Using catchment characteristics to model seasonality of dissolved organic carbon fluxes in semi-arid mountainous headwaters

Kazem Nosrati · Adrian L. Collins · Peter Fiener

Abstract Prediction of dissolved organic carbon (DOC) based on catchment characteristics is a useful tool for efficient and effective water management, but in the case of arid and semi-arid regions, such predictive capacity is scarce. Accordingly, the main objective of this study was to evaluate the significance of principal components for predicting DOC concentrations and fluxes in nine headwater catchments of the Hiv catchment located in the Southern Alborz Mountains in the west of Tehran, Iran. To achieve this aim, data were assembled on 24 headwater catchment characteristics comprising soil properties, physiography, seasonal rainfall, and flow attributes, as well as estimates of DOC concentrations and fluxes across four seasons. The results revealed a major positive correlation between DOC and soil organic matter parameters related to soil biological processes. Using general linear modelling, an organic matter component related to soil biology, a seasonal component related to the dummy effect of sampling seasons, and a soil physical component related to soil texture were found to be the best predictors for DOC responses in the study area.

Keywords Organic matter · Soil enzyme activities · Modelling · Headwater catchments · General linear model

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Introduction

Lateral organic carbon fluxes from land into inland waters and ultimately oceans are of growing interest in unravelling the global carbon (C) cycle (Brunet et al. 2009; Janeau et al. 2014; Raymond et al. 2013). Accordingly, these were explicitly addressed within the latest scientific report of the IPCC (IPCC 2007), wherein, carbon reaches the atmosphere indirectly as DOC (Wohl et al. 2017). Organic carbon delivery from catchments into inland waters results mostly from erosion-induced redistribution of particle bound or particulate carbon and from dissolved organic carbon fluxes via surface runoff, interflow, and groundwater transport (Manninen et al. 2018; Wang et al. 2014, 2017). Evaluation of the effect of anthropogenic (accelerated) soil erosion on C fluxes, based on a comprehensive global database, showed that erosion processes on agricultural land have had an enormous impact on the C cycle and during the period 6000 BC to AD 2015, the net absorption of C in terrestrial landscapes has therein increased by about 78 Pg C (Wang et al. 2017).

The effect of soil erosion on the global C cycle has been extensively debated for more than two decades

(Lal 2003; Stallard 1998; Van Oost et al. 2007) and recent reviews (Doetterl et al. 2016; Kirkels et al. 2014) still indicate that there is no consensus if soil erosion is a global CO_2 sink or source. Soil erosion and hence soil organic C redistribution studies mostly focus on small catchments, where soil erosion processes can be studied in detail (Dlugoß et al. 2009; Wilken et al. 2017). Based on such studies from many regions, well-established parsimonious erosion models for material transport into inland waters can be upscaled to a regional (Nadeu et al. 2015) or even global scale (Van Oost et al. 2007).

In contrast, information regarding organic C fluxes in large river systems is often derived from measurements in their rivers (Hope et al. 1997a), and such work demonstrates that dissolved organic carbon (DOC) fluxes are more dominant (Correll et al. 2001; Hope et al. 1997b). However, to understand the DOC transport in large river systems, it is essential to analyze the spatio-temporal dynamics of DOC in small headwater catchments, where clearer interactions with land use and management, erosion, and additional factors can be interrogated (Aitkenhead-Peterson et al. 2009; Aitkenhead et al. 1999; Cooper et al. 2007; Correll et al. 2001; Dawson et al. 2008; Doetterl et al. 2016; Don and Schulze 2008; Ma et al. 2018; Moody et al. 2013).

There is a large number of experimental studies available measuring DOC concentrations and fluxes in headwater catchments related to land use, soils, climate, and climate seasonality underlining the importance of these variables in different regions. These studies range from DOC measurements in streams of the Qinghai-Tibetan Plateau, where Ma et al. (2018) could show the importance of headwater catchment vegetation, to forest site studies comparing natural forest catchments with plantations in central Scotland (Zheng et al. 2018) or studies focusing on the seasonality of DOC fluxes in sub-tropical rivers (Moyer et al. 2015).

There is also a number of studies trying to model these fluxes based on catchment-specific features (Ågren et al. 2010; Aitkenhead-Peterson et al. 2005; Aitkenhead-Peterson et al. 2007; Aitkenhead and McDowell 2000; Aitkenhead et al. 2007; Ma et al. 2018; Parry et al. 2015; Worrall et al. 2012; Zhang et al. 2011). For example, Aitkenhead-Peterson et al. (2009), Mattsson et al. (2007), and Nosrati et al. (2012) showed that DOC concentrations in river waters have important positive correlations with the proportion of agricultural land cover because of the concomitant application of fertilizers and plowing for crop production. Cooper et al. (2007) showed that DOC in a stream network can be depended on the amount of precipitation and the soil water content. In addition, the ratio of soil C to nitrogen (C:N) (Aitkenhead-Peterson et al. 2005), soil organic C, total N, and soil enzyme activities (Nosrati et al. 2012), and topographic attributes (Ågren et al. 2010; Winn et al. 2009), as well as climatic and hydrological variables (Mattsson et al. 2009; Wagner et al. 2008) have also been used to predict DOC export in surface waters.

However, studies (experimental and modelling) from semi-arid areas (with little baseflow and substantial seasonal dynamics) are generally rare. Especially studies from the arid and semi-arid regions of the Iran are not available, as indicated by a literature search using search terms "DOC" and "Iran" (Scopus; Google, Google Scholar, and Iranian national database SID.ir). Given this evident gap, the aims of this study are (i) to analyze and understand the seasonal dynamics of DOC fluxes in nine meso-scale headwater catchments in the semi-arid Southern Alborz Mountains Chain (Iran) and (ii) to develop and test a data-driven model to estimate DOC fluxes from such catchments based on biogeochemical and physiographical characteristics.

