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Dissolved organic matter dynamics in storm water runoff in a dryland urban region

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ABSTRACT

The temporal and spatial dynamics of dissolved organic carbon (DOC) during storm events are well characterized in mesic urban regions, but equivalent studies in arid regions are less frequent, and our understanding of the impacts of arid-land urban storm events on downstream ecosystems remains poorly constrained. We sampled storm runoff in an urban dryland storm drainage system during four summer monsoon storms to determine DOC concentration and composition and to develop a conceptual carbon transport model during storm events. DOC patterns were consistent between storm events despite large differences in discharge and DOC concentration, with the lowest DOC concentrations (2.1–11.7 mg L^{-1}) during first flush, highest concentrations shortly after peak discharge (18.3–46.0 mg L^{-1}), and decreasing concentrations on the descending limb of the hydrograph. Fluorescence Index (FI) values suggested the DOC source shifted throughout events in three distinct phases: Phase 1- autochthonous DOC, Phase 2 - fresh allochthonous DOC, and Phase 3 - processed allochthonous DOC, representing the sequential input of previously disconnected sources during each storm event. Peak DOC concentrations generally lagged peak discharge, supporting distal allochthonous inputs of DOC to the drainage system. A single 11-h storm event delivered more than half the average daily Rio Grande discharge and approximately four times the average daily DOC load. Our findings indicate the significant impact monsoon storm events exert on DOC budgets in dryland rivers, particularly in watersheds drained by urban storm-water conveyances.

1. Introduction

Dryland regions, those with arid and semi-arid climates, often rely on surface water to meet environmental, agricultural, and drinking water demands. These areas cover more than 40% of the globe, house over two billion people, and have the fastest growing urban populations (Millennium Ecosystem Assessment, 2005). Rapid urbanization and population growth in these regions alter hydrology and aquatic biogeochemical cycles including the cycling of carbon, nitrogen, and phosphorous (Paul and Meyer, 2001, Grimm et al., 2004), which have important implications for ecosystems and human health. Thus, it is critical to understand controls on surface water quality in dryland urban regions. However, current conceptual models linking hydrology and biogeochemistry, largely based on natural watersheds, poorly represent the dynamics that occur in urban systems (Kaye et al., 2006).

Dissolved organic carbon (DOC) is an important component of surface water quality and plays an integral role in regional and global carbon cycles (Aitkenhead and McDowell, 2000). In surface waters, DOC is an energy source for heterotrophs, mediates nutrient cycling, and mobilizes and alters the bioavailability of metals and organic contaminants (e.g. Stewart and Wetzel, 1981; Stanley et al., 2012, and references therein). In addition, DOC is of growing concern during drinking water treatment, where it can consume coagulants, promote bacterial regrowth, and form carcinogenic disinfection byproducts (Rook, 1977, and references therein).

Surface water DOC is derived from a combination of autochthonous (aquatic production) and allochthonous (terrestrial production) sources (Aitkenhead-Peterson et al., 2003; Fellman et al., 2009). The balance between autochthonous and allochthonous sources varies among biomes and ecosystems due to factors such as light availability, riparian

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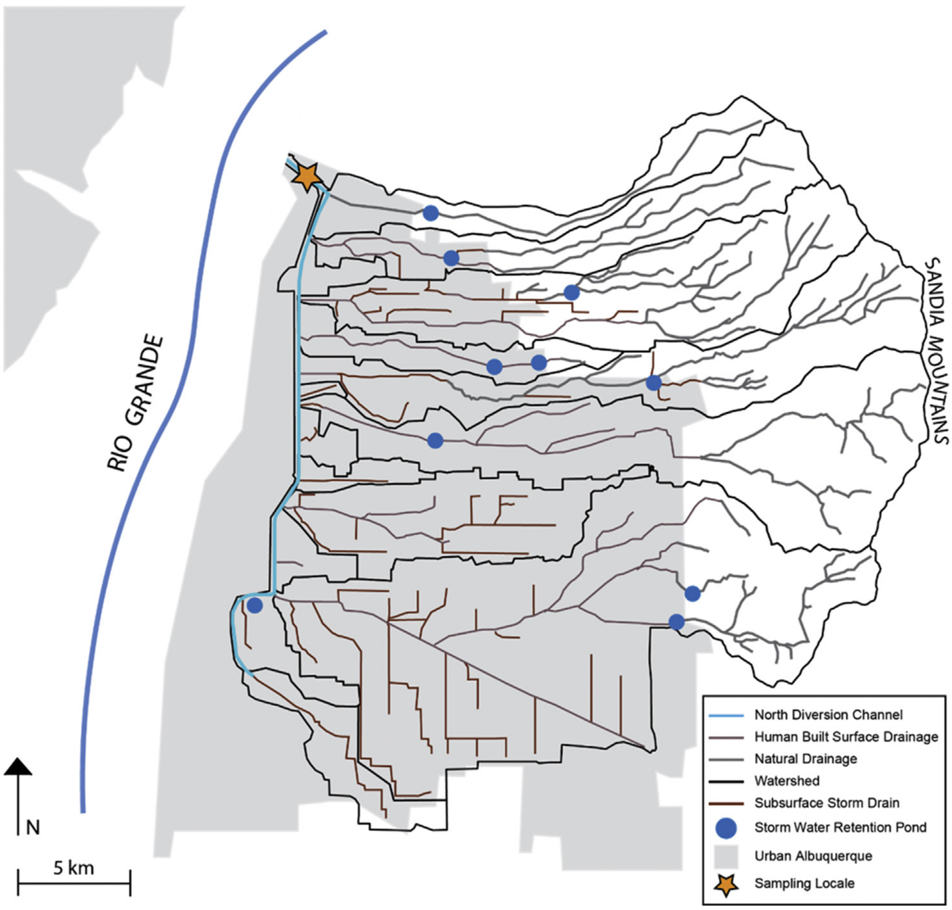

Fig. 1. Location of the NDC within the greater Albuquerque area. The storm drainage system encompasses the area from the Sandia Mountains to the Middle Rio Grande river valley. Watersheds drained by the storm drainage system are outlined in black, and the sampling location is marked with a star. Impervious surfaces associated with the Albuquerque urban area are shaded in gray.

characteristics, and storm events (Bertilsson and Jones, 2003; Hood et al., 2006). For instance, DOC in mesic regions is dominated by allochthonous inputs and reflects large contributions of carbon from terrestrial vegetation (Aitkenhead-Peterson et al., 2003; Kaplan et al., 2006), composed primarily of humic material (Wetzel, 1995). In contrast, DOC in dryland regions is largely derived from autochthonous growth due to high light availability that stimulates aquatic biomass and degradation of terrestrial carbon inputs (Jones et al., 1997). This autochthonous DOC is generally simpler in chemical structure and is more biologically labile than allochthonous DOC (Findlay and Sinsabaugh, 2003; Kaplan et al., 2006).

In river systems, DOC concentration generally increases with elevated discharge (Meyer and Tate, 1983; Hood et al., 2006). Storm events not only increase discharge but also increase hydrologic connectivity to the landscape, flushing distal sources of organic matter including riparian organic carbon-rich soils and the hyporheic zone, and transporting this carbon to downstream waterways via overland and subsurface flow (Schindler and Krabbenhoft, 1998; Hood et al., 2006; Fellman et al., 2009). Thus, storm events are an important control on DOC transport dynamics as they connect pools of previously inaccessible carbon on the landscape to rivers via runoff and subsurface flow paths. Consequently, storm events are responsible for a significant portion of the annual DOC export in many regions (e.g. Hinton et al., 1998; Raymond and Saiers, 2010; Raymond et al., 2016).

