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Dissolved organic carbon and nitrogen in urban and rural watersheds of south-central Texas: land use and land management influences

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Abstract Dissolved organic carbon (DOC) and nitrogen (DON) concentrations were quantified in urban and rural watersheds located in central Texas, USA between 2007 and 2008. The proportion of urban land use ranged from 6 to 100% in our 12 study watersheds which included nine watersheds without waste water treatment plants (WWTP) and three watersheds sampled downstream of a WWTP. Annual mean DOC concentrations ranged 20.4–52.5 mg L^{-1}. Annual mean DON concentrations ranged 0.6–1.9 mg L^{-1}. Only the rural watersheds without a WWTP had significantly lower DOC concentrations compared to those watersheds with a WWTP but all the streams except two had significantly reduced DON compared to those with a WWTP. Analysis of the nine watersheds without a WWTP indicated that 68% of the variability in mean annual DOC concentration was explained by urban open areas such as golf courses, sports fields and neighborhood parks under turf grass. There was no relationship between annual mean DON concentration and any land use. Urban open area also explained a significant amount of the variance in stream sodium and stream sodium adsorption ratio (SAR). Ninety-four percent of the variance in annual mean DOC concentration was explained by SAR. Irrigation of urban turf grass with domestic tap water high in sodium (>181 mg Na^{+} L^{-1}) may be inducing sodic soil conditions in watershed soils in this region resulting in elevated mean annual DOC concentrations in our streams.

Keywords DOC · DON · Land-use · Sodium · Streams · Urban

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Introduction

Allochthonous dissolved organic matter (DOM) supplied to streams and rivers has wide ranging consequences for aquatic chemistry and biology. While it represents a small loss from terrestrial organic carbon and nitrogen pools it affects the solubility and mobility of metals (Perdue et al. 1976; Driscoll et al. 1988) and the adsorption of pesticides to soils (Worrall et al. 1997). Positive effects of allochthonous DOM supply to aquatic systems include attenuation of ultraviolet-B (UV-B) radiation providing some protection for aquatic biota (Williamson and Zagarese 1994) and the provision of substrate for aquatic microbial heterotrophs (Volk et al. 1997).

Export of dissolved organic carbon (DOC) in relatively pristine streams and rivers with single dominant land use are extremely variable (Aitkenhead and McDowell 2000). This variability has been shown to be driven by land cover. For example, higher DOC exports and concentrations are usually found in watersheds with a high proportion of wetlands or peat (Dillon and Molot 1997; Kortelainen et al. 1997; Aitkenhead et al. 1999; Mattson et al. 2005; Williams et al. 2005; Aitkenhead-Peterson et al. 2007), whereas lower concentrations of DOC are typically reported in watersheds with a higher proportion of warm grasslands (Malcolm and Durum 1976). We have found no studies that have examined the effect of land management practices on DOC concentration or export in the subtropical savanna streams of the USA.

Dissolved organic nitrogen (DON) is typically a large proportion of aquatic total dissolved nitrogen (TDN) concentration in relatively undisturbed watersheds (Hedin et al. 1995; Pellerin et al. 2006; Stanley and Maxted 2008). However, as urban areas increase in a watershed so does the concentration of TDN; yet the ratio of DON:TDN tends to decrease and the dominant dissolved N species becomes nitrate (Pellerin et al. 2006; Stanley and Maxted 2008). Specific land use correlations with DON that have been reported include organic rich peat or wetland dominated watersheds (Kortelainen et al. 1997; Pellerin et al. 2004; Aitkenhead-Peterson et al. 2005; Stanley and Maxted 2008) which may be indicative of DON leaching from humified organic matter (Stanley and Maxted 2008).

Waste water treatment plants (WWTP) are suggested to be a major point source of DOC in urban watersheds by some authors (e.g. Westerhoff and Anning 2000; Sickman et al. 2007). Waste water treatment plants in the USA typically utilize primary (settling) and secondary (settling + aeration) treatments prior to point source discharge to local surface waters. Sickman et al. (2007) investigated point and non-point source loading of total organic carbon in the metropolitan area of the Sacramento River in California and concluded that the source of DOC in urban watersheds was predominately from WWTPs. Furthermore, the highest mean DOC concentration was found in effluent dominated creeks in a study investigating the influence of urbanization in Arizona (Westerhoff and Anning 2000).

