

Dissolved organic matter in relation to nutrients (N and P) and heavy metals in surface runoff water as affected by temporal variation and land uses – A case study from Indian River Area, south Florida, USA

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ABSTRACT

Transport of dissolved organic matter in runoff water plays a critical role in the increased inputs of nutrients (N and P) and metals (Fe, Cu and Zn) in water, and the deposition of muck sediments in the Saint Lucie Estuary and Indian River Lagoon, Florida. The objectives of this study were to investigate the variation of dissolved organic carbon (DOC) and dissolved nitrogen (DN) in surface runoff water with varying land uses, and to explore their possible relations with the leaching losses of nutrients N and P, and metals Fe, Cu, and Zn from different land uses. For this, surface runoff water from two major agricultural production systems (citrus grove and vegetable farm) in south Florida was collected weekly using pre-installed autosamplers during Jan. 2008–Mar. 2010. Meanwhile, runoff water from twelve field sites with varying land uses (such as ranch, golf course, and forest) was collected monthly using a grab sampler from Aug. 2008 to April, 2010, and soils were collected at the depth of 0–15 cm and 15–30 cm twice a year from autosampler-installed locations and on Nov. 25th, 2008 from grab sampling locations as well. In the field, water samples were measured for electrical conductivity, dissolved oxygen, and temperature; in the laboratory, water samples were analyzed for pH, total solids, turbidity, DOC, DN, total P (TP), and metals Cu, Fe and Zn with or without passing a 0.45 μm filter membrane. After passing a 2 mm sieve, fresh soil samples were analyzed for moisture, pH, electrical conductivity, 0.5 M K_2SO_4 solution extractable DOC/DN, and Mehlich 3 extractable P, Fe, Cu, and Zn. Spatial and temporal variations in the concentrations of DOC and DN in runoff water were observed, with the greatest average concentrations of DOC and DN from ranch (~ 28 and ~ 2.3 mg L^{-1}) and the lowest from golf course (~ 16 mg L^{-1}) for DOC and from forest and nursery for DN (~ 1.5 – 1.6 mg L^{-1}), respectively. Temporal fluctuations of DOC and DN in runoff water from varying land uses were in good accord with rainfall intensity and frequency of rainfall. Temporal variations of TP and metals Fe, Cu, and Zn were influenced by climatic condition as well. Citrus grove exported greater amounts of DOC and DN in runoff water (27.6 and 3.51 mg L^{-1} of median value) than vegetable farms (13.8 and 2.26 mg L^{-1} of median value). Annual cumulative loads of DOC and total N in 2008, 2009 or 2010 were >20 kg ha^{-1} , greater than those of TP (<13.5 kg ha^{-1}) and metals Fe, Cu, and Zn (<1.5 kg ha^{-1}). Ranch soil had the highest extractable DOC concentration (>100 mg kg^{-1}), accounting for 1% of its total organic carbon. Soil extractable DN had significant correlations with extractable P and Cu/Zn in soils. In conclusion, soil total organic carbon pool and its availability had an important effect on DOC and DN in runoff water. Land use type and rainfall event were the two influential factors affecting concentrations of DOC and DN, and the export of nutrients N and P, and metals in runoff water.

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1. Introduction

Water quality issues, such as water eutrophication, have been a major environmental concern throughout south Florida in the past years. The frequency and severity of eutrophication of the Saint

Lucie Estuary (SLE) and Indian River Lagoon (IRL) have increased with time. For instance, severe algae boom lasted for four months in 2005 and the water quality was the worst in history. Accumulation of organic matter in the water systems is one of the major causes for water quality degradation. Tens of millions cubic meters of fine organic materials called “muck” (41% of silt and 50% of clay) have been accumulated at the bottom of the SLE and IRL since 1920s, with a depth of the organic layer varying from a few centimeters to several meters (Schropp et al., 1994). These muck sediments

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contain high organic matter, nutrients and some heavy metals such as Cu and Zn (He et al., 2001) and serve as an important internal source of nutrients, and contaminants such as heavy metals. Muck sediments have been identified as having detrimental impacts to benthic biological communities and to the overlying water column, such as nutrient release into the water column from sediment re-suspension, reduction in light penetration in water column, and dissolved oxygen depletion due to high oxygen demand of muck sediment (Taylor Engineering, 1994). Stable isotope (^{13}C) tracing techniques indicated that the organic matter in the sediments of SLE and IRL were mainly originated from the surrounding agricultural land, and DOM, fine organic particles and clay particles in storm runoff from St. Lucie watershed were the contributions to the muck sediments in SLE and IRL (He et al., 2003).

Transport of dissolved organic matter (DOM) from land to the surface waters plays a critical role in the increased inputs of nutrients (N and P) and heavy metals (Cu and Zn), and accumulation of muck sediments in the SLE and IRL. It is observed that over 50% of N load in surface runoff water from citrus groves or vegetable farms is in organic form (Zhang et al., 2007). In the St. Lucie watershed, dominant land uses are pasture and citrus, with a large proportion of the land on acidic sandy soils (Wabasso) and flatwoods soils with high runoff potential (Janicki et al., 1999). Organic matter in soils from plant residuals and applied manures or composts is quickly decomposed by microorganisms due to high temperature and humidity in south Florida. Studies indicate that up to 23 kg of DOC or 39.8 kg of DOM per ha per year were exported from a watershed in Illinois (Royer and David, 2005). This number can be higher in South Florida because of the warmer and more humid climate conditions, as evidenced by black or brown colored drainage water from agricultural land.