Urbanization generally intensifies flows by reducing the extent of riparian and hyporheic zones, increasing impervious surface area, and increasing the number of surface drainage channels on the landscape (Paul and Meyer, 2001, Grimm et al., 2004). Additional anthropogenic sources of nutrients and organic carbon linked to urbanization, including wastewater treatment plant effluent and seepage from sewage and storm drains (Sickman et al., 2007; Kaushal and Belt, 2012) are mobilized through increased surface runoff and rapid flushing associated with increased impervious surfaces and stormwater conveyances, amplifying the effects of storms on biogeochemistry in urban regions (e.g. Lee et al., 2002; Hale et al., 2015; Song et al., 2015).

Despite the importance of surface water in urban dryland regions and the rate at which these regions are growing, little is known about how storm events impact DOC dynamics in such areas. To address this knowledge gap, we studied changes in DOC concentration and composition from the outlet of the largest collection channel in the storm water drainage system of Albuquerque, NM (a large urban center located in the arid southwestern United States). This channel, which delivers runoff directly to the Rio Grande, was sampled during four monsoon storm events in the summer of 2014. Our specific goals were to: 1) determine the concentration and quantity of DOC transported by storm events in an urban dryland region, and 2) identify the major sources of DOC transported during storm events. We find that DOC concentration increases with discharge and that the source of DOC shifts sequentially over the course of each storm event between autochthonous production occurring in pools that are persistent between events, fresh allochthonous material from near-channel sources, and processed allochthonous material from sources distal to the channel. We also find that the NDC drainage system is capable of transporting up to four times the Rio Grande's daily dissolved organic carbon load during a single storm event.

2. Methods

2.1. Site description

Surface water samples were collected near the outfall of the North Diversion Channel (NDC) on the east side of the Rio Grande in

Albuquerque, New Mexico (USA). The NDC is a 14 km low gradient concrete channel that receives runoff from a series of natural and human built conveyances draining ten watersheds (2462 ha in total) that cover the area from the base of the Sandia Mountains to the Rio Grande (Fig. 1). The NDC is the largest storm drainage channel in the network of engineered conveyances in the Albuquerque storm drainage system. The NDC dries out between storm events, and only has measureable flows on average 75 days out of the year (Storms et al., 2015).

The NDC enters the Rio Grande (35° 12′ 18.90″ N, 106° 36′ 2.33″ W) upstream of Albuquerque and the drinking water intake for city. NDC discharge is measured at 15 min intervals by the United States Geologic Survey (USGS) at the North Floodway Channel Near Alameda Gauging Station (USGS Site Number 08329900; 35°11′ 53″ N, 106° 35′ 59″ W). On an annual basis, the NDC contributes ~3% of the Rio Grande's discharge. On days with storm events, the NDC can contribute more than 50% of the Rio Grande's daily flow (Storms et al., 2015).

The NDC catchment covers a large area from the Sandia Mountains to the Rio Grande valley and ranges in elevation from ~3000 m in the mountains to ~1400 m in the river valley. Land use in the valley is a mixture of residential, agricultural, commercial, industrial, and undeveloped open space, with impervious surfaces accounting for about 60% of the drainage (Storms et al., 2015). East of the valley, the foothills and mountains are characterized by shrub lands in the foothills and piñon-juniper, ponderosa pine, and mixed conifer forests at increasing elevations (Storms et al., 2015).

The NDC drainage area has a mean annual air temperature of ~12 °C. Mean annual precipitation in the urban valley and foothills ranges between 16 and 25 cm yr^{-1} while the Sandia Mountains receive ~55 cm yr^{-1}. The precipitation in this region is largely controlled by the North American Monsoon, with more than 60% of annual precipitation in the area falling during thunderstorms that occur between July and September (Western Regional Climate Center, http://www.wrcc.dri.edu/narratives/newmexico/). All samples were collected during the summer monsoon season of 2014. For context, the cumulative precipitation during 2014 (as determined from daily precipitation data collected from the USGS 08329900 gauge referenced above) was 17.5 cm. Compared to the 2002–2017 mean value of 21.8 cm and median value of 19.1 cm, 2014 was a drier than average year.

2.2. Sample collection

Storm events were sampled on July 3, August 1 and 2, August 13, and September 4, 2014 (Fig. 2a) and are referred to as Events 1, 2, 3, and 4, respectively. Sampling was conducted from a bridge overlooking the center of the channel using a bottle attached to a telescoping rod. As monsoonal storms occur in the evening, storm pulses often peak close to midnight, so samples were collected throughout the night for each storm. We attempted to sample before, during, and after the rising limb of each storm. However, due to rapid rises in discharge (all storm hydrographs transition from baseflow to peak flow in minutes), it was difficult to collect samples during the rising limb. Duplicate samples were collected approximately hourly over the duration of the storm events using 130 ml plastic syringes rinsed 3 times with storm water prior to collection. Samples were immediately filtered through precombusted organic carbon free 0.7 μm pore size glass fiber filters and then through sterile 0.2 μm polytetrafluoroethylene filters (PTFE). Field blanks were also collected and consisted of deionized water (18 MΩ-cm). Samples were stored in combusted (4 h at 500 °C) amber glass bottles with PTFE caps and kept in the dark, on ice in the field, and refrigerated (4 °C) upon return to the laboratory.

2.3. Organic matter analysis

Samples for DOC concentration analysis were acidified (pH = 2) using 6N hydrochloric acid, packed on ice, and shipped overnight to the Kiowa Analytical Laboratory at the University of Colorado Boulder. DOC concentrations were measured by high temperature combustion followed by detection using infrared spectroscopy on a Shimadzu TOC-5000 analyzer within 28 days of collection, following the method of the Kiowa Environmental Chemistry Laboratory (http://niwot.colorado.edu/research/kiowa-lab). Carbon concentration is reported as milligrams of carbon per liter (mg L^{-1}).

Dissolved organic matter (DOM) fluorescence was measured using a Varian Eclipse fluorescence spectrophotometer with a 1 cm quartz cuvette. Only excitation and emission wavelengths needed to calculate the fluorescence index (FI) according to McKnight et al. (2001) were measured. Blanks were run to background-correct readings. The fluorescence index (FI) was calculated as the ratio of fluorescence emission intensity at 470 nm to that of 520 nm based on an excitation wavelength of 370 nm (McKnight et al., 2001). The FI can be used to assign DOM to allochthonous (1.2–1.5; e.g., fresh and degraded terrestrial plant and soil organic matter) or autochthonous and microbially processed (1.7–2.0) sources (McKnight et al., 2001). However, subsequent study of instrument-specific bias on FI measurements has found that FI values for terrestrial and microbial DOM standards run on a different Eclipse fluorometer were 1.28 and 1.52, respectively, suggesting that microbially-processed DOM FI signatures may be lower than 1.7. Additionally, instrumental bias correction factors were not used, so our interpretation of the origin of the fluorescence index is relative.

3. Results

3.1. Storm event discharge

Among storm events, there was large variation in seven-day antecedent discharge (range: 145 m^3 to 491,767 m^3), total water discharged during each event (range: 273 m^3–670 m^3), and peak discharge (range 4 m^3s^{-1} to 214 m^3s^{-1}) (Table 1). Peak discharge varied among events by approximately two orders of magnitude with the highest discharge occurring during Event 2, while Events 1, 3, and 4 had very similar total discharge (Table 1). The hydrograph for each storm was characterized by a nearly vertical ascending limb to the peak discharge followed by a gradual tapering of the descending limb (Fig. 2a; Table 1).

