Dissolved Organic Carbon Driven by Rainfall Events from a Semi-arid Catchment during Concentrated Rainfall Season in the Loess Plateau, China

Linhua Wang[1], Haw Yen[2], Xinhui E[1,3], Liding Chen[1,3], Yafeng Wang[1,3,4*]

[1]State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing 100085, China

[2]Blackland Research and Extension Center, Texas A&M AgriLife Research, Texas A&M University, Texas, 76502, USA

[3]College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 100049, China

[4]Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing 100101, China

** Corresponding author: Yafeng Wang: yfwang@rcees.ac.cn*

Abstract: Dissolved organic carbon (DOC) transported by runoff has been identified as an important role of the global carbon cycle. Despite there being many studies on DOC concentration and flux, but little information is available in semi-arid catchments of the Loess Plateau Region (LPR). The primary goal of this study was to quantify DOC exported driven by a sequence of rainfall events during the concentrated rainfall season. In addition, factors that affect DOC export from a small headwater catchment will be investigated accordingly. Runoff discharge and DOC concentration were monitored at the outlet of the Yangjuangou catchment in Yanan, Shaanxi Province, China. The results showed that DOC concentration was highly variable, with event-based DOC concentrations ranging from 5.14 to 13.14 mg L^{-1}. Hysteresis analysis showed a nonlinear relationship between DOC concentration and flow rate in the hydrological process. The monthly DOC flux loading from the catchment was varied from 94.73 to 110.17 kg km^{-2}, while the event-based DOC flux ranged from 0.18 to 2.84 kg km^{-2} in the period of June to September. Variations of event-driven DOC concentration contributed slightly to a difference in DOC flux, whereas intra-events of rainfall amount and runoff discharge led to evident difference in DOC export. In conclusion, our case results highlighted the advantages of high-frequency monitoring for DOC export and indicated that event-driven DOC export is largely influenced by the interaction of catchment hydrology and antecedent condition within a catchment. Engineering and scientists can take advantage of the derived results to better develop advanced field monitoring work. In addition, more studies are needed to investigate the magnitude of terrestrial DOC export in response to projected climate change at larger spatiotemporal scale, which may have implication for the carbon balance and carbon cycle model from an ecological restored catchment in LPR.

1. Introduction

Dissolved organic carbon (DOC), often defined as the solute filtered through <0.45μm pore size, is regarded as one of the active constituents and provides a biologically available carbon source for organisms (Raymond and Saiers, 2010). The estimated DOC flux of terrestrial organic carbon through major worldwide rivers to ocean is from 0.45 to 0.78 Pg C y^{-1} (Drake et al., 2018; Hedge et al., 1997; Ran et al., 2018). The substantial magnitude of flux suggests that the DOC export on a global scale acts as one of the crucial processes of linking between terrestrial and aquatic ecosystem (Battin et al., 2008; Raymond et al., 2013; Raymond and Saiers, 2010). For instance, high DOC concentrations can lead to water pollution and eutrophication, and thus have dramatic consequences on aquatic ecosystem services (Evans et al., 2005; Hu et al., 2016). In addition to ecological impacts, DOC in runoff also play an important role in social well-beings. High DOC concentrations will aggravate the complexation and adsorption of pesticides and heavy metals in hydrological process. Therefore, the quality of domestic water could be damaged and it might potentially lead to adverse impacts on human health, such as increased risk of cancer, diabetes, or other diseases

(Bennett et al., 2009; Ritson et al., 2014). Therefore, it is urgent to improve the associated knowledge on DOC export variability and develop a thorough understanding of DOC export from catchment.

DOC transport from catchment has been attracted great attention in the last two decades due to global concerns about potential influences on the global carbon cycle and climate change (Laudon et al., 2004; Raymond et al., 2013). The transport of terrestrial DOC to runoff is strongly influenced by hydrological process, soil carbon cycle and climatological factors. Hydrological process driven by rainfall event plays an important role in controlling terrestrial DOC from soil carbon pool to runoff. Previous studies have shown that the release of DOC concentrations ranged from 0.5 to 50 mg L^{-1} for global catchments (Mulholland, 2003). For instance, Clark et al. (2007) found that DOC concentration varied from 5 to 35 mg L^{-1} with a highly variable in rainfall events from a peatland catchment, and a study by Blaen et al. (2017) showed that the DOC concentration ranged from 5.4 to 18.9 mg L^{-1}. Similar results were reported by Ran et al. (2018), who found that DOC concentration ranged from 1.4 to 9.5 mg L^{-1} in the Wuding River in the LPR. Such studies highlighted that the importance of hydrological process on DOC transport (Billett et al., 2006; Dawson et al., 2002; Inamdar et al., 2006). Different rainfall events may alter hydrological connectivity or the flow path, which in turn lead to a varied hydrological condition and DOC source contributing to runoff. Moreover, the intensity and frequency of rainfall event not only influenced the current hydrological and DOC loading processes, but also changed the soil moisture conditions (Yang et al., 2018). The latter point may be particularly important in soil biogeochemical cycle. For example, DOC concentration may increase due to accumulated soil organic carbon after a dry period (Jager et al., 2009). In addition, variations in the magnitude and frequency of precipitation are one of manifestations of climate change, and thus, changes in hydrological process induced by climate change are also impact on the transport of terrestrial DOC. Therefore, understanding the dynamic and magnitude of DOC export from catchment is an important component of prediction DOC flux under the circumstance of future climate change.

The LPR, which has an area of 6.4×10^5 km^2, is situated in the middle reaches of the Yellow River, China, and approximately 90% of the river loading sediment is derived from this region (Tang, 2004). With regards to this fragile environment, the Chinese government has launched some ecological restoration projects since the beginning of this century, such as the 'Grain-for-Green' and 'Natural Forest Protection Project'. With the implementation of these projects, large areas of steep-sloping (higher than 20°) agricultural land was converted to forest, shrub, or grassland, and engineering measures were also applied to control erosion (Fu et al., 2017). For instance, check dams can retain sediment and also offer flat and fertile land behind the dam (Wang et al., 2011a). These measures have caused the Loess Plateau to experience a substantial change in land use, vegetation cover, soil properties, and catchment hydrology (Chen et al., 2007; Wang et al., 2011b; Wei et al., 2014). Consequently, the hydrological and carbon biogeochemical processes, which operate and interact with each other, were dramatically altered (Liang et al., 2015a; Liang et al., 2015b). These changes in hydrology and soil carbon cycle induced by land use and vegetation change may particularly important in the dynamics of DOC concentration and flux in an ecological restored catchment. Moreover, DOC transport from a catchment is sparsely measured due to the DOC concentration in hydrological process is not treated as a general parameter in monitoring networks of LPR. Therefore, less information is available on DOC export driven by rainfall events, which DOC flux is an important component in overall carbon balance for ecological restored catchment.

Therefore, the primary goal of this study is to investigate how variations of DOC concentration and flux response to a sequence of rainfall events from a restored catchment during concentrated rainfall season in the LPR. Specifically, the two objectives of this study were (1) to examine the dynamic changes in DOC concentration and flux and assess the difference in DOC export driven by various rainfall events, and (2) evaluate how rainfall, runoff, and antecedent factors affect DOC export from a catchment. To do so, we used high-frequency method to capture the temporal changes in DOC export and hydrological process driven by rainfall event within an ecological restored watershed in LPR. These results will provide evidence of DOC export response to rainfall events, especially driven by extreme events, which may be important for evaluating carbon balance and modeling DOC export through runoff at ecological restored catchment in LPR.