Materials and methods

Study area and sub-catchment attributes

The nine headwater sub-catchments studied are part of the Hiv catchment (35° 59′ to 36 07′ N; 50° 36′ to 50° 43′ E), which in turn is part of the Namak (Shoor) Drainage Basin, located in the Southern Alborz Mountains Chain about 70 km West of Tehran (Fig. 1). The nine headwater sub-catchments in the study area were selected in order to measure DOC concentrations and export at the stream outlets, and to collect soil samples and to determine the physiographic characteristics (Table 1 and Fig. 1). The main land use in all nine headwater sub-catchments is grazing land with the major vegetation types comprising *Astragalus effuses*, *Acantholimon festucaceum*, *Hulthemia lactuca*, *Astragalus Acanthophyllum*, *Bromus tectorum*, and *Astragalus lagopoides* (IFRWMO 2010). The general stream network pattern is dendritic. The lithostratigraphy in the headwater sub-catchments includes units from the Infra-Cambrian to Quaternary. The main Formations in the headwater sub-catchments are Laloun, Mila, Soltanieh, Barout, Jiroud, Doroud, Routeh, Elika, Shemshak, and Karaj. Soils comprise Typic Xerorthents, Lithic Xerorthents, Typic Xerochrepts, and Typic Calcixerepts (IFRWMO 2010). For each selected sub-catchment, attributes comprising area, mean elevation, mean slope gradient, stream length, drainage density, and seasonal rainfall were determined (Table 1). The seasonal rainfall was determined based on the isohyetal method (McCuen 1989) using data from eight meteorological stations comprising Karimabad, Fashand, Velian, Sorhe, Dehsomeh, Behjatabad, and Najmabad in the Hashtgerd Plain. Based on regional analysis, the corresponding equations using seasonal precipitation (P) and elevation (E) for the four main seasons were spring ($P = 0.04 \times E - 9.27$, $R^2 = 0.96$); summer ($P = 0.006 \times E - 6.45$, $R^2 = 0.89$); autumn ($P = 0.028 \times E - 13.4$, $R^2 = 0.95$); and winter ($P = 0.056 \times E - 43.27$, $R^2 = 0.96$). The relative importance of seasonal rainfall is ordered winter (22 December to 19 March) > spring (20 March to 21 June) > autumn (23 September to 21 December) > summer (22 June to 22 September). Winter (42%) and summer (2%) have the highest and lowest precipitation, respectively. The annual rainfall in the study area based on the equation ($P = 0.321 \times E - 146.01$, $R^2 = 0.93$) is ca. 444.5 mm. The annual mean of daily temperature is 9.6 °C. The climate groups in the nine headwater sub-catchments, based on the Emberger and De Marton climate classifications, are mountainous climate and Mediterranean climate, respectively (IFRWMO 2010).

Water sampling, DOC analysis, and discharge measurements

Water samples were taken in duplicates from the flow at the outlets (Fig. 1) of the nine headwater sub-catchments in spring (25–26 March), summer (26–27 May), and autumn (1–2 December) of 2018 and winter (13–14 January) 2019. Before selecting the dates for water sampling, the mean seasonal discharges in the nine headwater sub-catchments, estimated by the Iran Forests, Range and Watershed Management Organization (IFRWMO) and reported in Hiv and Shalamzar surface and groundwater hydrology report (IFRWMO 2010), were investigated to select seasonal sampling occasions. All water samples were collected in dark acid washed bottles and placed immediately in a portable cool box for transportation to the laboratory. At the laboratory, the samples were stored in a refrigerator at 4 °C while waiting for DOC measurements (maximum 2 days). After filtering the water samples using MN GF-6 glass-fiber filters (0.45 μm), and acidification of the samples to pH < 3 with chloric acid (Zieliński et al. 2016), DOC was measured by high-temperature combustion using a total carbon analyzer (ANATOC™ Series II, Australia) calibrated using potassium hydrogen phthalate based on repeated measurements. The measurement error was less than 2%.

Stream discharges were measured manually by the velocity-area method (Gordon et al. 2004) at the outlet of each of the nine headwater sub-catchments during the sampling days. In this method, there is a need to measure the cross-section area (S, m^2) and velocity (V, $m\ s^{-1}$) of the flow. For measuring the velocity, we used a portable current meter (Z30 counter, OTT, Germany). Finally, the discharge (Q, $m^3\ s^{-1}$) was calculated on the basis of $Q = V \times S$. The measured discharges were assumed to be representative of seasonal flows.

Soil sampling and measurement of soil properties

A total of 53 soil samples were retrieved from the nine sub-catchments (Fig. 1). The details on numbers of soil samples for each sub-catchment are presented in Table 1. Efforts were made to collect the samples from the same landforms whereby the slope, aspect, and elevation were similar. Here, similar landforms were selected based on the mean of slope and elevation for each sub-catchment plus or minus to the corresponding standard deviation. The samples were retrieved from the upper layer (0–20 cm depth) of the soils using a shovel. In order to improve the representativeness of the individual soil samples, each sample comprised a composite of four sub-samples collected within ca. 100 m^2 at the specific landform. Soil samples were air-dried and sieved to 2 mm. Several soil properties comprising physiochemical and enzyme activities were measured. The physiochemical properties comprised percentage of clay, silt, and sand (Kroetsch and Wang 2008), calcium carbonate content (Nelson 1982), soil water holding capacity (WHC) based on pressure plate readings (33 kPa and 1500 kPa) (Cassel and Nielsen 1986), soil bulk density (BD) (Forster 1995), electrical conductivity (EC), pH (Mettler Toledo, USA), total nitrogen (TN) (Rutherford et al. 2008), soil organic carbon (SOC) (Skjemstad and Baldock 2008), and the ratio of C:N. Four enzyme activities comprising urease at a wavelength of 690 nm (Alef and Nannipieri 1995), alkaline phosphatase and β-glucosidase at a wavelength of 400–420 nm, and dehydrogenase at a wavelength of

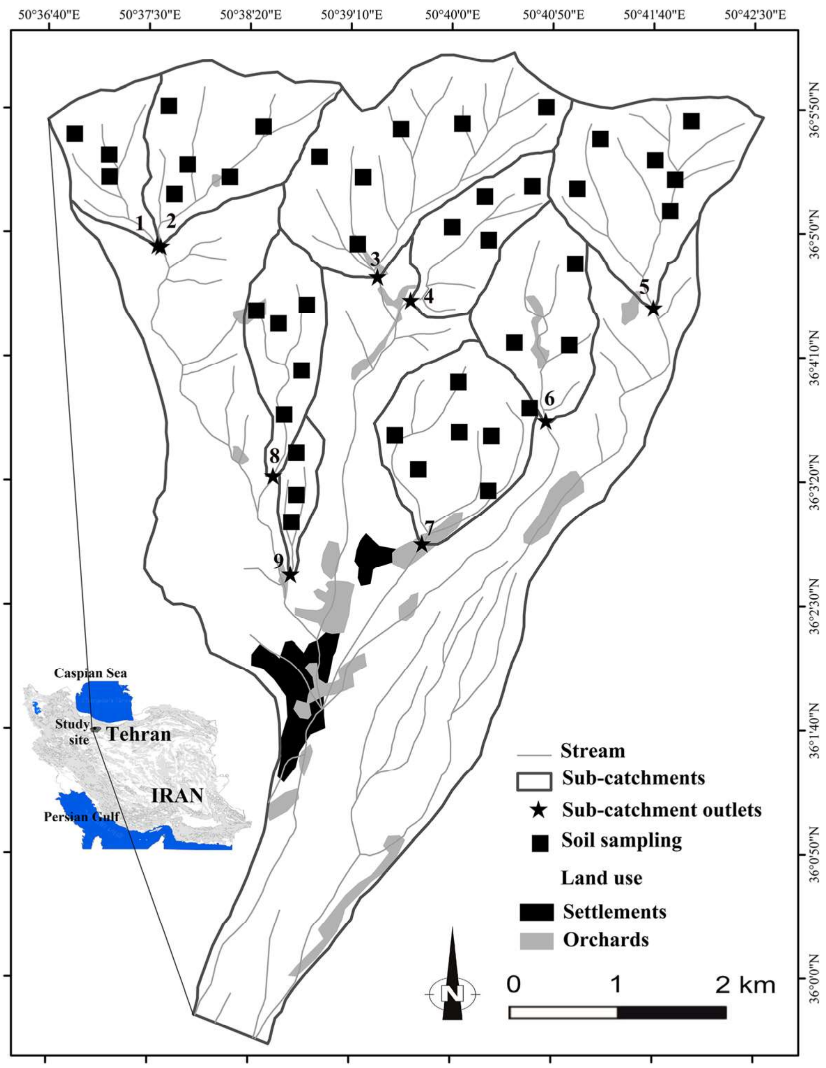


Fig. 1 Location of the Hiv study catchment in Iran and soil and stream outlet sampling sites in the nine sub-catchments

