/19/2011 12:00	NA	NA	NA	NA
6/23/2011 12:00	NA	NA	NA	NA
6/29/2011 12:00	NA	NA	NA	NA
7/25/2011 12:00	NA	NA	NA	NA
10/1/2011 12:00	-2.16	-2.16	-2.16	1
12/15/2011 12:00	-1.02	-0.90	-1.14	1
1/8/2012 22:19	NA	NA	NA	NA
1/9/2012 12:00	NA	NA	NA	NA
1/10/2012 0:00	NA	NA	NA	NA
1/14/2012 20:24	NA	NA	NA	NA
1/15/2012 12:00	NA	NA	NA	NA
1/19/2012 1:27	NA	NA	NA	NA
1/19/2012 11:27	NA	NA	NA	NA
1/19/2012 18:59	NA	NA	NA	NA
1/19/2012 20:24	NA	NA	NA	NA
1/20/2012 1:29	NA	NA	NA	NA
1/20/2012 10:41	NA	NA	NA	NA
1/21/2012 1:11	NA	NA	NA	NA
1/21/2012 6:59	NA	NA	NA	NA
1/21/2012 12:33	NA	NA	NA	NA

DateTime	Average water table height (m)	Maximum water table height (m)	water table height at location 95 (m)	water table depth good?
1/21/2012 18:44	NA	NA	NA	NA
1/22/2012 23:42	NA	NA	NA	NA
1/24/2012 23:25	NA	NA	NA	NA
1/26/2012 19:37	NA	NA	NA	NA
1/29/2012 22:53	NA	NA	NA	NA
1/30/2012 1:11	NA	NA	NA	NA
1/30/2012 4:30	NA	NA	NA	NA
1/30/2012 22:35	NA	NA	NA	NA
1/31/2012 20:27	NA	NA	NA	NA
2/3/2012 12:00	-0.54	0.00	-0.76	1
2/14/2012 9:30	NA	NA	NA	NA
2/14/2012 9:50	NA	NA	NA	NA
2/15/2012 12:00	-1.17	-0.90	NA	NA
2/21/2012 10:00	NA	NA	NA	NA
2/22/2012 12:00	-1.17	-0.46	-1.20	1
2/23/2012 17:25	NA	NA	NA	NA
2/25/2012 8:35	NA	NA	NA	NA
2/25/2012 12:44	NA	NA	NA	NA
3/2/2012 12:00	-1.29	-0.77	-1.19	1
3/3/2012 12:50	NA	NA	-1.13	NA
3/9/2012 12:00	-0.60	-0.18	-0.74	1
3/11/2012 12:55	NA	NA	NA	NA
3/13/2012 13:14	NA	NA	NA	NA
3/13/2012 13:44	NA	NA	NA	NA
3/14/2012 12:49	NA	NA	NA	NA
3/15/2012 2:11	NA	NA	NA	NA
3/15/2012 15:01	NA	NA	NA	NA
3/15/2012 21:11	NA	NA	NA	NA
3/16/2012 10:08	-1.13	-0.45	-0.76	1
3/17/2012 17:21	NA	NA	NA	NA
3/23/2012 12:00	-0.78	-0.45	-0.55	1
3/29/2012 11:05	NA	NA	NA	NA
3/29/2012 12:00	NA	NA	NA	NA
3/30/2012 17:17	NA	NA	NA	NA
4/1/2012 20:25	NA	NA	NA	NA
4/4/2012 12:00	-1.02	-0.50	-0.55	NA
4/6/2012 12:00	-1.02	-0.50	-0.55	NA

DateTime	Average water table height (m)	Maximum water table height (m)	water table height at location 95 (m)	water table depth good?
4/11/2012 12:06	NA	NA	NA	NA
4/13/2012 17:00	NA	NA	NA	NA
4/15/2012 16:07	NA	NA	NA	NA
4/23/2012 12:00	NA	NA	NA	NA
5/2/2012 18:40	NA	NA	NA	NA
5/3/2012 7:00	NA	NA	NA	NA
5/3/2012 18:00	NA	NA	NA	NA
5/8/2012 6:33	NA	NA	NA	NA
5/21/2012 12:00	-1.19	-1.18	-1.19	NA
5/30/2012 12:00	NA	NA	NA	NA
6/8/2012 12:00	NA	NA	NA	NA
6/11/2012 22:01	NA	NA	NA	NA
6/14/2012 12:31	NA	NA	NA	NA
6/22/2012 10:48	-1.57	-1.25	-1.25	1
6/24/2012 10:56	NA	NA	NA	NA
6/30/2012 20:16	NA	NA	NA	NA
7/7/2012 1:23	-1.82	-1.29	-1.29	NA
7/10/2012 14:35	NA	NA	NA	NA
7/25/2012 12:30	NA	NA	NA	NA
8/17/2012 2:00	NA	NA	NA	NA
8/30/2012 13:20	NA	NA	NA	NA
9/3/2012 15:21	NA	NA	NA	NA
9/10/2012 15:31	NA	NA	NA	NA
9/16/2012 12:00	-1.29	-0.83	-1.76	1
9/17/2012 8:45	NA	NA	NA	NA
9/23/2012 12:00	NA	NA	NA	NA
9/26/2012 12:00	NA	NA	NA	NA
9/29/2012 12:00	NA	NA	NA	NA
10/2/2012 12:00	NA	NA	NA	NA
10/5/2012 12:00	NA	NA	NA	NA
10/8/2012 12:00	NA	NA	NA	NA
10/11/2012 12:00	NA	NA	NA	NA
10/12/2012 12:10	-1.85	-0.84	-1.77	1
10/14/2012 12:00	NA	NA	NA	NA
10/23/2012 12:00	NA	NA	NA	NA
10/23/2012 12:00	NA	NA	NA	NA
10/24/2012 10:00	NA	NA	-1.67	NA

DateTime	Average water table height (m)	Maximum water table height (m)	water table height at location 95 (m)	water table depth good?
10/27/2012 10:00	NA	NA	NA	NA
10/30/2012 14:30	NA	NA	NA	NA
11/2/2012 10:00	NA	NA	NA	NA
11/5/2012 10:00	NA	NA	NA	NA
11/8/2012 10:00	NA	NA	NA	NA
11/12/2012 20:32	NA	NA	NA	NA
11/14/2012 10:00	NA	NA	NA	NA
11/17/2012 10:00	NA	NA	NA	NA
11/20/2012 10:00	NA	NA	NA	NA
11/21/2012 20:32	NA	NA	NA	NA
11/28/2012 16:33	NA	NA	NA	NA
11/29/2012 6:35	NA	NA	NA	NA
11/30/2012 10:00	NA	NA	NA	NA
12/3/2012 12:00	-1.26	-0.84	-1.47	1
12/12/2012 12:50	NA	NA	NA	NA
12/17/2012 13:38	NA	NA	NA	NA
12/18/2012 15:14	NA	NA	NA	NA
12/21/2012 12:00	NA	NA	NA	NA
12/22/2012 12:00	NA	NA	NA	NA
12/23/2012 12:00	NA	NA	NA	NA
12/24/2012 12:00	NA	NA	NA	NA
12/26/2012 12:00	NA	NA	NA	NA
12/28/2012 12:00	NA	NA	NA	NA
1/5/2013 12:00	-0.92	-0.34	-1.38	NA
1/5/2013 15:05	-0.92	-0.34	-1.38	NA
1/9/2013 5:31	NA	NA	NA	NA
1/9/2013 8:01	NA	NA	NA	NA
1/9/2013 9:27	NA	NA	NA	NA
1/9/2013 10:58	NA	NA	NA	NA
1/9/2013 13:15	NA	NA	NA	NA
1/9/2013 16:54	NA	NA	NA	NA
1/10/2013 8:24	NA	NA	NA	NA
1/10/2013 16:07	NA	NA	NA	NA
1/11/2013 2:24	NA	NA	NA	NA
1/11/2013 13:20	NA	NA	NA	NA
1/12/2013 6:42	NA	NA	NA	NA
1/14/2013 19:45	NA	NA	NA	NA

DateTime	Average water table height (m)	Maximum water table height (m)	water table height at location 95 (m)	water table depth good?
1/17/2013 0:00	NA	NA	NA	NA
1/23/2013 19:04	NA	NA	NA	NA
1/24/2013 0:00	-0.83	-0.54	-0.85	1
1/24/2013 9:30	-0.83	-0.54	-0.85	1
1/25/2013 12:16	NA	NA	NA	NA
1/25/2013 15:02	NA	NA	NA	NA
1/25/2013 18:31	NA	NA	NA	NA
1/25/2013 23:38	NA	NA	NA	NA
1/26/2013 3:01	NA	NA	NA	NA
1/26/2013 12:24	NA	NA	NA	NA
1/27/2013 0:32	NA	NA	NA	NA
1/27/2013 8:43	NA	NA	NA	NA
1/29/2013 12:45	NA	NA	NA	NA
1/29/2013 22:55	NA	NA	NA	NA
1/30/2013 0:23	NA	NA	NA	NA
1/30/2013 2:32	NA	NA	NA	NA
1/30/2013 5:32	NA	NA	NA	NA
1/31/2013 9:23	-0.04	-0.03	-0.04	NA
1/31/2013 12:00	-0.04	-0.03	-0.04	NA
2/1/2013 0:50	NA	NA	NA	NA
2/2/2013 0:54	NA	NA	NA	NA
2/4/2013 17:53	NA	NA	NA	NA
2/5/2013 8:45	-0.44	-0.04	-0.48	NA
2/5/2013 9:53	-0.44	-0.04	-0.48	NA
2/5/2013 9:57	-0.44	-0.04	-0.48	NA
2/12/2013 12:00	-0.45	-0.17	-0.54	1
2/19/2013 10:07	NA	NA	NA	NA
2/20/2013 3:10	-0.50	-0.32	-0.75	NA
2/20/2013 12:56	-0.50	-0.32	-0.75	NA
2/22/2013 17:18	NA	NA	NA	NA
2/22/2013 18:08	NA	NA	NA	NA
2/22/2013 20:24	NA	NA	NA	NA
2/22/2013 22:19	NA	NA	NA	NA
2/23/2013 8:25	NA	NA	NA	NA
2/23/2013 17:47	NA	NA	NA	NA
2/24/2013 0:31	NA	NA	NA	NA
2/25/2013 9:18	NA	NA	NA	NA

DateTime	Average water table height (m)	Maximum water table height (m)	water table height at location 95 (m)	water table depth good?
2/25/2013 12:10	NA	NA	NA	NA
2/25/2013 14:59	NA	NA	NA	NA
2/25/2013 15:19	NA	NA	NA	NA
2/26/2013 0:59	NA	NA	NA	NA
2/26/2013 12:03	NA	NA	NA	NA
2/26/2013 15:14	NA	NA	NA	NA
2/28/2013 22:08	NA	NA	NA	NA
3/1/2013 19:11	NA	NA	NA	NA
3/3/2013 20:30	NA	NA	NA	NA
3/8/2013 10:00	-0.45	-0.25	-0.57	1
3/9/2013 10:41	NA	NA	NA	NA
3/11/2013 12:00	-0.45	-0.13	-0.70	1
3/16/2013 10:49	NA	NA	NA	NA
3/21/2013 11:30	-0.56	-0.28	-0.76	1
3/25/2013 16:25	NA	NA	NA	NA
4/1/2013 10:24	NA	NA	NA	NA
4/5/2013 10:45	NA	NA	NA	NA
4/5/2013 22:28	NA	NA	NA	NA
4/6/2013 9:17	NA	NA	NA	NA
4/7/2013 8:05	NA	NA	NA	NA
4/7/2013 10:14	NA	NA	NA	NA
4/7/2013 11:30	NA	NA	NA	NA
4/7/2013 14:24	NA	NA	NA	NA
4/7/2013 17:09	NA	NA	NA	NA
4/8/2013 18:56	NA	NA	NA	NA
4/12/2013 22:04	NA	NA	NA	NA
4/13/2013 1:50	NA	NA	NA	NA
4/13/2013 11:12	NA	NA	NA	NA
4/15/2013 16:51	NA	NA	NA	NA
4/19/2013 11:46	NA	NA	NA	NA
4/21/2013 21:08	NA	NA	NA	NA
4/24/2013 15:40	NA	NA	NA	NA
4/25/2013 14:45	NA	NA	NA	NA
4/26/2013 10:45	NA	NA	NA	NA
4/28/2013 6:30	NA	NA	NA	NA
4/28/2013 12:19	NA	NA	NA	NA
4/30/2013 4:51	NA	NA	NA	NA

DateTime	Average water table height (m)	Maximum water table height (m)	water table height at location 95 (m)	water table depth good?
5/7/2013 4:57	NA	NA	NA	NA
5/14/2013 5:06	NA	NA	NA	NA
5/21/2013 2:03	NA	NA	NA	NA
5/22/2013 0:00	-1.15	-0.95	-1.29	1
5/23/2013 20:09	NA	NA	NA	NA
5/28/2013 13:21	NA	NA	NA	NA
6/3/2013 13:00	NA	NA	NA	NA
6/10/2013 12:34	NA	NA	NA	NA
6/15/2013 20:23	NA	NA	NA	NA
6/16/2013 15:21	NA	NA	NA	NA
6/29/2013 7:37	NA	NA	NA	NA
7/11/2013 12:00	-1.46	-1.26	-1.67	1
7/13/2013 8:45	NA	NA	NA	NA
7/20/2013 16:11	NA	NA	NA	NA
7/27/2013 15:56	NA	NA	NA	NA
9/30/2013 15:10	-1.85	-1.85	-1.85	1

Appendix D. Soil water data, water years 2011-2013

Ch	Water Year	Sample Date	Location ID	Instrument*	Easting	Northing	DOC (mg C/L)	DOC sd	DOC n
2	2011	7/26/2011	1012	WD	493794	5180813	NA	NA	1
2	2011	7/26/2011	201	WD	493418	5180835	5.590	NA	1
2	2012	10/1/2011	95	WD	493274	5180687	6.960	1.080	2
2	2012	12/15/2011	201	WD	493418	5180835	1.350	0.050	2
2	2012	12/15/2011	95	WD	493274	5180687	2.690	0.350	2
2	2012	2/3/2012	1012	LS	493794	5180813	7.070	0.040	2
2	2012	2/3/2012	201	LS	493418	5180835	13.090	0.380	2
2	2012	2/3/2012	1012	WD	493794	5180813	6.510	0.510	3
2	2012	2/3/2012	133	WD	493655	5180729	NA	NA	NA
2	2012	2/3/2012	201	WD	493418	5180835	9.720	0.140	3
2	2012	2/3/2012	95	WD	493274	5180687	3.340	0.910	2
2	2012	2/3/2012	1002	WS	493591	5180786	14.220	0.500	3
2	2012	2/3/2012	95	WS	493274	5180687	7.830	0.260	3
2	2012	2/15/2012	1012	LS	493794	5180813	8.030	NA	1
2	2012	2/15/2012	133	LS	493655	5180729	6.440	NA	1
2	2012	2/15/2012	201	LS	493418	5180835	9.920	NA	1
2	2012	2/15/2012	1012	WD	493794	5180813	2.680	NA	1
2	2012	2/15/2012	133	WD	493655	5180729	2.660	NA	1
2	2012	2/15/2012	201	WD	493418	5180835	6.950	NA	1
2	2012	2/22/2012	129	LS	493530	5180728	7.760	NA	1
2	2012	2/22/2012	133	LS	493655	5180729	6.570	NA	1
2	2012	2/22/2012	201	LS	493418	5180835	9.910	NA	1
2	2012	2/22/2012	1002	WD	493591	5180786	6.100	NA	1
2	2012	2/22/2012	1012	WD	493794	5180813	3.690	NA	1
2	2012	2/22/2012	133	WD	493655	5180729	2.390	NA	1
2	2012	2/22/2012	201	WD	493418	5180835	5.230	NA	1
2	2012	2/22/2012	95	WD	493274	5180687	5.660	NA	1
2	2012	2/22/2012	1002	WS	493591	5180786	18.000	NA	1
2	2012	2/22/2012	1014	WS	493480	5180834	36.030	NA	1
2	2012	2/22/2012	95	WS	493274	5180687	6.560	NA	1
2	2012	3/2/2012	163	LS	493796.6	5180768	6.580	NA	1
2	2012	3/2/2012	201	LS	493418	5180835	9.750	NA	1
2	2012	3/2/2012	215	LS	493858.6	5180845	7.180	NA	1
2	2012	3/2/2012	1002	WD	493591	5180786	6.340	NA	1
2	2012	3/2/2012	133	WD	493655	5180729	2.610	NA	1
2	2012	3/2/2012	201	WD	493418	5180835	2.910	NA	1
2	2012	3/2/2012	95	WD	493274	5180687	5.020	NA	1

Ch	Water Year	Sample Date	Location ID	Instrument*	Easting	Northing	DOC (mg C/L)	DOC sd	DOC n
2	2012	3/2/2012	1002	WS	493591	5180786	17.520	NA	1
2	2012	3/2/2012	129	WS	493530	5180728	5.180	NA	1
2	2012	3/2/2012	95	WS	493274	5180687	6.110	NA	1
2	2012	3/7/2012	79	LS	NA	NA	7.770	NA	1
2	2012	3/7/2012	1002	WD	493591	5180786	5.800	NA	1
2	2012	3/7/2012	1012	WD	493794	5180813	2.370	NA	1
2	2012	3/7/2012	95	WD	493274	5180687	4.920	NA	1
2	2012	3/7/2012	1002	WS	493591	5180786	16.910	NA	1
2	2012	3/7/2012	1014	WS	493480	5180834	18.400	NA	1
2	2012	3/7/2012	129	WS	493530	5180728	4.210	NA	1
2	2012	3/9/2012	1002	WD	493591	5180786	5.960	0.020	2
2	2012	3/9/2012	1012	WD	493794	5180813	2.480	0.200	2
2	2012	3/9/2012	133	WD	493655	5180729	2.500	NA	1
2	2012	3/9/2012	201	WD	493418	5180835	6.420	0.270	2
2	2012	3/9/2012	95	WD	493274	5180687	4.970	NA	1
2	2012	3/9/2012	1002	WS	493591	5180786	19.060	4.460	2
2	2012	3/9/2012	95	WS	493274	5180687	6.300	0.340	2
2	2012	3/16/2012	1002	WD	493591	5180786	4.140	NA	1
2	2012	3/16/2012	1012	WD	493794	5180813	2.040	NA	1
2	2012	3/16/2012	1015	WD	493659	5180804	NA	NA	1
2	2012	3/16/2012	133	WD	493655	5180729	2.560	NA	1
2	2012	3/16/2012	95	WD	493274	5180687	5.320	NA	1
2	2012	3/16/2012	1002	WS	493591	5180786	33.230	NA	1
2	2012	3/16/2012	1014	WS	493480	5180834	7.900	NA	1
2	2012	3/16/2012	129	WS	493530	5180728	4.380	NA	1
2	2012	3/16/2012	95	WS	493274	5180687	NA	NA	1
2	2012	3/23/2012	1012	LS	493794	5180813	7.330	NA	1
2	2012	3/23/2012	1002	WD	493591	5180786	6.390	NA	1
2	2012	3/23/2012	1012	WD	493794	5180813	3.420	NA	1
2	2012	3/23/2012	133	WD	493655	5180729	2.640	NA	1
2	2012	3/23/2012	201	WD	493418	5180835	3.870	NA	1
2	2012	3/23/2012	95	WD	493274	5180687	5.500	NA	1
2	2012	3/23/2012	1002	WS	493591	5180786	27.620	NA	1
2	2012	3/23/2012	1014	WS	493480	5180834	7.920	NA	1
2	2012	3/23/2012	129	WS	493530	5180728	4.730	NA	1
2	2012	3/23/2012	95	WS	493274	5180687	6.650	NA	1
2	2012	4/5/2012	1012	LS	493794	5180813	5.670	NA	1
2	2012	4/5/2012	201	LS	493418	5180835	9.950	NA	1
2	2012	4/5/2012	1002	WD	493591	5180786	6.470	NA	1