Other studies have suggested alternative non-point sources of DOC to urban surface waters (e.g. Kolpin et al. 2002; Hope et al. 2004; Chalmers et al. 2007; Wright et al. 2005, 2008). Hope et al. (2004) used a rainfall simulator to quantify DOC concentration in runoff from asphalt surfaces with increasing vehicular use (residential to light industrial). They found high but variable runoff DOC with concentrations ranging from 26 to 296 mg C L^{-1} with highest concentrations running off commercial sites. Newly laid turf grass that has been amended with biosolids may be an additional non-point source of DOC to urban aquatic systems (Wright et al. 2005; 2008). Pharmaceuticals and personal care products (PPCPs), poly aromatic hydrocarbons (PAH) and pesticides may also contribute to DOC concentrations through effluent discharge and asphalt runoff; however concentrations are typically in the parts per billion ranges and are not likely to be major contributors to bulk DOC concentrations.

Fewer studies have investigated what affect urbanization may have on dissolved organic nitrogen (Pellerin et al. 2004, 2006; Hayakawa et al. 2006). The Ipswich watershed and its sub-catchments in Massachusetts comprising 35% urban area showed a very low but nevertheless significant positive relationship ($r^2 = 0.09$, $p < 0.05$) between DON and developed land but the authors suggested that percentage wetland within the watershed and its sub-catchments was a better predictor of DON (Pellerin et al. 2004). Hayakawa et al. (2006) examined two watersheds in Japan with urban land use ranging 0.2–4.3% and found a significant positive correlation between DON and urban land use in both watersheds.

The majority of studies investigating land use effects on DOC and DON have been in humid temperate, semi-arid or tropical climatic zones and furthermore the majority of urban studies examining aquatic DOC and DON have been conducted in areas where the land use, prior to urbanization, was forest, agriculture or desert. Evaluation of DOC and DON concentrations in urban and rural streams in humid subtropical savannahs have received less attention (e.g. Malcolm and Durum 1976; Mulholland and Watts 1982). The objective of this study was to examine the effect of land use and management on mean annual DOC and DON concentrations in rural and rapidly urbanizing watersheds of a subtropical post oak savannah in south-central Texas.

Site description

The location of this study was the cities of and rural areas surrounding Bryan and College Station in south-central Texas (northern point N 30°50′36.63″ W 96°23′53.87″ and southern point 30°29′10.46″ W 96°16′16.15″). Population of the Bryan/College Station metropolis was 184,884 in 2000 and it was estimated at 203,371 in 2007 representing an increase of almost 10%. Much of the new growth has resulted in rangeland areas being cleared for sub-division development. Impervious surfaces in the region are typically concrete particularly in parking lots and neighborhoods. Asphalt surfaces only occur on major highways. Soils in the region include several soil series, but are dominated by alfisols underlain with marine clays. The climate is humid subtropical having a mean annual temperature of 20°C and annual precipitation of 1,000 mm. Precipitation is produced by high intensity, short duration storm events occurring in the spring and fall. In the urban streams, storm runoff is channeled directly to storm drains and receiving waters without treatment and stream flow during the dry summer months is predominately effluent downstream of a WWTP or irrigation runoff in those streams without a WWTP.

Twelve independent watersheds which are tributaries of the Brazos River were sampled for this study. Land use in these watersheds was variable (Table 1) ranging from 6 to 100% urbanized, 0 to 28% forested, 0 to 17% wetland (herbaceous and woody), 0 to 27% rangeland (grassland and shrub/scrub) and 0 to 67% agriculture (pasture and crop). Three of the 12 watersheds had waste water treatment plants within one mile upstream of our sampling sites; the remaining nine watersheds had no point source discharge. Fifty percent of our sampling days were during or just after a storm event.

Materials and methods

Field sampling

Grab samples were collected from the 12 streams mid-channel and mid depth using a sterile whirlpak bag every 2 weeks between March 2007 and February 2008. Samples were taken from bridges on the upstream side to aid ease of collection. Electrical conductivity and pH were quantified on unfiltered aliquots and the remainder of the sample was syringe filtered through ashed (400°C for 5 h) Whatman GF/F filters (0.7 μm nominal pore size). Further aliquots were filtered through 0.2 μm Pall filters in readiness for cation analysis. Samples were either analyzed on the day of collection or frozen in acid washed

Table 1 Proportion of land use and population density in our 12 study watersheds

Watershed	Area (km^2)	Urban				Population (#/km^2)	Forest (%)	Wetland (%)	Range (%)	Agricultural	
		Open (%)	Low (%)	Med (%)	High (%)					Pasture (%)	Crop (%)
Wickson	84.1	5.6	0.5	0.2	0	25	11.2	2.3	12.4	63.7	3.7
Peach	58.1	5.5	0.7	0.4	0	27	37.7	16.6	9.6	27.8	0
Thompson	19	9.1	3.8	1.8	0.4	123	6.7	1.3	27.5	48.1	0.9
Turkey	20.2	10.9	7	5.5	0.6	349	29.5	9.5	12.6	20.5	2.9
Spring	21.2	13.3	8.1	7.2	0.7	193	25.1	3.1	13.1	29	0
Hudson	7.5	11.7	10.7	7.9	0.4	334	10	7.7	10.2	35.3	0
White	2.5	17	8.5	5.5	0.2	1	17	0	8.5	41.2	2.3
Still	23.5	15.6	16.8	8.8	1.6	535	12.1	7.3	16.9	20.6	0
Carter	56.9	20.9	22.8	18.5	5.2	749	5.6	4.4	7.4	13.2	1.3
Cottonwood	7	20.6	25.4	17.7	4	989	10.3	8.2	12.3	1.3	0
Bee	21.1	19.2	27	27	3.9	1405	3.4	1.6	7.2	10.5	0
Wolfpen	6.5	29.9	25.5	31	13.6	2634	0	0	0	0	0