3.2. Storm event DOC concentration and transport

For all events, the lowest DOC concentrations were observed prior to the ascending limb of the hydrograph (Table 1, Fig. 3). Event 1 had the highest initial DOC concentration (11.7 mg L^{-1}) while events 2 and 3 had the lowest initial DOC concentrations (2.1 mg L^{-1}). The offset of peak DOC concentration from peak discharge varied slightly between storm events from no lag in Event 4 to a two-hour lag in Event 3. Events 1 and 2, which occurred in July and early August, had the greatest maximum DOC concentrations (46.0 and 41.1 mg L^{-1}) (Table 2). Events 3 and 4 had much lower maximum DOC concentrations (24.1 and 18.0 mg L^{-1}) and occurred in the second half of the monsoon season (Table 2). Concentrations returned to near initial values as each storm event tapered (Fig. 3). Mean DOC concentrations for each event followed maximum concentration patterns, with values of 23.6, 16.0, 10.3, and 13.0 mg L^{-1} for Events 1 through 4, respectively (Table 2). Hysteresis analysis used to explore discharge/concentration relationships revealed counter-clockwise patterns for all four storm events (Fig. 4). This is consistent with peaks in DOC concentrations observed shortly after the maximum discharge followed by concurrent decreases in discharge and DOC concentration (Fig. 3).

The total amount of carbon transported through the NDC during each storm event was calculated by integrating and multiplying the hourly measured DOC concentrations and the hourly discharge for each storm (Table 2). DOC loads during storm events varied by almost two orders of magnitude: the two storm events with the largest total discharges (Events 1 and 2) transported the largest quantities of carbon (2118 and 20181 kg, respectively; Table 2). Events 3 and 4 had much

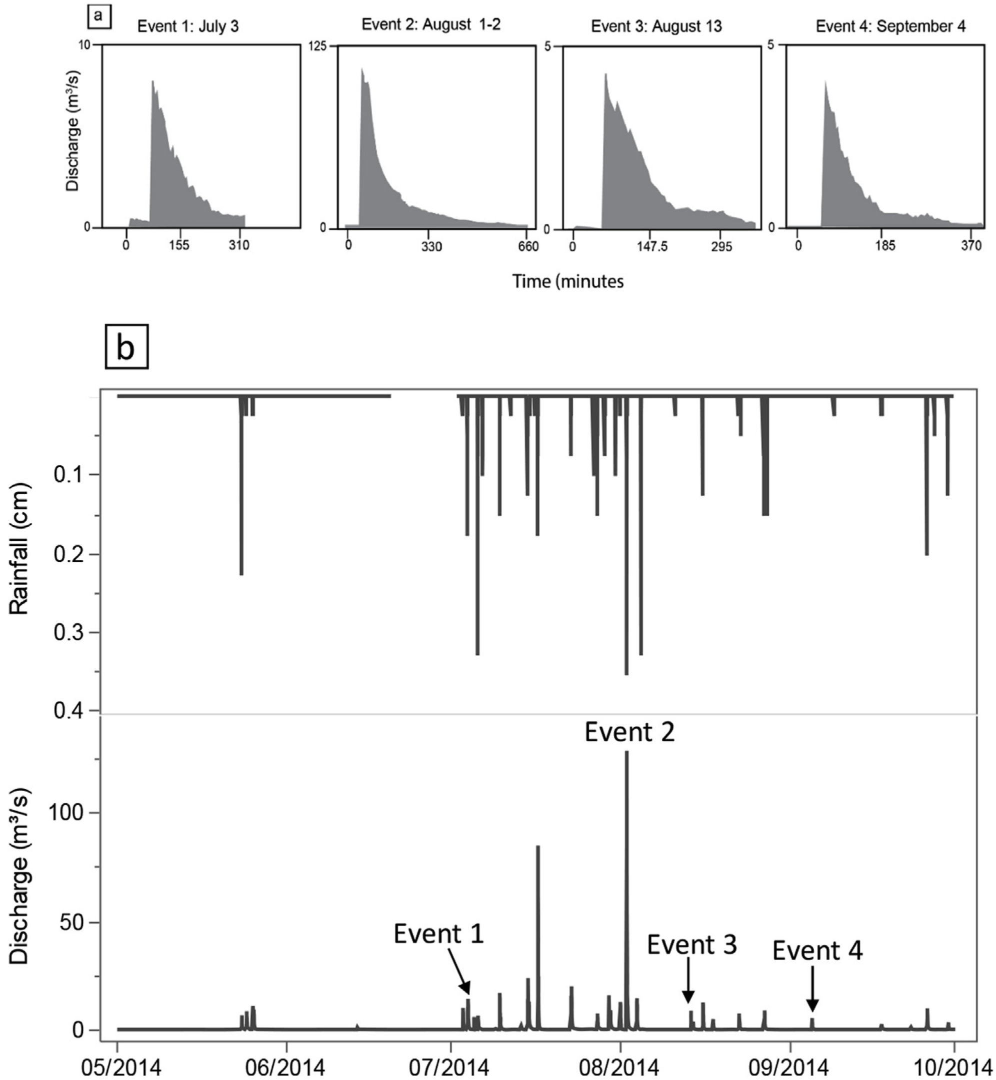

Fig. 2. A) Individual storm hydrographs exhibiting consistent discharge spikes with storm onset and extended tailing. B) Precipitation and discharge for the study period, with storm events marked for discharge.

Table 1
Hydrologic characteristics of four storm events.

Event	Date	Antecedent discharge (m^3/7 days)	Peak discharge (m^3/s)	Total discharge (m^3)
Event 1	7/3/14	145	9	62880
Event 2	8/1/14-8/2/14	491768	214	670100
Event 3	8/13/14	1998	4	27260
Event 4	9/4/14	7783	5	46560

lower discharge (Table 1), and transported much smaller quantities of carbon (285 and 666 kg, respectively).

3.3. DOC source: fluorescence index during storm events

Initial FI values ranging from 1.51 in Event 4 to 1.68 in Event 2 reflect a mixture of autochthonous and allochthonous sources (Table 2; Fig. 3) and the event with the highest initial FI value (Event 2) corresponds to the largest seven-day antecedent discharge. During all storm events, FI values decreased (became more terrestrial) with increasing DOC concentrations. Low FI values indicative of allochthonous inputs accompanied higher average DOC concentrations (1.37 and 1.38 for Events 1 and 2), while Events 3 and 4 had lower minimum FI values of 1.31 and 1.21, respectively (Table 2). Average values over the course of each event were consistently near 1.50 (Table 2; Fig. 3). As DOC concentrations fell with the receding discharge, FI values increased (Fig. 3). By the end of each storm event, FI values reached their maxima near 1.70 indicating an autochthonous or a microbially processed soil source (Cory et al., 2010). FI values reported throughout storm events are consistent with previous reports of FI values in urban stormwater (e.g. Zhao et al., 2015).