485 nm (Tabatabai 1994) were measured in soil samples using a Hach DR 6000 spectrophotometer (Hach, USA). The measured values of enzyme activities were reported based on an oven dry weight of the soil samples. Further

Table 1 Characteristics of each sub-catchment in the study area

Sub-catchment no.	Area (ha)	Number of soil samples collected within sub-catchment	Stream length (km)	Mean slope (%)	Drainage density (km km^{-2})	Sand (g kg^{-1})	Silt (g kg^{-1})	Clay (g kg^{-1})
1	176	5	2.1	60.1	1.3	620.8	221.2	158.0
2	335	5	2.7	62.7	3.2	572.8	289.2	138.0
3	566	8	3.2	53.0	3.6	453.3	318.0	228.8
4	194	5	2.2	35.9	3.7	580.8	253.2	166.0
5	416	7	2.8	47.6	2.6	532.2	297.8	170.0
6	274	5	2.5	25.5	3.2	646.8	214.0	139.2
7	334	8	2.8	19.9	2.8	562.1	281.7	156.3
8	196	6	2.8	21.1	2.7	600.8	254.2	145.0
9	62	4	1.3	19.6	3.4	415.8	349.2	235.0

details on the methods can be found in Nosrati et al. (2012).

Statistical analyses and modelling DOC concentrations and fluxes

Prior to any additional statistical analyses, variables were tested for normality using a Shapiro–Wilk *W* test, and homogeneity of variance using a Levene test (Härdle and Simar 2007). Since the study was designed as a reconnaissance survey to examine temporal and spatial variations in DOC concentrations and fluxes, one-way ANOVA (*F* test) and Tukey HSD post hoc tests were used. Correlation values (Pearson's *r*) were determined to measure the associations between the sub-catchment characteristics and DOC concentrations and fluxes.

To find predictors of DOC concentrations and fluxes using the sub-catchment biogeochemical and physiographical characteristics (see Table 2), we performed a principle component analysis (PCA) and used the PCs in a general linear regression model. In order to identify predictor variables (independent variables), PCA was used to cluster the biogeochemical and physiographical catchment characteristics into PCs. All significant PCs were subsequently used as predictors in a general linear model. General linear models based on PC scores, instead of basic independent variables, help to decrease the independent variables by removing those that are correlated.

Null hypotheses for PCA were tested via Kaiser-Meyer-Olkin (KMO) and Bartlett's test of sphericity. The KMO value (0.72) and Bartlett's statistics (72.3, p value < 0.001) indicated that the sub-catchment variables could be reduced to a smaller set of fundamental PCs. PCA was undertaken on standardized variables to remove the influence of different measurement units. The 25 sub-catchment biophysical characteristics analyzed comprised calcium carbonate, clay, silt, sand, WHC, BD, EC, pH, TN, SOC, C:N, UA, βGA, APA, DHA, D_{season} (spring and summer), D_{season} (autumn and winter), drainage area, mean slope, mean elevation, stream length, drainage density, stream discharge, discharge per unit area, and seasonal rainfall. PCs with eigenvalues > 1 were determined and afterwards subjected to a varimax rotation (Härdle and Simar 2007) to minimize the number of variables that have high loadings on each PC. In addition, the powers of each variable for the PCs were considered to show the importance of the variables in the selected PCs. The PC score values for each case were determined to use as independent variables in a general linear model, based on multivariate regression analyses; to find the best regression models for predicting DOC concentrations and fluxes, STATISTICA V. 8.0 (StatSoft 2008) was used for performing all statistical analyses.

Results

Spatio-temporal variation of DOC concentrations and fluxes

The minimum and maximum DOC concentrations among the monitoring sites for all seasons measured in stream flow ranged between 0.7 and 21.9 mg L^{-1} with a corresponding overall mean and standard deviation of 8.6 mg L^{-1} and 5.3 mg L^{-1}, respectively (Fig. 2a and Table 2). DOC concentration showed high variability (coefficient of variation, CV = 62.3%). Lowest DOC concentrations in all sub-catchments were observed during the spring and summer seasons, while the highest concentrations were consistently observed during the autumn season (Fig. 2a).

The minimum and maximum DOC fluxes across all seasons ($n = 72$) in the sampled streamflow were 0.5 g ha^{-1} day^{-1} and 195.2 g ha^{-1} day^{-1}, respectively, with a corresponding overall mean of 29.8 g ha^{-1} day^{-1} (Table 2). DOC fluxes (calculated from two replicates for each season at each of the nine monitoring sites) varied between 0.81 g ha^{-1} day^{-1} (i.e., summer season, sub-catchment 9) and 191.4 g ha^{-1} day^{-1} (i.e., winter season, sub-catchment 5) (Fig. 2b). DOC flux showed higher variability (CV = 144%) compared to DOC concentration. These particular results showed that DOC fluxes during winter exceeded those during the other seasons in all nine sub-catchments (Fig. 2b). This is because the concentrations were relatively high (not as high as in autumn) and the discharge was correspondingly highest in all nine sub-catchments.

Based on a two-way ANOVA, DOC concentrations and fluxes were significantly ($p < 0.01$) affected by location (sub-catchment), season, and the interaction between both. The most statistically most important effect was found for the different seasons. These results are confirmed via pairwise comparisons for interaction effects of temporal and spatial patterns in the measured DOC data, based on the Tukey HSD post hoc test (Table 3).