The export of DOM in storm runoff from land to surface waters has significant impacts on water quality, since a variable proportion of DOM (12–56%) is bioavailable (Kawahigashi et al., 2004), and the DOM in storm runoff from agricultural field is associated with nutrients (N and P), heavy metals (Cu and Zn), and pesticides. It is estimated that DOM contains up to 1% of N and 0.2% of P and the nutrients are released into the water when DOM is decomposed (Dillon and Molot, 1997). Heavy metals such as Cu and Zn can form stable complexes with DOM (Mattigod et al., 1981), and high concentrations of Cu and Zn (up to 300 mg Cu kg⁻¹ and 200 mg Zn kg⁻¹) were measured in the muck samples from the SLE (Haunert, 1986; He et al., 2006). This phenomenon suggested that heavy metals could be transported from agricultural land to surface waters through metal–DOM complexes and deposited in muck sediment (He et al., 2004). A column leaching study confirmed the central role of DOC for the mobilization of Cu and Zn from sandy soils (Zhang and Zhang, 2010). Furthermore, the DOM in storm runoff tends to flocculate and settle down to become muck when it reaches the SLE or IRL due to increased salt concentrations in the brackish water. This process increases water turbidity and contributes to muck accumulation in the surface water systems.

In south Florida, soil (sandy and acidic) and climate conditions (warm and humid) are favorable to DOM release; therefore, organic matter added to soil is readily inclined to lose into the environment. In addition, DOM release and transport is also affected by land use and agricultural practices (Michel et al., 2006; Zhang et al., 2006; Aitkenhead-Peterson et al., 2009). Cropping systems or land use that can add more fresh organic matter to the soil can result in more DOM release (Dillon and Molot, 1997; Chantigny, 2003; Zhang et al., 2006). Generally, forest soil results in higher DOM concentration than pasture/grassland soils (Chantigny, 2003) due to soil organic carbon sequestration in pasture/grassland soils (Ussiri and Lal, 2005). The amounts of DOC in forest soil were also greater than in arable soils (Seto and Yui, 1983), however, cultivation of forest

soil can lead to 2–5 times increase in DOM in soils (Delprat et al., 1997). Fertilization can influence soil organic matter quality and subsequently DOM release as well (Clay et al., 1995; Michel et al., 2006). Application of excess P fertilizer in sandy soils can lead to more DOM subject to leaching (Zhang and Zhang, 2010); whereas, liming resulted in elevation in DOC concentrations in upper soil horizon of forest soils (Erich and Trusty, 1997). Temporal variation in DOM in soils is also significant due to climate condition change and seasonal fertilization (Christ and David, 1996; Hejzlar et al., 2003; Wright et al., 2008). However, at present, very rare studies comparably reported DOM export from soils under a variety of land uses from forest, pasture, golf course, and cropping cultivation to residence (home lawn).

It is hypothesized that more DOM in runoff water would be expected from forest soils and agricultural soils with heavy P fertilizer application than from soils under pasture or golf course in south Florida. Also, raining season (especially, tropical storms) and cultivation season would cause more DOM export in runoff water than in dry season. Therefore, the objectives of this study were: (1) to investigate spatial and temporal variation of DOM in surface runoff water from soils under citrus grove, vegetable farms, pasture fields/ranches, golf courses, landscape nursery, and residential communities (home lawn), (2) to study the possibility of DOM export with the losses of nutrients N and P, and heavy metals Fe, Cu, and Zn from agricultural practices. The specific objective of this study was to correlate the rainfall event and export of DOC, nutrients N and P, and heavy metal pollutants (Fe, Cu, and Zn).

2. Materials and methods

2.1. Water sample collection

Two sets of runoff water were collected: one set is named as grab sampling water, which runoff water was collected by surface grabbing. Twelve sampling sites were selected in the watershed of St. Lucie Estuary for grab sampling from Aug., 2008 to April, 2010. These sites represent the main types of land uses in south Florida, and included citrus grove, vegetable farms, forest, pasture fields/ranches, golf courses, landscape nursery, residential communities (home lawn), and the upstream of Ten Mile Creek (Table 1). The water samples were collected in the middle of flow channel and 10 cm below water surface. A large clean funnel (pre-rinsed with site water) was used to thoroughly mix water in the bucket and dispense water into 1 L plastic sampling bottles. Water pH value, total dissolved oxygen (DO), and electricity conductivity (EC) were measured on the spot using portable environmental multi-probes (YSI Model EC300 and 550A-25, YSI Environmental, Yellow Springs, OH, USA).