2. Materials and Methods

2.1 Site Description

As shown in Figure 1, this study was conducted in the Yangjuangou catchment (N36° 42', E109° 31'), which is an Ecological Restoration and Soil and Water Conservation Monitoring Station situated in Yan'an, Shaanxi Province, China. The catchment located in the secondary tributary of the Yan River Watershed and covers an area of 2.02 km^2, ranging in elevation from 1050 to 1295 m above the mean sea level. The topography is characterized by a typical loess hilly and gully topography with a gully density of 2.74 km km^{-2} (Wang et al., 2011b). The climate of this catchment is situated in a semi-arid continental monsoonal climate with an average annual temperature of 9.6℃ and average annual precipitation is 535 mm during the period from 1951 to 2012 (Li and Wang, 2015). Furthermore, the precipitation is unevenly distributed throughout the year and 60-70% of annual precipitation concentrated from June to September (Shi and Shao, 2000). The soil is classified as a typical loess with a fine silt texture and is weakly resistant to detachment by raindrops or runoff. Two check-dams were built in the main gully in the 1960s and it are currently filled with sediment and used for agricultural land. Land use is dominated by forest with a mix of shrub, grassland, and arable land. The proportion of sloping cropland has remarkably decreased from 16.9% in 1998 to 0.1% in 2006. The forestland increased from 15.2% in 1998 to 37.4% in 2006 since implemented the 'Grain-for-Green' and engineering measures (Wang et al., 2011b). The major forest species are *Robiniapseudoacacia*, *Salix spp.*and*Populus spp.* The area with *Artemisaargyi*, *StipaBungeanatrin*., *Bothriochloaischaemum*, *Lespedezadavuricaschindl.*, and *Artemisia sacrorum*are classified as grassland. The major orchards are *Prunus armeniaca L.*, *Malus pumilaMill.*, and *Juglans rejia L.* The major crops are *Setariaitalica, Zea may L. Glycinemax (L) Merr. Panicum miliaceum L.* and *Solanum tuberosum* (Fu et al., 2014). Therefore, the Yangjuangou catchment was chosen as a study site, which represented an ecological restored catchment.

2.2 Field Monitoring and Sampling

To measure the temporal dynamics of DOC, a monitoring station was deployed at the outlet of the Yangjuangou catchment to sample runoff water and monitor discharge. The station was equipped with an ISCO 6712 (Lincoln, NE, USA) peristaltic pump for collecting water samples during a runoff process induced by rainfall events. Unlike the common sampling frequency is monthly or weekly at field observatory station, the high-frequency monitoring was carried out in a hydrological process driven by a rainfall event in this study. Researchers resided in the field observatory station and treated the samples immediately after a rainfall event to ensure that the DOC in the sampled water did not microbially degrade (Kieber et al., 2002; Willey et al., 2000). The time-consuming and laborious field work is also one of the reasons for the measurement scarcity of DOC export in the existing ecosystem monitoring networks. Thus, the ISCO was set to acquire samples every 10 min from the first 12 runoff samples and another 12 were sampled every 30 min. The equipment was programmed to monitor runoff discharge by capturing the flow rate (L s^{-1}) and interval time (min). The auto-sampler collects a runoff sample with a volume of 200 ml. The auto-sampler ceased sampling work after 24 samples were collected. Then, the experimenter poured the runoff water into high-density polyethylene bottles that were prewashed with ultra-pure water. The auto-sampler continued to monitor the hydrological process and sample runoff for the next rainfall event. There were 278 samples collected for 22 hydrological processes induced by rainfall event over the monitoring period of June to September, 2016. In addition, the aim of hydrological and meteorological factor monitoring was to characterize the temporal changes of catchment condition. A meteorological station was installed in the center of the catchment, which was away from high trees. It was used to continuously monitor the rainfall characteristics, air temperature, and soil moisture throughout the study period. Rainfall amount (Ra, mm) and air temperature were measured every 30 min. The volumetric soil moisture content at 20 cm depth of forestland was measured every 30 min, which accounts for a large proportion of land use. Because these factors drive the hydrological and carbon biogeochemical processes in the catchment, these monitoring works may offer another perspective for understanding the runoff and DOC export process within an individual or continuous temporal variation between rainfall events (Blaen et al., 2017).

2.3 Laboratory Analysis

In the Yangjuangou field station, 200 ml of the collected runoff water sample was immediately filtered through a 0.45μm membrane into high-density polyethylene bottles and stored in a cooler (4℃). Then, the samples were transported to the State Key Laboratory of Urban and Regional Ecology in Beijing for the following analysis. DOC was recognized as the difference between total dissolved carbon (TDC) and dissolved inorganic carbon (DIC) for each sample (DOC=TDC-DIC). TDC and DIC were determined by Vario Select (Elementar, Germany), which included a high-temperature combustion furnace, a self-contained acidification module and a highly sensitive CO_2 detector. TDC was automatically measured by the combustion of a sample, whereas DIC was measured after acidified by 1% H_3PO_4 solution (phosphoric acid). Then, validation was conducted by analyzing various concentrations of a standard solution to achieve accurate result. In order to control quality, each sample is determined through analysis of two replicate and the coefficient of variation of tested results was less than 10%.

2.4 Data Analysis

2.4.1 Event-driven DOC Concentration and Flux Calculation

In the present study, the flow-weight mean concentration (C_f) was used to determine the average DOC concentration in a rainfall event. C_f was calculated by dividing the total DOC load by the total discharge in an event time. The equations of the flow-weighted mean concentration and flux are defined as the following:

$$C_f = \frac{\sum_{i=1}^{n} C_i \times Q_i}{\sum_{i=1}^{n} Q_i} \qquad (1)$$

$$Flux = \frac{10^{-6} \times C_f \times \sum_{i=1}^{n} Q_i}{S} \qquad (2)$$

where, Q_i (L) is the discharge amount corresponding to sample *i*, which is calculated by flow rate and interval time; C_i (mg L^{-1}) is the DOC concentration in a runoff sample *i*; n is the total number of collected sample in a runoff event. *Flux* (kg km^{-2}) is the quantity of DOC driven by a rainfall event for in the study region, and, *s* is the catchment area (km^2).

2.4.2 Variables related to Event-driven DOC Transport

To better understand DOC concentrations and fluxes from a catchment, specific hydrological and meteorological variables were selected. For instance, rainfall and soil moisture content may be related to hydrological connectivity in a runoff event, while soil moisture and temperature conditions impact on soil organic carbon content through biological processes (Blaen et al., 2017; Cooper et al., 2007; Soulsby et al., 2003). These variables are Q (total discharge volume a rainfall), Ra (total rainfall amount in a rainfall event), R1, R7 and R14 (total rainfall amount in the 1, 7 and 14 days before the current rainfall event, respectively), SMC-7 and SMC-14 (soil moisture content in the 7 and 14 days before the current rainfall event), T_{air}-7 and T_{air}-14 (mean air temperature in the 7 and 14 days before the current rainfall event) and REI (interval days between the current and last rainfall event).

2.4.3 Statistical analysis

To analyze potential relationships among DOC concentration, flux, and selected variables, Pearson's test was performed using SPSS (Statistics Package for Social Science, Version 22). The corresponding figures were developed using Sigma Plot 10.0 (Systat, 2008).

