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Short communication

Snowpack enhanced dissolved organic carbon export during a variety of hydrologic of events in an agricultural landscape, Midwestern USA

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ABSTRACT

This study investigates the dynamics of riverine DOC concentrations during a series of stream discharge events (3–10 days) following rainstorms of different intensity and duration. We examined six events, when high-frequency (hourly) water samples for DOC (n = 321) were collected in spring (n = 166) and autumn (n = 155). Results identified three distinct water-mediated processes during stream discharges events that linked DOC source supply from agricultural land surfaces with sinks in a receiving river. These were as follows: 1) snowpack drives significant high DOC concentrations in base-flow during spring, 2) abundant organic matter in topsoil from crop residues determines a rapid DOC loading profile in the first flush, and 3) very large hydro-climatic events in snow-melting season over agricultural watersheds could increase the riverine DOC flux by 2.3 folds. These results revealed that ca. 76.5% of annual DOC was exported during a handful of storm-discharge events (78.9% for spring and 74.2% from autumn) over agricultural landscapes. Given the significant amount of riverine DOC exported from agricultural landscapes during severe weather events, our results suggest that changes in climate promote larger precipitation events that would likely enhance the export of terrestrial DOC to receiving water bodies. The study presents a semi-analytical model that is able to extrapolate the riverine DOC dynamics during storm discharge events of varying duration and intensity (R^2 up to 0.9).

1. Introduction

Dissolved organic carbon (DOC) is a significant source of energy to marine and fresh water environments, being the basic building block of food webs and influencing the bioavailability of nutrients and metals (Porcal et al., 2009; Benstead and Leigh, 2012). The annual transfer of dissolved and particulate organic carbon (DOC/POC) from terrestrial ecosystems to inland waters and the ocean is estimated as 0.37 $*10^{15}$ gC yr^{-1} (Schlünz and Schneider, 2000). Such large loadings of allochthonous organic carbon suggest that aquatic systems can act as net sources of CO_2 to the atmosphere (Duarte and Prairie, 2005) and thereby contribute significantly to the global carbon cycle and associated changes in climate (Meybeck, 1993). Aquatic DOC fuels detrital food webs that can augment autotrophic carbon production (Findlay, 2010); however, over long time scales, small but consistent losses of DOC/POC containing limiting or essential elements can reduce the capacity of ecosystems to support primary productivity (Jason et al., 2001; Hedin et al., 1995; Vitousek et al., 1998). That said, DOC can affect the biogeochemical conditions in aquatic ecosystems in other ways as well, by limiting the penetration of UV radiation and thereby limiting phytoplankton photosynthesis (Kaplan et al., 2006; Williamson and Zagarese, 1994). The chemical structure and reactivity of the some components of the DOC pool can contribute to the formation of Trihalomethanes (THMs) and other byproducts than can impede biological productivity (Gough et al., 2014; Galapate et al., 2001).

Climate-driven intensification of ground and oceanic warming has increased the frequency and magnitude of extreme events (e.g. heavy snow and large storm discharges, IPCC, 2014, US EPA (2014), Fabina et al., 2015). Similarly, there is an increasing trend in precipitation and water storage in the Midwestern USA (Slater and Villarini, 2016). It has been well documented that the majority of annual riverine and estuarine DOC fluxes occur during key, storm-discharge events (Dalzell et al., 2007; Inamdar et al., 2006; Joanna et al., 2007; Jeong et al., 2012), for example, Raymond and Saiers (2010) reported that about 86% of annual DOC from forested watersheds was exported during storm-discharge events in the Northeastern United States. A similar set of results was presented by Oeurng et al., (2011), who showed that the top 10%-20% of large storm events contributed > 70% to the annual

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DOC loading from mountain drainage area to rivers. These results are consistent to that sampled by Dhillon and Inamdar (2013), who monitored 14 storm events with varying magnitude and intensity: they concluded that the greatest DOC export was associated with Hurricane Irene on 27 August 2011 (precipitation: 155 mm). This was also true for temperate, grassland watersheds (central Ontario, Canada), where a large proportion of annual terrestrial DOC (31%–66%) was exported during large (storm-flow) discharge events (Eimers et al., 2008; Hinton et al., 1997).

Most of previous studies were focused on estimating carbon exports from forest land-uses (Aitkenhead-Peterson et al., 2005; Clark et al., 2007; Vidon et al., 2008; Worrall et al., 2002); however, our understanding is lacking of the processes that govern DOC flux from agricultural watersheds to receiving water bodies during stream discharge events (Dalzell et al., 2007; Royer and David, 2005; Tian et al., 2013). In order to study the DOC cycling processes in response to global climate changes, it is important to learn how riverine DOC changes with varying storm intensity and durations coupled with snow-melting (Hope et al., 1994; Laudon et al., 2004; Caverly et al., 2013). Given that row crop land cover account for 40% of the Earth's land surface (Foley et al., 2005), it is important to analyze what scale of storm-discharge events and seasonal effects would raise DOC export from croplands to levels that would affect ecological conditions in aquatic ecosystems. An important question is whether the seasonal variations of riverine DOC in the storm discharges over agricultural landscapes are significant.

A number of sources have shown that the frequency and magnitude of large snow or rainfall events have increased over the past 200 years (Groisman et al., 2004; Groisman et al., 2005; Karl, 2009; Yoon and Raymond, 2012). As snowpack expedites carbon transformation processes (Dalzell et al., 2005, 2007; Vidon et al., 2008), large precipitation events resulting from climate change would likely increase DOC loading to receiving water bodies, particularly from agricultural watersheds during seasonal snow-melt periods. Here, we investigated the seasonal dynamics of riverine DOC loading from agricultural watersheds during a series of stream discharge events that captured a range of rainstorm scales. We examined whether linkages existed between discharge events (surface runoff and groundwater pathways) and DOC fluxes to a receiving stream ecosystem. Our specific research questions were as following: 1) do hydro-climate events (and associated snow-melting processes) have significant impact on DOC exports from agricultural landscapes?, 2) does the availability of organic matter (present in surface soil and groundwater leachate) determine the rapid loading profiles of riverine DOC in the initial surface runoff and in the base flow during stream discharge events; and 3) does riverine DOC exports vary as function of stream discharge events (contrasting spring and autumn events)? Our approach was to address these questions using high frequency field collections taken at hourly intervals during six precipitation-driven, stream discharge events.

2. Materials and methods

2.1. Study site

The study site was conducted in the Chippewa River watershed (Michigan USA), located in a temperate continental and humid climate, with an average precipitation of 71.04 and 81.79 mm in spring and autumn (1981–2010, US Climate Data, at http://www.usclimatedata.com/climate). The Chippewa River is a fourth-order tributary of the Saginaw River, which flows into the Lake Huron. The river drains an area of 1037 km^2 along a riverine length of 62 km (Fig. 1), with an annual average discharge of 7.19 m^3/s (23.88 m^3/s and 5.97 m^3/s, spring and autumn, respectively) during the 1931–2013 period (USGS NWIS, available at http://waterdata.usgs.gov). The watershed has a relatively flat topography with the mean slope of 0.4 °, generally sloping from west to east.

The drainage area is dominated by agricultural land cover (approximately 45%) mixed with forest (40%), and residential (4%) and wetland areas (11%). The major agricultural products in the watershed are row crops (i.e., corns and beans), which are generally associated with high DOC inputs to receiving waters (Chow et al., 2006). The secondary land use, the mixed forest, also generates a significant amount of DOC inputs through seasonal leaf fall. It has been known that wetland is a potential source of DOC (Tian et al., 2012, 2013).