Table 2 Descriptive statistics for soil and water properties in the study area

Variables	Mean	Median	Minimum	Maximum	S.D.
Water characteristics ($n = 72$)					
DOC (mg L^{-1})	8.6	7.9	0.7	21.8	5.3
DOC (g ha^{-1} day^{-1})	29.8	13.5	0.5	195.2	42.8
Stream discharge (L s^{-1})	11.8	6.1	0.1	63.1	15.0
Q_{area}, discharge per unit area (L s^{-1} ha^{-1})	0.050	0.022	0.002	0.563	0.090
Soil properties ($n = 53$)					
Sand (g kg^{-1})	551.4	560.8	160.8	880.8	173.5
Silt (g kg^{-1})	277.2	249.2	49.2	569.2	116.5
Clay (g kg^{-1})	171.4	170.0	54.0	350.0	69.2
Soil organic carbon (g kg^{-1})	13.6	12.2	5.9	37.0	6.4
Soil total nitrogen (g kg^{-1})	1.3	1.2	0.4	4.1	0.6
C:N	11.0	10.8	5.8	15.5	1.9
Soil EC (dS m^{-1})	0.5	0.4	0.3	1.9	0.3
Soil pH	7.2	7.3	6.7	7.6	0.2
Calcium carbonate (g kg^{-1})	117.1	120.8	0.0	281.3	87.8
Water holding capacity (%)	0.2	0.2	0.1	0.2	0.0
Bulk density (Mg m^{-3})	1.8	1.8	0.2	2.7	0.4
Urease (μg $NH_4^+{-}N$ g^{-1} h^{-1} dry soil)	20.9	15.5	0.8	115.1	18.4
Alkaline phosphatase (μg PNP g^{-1} h^{-1} dry soil)	466.8	390.9	66.8	1443.6	292.9
β-Glucosidase (μg PNP g^{-1} h^{-1} dry soil)	453.1	367.8	57.1	1519.9	335.2
Dehydrogenase (μg TPF g^{-1} h^{-1} dry soil)	12.1	10.1	1.6	31.0	7.4

Dissolved organic carbon concentration (DOC), soil organic carbon content: soil total N, C:N ratio

Biogeochemical and physiographical catchment characteristics regulating DOC concentrations and fluxes

DOC concentrations were positively correlated with seasonal rainfall, mean elevation, stream length, SOC, soil TN, C:N, soil EC, WHC, urease, alkaline phosphatase, β-glucosidase, and dehydrogenase ($p < 0.01$), but negatively correlated with soil pH and soil bulk density ($p < 0.01$) (Table 4). DOC fluxes were positively correlated with stream discharge, discharge per unit area, seasonal rainfall, soil OC, soil TN, and soil EC ($p < 0.01$), and with mean elevation, stream length, C:N, alkaline phosphatase, and dehydrogenase ($p < 0.05$) (Table 4).

The results for the correlations among the sub-catchment attributes exhibited a large number of significant correlations (at the 95% level of confidence) whereby 142 of 300 sub-catchment attribute pairs were significantly correlated (Table 4). The high frequency of significant correlations indicates that the sub-catchment attributes can be clustered into uniform groups of PCs based on their correlation patterns. On this basis, these sub-catchment attributes can be grouped into PCs and used as predictors of DOC concentrations and fluxes in the study area.

Based on the 25 biophysical parameters of each sub-catchment (Table 5), the PCA results in four significant PCs explained ~71% of the variability in the original data. More specifically, the explanatory power for the sub-catchment attributes indicated that 14 attributes have a power of >0.7. The first PC explained 33.2% of the total variance. This PC has a strong positive loading (>0.75) on soil TN, alkaline phosphatase, SOC, dehydrogenase, urease, β-glucosidase, WHC, and soil EC (Table 5), and thus may be considered to represent the influence of organic matter related to soil biological attributes. There was further a moderate positive loading (0.50–0.75) on mean elevation and a moderate negative loading on bulk density (Table 5) which we interpret as secondary influences due to their relationship with organic matter variables. PC2 explained 17.7% of the total variance and returned a robust

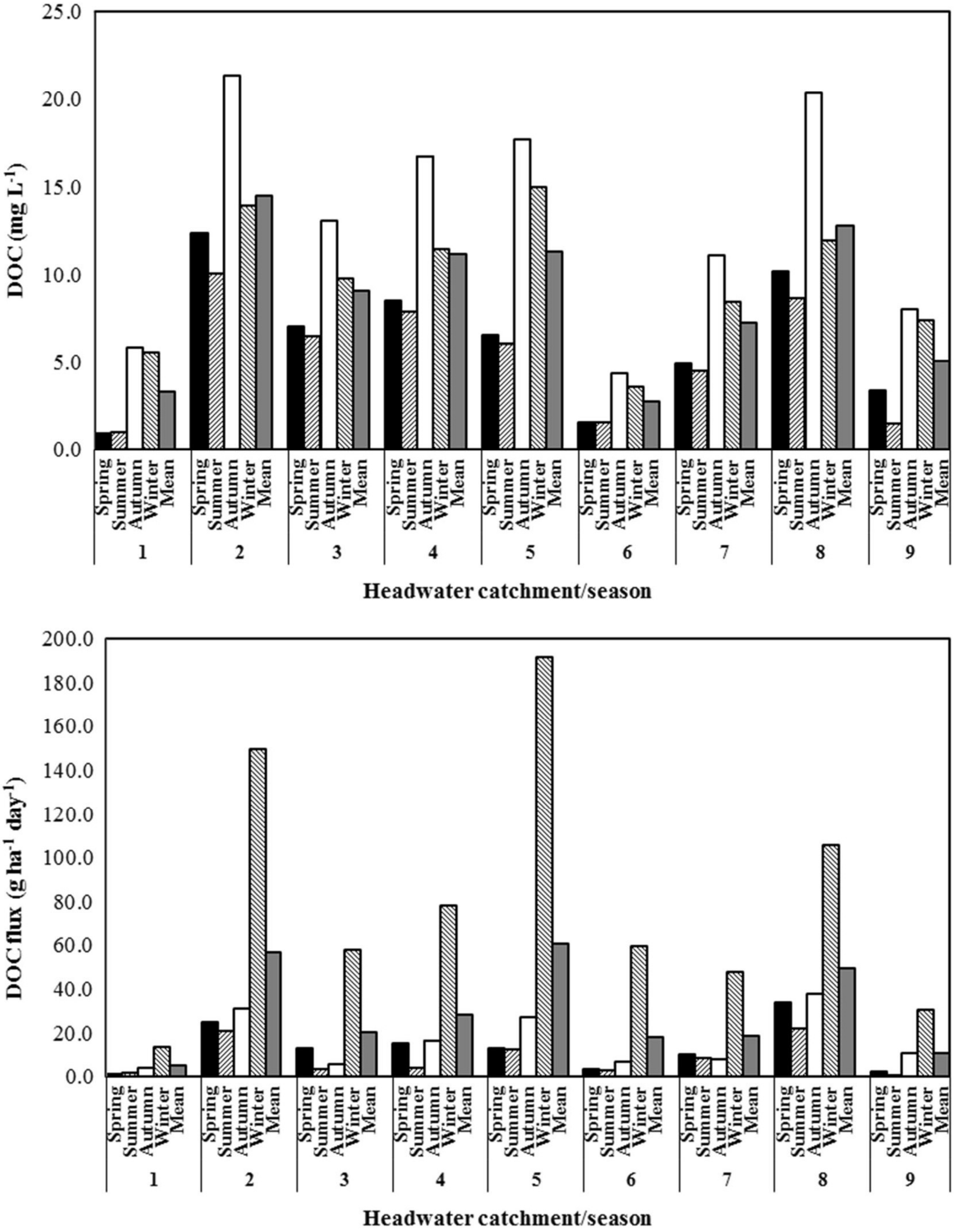


Fig. 2 Spatio-temporal variations in DOC concentrations and fluxes, in the study area, calculated from two replicates for each season at each of the nine monitoring sites

negative loading on sand and a strong positive loading on silt and clay (Table 5). On this basis, PC2 can be interpreted as representing soil physical attributes related to soil texture. There was further a moderate positive loading from PC2 on soil pH, and a moderate negative loading on C:N (Table 5) which we consider to be secondary impacts due to their relationships with soil texture. PC3 explained 11.4% of total variance and was interpreted to represent a seasonal component related to the dummy effect of sampling seasons ($D_{\text{season}} = 1$ for