4. Discussion

4.1. DOC dynamics during storm events

Based on our observations that DOC concentration and FI values vary predictably over the duration of each storm event and appear to be influenced by antecedent conditions, we present a conceptual model relating DOC concentration and source to storm runoff patterns (Fig. 5). In this model, we propose that the carbon present in the NDC during storm events comes from three main sources accessed during three distinct time-periods associated with the hydrograph. First, DOC originating from autochthonous sources within the storm drainage system is flushed prior to maximum discharge. Second, during peak discharge,

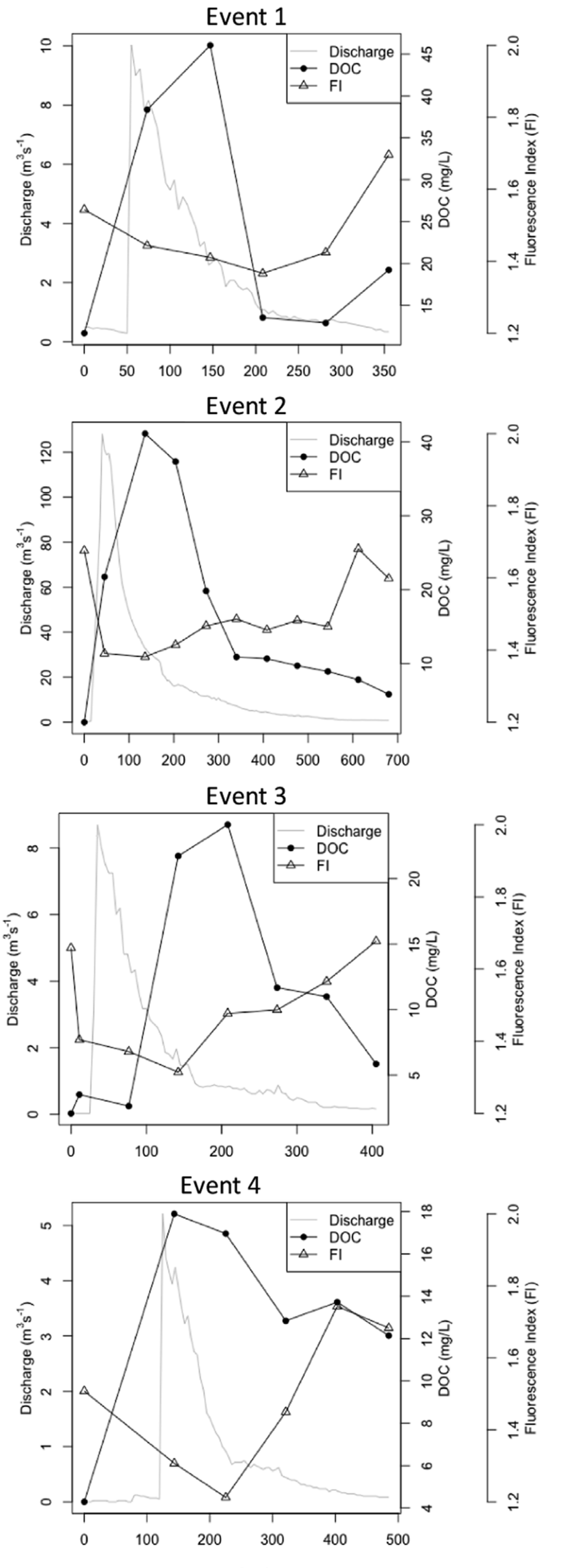

Fig. 3. Relationships between DOC concentration, FI, and discharge during the four storm events.

Table 2
DOC and FI characteristics of four storm events.

Event	DOC (mg L^{-1}	DOC range (mg L^{-1})	Total export (kg DOC)	FI initial	FI mean	FI range
Event 1	23.6	11.7–46.0	2118	1.54	1.48	1.37-1.70
Event 2	16.0	2.1–41.1	20181	1.68	1.50	1.38-1.68
Event 3	10.3	2.1–24.1	285	1.66	1.49	1.31-1.68
Event 4	13.0	4.3–18.1	666	1.51	1.48	1.21-1.74

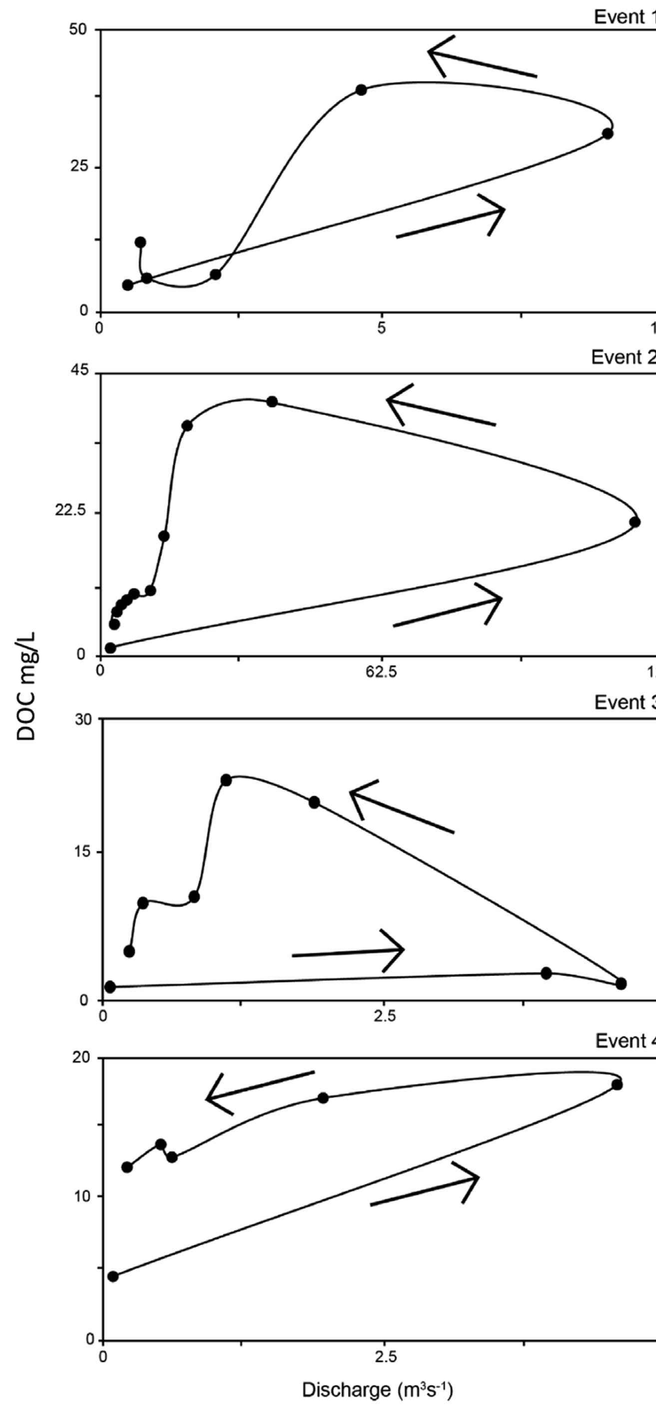

Fig. 4. Hysteresis plots illustrating the relationship between discharge and DOC concentration, with arrows indicating the direction of hysteresis. All hysteresis is counter-clockwise, indicating increasing DOC concentrations on the descending limb of the hydrograph.