Watersheds are ordered from lowest to highest total urbanization ultra-pure water rinsed (Barnstead Nanopure Diamond water filtration) HDPE bottles for later analysis. Samples of treated effluent and domestic tap water were also collected for analyses to compare with stream samples.

Chemical analysis

Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were measured using high temperature Platinum-catalyzed combustion with a Shimadzu TOC-V_{CSH} and Shimadzu total measuring unit TNM-1 (Shimadzu Corp. Houston, TX, USA). Dissolved organic carbon was measured as non-purgeable carbon using USEPA method 415.1 which entails acidifying the sample and sparging for 4 min with C-free air. Ammonium was analyzed using the phenate hypochlorite method with sodium nitroprusside enhancement (USEPA method 350.1) and nitrate was analyzed using Cd–Cu reduction (USEPA method 353.3). Alkalinity was quantified using methyl orange (USEPA method 310.2) and was assumed to be in the form of bicarbonate. All colorimetric methods were performed with a Westco Scientific Smartchem Discrete Analyzer (Westco Scientific Instruments Inc. Brookfield, CT, USA). DON is the product of TDN—(NH3-N + NO3-N). Calcium, magnesium and sodium were quantified by ion chromatography using an Ionpac CS16 analytical and Ionpac CG16 guard column for separation and 20 mM methanosulfonic acid as eluent at a flow rate of 1 mL min and injection volume of 10 µL using a DIONEX ICS 1000 (DIONEX Corp. Sunnyvale, CA, USA). Sodium adsorption ratio was determined using Eq. 1 after converting the cation concentration from mg L^{-1} to meq L^{-1}.

$$\mathrm{SAR} = \frac{[\mathrm{Na}^+]}{\sqrt{\frac{1}{2}\left(\left[\mathrm{Ca}^{2+}\right] + \left[\mathrm{Mg}^{2+}\right]\right)}} \qquad (1)$$

Proteins were estimated after instrument calibration with Bradford assay albumin standards at 595 nm UV–VIS using a Beckman 640 spectrophotometer (Beckman Coulter Inc. Fullerton, CA, USA). Sample replicates, blanks, NIST traceable and check standards were run every 12th sample to monitor instrument precision and co-efficient of variance among replicate samples which was set at a maximum of <4% CV or the sample was re-run.

Spatial analysis

ArcGIS 9.1 Desktop GIS software was used to determine the relative composition of land uses within each of the study watersheds. Watershed boundaries were plotted using a 1:25,000 scaled topographic map. The resultant polygon data was then overlaid on the digital LULC land use map published in 2000 by USGS, the latest officially published. Using Arc View's spatial analyst function the area of each of the land uses of each watershed was estimated. Land use areas were divided by the watershed area to derive the percentage of the watershed covered by each type. All LULC files were cast to the Universal Transverse Mercator (UTM) projection, and referenced to the North American Datum of 1983 (NAD83).

Statistical analysis

No flow data are available for these watersheds so values represent annual arithmetical mean concentrations. Independent sample *t*-tests were applied to each watershed without a WWTP and compared to each watershed with a WWTP in turn to test for a significant difference in stream chemistry. One-way analysis of variance (ANOVA) with post hoc Tukey HSD tests were applied separately (a) to the group of watersheds with a WWTP and (b) the group of watersheds without a WWTP to test for significant differences in stream chemistry. Correlations between mean annual DOC, DON and protein concentrations and land use classification were investigated using Pearson bivariate correlation. Correlations were examined on the nine watersheds without a WWTP only. All statistical analysis was performed using SPSS v.16.

Results

Stream chemistry in urban, suburban and rural surface waters with and without a WTTP

The range of mean annual concentrations from the 12 study watersheds were for DOC: 20.4 (±9.8 SD) to 52.5 (±49.8 SD) mg C L^{-1}, DON: 0.6 (±0.4 SD) to 1.9 (±2.5 SD) mg N L^{-1}, and proteins: 1.99 (± 0.8 SD) to 5.75 (± 3.8 SD) mg L^{-1}. Independent sample *t*-tests determined that DOC concentration in seven of the nine watersheds without a WWTP were not significantly different from those watersheds with a WWTP (Fig. 1). The two rural watersheds had significantly lower DOC than the watersheds with a WWTP (Fig. 1). While there was no significant difference in DOC concentration among those watersheds with a WWTP there was a significant difference in DOC among the watersheds without WWTP (Fig. 1).