Table 3 Effect of temporal patterns and spatial variations on the DOC concentrations and fluxes (± standard error) in the study sub-catchments

Variation		DOC (mg L^{-1})	DOC flux (g ha^{-1} day^{-1})
Sub-catchment	1	3.3 ± 0.9b	4.9 ± 2.2a
	2	14.4 ± 1.7c	56.4 ± 21.9c
	3	9.1 ± 1.0f	20.0 ± 9.0ab
	4	11.1 ± 1.4a	28.2 ± 11.2bd
	5	11.3 ± 1.9a	60.8 ± 28.5c
	6	2.8 ± 0.5b	18.1 ± 9.0ab
	7	7.2 ± 1.1e	18.6 ± 6.6ab
	8	12.8 ± 1.7ac	49.6 ± 13.4cd
	9	5.1 ± 1.1d	11.0 ± 4.9ab
Season	Spring	6.2 ± 0.9a	12.9 ± 2.7a
	Summer	5.3 ± 0.8a	8.5 ± 1.9a
	Autumn	13.2 ± 1.4b	16.2 ± 3.0a
	Winter	9.7 ± 0.9c	81.4 ± 14.0b

Different letters in each column indicate that the DOC is significantly different at the 99% level of confidence based on the Tukey HSD post hoc test

autumn and winter and $D_{\text{season}} = 0$ for spring and summer) because it returned a strong positive loading on D_{season}: spring and summer and a strong negative loading on D_{season}: autumn and winter (Table 5). PC3 also returned a moderate negative loading on stream discharge, discharge per unit area, and seasonal rainfall (Table 5), reflecting the strong relationships between seasonal components and these hydrological attributes. PC4 explained 9.4% of the total variance and characterized the effect of sub-catchment size because it returned a strong positive loading on drainage area (Table 5). The sub-catchment size attribute also returned a moderate positive loading on stream length, and mean slope (Table 5), reflecting the established relationships between area and these specific attributes.

In the final stage of the data analysis, concerned with selecting DOC concentrations and fluxes predictors, the PC scores were calculated for the samples (all cases). The selected PC scores were then used as independent variables in general linear modelling. Separate models were implemented for DOC concentrations and fluxes. The results are presented in Table 6.

Dataset analysis for DOC concentrations showed that PC1, PC2, and PC3 were the best predictors (Table 6). A model based on these three PCs was able to predict 79% of the variation in the DOC concentrations sampled in the nine sub-catchments. The stronger partial correlations for PC1 (0.70) and PC3 (− 0.58) indicated their greater contributions to DOC concentrations, while the lower negative partial correlation for PC2 (− 0.25) indicated that this PC exerted the least control on DOC concentrations. The Pareto chart of *t* values for coefficients of the independent variables (PCs) and the threshold of *t* values for the DOC concentration model are plotted in Fig. 3a.

The results for DOC export indicated that PC1 and PC3 were the most reliable flux predictors (accounting for 73% of variation in DOC export) based on the regression statistics (Table 6). Here, PC3 (with the highest partial correlation = − 0.68) explained more of the variance among DOC fluxes compared to PC1 (with a partial correlation of 0.41). The Pareto chart of *t* values for the coefficients of the independent variables (PCs) and the threshold of *t* values for the DOC flux model are plotted in Fig. 3a.

Discussion

Spatio-temporal variation of DOC concentrations and fluxes

DOC concentrations and fluxes in stream networks of different regions depend on many potential drivers including climate, meteorology, hydrology, soil type, land use, cover and vegetation, and season. Thus, it is challenging to directly compare our results with those reported by other studies. Equivalent data for either

Table 4 Correlation matrix of biogeochemical and physiographical characteristics of the sub-catchments. Dissolved organic carbon concentration (DOC; mg L^{-1}), flux (DOC flux; kg ha^{-1} year^{-1}), stream discharge (L s^{-1}), discharge per unit area (L s^{-1} ha^{-1}), seasonal rainfall (mm), drainage area (ha), mean elevation (m), stream length (km), mean slope (%), drainage density (km km^{-2}), sand (g kg^{-1}), silt (g kg^{-1}), and clay content (g kg^{-1}), soil organic carbon content (SOC, g kg^{-1}), soil total N (STN, g kg^{-1}), C:N ratio, soil EC (dS m^{-1}), soil pH (18), calcium carbonate content (Ca; g kg^{-1}), water holding capacity (WHC; %), bulk density (BD; Mg m^{-3}), urease content (UA; µg g^{-1} h^{-1} dry soil), alkaline phosphatase (APA; µg PNP g^{-1} h^{-1} dry soil), β-glucosidase (β GA; µg PNP g^{-1} h^{-1} dry soil), and dehydrogenase (DHA; µg TPF g^{-1} h^{-1} dry soil)