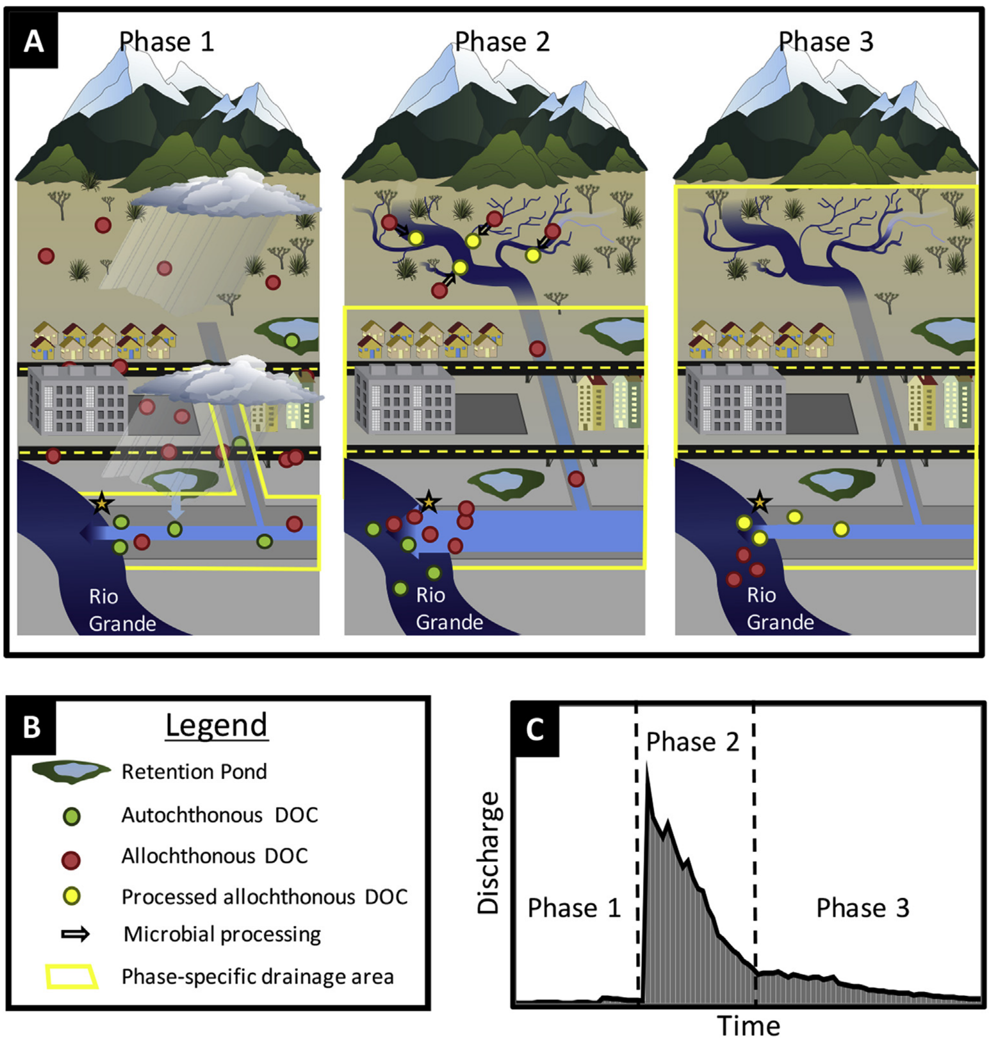

Fig. 5. Conceptual diagram illustrating the three phases of dissolved organic carbon (DOC) transport during monsoonal storm events in the North Diversion Channel (NDC) in Albuquerque, NM. All three phases are shown in A), with a legend explaining symbols provided in B). For reference, C) provides delineations between phases using an example hydrograph. During Phase 1, authothonous DOC in the NDC is exported to the river. During Phase 2, increased discharge flushes allochthonous sources (including urban and undeveloped soils). During Phase 3, microbially processed DOC is transported from permeable soils and natural flowpaths into the NDC and exported into the Rio Grande. The spatial extent of the area of DOC inputs increases with each phase.

DOC is transported from impervious surfaces within the Albuquerque urban area, along with some near-channel terrestrial organic matter. Finally, during the descending limb of the storm hydrograph, DOC is transported via runoff from soils in undeveloped areas surrounding Albuquerque, including the Sandia Mountains. Using this model, we have divided the following discussion into three phases of storm-driven organic matter transport: Phase 1 - flushing of autochthonous material from the NDC, Phase 2, Phase 2 – the initial flushing of adjacent and distal pools of allochthonous carbon sources, and Phase 3 – flushing of processed allochthonous material from longer or slower flowpaths. Consistent with previous literature, mean DOC concentrations were highest for the lowest antecedent discharge (Event 1, Tables 1 and 2), while higher antecedent discharge events (Events 2–4) showed lower mean DOC concentrations (Westerhoff and Anning, 2000), suggesting that antecedent conditions may be an important additional consideration that dictates the magnitude of carbon exported from the catchment during a storm event.

4.2. Phase 1- flushing of autochthonous material

The initial phase of each storm event in Fig. 3 is characterized by low discharge and low DOC concentrations with an elevated FI signal (ranging from 1.51 to 1.68) suggesting a mixture of allochthonous and autochthonous sources. Low DOC concentrations prior to peak discharge may be explained by high rates of organic matter processing within engineered storm channels, as suggested by Kaushal and Belt (2012). The concrete construction of the NDC blocks groundwater inputs, eliminating exchange of carbon and water with the hyporheic zone, and the NDC lacks a riparian zone. Thus, it is unlikely that the initial DOC signal originates from terrestrial organic matter or sources external to the storm drainage system. We therefore suggest the initial DOC pool is sourced primarily from organic matter originating throughout the drainage system during periods of no flow. Autochthonous inputs are likely derived from algal and macrophyte production in low lying sections of the system which hold water and support growth in between storm events (Personal observation). This is consistent with a recent review of DOM sources in urban waterways, which indicated an initial pulse of algal-derived and instream sources during storm events (Khamis et al., 2018). DOC inputs could also include contributions from subsurface storm drains and retention ponds connected to the NDC network. During dry periods, retention ponds located within the NDC watershed (Fig. 1) retain water which can promote microbial and algal production of autochthonous organic matter (Williams et al., 2013). Subsequent storm events may then flush retention pond DOC into the drainage system in a similar manner to flushing of riparian or hyporheic regions of natural streams and rivers (Song et al., 2015). Although we do not know the timing of retention pond inputs, the high FI values during Phase 1 and Phase 3 suggest these inputs either occur during these phases, or are minimal during Phase 2. Additionally, both wet and dry deposition have been reported as significant sources of carbon, particularly in urban systems (Lohse et al., 2008), and may also contribute to the partly allochthonous signal observed during first flush. A final possibility is that the high-FI DOC may be sourced from fecal or sewage-related inputs to the NDC via leakage or overflow of sewage lines. This possibility is supported by a 2005 study which found that samples from the NDC contained elevated levels of *Escherichia coli* (*E. coli*) from humans/sewage (23.7% of total *E. coli* contributions) as compared to a site located on the Rio Grande just downstream of the NDC outlet (16.5%, Middle Rio Grande Microbial Source Tracking Assessment Report). Limited total dissolved nitrogen data collected concurrently with DOC samples during the first three storms (Fig. S3) provide additional support for this theory, as previous studies have suggested linkages between increased nitrogen concentrations in urban stormwater and sewer inputs (e.g. Kaushal and Belt, 2012).

Antecedent hydrology plays an important role in DOC cycling (Hale et al., 2015; Guarch-Ribot and Butturini, 2016), and appears to influence DOC concentration and composition during Phase 1. During this phase, the lowest value for antecedent discharge (Event 1) corresponds to the highest initial DOC concentration (Table 2). Conversely, the event with the highest antecedent discharge (Event 2) has a considerably lower starting DOC concentration (Table 2). The large pulse of channel-derived DOC following low antecedent discharge suggests accumulation of DOC in lentic, low-lying regions of the NDC, which are hydrologically isolated during periods of low or no flow. Extended dry periods also enhance potential for photo-processing of DOC, which has been shown to decrease FI values in algal leachates (Hansen et al., 2016), potentially shifting values for autochthonous DOC sources to resemble those of allochthonous DOC. This explanation matches lower starting FI values for Event 1 compared to Event 2 (Fig. 3). Thus, we suggest that the initial increase in discharge associated with onset of a storm pulse mobilizes organic matter stored within the NDC, and that antecedent flow conditions influence the relative contributions of these sources.