Mean annual DON concentration was significantly different among watersheds with a WWTP, but not among watersheds without WWTP (Fig. 2). Two of the nine watersheds without WWTP had statistically similar DON concentration to those of Carter and Still creeks and seven of the nine watersheds without WWTP had statistically similar DON concentration to that of Turkey Creek (Fig. 2). DOC:DON ratios ranged from 31.7 to 194.2 in the nine watersheds without a WWTP and from 45.3 to 67.0 in the three watersheds with a WWTP. Ratios of DON:TDN were significantly lower in the three watersheds sampled below a WWTP compared to watersheds sampled without a WWTP. The DON:TDN in the two rural streams (6–7% urbanization) ranged from 0.63 ± 0.13 to 0.81 ± 0.10, in the streams without a WWTP, DON:TDN ranged from 0.57 ± 0.21 at the 100% urbanized Wolfpen creek to 0.74 ± 0.14 at the 77% urbanized Bee creek. The streams with a WWTP had DON:TDN ratios ranging from 0.13 ± 0.10 to 0.24 ± 0.23.

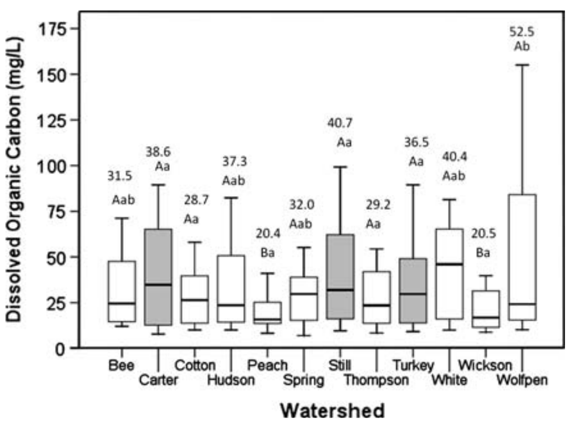

Fig. 1 Concentrations of dissolved organic carbon at each of our watersheds. *Error bars* represent the minimum and maximum concentration, the *solid bar* represents the 1st and 3rd quartile, the *bold line* the annual median concentration and the number at the top of each data point the mean annual concentration. *Grey data* points are those sampled downstream of a WWTP while *white data* points have no WWTP. Different *uppercase letters* show significant difference between those watersheds with a WWTP and those without a WWTP. Different *lowercase letters* show significant difference among sites with a WWTP or among sites without a WWTP

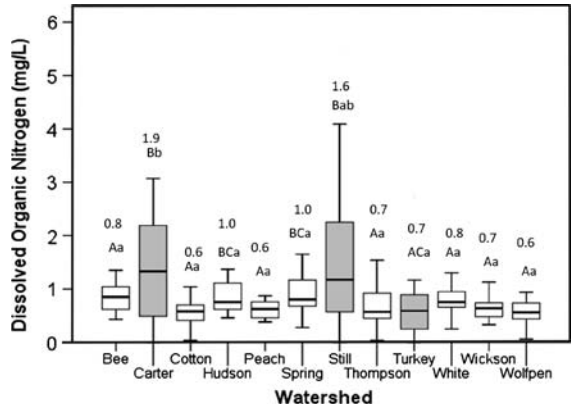

Fig. 2 Concentrations of dissolved organic nitrogen at each of our watersheds. *Error bars* represent the minimum and maximum concentration, the *solid bar* represents the 1st and 3rd quartile, the *bold line* the annual median concentration and the number at the top of each data point the mean annual concentration. *Grey data* points are those sampled downstream of a WWTP while *white data* points have no WWTP. Different *uppercase letters* show significant difference between those watersheds with a WWTP and those without a WWTP. Different *lowercase letters* show significant difference among sites with a WWTP or among sites without a WWTP

Protein concentrations were significantly higher in three of the watersheds without WWTP compared to all the watersheds with WWTP. The other six watersheds without a WWTP were not significantly higher in protein concentration than one or more of the watersheds with WWTP (Fig. 3). Among both the watersheds with and without a WWTP there were significant differences in protein concentrations (Fig. 3). Protein and DON concentrations were significantly correlated ($r = 0.84$, $p < 0.01$) in the watersheds without WWTP but not in the watersheds with a WWTP ($r = -0.14$, $p > 0.05$). Neither DON nor protein were correlated with DOC ($r = 0.11$, $p = 0.77$ and $r = 0.59$, $p = 0.09$, respectively).