		1	2	3	4	5	6	7	8	9	10	11	12	13
DOC	1	1.00												
DOC flux	2	**0.44**	1.00											
Discharge	3	0.16	**0.82**	1.00										
Qarea	4	0.02	**0.39**	**0.63**	1.00									
Seasonal rainfall	5	**0.33**	**0.35**	**0.31**	0.23	1.00								
Drainage area	6	0.23	0.14	*0.24*	−0.19	0.03	1.00							
Mean elevation	7	**0.42**	*0.23*	0.07	−0.02	0.15	0.19	1.00						
Stream length	8	**0.37**	*0.23*	0.20	*−0.25*	0.00	**0.86**	0.02	1.00					
Slope	9	0.18	0.10	0.05	−0.18	0.11	**0.44**	**0.73**	*0.27*	1.00				
Drainage density	10	0.23	0.05	0.10	0.12	0.00	0.19	0.00	0.07	*−0.27*	1.00			
Sand	11	−0.04	0.05	−0.03	−0.19	−0.05	−0.15	**0.32**	0.22	0.06	**−0.45**	1.00		
Silt	12	0.20	0.05	0.08	0.20	0.06	0.19	**0.38**	−0.12	−0.05	**0.47**	**−0.95**	1.00	
Clay	13	−0.15	−0.18	−0.03	0.17	0.03	0.09	0.21	**−0.31**	−0.06	**0.37**	**−0.93**	**0.77**	1.00
SOC	14	**0.65**	**0.34**	0.07	−0.05	0.08	0.14	**0.54**	**0.32**	**0.38**	*0.23*	0.04	0.19	**−0.31**
STN	15	**0.64**	**0.33**	0.07	−0.05	0.08	0.16	**0.50**	**0.34**	**0.36**	*0.24*	0.01	0.22	*−0.29*
C:N	16	**0.37**	*0.27*	0.03	−0.03	0.10	−0.19	**0.64**	−0.04	**0.39**	−0.05	**0.33**	*−0.27*	**−0.35**
EC	17	**0.65**	**0.36**	0.10	−0.08	0.05	0.23	**0.35**	**0.46**	0.22	0.12	0.12	0.16	**−0.45**
pH	18	**0.34**	−0.16	0.02	0.21	−0.03	−0.20	−0.22	**−0.45**	−0.22	−0.08	**−0.39**	**0.45**	*0.28*
Ca	19	0.04	0.06	0.16	0.04	0.02	*0.29*	0.10	0.05	0.05	0.18	*0.26*	**0.41**	0.05
WHC	20	**0.41**	0.16	0.03	0.10	0.09	0.13	**0.57**	−0.04	*0.28*	*0.30*	**−0.65**	**0.80**	**0.38**
BD	21	**0.34**	−0.08	0.02	−0.14	−0.02	−0.03	−0.15	−0.02	0.16	**−0.57**	**0.62**	**−0.67**	**−0.47**
UA	22	**0.47**	0.21	0.02	0.01	0.05	0.01	**0.36**	0.12	*0.30*	*0.29*	−0.03	*0.24*	−0.23
APA	23	**0.53**	*0.27*	0.08	0.03	0.06	0.07	**0.38**	0.17	0.23	**0.38**	−0.08	**0.32**	−0.22
βGA	24	**0.47**	0.22	0.04	0.03	0.06	−0.01	**0.38**	0.06	*0.27*	**0.37**	−0.04	*0.26*	*−0.24*
DHA	25	**0.52**	*0.26*	0.06	0.03	0.04	0.05	0.29	0.18	0.15	**0.36**	−0.05	*0.30*	*−0.26*

	14	15	16	17	18	19	20	21	22	23	24	25
DOC												
DOC flux												
Discharge												
Qarea												
Seasonal rainfall												
Drainage area												

Table 4 (continued)

	14	15	16	17	18	19	20	21	22	23	24	25
Mean elevation												
Stream length												
Slope												
Drainage density												
Sand												
Silt												
Clay												
SOC	1.00											
STN	**0.97**	1.00										
C:N	**0.48**	**0.41**	1.00									
EC	**0.91**	**0.92**	*0.28*	1.00								
pH	*−0.24*	−0.20	**−0.62**	−0.12	1.00							
Ca	0.04	0.07	**−0.32**	*0.26*	**0.60**	1.00						
WHC	**0.66**	**0.69**	−0.02	**0.59**	**0.34**	**0.36**	1.00					
BD	**−0.50**	**−0.53**	0.12	**−0.35**	−0.04	0.19	**−0.69**	1.00				
UA	**0.91**	**0.93**	0.22	**0.81**	0.06	0.12	**0.73**	**−0.57**	1.00			
APA	**0.93**	**0.94**	*0.24*	**0.87**	0.08	*0.27*	**0.75**	**−0.55**	**0.97**	1.00		
βGA	**0.89**	**0.90**	*0.25*	**0.80**	0.11	*0.28*	**0.72**	**−0.47**	**0.97**	**0.98**	1.00	
DHA	**0.91**	**0.93**	0.17	**0.88**	0.10	*0.26*	**0.73**	**−0.56**	**0.97**	**0.99**	**0.97**	1.00

Italics, correlation is significant at the 0.05 level (2-tailed); bold, correlation is significant at the 0.01 level (2-tailed)

Table 5 Proportion of DOC variance explained using PCA with varimax rotation.The variable power measures how well a variable is represented by the PCs. This is a quantity ranging from 0 to 1. The variables that are not well represented (i.e., have low values of power) are more likely to be insignificant. The variable importance ranks the variable power

Variables	PC1	PC2	PC3	PC4	Power	Importance
Soil total nitrogen	**0.96**	−0.26	0.01	−0.02	0.99	1
Alkaline phosphatase	**0.97**	−0.06	0.02	−0.19	0.98	2
Soil organic carbon	**0.95**	−0.29	0.00	−0.01	0.98	3
Dehydrogenase	**0.95**	−0.07	0.03	−0.26	0.97	4
Sand	−0.22	**−0.91**	−0.07	−0.27	0.96	5
Silt	0.45	**0.84**	0.06	0.20	0.96	6
Urease	**0.94**	−0.11	0.04	−0.23	0.95	7
β-Glucosidase	**0.93**	−0.08	0.03	−0.26	0.95	8
Water holding capacity	**0.84**	0.46	0.06	0.07	0.92	9
Clay	−0.08	**0.88**	0.07	0.31	0.89	10
Soil EC	**0.87**	−0.31	0.00	−0.03	0.85	11
D_{season}: spring and summer	−0.02	−0.06	**0.89**	0.06	0.80	12
D_{season}: autumn and winter	0.02	0.06	**−0.89**	−0.06	0.80	13
Drainage area	0.19	−0.02	−0.05	**0.84**	0.73	14
Bulk density	*−0.62*	−0.49	−0.09	0.07	0.63	15
Stream length	0.24	−0.39	−0.05	*0.61*	0.58	16
Mean slope	0.34	−0.32	−0.05	*0.60*	0.57	17
Soil pH	0.00	*0.63*	0.05	−0.37	0.53	18
Mean elevation	*0.54*	−0.02	−0.05	0.49	0.53	19
Stream discharge	0.11	0.07	−0.70	0.12	0.52	20
Discharge per unit area	0.03	0.33	*−0.58*	−0.26	0.51	21
C:N	0.27	*−0.57*	−0.10	0.07	0.41	22
Seasonal rainfall	0.10	0.04	*−0.62*	0.06	0.40	23
Drainage density	0.38	0.41	0.03	0.01	0.32	24
Calcium carbonate	0.24	0.33	−0.01	0.08	0.18	25
Eigenvalue	8.29	4.42	2.84	2.34		
% total variance	33.18	17.68	11.35	9.38		
Cumulative % variance	33.18	50.86	62.21	71.58		

Bold and italic values indicate strong (> 0.75) and moderate (0.50–0.75) loadings, respectively

similar, or indeed, contrasting areas in Iran are not reported and so we are forced to look further afield. For example Aitkenhead-Peterson et al. (2009) reported that annual mean DOC concentrations in residential watersheds located in central Texas, USA, ranged between 20.4 and 52.5 mg L^{-1}. Manninen et al. (2018) reported annual DOC loads between 69 and 143 g ha^{-1} day^{-1} for cultivated plots and 121 to 162 g ha^{-1} day^{-1} for permanent grassland plots. Royer and David (2005) reported DOC fluxes for three Illinois crop land catchments ranging between 246.5 and 301.4 g ha^{-1} day^{-1}. Dalzell et al. (2007) reported DOC fluxes for a lowland agricultural catchment in Indiana between 384 and 521 g ha^{-1} day^{-1}. Don and Schulze (2008) measured annual DOC exports for two grassland sites in Germany at between 219 and 1507 g ha^{-1} day^{-1}. Hope et al. (1997a), working on forest land, measured DOC export ranges between 411 and 1452 g ha^{-1} day^{-1}. Our measured values for both DOC concentrations (with a mean 8.6 mg L^{-1}) and fluxes (with a mean of 29.8 g ha^{-1} day^{-1}) are therefore at the lower end of the data reported in the existing international literature. However, here it should be borne in mind that in our study, the measured discharge in the sub-catchments are baseflows during summer and a mixture of baseflow/surface runoff in winter.