3. Results

3.1 Rainfall and Discharge in the Study Catchment

Rainfall is the main driving force of hydrological process in a catchment. Event-based rainfall amount varied from 62.6 mm (18-July) to 0.60 mm (17-August) from the June to September, 2016 (Figure 2-a). Over this period, the total rainfall amount was 372.1 mm, with approximately 70% of the annual rainfall amount. All the rainfall events in between June to September were grouped into four grades: <5mm (Light rainfall), 5-10mm (Moderate rainfall), 10-20mm (Heavy rainfall), and >20mm (Violent rainfall) according to rainfall amount classification (Yang et al., 2018). Figure 3-a showed that the total rainfall amount was 41.1, 44.8, 99.6, and 186.6 mm for each grade, respectively. The occurrence frequency of rainfall in each grade was 52.4% (<5 mm), 17.1% (5-10 mm), 16.7% (10-20 mm), and 14.3% (>20 mm) (Figure 3-b). These results indicated that the light and moderate rainfall occurs frequently with a less total rainfall amount, whereas the majority of rainfall amount occurs with a less chance in violent rainfall.

In general, flow discharge tended to follow the pattern of rainfall amount in the study catchment. The mean flow rate at the outlet of the catchment was 0.46 L s^{-1}, but it was also more variable and ranged from 0 to 4.5 L s^{-1} during June to September, 2016. In particular, there was no runoff in the catchment, due to the higher temperature, evapotranspiration and lower rainfall amount in early July. The higher flow rate is caused by continuous heavy rainfall. For instance, the cumulative rainfall amount was 91.8mm and the mean flow rate was 4.05 L s^{-1} from 18-19 July. Therefore, the flow rate increased rapidly with short duration and violent rainfall. In addition, Figure 4-a showed the relationship between flow rate and rainfall amount during June to September. This indicated that event-driven flow rate varied with rainfall amount, and thus suggested that runoff discharges are highly sensitive to rainfall amount with greater than 20 mm in this area.

3.2 DOC Concentrations in Runoff Discharges

3.2.1 Event-based DOC Concentrations during Concentrated Rainfall Season

In general, the monthly mean DOC concentration tended to decrease from 11.52 mg L^{-1} in June to 6.81 mg L^{-1} in August, and then slightly increased to 7.49 mg L^{-1} in September. There were less variations in the mean DOC concentration among monitoring months. For the event-driven DOC concentration, the flow-weight mean DOC concentration (C_f) ranged from 5.14 to 13.14 mg L^{-1} for all sampled rainfall events during June to September. The relationship between flow rate and C_f for sampled rainfall events was shown in Figure 4-b. The C_f exhibited a poor relationship with flow rate, and the C_f was a more variable at low flow rate period compared to the high flow rate period, which was typically observed during consecutive rainfall events with high rainfall amount. In addition, Table 2 showed the correlation between C_f and a set of factors in all sampled rainfall events during the study period. On one hand, the C_f was positively correlated with rainfall amount (Ra) and R7. On the other hand, the

C_f was extreme significantly and negatively correlated with SMC7 and SMC14. These results showed that different rainfall and soil moisture condition may affect DOC concentration for a rainfall event.

3.2.2 Dynamic Changes of DOC Concentrations in a Rainfall Event

Four rainfall events of total sampled events were chosen for detailed examine the relationship between DOC concentration (C_i) and flow rate in the hydrological process. These selected rainfall events represented 83% of the occurrence frequency of rainfall amount and the collected samples with high-frequency cover a complete of hydrological process during the monitoring period. Figure 5 shows the dynamic changes in DOC concentration and flow rate via the hydrograph over an event-driven hydrological process. In general, C_i varied between the runoff discharge process induced by different rainfall amount. The C_i increased quickly in the rising limb of the hydrograph and the maximum concentration occurred behind the peak of the hydrograph on 7-June (Figure 5-a) and 2-August (Figure 5-c), a period with less rainfall and of a long duration. Then, the C_i then decreased from 1.35 to 0.41 mg L^{-1} at the falling limb on 2-August, while the C_i remained relatively high values at 1.41-1.50 mg L^{-1} in the falling limb on 7-June. In rainfall events on 13-July (Figure 5-b) and 10-September (Figure 5-d), the discharge hydrograph exhibited a higher fluctuation due to the high rainfall amount and short rainfall duration. The C_i was kept relatively stable despite the facts that it increased from 1.05 to 1.30 mg L^{-1} at the rising limb on 13-July. However, the C_i sharply increased from 0.61 to 1.24 mg L^{-1} and the maximum C_i was observed before the peak of the hydrograph. The C_i then declined and remained stable ranging from 0.61 to 0.75 mg L^{-1} at the falling limb on 10-September. Overall, the dynamic changes in C_i in the hydrograph show that the DOC export process varied with different rainfall and runoff condition.

3.3 Hysteresis of event-driven DOC Concentrations

The above results showed a nonlinear correlation with flow rate and DOC concentrations (C_i) over a rainfall event. Therefore, a hysteresis analysis was used to examine the dynamic changes of the C_i response to a hydrological process, which has been applied to investigate the temporal variation in solute concentration with flow rate (Blaen et al., 2017; Lloyd et al., 2016a; Lloyd et al., 2016b; Tunaley et al., 2017). Figure 7 shows that the C_i varied in the rising and falling hydrograph during four selected rainfall events. Three hysteresis patterns were observed, including clockwise (13-July and 10-September), anti-clockwise (7-June) and figure-of-eight (2-August). As shown in Figure 6-a, the C_i was higher during the falling limb than during the rising limb of the hydrograph, thus resulting in an anti-clockwise pattern. A figure-of-eight pattern and indicated that C_i generally varied in pace with runoff discharge on 2-August, 2016 (Figure 6-c). The difference of C_i between rising and falling limb at a given flow rate was small, as supported by the results shown in Figure 5-c. On 13-July (Figure 6-b) and 10-September (Figure 6-d), the C_i exhibited a clockwise pattern, which implied that the C_i was higher in the rising limb than in the falling limb. The relationships between concentration and flow rate highlighted that the DOC export behavior was different in a complete hydrological process driven by a single rainfall event.

3.4 DOC Fluxes from Catchment

A rainfall event-based monitoring method is helpful to better understand the hydrological, DOC concentration and flux process. The rainfall event-based DOC flux ranged from 0.18 to 2.84 kg km^{-2} with a mean DOC flux of 0.43 kg km^{-2} for all sampled rainfall events from June to September, 2016. The relationship between event-based DOC flux and runoff discharge amount is shown in Figure 4-c. The DOC flux showed a positive linear relationship with the runoff discharge amount, especially for violent rainfall events. The DOC flux was more variable in lower runoff discharge conditions. In general, event-based DOC flux was significantly and positively correlated with Q, Ra, R1 and R, as showed in Table 2. For the monthly DOC flux, the total DOC loading from the catchment ranged from 94.73 kg km^{-2} in August to 110.17 kg km^{-2} in September (Table 1). Although the total runoff discharge was lowest in June in these four months, the DOC monthly flux was 102.39 kg km^{-2} and had a higher flow-weighted DOC concentration (11.52 mg L^{-1}). However, the DOC flux was higher in September, with an increased runoff discharge and a lower flow-weighted DOC concentration. The larger runoff discharge amount may offset the effects of lower DOC concentration.