Relationships between mean annual stream DOC, DON and land use

Mean annual DOC concentration was significantly and positively correlated with each urban open area

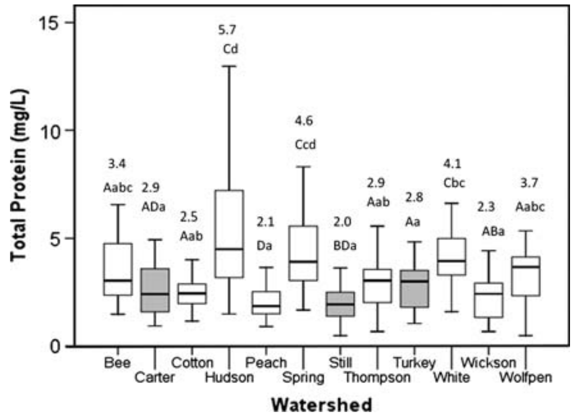

Fig. 3 Concentrations of total proteins at each of our watersheds. *Error bars* represent the minimum and maximum concentration, the *solid bar* represents the 1st and 3rd quartile, the *bold line* the annual median concentration and the number at the top of each data point the mean annual concentration. *Grey data* points are those sampled downstream of a WWTP while *white data* points have no WWTP. Different *uppercase letters* show significant difference between those watersheds with a WWTP and those without a WWTP. Different *lowercase letters* show significant difference among sites with a WWTP or among sites without a WWTP

land use, high density urban area and population density (Table 2). There were significant negative correlations between mean annual DOC concentration and herbaceous wetland cover and rangeland shrub and scrub (Table 2). Mean annual DON was not significantly correlated with any of the land use classes (Table 2). Ratios of DOC:DON were significantly correlated with the same independent variables as DOC (Table 2). The ratio of DON:TDN was positively and significantly correlated to deciduous forest ($r = 0.77$, $p = 0.015$).

Effect of irrigation water and waste water effluent on stream DOC, DON and proteins

Due to the long hot summers and the plethora of urban open areas such as golf courses, sports fields and neighborhood parks in the region, the turf grass was typically irrigated from early March through late November. Irrigation water chemistry in our study area was very high in sodium, bicarbonate and SAR but not DOC (Table 3). In the nine watersheds without a WWTP, mean annual sodium concentrations ranged from 32 to 174 mg L^{-1}, bicarbonate concentrations from 45 to 191 mg L^{-1} and SAR from 2.5 to 17.2 (Table 4). There were significant differences in mean annual pH, conductivity, SAR and mean annual concentrations of sodium and bicarbonate among the nine watersheds without a WWTP (Table 4). Mean annual sodium and bicarbonate concentrations and SAR were significantly correlated to urban open area and urban high density land use and significantly negatively correlated to rangeland shrub and herbaceous wetland (Table 2). Mean annual sodium and bicarbonate concentrations explained a significant amount of the variance in DOC concentrations ($r^2 = 0.84$, $p < 0.01$; $r^2 = 0.93$,

Table 2 Pearson bivariate correlations between mean annual stream chemistry in the watersheds without A WWTP and watershed land use

Stream chemistry	Urban			Population density (#/km^2)	Herbaceous wetland (%)	Range shrub (%)	Agriculture	
	Open (%)	Medium (%)	High (%)				Pasture (%)	Crop (%)
pH	0.88	0.66	0.68	ns	-0.78	ns	-0.67	ns
Conductivity	0.68	0.72	0.73	0.74	ns	ns	-0.85	-0.74
DOC	0.82	ns	0.72	0.67	-0.73	-0.73	ns	ns
DON	ns	ns	ns	ns	ns	ns	ns	ns
DOC:DON	0.84	ns	0.88	0.79	ns	ns	ns	ns
Protein	ns	ns	ns	ns	ns	ns	ns	ns
SAR	0.81	ns	0.72	ns	-0.69	-0.72	ns	ns
Bicarbonate	0.75	ns	ns	ns	-0.72	ns	ns	ns
Sodium	0.83	0.71	0.82	0.77	ns	-0.81	ns	ns

Only those land uses that showed a significant correlation ($p < 0.05$) with stream chemistry are shown. *ns* No significant correlation

Table 3 Chemistry of treated effluent obtained from one of the waste water treatment plants and municipal tap water used in the region for irrigating turf grass

Watershed	pH	EC (μS cm^{-1})	DOC (mg L^{-1})	DON (mg L^{-1})	Na^+ (mg L^{-1})	HCO_3^- (mg L^{-1})	SAR
Effluent	7.5	980	72.5	3.34	235.0	244.1	22.6
Irrigation	8.4	590	1.14	0	181.32	317.7	45.2