2.2. Measurements of stream discharge and DOC

Field measurements of riverine DOC dynamics and associated river flows were made at the eastern-most outlet of the Chippewa River watershed (Fig. 1), located ~ 50 m from a USGS gauge station (station 04154000, latitude 43°37′34", longitude 84°42′28") where river flow data are available at an interval of five minutes. Six stream discharge events were evaluated after storms in the spring and autumn periods from 2013 to 2015 (Fig. 2). In the spring, DOC sampling occurred from late March to early May when stream/river systems thawed from winter ice formation and snow turned to rainfall (Table 1). Sampling for fall stream discharge events occurred from early October to November prior to freezing conditions and the onset of winter. The term of stream discharge event was defined as the criteria for graphical hydrograph separation to define periods of storm-flow and base-flow (Hinton et al., 1997). Therefore, a stream discharge event was initiated when the river hydrograph rose above normal river base-flow (rising limb of curve). The end of the stream discharge event was determined when the river hydrograph returned to within 10% of pre-event conditions. The end of any given stream discharge event occurred when no perceptible decrease in discharge was observed over a period of 2 h (Dhillon and Inamdar, 2013).

Daily precipitation was calculated from hourly data obtained from a rain gauge station (Lat: 43.63° N, Lon: 87.71° W), maintained by the Department of Earth and Atmospheric Sciences, Central Michigan University (CMU) located within the study watershed (Fig. 1). Daily precipitation for the period from 3/11/2013 to 3/13/2013 from CMU station went missing due to an operation issue. The missing precipitation was replaced with data obtained from the U.S. climate data website. Given the relatively small size of the watershed (1037 km^2), we assumed the precipitation data logged at the station was representative for the entire watershed. Variations of DOC fluxes in relation to precipitation scales was conducted for three different precipitation levels classified at equal intervals: light ($<$ 27.6 mm), moderate (27.6 mm $< X <$ 50.38 mm), and heavy (50.38 mm $< X <$ 73.152 mm). Here we defined a precipitation (storm) event as all rainfalls (including short breaks, $<$ 10 h) associated with a common stream discharge event pattern. Each stream discharge event corresponded with a single precipitation event. Overall, the precipitation events corresponding with the six stream discharge events ranged from 0.58 mm to 51.54 mm (Fig. 2); three events occurred in spring (14 March 2013, light; 2 April 2014, light; and 7 April 2015, heavy), while the other three occurred in the autumn (2 October 2014, moderate; 11 November 2014, light; and 28 October 2015, moderate).

We have documented the information during each of the discharge events, acknowledging the antecedent (10–20 days) meteorological conditions prior to the events we measured in Table 1 (e.g., starting date/duration, precipitation, snowpack). There were at least two snow storms accumulating 2.2–9.5 in. of snow) prior to the sampling dates. The snowpack information indicates the timing of snow-melt relative to the sampling dates. In fact, there were many areas still covered by thin layer of snowpack. Antecedent daily temperatures ranged between 10° to 50° F. The table better informs the potential interaction among key environmental factors during riverine DOC cycling processes.

Sequential water samples were collected using an auto-sampler (ISCO 6712) equipped with twenty-four, 500 ml polypropylene bottles. All bottles used here (field and laboratory) were prepared using clean laboratory techniques (see Fitzwater et al., 1982; Carrick et al., 1993),

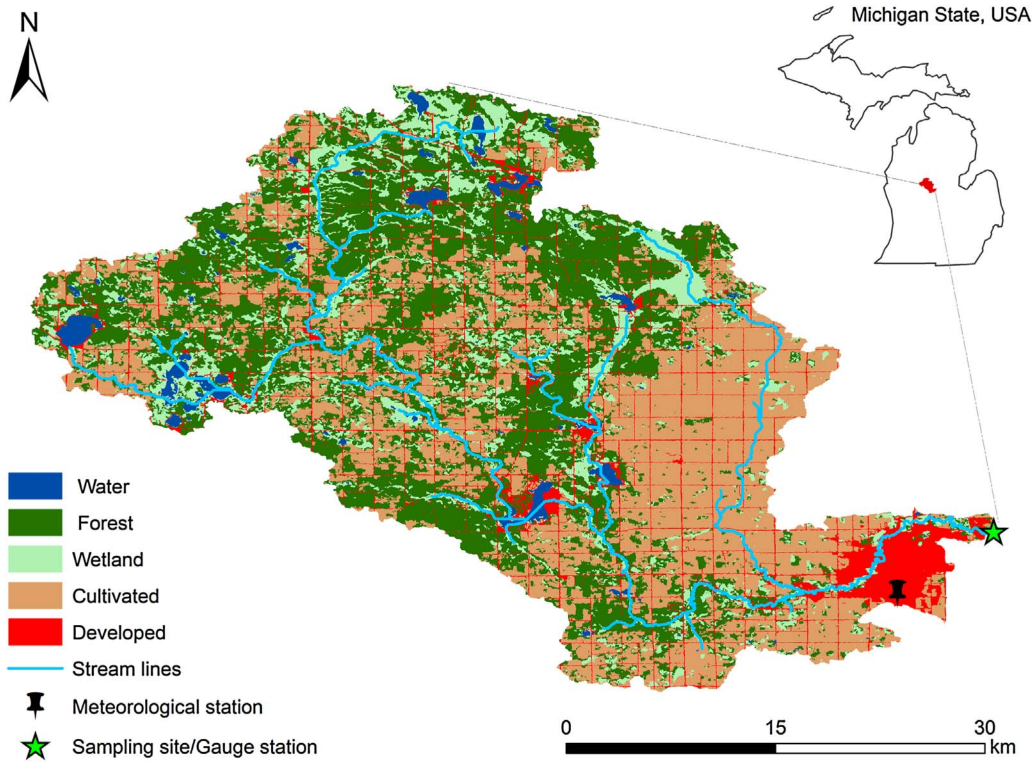

Fig 1. Study site: Chippewa River Watershed, MI. It consists of agricultural land uses (approximately 45%) mixed with forest (40%), and residential (4%) and wetland areas (11%). The meteorological station is located at: Lat: 43.63° N, Lon: 84.71°W. The USGS 04154000 for river discharges is located at Latitude 43°37′34”, Longitude 84°42′28”.

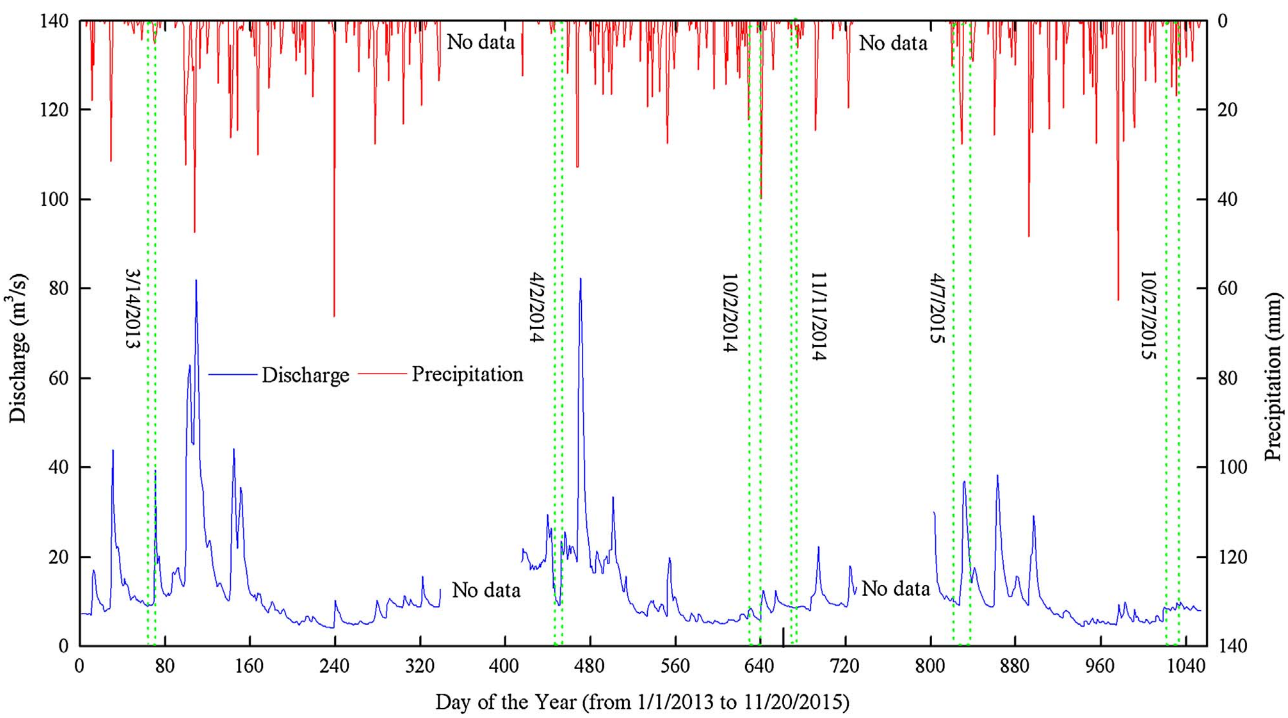

Fig. 2. Precipitation and discharge events from January 1st, 2013 to November 20th, 2015 except winter times (highlighted in green dished vertical lines are the six events considered in this study). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