Ch	Water Year	Sample Date	Location ID	Instrument*	Easting	Northing	DOC (mg C/L)	DOC sd	DOC n
2	2012	4/5/2012	1012	WD	493794	5180813	2.120	NA	1
2	2012	4/5/2012	1014	WD	493480	5180834	12.870	NA	1
2	2012	4/5/2012	1015	WD	493659	5180804	13.720	NA	1
2	2012	4/5/2012	133	WD	493655	5180729	2.470	NA	1
2	2012	4/5/2012	201	WD	493418	5180835	4.210	NA	1
2	2012	4/5/2012	95	WD	493274	5180687	5.990	NA	1
2	2012	4/5/2012	1002	WS	493591	5180786	22.730	NA	1
2	2012	4/5/2012	1014	WS	493480	5180834	5.930	NA	1
2	2012	4/5/2012	129	WS	493530	5180728	5.020	NA	1
2	2012	4/5/2012	95	WS	493274	5180687	5.890	NA	1
2	2012	5/21/2012	201	WD	493418	5180835	1.620	0.410	2
2	2012	5/21/2012	95	WD	493274	5180687	6.990	0.120	2
2	2012	6/22/2012	1012	WD	493794	5180813	1.860	NA	1
2	2012	6/22/2012	1015	WD	493659	5180804	8.640	NA	1
2	2012	6/22/2012	201	WD	493418	5180835	1.030	NA	1
2	2012	6/22/2012	201	WD	493418	5180835	NA	NA	1
2	2012	6/22/2012	95	WD	493274	5180687	5.420	NA	1
2	2012	6/22/2012	129	WS	493530	5180728	3.890	NA	1
2	2012	7/6/2012	1014	WD	493480	5180834	NA	NA	1
2	2012	7/8/2012	1002	WD	493591	5180786	7.870	NA	1
2	2012	7/8/2012	1012	WD	493794	5180813	1.930	NA	1
2	2012	7/8/2012	1015	WD	493659	5180804	8.110	NA	1
2	2012	7/8/2012	133	WD	493655	5180729	2.250	NA	1
2	2012	7/8/2012	201	WD	493418	5180835	1.000	NA	1
2	2012	7/8/2012	95	WD	493274	5180687	4.810	NA	1
2	2012	8/20/2012	1012	WD	493794	5180813	3.190	NA	1
2	2012	9/16/2012	201	WD	493418	5180835	1.000	0.250	2
2	2012	9/16/2012	95	WD	493274	5180687	3.640	0.090	2
2	2013	10/12/2012	1012	WD	493794	5180813	3.750	NA	1
2	2013	10/12/2012	1015	WD	493659	5180804	11.130	NA	1
2	2013	10/12/2012	133	WD	493655	5180729	4.750	NA	1
2	2013	10/12/2012	201	WD	493418	5180835	2.810	NA	1
2	2013	10/12/2012	95	WD	493274	5180687	3.920	NA	1
2	2013	10/23/2012	95	WD	493274	5180687	3.150	NA	1
2	2013	11/2/2012	1012	WD	493794	5180813	2.990	NA	1
2	2013	11/2/2012	1015	WD	493659	5180804	8.370	NA	1
2	2013	11/2/2012	95	WD	493274	5180687	3.410	NA	1
2	2013	12/3/2012	1012	WD	493794	5180813	2.050	0.010	2
2	2013	12/3/2012	1015	WD	493659	5180804	8.680	0.090	2

Ch	Water Year	Sample Date	Location ID	Instrument*	Easting	Northing	DOC (mg C/L)	DOC sd	DOC n
2	2013	12/3/2012	95	WD	493274	5180687	2.430	0.060	2
2	2013	12/4/2012	201	WD	493418	5180835	NA	NA	1
2	2013	1/5/2013	1002	WD	493591	5180786	7.170	0.870	2
2, 3	2013	1/5/2013	1012	WD	493794	5180813	2.100	0.100	2
2	2013	1/5/2013	1015	WD	493659	5180804	7.240	0.450	2
2, 3	2013	1/5/2013	133	WD	493655	5180729	2.930	0.140	2
2, 3	2013	1/5/2013	201	WD	493418	5180835	3.180	0.020	2
2, 3	2013	1/5/2013	95	WD	493274	5180687	1.640	0.210	3
2	2013	1/24/2013	1002	WD	493591	5180786	7.640	NA	1
2, 3	2013	1/24/2013	1012	WD	493794	5180813	2.620	NA	1
2	2013	1/24/2013	1015	WD	493659	5180804	6.860	NA	1
2, 3	2013	1/24/2013	133	WD	493655	5180729	3.190	NA	1
2, 3	2013	1/24/2013	201	WD	493418	5180835	2.170	NA	1
2, 3	2013	1/24/2013	95	WD	493274	5180687	4.730	NA	1
2, 3	2013	1/24/2013	95	WS	493274	5180687	10.540	NA	1
2	2013	1/31/2013	95	LS	493274	5180687	9.020	NA	1
2, 3	2013	1/31/2013	201	WD	493418	5180835	4.700	NA	1
2, 3	2013	1/31/2013	95	WD	493274	5180687	5.870	NA	1
2, 3	2013	1/31/2013	95	WS	493274	5180687	8.640	NA	1
2	2013	2/5/2013	1012	WD	493794	5180813	2.220	0.220	2
2	2013	2/5/2013	1015	WD	493659	5180804	5.870	0.010	2
2	2013	2/5/2013	133	WD	493655	5180729	3.020	0.610	2
2	2013	2/5/2013	201	WD	493418	5180835	4.420	0.110	2
2	2013	2/5/2013	95	WD	493274	5180687	6.100	0.270	2
2	2013	2/5/2013	95	WS	493274	5180687	6.750	0.070	2
2	2013	2/12/2013	1002	WD	493591	5180786	6.820	NA	1
2	2013	2/12/2013	1012	WD	493794	5180813	3.050	NA	1
2	2013	2/12/2013	1014	WD	493480	5180834	7.890	NA	1
2	2013	2/12/2013	1015	WD	493659	5180804	6.280	NA	1
2	2013	2/12/2013	133	WD	493655	5180729	3.970	NA	1
2	2013	2/12/2013	201	WD	493418	5180835	3.820	NA	1
2	2013	2/12/2013	95	WD	493274	5180687	5.500	NA	1
2	2013	2/12/2013	1002	WS	493591	5180786	11.610	NA	1
2	2013	2/12/2013	95	WS	493274	5180687	5.840	NA	1
2	2013	2/20/2013	1002	WD	493591	5180786	6.160	0.130	2
2	2013	2/20/2013	1012	WD	493794	5180813	3.030	0.100	2
2	2013	2/20/2013	133	WD	493655	5180729	3.440	0.340	2
2	2013	2/20/2013	201	WD	493418	5180835	3.380	0.330	2
2	2013	2/20/2013	95	WD	493274	5180687	5.860	0.450	2

Ch	Water Year	Sample Date	Location ID	Instrument*	Easting	Northing	DOC (mg C/L)	DOC sd	DOC n
2	2013	2/20/2013	95	WS	493274	5180687	5.180	NA	1
2	2013	3/7/2013	95	WS	493274	5180687	5.370	NA	1
2	2013	3/8/2013	133	LS	493655	5180729	4.010	NA	1
2	2013	3/8/2013	95	LS	493274	5180687	6.720	NA	1
2	2013	3/8/2013	1002	WD	493591	5180786	6.230	NA	1
2	2013	3/8/2013	1012	WD	493794	5180813	2.050	NA	1
2	2013	3/8/2013	1014	WD	493480	5180834	5.780	NA	1
2	2013	3/8/2013	1015	WD	493659	5180804	5.540	NA	1
2	2013	3/8/2013	133	WD	493655	5180729	2.920	NA	1
2	2013	3/8/2013	201	WD	493418	5180835	2.800	NA	1
2	2013	3/8/2013	95	WD	493274	5180687	5.120	NA	1
2	2013	3/8/2013	1002	WS	493591	5180786	11.220	NA	1
2	2013	3/11/2013	1002	WD	493591	5180786	5.470	0.280	2
2	2013	3/11/2013	1012	WD	493794	5180813	2.470	0.180	2
2	2013	3/11/2013	133	WD	493655	5180729	3.190	0.150	2
2	2013	3/11/2013	201	WD	493418	5180835	2.530	0.380	2
2	2013	3/11/2013	95	WD	493274	5180687	5.800	0.080	2
2	2013	3/11/2013	1002	WS	493591	5180786	11.300	1.350	2
2	2013	3/11/2013	95	WS	493274	5180687	6.690	NA	1
2	2013	3/21/2013	133	LS	493655	5180729	4.230	NA	1
2	2013	3/21/2013	201	LS	493418	5180835	7.900	NA	1
2	2013	3/21/2013	95	LS	493274	5180687	5.950	NA	1
2	2013	3/21/2013	1002	WD	493591	5180786	5.950	NA	1
2	2013	3/21/2013	1012	WD	493794	5180813	2.170	NA	1
2	2013	3/21/2013	1014	WD	493480	5180834	6.440	NA	1
2	2013	3/21/2013	1015	WD	493659	5180804	5.520	NA	1
2	2013	3/21/2013	133	WD	493655	5180729	2.670	NA	1
2	2013	3/21/2013	201	WD	493418	5180835	1.550	NA	1
2	2013	3/21/2013	95	WD	493274	5180687	4.880	NA	1
2, 3	2013	3/21/2013	1002	WS	493591	5180786	11.180	NA	1
2, 3	2013	3/21/2013	95	WS	493274	5180687	5.760	NA	1
2	2013	3/26/2013	133	LS	493655	5180729	3.920	NA	1
2	2013	3/26/2013	1002	WD	493591	5180786	6.480	NA	1
2, 3	2013	3/26/2013	1012	WD	493794	5180813	2.270	NA	1
2	2013	3/26/2013	1014	WD	493480	5180834	6.780	NA	1
2	2013	3/26/2013	1015	WD	493659	5180804	5.900	NA	1
2, 3	2013	3/26/2013	133	WD	493655	5180729	3.280	NA	1
2	2013	5/22/2013	1014	WD	493480	5180834	7.330	0.090	2
2	2013	5/22/2013	201	WD	493418	5180835	0.914	0.001	2

Ch	Water Year	Sample Date	Location ID	Instrument[*]	Easting	Northing	DOC (mg C/L)	DOC sd	DOC n
2	2013	5/22/2013	95	WD	493274	5180687	4.660	0.330	2
2	2013	6/22/2013	201	WD	493418	5180835	1.000	NA	1
2	2013	6/22/2013	95	WD	493274	5180687	5.290	NA	1
2	2013	7/9/2013	201	WD	493418	5180835	1.690	NA	1
2	2013	7/9/2013	95	WD	493274	5180687	4.940	NA	1
2	2013	7/11/2013	201	WD	493418	5180835	1.180	0.120	2
2	2013	7/11/2013	95	WD	493274	5180687	4.090	0.030	2
2	2013	9/30/2013	95	WD	493274	5180687	5.650	0.330	3
NA	2012	2/7/12 12:00	SR[#]	ISCO	493418	5180835	17.253	NA	1
NA	2012	3/21/12 15:52	SR	ISCO	493418	5180835	12.6624	NA	1
NA	2012	3/26/12 13:35	SR	ISCO	493418	5180835	20.7993	NA	1
NA	2012	3/26/12 14:37	SR	ISCO	493418	5180835	15.2874	NA	1
NA	2012	3/26/12 19:44	SR	ISCO	493418	5180835	11.704	0.33304	2
NA	2012	3/27/12 1:44	SR	ISCO	493418	5180835	13.807	NA	1
NA	2012	3/28/12 0:55	SR	ISCO	493418	5180835	14.6994	NA	1
NA	2012	3/28/12 1:44	SR	ISCO	493418	5180835	42.6019	NA	1
NA	2012	3/28/12 7:44	SR	ISCO	493418	5180835	15.08	NA	1
NA	2012	3/28/12 19:44	SR	ISCO	493418	5180835	16.1985	NA	1
NA	2012	3/29/12 18:10	SR	ISCO	493418	5180835	13.73	NA	1
NA	2012	3/30/12 14:10	SR	ISCO	493418	5180835	15.3763	NA	1
NA	2012	3/30/12 18:10	SR	ISCO	493418	5180835	13.12	NA	1
NA	2012	5/26/12 12:55	SR	ISCO	493418	5180835	14.9131	NA	1
2, 3	2013	1/26/13 4:08	SR	ISCO	493418	5180835	13.74	NA	1

[*] Instruments are: deep wells (WD), shallow wells (WS), deep lysimeters (LD), shallow lysimeters (LS), autosampler (ISCO)

[#] SR = Surface runoff

Sample Date	Location ID	Instrument	TN (mg N/L)	TN sd	TN n	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n
7/26/2011	1012	WD	3.650	NA	1	3.260	NA	1	0.080	NA	1
7/26/2011	201	WD	3.000	NA	1	2.800	NA	1	0.040	NA	1
10/1/2011	95	WD	0.380	0.060	2	0.140	0.010	2	0.180	0.070	2
12/15/2011	201	WD	2.750	0.010	2	2.660	0.050	2	0.010	0.000	2
12/15/2011	95	WD	0.350	0.020	2	0.060	0.010	2	0.050	0.000	2
2/3/2012	1012	LS	10.060	0.110	2	10.060	NA	1	0.100	0.030	2
2/3/2012	201	LS	48.290	1.420	2	49.000	NA	1	1.500	0.020	2
2/3/2012	1012	WD	2.830	0.090	3	2.230	0.030	3	0.250	NA	1
2/3/2012	133	WD	11.100	0.970	2	11.100	0.970	2	0.040	0.000	2
2/3/2012	201	WD	23.560	0.730	3	23.540	NA	1	0.070	NA	1
2/3/2012	95	WD	8.030	0.240	2	7.610	0.140	2	0.050	0.000	2
2/3/2012	1002	WS	10.770	0.190	3	9.920	0.240	3	0.160	0.110	3
2/3/2012	95	WS	2.930	0.350	3	2.740	0.440	2	0.330	0.090	2
2/15/2012	1012	LS	9.100	NA	1	9.870	NA	1	0.080	NA	1
2/15/2012	133	LS	5.280	NA	1	5.030	NA	1	0.020	NA	1
2/15/2012	201	LS	NA	NA	1	NA	NA	1	NA	NA	1
2/15/2012	1012	WD	6.760	NA	1	6.880	NA	1	0.160	NA	1
2/15/2012	133	WD	11.780	NA	1	11.810	NA	1	0.020	NA	1
2/15/2012	201	WD	21.920	NA	1	20.080	NA	1	0.010	NA	1
2/22/2012	129	LS	52.650	NA	1	51.140	NA	1	0.030	NA	1
2/22/2012	133	LS	4.440	NA	1	4.150	NA	1	0.020	NA	1
2/22/2012	201	LS	NA	NA	1	NA	NA	1	NA	NA	1
2/22/2012	1002	WD	NA	NA	1	NA	NA	1	0.020	NA	1
2/22/2012	1012	WD	6.780	NA	1	5.350	NA	1	0.110	NA	1
2/22/2012	133	WD	12.710	NA	1	12.570	NA	1	0.010	NA	1
2/22/2012	201	WD	16.010	NA	1	15.370	NA	1	0.040	NA	1
2/22/2012	95	WD	18.880	NA	1	18.650	NA	1	0.030	NA	1
2/22/2012	1002	WS	7.300	NA	1	6.300	NA	1	0.190	NA	1
2/22/2012	1014	WS	13.710	NA	1	13.400	NA	1	0.050	NA	1
2/22/2012	95	WS	17.700	NA	1	17.920	NA	1	0.070	NA	1
3/2/2012	163	LS	2.550	NA	1	1.670	NA	1	0.070	NA	1
3/2/2012	201	LS	NA	NA	1	NA	NA	1	NA	NA	1
3/2/2012	215	LS	11.100	NA	1	10.530	NA	1	0.030	NA	1
3/2/2012	1002	WD	35.050	NA	1	34.400	NA	1	0.050	NA	1
3/2/2012	133	WD	13.010	NA	1	12.930	NA	1	0.010	NA	1
3/2/2012	201	WD	NA	NA	1	NA	NA	1	NA	NA	1
3/2/2012	95	WD	15.860	NA	1	16.310	NA	1	0.010	NA	1
3/2/2012	1002	WS	4.540	NA	1	3.840	NA	1	0.120	NA	1
3/2/2012	129	WS	12.090	NA	1	11.510	NA	1	0.030	NA	1