Table 6 Best sets of predictive variables for DOC concentrations and fluxes defined by general linear modelling, using multiple regression analysis

Regression parameters							Regression statistics			
Dependent variable	Predictor	*B*	*t* value	*p* value	Partial correlation	VIF	R^2	Adjusted R^2	*F*	*p* value
DOC	Intercept	8.57	21.4	< 0.0001			0.79	0.59	27	< 0.0001
	PC1	1.13	8.1	< 0.0001	0.70	1.0				
	PC2	− 0.4	− 2.1	0.035	− 0.025	1.0				
	PC3	− 1.4	− 5.9	< 0.0001	− 0.58	1.0				
DOC fluxes	Intercept	10.9	8.4	< 0.0001			0.73	0.51	19	< 0.0001
	PC1	1.7	3.7	< 0.001	0.41	1.0				
	PC3	− 6.0	− 7.8	< 0.0001	− 0.68	1.0				

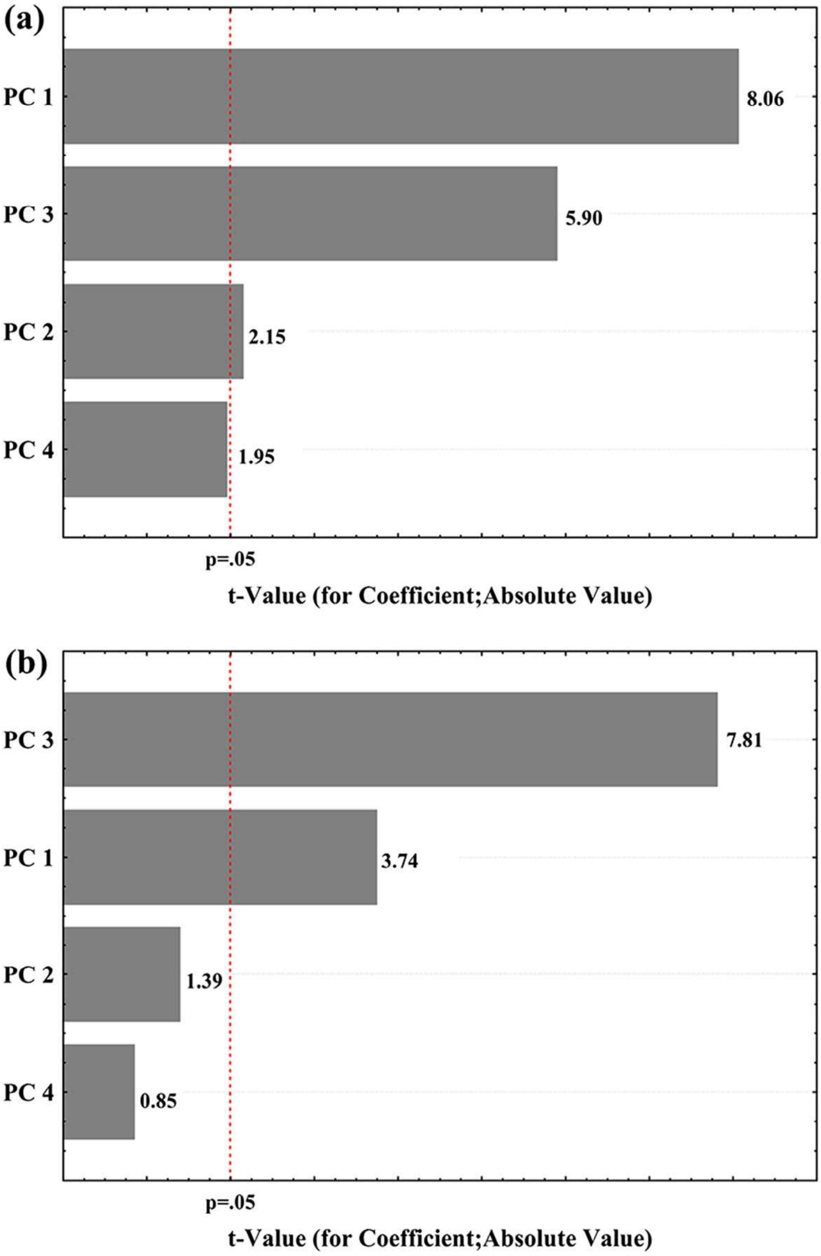
B, raw regression coefficient; *VIF*, variance inflation factor

Our results for the spatio-temporal variation of DOC concentrations and fluxes are consistent with the findings of Huntington et al. (2016) who reported that despite large inter-annual variability, all rivers had increasing DOC loads during the winter season in the case of rivers draining into the Gulf of Maine, USA. Similar results were also reported by Sachse et al. (2005) in Germany. The higher winter DOC fluxes are likely to be a product of higher winter runoff volumes. Buckingham et al. (2008), using analysis of variance, showed that soil types, land use types, and their interactions have significant effects on DOC loads. The same authors reported, using the post hoc test, that there is no significant difference between the DOC responses for organo-mineral and mineral soils. Nosrati et al. (2012) in a catchment neighboring the study area used herein, and using ANOVA, showed that temporal variations (seasons) have significant effects on DOC concentrations but that spatial (location) variations have significant effects on DOC fluxes. Here, we should keep in mind that the sub-catchments used by Nosrati et al. (2012) were covered by higher proportions of cropped land which had higher DOC concentrations. In contrast, in the current study, all nine sub-catchments were dominated by rangelands. Zheng et al. (2018) reported that spatial and temporal factors affect DOC responses in a sub-catchment in central Scotland, UK. Ma et al. (2018) showed that land cover controlled riverine DOC in the Three Rivers Headwater Region of the Qinghai-Tibetan Plateau, whereby the highest DOC fluxes were measured in alpine wet meadow and meadow areas and the lowest in river catchments dominated by steppe and desert. Jiang et al. (2014) reported that the annual patterns of DOC loads are temporally significantly different between agricultural and forested watersheds located in the Shibetsu watershed of eastern Hokkaido, Japan. Biogeochemical transformations that occur in top soil layers and stream sediments most likely influence temporal patterns in DOC concentrations. Our field work showed that there are substantial amounts of leaf litter inside and nearby the stream channels in the autumn season, the season during which the highest DOC concentrations were observed (Table 3). It is possible that the highest concentrations in autumn result from large amounts of plant litter and general dead biomass at the end of the growing season when discharge is still low. So, the fluxes are not significantly different from spring and summer (Table 3). However, this C accumulation at the end of the growing season is then transported out of the catchments in winter when there is no transport limitation. The highest concentrations of DOC can be observed in the season that the first flush precipitation occurs in, reflecting the role of fresh litter material in producing high amounts of soluble organic matter (Chow et al. 2011). Here, it has been reported that some additional parameters including temperature, rainfall intensity, and number of dry days between the rainfall events can affect DOC mobilization (Xu and Saiers 2010).