whereby bottles were washed through a series of sequential washes using liquinox soap-wash (rinsed 3 x with reverse osomosis water) followed by an acid-wash (rinsed 3X with reverse osomosis water). Sampling was conducted at 1-h intervals except during those events in 2015, when the interval was 2 h (Table 1). A total of 321 samples were collected during six stream discharge events. Following sample collection, water subsamples were transferred into clean, amber 500 ml polypropylene bottles, and stored in a cooler at ambient water temperatures until further processed in the laboratory (within 3–6 h). Discharge was obtained from a USGS gauge station (04154000) at 15-min intervals; the station was located about 50 m from the auto-sampler.

Once in the laboratory, water samples were filtered through GF/F glass microfiber membranes (0.70 μm effective pore size) under low pressure ($<$ 5 atm), acidified (2 drops of H_2SO_4), and refrigerated at 4 °C until analyses could be completed (within 3 days). Dissolved

Table 1
Measurements during storm events: the range of DOC concentration, Range of river flow, Event scale discharge, Number of samples collected in each event, mean DOC concentration of each discharge event, Precipitation during each discharge event (Precip.), Total DOC fluxes from each event (DOC fluxes), DOC fluxes per unit area from the event (DOC fluxes (kg/ha), Total antecedent precipitations 10-days prior to each sampling event (Antec. Precip.), Accumulative snow 20-days prior to each sampling event (Antec snow), Antecedent number of snow storms 20-days prior to each sampling event (Antec. #snow), and total snow of the winter (winter snow).

Event date	Duration	DOC range (mg C L^{-1})	River flow range (m3/s)	Discharge (m^3)	Sample n	Mean DOC (mg/L)	Precip. (mm)	DOC fluxes (tons)	DOC fluxes (kg/ha)	Antec. Precip. (mm)	Antec snow (in)	Antec #snow	Winter snow(in)
3/14/2013	33	7.00–9.00	17.1–22.0	11729966.12	24	7.78	11.48*	88.80	0.86	11.48	9.52	5	41.39
3/31/2014	96	6.02–9.48	20.0–24.0	7992699.786	22	6.61	0.508	55.60	0.54	2.03	2,2	2	38.53
10/2/2014	278	4.00–9.14	5.7–13.0	9797059.026	72	6.00	40.90	51.75	0.50	2.54	0	0	0
11/11/2014	96	4.50–6.50	8.2–9.1	2905731.965	48	5.16	3.3	14.93	0.14	14.22	0	0	0
4/7/2015	230	5.03–8.89	9.2–37.4	21515913.55	120	6.83	51.54	150.34	1.45	18.29	4.21	2	21.64
10/28/2015	136	5.12–6.10	6.85–8.72	4613450.947	34	5.67	17.53	24.88	0.24	15.75	0	0	0

**Note*: Precipitation amount (mm) corresponding to the stream discharge event of 3/14/2013 was the accumulation (11.48 mm) from 3/11/2013 to 3/13/2013 from U.S. climate data. The precipitations of low intense and long duration for each of the three days are 0.2” (5.08 mm), 0.14” (3.556 mm), 0.01” (0.254 mm) precipitations plus 0.51” snow (0.51”*0.2 = 0.102” = 2.59 mm precipitation). USDA defined that the density of new snow ranges from about 5% when the air temperature is 14° F, to about 20% when the temperature is 32° F (USDA-NRCS website). Since the mean temperature of the three precipitation days is 35.3° F, we used 0.2 as snow density.

organic carbon (DOC) concentrations were measured using a Shimadzu TOC-V analyzer with high temperature combustion (Vlahos et al., 2002). Briefly, water sample aliquots (50 µl) were injected in the instrument and subsequently combusted at 800 °C; concentrations of DOC were calculated from the resultant CO_2 analyzed with a non-dispersive infrared detector. Both response factors and reverse osmosis water blanks were compared with inter-comparison standards provided by Sharp et al., (2002).

2.3. Accumulative DOC fluxes in a range of stream discharge events

Overall, we developed this semi-analytical model in order to fit parameters with field measurements to estimate the change of DOC concentrations during stream discharge events in response to storms, and ultimately, link these estimates with key environmental variables. Event-scale DOC fluxes (C_X) were estimated by integrating fluxes across successive, intervals spanning the entire stream discharge event (see below). First, DOC concentrations (measured in our samples) were multiplied by the corresponding river flow volumes for each time interval to derive time-specific DOC fluxes.

$$C_X = \sum_{i=S_1}^{s_N} (c_i * Q_i) \quad (1)$$

Where c_i is DOC concentration sampled at i^{th} interval, Q_i is the discharge volume at i^{th} interval. The s_1 is the interval when the first sample was taken. The s_N is the interval when the last sample was taken. Ideally the first sample would be the first interval from the starting point of a stream discharge event and the last sample would encapsulate the termination of the discharge event. However, it was very common that our sampling was not adequate to cover the entire discharge event period; such was the case for the periods 2–3 April, 11 November 2014, and 2 October 2014. Incomplete sample coverage was mainly due to variation in weather forecasting, where storms started at times with little preemptive warning (e.g., middle of night). Therefore, we investigated if Weibull distribution patterns (Weibull, 1951) could be modified to extrapolate DOC concentrations for the periods in which there were no empirical samples to describe a discharge event. The Weibull distribution is a well-known continuous probability distribution that was initially applied for describing particle size distribution patterns (Rosin and Rammler, 1933). The Weibull distribution has been used more recent to augment a wide variety of applications, such as wind power analysis (Wais, 2017) and natural gas flow simulation (Yang et al., 2017). The standard Weibull distribution has two parameters as described below:

$$f(x; \alpha, \gamma) = \frac{\gamma}{\alpha}\left(\frac{x}{\alpha}\right)^{\gamma-1} e^{-(x/\alpha)^{\gamma}} \quad x \geq 0 \quad (2)$$

where $\gamma > 0$ controls the distribution curve shape and $\alpha > 0$ controls the scale of the distribution.