Sample Date	Location ID	Instrument	TN (mg N/L)	TN sd	TN n	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n
3/2/2012	95	WS	13.540	NA	1	12.960	NA	1	0.060	NA	1
3/7/2012	79	LS	1.780	NA	1	1.490	NA	1	0.040	NA	1
3/7/2012	1002	WD	33.880	NA	1	32.900	NA	1	0.020	NA	1
3/7/2012	1012	WD	7.620	NA	1	7.570	NA	1	0.180	NA	1
3/7/2012	95	WD	16.570	NA	1	16.730	NA	1	0.010	NA	1
3/7/2012	1002	WS	4.260	NA	1	3.430	NA	1	0.200	NA	1
3/7/2012	1014	WS	NA	NA	1	NA	NA	1	NA	NA	1
3/7/2012	129	WS	10.760	NA	1	10.210	NA	1	0.030	NA	1
3/9/2012	1002	WD	33.950	0.920	2	31.850	0.470	2	0.020	0.000	2
3/9/2012	1012	WD	7.130	0.010	2	7.380	0.240	2	0.030	0.000	2
3/9/2012	133	WD	12.800	NA	1	13.170	NA	1	0.010	NA	1
3/9/2012	201	WD	7.190	0.070	2	7.180	0.000	2	0.020	0.000	2
3/9/2012	95	WD	16.240	NA	1	16.880	NA	1	0.010	NA	1
3/9/2012	1002	WS	2.870	1.110	2	1.750	0.960	2	0.110	0.020	2
3/9/2012	95	WS	10.950	0.410	2	10.730	0.180	2	0.080	0.010	2
3/16/2012	1002	WD	NA	NA	1	NA	NA	1	0.010	NA	1
3/16/2012	1012	WD	6.900	NA	1	6.950	NA	1	0.010	NA	1
3/16/2012	1015	WD	35.280	NA	1	35.200	NA	1	0.010	NA	1
3/16/2012	133	WD	13.410	NA	1	13.000	NA	1	0.020	NA	1
3/16/2012	95	WD	17.440	NA	1	17.000	NA	1	0.010	NA	1
3/16/2012	1002	WS	NA	NA	1	NA	NA	1	0.190	NA	1
3/16/2012	1014	WS	20.500	NA	1	19.380	NA	1	0.090	NA	1
3/16/2012	129	WS	7.740	NA	1	NA	NA	1	0.040	NA	1
3/16/2012	95	WS	10.950	NA	1	10.560	NA	1	0.040	NA	1
3/23/2012	1012	LS	12.180	NA	1	10.750	NA	1	0.020	NA	1
3/23/2012	1002	WD	35.730	NA	1	31.150	NA	1	0.010	NA	1
3/23/2012	1012	WD	8.670	NA	1	7.520	NA	1	0.020	NA	1
3/23/2012	133	WD	12.780	NA	1	13.270	NA	1	0.010	NA	1
3/23/2012	201	WD	8.670	NA	1	8.580	NA	1	0.010	NA	1
3/23/2012	95	WD	17.620	NA	1	17.110	NA	1	0.010	NA	1
3/23/2012	1002	WS	1.450	NA	1	0.010	NA	1	0.170	NA	1
3/23/2012	1014	WS	17.330	NA	1	17.890	NA	1	0.050	NA	1
3/23/2012	129	WS	12.030	NA	1	10.120	NA	1	0.040	NA	1
3/23/2012	95	WS	20.140	NA	1	17.790	NA	1	0.340	NA	1
4/5/2012	1012	LS	10.830	NA	1	10.560	NA	1	0.020	NA	1
4/5/2012	201	LS	31.590	NA	1	24.710	NA	1	0.330	NA	1
4/5/2012	1002	WD	34.280	NA	1	32.510	NA	1	0.010	NA	1
4/5/2012	1012	WD	8.310	NA	1	8.160	NA	1	0.040	NA	1
4/5/2012	1014	WD	4.920	NA	1	5.460	NA	1	0.060	NA	1

Sample Date	Location ID	Instrument	TN (mg N/L)	TN sd	TN n	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n
4/5/2012	1015	WD	24.830	NA	1	24.090	NA	1	0.010	NA	1
4/5/2012	133	WD	14.850	NA	1	12.390	NA	1	0.020	NA	1
4/5/2012	201	WD	10.060	NA	1	8.470	NA	1	0.260	NA	1
4/5/2012	95	WD	15.470	NA	1	15.260	NA	1	0.020	NA	1
4/5/2012	1002	WS	1.830	NA	1	0.490	NA	1	0.020	NA	1
4/5/2012	1014	WS	35.160	NA	1	34.810	NA	1	0.020	NA	1
4/5/2012	129	WS	15.220	NA	1	12.630	NA	1	0.100	NA	1
4/5/2012	95	WS	19.710	NA	1	16.510	NA	1	0.010	NA	1
5/21/2012	201	WD	0.310	0.080	2	0.260	0.100	2	0.030	0.000	2
5/21/2012	95	WD	10.480	0.200	2	9.790	0.340	2	0.020	0.000	2
6/22/2012	1012	WD	6.060	NA	1	5.600	NA	1	0.070	NA	1
6/22/2012	1015	WD	13.570	NA	1	16.580	NA	1	0.010	NA	1
6/22/2012	201	WD	0.750	NA	1	0.670	NA	1	0.010	NA	1
6/22/2012	201	WD	NA	NA	1	NA	NA	1	NA	NA	1
6/22/2012	95	WD	6.730	NA	1	5.890	NA	1	0.170	NA	1
6/22/2012	129	WS	16.830	NA	1	15.140	NA	1	0.010	NA	1
7/6/2012	1014	WD	1.880	NA	1	0.050	NA	1	1.390	NA	1
7/8/2012	1002	WD	30.950	NA	1	30.390	NA	1	0.010	NA	1
7/8/2012	1012	WD	6.200	NA	1	5.450	NA	1	0.120	NA	1
7/8/2012	1015	WD	12.000	NA	1	15.270	NA	1	0.010	NA	1
7/8/2012	133	WD	13.570	NA	1	11.880	NA	1	0.010	NA	1
7/8/2012	201	WD	0.470	NA	1	0.440	NA	1	0.020	NA	1
7/8/2012	95	WD	4.030	NA	1	3.840	NA	1	0.230	NA	1
8/20/2012	1012	WD	6.760	NA	1	6.070	NA	1	0.050	NA	1
9/16/2012	201	WD	0.150	0.020	2	0.020	0.020	2	0.050	0.010	2
9/16/2012	95	WD	0.780	0.080	2	0.740	0.090	2	0.090	0.000	2
10/12/2012	1012	WD	6.700	NA	1	6.010	NA	1	0.000	NA	1
10/12/2012	1015	WD	13.590	NA	1	12.450	NA	1	0.340	NA	1
10/12/2012	133	WD	13.830	NA	1	12.860	NA	1	0.120	NA	1
10/12/2012	201	WD	0.470	NA	1	0.040	NA	1	0.050	NA	1
10/12/2012	95	WD	1.250	NA	1	0.740	NA	1	0.070	NA	1
10/23/2012	95	WD	0.530	NA	1	0.470	NA	1	0.070	NA	1
11/2/2012	1012	WD	6.090	NA	1	5.390	NA	1	0.020	NA	1
11/2/2012	1015	WD	14.820	NA	1	13.060	NA	1	0.300	NA	1
11/2/2012	95	WD	0.980	NA	1	0.700	NA	1	0.050	NA	1
12/3/2012	1012	WD	5.920	0.050	2	5.570	0.130	2	0.010	0.000	2
12/3/2012	1015	WD	15.790	0.030	2	14.240	0.550	2	0.270	0.020	2
12/3/2012	95	WD	0.730	0.080	2	0.460	NA	1	0.010	0.000	2
12/4/2012	201	WD	NA	NA	1	18.720	NA	1	0.160	NA	1

Sample Date	Location ID	Instrument	TN (mg N/L)	TN sd	TN n	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n
1/5/2013	1002	WD	27.260	4.750	2	24.790	3.790	2	0.010	0.000	2
1/5/2013	1012	WD	5.900	0.290	2	5.570	0.200	2	0.020	0.000	2
1/5/2013	1015	WD	15.990	0.080	2	12.960	0.700	2	0.010	0.000	2
1/5/2013	133	WD	16.400	0.740	2	14.880	0.470	2	0.000	0.000	2
1/5/2013	201	WD	8.500	0.120	2	8.450	NA	1	0.010	0.000	2
1/5/2013	95	WD	0.700	0.150	3	0.610	0.170	3	0.010	0.000	3
1/24/2013	1002	WD	37.150	NA	1	33.610	NA	1	0.160	NA	1
1/24/2013	1012	WD	6.640	NA	1	6.040	NA	1	0.090	NA	1
1/24/2013	1015	WD	21.880	NA	1	20.080	NA	1	0.090	NA	1
1/24/2013	133	WD	18.490	NA	1	15.920	NA	1	0.010	NA	1
1/24/2013	201	WD	5.750	NA	1	5.360	NA	1	0.010	NA	1
1/24/2013	95	WD	4.560	NA	1	3.900	NA	1	0.130	NA	1
1/24/2013	95	WS	11.770	NA	1	10.050	NA	1	0.050	NA	1
1/31/2013	95	LS	31.490	NA	1	28.160	NA	1	0.170	NA	1
1/31/2013	201	WD	15.380	NA	1	12.980	NA	1	0.160	NA	1
1/31/2013	95	WD	7.560	NA	1	6.700	NA	1	0.010	NA	1
1/31/2013	95	WS	22.850	NA	1	19.900	NA	1	0.080	NA	1
2/5/2013	1012	WD	4.900	1.330	2	4.630	1.120	2	0.010	0.000	2
2/5/2013	1015	WD	21.540	0.270	2	21.360	0.020	2	0.010	0.000	2
2/5/2013	133	WD	8.520	2.380	2	7.990	2.220	2	0.000	0.000	2
2/5/2013	201	WD	10.170	0.020	2	9.830	0.020	2	0.120	0.000	2
2/5/2013	95	WD	8.870	0.260	2	8.390	0.240	2	0.010	0.010	2
2/5/2013	95	WS	24.420	NA	1	23.550	1.140	2	0.030	0.000	2
2/12/2013	1002	WD	31.680	NA	1	31.000	NA	1	0.090	NA	1
2/12/2013	1012	WD	6.600	NA	1	6.200	NA	1	0.050	NA	1
2/12/2013	1014	WD	9.670	NA	1	8.760	NA	1	0.050	NA	1
2/12/2013	1015	WD	22.960	NA	1	21.340	NA	1	0.050	NA	1
2/12/2013	133	WD	13.100	NA	1	11.880	NA	1	0.050	NA	1
2/12/2013	201	WD	10.320	NA	1	9.690	NA	1	0.030	NA	1
2/12/2013	95	WD	9.040	NA	1	7.730	NA	1	0.030	NA	1
2/12/2013	1002	WS	7.950	NA	1	6.330	NA	1	0.180	NA	1
2/12/2013	95	WS	27.370	NA	1	26.140	NA	1	0.050	NA	1
2/20/2013	1002	WD	32.960	1.700	2	29.850	1.940	2	0.000	0.000	2
2/20/2013	1012	WD	6.380	0.240	2	5.930	0.240	2	0.000	0.000	2
2/20/2013	133	WD	11.290	1.940	2	10.540	1.840	2	0.010	0.000	2
2/20/2013	201	WD	6.650	0.370	2	6.360	0.270	2	0.000	0.000	2
2/20/2013	95	WD	9.920	NA	1	9.340	0.130	2	0.010	0.000	2
2/20/2013	95	WS	21.560	NA	1	20.950	NA	1	0.030	NA	1
3/7/2013	95	WS	26.230	NA	1	24.650	NA	1	0.010	NA	1

Sample Date	Location ID	Instrument	TN (mg N/L)	TN sd	TN n	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n
3/8/2013	133	LS	4.770	NA	1	4.290	NA	1	0.040	NA	1
3/8/2013	95	LS	27.420	NA	1	24.090	NA	1	0.040	NA	1
3/8/2013	1002	WD	34.890	NA	1	32.090	NA	1	0.010	NA	1
3/8/2013	1012	WD	6.750	NA	1	6.360	NA	1	0.010	NA	1
3/8/2013	1014	WD	13.490	NA	1	12.080	NA	1	0.030	NA	1
3/8/2013	1015	WD	24.930	NA	1	22.720	NA	1	0.020	NA	1
3/8/2013	133	WD	13.020	NA	1	11.560	NA	1	0.010	NA	1
3/8/2013	201	WD	5.890	NA	1	5.300	NA	1	0.020	NA	1
3/8/2013	95	WD	12.480	NA	1	10.810	NA	1	0.010	NA	1
3/8/2013	1002	WS	9.700	NA	1	8.150	NA	1	0.270	NA	1
3/11/2013	1002	WD	29.210	1.390	2	27.010	0.530	2	0.010	0.000	2
3/11/2013	1012	WD	6.650	0.730	2	6.330	0.310	2	0.000	0.000	2
3/11/2013	133	WD	12.930	0.040	2	12.460	0.190	2	0.000	0.000	2
3/11/2013	201	WD	4.940	0.040	2	4.750	0.120	2	0.010	0.000	2
3/11/2013	95	WD	11.570	0.090	2	10.620	0.350	2	0.010	0.010	2
3/11/2013	1002	WS	6.140	1.350	2	4.700	1.470	2	0.260	0.050	2
3/11/2013	95	WS	23.650	NA	1	22.950	0.740	2	0.080	0.010	2
3/21/2013	133	LS	5.890	NA	1	5.000	NA	1	0.100	NA	1
3/21/2013	201	LS	3.460	NA	1	2.870	NA	1	0.100	NA	1
3/21/2013	95	LS	33.860	NA	1	29.160	NA	1	0.030	NA	1
3/21/2013	1002	WD	36.490	NA	1	33.490	NA	1	0.060	NA	1
3/21/2013	1012	WD	7.310	NA	1	6.720	NA	1	0.010	NA	1
3/21/2013	1014	WD	12.050	NA	1	11.440	NA	1	0.020	NA	1
3/21/2013	1015	WD	24.500	NA	1	22.720	NA	1	0.010	NA	1
3/21/2013	133	WD	13.530	NA	1	12.310	NA	1	0.020	NA	1
3/21/2013	201	WD	3.610	NA	1	3.290	NA	1	0.010	NA	1
3/21/2013	95	WD	11.260	NA	1	10.160	NA	1	0.010	NA	1
3/21/2013	1002	WS	6.400	NA	1	5.460	NA	1	0.300	NA	1
3/21/2013	95	WS	21.260	NA	1	18.560	NA	1	0.040	NA	1
3/26/2013	133	LS	5.010	NA	1	4.310	NA	1	0.020	NA	1
3/26/2013	1002	WD	32.520	NA	1	30.960	NA	1	0.030	NA	1
3/26/2013	1012	WD	7.080	NA	1	6.290	NA	1	0.000	NA	1
3/26/2013	1014	WD	11.940	NA	1	10.990	NA	1	0.030	NA	1
3/26/2013	1015	WD	23.810	NA	1	22.850	NA	1	0.010	NA	1
3/26/2013	133	WD	12.350	NA	1	11.600	NA	1	0.040	NA	1
5/22/2013	1014	WD	11.840	0.090	2	10.890	0.050	2	0.160	0.040	2
5/22/2013	201	WD	0.484	0.024	2	0.348	0.045	2	0.041	0.012	2
5/22/2013	95	WD	6.370	0.430	2	5.770	0.420	2	0.010	0.000	2
6/22/2013	201	WD	0.000	NA	1	0.010	NA	1	0.010	NA	1

Sample Date	Location ID	Instrument	TN (mg N/L)	TN sd	TN n	NO3 (mg N/L)	NO3 sd	NO3 n	NH4 (mg N/L)	NH4 sd	NH4 n
6/22/2013	95	WD	4.390	NA	1	3.710	NA	1	0.010	NA	1
7/9/2013	201	WD	0.000	NA	1	0.010	NA	1	0.010	NA	1
7/9/2013	95	WD	4.300	NA	1	3.750	NA	1	0.010	NA	1
7/11/2013	201	WD	0.250	0.000	2	0.010	0.000	2	0.070	0.010	2
7/11/2013	95	WD	3.950	0.060	2	3.820	0.000	2	0.170	0.000	2
9/30/2013	95	WD	0.900	0.130	3	0.190	0.060	3	0.270	0.050	3
2/7/12 12:00	SR	ISCO	24.242	NA	1	24.546	NA	1	1.352	NA	1
3/21/12 15:52	SR	ISCO	32.136	NA	1	28.604	NA	1	3.121	NA	1
3/26/12 13:35	SR	ISCO	11.849	NA	1	9.809	NA	1	0.250	NA	1
3/26/12 14:37	SR	ISCO	12.198	NA	1	10.462	NA	1	0.122	NA	1
3/26/12 19:44	SR	ISCO	25.458	0.674	2	24.072	NA	1	0.780	NA	1
3/27/12 1:44	SR	ISCO	27.203	NA	1	23.958	NA	1	0.024	NA	1
3/28/12 0:55	SR	ISCO	21.869	NA	1	19.471	NA	1	0.874	NA	1
3/28/12 1:44	SR	ISCO	10.125	NA	1	1.649	NA	1	9.005	NA	1
3/28/12 7:44	SR	ISCO	19.880	NA	1	17.627	NA	1	0.187	NA	1
3/28/12 19:44	SR	ISCO	15.421	NA	1	15.666	NA	1	0.044	NA	1
3/29/12 18:10	SR	ISCO	12.760	NA	1	10.771	NA	1	0.191	NA	1
3/30/12 14:10	SR	ISCO	8.788	NA	1	7.491	NA	1	0.112	NA	1
3/30/12 18:10	SR	ISCO	15.151	NA	1	13.480	NA	1	0.346	NA	1
5/26/12 12:55	SR	ISCO	10.118	NA	1	8.024	NA	1	0.313	NA	1
1/26/13 4:08	SR	ISCO	5.320	NA	1	4.296	NA	1	0.153	NA	1

Sample Date	Location ID	Instrument	DON (mg N/L)	DON sd	C:N	FI	Freshness Index	SUVA (a254 nm)
7/26/2011	1012	WD	0.310	NA	43.77	1.529	0.691	1.084
7/26/2011	201	WD	0.160	NA	41.80	1.590	0.740	NA
10/1/2011	95	WD	0.060	0.100	126.93	1.620	0.800	0.840
12/15/2011	201	WD	0.080	0.050	20.09	1.600	0.800	2.970
12/15/2011	95	WD	0.250	0.020	12.74	1.570	0.980	1.670
2/3/2012	1012	LS	0.000	NA	NA	NA	NA	NA
2/3/2012	201	LS	0.000	NA	NA	1.520	0.688	2.210
2/3/2012	1012	WD	0.350	NA	21.57	1.515	0.689	1.567
2/3/2012	133	WD	0.000	1.370	NA	1.510	0.690	1.260
2/3/2012	201	WD	0.000	NA	NA	1.470	0.640	4.090
2/3/2012	95	WD	0.380	0.280	10.38	1.660	0.790	2.150
2/3/2012	1002	WS	0.700	0.330	23.83		NA	NA
2/3/2012	95	WS	0.000	0.570	NA	1.230	0.800	NA
2/15/2012	1012	LS	0.000	NA	NA	NA	NA	NA
2/15/2012	133	LS	0.230	NA	33.03	NA	NA	NA
2/15/2012	201	LS	NA	NA	NA	NA	NA	NA
2/15/2012	1012	WD	0.000	NA	NA	NA	NA	NA
2/15/2012	133	WD	0.000	NA	NA	NA	NA	NA
2/15/2012	201	WD	1.830	NA	4.43	NA	NA	NA
2/22/2012	129	LS	1.480	NA	6.10	NA	NA	NA
2/22/2012	133	LS	0.280	NA	27.87	NA	NA	NA
2/22/2012	201	LS	NA	NA	NA	NA	NA	NA
2/22/2012	1002	WD	NA	NA	NA	NA	NA	NA
2/22/2012	1012	WD	1.330	NA	3.25	NA	NA	NA
2/22/2012	133	WD	0.000	NA	NA	NA	NA	NA
2/22/2012	201	WD	0.600	NA	10.12	NA	NA	NA
2/22/2012	95	WD	0.200	NA	33.52		NA	NA
2/22/2012	1002	WS	0.810	NA	25.88		NA	NA
2/22/2012	1014	WS	0.270	NA	157.69	NA	NA	NA
2/22/2012	95	WS	0.000	NA	NA	NA	NA	NA
3/2/2012	163	LS	0.810	NA	9.49	NA	NA	NA
3/2/2012	201	LS	NA	NA	NA	NA	NA	NA
3/2/2012	215	LS	0.540	NA	15.48	NA	NA	NA
3/2/2012	1002	WD	0.600	NA	12.42	NA	NA	NA
3/2/2012	133	WD	0.070	NA	41.95	NA	NA	NA
3/2/2012	201	WD	NA	NA	NA	NA	NA	NA
3/2/2012	95	WD	0.000	NA	NA		NA	NA
3/2/2012	1002	WS	0.580	NA	35.01	NA	NA	NA
3/2/2012	129	WS	0.550	NA	10.98	NA	NA	NA