4. Discussion

4.1 Relationship between Rainfall and DOC Export

It has been known that hydrological and carbon processes are important aspects of the regional carbon cycle and for restoring ecosystem service. However, the event-driven DOC exported from a catchment in the LRP has rarely been studied. In this study, we used an in-situ auto- and high-frequency monitoring method to observe temporal changes in hydrological and DOC concentration for an event-based sampling period during the concentrated rainfall season (June-September, 2016) (Figure 2-b). For DOC export on a monthly scale, the DOC was calculated as the product of total discharge and flow-weighted mean concentration in a month, and thus, these two variables represented hydrological and carbon biogeochemical processes. Monthly DOC fluxes were not clearly correlated with discharge amount. The flow-weighted DOC concentrations decreased during the experimental period, which differed from the greater DOC flux with a large discharge (Chen et al., 2012; Cooper et al., 2007). Furthermore, the monthly DOC fluxes were negatively correlated with the discharge amount from June to August, 2016. The DOC concentration was higher in June and decreased in August. This was reasonable because the accumulated soil organic carbon can be flushed by runoff in early rainfall period, and the DOC concentration may be diluted by increased runoff (Blaen et al., 2017; Chen et al., 2012). In addition, in combination with the increased discharge amount, the decreased concentration led to a decrease in monthly DOC flux from June to August. This could be explained by the relative changes in DOC concentrations being higher than changes in monthly discharge, indicating that the decreased concentration may outweigh the effect of increased discharge. However, the exception occurred in September, while increased DOC flux over the other three months was mainly due to a smaller increase in DOC concentration. These results were also probably associated with rainfall amount, land cover and runoff flow path (Laudon et al., 2004; Soulsby et al., 2003). For example, crops planted in the check-dam field were harvested, and the ratio of rainfall to runoff increased in September. The soil soluble organic carbon is more likely to leach through macropores from check-dam farmland into runoff, which further increased the DOC concentration in runoff. Thus, it led to a slight increase in DOC flux in September. Therefore, it could be inferred from these results that DOC flux may depend on runoff flushing capacity and flow path in a restored and check-dam catchment.

Despite the facts that the DOC export varied in different months, there were also differences in DOC concentration and flux response to a rainfall event. DOC concentrations exhibited different dynamic changes throughout an event-driven hydrological process. In our result, the anticlockwise hysteresis between DOC concentration and flow rate was observed at 7-June. The peak DOC concentration was delayed compare to peak flow rate. These results may be attributed to a 5.2 mm rainfall was happen earlier than the maximum rainfall at 7-June (Figure 5-a). The antecedent rainfall may increase connectivity in hydrology and DOC source contributed to runoff. Thus, the dilution effect diminished as flow rate decreased and the increased connectivity lead to a relatively higher DOC concentration during the falling limb (Hope et al., 1994; Ma et al., 2018; Williams et al., 2017). A clockwise hysteresis was observed in 13-July and 10-September. The rapid response of flow rate to rainfall can be attributed to the rainfall event with a shorter duration and larger rainfall amount. The higher discharge may bring a higher flushing capacity, thus an increased DOC concentration was observed during the rising limb (Blaen et al., 2017; Tunaley et al., 2017). Moreover, the close link of DOC source to runoff may lead to a rapid increased in DOC concentration. A figure-of-eight hysteresis was observed in 2-August due to the DOC concentration keep pace with flow rate during the rising and falling limb. Moreover, the event-driven DOC concentration at 2-August showed no distinct difference with other three higher rainfall amount events. These results suggested that a lower discharge induced by lower rainfall amount have a more complex and larger influence on DOC concentration from a catchment in LPR.

For event-driven flux, the DOC flux is a function of total runoff discharge and DOC concentration (C_f). DOC flux showed a positive linear relationship with runoff discharges, which is not surprising and parallel with studies reported by Clark et al. (2007) and Ma et al. (2018). In addition, it should be noted that the DOC flux induced by larger rainfall amount was higher than flux driven by light rainfall, whereas the C_f showed no evident difference for the selected rainfall events. Thus, the greater DOC flux clearly showed that the DOC export was closely linked to hydrologic process induced by various amount of rainfall events in LPR. For an ecological restored catchment in LPR, the soil carbon driven by increased vegetation was significantly increased and acted as a positive pathway to sequestration soil carbon on terrestrial ecosystem (Wang et al., 2011b). Meanwhile, the reduced hydrology responded to an increased vegetation may diminish soil carbon transported by hydrological process in a catchment. The event-driven DOC transport is an important component for evaluating carbon balance of the ecological restored catchment in LPR. Hence, further study should be long-term undertaking to investigate the hydrological response and its impact on terrestrial carbon loss from a catchment in LPR.

4.2 Potential Factors Influence on DOC Export

The mechanisms of DOC export from terrestrial ecosystem may be complicated and depend on many factors, such as soil organic carbon, vegetation, rainfall, hydrological condition and sampling period (Blaen et al., 2017; Cooper et al., 2007; Ma et al., 2018). Comparatively few previous studies have investigated how changes in hydrological factors and rainfall affect on DOC export. For instance, a current rainfall event leads to changes in a hydrological process, and it may also simultaneously change soil moisture content, which may influence the soil carbon biogeochemical process. For the next rainfall event, the antecedent conditions, such as hydrological condition and the soil organic carbon content, may also influence the DOC concentration and flux. In general, antecedent conditions drive DOC export through exerting influences on availability of DOC and impacts on hydrologic connectivity (Brocca et al., 2010; McMillan et al., 2018). Therefore, DOC export from a catchment during rainfall event was the result of carbon biogeochemical processes, and the antecedent hydrological and rainfall characteristics.

The infrequent and amount of violent rainfall events strongly influence the runoff discharges and soil moisture, which in turn impact on DOC during or later export from a catchment. In this study, temporal variations of rainfall, air temperature and soil moisture content were continuously monitored throughout the study period to provide detailed information describing the antecedent and current conditions. Positive correlation between Ra, R7 and C_f suggested that the combination of the current rainfall amount and the accumulated rainfall before a current rainfall event played important roles in DOC concentration for a rainfall event. R7 may reflect the antecedent hydrological condition and Ra represent the current rainfall input into the catchment. Higher Ra and R7 may lead to a well hydrological connectivity, and thus more DOC source may contribute to runoff. Therefore, C_f can by strongly influenced by Ra and R7 due to the hydrological properties of the catchment. Apart from the hydrological changes, the antecedent soil moisture also played an important role in C_f and showed an extreme significantly and negatively correlated with SMC7 and SMC14 (Table 2). The soil moisture content was continuously dried and then effectively rewetted under a specific rainfall amount, as supported by the soil moisture variations shown in Figure 2-c. These results were also consistent with Yang et al. (2018), who found that the threshold of rainfall effectively recharged into soil was 20-26 mm for grassland and forestland in LPR. Therefore, the pattern of soil moisture dry-wet cycle may affect event-driven DOC concentration, and this highlights the importance of soil moisture condition in DOC export (Figure 7). The higher DOC concentrations from June to middle July coincided with light rainfall, and thus rainfall recharge into soil moisture. This is probably attributed to inactive microbial activity, caused by the relatively lower soil moisture (Jager et al., 2009). The DOC concentration decreased with increased soil moisture content, particularly in July-18 with a total rainfall amount of 56.4 mm. On one hand, violent rainfall events may induce a higher discharge, causing a dilution effects on DOC concentration. On the other hand, the rainfall water may effectively replenish soil moisture content, and thus stimulate a higher decomposition of soil carbon under wet and higher temperature condition. Then, the relative decreased DOC concentrations were observed in a drying soil moisture condition for the next rainfall events, which may attribute to an exhaustion of DOC (Laudon et al., 2004). These findings were similar to previous studies by Tunaley et al. (2017), who reported a strong influence of dry antecedent conditions on DOC export response to rainfall event.