Based on our field measurements, we modified the Weibull distribution to formulate a model to extrapolate DOC concentrations for the periods in which there are no samples in a stream discharge event as displayed in Eq. (3).

$$c(t_j) = \frac{\gamma}{\alpha} * \left(\frac{t_j - \mu}{\alpha}\right)^{(\gamma-1)} exp^{\left(-\left(\left(t_j-\mu\right)/\alpha\right)^{\gamma}\right)} * (Q_j * G * + b) \quad \gamma, \alpha > 0 \quad (3)$$

We extended Weibull distribution model by introducing environmental factors as key variables of the above model (Eq. (3)). Where the shape parameter, γ referred to discharge duration, and location parameter μ referred to the curve skewness govern by discharge intensity, and α was a typical scale factor. Our model extension featured on three new parameters in the second portion of the model in order to compare with the Weibull distribution, where: Q_j is the discharge (m^3/s) at j^{th} interval, t_j is the hours from beginning of the storm discharge event to the j^{th} interval, b is the base flow (m^3/s), and G is the scale factor for DOC concentrations. These parameters were manually calibrated to fit the model describing sampled DOC concentrations, so that it was capable of extrapolating DOC concentrations during intervals where there were no empirical samples, C_Y. Estimation was based on the basic formula below

$$C_Y = \sum_{j=D_1}^{D_M} (c(t_j) * Q_j) \quad (4)$$

Where $c(t_j)$ is the mean DOC concentration at j^{th} time interval for the period with no samples, Q_j is the discharge volumes for the same interval, D_1 and D_m are the first and the last interval of missing sample period in an event. Therefore, the total DOC fluxes generated during a storm event was the summation of C_X and C_Y. While the majority of interval-specific DOC fluxes were calculated using empirical field samples where DOC concentrations C_i were measured in the laboratory, approximately one fourth of these values were estimated with modeled concentrations $C(t_j)$. This means $C_Y/(C_X + C_Y) < 30\%$.

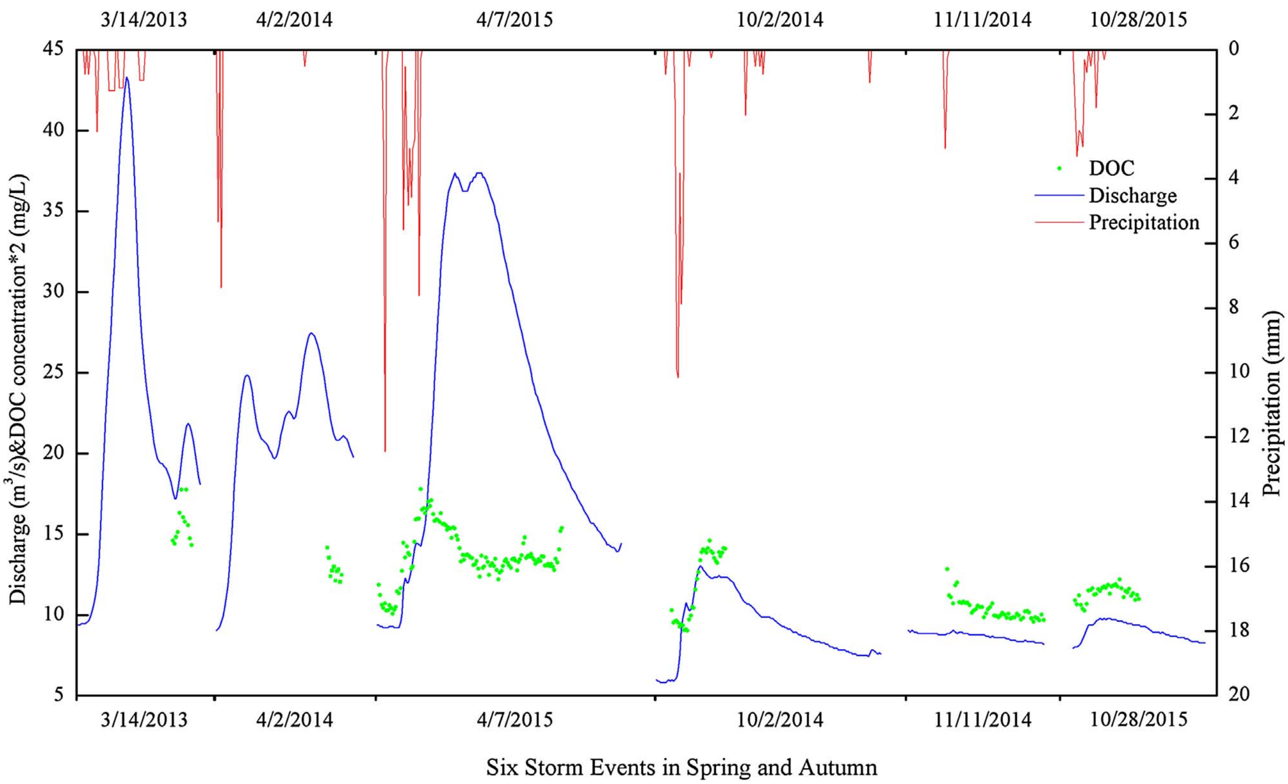

Fig. 3. Characteristics of rainfall, river flow (m^3/s) and DOC concentrations sampled at 1–2 h of intervals in spring and fall. DOC concentrations were multiplied by 2 for the purposes of display in the same figure. The precipitations associated with the river discharge event started on March 14th, 2013 were from U.S. Climate Data website (at daily interval).

3. Results and discussion

3.1. Snowpack-enhanced DOC production

During spring stream discharge events, changes of DOC concentrations were positively skewed, indicating a rapid DOC increment during the initial portion of the rising limb (Fig. 3). This discharge pattern appeared to reflect the interaction between seasonal snowpack and the export of DOC from croplands, further underscoring the important connection between agricultural practices and the available soil organic matter. For instance, Neill (2011) reported that crop residues (stalk stubble and leafy matter) from agricultural landscapes were usually left on fields following fall harvesting (dominated by corn and bean plants). During the winter period (December-March), these organic residues were eventually covered with the typical, seasonal snowpack that occurred. Antecedent meteorological conditions (precipitation and snowpack) prior to sampling stream discharge events (Table 1) suggest that abundant snowpack made soil moisture near field capacity. By the following spring period, this organic matter was subsequently associated with abundant dissolved organic carbon in the O and A horizons (Martins et al., 2012). As such, high DOC concentrations were present in stream discharges following spring snow-melt. This appeared to be the case, because of elevated soil moisture from the previous months of snowpack that extended the duration of water contact with surface soil horizons through capillary action, standing water, and sheet-wash (Kätterer et al., 2011). Snow-melt conditions also enhanced metabolic and decomposition processes, so that more DOC was eventually exported by stream discharge events in the spring (Hongve et al., 2004; Tranvik and Jansson, 2002). The observations by Henry et al., (2008) also showed that the relationship between DOC concentration and discharge was largely driven by land moisture conditions. Our empirical results presented here further supports this notion, that seasonal snowpack catalyzed the transformation of DOC from agricultural residues making it more available to surface runoff.

Our results also indicate an important seasonal pattern, whereby the event-scale DOC flux in spring was much greater compared with those fluxes observed in the fall period, despite the similarity in discharges conditions during the two periods. Interestingly, riverine DOC concentrations in the spring (ranged 5.0-9.0 mg C L^{-1}) were consistent greater in contrast to those measured in autumn (4.0-7.0 mg C L^{-1}, Fig. 3). It is clear that with similar precipitation events, the range of spring river discharge intensities were greater (between 5.7 and 37.38 m^3/s) than those in the fall (Table 1). Similarly, the duration of stream discharge and flow intensity were greater for a comparable spring event (230 h, 4/7/2015), relative to an event in the fall (278 h, 10/2/2014). Taken together, these data demonstrated that the snow-melting processes resulted in spring discharges events that were of greater intensity and duration, relative to those in the fall. For example, the discharge event right before the 14 March 2013 was significantly greater ($11.7*10^6$ m^3) than the event started on 2 October 2014 (9.8 $*10^6$ m^3), although the associated precipitation was smaller in spring (11.9 mm) versus that in the fall (41.0 mm, Fig. 3). These results reflect important seasonal differences in the mechanisms that regulate DOC dynamics in agricultural landscapes and receiving rivers; larger DOC fluxes in the spring appear to be driven by the greater reservoir of available DOC, while fluxes in the fall were driven by capillary action from higher net primary production (NPP) by standing plants that supported a limited pool of soil organic matter.