Biogeochemical and physiographical sub-catchment characteristics regulating DOC concentrations and fluxes

Comparing our results regarding the biogeochemical and physiographical catchment characteristics

Fig. 3 Pareto charts of *t* values for the coefficients of the general linear modelling. **a** DOC concentrations. **b** DOC fluxes; df = 67



dominating DOC fluxes with the findings of others shows some general patterns: the significant positive correlation between DOC parameters and SOC and TN is related to the organic C and N pools in soil at catchment scale (Aitkenhead et al. 1999; Manninen et al. 2018; Sobek et al. 2007). It is logical that soil enzyme activities are strongly correlated with soil organic matter content. Higher organic matter content can support greater microbial biomass. The production of leachable organic materials can control the leaching of DOC from soils and hence the decomposition and degradation of organic materials can be an important control on DOC responses (Salazar et al. 2011; Yuan and Yue 2012). Here, previous work has noted the interaction among hydrological and meteorological factors and soil water content and related biological processes in controlling DOC release from soils (Cooper et al. 2007). Bulk density showed a negative correlation with DOC and this indirectly reflects the negative relationship with organic material indices (including OC, TN, WHC, and enzyme activities). The soil biochemical properties (measured enzyme activities) were highly correlated with DOC concentrations (Table 5). There was a robust relationship between soil enzyme activities and SOC and TN and it is hence not surprising that fairly robust relationships exist between DOC and enzyme activity due to the fundamental impact of microbial activities on many soil functions. Soil enzymes can be increased by the rate of plant residue decomposition and so play a fundamental role in organic matter decomposition and nutrient cycling. Soil enzyme sources comprise living and dead soil microbes, animals, plant roots, and residues that either add or form compounds with organic matter when they become stabilized. Consequently, enzymes are the cumulative impact of long-term microbial activity with the exception of dehydrogenase which occurs in viable cells (Bandick and Dick 1999; Tabatabai 1994).

Increases in DOC concentrations and export with increasing rainfall evident in our study are consistent with the results from a study undertaken by Jiang et al. (2014). The strong correlation between DOC and WHC is also consistent with the work of Jiang et al. (2014) who also reported a strong relationship between DOC and soil moisture (antecedent precipitation index). The topographic indices were found to exert contrasting controls on DOC concentrations and fluxes. Tajik et al. (2012) showed that topographic parameters were the most important factors for predicting the soil enzyme activity prediction. Elevation and stream length had positive correlations with DOC in our study, but other work has reported an inverse correlation between elevation and DOC (Aitkenhead et al. 1999; Parry et al. 2015). In the case of our study sub-catchments, the dominant precipitation is in the form of snow and in high altitudes, melting can impact on the soil moisture content and thereby affect DOC response. Increasing stream length can provide opportunities for additions of riverine DOC. Our field surveys showed that the stream banks are covered by trees and grasses that can supply DOC. Although our results did not return a strong correlation between DOC concentrations and sub-catchment area, the correlation coefficient value (0.23) is close to the lower limit of the significant correlation coefficient threshold of 0.24 (Table 4). Slope returned a poor correlation with DOC in contrast with the findings of some other studies. Aitkenhead et al. (1999) and Ogawa et al. (2006) have argued previously that small catchment areas can counteract the potential influence of slope in DOC responses. In combination, topographic indices can affect the mean residence time of water and WHC (which returned a strong correlation with DOC) in addition to controlling soil organic matter content.

The results showed that organic matter related to soil biology, a seasonal component related to the dummy effect of seasons ($D_{\text{season}} = 1$ for autumn and winter and $D_{\text{season}} = 0$ for spring and summer), and soil physical attributes related to soil texture-controlled DOC concentrations sampled in the study area (Table 6). The results also revealed that organic matter related to soil biology and a seasonal component related to the dummy effect of seasons controlled DOC fluxes in the nine sub-catchments (Table 6). In both models, organic matter related to soil biology (comprising soil enzyme activities) was selected as the best predictor of DOC concentrations and fluxes in the study area. Most soil enzymes were strongly correlated with SOC. A significant relationship among SOC, STN, and soil enzymes has been reported by previous studies (e.g., Chaer et al. 2009; Miralles et al. 2007). Soil enzyme activities play an important role in the biogeochemical cycles of major elements (Killham and Staddon 2002). Soil organic matter content, and especially organic C, acts as a principal driver of soil enzyme activities and the biological activities of soils can be increased by inputs of SOM and consequently SOC, since these increase the availability of energy and major nutrients (Nourbakhsh 2007). Our results also demonstrated that DOC is strongly associated with biochemical properties and this is consistent with previous work which has suggested that DOC yield is directly linked to soil organic matter parameters such as C:N ratios in soils (Aitkenhead-Peterson et al. 2005; Aitkenhead and McDowell 2000), soil moisture-dependent biological processes (Cooper et al. 2007), vegetation canopy cover (Winn et al. 2009), and watershed C density (Aitkenhead et al. 1999; Hope et al. 1997a).

Conclusions

Measurements and predictions of DOC concentrations and fluxes in arid and semi-arid lands are only just beginning to emerge in the international literature. The work presented herein suggests that DOC in surface waters in semi-arid areas is at the lower end of the data reported in existing international. Numerous factors can play a fundamental role in controlling DOC at sub-catchment scale, including biogeochemical and physiographical catchment characteristics. The results demonstrated that organic matter related to soil biology, a seasonal component related to the dummy effect of seasons, and soil physical attributes related to soil texture predicted DOC concentrations in the headwater sub-catchments of study area. The results also demonstrated that organic matter related to soil biology and a seasonal component related to the dummy effect of seasons predicted DOC fluxes. The selected predictors for DOC parameters confirmed that the inclusion of soil enzyme activities has the potential to supplement modelling using more conventional catchment characteristics for predicting DOC responses at landscape scale. In future studies, we suggest it would be informative to elucidate the exact role of organic matter related to soil biology and to examine seasonality using detailed runoff and leaching experiments to confirm how these factors affect DOC losses.

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