DOC flux was significantly and positively correlated with Q, Ra, R1 and R7. The Q and Ra reflect the direct effect of current rainfall and hydrological processes during a rainfall event, while R1 and R7 refer to the antecedent rainfall conditions and reflect indirect effects on DOC export. These results agreed with previous studies demonstrated by Blaen et al. (2017), who noted that antecedent conditions and rainfall were key drivers of DOC export during a rainfall event. Cooper et al. (2007) also concluded that DOC export is largely governed by interactions between hydrological and meteorological factors and carbon biogeochemical process. Overall, these results suggested that rainfall is a key factor influencing hydrological process, and thus DOC export from an ecological restored catchment in LPR. Apart from the increased soil carbon driven by increased vegetation (Wang et al., 2011b), the weaken hydrological process induced by increased vegetation may also cause a less terrestrial carbon export from a catchment. Therefore, our results highlight the need for research not only into the hydrological process and soil carbon cycle, but the integration of carbon export driven by a sequence of rainfall events across spatiotemporal scales to understand the carbon balance in a restored catchment in LPR.

5. Conclusion

The DOC concentration and flux for individual rainfall events from a semi-arid catchment of the LPR was initially monitored during the concentrated rainfall season. DOC concentration showed a weak correlation with discharge, except in higher runoff discharge induced by extreme rainfall events. The findings of this study indicate that DOC concentrations were highly variable, particularly during low runoff discharge periods. Hysteresis analysis showed that the relationship between DOC concentration and runoff discharge for a rainfall event is nonlinear and varied with conditions in rainfall amount, discharge process. DOC flux increased with runoff discharge and showed a positive linear correlation with runoff discharge. These results showed that higher DOC flux with low DOC concentration related to higher discharge and its dilution effects in a hydrological process driven by larger rainfall amount. The diluted DOC concentration induced by increased discharges contributed slightly to difference in DOC flux, due to total runoff discharge is a major variable for flux. These results showed that the temporal variation magnitude of DOC is related to hydrological condition and antecedent condition, and suggested that the event-driven DOC export are largely influenced by rainfall through direct effects on catchment hydrology and indirect effects on soil carbon cycles. Changes in catchment hydrology and soil carbon processes responded to climate change may play an important role in terrestrial carbon export, particularly for a restored catchment. Thus, further work should focus on carbon export response to various rainfall events at a larger spatiotemporal scale for better estimating future terrestrial carbon to aquatic ecosystem and evaluating carbon balance in ecological restored catchment in LPR. In addition, engineers and scientists can take advantage of the derived results to better develop advanced field monitoring work.

Data availability: The dataset used for this manuscript can be provided by e-mail contact with the first or corresponding author.

Author contributions. Linhua Wang: analyzing data and organizing the manuscript; Haw Yen: discussing the relationship between DOC concentration/flux and runoff discharges induced by a sequence of rainfall events; Xinhui E: sampling and lab testing work; Liding Chen and Yafeng Wang: discussing and guiding the field monitoring work.

Competing interests: The authors declare that they have no conflict of interest.

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Table 1 Characteristics of rainfall amount (Ra), flow rate, DOC concentration (C_f) and *Flux* for event-based samples collected during the concentrated rainfall season (June-September, 2016).

Table 2 Summary of correlation coefficients between C_f, *Flux* and a set of factors.

Figure 1 Geographic location of the Yangjuangou catchment in the Loess Plateau Region, China and the red and yellow dot denote the weather station and runoff sampling site.

Figure 2 Temporal variations in Ra (rainfall amount) and flow rate (a), C_f (flow-weighted mean concentration) and *Flux* (b), SMC (soil moisture content) (c) and air temperature (d) during the concentrated rainfall season (June-September, 2016).

Figure 3 Statistical characteristics of rainfall events from June to September,2016: (a) characteristics of total and sampled rainfall amount, (b) characteristics of rainfall amount grades and its occurrence frequency.

Figure 4 Relationships between Ra (rainfall amount) and flow rate (a), C_f (flow-weighted mean concentration) and flow rate (b), *Flux* and total discharge (c)for sampled rainfall events during the monitoring period (June-September, 2016).

Figure 5 Dynamic changes of DOC concentration (C_i) in an individual runoff event: (a)7-June, (b)13-July, (c)2-August, (d) 10-September.

Figure 6 Hysteresis loops for four selected runoff events from June to September: (a)7-June, (b)13-July, (c)2-August, (d) 10-September.

Figure 7 The changes of event-driven C_f (flow-weighted mean concentration) response to dry-wet and wet-dry variations in soil moisture content.

Table 1

Date	Ra (mm)	Flow rate (L s^{-1})	C_f (mg L^{-1})	*Flux* (kg km^{-2})
1-Jun.	1.0	0.56	10.87	0.52
2-Jun.	7.0	0.59	9.97	0.51
3-Jun.	3.0	0.53	10.53	0.48
5-Jun.	3.2	0.53	11.59	0.53
7-Jun.	13.8	0.65	12.96	0.73
Jun.	82.9	0.35	11.52	102.39
11-Jul.	24.6	0.44	11.92	0.45
13-Jul.	19.8	1.28	11.84	1.31
14-Jul.	11.0	0.46	13.00	0.52
18-Jul.	62.6	1.46	11.64	1.47
19-Jul.	29.2	4.05	8.12	2.84
31-Jul.	2.2	0.54	6.70	0.31
Jul.	184.2	0.41	8.95	96.57
1-Aug.	0.8	0.54	5.14	0.24
2-Aug.	4.2	0.63	9.72	0.53
6-Aug.	0.8	0.47	7.95	0.32
12-Aug.	0.8	0.40	5.30	0.18
13-Aug.	1.2	0.35	5.93	0.18
16-Aug.	18.8	0.96	6.46	0.54
17-Aug.	0.6	0.55	9.69	0.46
18-Aug.	1.2	0.57	7.44	0.37
Aug.	53.8	0.53	6.81	94.73
9-Sept.	6.8	0.44	13.14	0.50
10-Sept.	21.8	1.24	7.21	0.77
17-Sept.	6.2	0.48	9.10	0.38
Sept.	51.2	0.57	7.49	110.17

Table 2

	Flux	Q	Ra	R1	R7	R14	REI	T_{air}-7	T_{air}-14	SMC-7	SMC-14
C_f	0.30	-0.01	0.30	-0.01	0.23	-0.05	-0.32*	-0.25	-0.24	-0.44**	-0.65**
Flux		0.94**	0.69**	0.76**	0.57**	0.29	-0.14	-0.07	-0.04	0.06	-0.24
Q			0.60**	0.85**	0.53**	0.33*	-0.07	-0.02	0.01	0.19	-0.03
Ra				0.38*	0.39*	0.14	-0.06	0.02	0.07	-0.05	-0.30
R1					0.58**	0.42**	-0.27	0.11	0.10	0.12	-0.01
R7						0.69**	-0.28	0.24	0.23	0.40**	0.02
R14							-0.20	0.19	0.13	0.56**	.420**
REI								-0.02	0.03	0.26	0.25
T_{air}-7									0.96**	0.09	0.20
T_{air}-14										0.09	0.17
SMC-7											0.79**

Note: ** ($P<0.01$), * ($P<0.05$).
C_f: Flow-weighted mean concentration driven by an event, *Flux*: Event-driven DOC quantity,
Q: Total discharge volume, Ra: Total rainfall amount,
R1: Total rainfall amount in the 1 day before the current rainfall event,
R7: Total rainfall amount in the 7 days before the current rainfall event,
R14: Total rainfall amount in the 14 days before the current rainfall event,
SMC-7 and SMC-14: Soil moisture content in the 7 and 14 days before the current rainfall event,
T_{air}-7 and T_{air}-14: Mean air temperature in the 7 and 14 days before the current rainfall event,
REI: Interval days between the current and last rainfall event.