3.2. Elevated DOC concentrations during spring base flow

Riverine DOC concentrations appeared to reach some equilibrium as observed in the middle region of the receding limb of the spring stream discharge vs. DOC plot (Fig. 4a). It suggests that wet-snow enhances water infiltration, so the base-flow starts to dominate the end of storm discharge events, especially on flat areas (Ikeda et al., 2014). Additionally, interaction of wet-snow with agricultural residues could be also a factor that accelerates DOC production rates. The equilibrium status of DOC concentrations in base-flow suggests that snow melting hydrology increases the transformation of dissolved carbon from

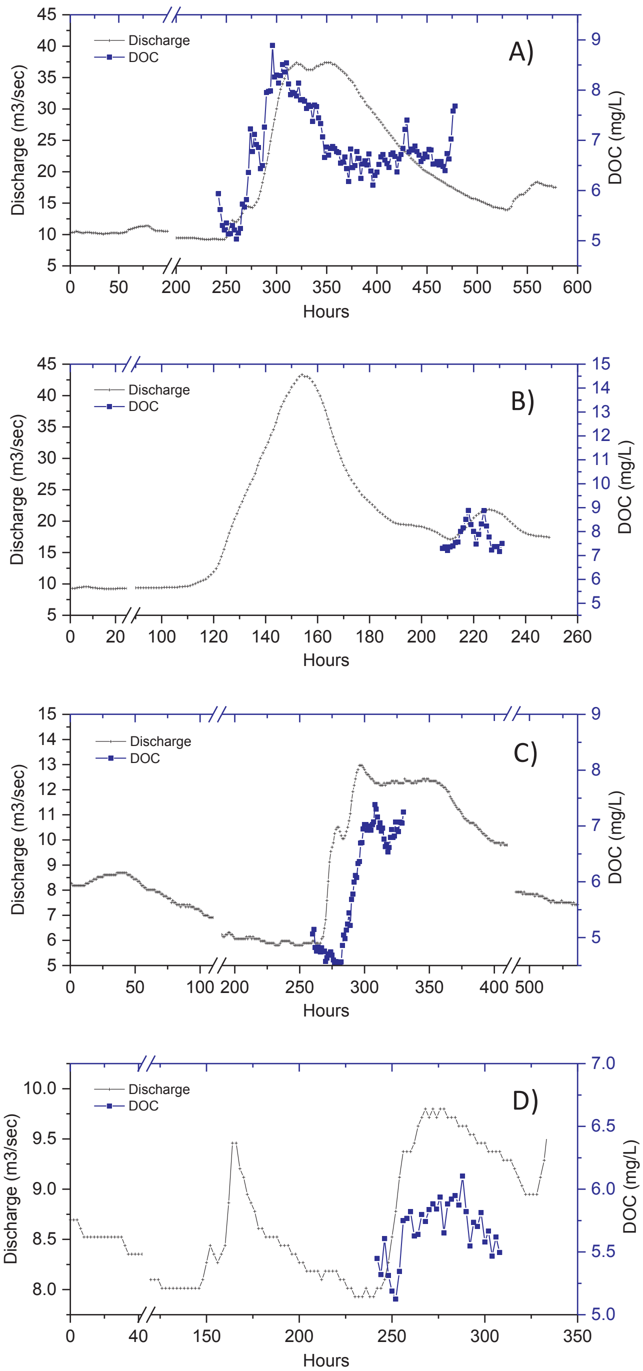

Fig. 4. Profiles of the riverine DOC concentrations during 4 stream discharge events in spring and autumn. The corresponding start dates for each of the four events are: A) is for 04/07/2015, B) is for 03/14/2013, C) is for 10/02/2014, and D) is for 10/28/2015.

surface to groundwater. The elevated DOC concentrations in groundwater governed the equilibrium status (at 6.5–7 mg C L^{-1}) through base flow in the later periods of the storm discharge events (the middle of the receding discharge limbs). The equilibrium status of DOC loading to the river represents a mixing process of surface runoff and base-flow (Fig. 4a). Fig. 3 showed that the average base-flows in spring were about 5 m^3/s higher than that in autumn, and average DOC concentrations (6–9 mg C L^{-1}) were about 20% higher than events in autumn (4–7 mg C L^{-1}). These results support the idea that high base-flow associated with snowpack in spring increases the event-scale DOC flux significantly in river flow.

Contrasted with forested landscapes, our results have demonstrated the how snowpack can increase the transform rates of DOC from crop residues (including maize leaf litter), particularly within agricultural watersheds. This is consistent with studies, where high incorporation rates of organic matters has been measured into farm topsoil during the winter fallow period (Kamota et al., 2014). The impacts of snowpack in agricultural landscapes differs from that in forested landscapes, given that mineralization within forested areas occurred within a shallow, subsurface DOC reservoir, in contrast with the larger, groundwater DOC reservoir that developed in agricultural landscapes (Stottlemyer, 1987; Stottlemyer and Toczydlowski, 1991). The relatively shallow DOC reservoir over forest landscapes was transported to adjacent streams mostly through surface runoff instead of through base flow in response to rapid snow-melt (Stottlemyer and Toczydlowski, 1996; Stottlemyer and Toczydlowski, 1999). In addition to different land uses, the enhanced winter-spring run-off appeared to be a common feature of seasonal hydrodynamics observed elsewhere, such as bog vegetation or boreal heather moor (Helliwell et al., 1998) and forest landscapes (Stadler et al., 1996). These seasonal discharge events, such as these, have been well documented for other temperate, forested watersheds, where DOC flux has been shown to lower the pH of poorly-buffered, headwater streams, which in turn have had a negative impact on fisheries productivity (see MacDougall et al., 2008).

3.3. Land surface soil carbon availability and DOC run-off

The observation showed a clear hysteresis between rising limbs in the discharges versus DOC concentration relationships measured during the fall events [clockwise panels, Figs. 4 c, d and Fig. 5]. The delayed DOC increase in the initial flush corresponded well with the limited reservoir of stored organic carbon in surface soil horizon (seasonal deficiency). This was likely residual organic matter in surface soils that was not flushed during storms in spring, summer and early fall, resulting in a seasonal deficiency in soil DOC concentrations just prior to leaf fall (Neill, 2011). In this case, the low availability of organic matter in the surface soil layer (A and O horizons) made diluted DOC in surface runoff in the beginning of storms. We believe that carbon sources supporting the delayed increase of DOC concentrations are from subsurface soils that have sufficient moisture for metabolic processes. If this is true, it explains that shortly following first flush, organic carbon stored in the subsurface soils was gradually transported to the river with interflow (Kätterer et al., 2011). This means that DOC from interflow and groundwater contribute to the delayed rising limb of the DOC concentrations (Martins, 2012). Similarly, DOC concentrations in spring events started increasing at rising limbs almost simultaneously with increasing discharges is supported by the higher availability of organic matter on top soil than that in fall events (Fig. 4).

The seasonal differences of DOC levels in first flush suggest that high carbon availability on surface soil in the agricultural watersheds in spring is strongly related to snowpack and agricultural practices. Another interesting point in the results is that the peaks of DOC concentrations usually came before the peaks of stream discharges in an event. This fact indicates that terrestrial DOC supply conveyed by spring storm discharges could become insufficient when event duration or intensity is over a certain threshold because of the slow turnover rates. The thresholds seem in the range between 15 and 20 m^3/s, in which riverine DOC concentrations usually reach peak. These thresholds might be ecosystem-specific, and thus, vary according to the characteristics of individual watershed such as drainage area and physical conditions. That said, discharge events of this magnitude have been observed to deliver significant fraction of the annual nutrient load to receiving water bodies in other temperate, mixed land use, watersheds (Godwin and Carrick, 2008; Godwin et al., 2009).