Another set is named autosampler sampling water, in which runoff water was captured by pre-installed autosamplers in traditional agricultural practice fields (specifically, citrus grove and vegetable farm 1 in Table 1) in Saint Lucie county, south Florida. Real-time discharge water samples from surface runoff after each rainfall events were taken in Jan. 2008–Mar. 2010. Rainfall and flow information of each rainfall events was recorded by four autosamplers (Sigma 900 MAX portable sampler, Hach Company, Loveland, CO, USA).

Water sampling was conducted weekly from traditional agricultural practice field where autosamplers were installed. Sampling in the twelve selected sites was carried out on a monthly basis.

2.2. Soil sample collection

Soil samples from autosampler locations were collected twice a year. Soil samples from grab sampling locations were collected

Table 1
Description of grab sampling locations in Indian River watershed in St. Lucie County, Florida.

Location ID	Land use	Description
No. 1	Residence 1	A water holding ditch receiving runoff from a residential area may be influenced by drainage of septic tanks during flooding period. Bank soil is sandy, siliceous, hyperthermic Aeric Alaquods, no fertilizer application, no tillage.
No. 2	Golf course 1	A retention pond receiving runoff from a golf course. The soil in the golf course is sandy, siliceous, hyperthermic Aeric Alaquods, covered with Bermuda grass, with application of manure at 3 tons/ha/yr and solid fertilizer (15N–5P–15K) at 336 kg ha ⁻¹ at twice a year. And it is also subjected to best management practice (BMP) management with no tillage.
No. 3	Golf course 2	A retention pond receiving runoff from a golf course. The soil in the golf course is sandy, siliceous, hyperthermic Alfic Arenic Alaquods, covered with Bermuda grass, with application of chicken litter at 2 tons/ha/yr and solid fertilizer (15N–5P–15K) at 336 kg ha ⁻¹ at twice a year. And it is also subjected to BMP management without tillage.
No. 4	Ranch 1	A water holding ditch receiving runoff from pasture ground, where beef cattle residues may influence water quality. The soil type is loamy, siliceous, active, hyperthermic Arenic Glossaqualfs, with chicken litter application at 1 ton/yr and chemical fertilizer (21N–0P–0K) at 280 kg ha ⁻¹ at once per year.
No. 5	Forest	A water holding ditch receiving runoff discharging from a pine forest, where it is supposed to be no disturbance or human interference. The soil is loamy, siliceous, active, hyperthermic Arenic Glossaqualfs.
No. 6	Vegetable farm 1	A water holding ditch receiving runoff from drainages of a commercial vegetable field. Squash is seasonally grown with plastic mulching, with fertilizer application (6N:8P:6K) at 840 kg ha ⁻¹ . The soil is sandy, siliceous, hyperthermic, ortstein Arenic Ultic Alaquods.
No. 7	River water	A river receiving runoff from agricultural fields. The bank soil is subjected to flushing in rain seasons, and it is fine-loamy, siliceous, superactive, hyperthermic Typic Glossaqualfs.
No. 8	Nursery	A retention pond receiving drainage from nursing irrigation. The soil type is fine-loamy, siliceous, superactive, hyperthermic Typic Glossaqualfs. With chemical fertilizer application (6N:6P:6K) at 0.244 kg/m ² .
No. 9	Vegetable farm 2	A water holding ditch receiving runoff from drainages of a vegetable field. The soil type is sandy, siliceous, hyperthermic Alfic Arenic Alaquods. Bell peppers and cucumbers are seasonally grown. The soil was mulched with plastic in plant growing seasons, with fertilizer application (6N:8P:6K) at 1120 kg ha ⁻¹ .
No. 10	Citrus grove	A water holding ditch receiving runoff from drainages of citrus land. The soil is loamy, siliceous, active, hyperthermic Arenic Glossaqualfs. Fertilizers applied at 168 kg ha ⁻¹ /yr of N and K, and 134 kg P ₂ O ₅ /ha/yr.
No. 11	Ranch 2	A water holding ditch receiving runoff from pasture ground, overflow when flooding. The soil is fine-loamy, siliceous, superactive, hyperthermic Typic Glossaqualfs, with chicken litter application at 1 ton/yr and chemical fertilizer (21N–0P–0K) at 280 kg ha ⁻¹ at once per year.
No. 12	Residence 2	A water holding ditch receiving runoff from an old residential area may be influenced by drainage of septic tanks during flooding period. The soil is sandy, siliceous, hyperthermic Aeric Alaquods. No fertilizer application, no tillage.

on Nov. 25th, 2008 at each bank of the twelve water grab sampling locations. Soils were sampled at the depth of 0–15 cm and 15–30 cm using a stainless steel auger with a diameter of 8 cm. Each soil sample was a composite of 4 sampling cores. After collected, samples were stored in a cooler and transported into laboratory for further chemical analyses.