Table 4 Mean annual pH, conductivity, sodium, bicarbonate and SAR concentrations in our 12 study streams

Watershed	WWTP	Number of samples	pH	EC (μS cm^{-1})	Na^+ (mg L^{-1})	HCO_3^- (mg L^{-1})	SAR
Wickson	No	26	[a]7.0 (*0.2*)	[a]368 (*165*)	[a]32.4 (*15.7*)	[a]45.1 (*19.8*)	[a]2.5 (*1.2*)
Peach	No	24	[b]7.4 (*0.2*)	[bcd]851 (*511*)	[abc]76.4 (*30.9*)	[a]49.8 (*21.9*)	[ab]4.2 (*1.1*)
Thompson	No	25	[b]7.4 (*0.4*)	[ab]539 (*421*)	[ab]61.8 (*51.6*)	[abc]87.0 (*72.3*)	[abc]5.8 (*6.1*)
Turkey	Yes	26	[e]8.2 (*0.5*)	[bcd]884 (*452*)	[cde]128.0 (*57.0*)	[cde]136.2 (*69.5*)	[cd]11.0 (*5.3*)
Spring	No	26	[bc]7.6 (*0.2*)	[abcd]695 (*522*)	[abc]78.6 (*54.0*)	[ab]79.5 (*41.2*)	[abc]5.7 (*3.5*)
Hudson	No	26	[bc]7.6 (*0.3*)	[abc]619 (*316*)	[bcd]99.7 (*53.2*)	[bcd]124.6 (*71.6*)	[bcd]10.2 (*6.3*)
White	No	26	[de]7.9 (*0.3*)	[abc]624 (*247*)	[bcd]103.9 (*38.6*)	[de]154.9 (*56.2*)	[de]12.7 (*5.8*)
Still	Yes	26	[cd]7.8 (*0.2*)	[d]1098 (*492*)	[d]165.1 (*70.2*)	[de]183.7 (*84.6*)	[de]14.9 (*7.4*)
Carter	Yes	26	[cd]7.7 (*0.2*)	[bcd]919 (*483*)	[de]138.8 (*65.2*)	[de]172.0 (*81.3*)	[de]14.2 (*7.1*)
Cottonwood	No	26	[cd]7.7 (*0.4*)	[cd]691 (*578*)	[abc]77.3 (*60.7*)	[abc]89.4 (*61.8*)	[abc]7.0 (*8.3*)
Bee	No	26	[bc]7.6 (*0.3*)	[bcd]815 (*468*)	[bcd]88.9 (*40.2*)	[abc]73.8 (*31.4*)	[abc]6.8 (*2.9*)
Wolfpen	No	26	[e]8.1(*0.4*)	[cd]1005 (*725*)	[d]174.2 (*115.7*)	[e]190.8 (*138.2*)	[e]17.2 (*11.1*)

Numbers in parenthesis are standard deviation. Streams are in order of lowest to highest total urbanization. Differences in lowercase letter indicates a significant difference ($p < 0.05$) in stream chemistry among study watersheds

$p < 0.001$, respectively) but explained none of the variance in mean annual DON or protein concentrations. Mean annual SAR explained 94% of the variance in DOC (Fig. 4).

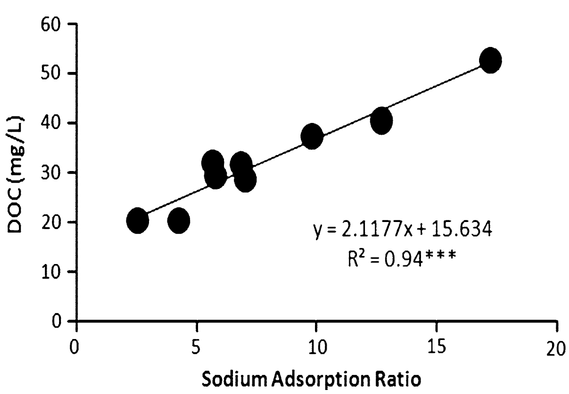

Fig. 4 The relationship between mean annual DOC concentrations and mean annual SAR values for the nine watersheds without WWTP

Treated effluent obtained from one of the waste water treatment plants also had high concentrations of sodium, bicarbonate and sodium adsorption ratio, a consequence of the chemistry of the municipal water supply. The treated effluent also had very high DOC and DON concentrations (Table 2) likely contributing to the high DOC and DON concentrations observed downstream in the three watersheds with a WWTP.