The early peak and the delayed rising limb in the discharge versus DOC concentrations curves appear to be characteristic of agricultural watersheds compared with those yielded from forested watersheds. In forested watersheds, DOC concentrations were linearly related to

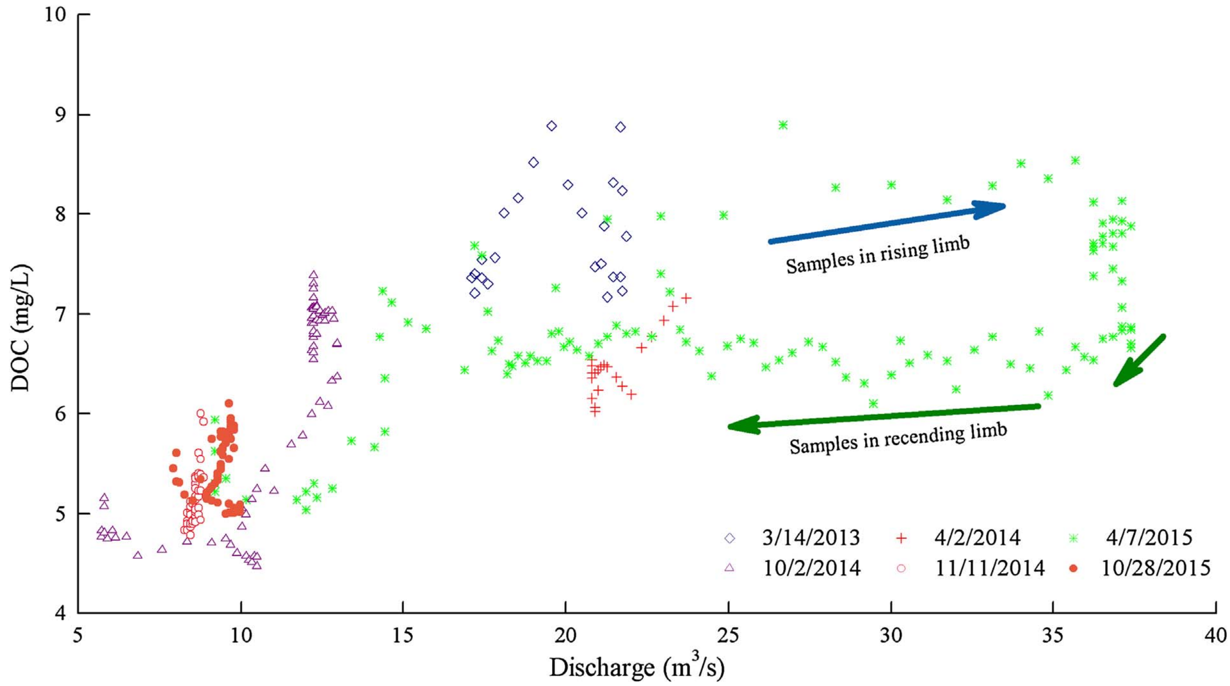

Fig. 5. Changes of DOC concentrations against the magnitudes of river flow in different seasons.

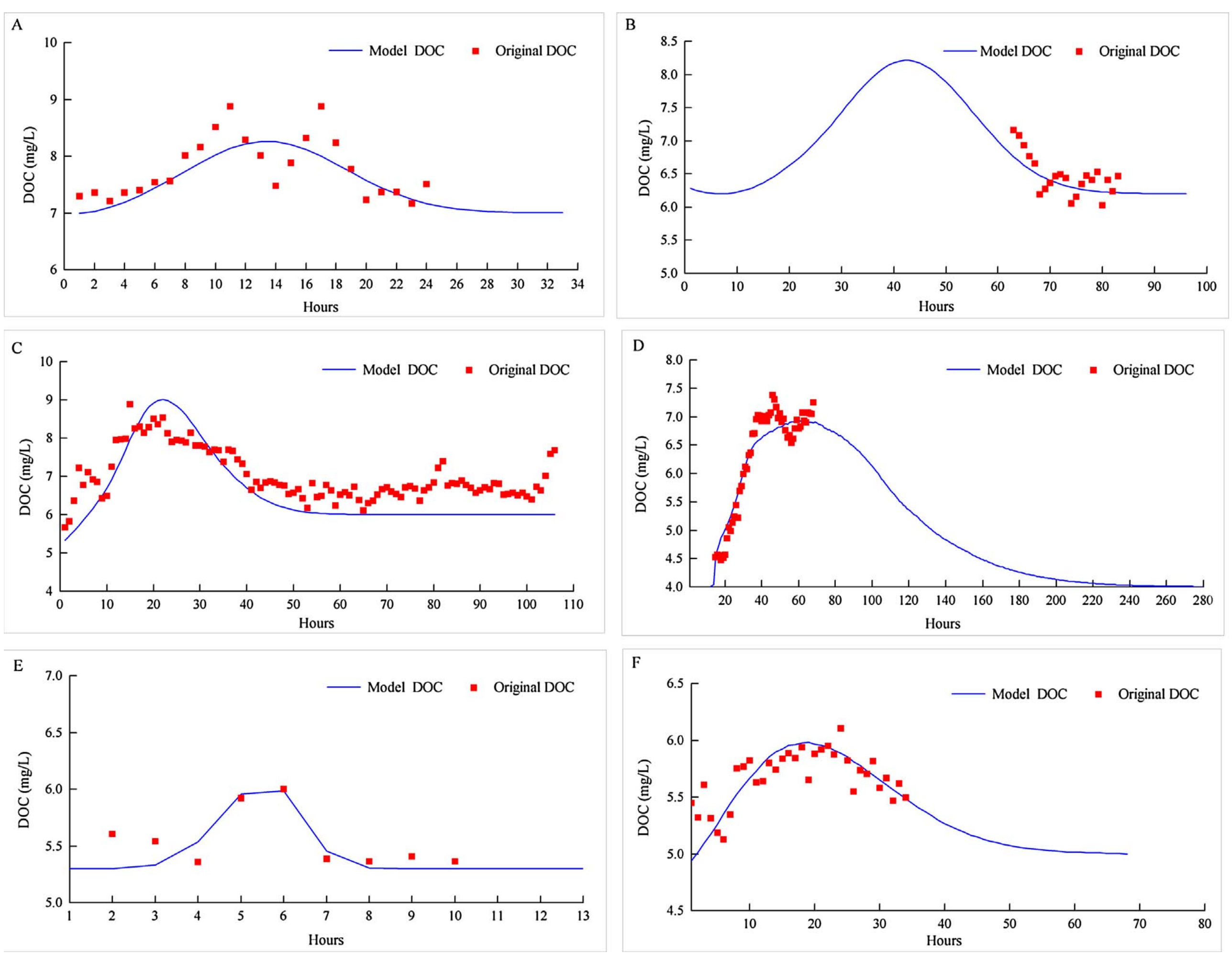

Fig. 6. Modelled DOC fitted to the sampled (original) concentrations for the duration of stream discharge events. X-axis is the hours since the storm-discharge started. For each of the six events started on A)3/14/2013, B) 3/31/2014; C) 4/7/2015; D) 10/2/2014; E) 11/11/2014; and F) 10/28/2015 respectively. For the event B, stream discharge started from 3/31/2014 and ended 4/3/2014 (96 h), but the hourly sampling for DOC was started on 4/2/2014.