2.3. Chemical analyses of water samples

Concentrations of DOC and DN in water samples were determined using a liquid TOC analyzer (liquid TOC Trace, Elementar Analysensysteme GmbH, Hanau, Germany) after filtered through a 0.45 μm membrane filter (EPA 415.1). Total solids of unfiltered water samples were measured using a gravimetric method (EPA 160.3). Turbidity was determined using a turbidimeter (Drt 100B, HF Scientific, Inc., Fort Myers, FL, USA) after water samples were totally mixed (EPA 180.1). Total Kjeldahl N (TKN) was determined using an N/P Discrete Analyzer (Easychem Plus, Systea Scientific, LLC, IL, USA) following USEPA method 351.2 after digested with acidified cupric sulfate and potassium sulfate (USEPA, 1993). The concentrations of NO₃⁻-N in water samples were determined using Ion Chromatography (IC, DX 500; Dionex Corporation Sunnyvale, CA) following USEPA method 300 after filtered through a 0.45 μm

membrane filter. Total N (TN) was calculated by the sum of TKN and NO₃⁻-N. Total P (TP) in water samples was determined using the USEPA method 365.3 after the unfiltered water samples were digested with acidified ammonium persulfate (USEPA, 1978) and measured using colorimetry method (Kuo, 1996). Metal concentrations (especially Fe, Cu and Zn) in water samples were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, Ultima, JY Horiba Inc., Edison, NJ, USA) after the sample was filtered through a 0.45 μm membrane filter (EPA 200.7, USEPA, 1998). Basic physical and chemical properties of water samples were reported in Table 2.

For the autosampler captured surface runoff, loads of DOC, TP, TN, and suspended solid for each runoff event were determined as a product of nutrient or solid concentration in each runoff sample and each runoff discharge per event:

$$\text{Load (g ha}^{-1}\text{)} = \frac{\text{Concentration (mg L}^{-1}\text{)} \times \text{Discharge (m}^3\text{)} \times 10^4}{\text{Site area (m}^2\text{)}}$$

2.4. Chemical analyses of soil samples

After passing through a 2-mm sieve, soil samples were analyzed for moisture and 0.5 M K₂SO₄ extractable dissolved organic

Table 2

Basic physical and chemical properties of surface runoff water samples from autosampler locations and grab sampling locations in 2008–2010.

Water samples from auto sampler locations (N = 397)					
Locations	pH	EC ($\mu\text{S cm}^{-1}$)	Total solid (g L^{-1})	Turbidity (NTU)	Total P (mg L^{-1})
Citrus grove	7.30 \pm 0.57a	1262 \pm 938a	0.59 \pm 0.48a	38.2 \pm 76.1a	1.36 \pm 1.27a
Vegetable farm	6.76 \pm 0.56b	486 \pm 492b	0.38 \pm 0.29b	93.4 \pm 177b	1.49 \pm 1.60a
Water samples from auto sampler locations (N = 397)					
Locations	DOC (mg L^{-1})	DN (mg L^{-1})	Cu (mg L^{-1})	Fe (mg L^{-1})	Zn (mg L^{-1})
Citrus grove	27.6 \pm 10.7a	3.51 \pm 2.18a	0.14 \pm 0.11a	0.29 \pm 0.73a	0.09 \pm 0.12a
Vegetable farm	13.8 \pm 8.79b	2.26 \pm 2.05b	0.05 \pm 0.10b	0.10 \pm 0.19b	0.04 \pm 0.05b
Water samples from grab sampling locations (N = 261)					
Locations	pH	EC ($\mu\text{S cm}^{-1}$)	Total solid (g L^{-1})	Turbidity (NTU)	Total P (mg L^{-1})
No. 1. Residence 1	6.42 \pm 0.27e	877 \pm 253de	0.60 \pm 0.10cde	12.4 \pm 6.20ab	0.17 \pm 0.15bcd
No. 2. Golf course 1	6.67 \pm 0.19d	885 \pm 147de	0.58 \pm 0.10de	4.06 \pm 4.54b	0.09 \pm 0.07d
No. 3. Golf course 2	7.19 \pm 0.56a	341 \pm 103f	0.24 \pm 0.10f	4.46 \pm 1.71b	0.08 \pm 0.05d
No. 4. Ranch 1	6.85 \pm 0.34cd	2670 \pm 1908a	1.74 \pm 1.24a	18.7 \pm 50.3a	1.03 \pm 1.15a
No. 5. Forest	7.06 \pm 0.34abc	975 \pm 365cde	0.63 \pm 0.24cde	11.5 \pm 5.45ab	0.14 \pm 0.12cd
No. 6. Vegetable farm 1	7.28 \pm 0.52a	657 \pm 227ef	0.43 \pm 0.15ef	5.96 \pm 5.33b	0.14 \pm 0.12cd
No. 7. River water	7.19 \pm 0.29a	1814 \pm 722b	1.18 \pm 0.47b	4.81 \pm 5.38b	0.39 \pm 0.28bc
No. 8. Nursery	7.29 \pm 0.28a	682 \pm 204ef	0.46 \pm 0.10ef	8.76 \pm 2.55ab	0.20 \pm 0.16bcd
No. 9. Vegetable farm 2	7.27 \pm 0.33a	1368 \pm 556c	0.89 \pm 0.35c	5.49 \pm 3.82b	0.41 \pm 0.30b
No. 10. Citrus grove	7.15 \pm 0.27ab	1250 \pm 381cd	0.80 \pm 0.27cd	8.58 \pm 7.36ab	0.27 \pm 0.20bcd
No. 11. Ranch 2	6.96 \pm 0.31bc	2186 \pm 1331b	1.39 \pm 0.81b	9.69 \pm 14.9ab	0.35 \pm 0.24bc
No. 12. Residence 2	6.19 \pm 0.31f	516 \pm 95.2ef	0.34 \pm 0.06ef	6.17 \pm 7.00b	0.20 \pm 0.16bcd
Water samples from grab sampling locations (N = 261)					
Locations	DOC (mg L^{-1})	DN (mg L^{-1})	Cu (mg L^{-1})	Fe (mg L^{-1})	Zn (mg L^{-1})
No. 1. Residence 1	22.9 \pm 7.39bcd	1.78 \pm 0.70b	0.02 \pm 0.02a	0.65 \pm 0.38a	0.04 \pm 0.04a
No. 2. Golf course 1	20.1 \pm 2.35cd	1.67 \pm 0.70b	0.02 \pm 0.02a	0.02 \pm 0.02b	0.02 \pm 0.01b
No. 3. Golf course 2	13.8 \pm 3.92e	1.82 \pm 1.52b	0.02 \pm 0.02a	0.01 \pm 0.01b	0.02 \pm 0.02b
No. 4. Ranch 1	33.9 \pm 19.5a	2.56 \pm 1.89a	0.02 \pm 0.02a	0.67 \pm 0.77a	0.02 \pm 0.01b
No. 5. Forest	25.9 \pm 11.5bc	1.50 \pm 0.79b	0.01 \pm 0.01a	0.52 \pm 0.51a	0.03 \pm 0.01ab
No. 6. Vegetable farm 1	26.6 \pm 8.23b	1.67 \pm 0.71b	0.02 \pm 0.02a	0.18 \pm 0.14b	0.03 \pm 0.01ab
No. 7. River water	19.3 \pm 9.78de	1.67 \pm 0.80b	0.02 \pm 0.01a	0.13 \pm 0.13b	0.03 \pm 0.02ab
No. 8. Nursery	20.5 \pm 6.28bcd	1.64 \pm 0.79b	0.01 \pm 0.01a	0.10 \pm 0.11b	0.03 \pm 0.01ab
No. 9. Vegetable farm 2	21.6 \pm 6.70bcd	1.81 \pm 0.86b	0.02 \pm 0.01a	0.14 \pm 0.15b	0.03 \pm 0.02ab
No. 10. Citrus grove	20.8 \pm 8.66bcd	1.71 \pm 0.73b	0.02 \pm 0.01a	0.15 \pm 0.17b	0.02 \pm 0.02b
No. 11. Ranch 2	25.3 \pm 9.58bcd	1.95 \pm 1.07b	0.02 \pm 0.02a	0.19 \pm 0.14b	0.03 \pm 0.02ab
No. 12. Residence 2	19.0 \pm 3.36de	1.73 \pm 0.85b	0.02 \pm 0.02a	0.17 \pm 0.16b	0.03 \pm 0.01ab