4.3. Phase 2 – first flush of allochthonous material

The start of Phase 2 was consistently marked by a sharp increase in discharge and DOC concentrations and lower FI values indicative of a predominantly allochthonous DOC source (Fig. 3). Similar rapid shifts from primarily autochthonous to a more allochthonous DOC signature have been documented during storm pulses in other arid-land aquatic systems (Westerhoff and Anning, 2000), including decreased FI in an urban drainage (Zhao et al., 2016). The increase in DOC concentration with discharge observed in the current study is also in agreement with patterns observed in other watersheds, including arid-land rivers (Meixner et al., 2007), forested catchments (Hinton et al., 1998; Buffam et al., 2001; Inamdar et al. 2006), humid urban areas (Hook and Yeakley, 2005), and agricultural landscapes with combined natural and artificial drainages (Dalzell et al., 2007; Vidon et al., 2008). The rapid increase in discharge and DOC transport suggests higher hydrologic connectivity of the surrounding landscape to the NDC, and the consistency of FI trends indicates allochthonous DOC sources with a relatively constant FI value throughout the monsoon season, regardless of antecedent conditions. It is unlikely the allochthonous fingerprint during Phase 2 is primarily driven by biodegradation or photodegradation of in-channel organic matter due to short residence times associated with the dramatic increase in discharge (Fig. 2). Moreover, all events occurred during the night which limits potential inputs from primary productivity. As such, allochthonous sources likely include runoff from nearby impervious and pervious surfaces within the urbanized region as well as hydrologically connected distal terrestrial carbon pools adjacent to drainage channels like shrub-lands and foothills.

Previous studies of baseflow water chemistry found runoff from impervious surfaces generally has a more microbial signature, with a higher occurrence of fulvic-like and protein-like components (Hosen et al., 2014), as well as generally higher FI values (Parr et al., 2015). However, photodegradation studies have clearly demonstrated that FI values decline following photoexposure (Hansen et al., 2016) and thus, the low FI values observed during Phase 2 may be due to the high degree of photodegradation that occurs in this high-desert environment. Additionally, DOC sources present on impervious surfaces including leaf litter and detergents (e.g. Duan et al., 2014), as well as from anthropogenic green spaces and upper soil horizons are all likely to contribute low FI, humic-like compounds (Kaiser and Kalbitz, 2012; Khamis et al., 2018). Moreover, intermittent streams located near stormwater diversion channels may exhibit an increase in humic-like material during re-wetting (Guarch-Ribot and Butturini, 2016), suggesting that pervious surfaces in and near the urban area contribute the majority of DOM to the NDC during Phase 2.

During all storm events, clear counter-clockwise hysteresis between DOC concentration and hydrology was observed (Fig. 4), although it is important to note that the limited number of samples on the rising limb limits our ability to interpret hysteresis patterns. As such, we do not include quantitative metrics, but only discuss direction of hysteresis. Clockwise hysteresis has been observed in natural river systems where the highest DOC concentrations occur on the ascending limb of the hydrograph, and are associated with flushing of organic rich riparian soils and strong hyporheic DOC exchange (e.g. Hood et al., 2006; Fellman et al., 2009). In these systems, DOC concentrations are depleted on the descending limb as runoff shifts to areas with lower DOC content such as mineral soils (e.g., Hinton et al., 1998). Counter-clockwise hysteresis, in contrast, occurs when DOC flushing lags peak discharge, and has been observed for urban, agricultural and forested sites (e.g., Vaughan et al., 2017). Consistent hysteretic patterns in the current study indicate that the majority of DOC is being flushed after peak discharge. Rapid runoff evidenced by nearly vertical rising limbs of storm hydrographs (Fig. 3) contrasts with natural ecosystems, where hydrograph rising limbs are more gradual due to attenuation of runoff by porous riparian soils (e.g., Inamdar et al., 2006; Meixner et al., 2007). Thus, the hysteresis in Fig. 4 can be explained by rapid runoff coupled with a physical disconnect between organic carbon sources and the NDC due to impervious banks (i.e., no riparian zone).

4.4. Phase 3 – flushing processed allochthonous material

During Phase 3, discharge and DOC concentrations decrease and FI values increase, representing a shift from the humified allochthonous signal observed in Phase 2 to values similar to autochthonous material in Phase 1. As Phase 3 occurs after peak discharge (and thus after the initial flush of autochthonous material from water conveyance structures), it is unlikely that Phase 3 DOC is truly autochthonous. Instead, we suggest three potential explanations for the consistent increase in FI during the descending limb of the hydrograph. First, longer transport times compared to Phase 1 and Phase 2 suggest increased contributions from deeper soil profiles drained by longer and/or slower flowpaths. Deeper soil horizons are generally associated with DOC of a more microbially processed signature (Kaiser and Kalbitz, 2012). As many of the major DOC sources close to the channel are exhausted at this point in the hydrograph (e.g., Khamis et al., 2018), microbially processed DOC exported from subsurface flow paths likely constitutes a larger percentage of the DOC pool, increasing FI values. Second, during the later stages of the storm event, contributions from a greater extent of the watershed make their way to the NDC, likely containing DOC from more distant regions in the Sandia mountains (Fig. 1). Shifts in contributions from differing vegetation and soil type, combined with flushing of higher elevation intermittent or perennial streams, may explain the increase observed in FI values (e.g. Guarch-Ribot and Butturini, 2016). Third, it is possible that the higher FI values are linked to more biologically available DOC, which has been shown to increase with water residence time (Hosen et al., 2014; Helton et al., 2015). Thus, we suggest that the autochthonous-like FI signal during Phase 3 is a combination of inputs from increasingly distal sources, longer flow paths, and biological processing occurring during transport.

4.5. Organic carbon exported from the North Diversion Channel

Mean DOC concentrations from this study are more similar to those found in mesic environments than those found in other dryland areas (Table S1). In fact, stormwater DOC concentrations in the NDC (ranging from 2.1 to 40.0 mg L^{-1}, Table 2) are similar, and at times higher than DOC concentrations reported in Alaskan wetlands (2.4–27.7 mg L^{-1}) (Fellman et al., 2009). The high DOC concentrations during Phase 2 in the NDC are explained by a combination of rapid flushing of DOC from nearby urban and natural surfaces. Elevated DOC values during Phase 2, despite a general lack of organic-rich soils in the watershed, highlight the efficacy of manmade drainage systems in liberating and transporting organic carbon from multiple sources. Normalized to watershed area, DOC exported during individual storm events ranged from 0.012 kg ha^{-1} to 0.82 kg ha^{-1}, which is comparable to carbon transport by a forested urban stream (Table S1; Hook and Yeakley, 2005), though all events (except Event 2) are lower than other reported values for forested streams in the Adirondacks (Inamdar et al., 2006). The large quantity of DOC exported during Event 2 indicates that summer monsoonal events in Albuquerque have the potential to mobilize DOC yields equivalent to some forested regions, despite the absence of dense forests or carbon-rich terrestrial biomass.

The importance of storm events in annual DOC export has been well documented. Dalzell et al. (2007) estimated 80% of DOC loads could be contributed by only 20% of stream flow associated with storm events in an agriculturally influence watershed. Similarly, Raymond and Saiers (2010) found 86% of annual DOC export occurred during storm events in small forested watersheds, with up to 70% attributed to a few large events. The current study finds that storm pulses transport large amounts of DOC via the NDC to the Rio Grande, though quantity is strongly event-dependent, with variability spanning almost two orders of magnitude (285 kg–20,181 kg, Table 2). Based on daily DOC loads in the Rio Grande averaging 5,113 kg/day during the summer monsoon (using USGS DOC and discharge data for July-September, 2014 from gauge 08329918), a single storm event (i.e., 20,181 kg in Event 2, Table 2) is capable of delivering approximately four days' worth of DOC loading in a matter of hours. Massive, rapid inputs of both autochthonous and allochthonous DOM, in combination with sources of nutrients flushed from the urban landscape, could cause dramatic shifts in water chemistry, affecting natural biota through nutrient enrichment, and potentially impacting drinking water quality (the Albuquerque drinking water treatment plant intake is downstream of the NDC). In contrast, Event 3 DOC inputs account for less than 8% of the average daily DOC load in the Rio Grande, resulting in minimal impacts on river nutrient budgets. Thus, runoff delivered via the NDC to the Rio Grande during storm events has the capacity to dramatically alter downstream ecosystems, but is highly event-dependent.