Figure 1

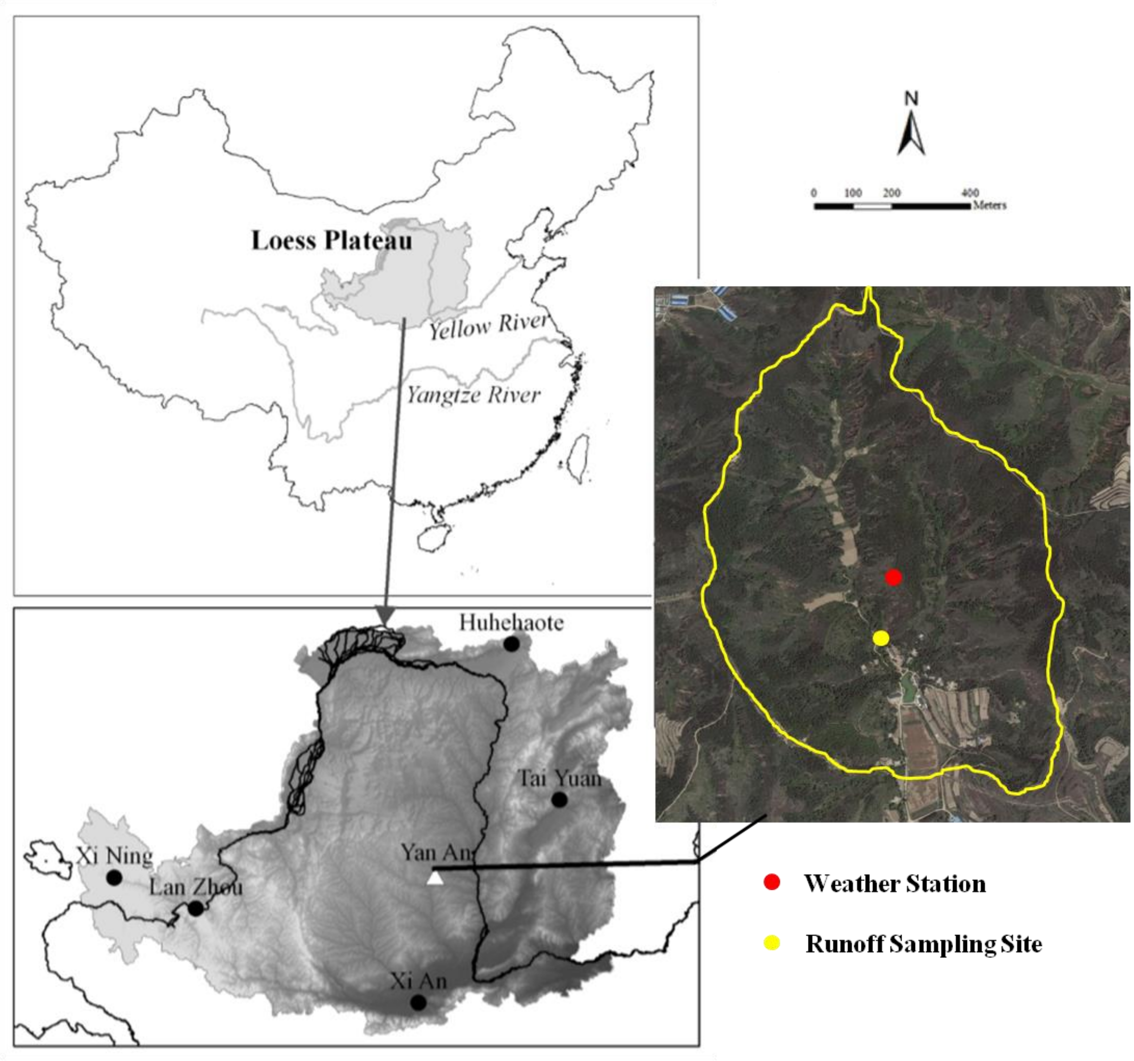
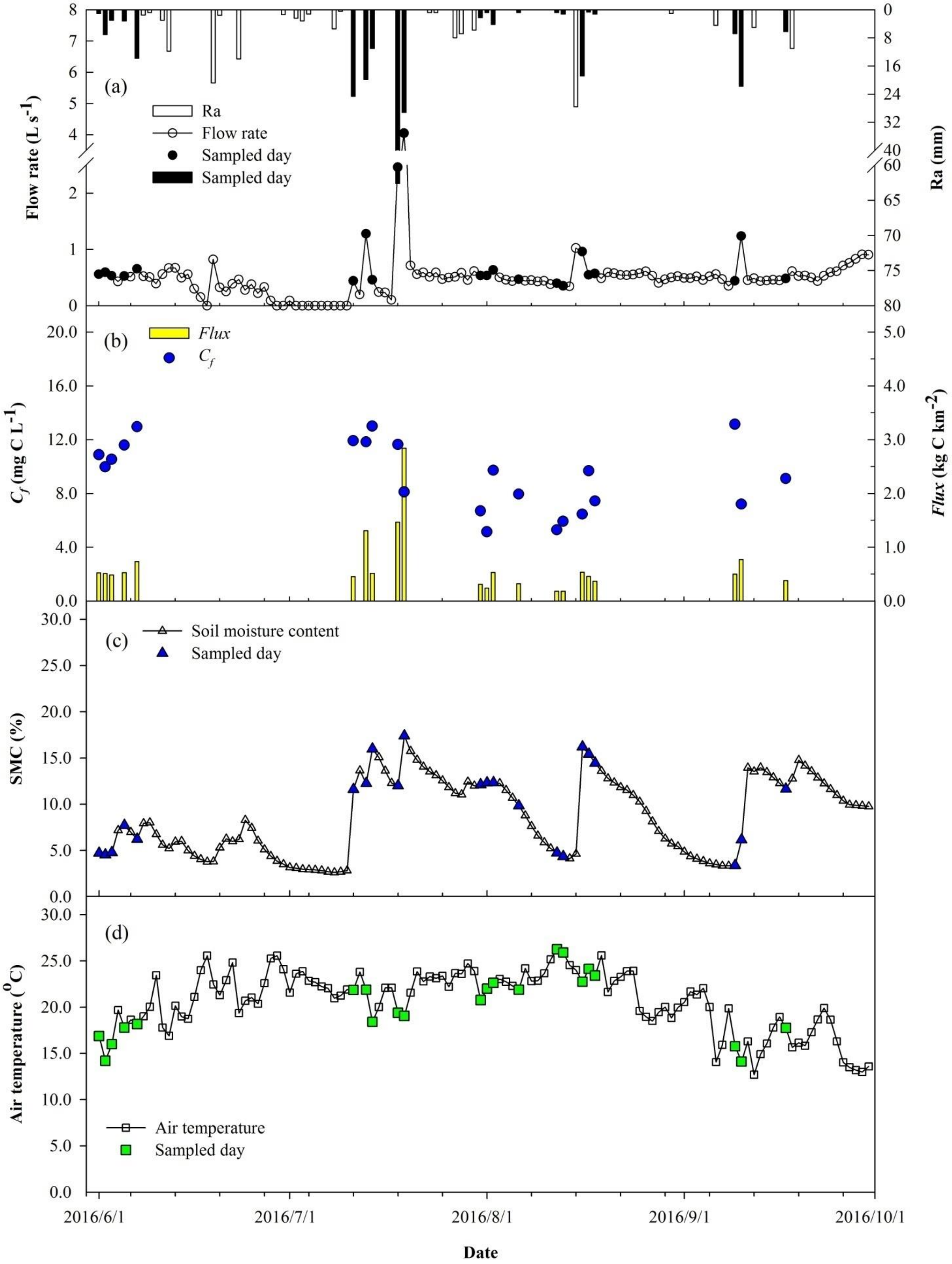