Data are present as mean \pm standard deviation. Varying letters in the same column represent differences at a significance level of $P < 0.05$ by using post hoc multiple comparison procedure. N: number of samples; EC: electrical conductivity; DOC: dissolved organic carbon; DN: dissolved nitrogen; Cu: copper; Fe: iron; Zn: zinc.

carbon/nitrogen ($\text{K}_2\text{SO}_4\text{-DOC}/\text{K}_2\text{SO}_4\text{-DN}$). For the determination of moisture, 20 g of fresh soil was weighed out into an aluminum can, dried at 105 °C for 12 h, and weighed after cooled down in a desiccator, soil moisture was then calculated. For the determination of $\text{K}_2\text{SO}_4\text{-DOC}/\text{K}_2\text{SO}_4\text{-DN}$, fresh soils were extracted with 0.5 M K_2SO_4 solution at a soil/solution ratio of 1:5. The DOC/DN in the extracts was measured using a liquid TOC analyzer (liquid TOC Trace, Elementar Analysensysteme GmbH, Hanau, Germany) after samples were filtered through a 0.45 μm membrane. Soil total organic carbon/total nitrogen (TOC/TN) were measured using a C/N Analyzer (Vario Max CN Macro Elemental Analyzer, Elementar Analyses system GmbH, Hanau, Germany) after samples were air dried and passed through a 1-mm sieve. Soil pH was measured using a pH/Conductivity meter (Model 220, Denver Instrument, Denver, CO, USA) following EPA method 150.1 in slurry of soil: water ratio of 1:1. Electrical conductivity (EC) of soil samples was determined at the soil: water ratio of 1:2 using the pH/Conductivity meter following EPA method 120.1. For the determination of Mehlich 3 extractable elements (P, Fe, Cu, and Zn), fresh soils were extracted with Mehlich 3 solution at a water to soil ratio of 1:10, the concentrations of the elements in the extract were then determined on the ICP-OES. Basic chemical properties of soil samples were reported in Table 3.

2.5. Quality assurance and quality control

The National Environmental Laboratory Accreditation Conference standards (2003 version) was strictly followed in chemical analyses: quality control samples (second standard), sample duplicate, reagent blank, laboratory fortified blank, continued control verification, and matrix spike were determined. Recoveries of quality control samples were in the range of 95–105%, and those of laboratory fortified blank, continued control verification, and matrix spike were within the range of 90–110%.