5. Conclusions

Analysis of DOC concentration and FI values during storm events reveal a predictable shift in concentration and source of the organic carbon pool throughout each event. DOC concentrations track discharge and reach their maxima just after peak discharge. During each storm event, dominant DOC sources appear to shift from autochthonous to allochthonous, and then to processed allochthonous carbon. We suggest this shift is closely related to changes in hydrologic connectivity that deliver runoff from different DOC pools located throughout both developed and undeveloped regions of the Albuquerque landscape. In our conceptual model, water 1) flushes residual organic matter from the storm drainage system, 2) elutes organic matter from urban surfaces and causes a first-flush of the shrub-land terrestrial environment, and 3) transports DOC processed by microbes from slower or more distant flow paths to the NDC.

During storm events in both dryland and mesic regions, there is a connection between discharge, DOC concentration, and increased allochthonous contributions to the DOC pool. However, in dryland regions, carbon export can be rapid, particularly in urbanized areas, and the observed delay in peak DOC relative to peak discharge may be due to the absence of organic-rich hyporheic zones and/or riparian soils, increasing the relative importance of distal sources of carbon. The combination of large DOC loads and rapidly changing lability entering the Rio Grande during a short time-period indicates potential for strong impacts of storm events on river biogeochemistry. Based on our findings, monsoon storms can exert a strong influence over the quantity and quality of carbon exported to rivers. Stormwater conveyances can concentrate such pulses of carbon, resulting in potentially detrimental impacts to downstream ecosystems and populations.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jaridenv.2019.03.003.

References

Aitkenhead, J.A., McDowell, W.H., 2000. Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scales. Glob. Biogeochem. Cycles 14, 127–138. https://doi.org/10.1029/1999GB900083.

Aitkenhead-Peterson, J.A., McDowell, W.H., Neff, J.C., 2003. 2 - sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters. In: Findlay, S.E.G., Sinsabaugh, R.L. (Eds.), Aquatic Ecosystems, Aquatic Ecology. Academic Press, Burlington, pp. 25–70. https://doi.org/10.1016/B978-012256371-3/50003-2.

Bertilsson, S., Jones Jr., J.B., 2003. 1 - supply of dissolved organic matter to aquatic ecosystems: autochthonous sources. In: Findlay, S.E.G., Sinsabaugh, R.L. (Eds.), Aquatic Ecosystems, Aquatic Ecology. Academic Press, Burlington, pp. 3–24. https://doi.org/10.1016/B978-012256371-3/50002-0.

Buffam, I., Galloway, J.N., Blum, L.K., McGlathery, K.J., 2001. A stormflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appalachian stream. Biogeochemistry 53, 269–306. https://doi.org/10.1023/A:1010643432253.

Cory, R.M., Miller, M.P., McKnight, D.M., Guerard, J.J., Miller, P.L., 2010. Effect of instrument-specific response on the analysis of fulvic acid fluorescence spectra. Limnol Oceanogr. Methods 8 (2), 67–78. https://doi.org/10.4319/lom.2010.8.67.

Dalzell, B.J., Filley, T.R., Harbor, J.M., 2007. The role of hydrology in annual organic carbon loads and terrestrial organic matter export from a midwestern agricultural watershed. Geochem. Cosmochim. Acta 71, 1448–1462. https://doi.org/10.1016/j.gca.2006.12.009.

Duan, S., Delaney-Newcomb, K., Kaushal, S.S., Findlay, S.E.G., Belt, K.T., 2014. Potential effects of leaf litter on water quality in urban watersheds. Biogeochemistry 121, 61–80. https://doi.org/10.1007/s10533-014-0016-9.

Fellman, J.B., Hood, E., Edwards, R.T., D'Amore, D.V., 2009. Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds. J. Geophys. Res. 114, G01021. https://doi.org/10.1029/2008JG000790.

Findlay, S., Sinsabaugh, R.L., 2003. Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. Academic Press.

Grimm, N.B., Arrowsmith, J.R., Eisinger, C., Heffernan, J., Macleod, A., Lewis, D.B., et al., 2004. Effects of urbanization on nutrient biogeochemistry of aridland streams. In: Ecosystems and Land Use Change. American Geophysical Union, pp. 129–146. https://doi.org/10.1029/153GM11.

Guarch-Ribot, A., Butturini, A., 2016. Hydrological conditions regulate dissolved organic