Loess Plateau
Yellow River
Yangtze River
Huhehaote
Tai Yuan
Yan An
Xi Ning
Lan Zhou
Xi An
N
0
100
200
400
Meters
Weather Station
Runoff Sampling Site

Figure 2



(a)
Ra
Flow rate
Sampled day
Sampled day
Flow rate (L s^{-1})
Ra (mm)
(b)
Flux
C_f
C_f (mg C L^{-1})
Flux (kg C km^{-2})
(c)
Soil moisture content
Sampled day
SMC (%)
(d)
Air temperature
Sampled day
Air temperature (^{o}C)
2016/6/1
2016/7/1
2016/8/1
2016/9/1
2016/10/1
Date

Figure 3

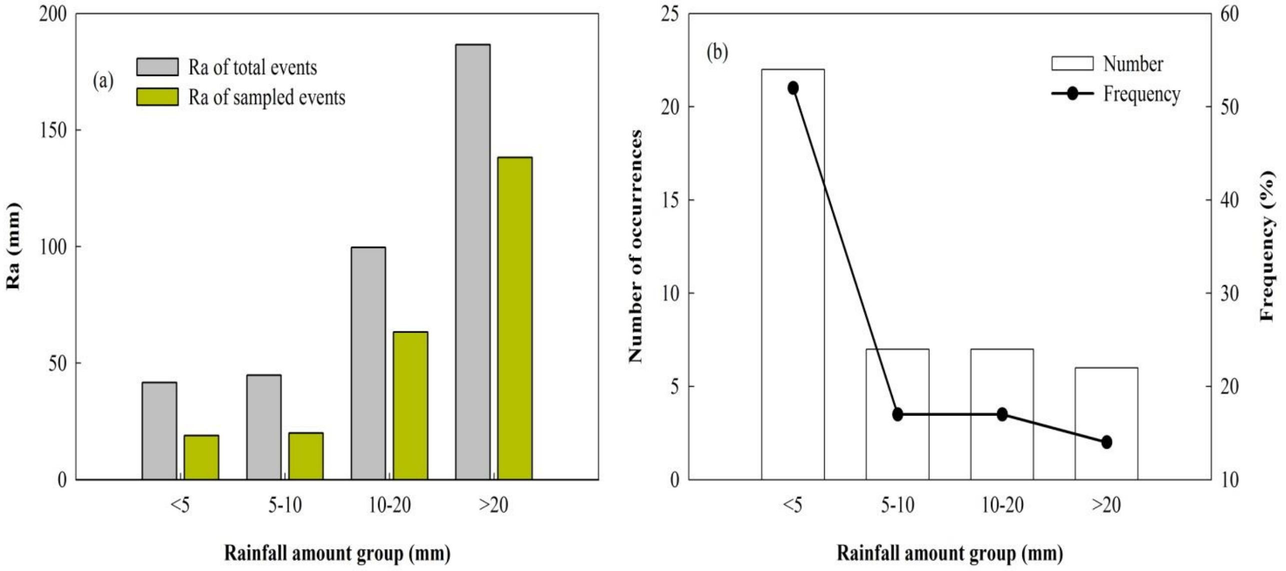


Figure 4

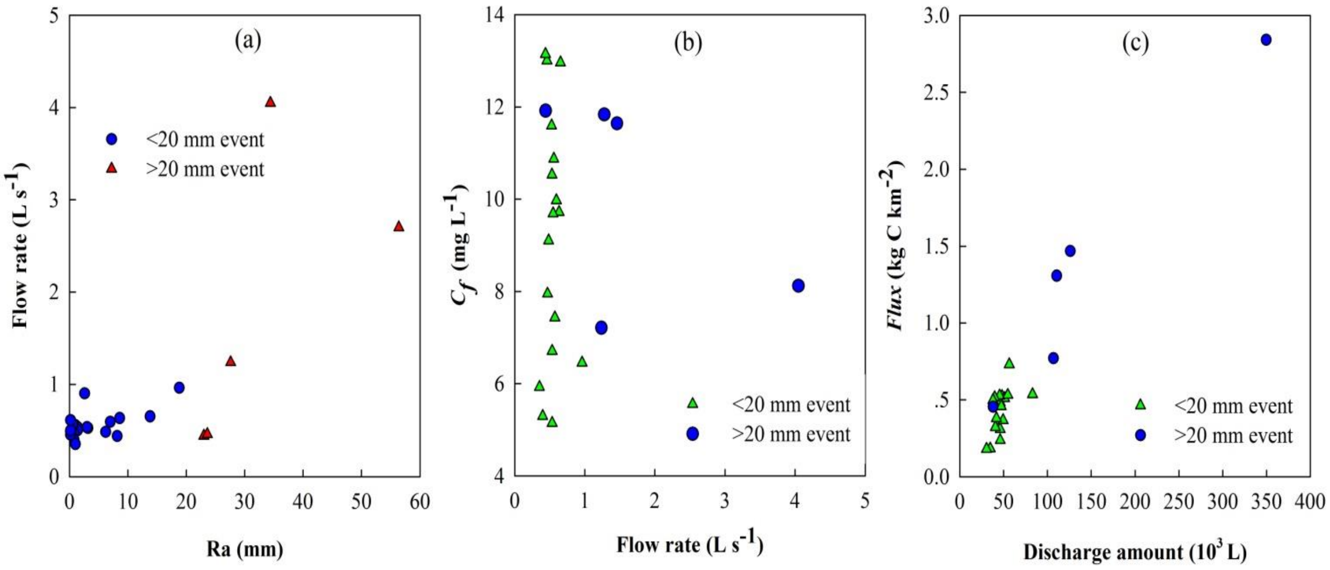
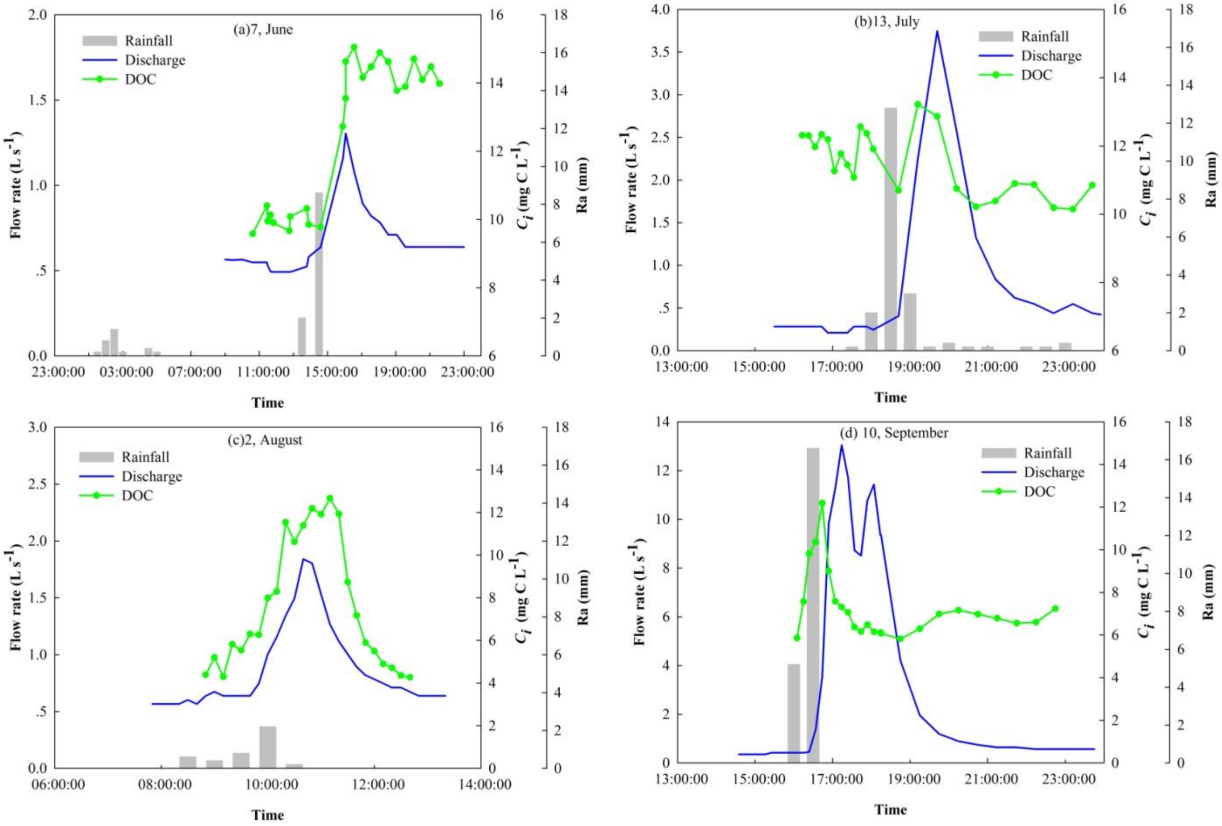