2.6. Data processing

Raw data were subjected to normality test using SPSS 16.0 software (SPSS Inc., Richmond, CA, USA), and relevant transformations were conducted so that all data set had the feature of normal distribution. Then the transformed data were used for one-way analysis of variance and the post hoc multiple comparison procedure. Duncan's test was used to compare the difference of chemical parameters among varying land uses and sampling years at a significance level of $P < 0.05$. Bivariate correlation analyses were performed to distinguish relationships among water and soil

Table 3
Basic chemical properties of soil samples from autosampler locations and grab sampling locations in 2008–2010.

Soil samples from autosampler locations (N=160)				
Location	pH	EC ($\mu\text{S cm}^{-1}$)	TN (g kg^{-1})	TOC (g kg^{-1})
Citrus grove	5.86 \pm 0.96a	63.8 \pm 41.0b	0.41 \pm 0.22a	4.09 \pm 2.52b
Vegetable farm	5.74 \pm 1.00a	294 \pm 279a	0.46 \pm 0.33a	6.08 \pm 2.47a
Mehlich 3 extractable (mg kg^{-1})				
Location	P	Cu	Fe	Zn
Citrus grove	35.4 \pm 17.6b	32.3 \pm 20.7a	339 \pm 485b	10.5 \pm 10.4a
Vegetable farm	75.7 \pm 65.7a	8.15 \pm 10.3b	664 \pm 806a	5.86 \pm 6.63b
Soil samples from grab sampling locations (N=96)				
Location	pH	EC ($\mu\text{S cm}^{-1}$)	TN (g kg^{-1})	TOC (g kg^{-1})
No. 1. Residence 1	7.67 \pm 0.02a	74.4 \pm 8.93bc	0.38 \pm 0.14c	11.4 \pm 4.28bcde
No. 2. Golf course 1	6.90 \pm 0.32c	103 \pm 27.7bc	0.75 \pm 0.31bc	14.4 \pm 9.44abcd
No. 3. Golf course 2	5.87 \pm 0.70e	70.8 \pm 38.0bc	0.62 \pm 0.36bc	16.7 \pm 6.18abc
No. 4. Ranch 1	7.45 \pm 0.25ab	91.0 \pm 20.7bc	1.51 \pm 1.04a	18.3 \pm 13.0ab
No. 5. Forest	3.82 \pm 0.08g	17.2 \pm 4.03c	0.17 \pm 0.08c	3.53 \pm 3.56e
No. 6. Vegetable farm 1	5.21 \pm 0.19f	153 \pm 78.2abc	0.36 \pm 0.13c	5.94 \pm 2.66de
No. 7. River water ^a	6.91 \pm 0.21c	108 \pm 15.2bc	1.32 \pm 0.57ab	23.2 \pm 4.55a
No. 8. Nursery	7.17 \pm 0.18bc	54.4 \pm 13.2c	0.37 \pm 0.10c	7.54 \pm 1.65cde
No. 9. Vegetable farm 2	6.24 \pm 0.24de	277 \pm 294a	0.44 \pm 0.25c	5.31 \pm 2.96de
No. 10. Citrus grove	6.33 \pm 0.19d	58.2 \pm 22.1bc	1.52 \pm 0.95a	18.4 \pm 11.4ab
No. 11. Ranch 2	6.99 \pm 0.32c	234 \pm 198ab	0.59 \pm 0.16bc	9.47 \pm 1.15bcde
No. 12. Residence 2	6.97 \pm 0.25c	76.0 \pm 11.2bc	0.42 \pm 0.09c	7.79 \pm 2.55bcde
Mehlich 3 extractable (mg kg^{-1})				
Location	P	Cu	Fe	Zn
No. 1. Residence 1	8.77 \pm 2.14e	2.73 \pm 0.47c	107 \pm 33.3bc	4.21 \pm 1.44c
No. 2. Golf course 1	36.5 \pm 32.7cd	4.96 \pm 1.57c	51.6 \pm 17.7d	13.8 \pm 16.8b
No. 3. Golf course 2	2.55 \pm 0.91e	2.72 \pm 0.33c	38.1 \pm 11.0d	1.00 \pm 0.46c
No. 4. Ranch 1	48.6 \pm 13.0c	2.71 \pm 0.45c	191 \pm 66.6a	2.77 \pm 1.48c
No. 5. Forest	0.74 \pm 1.51e	3.91 \pm 1.56c	35.7 \pm 32.4d	0.86 \pm 0.58c
No. 6. Vegetable farm 1	77.8 \pm 29.7b	7.38 \pm 0.99c	104 \pm 25.4bc	4.29 \pm 2.61c
No. 7. River water ^a	45.6 \pm 29.6c	11.4 \pm 4.00c	188 \pm 80.9a	15.3 \pm 6.93b
No. 8. Nursery	18.8 \pm 12.1de	2.60 \pm 3.05c	72.0 \pm 39.4cd	3.68 \pm 6.73c
No. 9. Vegetable farm 2	161 \pm 13.1a	20.8 \pm 1.75b	176 \pm 24.5a	15.8 \pm 3.02b
No. 10. Citrus grove	36.3 \pm 9.00cd	57.9 \pm 28.5a	135 \pm 26.1b	26.0 \pm 14.4a
No. 11. Ranch 2	9.24 \pm 6.13e	1.73 \pm 0.59c	103 \pm 8.63bc	1.61 \pm 1.28c
No. 12. Residence 2	9.91 \pm 4.32e	1.93 \pm 0.53c	106 \pm 21.7bc	3.26 \pm 1.51c