Sample Date	Location ID	Instrument	DON (mg N/L)	DON sd	C:N	FI	Freshness Index	SUVA (a254 nm)
3/2/2012	95	WS	0.520	NA	13.80	NA	NA	NA
3/7/2012	79	LS	0.240	NA	37.26	NA	NA	NA
3/7/2012	1002	WD	0.960	NA	7.07	NA	NA	NA
3/7/2012	1012	WD	0.000	NA	NA	NA	NA	NA
3/7/2012	95	WD	0.000	NA	NA		NA	NA
3/7/2012	1002	WS	0.640	NA	30.95	NA	NA	NA
3/7/2012	1014	WS	NA	NA	NA	NA	NA	NA
3/7/2012	129	WS	0.520	NA	9.38	NA	NA	NA
3/9/2012	1002	WD	2.080	1.030	3.34	NA	NA	NA
3/9/2012	1012	WD	0.000	0.240	NA	1.519	0.686	4.590
3/9/2012	133	WD	0.000	NA	NA	1.590	0.760	3.280
3/9/2012	201	WD	0.000	0.070	NA	1.420	0.690	6.670
3/9/2012	95	WD	0.000	NA	NA	1.620	0.760	2.610
3/9/2012	1002	WS	1.020	1.470	21.91	1.420	0.840	11.090
3/9/2012	95	WS	0.140	0.450	52.92	1.480	0.780	8.510
3/16/2012	1002	WD	NA	NA	NA	NA	NA	NA
3/16/2012	1012	WD	0.000	NA	NA	NA	NA	NA
3/16/2012	1015	WD	0.070	NA	NA	NA	NA	NA
3/16/2012	133	WD	0.400	NA	7.54	NA	NA	NA
3/16/2012	95	WD	0.440	NA	14.20		NA	NA
3/16/2012	1002	WS	NA	NA	NA	NA	NA	NA
3/16/2012	1014	WS	1.030	NA	8.91	NA	NA	NA
3/16/2012	129	WS	2.270	NA	2.25	NA	NA	NA
3/16/2012	95	WS	0.350	NA	7.53	NA	NA	NA
3/23/2012	1012	LS	1.400	NA	6.10	NA	NA	NA
3/23/2012	1002	WD	4.570	NA	1.63	NA	NA	NA
3/23/2012	1012	WD	1.140	NA	3.51	NA	NA	NA
3/23/2012	133	WD	0.000	NA	NA	NA	NA	NA
3/23/2012	201	WD	0.080	NA	57.38	NA	NA	NA
3/23/2012	95	WD	0.500	NA	12.87		NA	NA
3/23/2012	1002	WS	1.270	NA	25.42	NA	NA	NA
3/23/2012	1014	WS	0.000	NA	NA	NA	NA	NA
3/23/2012	129	WS	1.880	NA	2.93	NA	NA	NA
3/23/2012	95	WS	2.010	NA	3.86	NA	NA	NA
4/5/2012	1012	LS	0.250	NA	26.52	NA	NA	NA
4/5/2012	201	LS	6.550	NA	1.77	NA	NA	NA
4/5/2012	1002	WD	1.760	NA	4.29	NA	NA	NA
4/5/2012	1012	WD	0.100	NA	24.47	NA	NA	NA
4/5/2012	1014	WD	0.000	NA	NA	NA	NA	NA

Sample Date	Location ID	Instrument	DON (mg N/L)	DON sd	C:N	FI	Freshness Index	SUVA (a254 nm)
4/5/2012	1015	WD	0.730	NA	21.95	NA	NA	NA
4/5/2012	133	WD	2.440	NA	1.18	NA	NA	NA
4/5/2012	201	WD	1.330	NA	3.69	NA	NA	NA
4/5/2012	95	WD	0.200	NA	35.65		NA	NA
4/5/2012	1002	WS	1.320	NA	20.13	NA	NA	NA
4/5/2012	1014	WS	0.340	NA	20.49	NA	NA	NA
4/5/2012	129	WS	2.490	NA	2.35	NA	NA	NA
4/5/2012	95	WS	3.190	NA	2.16	NA	NA	NA
5/21/2012	201	WD	0.020	0.130	82.34	1.410	0.710	11.980
5/21/2012	95	WD	0.680	0.400	12.04	1.600	0.740	2.000
6/22/2012	1012	WD	0.400	NA	5.46	NA	NA	NA
6/22/2012	1015	WD	0.000	NA	NA	NA	NA	NA
6/22/2012	201	WD	0.070	NA	16.14	NA	NA	NA
6/22/2012	201	WD	NA	NA	NA	NA	NA	NA
6/22/2012	95	WD	0.660	NA	9.56		NA	NA
6/22/2012	129	WS	1.680	NA	2.69	NA	NA	NA
7/6/2012	1014	WD	0.440	NA	56.34	NA	NA	NA
7/8/2012	1002	WD	0.560	NA	16.51	NA	NA	NA
7/8/2012	1012	WD	0.630	NA	3.59	NA	NA	NA
7/8/2012	1015	WD	0.000	NA	NA	NA	NA	NA
7/8/2012	133	WD	1.690	NA	1.56	NA	NA	NA
7/8/2012	201	WD	0.010	NA	86.03	NA	NA	NA
7/8/2012	95	WD	0.000	NA	NA		NA	NA
8/20/2012	1012	WD	0.640	NA	5.77	NA	NA	NA
9/16/2012	201	WD	0.070	0.030	16.63	1.530	0.700	4.090
9/16/2012	95	WD	0.000	0.120	NA	1.670	0.760	2.030
10/12/2012	1012	WD	0.680	NA	6.40	NA	NA	NA
10/12/2012	1015	WD	0.800	NA	16.22	NA	NA	NA
10/12/2012	133	WD	0.850	NA	6.50	NA	NA	NA
10/12/2012	201	WD	0.380	NA	8.54	NA	NA	NA
10/12/2012	95	WD	0.440	NA	10.39		NA	NA
10/23/2012	95	WD	0.000	NA	NA		NA	NA
11/2/2012	1012	WD	0.680	NA	5.15	NA	NA	NA
11/2/2012	1015	WD	1.460	NA	6.71	NA	NA	NA
11/2/2012	95	WD	0.230	NA	17.29	1.670	0.810	1.770
12/3/2012	1012	WD	0.350	0.140	6.91	1.527	0.687	2.494
12/3/2012	1015	WD	1.280	0.550	7.93	1.590	0.770	1.350
12/3/2012	95	WD	0.260	0.080	10.93	1.660	0.770	1.730
12/4/2012	201	WD	0.340	NA	34.90	1.550	0.690	2.550

Sample Date	Location ID	Instrument	DON (mg N/L)	DON sd	C:N	FI	Freshness Index	SUVA (a254 nm)
1/5/2013	1002	WD	2.470	4.750	3.39	1.501	0.697	2.900
1/5/2013	1012	WD	0.320	0.350	7.63	1.533	0.689	2.987
1/5/2013	1015	WD	3.020	0.700	2.80	1.590	0.770	1.650
1/5/2013	133	WD	1.520	0.880	2.25	1.590	0.730	2.810
1/5/2013	201	WD	0.050	0.120	76.80	1.570	0.720	2.700
1/5/2013	95	WD	0.080	0.220	23.74	1.620	0.790	2.240
1/24/2013	1002	WD	3.380	NA	2.64	1.563	0.713	1.806
1/24/2013	1012	WD	0.510	NA	5.97	1.638	0.745	1.729
1/24/2013	1015	WD	1.710	NA	4.67	NA	NA	NA
1/24/2013	133	WD	2.570	NA	1.45	1.650	0.740	2.110
1/24/2013	201	WD	0.380	NA	6.72	1.640	0.750	1.830
1/24/2013	95	WD	0.530	NA	10.37	1.670	0.770	1.600
1/24/2013	95	WS	1.680	NA	7.34	1.560	0.730	1.970
1/31/2013	95	LS	3.160	NA	3.33	1.564	0.705	2.320
1/31/2013	201	WD	2.240	NA	2.45	1.580	0.690	2.480
1/31/2013	95	WD	0.850	NA	8.08	1.640	0.760	1.360
1/31/2013	95	WS	2.870	NA	3.51	1.550	0.700	2.060
2/5/2013	1012	WD	0.260	1.740	10.13	1.539	0.695	2.585
2/5/2013	1015	WD	0.160	0.270	42.12	1.610	0.780	1.850
2/5/2013	133	WD	0.530	3.250	6.64	1.570	0.740	5.020
2/5/2013	201	WD	0.220	0.020	23.19	1.530	0.680	2.880
2/5/2013	95	WD	0.470	0.360	15.29	1.610	0.750	1.980
2/5/2013	95	WS	0.840	NA	9.43	1.560	0.760	2.840
2/12/2013	1002	WD	0.600	NA	13.33	NA	NA	NA
2/12/2013	1012	WD	0.350	NA	10.25	NA	NA	NA
2/12/2013	1014	WD	0.860	NA	10.68	NA	NA	NA
2/12/2013	1015	WD	1.570	NA	4.67	NA	NA	NA
2/12/2013	133	WD	1.170	NA	3.97	NA	NA	NA
2/12/2013	201	WD	0.610	NA	7.35	NA	NA	NA
2/12/2013	95	WD	1.290	NA	4.98		NA	NA
2/12/2013	1002	WS	1.440	NA	9.37	NA	NA	NA
2/12/2013	95	WS	1.170	NA	5.81	NA	NA	NA
2/20/2013	1002	WD	3.110	2.590	2.31	1.530	0.704	2.367
2/20/2013	1012	WD	0.440	0.340	8.02	1.525	0.704	1.990
2/20/2013	133	WD	0.740	2.680	5.39	1.580	0.740	2.800
2/20/2013	201	WD	0.290	0.460	13.74	1.560	0.700	2.130
2/20/2013	95	WD	0.570	NA	12.08	1.610	0.750	2.140
2/20/2013	95	WS	0.580	NA	10.42	1.580	0.760	2.580
3/7/2013	95	WS	1.570	NA	3.99	1.650	0.760	2.080

Sample Date	Location ID	Instrument	DON (mg N/L)	DON sd	C:N	FI	Freshness Index	SUVA (a254 nm)
3/8/2013	133	LS	0.440	NA	10.71	1.640	0.730	1.960
3/8/2013	95	LS	3.280	NA	2.39	1.566	0.710	2.490
3/8/2013	1002	WD	2.790	NA	2.60	1.555	0.712	2.399
3/8/2013	1012	WD	0.380	NA	6.35	1.618	0.743	2.299
3/8/2013	1014	WD	1.380	NA	4.90	NA	NA	NA
3/8/2013	1015	WD	2.190	NA	2.94	NA	NA	NA
3/8/2013	133	WD	1.450	NA	2.36	1.630	0.740	2.210
3/8/2013	201	WD	0.570	NA	5.72	1.630	0.730	1.790
3/8/2013	95	WD	1.670	NA	3.58	1.630	0.770	2.120
3/8/2013	1002	WS	1.290	NA	10.19	1.520	0.680	2.760
3/11/2013	1002	WD	2.190	1.490	2.91	1.533	0.700	2.524
3/11/2013	1012	WD	0.320	0.790	9.00	1.525	0.693	2.287
3/11/2013	133	WD	0.460	0.190	8.03	1.580	0.740	2.280
3/11/2013	201	WD	0.180	0.130	16.01	1.570	0.700	1.740
3/11/2013	95	WD	0.940	0.360	7.21	1.610	0.750	1.890
3/11/2013	1002	WS	1.180	1.990	11.13	1.500	0.680	3.990
3/11/2013	95	WS	0.620	NA	8.60	1.570	0.740	3.230
3/21/2013	133	LS	0.790	NA	6.24	1.620	0.730	2.140
3/21/2013	201	LS	0.480	NA	19.01	1.550	0.700	2.700
3/21/2013	95	LS	4.680	NA	1.48	1.593	0.717	2.340
3/21/2013	1002	WD	2.930	NA	2.37	1.549	0.719	2.410
3/21/2013	1012	WD	0.580	NA	4.33	1.607	0.742	2.303
3/21/2013	1014	WD	0.600	NA	12.54	NA	NA	NA
3/21/2013	1015	WD	1.760	NA	3.65	NA	NA	NA
3/21/2013	133	WD	1.200	NA	2.59	1.650	0.750	2.160
3/21/2013	201	WD	0.320	NA	5.71	1.610	0.730	2.300
3/21/2013	95	WD	1.090	NA	5.22	1.660	0.770	2.260
3/21/2013	1002	WS	0.640	NA	20.25	1.530	0.690	2.560
3/21/2013	95	WS	2.660	NA	2.52	1.620	0.750	2.250
3/26/2013	133	LS	0.670	NA	6.82	1.630	0.730	2.110
3/26/2013	1002	WD	1.530	NA	4.93	NA	NA	NA
3/26/2013	1012	WD	0.790	NA	3.37	1.607	0.746	2.854
3/26/2013	1014	WD	0.920	NA	8.56	NA	NA	NA
3/26/2013	1015	WD	0.950	NA	7.26	NA	NA	NA
3/26/2013	133	WD	0.720	NA	5.34	1.650	0.750	2.330
5/22/2013	1014	WD	0.800	0.110	10.71	1.520	0.680	2.940
5/22/2013	201	WD	0.095	0.053	11.23	1.540	0.710	1.600
5/22/2013	95	WD	0.590	0.600	9.18	1.640	0.760	1.900
6/22/2013	201	WD	0.000	NA	NA		NA	NA

Sample Date	Location ID	Instrument	DON (mg N/L)	DON sd	C:N	FI	Freshness Index	SUVA (a254 nm)
6/22/2013	95	WD	0.680	NA	9.09		NA	NA
7/9/2013	201	WD	0.000	NA	NA		NA	NA
7/9/2013	95	WD	0.540	NA	10.69		NA	NA
7/11/2013	201	WD	0.820	0.000	1.69	1.610	0.710	1.390
7/11/2013	95	WD	NA	0.030	NA	1.660	0.780	1.800
9/30/2013	95	WD	0.430	0.150	15.18	1.550	0.650	2.000
2/7/12 12:00	SR	ISCO	0.00	NA	NA	NA	NA	NA
3/21/12 15:52	SR	ISCO	0.41	NA	35.97	NA	NA	NA
3/26/12 13:35	SR	ISCO	1.79	NA	13.56	NA	NA	NA
3/26/12 14:37	SR	ISCO	1.61	NA	11.05	NA	NA	NA
3/26/12 19:44	SR	ISCO	0.61	NA	22.56	NA	NA	NA
3/27/12 1:44	SR	ISCO	3.22	NA	5.00	NA	NA	NA
3/28/12 0:55	SR	ISCO	1.52	NA	11.25	NA	NA	NA
3/28/12 1:44	SR	ISCO	0.00	NA	NA	NA	NA	NA
3/28/12 7:44	SR	ISCO	2.07	NA	8.51	1.470	0.606	1.809
3/28/12 19:44	SR	ISCO	0.00	NA	NA	NA	NA	NA
3/29/12 18:10	SR	ISCO	1.80	NA	8.91	1.404	0.542	3.263
3/30/12 14:10	SR	ISCO	1.18	NA	15.14	NA	NA	NA
3/30/12 18:10	SR	ISCO	1.32	NA	11.56	NA	NA	NA
5/26/12 12:55	SR	ISCO	1.78	NA	9.77	NA	NA	NA
1/26/13 4:08	SR	ISCO	0.87	NA	18.41	1.372	0.562	2.853

Sample Date	Location ID	Instrument	C1	C2	C3	C4	C5
7/26/2011	1012	WD	0.808	0.684	0.266	0.277	0.257
7/26/2011	201	WD	0.222	0.235	0.016	0.102	0.064
10/1/2011	95	WD	0.221	0.277	0.156	0.227	0.946
12/15/2011	201	WD	0.136	0.130	0.115	0.057	0.139
12/15/2011	95	WD	0.097	0.037	0.469	0.505	2.361
2/3/2012	1012	LS	NA	NA	NA	NA	NA
2/3/2012	201	LS	1.519	1.393	0.000	0.507	0.505
2/3/2012	1012	WD	0.802	0.733	0.000	0.288	0.089
2/3/2012	133	WD	0.675	0.527	0.207	0.227	0.333
2/3/2012	201	WD	1.559	1.307	0.724	0.456	0.457
2/3/2012	95	WD	0.408	0.430	0.014	0.168	0.178
2/3/2012	1002	WS	NA	NA	NA	NA	NA
2/3/2012	95	WS	1.894	0.716	10.246	0.248	3.971
2/15/2012	1012	LS	NA	NA	NA	NA	NA
2/15/2012	133	LS	NA	NA	NA	NA	NA
2/15/2012	201	LS	NA	NA	NA	NA	NA
2/15/2012	1012	WD	NA	NA	NA	NA	NA
2/15/2012	133	WD	NA	NA	NA	NA	NA
2/15/2012	201	WD	NA	NA	NA	NA	NA
2/22/2012	129	LS	NA	NA	NA	NA	NA
2/22/2012	133	LS	NA	NA	NA	NA	NA
2/22/2012	201	LS	NA	NA	NA	NA	NA
2/22/2012	1002	WD	NA	NA	NA	NA	NA
2/22/2012	1012	WD	NA	NA	NA	NA	NA
2/22/2012	133	WD	NA	NA	NA	NA	NA
2/22/2012	201	WD	NA	NA	NA	NA	NA
2/22/2012	95	WD	NA	NA	NA	NA	NA
2/22/2012	1002	WS	NA	NA	NA	NA	NA
2/22/2012	1014	WS	NA	NA	NA	NA	NA
2/22/2012	95	WS	NA	NA	NA	NA	NA
3/2/2012	163	LS	NA	NA	NA	NA	NA
3/2/2012	201	LS	NA	NA	NA	NA	NA
3/2/2012	215	LS	NA	NA	NA	NA	NA
3/2/2012	1002	WD	NA	NA	NA	NA	NA
3/2/2012	133	WD	NA	NA	NA	NA	NA
3/2/2012	201	WD	NA	NA	NA	NA	NA
3/2/2012	95	WD	NA	NA	NA	NA	NA
3/2/2012	1002	WS	NA	NA	NA	NA	NA
3/2/2012	129	WS	NA	NA	NA	NA	NA