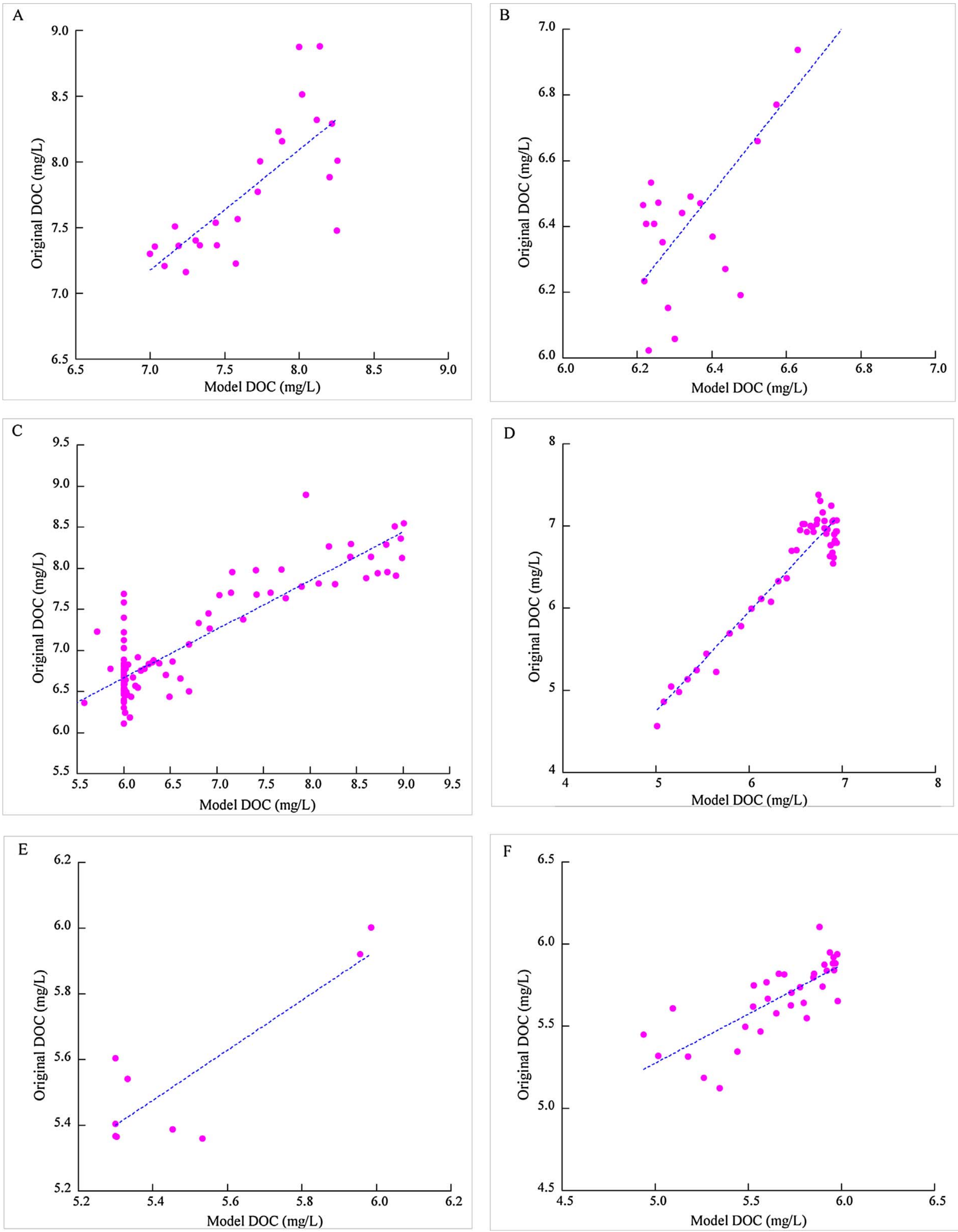

Fig. 7. Evaluations of modeled DOC against measured during each event. R^2 values for A) is 0.56 for 3/14/2013 event, B) 0.62 for 3/31/2014, C) 0.81 for 4/7/2015, D) 0.9 for 10/2/2014, E) 0.74 for 11/11/2014 and F) 0.6 for 10/28/2015. The A, B and C are for spring events. D, E, and F for autumn events.

storm-flow for both rising and receding limbs of hydrographs (Caverly et al., 2013). Different DOC dynamics occur in forested landscapes exist, because live stands of plants appear to support a more constant turnover rate of carbon to soils, that can be leached during storm discharge events (Dhillon and Inamdar, 2013; Hinton et al., 1997; Yoon and Raymond, 2012). Our results imply that the DOC flux from agricultural landscapes is more complicated, and therefore requires an approach that considers some conservation of mass function for modeling DOC cycling processes, rather than relying on simple discharge volumes as a the main variable (Hinton et al., 1997; Xu et al., 2010). This improved understanding is important to evaluating carbon cycling processes from agricultural lands to receiving water bodies (lakes or

Table 2
Parameters calibrated in modeling the dynamics of DOC concentrations during a rainfall event.

Event date	γ	*μ*	α	*G*	*b*	r^2
3/14/2013	2.7	1	14	0.8	7	0.56
3/31/2014	3	7	40	2.5	6.2	0.62
4/7/2015	2	20	20	2	6	0.81
10/2/2014	1.7	12	82	25	4	0.90
11/11/2014	5	1.5	4.25	0.2	5.3	0.74
10/28/2015	2	1.8	24	2.8	5	0.60

oceans), particularly at the global scale, where land cover is being converted from forest to agriculture.

3.4. Modeling event-scale DOC fluxes

A question following the improved understanding from field observations is if it is feasible to quantitatively model the riverine DOC dynamics during storm discharge events of varying duration and intensity. We proposed a model based on the Weibull distribution and examined its performance for the study river whose drainage areas are agricultural landscapes (see Eq. (3), above). This model was calibrated using a curve fitting procedure against our field measurements, and this in turn, was applied to extrapolate DOC concentrations during the periods where data were missing (no samples were available). As such, our field sampling was combined with the modeled time series of DOC concentrations in order to estimate event-scale DOC fluxes. We used this extrapolation method to populate datasets where storm event sampling was unavailable (Fig. 6).

The model we developed here has three advancements over current estimation methods for DOC flux. First, it is a semi-analytical model compared with currently available methods that rely mainly upon seasonal regressions between DOC and stream discharge (Hinton et al., 1997), such as computer programs, e.g. LoadRunner (Yoon and Raymond, 2012) or artificial neural network interpolation models (Strohmeier et al., 2012). The second, this model went a step further by evaluating ecosystem-scale dynamics in mixed watersheds dominated by agricultural, compared with modeling of DOC fluxes at annual scales in primarily forested landscapes. The strength of our proposed semi-analytical model is that it described riverine DOC dynamics during stream discharge events, as influenced by terrestrial snow-melt processes over agricultural dominated land cover. The third, the proposed model resulted in excellent performance in describing the six stream discharge events evaluated here.

Table 3
The percentages of DOC fluxes during all storm events (not only studying events) in spring and autumns respectively in 2014. Spring: was from March 1 to May 31 and autumn: was from September 1 to November 30 (Based on the Northern Meteorological seasons). The minimum DOC concentrations were used for calculating the DOC fluxes in the base flow in spring and autumn respectively. Similarly, the average DOC concentration sampled in spring was used to calculate the total DOC fluxes for all storm discharge events in spring 2014. This calculation method was also applied for calculating the percent of storm DOC fluxes in autumn 2014.

Season	(E) Storm DOC fluxes (kg)	(B) Base-flow DOC fluxes (kg)	E/(E + B)%
S (Spring)	858931.42	229329.58	78.9%
A (Autumn)	266633.46	92783.16	74.2%
A/S%	31%	40%	

Our modeling results matched well to the temporal patterns of sampled DOC concentrations during stream discharge events over varying storm scales (Fig. 7). For example, R^2 values for the two large events around 2 October 2014 and 7 April 2015, were 0.90 and 0.81, respectively. The other three stream discharge events were less intense and had a smaller number of field samples with greater residual of unexplained variation. Regardless, the model was able to adequately explain changes in DOC concentrations for these discharge events as well (range in R^2 of 56% to 70%). Hence, the model was appropriate to fit the positively skewed distributions of DOC concentrations for both small and large discharge events, and as such, it calibrated nicely with DOC dynamics along both rising and receding limbs. This performance meets the requirements of estimating the DOC concentrations for the period when field samples were unavailable.

The proposed model has significant improvement over the conventional linear regression approaches adapted by Hinton et al., (1997). Using linear regression, a limited amount of variation in DOC concentration was explained for both spring (R^2: 0.05-0.56) and for fall (R^2: 0.52-0.61) events. Our data clearly showed that the relationship between DOC concentrations and corresponding stream discharges was non-linear. Thus, our semi-analytical model (Eq. (3)) significantly improved the description of riverine DOC dynamics during stream discharge events (up to 90% for spring and 70% for autumn) compared with the simple, linear regression approach.