Discussion

Land use effect on DOC and DON concentrations

Dissolved organic carbon in most undisturbed streams and rivers is dominated by allochthonous sources and typically comprises recent photosynthate during high flow and older C during baseflow particularly in upland watersheds (Evans et al. 2007). DOC can be considered to be a loss from watershed soil C pools (Hope et al. 1997; Aitkenhead et al. 1999). Some of our study streams had higher mean annual DOC concentrations than any reported in the literature. For example, Wolfpen creek, a watershed which is 100% urbanized, has 29% of land under urban open areas and mean annual DOC of 52.5 mg C L^{-1} with a range of 10–155 mg C L^{-1}. Our rural watersheds, Wickson and Peach both 6% urbanized with roughly similar urban open areas (5.6 and 5.5%, respectively), had mean annual DOC concentrations of 20.5 and 20.4 mg C L^{-1}, respectively with a range of 8.9–39.8 mg C L^{-1} (Wickson) and 8.3–43.9 mg C L^{-1} (Peach). The dominant land uses in Wickson and Peach creeks are agricultural pasture and forest, respectively. Globally, land covers with a significant positive effect on stream DOC concentration or export have included wetland and peatland (Mulholland and Keunzler 1979; Kortelainen et al. 1997; Aitkenhead et al. 1999). Kortelainen et al. (1997) reported annual median DOC concentrations ranging 5–31 mg C L^{-1} from Finnish watersheds and Mulholland and Keunzler (1979) reported mean annual concentrations of 10–19.7 mg C L^{-1} from North Carolina swamp draining streams. Five of our nine watersheds without a WWTP had higher mean annual DOC concentrations than those reported from peat land or wetland watersheds. The key is likely pH which ranged from 7.0 to 8.1 in our watersheds, much higher than the range of 5.2–7.1 reported by Kortelainen et al. (1997). Our higher pH may be responsible for solubilization of humic acids which are less soluble in water at lower pH ranges compared to fulvic acids which are readily soluble in water under all pH conditions (Stevenson 1994).

Dissolved organic nitrogen concentrations ranged 0.59–4.33 across a range of land uses in Wisconsin, where wetland streams displayed significant increases in DON (Stanley and Maxted 2008). Our annual mean DON concentrations ranged from 0.62 to 1.90 mg L^{-1} and were within the range reported by Stanley and Maxted (2008). Typically the ratio of DON:TDN is reduced when a watershed has anthropogenic impacts (Pellerin et al. 2006). In a study of 348 watersheds with varying land use and management, Pellerin et al. (2006) reported a DON:TDN ratio of 0.35 for urban streams compared to a ratio of 0.55 for forested streams. Our values for DON:TDN ratios were slightly lower for urban streams with a WWTP and higher for our urban streams without a WWTP compared to the values reported by Pellerin et al. (2006).

Effect of urban land management on dissolved organic carbon

Direct loading of DOC from urban and industrial sources or urban contribution to aquatic DOC has had less attention (Westerhoff and Anning 2000; Hope et al. 2004; Sickman et al. 2007) relative to DOC concentrations and exports reported from relatively undisturbed ecosystems. Waste water treatment plants are postulated as a major source of DOC in urban streams in Arizona with effluent dominated streams producing DOC concentrations ranging 3.2–8.6 mg C L^{-1} (Westerhoff and Anning 2000). Median concentration of DOC in waste water treatment effluent in California is 23 mg C L^{-1} with a range of 15–50 mg C L^{-1} (Sickman et al. 2007). The DOC in our streams sampled downstream of WWTP ranged 36.5–40.7 mg C L^{-1} and were within the concentrations reported by Sickman et al. (2007). Treated (secondary treatment but not disinfected) effluent from one of the WWTPs in this study had DOC and DON concentrations of 72.5 and 3.3 mg L^{-1}, respectively (Table 2) but the color of the solution was clear and not the dark amber color seen in our study creeks. The dark amber color of our creeks indicates that a higher proportion of humic acids are likely in our creeks, this assumption is supported by our high creek pH values and the strong and significant positive relationship between DOC and pH (r = 0.81, $p < 0.01$). Non-point source runoff from impervious surfaces is also recognized as a contributor to aquatic DOC (Hope et al. 2004; Sickman et al. 2007). Hope et al. (2004) reported mean concentrations of 47.6, 81.2, and 59.1 mg C L^{-1} in simulated storm runoff from light industrial, commercial and residential parking lots in Arizona while Sickman et al. (2007) suggested that 4–49 mg DOC L^{-1} is derived from non-point sources in California. Poly aromatic hydrocarbons (PAH) derived from asphalt sealants in urban watersheds can contribute to the DOC concentration, but a high proportion of PAH is found in aquatic sediments (e.g. Chalmers et al. 2007) and not the water column which was the focus of this study. Our watersheds were in a region that utilizes concrete for driveways, parking lots and minor roads with asphalt surfaces contributing little to the impervious road surfaces in the region.