Sample Date	Location ID	Instrument	C1	C2	C3	C4	C5
3/2/2012	95	WS	NA	NA	NA	NA	NA
3/7/2012	79	LS	NA	NA	NA	NA	NA
3/7/2012	1002	WD	NA	NA	NA	NA	NA
3/7/2012	1012	WD	NA	NA	NA	NA	NA
3/7/2012	95	WD	NA	NA	NA	NA	NA
3/7/2012	1002	WS	NA	NA	NA	NA	NA
3/7/2012	1014	WS	NA	NA	NA	NA	NA
3/7/2012	129	WS	NA	NA	NA	NA	NA
3/9/2012	1002	WD	NA	NA	NA	NA	NA
3/9/2012	1012	WD	0.592	0.506	0.178	0.209	0.218
3/9/2012	133	WD	0.366	0.347	0.084	0.110	0.472
3/9/2012	201	WD	1.193	0.884	1.317	0.255	0.807
3/9/2012	95	WD	0.752	0.761	0.019	0.255	0.479
3/9/2012	1002	WS	4.133	2.747	10.177	0.775	2.857
3/9/2012	95	WS	0.956	0.797	2.153	0.220	0.506
3/16/2012	1002	WD	NA	NA	NA	NA	NA
3/16/2012	1012	WD	NA	NA	NA	NA	NA
3/16/2012	1015	WD	NA	NA	NA	NA	NA
3/16/2012	133	WD	NA	NA	NA	NA	NA
3/16/2012	95	WD	NA	NA	NA	NA	NA
3/16/2012	1002	WS	NA	NA	NA	NA	NA
3/16/2012	1014	WS	NA	NA	NA	NA	NA
3/16/2012	129	WS	NA	NA	NA	NA	NA
3/16/2012	95	WS	NA	NA	NA	NA	NA
3/23/2012	1012	LS	NA	NA	NA	NA	NA
3/23/2012	1002	WD	NA	NA	NA	NA	NA
3/23/2012	1012	WD	NA	NA	NA	NA	NA
3/23/2012	133	WD	NA	NA	NA	NA	NA
3/23/2012	201	WD	NA	NA	NA	NA	NA
3/23/2012	95	WD	NA	NA	NA	NA	NA
3/23/2012	1002	WS	NA	NA	NA	NA	NA
3/23/2012	1014	WS	NA	NA	NA	NA	NA
3/23/2012	129	WS	NA	NA	NA	NA	NA
3/23/2012	95	WS	NA	NA	NA	NA	NA
4/5/2012	1012	LS	NA	NA	NA	NA	NA
4/5/2012	201	LS	NA	NA	NA	NA	NA
4/5/2012	1002	WD	NA	NA	NA	NA	NA
4/5/2012	1012	WD	NA	NA	NA	NA	NA
4/5/2012	1014	WD	NA	NA	NA	NA	NA

Sample Date	Location ID	Instrument	C1	C2	C3	C4	C5
4/5/2012	1015	WD	NA	NA	NA	NA	NA
4/5/2012	133	WD	NA	NA	NA	NA	NA
4/5/2012	201	WD	NA	NA	NA	NA	NA
4/5/2012	95	WD	NA	NA	NA	NA	NA
4/5/2012	1002	WS	NA	NA	NA	NA	NA
4/5/2012	1014	WS	NA	NA	NA	NA	NA
4/5/2012	129	WS	NA	NA	NA	NA	NA
4/5/2012	95	WS	NA	NA	NA	NA	NA
5/21/2012	201	WD	0.389	0.281	0.756	0.083	0.216
5/21/2012	95	WD	0.989	0.944	0.085	0.304	0.205
6/22/2012	1012	WD	NA	NA	NA	NA	NA
6/22/2012	1015	WD	NA	NA	NA	NA	NA
6/22/2012	201	WD	NA	NA	NA	NA	NA
6/22/2012	201	WD	NA	NA	NA	NA	NA
6/22/2012	95	WD	NA	NA	NA	NA	NA
6/22/2012	129	WS	NA	NA	NA	NA	NA
7/6/2012	1014	WD	NA	NA	NA	NA	NA
7/8/2012	1002	WD	NA	NA	NA	NA	NA
7/8/2012	1012	WD	NA	NA	NA	NA	NA
7/8/2012	1015	WD	NA	NA	NA	NA	NA
7/8/2012	133	WD	NA	NA	NA	NA	NA
7/8/2012	201	WD	NA	NA	NA	NA	NA
7/8/2012	95	WD	NA	NA	NA	NA	NA
8/20/2012	1012	WD	NA	NA	NA	NA	NA
9/16/2012	201	WD	0.139	0.127	0.070	0.055	0.140
9/16/2012	95	WD	0.537	0.567	0.053	0.209	0.245
10/12/2012	1012	WD	NA	NA	NA	NA	NA
10/12/2012	1015	WD	NA	NA	NA	NA	NA
10/12/2012	133	WD	NA	NA	NA	NA	NA
10/12/2012	201	WD	NA	NA	NA	NA	NA
10/12/2012	95	WD	NA	NA	NA	NA	NA
10/23/2012	95	WD	NA	NA	NA	NA	NA
11/2/2012	1012	WD	NA	NA	NA	NA	NA
11/2/2012	1015	WD	NA	NA	NA	NA	NA
11/2/2012	95	WD	0.374	0.470	0.118	0.213	0.294
12/3/2012	1012	WD	0.476	0.397	0.010	0.175	0.081
12/3/2012	1015	WD	0.853	0.900	0.098	0.379	0.152
12/3/2012	95	WD	0.356	0.368	0.027	0.148	0.148
12/4/2012	201	WD	1.197	1.035	0.151	0.400	0.236

Sample Date	Location ID	Instrument	C1	C2	C3	C4	C5
1/5/2013	1002	WD	1.359	1.082	0.090	0.428	0.034
1/5/2013	1012	WD	0.438	0.378	0.044	0.158	0.162
1/5/2013	1015	WD	0.855	0.889	0.083	0.372	0.113
1/5/2013	133	WD	0.484	0.432	0.031	0.166	0.059
1/5/2013	201	WD	0.496	0.440	0.042	0.172	0.116
1/5/2013	95	WD	0.277	0.283	0.023	0.130	0.410
1/24/2013	1002	WD	0.989	0.852	0.013	0.297	0.025
1/24/2013	1012	WD	0.383	0.383	0.045	0.141	0.075
1/24/2013	1015	WD	NA	NA	NA	NA	NA
1/24/2013	133	WD	0.437	0.417	0.026	0.142	0.056
1/24/2013	201	WD	0.271	0.265	0.028	0.097	0.077
1/24/2013	95	WD	0.524	0.554	0.040	0.211	0.121
1/24/2013	95	WS	1.479	1.370	0.053	0.519	0.142
1/31/2013	95	LS	1.068	1.097	0.000	0.360	0.128
1/31/2013	201	WD	0.786	0.703	0.038	0.238	0.089
1/31/2013	95	WD	0.678	0.670	0.014	0.254	0.212
1/31/2013	95	WS	1.215	1.056	0.000	0.386	0.092
2/5/2013	1012	WD	0.460	0.403	0.044	0.174	0.127
2/5/2013	1015	WD	0.734	0.785	0.084	0.280	0.588
2/5/2013	133	WD	0.542	0.468	0.364	0.162	0.189
2/5/2013	201	WD	0.646	0.560	0.179	0.202	0.165
2/5/2013	95	WD	0.850	0.828	0.000	0.238	0.735
2/5/2013	95	WS	0.929	0.863	0.000	0.311	0.141
2/12/2013	1002	WD	NA	NA	NA	NA	NA
2/12/2013	1012	WD	NA	NA	NA	NA	NA
2/12/2013	1014	WD	NA	NA	NA	NA	NA
2/12/2013	1015	WD	NA	NA	NA	NA	NA
2/12/2013	133	WD	NA	NA	NA	NA	NA
2/12/2013	201	WD	NA	NA	NA	NA	NA
2/12/2013	95	WD	NA	NA	NA	NA	NA
2/12/2013	1002	WS	NA	NA	NA	NA	NA
2/12/2013	95	WS	NA	NA	NA	NA	NA
2/20/2013	1002	WD	1.019	0.862	0.000	0.320	0.067
2/20/2013	1012	WD	0.469	0.415	0.054	0.180	0.155
2/20/2013	133	WD	0.486	0.434	0.138	0.170	0.083
2/20/2013	201	WD	0.433	0.392	0.046	0.083	0.823
2/20/2013	95	WD	0.859	0.854	0.000	0.267	0.614
2/20/2013	95	WS	0.635	0.623	0.097	0.285	0.650
3/7/2013	95	WS	0.723	0.715	0.006	0.254	0.100

Sample Date	Location ID	Instrument	C1	C2	C3	C4	C5
3/8/2013	133	LS	0.549	0.516	0.000	0.180	0.057
3/8/2013	95	LS	0.977	0.941	0.000	0.326	0.101
3/8/2013	1002	WD	0.993	0.841	0.013	0.300	0.009
3/8/2013	1012	WD	0.375	0.364	0.063	0.145	0.071
3/8/2013	1014	WD	NA	NA	NA	NA	NA
3/8/2013	1015	WD	NA	NA	NA	NA	NA
3/8/2013	133	WD	0.402	0.388	0.046	0.152	0.061
3/8/2013	201	WD	0.321	0.293	0.036	0.106	0.063
3/8/2013	95	WD	0.760	0.774	0.185	0.238	0.009
3/8/2013	1002	WS	2.121	1.849	0.000	0.695	0.112
3/11/2013	1002	WD	0.989	0.843	0.000	0.299	0.093
3/11/2013	1012	WD	0.478	0.413	0.034	0.186	0.156
3/11/2013	133	WD	0.429	0.398	0.051	0.139	0.310
3/11/2013	201	WD	0.296	0.265	0.039	0.101	0.088
3/11/2013	95	WD	0.813	0.792	0.000	0.294	0.115
3/11/2013	1002	WS	2.360	2.031	0.561	0.745	0.755
3/11/2013	95	WS	0.762	0.762	0.125	0.272	0.141
3/21/2013	133	LS	0.587	0.545	0.004	0.187	0.066
3/21/2013	201	LS	1.810	1.603	0.022	0.566	0.014
3/21/2013	95	LS	0.833	0.810	0.000	0.272	0.067
3/21/2013	1002	WD	1.037	0.872	0.008	0.311	0.001
3/21/2013	1012	WD	0.371	0.363	0.064	0.143	0.072
3/21/2013	1014	WD	NA	NA	NA	NA	NA
3/21/2013	1015	WD	NA	NA	NA	NA	NA
3/21/2013	133	WD	0.365	0.356	0.042	0.123	0.044
3/21/2013	201	WD	0.243	0.222	0.027	0.084	0.072
3/21/2013	95	WD	0.695	0.718	0.037	0.247	0.059
3/21/2013	1002	WS	2.077	1.791	0.000	0.662	0.065
3/21/2013	95	WS	0.867	0.829	0.000	0.299	0.087
3/26/2013	133	LS	0.569	0.530	0.000	0.182	0.061
3/26/2013	1002	WD	NA	NA	NA	NA	NA
3/26/2013	1012	WD	0.362	0.380	0.194	0.121	0.058
3/26/2013	1014	WD	NA	NA	NA	NA	NA
3/26/2013	1015	WD	NA	NA	NA	NA	NA
3/26/2013	133	WD	0.372	0.365	0.040	0.123	0.049
5/22/2013	1014	WD	1.742	1.372	0.145	0.593	0.371
5/22/2013	201	WD	0.115	0.104	0.017	0.019	0.267
5/22/2013	95	WD	0.654	0.660	0.000	0.226	0.285
6/22/2013	201	WD	NA	NA	NA	NA	NA

Sample Date	Location ID	Instrument	C1	C2	C3	C4	C5
6/22/2013	95	WD	NA	NA	NA	NA	NA
7/9/2013	201	WD	NA	NA	NA	NA	NA
7/9/2013	95	WD	NA	NA	NA	NA	NA
7/11/2013	201	WD	NA	NA	NA	NA	NA
7/11/2013	95	WD	NA	NA	NA	NA	NA
9/30/2013	95	WD	0.776	0.710	0.032	0.292	0.387
2/7/12 12:00	SR	ISCO	NA	NA	NA	NA	NA
3/21/12 15:52	SR	ISCO	NA	NA	NA	NA	NA
3/26/12 13:35	SR	ISCO	NA	NA	NA	NA	NA
3/26/12 14:37	SR	ISCO	NA	NA	NA	NA	NA
3/26/12 19:44	SR	ISCO	NA	NA	NA	NA	NA
3/27/12 1:44	SR	ISCO	NA	NA	NA	NA	NA
3/28/12 0:55	SR	ISCO	NA	NA	NA	NA	NA
3/28/12 1:44	SR	ISCO	NA	NA	NA	NA	NA
3/28/12 7:44	SR	ISCO	1.419	1.414	0.207	0.405	0.490
3/28/12 19:44	SR	ISCO	NA	NA	NA	NA	NA
3/29/12 18:10	SR	ISCO	2.472	2.078	0.048	0.643	0.537
3/30/12 14:10	SR	ISCO	NA	NA	NA	NA	NA
3/30/12 18:10	SR	ISCO	NA	NA	NA	NA	NA
5/26/12 12:55	SR	ISCO	NA	NA	NA	NA	NA
1/26/13 4:08	SR	ISCO	2.098	1.562	0.000	0.585	0.237

Sample Date	Location ID	Instrument	raw EC (µS/cm)	Temp (°C)	Temp Correction factor	EC (µS/cm)	Water Table Elevation (masl)	Water table Depth Below Surface (m)
7/26/2011	1012	WD	NA	NA	NA	NA	NA	NA
7/26/2011	201	WD	NA	NA	NA	NA	NA	NA
10/1/2011	95	WD	410.3	NA	NA	410.0	772.40	-2.16
12/15/2011	201	WD	309.8	2.1	NA	310.0	778.79	-0.90
12/15/2011	95	WD	326.9	2.7	NA	327.0	773.42	-1.14
2/3/2012	1012	LS	101.0	3.1	1.72	175.0	NA	NA
2/3/2012	201	LS	314.0	NA	NA	NA	NA	NA
2/3/2012	1012	WD	387.0	NA	NA	387.0	793.85	-0.38
2/3/2012	133	WD	340.0	NA	NA	340.0	788.85	-1.02
2/3/2012	201	WD	244.0	NA	NA	244.0	779.13	-0.56
2/3/2012	95	WD	379.0	NA	NA	379.0	773.80	-0.76
2/3/2012	1002	WS	161.0	NA	NA	161.0	782.46	0.00
2/3/2012	95	WS	66.0	3.7	1.69	112.0	NA	NA
2/15/2012	1012	LS	NA	NA	NA	NA	NA	NA
2/15/2012	133	LS	75.0	1.4	1.81	135.0	NA	NA
2/15/2012	201	LS	300.0	1.2	1.82	546.0	NA	NA
2/15/2012	1012	WD	239.0	6.4	1.57	374.0	792.72	-1.52
2/15/2012	133	WD	293.0	6.8	1.55	454.0	788.77	-1.10
2/15/2012	201	WD	300.0	5.1	1.63	488.0	778.79	-0.90
2/22/2012	129	LS	359.0	5.7	1.60	574.0	NA	NA
2/22/2012	133	LS	NA	NA	NA	NA	NA	NA
2/22/2012	201	LS	315.0	5.2	1.62	511.0	NA	NA
2/22/2012	1002	WD	569.0	5.9	1.59	905.0	780.46	-2.00
2/22/2012	1012	WD	247.0	5.7	1.60	395.0	792.73	-1.50
2/22/2012	133	WD	288.0	7.6	1.52	437.0	789.15	-0.72
2/22/2012	201	WD	315.0	5.0	1.63	515.0	778.93	-0.76
2/22/2012	95	WD	419.0	6.1	1.58	662.0	773.36	-1.20
2/22/2012	1002	WS	208.0	3.8	1.69	351.0	782.00	-0.46
2/22/2012	1014	WS	193.0	3.0	1.73	333.0	779.73	-1.49
2/22/2012	95	WS	118.0	3.7	1.69	200.0	773.36	-1.20
3/2/2012	163	LS	NA	NA	NA	NA	NA	NA
3/2/2012	201	LS	335.0	NA	NA	NA	NA	NA
3/2/2012	215	LS	42.0	1.1	1.82	77.0	NA	NA
3/2/2012	1002	WD	569.0	5.8	1.60	908.0	780.48	-1.98
3/2/2012	133	WD	272.0	6.5	1.56	425.0	788.77	-1.10
3/2/2012	201	WD	297.0	4.5	1.66	492.0	778.60	-1.09

Sample Date	Location ID	Instrument	raw EC (µS/cm)	Temp (°C)	Temp Correction factor	EC (µS/cm)	Water Table Elevation (masl)	Water table Depth Below Surface (m)
3/2/2012	95	WD	376.8	6.0	1.59	598.0	773.38	-1.19
3/2/2012	1002	WS	199.1	2.8	1.74	346.0	781.69	-0.77
3/2/2012	129	WS	216.0	3.4	1.71	369.0	783.84	-1.69
3/2/2012	95	WS	144.4	4.4	1.66	240.0	773.35	-1.21
3/7/2012	79	LS	NA	NA	NA	NA	NA	NA
3/7/2012	1002	WD	560.0	5.6	1.60	898.0	780.83	-1.63
3/7/2012	1012	WD	266.0	5.8	1.60	424.0	792.73	-1.50
3/7/2012	95	WD	387.0	5.8	1.60	617.0	773.43	-1.13
3/7/2012	1002	WS	195.0	3.0	1.73	337.0	781.67	-0.79
3/7/2012	1014	WS	54.0	3.4	1.71	92.0	779.31	-1.91
3/7/2012	129	WS	215.0	4.3	1.66	358.0	783.94	-1.59
3/9/2012	1002	WD	519.0	4.5	1.66	859.0	781.34	-1.12
3/9/2012	1012	WD	257.3	3.8	1.69	434.0	793.67	-0.56
3/9/2012	133	WD	279.2	5.9	1.59	444.0	789.34	-0.53
3/9/2012	201	WD	228.6	4.4	1.66	379.0	779.32	-0.37
3/9/2012	95	WD	189.0	6.1	1.58	299.0	773.82	-0.74
3/9/2012	1002	WS	166.0	3.5	1.70	283.0	782.28	-0.18
3/9/2012	95	WS	174.2	4.3	1.66	290.0	773.86	-0.70
3/16/2012	1002	WD	559.0	5.7	1.60	894.0	781.04	-1.42
3/16/2012	1012	WD	276.0	6.0	1.59	438.0	792.85	-1.38
3/16/2012	1015	WD	545.0	6.1	1.58	862.0	784.68	-2.04
3/16/2012	133	WD	291.0	7.3	1.53	444.0	789.22	-0.65
3/16/2012	95	WD	370.0	5.3	1.62	598.0	773.81	-0.76
3/16/2012	1002	WS	174.0	4.2	1.67	290.0	782.01	-0.45
3/16/2012	1014	WS	326.0	4.7	1.65	537.0	779.34	-1.88
3/16/2012	129	WS	213.0	4.7	1.65	351.0	784.63	-0.90
3/16/2012	95	WS	167.0	4.2	1.67	279.0	773.83	-0.74
3/23/2012	1012	LS	114.0	3.0	1.73	196.0	NA	NA
3/23/2012	1002	WD	562.0	5.7	1.60	899.0	780.96	-1.50
3/23/2012	1012	WD	258.0	5.7	1.60	413.0	793.04	-1.19
3/23/2012	133	WD	274.0	6.5	1.56	428.0	789.34	-0.53
3/23/2012	201	WD	278.0	5.3	1.62	450.0	778.99	-0.69
3/23/2012	95	WD	376.0	4.8	1.64	617.0	774.01	-0.55
3/23/2012	1002	WS	171.0	3.8	1.69	289.0	782.01	-0.45
3/23/2012	1014	WS	251.0	3.0	1.73	433.0	780.22	-1.00
3/23/2012	129	WS	210.0	4.7	1.65	345.0	784.88	-0.65