Figure 5


(a)7, June
Rainfall
Discharge
DOC
Flow rate (L s^{-1})
C_i (mg C L^{-1})
Ra (mm)
Time
2.0
1.5
1.0
.5
0.0
16
14
12
10
8
6
18
16
14
12
10
8
6
4
2
0
23:00:00
03:00:00
07:00:00
11:00:00
15:00:00
19:00:00
23:00:00
(b)13, July
Rainfall
Discharge
DOC
Flow rate (L s^{-1})
C_i (mg C L^{-1})
Ra (mm)
Time
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
16
14
12
10
8
6
18
16
14
12
10
8
6
4
2
0
13:00:00
15:00:00
17:00:00
19:00:00
21:00:00
23:00:00
(c)2, August
Rainfall
Discharge
DOC
Flow rate (L s^{-1})
C_i (mg C L^{-1})
Ra (mm)
Time
3.0
2.5
2.0
1.5
1.0
.5
0.0
16
14
12
10
8
6
4
2
0
18
16
14
12
10
8
6
4
2
0
06:00:00
08:00:00
10:00:00
12:00:00
14:00:00
(d) 10, September
Rainfall
Discharge
DOC
Flow rate (L s^{-1})
C_i (mg C L^{-1})
Ra (mm)
Time
14
12
10
8
6
4
2
0
16
14
12
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8
6
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2
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18
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13:00:00
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23:00:00

Figure 6

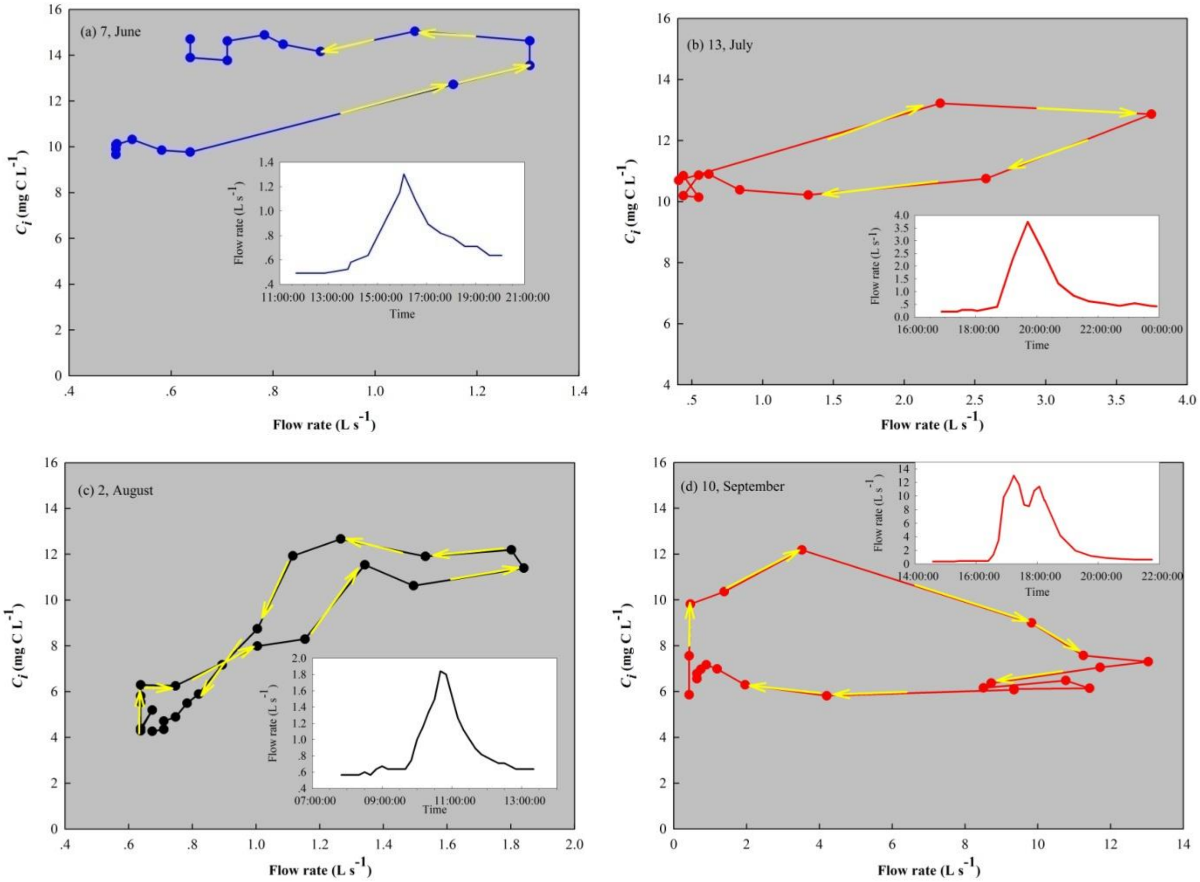

Figure 7