Turf grass type and management as well as soil conditions may be contributing to the elevated DOC concentrations in our streams which are significantly correlated with urban open area land use. During irrigation and rain events, the leaking of highly colored solution from turf grass was readily observed. Urban turf grass in our watersheds is dominated by warm-season C_4 grasses which may have an impact on enhancing DOC concentrations. *Cynodon dactylon* is commonly used in parks and on golf courses whereas *Stenotaphrum secundatum* is typically used as turf for new sub-division housing. It is not clear whether C_4 grasses will induce greater DOC release through root exudation and decomposition or whether the practice of mowing and mulching enhances DOC release from grass residue to local streams. A few studies have examined DOC production in soil under turf grass (Wright et al. 2005, 2007, 2008). These studies include compost amended and un-amended *Cynodon dactylon and Stenotaphrum secundatum* plots. Soil samples were removed six times over a period of 29 months to obtain water extractable DOC (WEDOC) at a 3:1 solution soil ratio (Wright et al. 2005, 2008). The authors do not reveal whether grass residue or thatch was removed from the soil prior to water extraction. Their water extractable total organic carbon (WETOC) was significantly higher from composted amended plots compared to un-amended plots as would be expected but there was nevertheless a trend of increased WEDOC from the un-amended *Stenotaphrum secundatum* plots over the study period (300–500 mg C kg^{-1}) (Wright et al. 2008). Similarly, their study of WEDOC under *Cynodon dactylon* plots yielded a trend of increased WEDOC (250–500 mg C kg^{-1}) from un-amended plots over the same time period (Wright et al. 2005). Both studies attribute the DOC source to turf grass residue and not compost addition.

The chemistry of municipal tap water used for irrigation in this south central Texas region and its interaction with watershed soil may be implicated in our high annual mean DOC concentrations. Municipal tap water for the study region is abstracted from the 900 m deep Carrizo-Wilcox Aquifer. Sodic soil conditions created by this high pH, high sodium municipal water which is used to irrigate urban turf grass in our watersheds may be inducing solubilization of humic as well as fulvic acids resulting in the high DOC concentrations in our streams. Sodium adsorption ratio explained most of the variance in our annual mean stream DOC concentration. Skene and Oades (1995) also reported a relationship between stream DOC and SAR. They found stream SAR values ranging 1.2–4.0 and DOC concentrations from 7 to 25 mg C L^{-1} in streams of the Mt. Lofty Range of Australia, which fit well with our findings (Fig. 4). Other studies on soil DOC release from soils at plot, mesocosm and field scale suggest that sodium application, either as an irrigant or deicer may contribute to increases in aquatic DOC. For example, Wright et al. (2008) reported that water extractable DOC is significantly correlated to water extractable sodium under composted amended turf grass ($r = 0.74$, $p < 0.05$). Recent work by Green et al. (2008) investigated the long term effect of road salting on the dispersion of organic matter (DOC and DON) into drainage water. They reported that at high NaCl exposure lower DOC concentrations are mobilized from the previously salt impacted soils than from the control soil and suggested that so much carbon has been removed over 40 years of road salt application that salt induced dispersion of C is less significant. Based on the diffuse double layer theory, solutions with a high SAR applied to a soil will increase the proportion of sodium on the soil exchange complex, which will result in greater clay dispersion. Skene and Oades (1995) tested the amount of total organic carbon (TOC) and clay dispersed and released from soil cores and reported significant correlations between TOC and suspended clay. Soil aggregate stability is also impacted with high sodium and bicarbonate irrigation water which in turn reduces water infiltration (Pilatti et al. 2006). Aggregate stability is associated with glomalin reactive soil proteins and carbon associated with wax compounds (Pikul et al. 2009); however the potential release of proteins from soil disaggregation into our surface waters by irrigating turf grass with sodic water was not supported by our findings. Proteins, which we analyzed as a surrogate for glomalin-like proteins were not correlated to any of the land use categories or DOC but they did explain a significant amount of the variance in stream DON. Aggregate stability may be impacted by irrigation water chemistry in our region, which in turn reduces water infiltration into our watershed soils. The high DOC concentrations in our watersheds without a WWTP may be due to irrigation water flow paths through the top layers of organic material as a result of reduced water infiltration due to soil disaggregation. Runoff from irrigated turf grass, high in DOC, will then enter storm drains as a non-point source to streams.

More research needs to be done using laboratory controlled experiments to investigate the linkages between sodium and DOC losses.

Conclusions

In this study of rural and rapidly urbanizing watersheds in a subtropical savanna biome of south-central Texas we have quantified:

- High DOC concentrations in urban watershed streams were significantly related to the proportion of high density and open area urban land uses.
- Within the streams, DOC concentration was most strongly related to sodium adsorption ratio suggesting that irrigating turf grass with high sodium and bicarbonate irrigation water may result in elevated DOC concentrations in urban streams.
- Dissolved organic nitrogen was not correlated to any watershed land use.

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