Sample Date	Location ID	Instrument	raw EC (µS/cm)	Temp (°C)	Temp Correction factor	EC (µS/cm)	Water Table Elevation (masl)	Water table Depth Below Surface (m)
3/23/2012	95	WS	174.0	4.2	1.67	290.0	774.07	-0.49
4/5/2012	1012	LS	NA	NA	NA	NA	NA	NA
4/5/2012	201	LS	NA	NA	NA	NA	NA	NA
4/5/2012	1002	WD	561.0	5.8	1.60	895.0	780.96	-1.50
4/5/2012	1012	WD	252.0	6.1	1.58	399.0	793.17	-1.06
4/5/2012	1014	WD	297.0	5.1	1.63	483.0	779.92	-1.30
4/5/2012	1015	WD	651.0	6.3	1.57	1024.0	784.53	-2.19
4/5/2012	133	WD	251.0	6.1	1.58	397.0	789.37	-0.50
4/5/2012	201	WD	278.0	5.4	1.61	448.0	778.74	-0.95
4/5/2012	95	WD	335.0	5.8	1.60	535.0	774.01	-0.55
4/5/2012	1002	WS	197.0	5.4	1.61	318.0	781.96	-0.50
4/5/2012	1014	WS	332.0	4.9	1.64	543.0	779.82	-1.40
4/5/2012	129	WS	214.0	4.9	1.64	351.0	784.83	-0.70
4/5/2012	95	WS	180.0	5.2	1.62	292.0	773.95	-0.61
5/21/2012	201	WD	291.7	NA	NA	292.0	778.51	-1.18
5/21/2012	95	WD	555.6	NA	NA	556.0	773.37	-1.19
6/22/2012	1012	WD	333.0	8.8	1.47	488.0	792.73	-1.50
6/22/2012	1015	WD	671.0	8.6	1.47	989.0	784.82	-1.90
6/22/2012	201	WD	205.0	9.7	1.43	293.0	778.09	-1.60
6/22/2012	201	WD	205.0	9.7	1.43	293.0	778.09	-1.60
6/22/2012	95	WD	NA	NA	NA	NA	773.32	-1.25
6/22/2012	129	WS	290.0	11.3	1.37	397.0	783.93	-1.60
7/6/2012	1014	WD	424.0	13.0	1.31	554.0	778.82	-2.40
7/8/2012	1002	WD	706.0	11.3	1.37	966.0	779.76	-2.70
7/8/2012	1012	WD	332.0	10.0	1.42	471.0	792.43	-1.80
7/8/2012	1015	WD	677.0	9.1	1.45	984.0	784.72	-2.00
7/8/2012	133	WD	292.0	9.5	1.44	420.0	788.47	-1.40
7/8/2012	201	WD	209.0	10.7	1.39	291.0	777.99	-1.70
7/8/2012	95	WD	NA	NA	NA	NA	773.27	-1.29
8/20/2012	1012	WD	NA	NA	NA	NA	NA	NA
9/16/2012	201	WD	284.4	NA	NA	284.0	778.86	-0.83
9/16/2012	95	WD	474.7	NA	NA	475.0	772.81	-1.76
10/12/2012	1012	WD	NA	NA	NA	NA	793.28	-1.00
10/12/2012	1015	WD	NA	NA	NA	NA	785.27	-1.44
10/12/2012	133	WD	NA	NA	NA	NA	785.68	-4.19
10/12/2012	201	WD	NA	NA	NA	NA	778.84	-0.84

Sample Date	Location ID	Instrument	raw EC (µS/cm)	Temp (°C)	Temp Correction factor	EC (µS/cm)	Water Table Elevation (masl)	Water table Depth Below Surface (m)
10/12/2012	95	WD	NA	NA	NA	NA	772.79	-1.77
10/23/2012	95	WD	299.8	9.1	1.45	436.0	772.89	-1.67
11/2/2012	1012	WD	NA	NA	NA	NA	NA	NA
11/2/2012	1015	WD	NA	NA	NA	NA	NA	NA
11/2/2012	95	WD	NA	NA	NA	NA	NA	NA
12/3/2012	1012	WD	NA	NA	NA	NA	793.44	-0.84
12/3/2012	1015	WD	NA	NA	NA	NA	785.24	-1.47
12/3/2012	95	WD	NA	NA	NA	NA	773.10	-1.47
12/4/2012	201	WD	NA	NA	NA	NA	779.55	-0.14
1/5/2013	1002	WD	NA	NA	NA	NA	781.60	-0.86
1/5/2013	1012	WD	NA	NA	NA	463.0	NA	NA
1/5/2013	1015	WD	NA	NA	NA	NA	785.27	-1.45
1/5/2013	133	WD	NA	NA	NA	NA	789.31	-0.56
1/5/2013	201	WD	NA	NA	NA	NA	779.34	-0.34
1/5/2013	95	WD	NA	NA	NA	NA	773.18	-1.38
1/24/2013	1002	WD	NA	NA	NA	NA	781.58	-0.88
1/24/2013	1012	WD	NA	NA	NA	NA	793.53	-0.75
1/24/2013	1015	WD	NA	NA	NA	NA	785.33	-1.39
1/24/2013	133	WD	NA	NA	NA	NA	789.30	-0.57
1/24/2013	201	WD	NA	NA	NA	NA	779.15	-0.54
1/24/2013	95	WD	NA	NA	NA	NA	773.72	-0.85
1/24/2013	95	WS	NA	NA	NA	NA	NA	NA
1/31/2013	95	LS	NA	NA	NA	NA	NA	NA
1/31/2013	201	WD	NA	NA	NA	NA	779.65	-0.03
1/31/2013	95	WD	NA	NA	NA	NA	774.52	-0.04
1/31/2013	95	WS	NA	NA	NA	NA	NA	NA
2/5/2013	1012	WD	284.7	5.0	1.63	465.0	794.24	-0.04
2/5/2013	1015	WD	NA	NA	NA	894.4	785.52	-1.19
2/5/2013	133	WD	NA	NA	NA	366.4	789.64	-0.23
2/5/2013	201	WD	NA	NA	NA	395.5	779.47	-0.22
2/5/2013	95	WD	NA	NA	NA	543.8	774.09	-0.48
2/5/2013	95	WS	NA	NA	NA	361.9	774.10	-0.46
2/12/2013	1002	WD	NA	NA	NA	NA	782.03	-0.43
2/12/2013	1012	WD	NA	NA	NA	NA	794.10	-0.18
2/12/2013	1014	WD	NA	NA	NA	NA	780.74	-0.47
2/12/2013	1015	WD	NA	NA	NA	NA	785.58	-1.13

Sample Date	Location ID	Instrument	raw EC (µS/cm)	Temp (°C)	Temp Correction factor	EC (µS/cm)	Water Table Elevation (masl)	Water table Depth Below Surface (m)
2/12/2013	133	WD	NA	NA	NA	NA	789.69	-0.17
2/12/2013	201	WD	NA	NA	NA	NA	779.48	-0.20
2/12/2013	95	WD	NA	NA	NA	NA	774.02	-0.54
2/12/2013	1002	WS	NA	NA	NA	NA	NA	NA
2/12/2013	95	WS	NA	NA	NA	NA	NA	NA
2/20/2013	1002	WD	NA	NA	NA	558.0	781.93	-0.53
2/20/2013	1012	WD	NA	NA	NA	459.0	793.88	-0.41
2/20/2013	133	WD	NA	NA	NA	377.0	789.54	-0.33
2/20/2013	201	WD	NA	NA	NA	369.0	779.37	-0.32
2/20/2013	95	WD	NA	NA	NA	554.0	773.81	-0.75
2/20/2013	95	WS	NA	NA	NA	452.0	773.88	-0.69
3/7/2013	95	WS	NA	NA	NA	NA	NA	NA
3/8/2013	133	LS	NA	NA	NA	NA	NA	NA
3/8/2013	95	LS	NA	NA	NA	NA	NA	NA
3/8/2013	1002	WD	NA	NA	NA	NA	782.00	-0.46
3/8/2013	1012	WD	NA	NA	NA	NA	793.97	-0.31
3/8/2013	1014	WD	NA	NA	NA	NA	780.96	-0.26
3/8/2013	1015	WD	NA	NA	NA	NA	785.68	-1.03
3/8/2013	133	WD	NA	NA	NA	NA	789.62	-0.25
3/8/2013	201	WD	NA	NA	NA	NA	779.41	-0.27
3/8/2013	95	WD	NA	NA	NA	NA	773.99	-0.57
3/8/2013	1002	WS	NA	NA	NA	NA	NA	NA
3/11/2013	1002	WD	NA	NA	NA	NA	781.93	-0.53
3/11/2013	1012	WD	NA	NA	NA	NA	793.88	-0.41
3/11/2013	133	WD	NA	NA	NA	NA	789.54	-0.33
3/11/2013	201	WD	NA	NA	NA	NA	779.29	-0.39
3/11/2013	95	WD	NA	NA	NA	NA	773.86	-0.70
3/11/2013	1002	WS	NA	NA	NA	NA	782.33	-0.13
3/11/2013	95	WS	NA	NA	NA	NA	773.88	-0.69
3/21/2013	133	LS	NA	NA	NA	NA	NA	NA
3/21/2013	201	LS	NA	NA	NA	NA	NA	NA
3/21/2013	95	LS	NA	NA	NA	NA	NA	NA
3/21/2013	1002	WD	NA	NA	NA	NA	781.90	-0.56
3/21/2013	1012	WD	NA	NA	NA	NA	793.93	-0.35
3/21/2013	1014	WD	NA	NA	NA	NA	780.71	-0.50
3/21/2013	1015	WD	NA	NA	NA	NA	785.58	-1.13

Sample Date	Location ID	Instrument	raw EC (µS/cm)	Temp (°C)	Temp Correction factor	EC (µS/cm)	Water Table Elevation (masl)	Water table Depth Below Surface (m)
3/21/2013	133	WD	NA	NA	NA	NA	789.55	-0.32
3/21/2013	201	WD	NA	NA	NA	NA	779.40	-0.28
3/21/2013	95	WD	NA	NA	NA	NA	773.80	-0.76
3/21/2013	1002	WS	NA	NA	NA	NA	NA	NA
3/21/2013	95	WS	NA	NA	NA	NA	NA	NA
3/26/2013	133	LS	NA	NA	NA	NA	NA	NA
3/26/2013	1002	WD	NA	NA	NA	NA	781.75	-0.71
3/26/2013	1012	WD	NA	NA	NA	NA	793.85	-0.43
3/26/2013	1014	WD	NA	NA	NA	NA	780.66	-0.55
3/26/2013	1015	WD	NA	NA	NA	NA	785.49	-1.22
3/26/2013	133	WD	NA	NA	NA	NA	789.43	-0.44
5/22/2013	1014	WD	NA	NA	NA	NA	780.00	-1.22
5/22/2013	201	WD	NA	NA	NA	281.0	778.73	-0.95
5/22/2013	95	WD	NA	NA	NA	524.0	773.27	-1.29
6/22/2013	201	WD	NA	NA	NA	NA	NA	NA
6/22/2013	95	WD	NA	NA	NA	NA	NA	NA
7/9/2013	201	WD	NA	NA	NA	NA	NA	NA
7/9/2013	95	WD	NA	NA	NA	NA	772.89	-1.67
7/11/2013	201	WD	NA	NA	NA	290.6	778.43	-1.26
7/11/2013	95	WD	NA	NA	NA	492.8	772.89	-1.67
9/30/2013	95	WD	NA	13.6	NA	430.8	772.71	-1.85
2/7/12 12:00	SR	ISCO	NA	NA	NA	NA	NA	NA
3/21/12 15:52	SR	ISCO	NA	NA	NA	NA	NA	NA
3/26/12 13:35	SR	ISCO	NA	NA	NA	NA	NA	NA
3/26/12 14:37	SR	ISCO	NA	NA	NA	NA	NA	NA
3/26/12 19:44	SR	ISCO	NA	NA	NA	NA	NA	NA
3/27/12 1:44	SR	ISCO	NA	NA	NA	NA	NA	NA
3/28/12 0:55	SR	ISCO	NA	NA	NA	NA	NA	NA
3/28/12 1:44	SR	ISCO	NA	NA	NA	NA	NA	NA
3/28/12 7:44	SR	ISCO	NA	NA	NA	NA	NA	NA
3/28/12 19:44	SR	ISCO	NA	NA	NA	NA	NA	NA
3/29/12 18:10	SR	ISCO	NA	NA	NA	NA	NA	NA
3/30/12 14:10	SR	ISCO	NA	NA	NA	NA	NA	NA
3/30/12 18:10	SR	ISCO	NA	NA	NA	NA	NA	NA
5/26/12 12:55	SR	ISCO	NA	NA	NA	NA	NA	NA
1/26/13 4:08	SR	ISCO	NA	NA	NA	NA	NA	NA

CHAPTER FOUR

Managing nonpoint source pollution in the face of climate change through adaptive management

4 Managing nonpoint source pollution in the face of climate change through adaptive management

4.1 PREFACE

Solving environmental problems can be complex, both scientifically and socially. Approaching the science of environmental problems from an interdisciplinary perspective and communicating that science to stakeholders and policy makers in a meaningful way is necessary if science is to inform decision-making. As a graduate student, I was fortunate to participate in WSU's Integrative Graduate Education and Research Traineeship (IGERT) program, Nitrogen Systems: Policy-oriented Integrated Research and Education (NSPIRE). This program was conceived to provide doctoral students in science and engineering with training and experience communicating science to policy makers. An important component of this training is a three-month fellowship with an organization that operates at the science-policy interface.

I completed my fellowship with the U.S. Global Change Research Program (GCRP) in Washington, D.C. GCRP's mission is to coordinate global change research, including climate change research, among federal agencies and to periodically update Congress on the state of climate science in a National Climate Assessment. GCRP is very much a federal organization; it was authorized by executive order, is located just blocks from the White House, and agency representatives are largely from "inside the beltway." GCRP is often focused on high-level priorities and strategies for agencies' research and core programs. However, from my experience, the program is also very outward-looking, drawing on the experiences of and also supporting regional programs like NOAA's Land Conservation Cooperatives and regional Climate Science Centers, and soliciting the expertise of academic, private sector, and government scientists from across the nation to develop the National Climate Assessment. Consequently, GCRP provides an important two-way link between scientists and high-level federal officials who can make decisions about agency priorities.

While at GCRP I helped organize Adaptation Science Interagency Work Group activities and contributed to the National Climate Assessment, both scientifically and via coordination efforts, and my experiences at GCRP have informed the following chapter in both overt and subtle ways. First, and most obviously, working on the National Climate Assessment provided me with an understanding of the diverse and interacting ways in which climate change will affect our environment and lives, and that addressing climate change now, through mitigation and adaptation, is the best way to avoid the worst effects in the future. Secondly, from working with the Adaptation Science Interagency Work Group, it became apparent to me that federal-level priorities and strategies may be well thought out and clearly stated, but implementation on the ground can be anything but clear. Case studies with examples of implementation can be valuable learning tools for others, bringing these vague directives into the real world. In the following chapter, I review observed and potential effects of climate change on water quality, specifically related to nonpoint source nutrient loading, and point out that there have been high-level calls to address climate change in water quality management. However, to date, very few water quality management programs have done so. I draw on lessons from the few examples of programs that have integrated climate change assessments to identify approaches that water quality managers can take to address climate change, hopefully providing managers with more concrete ways to implement goals set at the federal level.

4.2 ABSTRACT

Nonpoint source nutrient pollution is a major contributor to water quality impairment nationwide, and climate change is expected to exacerbate nonpoint source nutrient pollution in many systems. Federal and state government agencies have called for addressing climate change in water quality management plans; however this is rarely done, due in part to uncertainty about future climate change and effects on specific systems. In addition to evolving uncertainty about climate effects on nonpoint source nutrient loading, important catchment variables that affect nutrient loading (e.g. land-use) also change over time. Consequently, I argue that integrating climate change analyses throughout an adaptive management process is critical to successfully protecting water quality in the future. I identify several actions that can be taken to bring climate change issues into the process of nonpoint source pollution management and provide examples from three current total maximum daily load (TMDL) programs – the Lake Tahoe TMDL for nitrogen, phosphorus and sediment (to address lake clarity) (2011), the Chesapeake Bay Watershed TMDL for nitrogen, phosphorus, and sediment (2010), and the Lake Champlain TMDL for phosphorus (2014). Even with limited resource investment, important mechanisms for climate effects on nonpoint source nutrient loading can be identified and inform the selection of management strategies and a monitoring regime to capture baseline conditions. Additional model improvements can be identified and implemented in conjunction with on-the-ground management to inform subsequent assessments. Finally, programs need to commit to the adaptive part of adaptive management to identify, understand, and address climate impacts on nonpoint source nutrient loading and management.

4.3 INTRODUCTION

Climate change is expected to exacerbate nonpoint source pollution in many regions (Melillo et al. 2014); however, few water quality management programs have addressed climate change issues (Johnson et al. 2012). Uncertainty about the trajectory of climate change and how it will affect systems remains a major hurdle to addressing climate change in current water quality management plans, but I argue that in spite (and because) of this uncertainty, actions can and should be taken now to identify and mitigate negative effects of climate change on water quality via nonpoint source nutrient pollution. These efforts should ideally occur within an adaptive management framework to best cope with uncertainty in a timely and meaningful way.

4.3.1 Nonpoint source pollution and climate change

Nonpoint source nutrient pollution remains a major contributor to water quality impairment in the U.S. (EPA 2014). In the most recent summary of national water quality, nutrients were identified as the third most common pollutant in streams and rivers, and second most common in lakes and reservoirs (EPA 2014). Consistent with this finding, agricultural sources and atmospheric deposition (both nonpoint source) were identified as the most probable causes of water quality impairment in 23% and 18% of impaired stream and river miles, respectively, making these the most and third most common contributors to stream water quality impairment.

Climate change is expected to affect nonpoint source nutrient pollution via a number of different mechanisms (Murdoch et al. 2000; Baron et al. 2013). Changes to the hydrologic regime, including more intense precipitation events, more intense drought periods, and changes in total annual runoff are anticipated for different regions in the U.S. and are likely to have direct effects on nutrient loading (Walsh et al. 2014). More overall precipitation and runoff is likely to lead to greater nutrient loading (e.g. Chang, Evans, & Easterling, 2001; Prathumratana, Sthiannopkao, & Kim, 2008), while more intense precipitation events and snow-on-rain events may lead to more instances of episodic water quality impairment (Royer et al. 2006; Bloomfield et al. 2006; Raymond & Saiers 2010; Casson et al. 2012). Additionally, dry periods can allow nutrients to build-up in the landscape, and, when followed by precipitation events, can result in high nutrient concentrations (Whitehead et al. 2006; Davis et al. 2014).