We believe our model has application towards describing DOC-discharge dynamics in other watersheds for two main reasons. First, two of the variables were linked to important hydrological properties: instantaneous river flow (m^3/s) for each time interval and base-flow (m^3/s) for each storm discharge event. Second, the calibrated

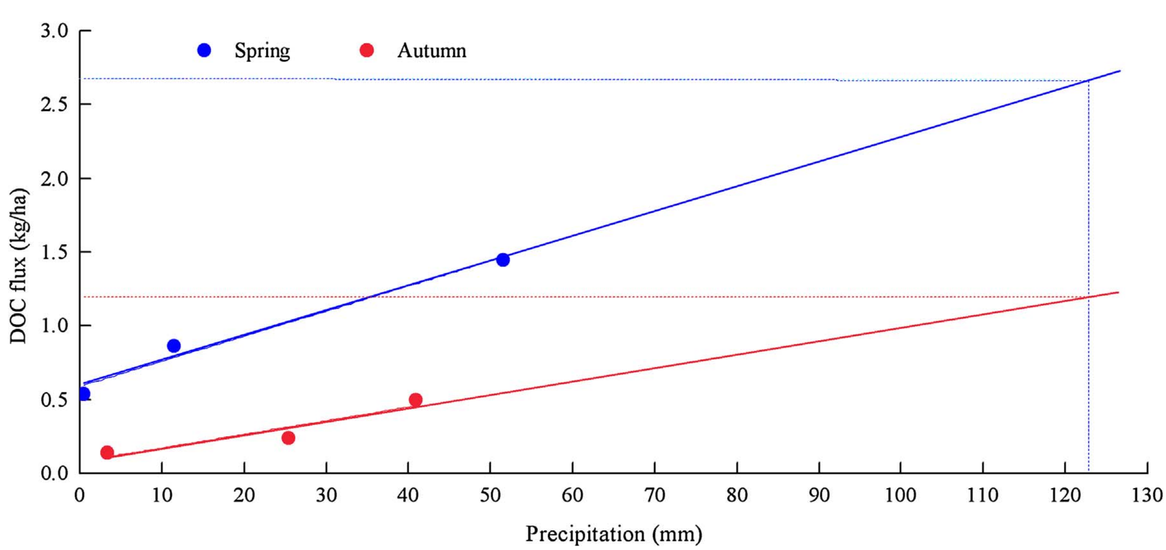

Fig. 8. Trends of accumulative DOC loadings to the river between spring and autumn events with varying scales of precipitation.

parameters appear to have linkages to physical scenarios. For example, parameter γ has an inverse relationship to the scale of the events, the μ term was positively related to the event scales (discharge volumes with regards to both intensity and duration), and the α term could be determined with storm discharge intensity (Table 2). These model parameters, therefore, appear to describe ecosystem features that are relevant to our understanding of river hydrology and discharge characteristics. As such, we are convinced the model should be further calibrated using field measurements from different watersheds collected under varying land uses and storm scales, so that the model can be more fully developed as a functional, analytical tool.

3.5. Assessing seasonal variation in event-scale DOC fluxes

Our analysis demonstrated that even small variation in DOC concentrations can translate into large impacts in the DOC flux for both small and large scale precipitation events. For example, the variation in the mean DOC concentrations was small among spring events (14 March 2013, 2 April 2014, and 7 April 2015, range 6.1–7.6 mg C L^{-1}); however, the difference between event-scale DOC fluxes associated with the three events was quite large. The DOC loadings were 17.64, 55.60 and 150.34 tons among the three events, respectively. Similarly, the differences in DOC concentrations (5.2, 5.5, and 5.67 mg C L^{-1}) during the fall events were also small for light (11 November 2014) compared with medium (2 October 2014) storm events. In contrast, the associated variation in DOC fluxes (14.93 and 51.75 tons) from these fall events were relatively small. Finally, DOC fluxes from small to large discharge events spanned an order of magnitude when applied to the study watershed scale (0.14–1.45 kg per hectare).

The trends of event-scale DOC fluxes were significantly departing while the scales of precipitation events are increasing (Fig. 8). Therefore, a very large precipitation event would have significantly larger impacts on DOC export if it occurred in spring rather than in the autumn period. If we posit that the historic high rainfall event of 10 August 2010 occurred in spring as result of climate change, the consequence would be a DOC export of 280.17 tons from the study watershed, a 2.3 fold increase from autumn (124.5 tons, Fig. 8). The records for the year 2014/2015 (Table 3) showed that about 76.5% of the annual DOC occurred during stormflow events (78.9% for spring and 74.2% from autumn). The average seasonal DOC fluxes are not significantly different between spring and autumn; however, differences were large for individual events between the two seasons. Large DOC flux in spring was most likely attributable to agricultural practices (beans and corn products). This result implies that a very large rainstorm is capable of transporting a significant amount of DOC loading to lakes or rivers, thereby affecting water quality and/or fishery productivity. For example, assuming a similar precipitation event occurred within the Saginaw River Watershed (22,260 km^2), it would generate 3338 tons of DOC in spring (total seasonal export: 6010.4 tons) compared with that in autumn (2672.5 tons). Assuming similar land cover, if the same rate was applied to regional Northeastern U.S. (42,024,000 ha), 113,468.853 and 50453.115 tons, respectively of DOC would be mobilized during spring and autumn of that year. Results such as these, illustrate how event-scale DOC flux analysis can be helpful in evaluating how global climate change will likely impact terrestrial dissolved carbon cycling from agricultural landscapes to the sea.

4. Conclusion

The samples were collected and analyzed to identify the impacts of snowpack on the dynamics of riverine DOC during stream discharge events of varying scales. The results revealed three distinct processes of riverine DOC from agricultural watersheds in spring compared to autumn: 1) significant high concentrations in base-flow, 2) availability of topsoil organic matters determines the levels of DOC in the first flush, and 3) large hydro-climatic events would result in significant raise of riverine DOC loading. The trend analysis indicated that a very large event could have a significant impact on distribution of soil carbon in a variety of spatiotemporal scales.

Spring snowmelt and abundant agricultural organic matter are significant factors that explain the elevated DOC levels in the first flush of the storm event. The results suggested the linkages of snowpack increased the soil moisture contents and catalytic/metabolism to the rapid raise of DOC concentrations during heavy overland flow in the beginning of early spring storm discharge events. In addition to the overland flow pathway, the equilibrium status of DOC concentrations on hydrograph's falling limb showed that snowmelt also drives a proportion of DOC from the surface through infiltration to groundwater, which is then loaded to the river through base flow. The result revealed that about 76.5% of annual DOC exported during storm-discharge events (78.9% for spring and 74.2% from autumn) over agricultural landscapes.

This study suggests that the low availability of metabolic organic matters in top soil in autumn led to the diluted DOC concentrations in the water entering the stream during the early part of the storm. The supply shortages could also occur in a long and intense storm discharge event when DOC production and metabolic processes could not keep up with the surface runoff. The evidence here is that riverine DOC concentrations came to equilibrium before the discharge peak and declined rapidly afterward as suggested by the hydrograph's the receding limb (See Fig. 4).

The study shows a different trend of riverine DOC fluxes between spring and autumn with regards to magnitudes of storm discharges. It concluded that an occurrence of a local historic event in spring would have a greater than a 2.3 fold increase of riverine DOC fluxes compared to the occurrence in the autumn. This riverine DOC loading trend from agricultural landscapes during a very large stream discharge event in spring would significantly affect the terrestrial and aquatic ecosystems, if the drainage watersheds are at regional and global scales. Further research is needed to understand resilience of ecosystem against DOC exports from agricultural watersheds in response to very large events.

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