Varying letters in the same column represent differences at a significance level of $P < 0.05$ by using post hoc multiple comparison procedure. N: number of samples; EC: electrical conductivity; TOC: total organic carbon; TN: total nitrogen; P: phosphorus; Cu: copper; Fe: iron; Zn: zinc.

^a Soils were collected on the both sides of the river bank. Data are presented as mean \pm standard deviation.

chemical parameters. Back transformed data were recorded and graphed using SigmaPlot 10.0 (SPSS Inc., Richmond, CA, USA).

3. Results

3.1. Temporal and spatial variations of DOC and DN in runoff water

Concentrations of DOC in runoff water from grab sampling varied with land uses (with their averages $< 30 \text{ mg L}^{-1}$, Fig. 1) and seasons (Fig. 2). Runoff water from ranch had the greatest DOC concentration, followed by forest and vegetable farms; whereas, the lowest from golf course (Fig. 1). However, no significant differences in DN concentrations in runoff water among the land uses were observed (Fig. 1). Four peaks of temporal variations in DOC concentrations in runoff water were observed: 71.7 mg L^{-1} (on Sept. 3rd, 2008), 28.6 mg L^{-1} (on Feb. 4th, 2009), 57.9 mg L^{-1} (on Jul. 9th, 2009), and 59.2 mg L^{-1} (on April 6th, 2010) (Fig. 2). A decrease in DOC (7.82 mg L^{-1}) after tropical storm Fay (it hit the region on Aug. 20th, 2008) may be due to the storm water dilution effect (Fig. 2). Whereas, four peaks of DN in the runoff water were shown on Oct. 1st, 2008, Apr. 7th, 2009, Jun. 4th, 2009, and Mar. 17th, 2010 (Fig. 2).

The peak shifts of DN from DOC in runoff water might be due to the seasonal application of N fertilizers in the field.

In the autosampler sampling locations, concentrations of DOC and DN in runoff water from the citrus grove (30.6 ± 12.7 and $4.11 \pm 2.78 \text{ mg L}^{-1}$, respectively, $N=271$) were higher than those from the vegetable farm (17.4 ± 13.7 and $3.22 \pm 3.05 \text{ mg L}^{-1}$, respectively, $N=126$). Temporally, DOC in water was highest in Year 2010 ($35.0 \pm 14.1 \text{ mg L}^{-1}$, $N=54$), followed by Year 2009 ($30.5 \pm 13.7 \text{ mg L}^{-1}$, $N=216$), and the lowest in Year 2008 ($17.6 \pm 9.80 \text{ mg L}^{-1}$, $N=127$). However, DN in water was higher in Year 2008 ($3.47 \pm 1.28 \text{ mg L}^{-1}$, $N=127$) and Year 2009 ($4.30 \pm 3.42 \text{ mg L}^{-1}$, $N=216$) than in Year 2010 ($2.29 \pm 2.82 \text{ mg L}^{-1}$, $N=54$). Monthly variation of DOC in water had the tendency of increasing with time, and the difference in DOC in water between vegetable farm and citrus grove became evident, whereas, the differences in monthly variation of DN in water between the two land uses were not apparent (Fig. 3).

Loads of DOC, TN, and TP were closely associated with rainfall events, as well as loads of Cu, Fe, and Zn; and the peaks of these loads were in accord with rainfall events (Fig. 4). The loads of DOC in Year 2008 and 2009 were less than in Year 2010; however, the load of TN in Year 2008 was higher than in Years 2009 and 2010 (Table 4). Loads of Cu, Fe, and Zn had similar temporal variations