In addition to direct effects on the mobilization and delivery of nutrients to surface water, climate change will affect the nutrient assimilation capacity of water bodies, as well as important biological responses to changes in water quality (Baron et al. 2013). For example, denitrification, a microbial process that permanently removes nitrate from surface water, increases with temperature and may be enhanced by long residence times associated with low flows, or reduced during high flow periods (Baron et al. 2013). Similarly, coupled increases in temperature and nutrient loading favor nuisance, sometimes toxic, algal blooms, which can be exacerbated by low flows or mitigated by flushing events (Paerl & Paul 2012; Baron et al. 2013).

The effects of climate change on nonpoint source nutrient inputs have already been observed in some catchments, although identifying causal mechanisms and separating the effects of non-climate related drivers can be challenging. For example, Paerl et al. (2006) report an unexpected decline in nutrient loading to the Neuse River in response to intensifying hurricane activity in recent decades, which they attribute to an increase in landscape-scale nutrient retention capacity that resulted from hurricane-related disturbances. In forested catchments in Norway, in-stream nitrate concentration was observed to increase in some catchments in response to declining snowpack but decrease in others; the mechanisms responsible for these divergent responses are not clear and require further investigation (de Wit et al. 2008). Dissolved organic carbon concentrations have been increasing in many streams and rivers in the northern hemisphere, possibly as a result of changing hydrology (Hejzlar et al. 2003; Evans et al. 2005), although declining acid deposition is likely contributing to this pattern in some areas (Monteith et al. 2007). In New Zealand, a significant relationship between total phosphorus concentration and the Southern Oscillation Index (SOI) – which is related to El Niño events – was observed over a 13 year period (Scarsbrook et al. 2003), and the incidence of intense "super El Niño" events is projected to increase in the future (Cai et al. 2014). Finally, warmer springs have resulted in earlier onset of *Microcystis* blooms, which can produce toxins, in the nutrient-enriched Lake Taihu (Deng et al. 2014).

4.3.2 Modeled effects

Potential effects of future climate change on nutrient loading have been examined by coupling climate model output and water quality models. The direction, magnitude, and seasonality of anticipated changes vary widely from watershed to watershed, highlighting the importance of local and regional assessments of climate effects on water quality. A recent study of 20 large watersheds in the US indicates that changes in sediment, phosphorus, and nitrogen loads by the mid 21st century will vary greatly from basin to basin; changes in nitrogen loads range from a decrease by half in the Rio Grande to a doubling in the Kenai River (Johnson et al. 2012). Even within a single region, the direction and magnitude of change may vary drastically; future nitrogen and phosphorus loads in six subbasins in the Susquehanna River Basin range from a decline of over 20% to an increase of over 100% (Chang et al. 2001). Analyses also suggest effects may vary from season to season; for example, in the River Thames, nitrate concentration is projected to increase in the winter but decrease in the summer under most future climate scenarios (Jin et al. 2012).

While changes to nonpoint source nutrient loading in the previous examples are largely driven by shifts in the hydrologic regime, effects of temperature and moisture availability on terrestrial and aquatic nutrient processing are likely to affect nutrient loading as well. In the semi-arid southwestern, US, nitrogen loads are projected to decrease through the 21st century as a result of declining precipitation and runoff, as well as lower soil nitrogen mineralization rates (Ye & Grimm 2013), while Whitehead et al. (2006) project increases in mineralization rates as a result of higher temperatures, leading to higher nitrogen concentrations in the River Kennet in England. Additionally, modeling suggests that in-stream nitrate concentrations are sensitive to denitrification rates, which are highly uncertain for future climate scenarios (Jin et al. 2012).

Climate change represents just one of many stressors that need to be considered to manage water quality and particularly nonpoint source nutrient pollution (Palmer et al. 2009), so models have been developed to assess the combined effects of climate change, land-use change, and alternative management practices, among other factors. Generally, urban development and agricultural intensification are projected to exacerbate climate change effects on water quality. For example, in a mixed land-use watershed in southwestern Ohio, nitrogen and phosphorus concentrations are expected to increase up to 8 and 14%, respectively, by the 2050's due to climate change alone, while urbanization alone is expected to increase concentrations by just 3 and 4%, respectively; however, combined effects of climate and urbanization on P concentrations are greater than the sum of the effects alone (Tong et al. 2012). Studies have identified practices that could mitigate these negative effects. In a heavily agricultural watershed in the Midwest, nitrogen and phosphorus loads are projected to increase from current conditions by 11-37% and 12-30%, respectively, by 2050 depending on the climate scenario, but water quality impairment can be mitigated to greater or lesser degrees by implementing various best management practices (e.g. nutrient reductions of ~50% with terracing but only ~1% with filter strips) (Woznicki et al. 2011). Similarly, Praskievicz and Chang (2011) report that conservation-based urban planning can ameliorate to some extent the anticipated negative effects of climate change on sediment and phosphorus loading in an urbanizing western Oregon watershed. For example, they project a 50% increase in winter orthophosphate loads by 2040 under a combined high climate change – high development scenario, but only a 40% increase with a conservation-minded development strategy. Importantly, the relative effects of climate change and land-use/management on nonpoint source nutrient pollution depend on the scale considered; water quality in large watersheds showed less sensitivity to urbanization than future climate change because the scale of land-use change was small relative to the size of the watersheds (EPA 2013).

4.4 CALL TO ADDRESS CLIMATE CHANGE IN WATER QUALITY MANAGEMENT

Because climate change has already begun and is projected to continue to negatively affect water quality in many regions, federal and state agencies have recognized the importance of incorporating climate change analyses in water resource management decisions (e.g. EPA 2012a). The EPA's *National Water Program 2012 Strategy: Response to Climate Change* outlines goals and strategic actions to mitigate the risks of climate change to water resources, including water quality, by "encouraging states and communities to incorporate climate change considerations into their water quality planning," including load and wasteload allocations for Total Maximum Daily Loads (TMDL) (EPA 2012b). (TMDL refers to water quality criteria set for impaired waterbodies, and the management programs designed to meet water quality goals.) New guidelines for the Nonpoint Source Program and Grants encourage climate change planning activities to be integrated with watershed management planning, and to consider the effects of climate change on water resources (EPA 2013b). Additionally, the EPA's Office of Water Climate Change Adaptation Implementation Plan 2013 Draft calls for "mainstreaming" climate change into core water programs, including water quality management programs, meaning climate change should be routinely considered and incorporated into activities (EPA 2013c).

Some states have initiated efforts to address climate change effects on water quality, typically through integrated water resource planning. California has developed Integrated Regional Water Management approaches, brought together a Climate Change Technical Advisory Group to provide scientific support for managers, and has compiled climate-relevant resources for managers, including a *Climate Change Handbook for Regional Water Planning* (EPA and CDWR 2011). Washington state has identified climate change as a threat to water quality in its recent report, *Preparing for a Changing Climate* (WA DOE, 2012), stating the need to integrate climate change effects on water quality into planning for other sectors, such as forestry. Similarly, Oregon recently released its *Integrated Water Resources Strategy* (OR WRD, 2012), which identified the need to understand how future stressors, including climate change, will affect water resource availability.

Despite this call to address climate change in watershed management plans, up to now the effects of climate change have rarely been accounted for explicitly in water quality management plans, with the majority assuming that hydrologic regimes and temperature conditions will continue to reflect historical distributions. (Johnson et al. 2012, but see Klein et al. 2012, Table 4.1). Widespread failure to assess climate change impacts during planning for the future is probably due to a combination of factors, including a lack of guidance as to how this can be rigorously accomplished, limited data associated uncertainty surrounding hydrologic and ecological responses to climate change, and a lack of resources required to carry out these assessments (e.g. Lake Tahoe TMDL, Chesapeake Bay TMDL, Table 4.1.). However, developing feasible approaches to address climate change in water quality management plans is critical for protecting water quality in the future.

There exist very few examples of water quality management programs focused on nonpoint source pollution that have attempted to address climate change effects. I used these examples to illustrate different approaches that can be taken and to provide insights into how research and regulatory communities can help climate change assessments become mainstreamed in water quality management programs. These programs include three current TMDLs – the Lake Tahoe TMDL for nitrogen, phosphorus and sediment (to address lake clarity) (2011), the Chesapeake Bay Watershed TMDL for nitrogen, phosphorus, and sediment (2010), and the Vermont Lake Champlain TMDL for phosphorus (2014).

4.5 AN ADAPTIVE MANAGEMENT FRAMEWORK

Adaptive management – "learning by doing" (Holling 1978) – has been accepted as an appropriate way to manage watersheds and water resources when large uncertainties, like those associated with the effects of climate change, are at play (e.g. NRC 2001; Pahl-Wostl 2007; Bruch & Troell 2011; Nanni 2012). Adaptive management of nonpoint source nutrient pollution in the context of climate change is particularly appropriate because both the system (land-use/management, climate, biogeochemical feedbacks) and our understanding of system are changing over time. Adaptive management cycles have been variously characterized, but contain the essential elements of deciding, doing, evaluating, and re-assessing decisions based on new information before continuing. I define the steps as: 1. Problem Assessment, where contributions to the problem and risks to successful mitigation are analyzed; 2. Management Strategy Selection and Implementation, where possible strategies are evaluated and chosen for implementation; 3. Monitoring, which occurs before/following implementation and is designed to provide information about implementation success; 4. Data evaluation and effectiveness assessment; where data collected in the field are analyzed to determine whether selected strategies are having their intended effect and what issues might be interfering with success; and 5. Re-evaluation of the problem based on new information (Fig. 4.1). In the context of climate change and nonpoint source nutrient loading, I suggest that incorporating a modeling loop in conjunction with field activities is critical for improving decision making during subsequent rounds of adaptive management (Fig. 4.1).

4.5.1 1.) Problem assessment

Once routine monitoring indicates that water quality needs improvement, the causes of impairment and potential risks to future impairment, including climate change, must be identified. Two important climate-related questions should to be addressed at this stage: 1) How sensitive is the water quality problem to climate change? and 2) By what mechanisms is climate change expected to affect water quality? (Table 4.2) Depending on the resources available, efforts to address these questions can range from a review of relevant, available literature to characterize projected changes in the regional hydrologic regime and possible mechanisms for effects on nonpoint source nutrient pollution, to a developing an watershed-specific mechanistic model to better characterize the range of nutrient loading under future scenarios and specific mechanisms that mediate these changes (Table 4.2). The three TMDL case studies represent a range of approaches to address these first-order questions, resulting in varying degrees of certainty about the direction, magnitude, and timeframe of expected climate effects, and the mechanisms by which climate change is expected to affect water quality.

Uncertainty about the climate change effects on water quality will inevitably be high due to multiple aspects of the modeling process (Hawkins & Sutton 2009; Praskievicz & Chang 2011). The future trajectories of greenhouse gases and human land use and management are unknown, and incorporating scenarios that span plausible futures can provide a range of reasonable projected effects on water quality (Yuan et al. 2011; Jin et al. 2012). Additionally, the climate models themselves are uncertain and can produce a range temperature and precipitation output given the same greenhouse gas scenario (Räisänen 2007); this can be managed by using as many GCMs as feasible to capture a range of potential futures and identify likely trends (e.g. Whitehead et al. 2006; Johnson et al. 2012) . Finally downscaling GCM output to relevant watershed scales also includes uncertainty (Johnson et al. 2012), which is important to recognize when addressing small watershed-scale management problems.

For the Lake Tahoe TMDL, the literature pertaining to observed and potential effects of climate change on basin hydrology and sediment and nutrient loading to the lake was reviewed, and an exploratory analysis of precipitation regimes under a range of climate scenarios was conducted. These efforts provided insights into the anticipated direction of climate effects; it was concluded that warming was likely to continue, leading to stronger lake stratification and reduced clarity, and a shift from a snow-dominated system to rain and snow at lower elevations, which could lead to increased nutrient and sediment inputs during the winter, further degrading water clarity. While the direction and likely mechanisms for effects were identified, considerable uncertainty about the magnitude and timing of these effects remained.

In the early stages of the Chesapeake Bay Watershed TMDL, a modeling analysis was conducted to assess nitrogen, phosphorus, and sediment loading in the Monocacy River sub-basin under multiple climate change and land-use scenarios for the 2030's, and in the major rivers under a subset of these scenarios. Median projected annual nitrogen and phosphorus loads for the major tributaries were 1.6% and 2.1% lower than current conditions, suggesting climate change will result in slightly less pressure on water quality by the 2030's. Although the models indicated precipitation was likely to increase, this was offset by increased evapotranspiration, resulting in a minimal impact on flow and nutrient transport to rivers. Ultimately, the Chesapeake Bay Program's watershed-specific modeling efforts provided some insight into the direction, magnitude, timeframe and mechanisms for climate change effects on nutrient loading, which could then be accounted for in subsequent load and wasteload allocations (as intrinsic Margin of Safety).

For the revised 2011 Lake Champlain TMDL, site-specific modeling of flow, total suspended solids, and phosphorus loading in tributaries to Lake Champlain under multiple climate scenarios for mid 21st century was conducted. When averaged across all watersheds, median annual increases of 13 and 30% for total suspended solids and phosphorus, respectively; all scenarios predict increases in phosphorus loads, but the range of projected change for total suspended solids includes zero. Researchers note that due to multiple uncertainties (e.g. GHG trajectory, differences among global climate models, downscaling, future land-use patterns), there is no single "best" prediction, and this scenarios approach was meant to provide an envelope of plausible futures for the watersheds, which could be considered in management decisions.

Obstacles All of the TMDLs identified obstacles to meaningfully characterizing potential climate effects on their respective water quality issues. Climate models were not able to simulate critical processes (e.g. the interaction between intense precipitation events and evapotranspiration in the Chesapeake Bay watershed) and uncertainty about the magnitude and timing of future climate change effects were identified in all three as issues, although each used a scenarios approach to cope with this uncertainty to some extent, as is standard practice (Johnson & Weaver 2009). Additionally, in the Chesapeake Bay TMDL, a lack of resources – human, monetary, and time - was identified as the reason more in-depth analyses were not conducted for each of the major river tributaries. Although uncertainties can limit how explicitly the anticipated effects of climate change on water quality are addressed in subsequent load and wasteload calculations and selection of management strategies, it is necessary to identify specific uncertainties and model shortcomings so they can be addressed, if possible, through future monitoring and modeling efforts.

4.5.2 2) Management strategy selection and implementation

After the important sources and drivers of nutrient pollution are characterized, appropriate management strategies need to be identified and implemented. Here, the anticipated effects of climate change and mechanisms can be considered in a “no regrets” approach (Table 4.2). Selecting strategies that are effective in the present as well as under future climate scenarios can help avoid actions that may unintentionally exacerbate climate effects and the costs of having to implement alternative strategies in the future. At a minimum, current understanding of mechanisms for climate effects on water quality, such as increasing erosion, can be qualitatively considered when assessing management strategies. If more modeling resources are available, the effectiveness (and uncertainty about effectiveness) of various management practices in the face of a range of climate scenarios can be explored for watersheds (e.g. Whitehead et al. 2006; Woznicki & Pouyan Nejadhashemi 2014). The three TMDLs illustrate a wide range of the extent to which projected climate change effects can be considered during the process of selecting and implementing management strategies.

The Lake Tahoe TMDL explicitly assumes no effects of climate change in their selection of management strategies and assumptions about the timeframe for success, citing uncertainty as being too great for climate change to be addressed in the current response. This is despite initial investigations suggested that climate change was likely to exacerbate water clarity issues by enhancing erosion and nutrient transport to the lake, and altering critical in-lake processes, Instead it is assumed that future monitoring will indicate when, if ever, additional actions need to be taken to address climate change impacts.

The Chesapeake Bay incorporated expected climate effects on nutrient loading (expected to be minimal and probably decrease loading) into the intrinsic margin of safety, asserting that estimates of loading in the absence of climate change were conservative. Therefore, proposed actions that were expected to ameliorate the problem under current circumstances would be even more likely to succeed under future climate change.

The Lake Champlain TMDL represents the most aggressive approach to management under the assumption of climate change; the plan assumes climate trends will continue and explicitly takes a “no regrets” strategy to selecting management tools. Because climate change is expected to exacerbate phosphorus loading primarily by increasing the risk of flooding and erosion, planners identify strategies to mitigate negative effects: they propose restoring natural hydrologic processes that reduce the risks of flooding and erosion, for example, via wetland and floodplain reconstruction.

Obstacles Several difficulties associated with management selection and implementation are identified in the case study TMDLs. The Lake Tahoe TMDL indicates that climate model output is too uncertain to even be considered when selecting current management strategies. The Chesapeake Bay Watershed TMDL noted that climate models need to be downscaled to the level of management to improve decision-making. Additionally, the Lake Champlain TMDL noted that stakeholders, particularly farmers, needed additional education about management options and tools, as well as resources, to help them tailor plans to individual farms to improve chances of overall success of the program. This includes a downscaled Best Management Practice (BMP) selection tool. Finally, a survey conducted for the Lake Champlain TMDL indicated that the public viewed climate change as the least pressing risk (of the 13 presented) to water quality, while staff on the project rated it 9th most important, suggesting some lack of support among stakeholders for addressing climate change issues meaningfully.

4.5.3 3) Monitoring

Monitoring is critical for providing feedback on the effectiveness of management strategies and any issues that may be interfering, including climate change. To date, few studies have been able to quantify the effects of climate change on nutrient loading, and effective monitoring can provide critical baseline information and, eventually, long-term data necessary to analyze trends and quantify the contribution of climate to changes in water quality (Table 4.2). Additionally, monitoring can address any data needs identified during the problem assessment to better model future climate impacts and/or target critical conditions that are expected to be most strongly affected by climate change. For example, if increasing precipitation intensity or drought periods followed by heavy precipitation are expected to be the major effects of climate change, water quality sampling can be targeted during these periods.

The Lake Tahoe TMDL provides an example of explicitly designing monitoring to be able to detect climate change effects. The TMDL indicates that long-term monitoring will continue, funding permitting, and should be able to detect trends in water quality as well as drivers of trends, including climate change. This is particularly critical since this TMDL did not address future climate change in the implementation strategy itself, and monitoring is required to determine whether additional actions need to be taken. Monitoring in relation to climate change effects was not mentioned specifically in either of the other two TMDLs, although extensive monitoring networks in the watersheds are expected to be maintained in the future.