matter quality in an intermittent headwater stream. From drought to storm analysis. Sci. Total Environ. 571, 1358–1369. https://doi.org/10.1016/j.scitotenv.2016.07.060.
Hale, R.L., Turnbull, L., Earl, S.R., Childers, D.L., Grimm, N.B., 2015. Stormwater infrastructure controls runoff and dissolved material export from arid urban watersheds. Ecosystems 18 (1), 62–75. https://doi.org/10.1007/s10021-014-9812-2.
Hansen, A.M., Kraus, T.E.C., Pellerin, B.A., Fleck, J.A., Downing, B.D., Bergamaschi, B.A., 2016. Optical properties of dissolved organic matter (DOM): effects of biological and photolytic degradation. Limnol. Oceanogr. 61, 1015–1032. https://doi.org/10.1002/lno.10270.
Helton, A.M., Wright, M.S., Bernhardt, E.S., Poole, G.C., Cory, R.M., Stanford, J.A., 2015. Dissolved organic carbon lability increases with water residence time in the alluvial aquifer of a river floodplain ecosystem. J. Geophys. Res.: Biogeosciences 120, 693–706. https://doi.org/10.1002/2014JG002832.
Hinton, M.J., Schiff, S.L., English, M.C., 1998. Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield. Biogeochemistry 41, 175–197. https://doi.org/10.1023/A:1005903428956.
Hood, E., Gooseff, M.N., Johnson, S.L., 2006. Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds. Oregon. J. Geophys. Res. 111, G01007. https://doi.org/10.1029/2005JG000082.
Hook, A.M., Yeakley, J.A., 2005. Stormflow dynamics of dissolved organic carbon and total dissolved nitrogen in a small urban watershed. Biogeochemistry 75, 409–431. https://doi.org/10.1007/s10533-005-1860-4.
Hosen, J.D., McDonough, O.T., Febria, C.M., Palmer, M.A., 2014. Dissolved organic matter quality and bioavailability changes across an urbanization gradient in headwater streams. Environ. Sci. Technol. 48, 7817–7824. https://doi.org/10.1021/es501422z.
Inamdar, S.P., O'Leary, N., Mitchell, M.J., Riley, J.T., 2006. The impact of storm events on solute exports from a glaciated forested watershed in western New York, USA. Hydrol. Process. 20, 3423–3439. https://doi.org/10.1002/hyp.6141.
Jones, J.B., Schade, J.D., Fisher, S.G., Grimm, N.B., 1997. Organic matter dynamics in sycamore creek, a desert stream in Arizona, USA. J. North Am. Benthol. Soc. 16, 78–82. https://doi.org/10.2307/1468238.
Kaiser, K., Kalbitz, K., 2012. Cycling downwards - dissolved organic matter in soils. Soil Biol. Biochem. 52, 29–32. https://doi.org/10.1016/j.soilbio.2012.04.002.
Kaplan, L.A., Newbold, J.D., Horn, D.J.V., Dow, C.L., Aufdenkampe, A.K., Jackson, J.K., 2006. Organic matter transport in New York City drinking-water-supply watersheds. J. North Am. Benthol. Soc. 25, 912–927. https://doi.org/10.1899/0887-3593(2006)025[0912:OMTINY]2.0.CO;2.
Kaushal, S.S., Belt, K.T., 2012. The urban watershed continuum: evolving spatial and temporal dimensions. Urban Ecosyst. 15 (2), 409–435. https://doi.org/10.1007/s11252-012-0226-7.
Kaye, J.P., Groffman, P.M., Grimm, N.B., Baker, L.A., Pouyat, R.V., 2006. A distinct urban biogeochemistry? Trends Ecol. Evol. 21 (4), 192–199. https://doi.org/10.1016/j.tree.2005.12.006.
Khamis, K., Bradley, C., Hannah, D.M., 2018. Understanding dissolved organic matter dynamics in urban catchments: insights from in situ fluorescence sensor technology. Wiley Interdiscipl. Rev.: Water 5. https://doi.org/10.1002/wat2.1259.
Lee, J.H., Bang, K.W., Ketchum, L.H., Choe, J.S., Yu, M.J., 2002. First flush analysis of urban storm runoff. Sci. Total Environ. 293, 163–175. https://doi.org/10.1016/S0048-9697(02)00006-2.
Lohse, K.A., Hope, D., Sponseller, R., Allen, J.O., Grimm, N.B., 2008. Atmospheric deposition of carbon and nutrients across an and metropolitan area. Sci. Total Environ. 402, 95–105. https://doi.org/10.1016/j.scitotenv.2008.04.044.
McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T., Andersen, D.T., 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol. Oceanogr. 46, 38–48. https://doi.org/10.4319/lo.2001.46.1.0038.
Meixner, T., Huth, A.K., Brooks, P.D., Conklin, M.H., Grimm, N.B., Bales, R.C., Haas, P.A., Petti, J.R., 2007. Influence of shifting flow paths on nitrogen concentrations during monsoon floods, San Pedro River, Arizona. J. Geophys. Res.-Biogeosci. 112, G03S03. https://doi.org/10.1029/2006JG000266.
Meyer, J.L., Tate, C.M., 1983. The effects of watershed disturbance on dissolved organic carbon dynamics of a stream. Ecology 64, 33–44. https://doi.org/10.2307/1937326.
Millennium Ecosystem Assessment, 2005. Ecosystems and Human Well-Being: Desertification Synthesis. World Resources Institute, Washington, DC.
Paul, M.J., Meyer, J.L., 2001. Streams in the urban landscape. Annu. Rev. Ecol. Systemat. 32, 333–365. https://doi.org/10.1146/annurev.ecolsys.32.081501.114040.
Parr, T.B., Cronan, C.S., Ohno, T., Findlay, S.E.G., Smith, S.M.C., Simon, K.S., 2015. Urbanization changes the composition and bioavailability of dissolved organic matter in headwater streams. Limnol. Oceanogr. 60, 885–900. https://doi.org/10.1002/lno.10060.
Raymond, P.A., Saiers, J.E., 2010. Event controlled DOC export from forested watersheds. Biogeochemistry 100, 197–209. https://doi.org/10.1007/s10533-010-9416-7.
Raymond, P.A., Saiers, J.E., Sobczak, W.V., 2016. Hydrological and biogeochemical controls on watershed dissolved organic matter transport: pulse-shunt concept. Ecology 97 (1), 5–16. https://doi.org/10.1890/14-1684.1.
Rook, J.J., 1977. Chlorination reactions of fulvic acids in natural waters. Environ. Sci. Technol. 11, 478–482. https://doi.org/10.1021/es60128a014.
Schindler, J.E., Krabbenhoft, D.P., 1998. The hyporheic zone as a source of dissolved organic carbon and carbon gases to a temperate forested stream. Biogeochemistry 43, 157–174. https://doi.org/10.1023/A:1006005311257.
Sickman, J.O., Zanoli, M.J., Mann, H.L., 2007. Effects of urbanization on organic carbon loads in the sacramento river, California. Water Resour. Res. 43, W11422. https://doi.org/10.1029/2007WR005954.
Song, K., Xenopoulos, M.A., Marsalek, J., Frost, P.C., 2015. The fingerprints of urban nutrients: dynamics of phosphorus speciation in water flowing through developed landscapes. Biogeochemistry 125, 1–10. https://doi.org/10.1007/s10533-015-0114-3.
Stanley, E.H., Powers, S.M., Lottig, N.R., Buffam, I., Crawford, J.T., 2012. Contemporary changes in dissolved organic carbon (DOC) in human-dominated rivers: is there a role for DOC management? Freshw. Biol. 57, 26–42. https://doi.org/10.1111/j.1365-2427.2011.02613.x.
Stewart, A., Wetzel, R., 1981. Dissolved humic materials - photodegradation, sediment effects, and reactivity with phosphate and calcium-carbonate precipitation. Arch. Hydrobiol. 92, 265–286.
Storms, E.F., Oelsner, G.P., Locke, E.A., Stevens, M.R., Romero, O.C., 2015. Summary of urban stormwater quality in Albuquerque, New Mexico, 2003–12. U.S. Geological Survey Scientific Investigations Report 2015– 5006, 48pp.
Vaughan, M.C.H., Bowden, W.B., Shanley, J.B., Vermilyea, A., Sleeper, R., Gold, A.J., Pradhanang, S.M., Inamdar, S.P., Levia, D.F., Andres, A.S., Birgand, F., Schroth, A.W., 2017. High-frequency dissolved organic carbon and nitrate measurements reveal differences in storm hysteresis and loading in relation to land cover and seasonality. Water Resour. Res. 53, 5345–5363. https://doi.org/10.1002/2017WR020491.
Vidon, P., Wagner, L.E., Soyeux, E., 2008. Changes in the character of DOC in streams during storms in two Midwestern watersheds with contrasting land uses. Biogeochemistry 88, 257–270. https://doi.org/10.1007/s10533-008-9207-6.
Westerhoff, P., Anning, D., 2000. Concentrations and characteristics of organic carbon in surface water in Arizona: influence of urbanization. J. Hydrol. 236, 202–222. https://doi.org/10.1016/S0022-1694(00)00292-4.
Wetzel, R.G., 1995. Death, detritus, and energy flow in aquatic ecosystems. Freshw. Biol. 33, 83–89. https://doi.org/10.1111/j.1365-2427.1995.tb00388.x.
Williams, C.J., Frost, P.C., Xenopoulos, M.A., 2013. Beyond best management practices: pelagic biogeochemical dynamics in urban stormwater ponds. Ecol. Appl. 23, 1384–1395. https://doi.org/10.1890/12-0825.1.
Zhao, C., Wang, C.-C., Li, J.-Q., Wang, C.-Y., Wang, P., Pei, Z.-J., 2015. Dissolved organic matter in urban stormwater runoff at three typical regions in Beijing: chemical composition, structural characterization and source identification. RSC Adv. 5 (90), 73490–73500. https://doi.org/10.1039/C5RA14993B.
Zhao, C., Wang, C.-C., Li, J.-Q., Wang, C.-Y., Zhu, Y.-R., Wang, P., Zhang, N., 2016. Chemical characteristics of chromophoric dissolved organic matter in stormwater runoff of a typical residential area, Beijing. Desalination and Water Treatment 57 (42), 19727–19740. https://doi.org/10.1080/19443994.2015.1106345.