4.5.4 4) Data analysis, effectiveness assessment and problem reassessment

Analyzing data to determine whether management strategies are resulting in their intended effects is a critical step in adaptive management. Monitoring data can be analyzed to assess whether climate change impacts are interfering with (or promoting) success. Modeling efforts undertaken simultaneous to implementation and monitoring (discussed below) should be used to re-evaluate projected climate change impacts for the watershed and whether the current strategy is likely to continue to be effective under future conditions. These evaluation and adaptive steps are theoretically built into the TMDL and nonpoint source nutrient management programs (e.g. Nonpoint Source Grant Guidelines), but the cycle is often slow on the ground. A review of stream restoration projects across the country suggests very few projects receive adequate funding for monitoring and assessment or make information available for learning (Bernhardt et al. 2005, Palmer et al. 2007). Even when adaptive management is codified, the process is slow. For example, in Washington State, the Department of Ecology is supposed to conduct effectiveness monitoring for TMDLs every 5 to 10 years, but effectiveness reports are only available for 12% of the listed watershed management plans across the state (WA DOE

2014). Similarly, in Idaho, reassessments of watershed management plans are required to take place every 5 years (Idaho Statute *39-3611*), but in reality are occurring on average once every 10 years (ID DEQ 2014). Due to current uncertainties about the effects of climate change on water quality, a commitment to re-evaluate and re-examine climate on a timescale relevant to water quality changes is critical for avoiding the worst water quality impacts.

Each of the TMDLs have outlined timeframes for evaluation and reassessment prior to the next phase. The Lake Tahoe TMDL is developing the Lake Tahoe Management System to keep track of implementation projects and data and provide milestone reports every 5 years, when climate change effects can be re-assessed. Similarly, the Lake Champlain TMDL describes a tactical basin planning process that will re-evaluate and prioritize management actions every 5 years, although climate change assessment is not explicitly described as a component of this process. Finally, the Chesapeake Bay Watershed TMDL is committed to re-evaluating climate change at the mid-course assessment in 2017, presumably with more sophisticated modeling tools at their disposal.

4.4.5 Modeling

All of the case study TMDLs identified insufficient modeling capability as a barrier to assessing the potential effects of climate change on future water quality and selecting local management strategies that would protect water quality in the future. The specific problems identified – the need for more detailed downscaling and lack of capacity to model important landscape processes and interactions – cannot be ameliorated with additional monitoring, suggesting a need to explicitly include a modeling component alongside field activities to improve the management of nonpoint source nutrient pollution. Modeling needs should be identified during the initial problem assessment phase, and monitoring can be designed to inform the modeling effort.

The Lake Tahoe TMDL represents the least explicit and aggressive approach to addressing and improving climate model uncertainty. Uncertainties associated with climate-water quality models are cited as being too great to affect current management decisions, despite observed (and significant) trends in lake temperature and stratification in recent decades. The Lake Tahoe TMDL Management System has a component for additional research outside of regular monitoring that is needed to inform future decision-making, which could hypothetically include efforts to improve climate change models, but this is not explicitly addressed as part of the TMDL.

The Chesapeake Bay Watershed TMDL only implicitly accounts for climate change during the first round of implementation, but identifies specific model improvements that can be made to improve decision-making in future cycles. These include improved spatial downscaling to better inform local management decisions and capacity to simulate interactions between high intensity precipitation events and evapotranspiration, effects of tidal water column temperatures, and temperature-dependent effects on important species and ecological communities. Importantly, the TMDL moved forward with the assumption that climate trends would continue and effects on water quality would be felt (e.g. implicit assumption in the Margin of Safety) while supplemental modeling efforts are undertaken.

The Lake Champlain TMDL clearly addresses projected effects of climate change in management decisions in the 2014 Implementation Phase I, but commits to needed climate-related model improvements less explicitly. Anticipated effects of climate change on phosphorus loading are integrated into the “no regrets” approach to BMP selection, with an emphasis on strategies that will be effective at reducing flooding and erosion under current and future conditions. However, the need for more localized information to select the most effective BMPs is identified; EPA's Scenarios Tool was used to assess relative effectiveness at a coarse scale, and the program is committed to develop higher resolution SWAT models for the entire basin to prioritize BMPs before Phase II, as has already been done for Missisquoi basin. Climate-related issues are not explicitly incorporated into this model, but hypothetically could be integrated.

4.6 RECOMMENDATIONS AND CONCLUSIONS

Managing nonpoint source nutrient pollution in the context of climate change is challenging; there are large uncertainties, multiple variables are changing through time and interacting, and there exist multiple solutions to the problem (with varying degrees social acceptability). Adaptive management is an appropriate approach to cope with these difficulties, and I have identified specific actions that can be taken at each stage to ensure climate analyses are adequately considered and future water quality is protected. Observations and modeling efforts in the literature suggest considerable uncertainties remain about the magnitude and timeframe for climate change impacts on nonpoint source nutrient pollution, particularly at local scales. This is evident in case studies, where model uncertainty is identified as a major obstacle to meaningfully integrating climate change into management planning, even in these large well-funded programs. However, initial climate assessments are critical so that needed improvements can be identified and incorporated into models that can contribute to problem assessment and decision-making during subsequent adaptive management cycles. Additionally, even limited initial climate assessments can inform a "no regrets" approach to selecting management strategies, and any monitoring needed to improve models and baseline monitoring of climate-relevant critical conditions can begin. Importantly, monitoring data and new tools and models that are developed should be made available to the broader research and management community. Finally, the TMDLs discussed here all developed specific timelines for evaluating success, which may be hindered by climate change. Re-evaluating on time is particularly critical, particularly if climate analyses do not initially inform load and wasteload calculations or selection of management strategies.

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4.8 TABLES

Table 4.1. Examples of climate change analyses being incorporated into adaptive management strategies associated with TMDLs targeting nonpoint source pollution.

TMDL	Climate Change Component	Relevant Adaptive Management Step	Stated Difficulties/Needs
Lake Tahoe (2011) for Nitrogen, Phosphorus, and Sediment to attain water clarity[1]	Literature review of observed and potential effects on hydrology and sediment and nutrient loading Exploratory modeling analysis of basin hydrology under a range of climate scenarios	Problem Assessment	Effects of climate change on future nonpoint source nutrient loading are highly uncertain and cannot currently be determined
	Pollution reduction timeline assumes climate change does not adversely affect progress (climate change NOT incorporated)	Strategy selecting and implementation	
	“status and trend monitoring” to detect changes in water quality and drivers, including climate change, to be integrated in monitoring plan	Monitoring	Contingent on continued funding for extensive monitoring
	Climate change will be addressed within an adaptive management framework, with milestone reports every 5 years based on the Lake Tahoe TMDL Management System Implementation plan can be adjusted if milestones are not being met.	Evaluate Effectiveness and Re-Assess Problem	

Chesapeake Bay Watershed (2010) for Sediment, Nitrogen and Phosphorus[2]	Modeled sediment, nitrogen and phosphorus loading to the Monocacy River under many climate-land-use scenarios and all river basins under a subset of scenarios and using BASINS-CAT; results suggest nutrient loading is likely to decline while sediment loading may increase.	Problem Assessment	Staff resources and time constraints[c] Model limitations to fully simulate the effects of climate change[c] Need capacity to evaluate climate change effects at the scale watershed implementation plans (downscaling to 92 segments in the watershed)[d] Need to develop and/or improve model simulations of interactions between evapotranspiration and high intensity precipitation, effects of tidal water column temperatures, temperature-dependent effects on important species and ecological communities[e]
	Incorporate climate change assessment implicitly into the Margin of Safety for nitrogen and phosphorus Incorporate climate change assessment explicitly into Margin of Safety for sediment	Selection and implementation of management strategies	
	Commitment to re-evaluate climate change effects at the mid-course assessment (2017)[d]	Evaluate Effectiveness and Re-Assess Problem	

Lake Champlain (2002) for Phosphorus[3]	No mention of climate change issues		
Lake Champlain Updated Implementation Plan (2010)[4]	Stated need to use “best available” science to incorporate anticipated effects of climate change into management strategies[g]	Problem Assessment, Selection of Management Strategies	Need to further develop climate change model for the lake[g] Funding needs to be made available for modeling effort[g] Climate change was viewed as the least pressing risk (of 13 presented) to success by the public, and 9th most pressing by staff
Lake Champlain Phase I Implementation Plan (2014) for Phosphorus[5]	Modeled flow, total suspended solids, and phosphorus loading in tributaries to Lake Champlain under multiple climate scenarios for mid 21st century; SWAT was used[6]	Problem Assessment	Large uncertainty about magnitude and timing of future climate change impacts; used scenarios approach to bound plausible futures[6]
	Identified a “no regrets” strategy for selecting management strategies. These include approaches to reduce the risks of flooding and erosion by: implementing BMPs that increase infiltration capacity and reducing runoff in agricultural lands; restoring and protecting wetlands, floodplains and shorelines; making forests more resilient to climate change.	Management Strategy Selection and Implementation	More education, tools and resources for farmers to implement BMPs Need to consider human response to climate change – converting forest to agricultural land, switching crops, altering land management (e.g installing more tile drains)

	EPA Scenarios Tool could be used to assess effectiveness under climate change currently isn't (explicitly)[7]	Effectiveness Evaluation and Problem Re-Assessment	Scenarios Tool needs to be downscaled to provide local information about P sources and BMP effectiveness
	Milestones to be assessed every 5 years	Problem Re-Assessment	

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[1] All information from the Lake Tahoe TMDL for Nitrogen, Phosphorus, and Sediment (NV DEP, 2011)

[2] All information from the Chesapeake Bay Watershed TMDL for Nitrogen, Phosphorus, and Sediment (EPA, 2010)

[3] All information from the Lake Champlain TMDL for Phosphorus (VT ANR & NY DEC 2002)

[4] All information from the Lake Champlain Revised Implementation Plan for Phosphorus (VT ANR 2010)

[5] All information from the Lake Champlain Phosphorus TMDL Phase I Implementation Plan (VT ANR 2014) unless otherwise noted.

[6] Lake Champlain Basin SWAT Climate Response Modeling (Tetra Tech, 2013a)

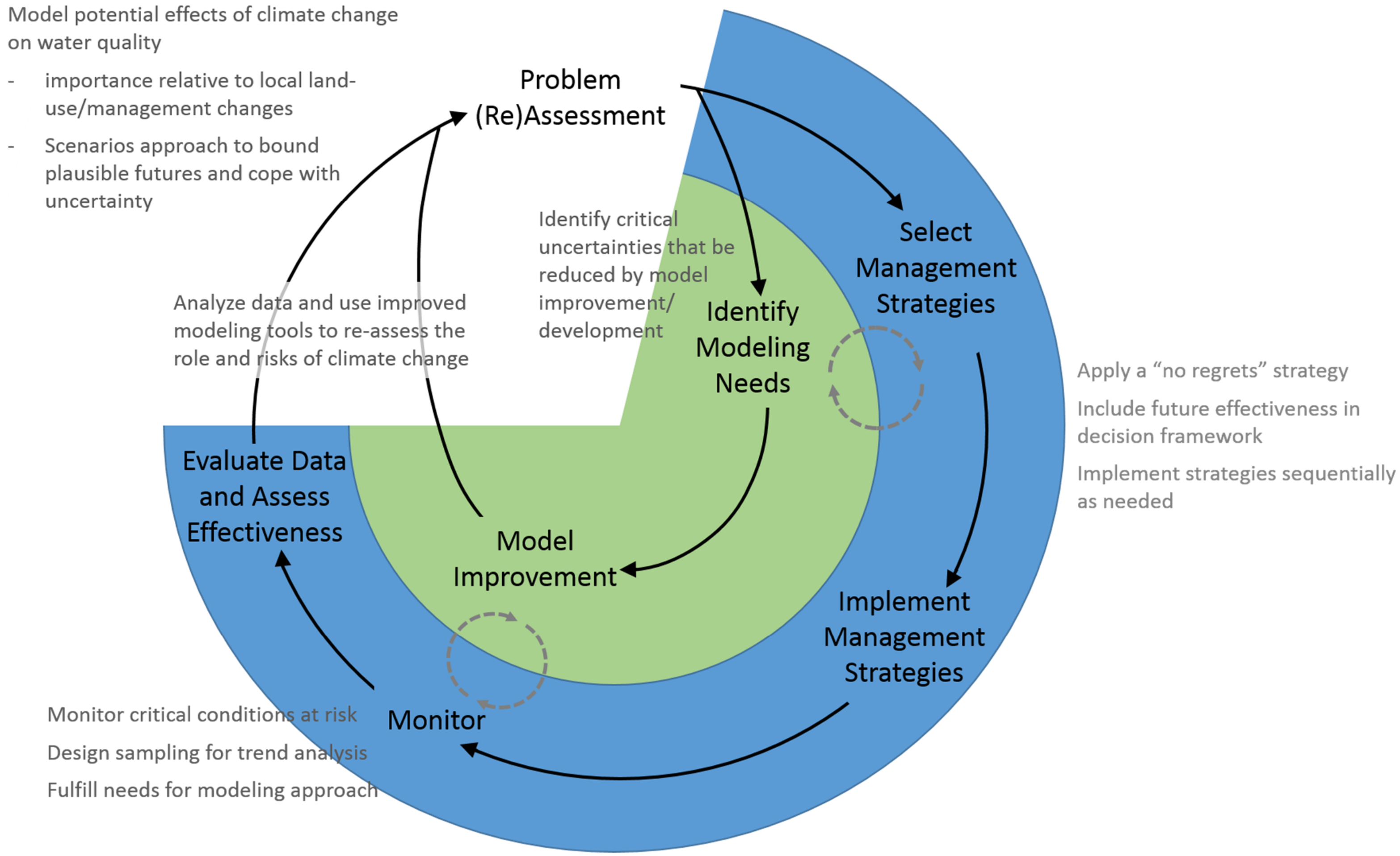
[7] Lake Champlain BMP Scenario Tool, Draft (Tetra Tech, 2013b)

Table 4.2. Recommendations for addressing climate change in water quality management plans.

	Approaches	
	Less resource intensive	**More resource intensive**
Questions to Address		
How is climate change expected to affect water quality in the watershed? - Direction - Magnitude - Timeframe	Explore literature for any existing regional or local analyses. Even regional hydrologic simulations can provide some insights (e.g. more intense precipitation predicted, significantly less overall precipitation predicted)	Conduct watershed-specific climate change-water quality modeling
By what mechanisms is climate change expected to affect water quality?	Expert understanding of the system	Develop mechanistic watershed model that includes climate as an input and water quality as an output.
Actions to Take		
If important mechanisms by which climate change is expected to affect water quality can be managed and/or mitigated, incorporate this information into a "no regrets" approach to managing water quality, as the timeframe and magnitude of effects are likely to be highly uncertain.	Based on current understanding of the system, choose approaches likely to be effective under both current conditions and future climate pressures. (e.g. select approaches that will minimize erosion)	Model water quality under future climate scenarios and various management strategies to prioritize appropriately.
Begin/continue water quality monitoring to establish baseline/current conditions that can be compared to future conditions.	Maintain sampling effort (current number of samples per month/year) but ensure critical conditions are included	Enhance sampling intensity and target critical conditions expected to be affected by climate change
Commit to and follow through on adaptive management cycle		

Critical Research to Pursue		
Downscale climate-water quality models	To watershed, climate scenarios alone	To scale of management, climate and land-use/management scenarios
Model and quantify effects of management strategies on water quality	Under current conditions, singly	Under future scenarios, various combinations, spatially explicit
Research Community Efforts		
Make monitoring data and newly developed tools/approaches available	Submit to department databases and websites	Submit to relevant climate information portals, such as California's Climate Change Portal, the World Bank's Climate Change Knowledge Portal, etc.

4.9 FIGURES



Model potential effects of climate change on water quality

- importance relative to local land-use/management changes
- Scenarios approach to bound plausible futures and cope with uncertainty

Identify critical uncertainties that be reduced by model improvement/ development

Analyze data and use improved modeling tools to re-assess the role and risks of climate change

Apply a "no regrets" strategy

Include future effectiveness in decision framework

Implement strategies sequentially as needed

Monitor critical conditions at risk

Design sampling for trend analysis

Fulfill needs for modeling approach

Figure 4.1. Diagram showing the Adaptive Management cycle, including co-occurring modeling (green) and field (blue) activities. Gray text describes approaches to incorporate climate change analyses into each step of the Adaptive Management cycle.

GENERAL CONCLUSION

The meta-analysis examining the response of in-stream dissolved organic nitrogen concentration ([DON]) to high flow events across ecosystems indicates that [DON] increases significantly with flow across a wide range of ecosystem types, resulting in order of magnitude increases in DON fluxes during high flow events relative to baseflow. In many cases, DON apparently became decoupled from dissolved organic carbon (DOC), with the two species displaying different responses to discharge. These patterns can likely be attributed to novel DOM sources in the landscape being mobilized and transported to streams and rivers, although the meta-analysis approach cannot distinguish controlling mechanisms.

Mechanisms controlling DOM export, including DOC and DON concentrations and the quality of DOM, were examined in a small agricultural catchment in eastern Washington State. In the soil column, DOC concentration declined and the quality of DOM shifted from humic-like and plant-derived to microbially-derived with depth through the profile, similar to patterns observed in natural forested catchments. DOM exported via drain discharge during low flows resembled that found deep in the soil profile, and DOM exported during high flows resembles topsoil and litter sources. Across seasons and years, [DOC], FI, β/α, and humic-like fluorescence components were significantly and strongly correlated with drain flow rate. An analysis of anticipated effects of climate change on the flow regime in the catchment projects more runoff during both the wettest and driest years relative to current conditions, with even larger increases in DOC export due to increasing incidence of intense high flow events, which export disproportionately more DOC.

A simple mixing model suggests that litter leachate can contribute over 50% of DOM during peak flow, highlighting the potential for topically-applied organic nutrients to be directly exported to surface water via subsurface drainage. Based on modeled contributions of litter, topsoil and subsoil sources of DOM to drain discharge DOM during storm events, drain discharge [DOC] is over-predicted, except for peak flows, suggesting removal via sorption and/or microbial decomposition in the soil column control DOC export on the timescale of events. Distinguishing the relative importance of biotic and abiotic removal is needed to partition the fate of DOC during transport. Although the source and character of exported DOM shifts with flow conditions, laboratory incubations suggest bioavailability to the stream sediment microbial community is consistently low, with a maximum loss of 7% over 6 days, indicating exported DOM is likely transported beyond the immediate stream reach, but future research is needed to assess how photodecomposition and the presence of labile autochthonous DOM could alter decomposition rates of drain discharge DOM in the receiving stream.

Finally, observational and modeling studies indicate that climate change is likely to exacerbate nonpoint source pollution in many regions. Federal agencies and some states have explicitly recognized this threat to water quality and have called for the consideration of potential climate change effects when developing water quality management plans. However, very few management plans have addressed climate change effects in a meaningful way. Using a case study approach that includes three Total Maximum Daily Load (TMDL) programs that have addressed climate change to varying degrees, I identify approaches that water quality managers can take to incorporate climate change assessments within an adaptive management framework. These include: identifying a range of plausible futures and mechanisms for climate change effects, considering these plausible futures and mechanisms to select “no-regrets” management strategies and tools, and monitoring water quality for trend analyses in the future and to assess the effectiveness of management actions. Additionally, due to the complexity of and uncertainties about climate effects on water quality, I recommend that a modeling component accompany on-the-ground management to help improve decision-making. Finally, completing the adaptive management cycle will be critical for avoiding the worst impacts of climate change, as the timeframe for projected climate effects and human responses to climate change that affect water quality remain highly uncertain.