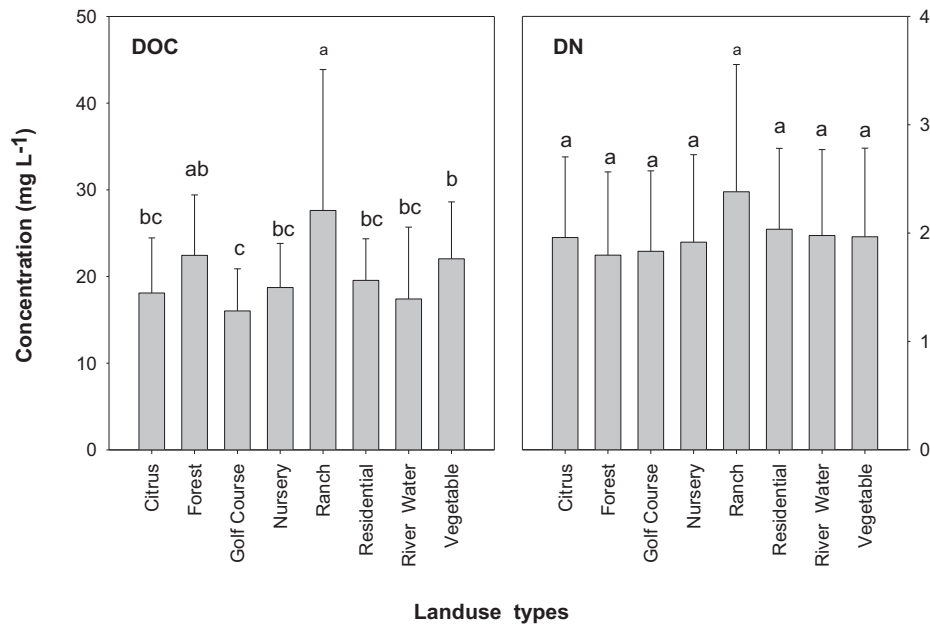


Fig. 1. Concentrations of DOC and DN in the water of grabbing samples collected in 2008–2010 in relation to different land uses. DOC: dissolved organic carbon; DN: dissolved nitrogen; data are presented as mean \pm standard deviation. Different letters represent differences at a significance level of $P < 0.05$.

to that of DOC (Table 4). In comparison, cumulative loads of DOC were far greater than those of TN, TP and metals (Table 4).

3.2. Correlations of DOC and DN with chemical properties in runoff water and hydrological parameters

Water pH demonstrated no correlations with DOC, DN, or C/N in runoff water, however, EC was positively correlated with DOC, DN, or C/N in autosampler captured water, but not to those from grab sampling (Table 5). DOC in runoff water showed significant correlations with water total solid ($P < 0.01$), DO ($P < 0.05$), turbidity ($P < 0.01$), TP ($P < 0.01$), and metals Cu ($P < 0.01$), Fe ($P < 0.01$), and Zn ($P < 0.01$), and a similar trend was observed for DN (Table 5). C/N also demonstrated significant correlations with total solid ($P < 0.05$), Cu ($P < 0.01$), and Zn ($P < 0.01$) (Table 5). Besides, loads of DOC had positively significant correlations with loads of total solids, TP, TN, and metals Cu, Fe, and Zn in runoff water ($R = 0.553, 0.767, 0.608, 0.842, 0.888, \text{ and } 0.687, P < 0.01$, respectively). Such correlations suggested the importance of DOM in the transport of P, Cu, Fe, and Zn in runoff water.

3.3. Concentrations of DOC and DN in soils

As shown in Fig. 5, soils with different land uses had varying levels of extractable DOC and DN. Ranch soil and river bank soil had the most extractable DOC ($\sim 140 \text{ mg kg}^{-1}$ at 0–15 cm, and $\sim 110 \text{ mg kg}^{-1}$ at 15–30 cm), whereas, forest soil the lowest extractable DOC ($< 50 \text{ mg kg}^{-1}$) (Fig. 5). However, vegetable soil had the highest extractable DN ($\sim 220 \text{ mg kg}^{-1}$ at 0–15 cm, and $\sim 40 \text{ mg kg}^{-1}$ at 15–30 cm), followed by ranch soil (Fig. 5). The percentage of extractable DOC in the soil TOC was a different case. The greatest percentage of extractable DOC was observed in the forest soil ($\sim 4\%$ at 15–30 cm), whereas the lowest percentages of extractable DOC were in the soils from citrus grove, golf course, and river bank at the 15–30 cm ($< 0.5\%$). Most soils had small percentages of extractable DOC in the soil TOC ($< 1.0\%$ at the 0–15 cm, and $< 2\%$ at the 15–30 cm) (Fig. 5). A large proportion of DN in the soil TN was observed in the vegetable soil ($\sim 30\%$ at the 0–15 cm, $\sim 12.5\%$ at the 15–30 cm), followed by the ranch soil ($\sim 12\%$ at the 0–15 cm, $\sim 5\%$ at the 15–30 cm) (Fig. 5), which suggested a great availability of N in these soils.

Availability of organic matter in soils may affect the loss potential of trace metals in surface runoff through association with DOC

Table 4
Loads of total solids (TS), TP, TN, DOC, Cu, Fe, and Zn in surface runoff water from autosamplers in 2008–2010.

Average loads in runoff water ^a							
Year	TS (kg ha ⁻¹)	TP (g ha ⁻¹)	DOC (g ha ⁻¹)	TN (g ha ⁻¹)	Cu (g ha ⁻¹)	Fe (g ha ⁻¹)	Zn (g ha ⁻¹)
2008	67.2 \pm 231a	184 \pm 733a	2414 \pm 7112b	1142 \pm 3708a	6.61 \pm 18.4b	22.6 \pm 74.7b	7.44 \pm 24.5b
2009	85.3 \pm 226a	155 \pm 414a	3667 \pm 8143b	461 \pm 1062b	8.13 \pm 19.1b	9.89 \pm 29.6b	4.20 \pm 8.59b
2010	48.7 \pm 98.2a	136 \pm 351a	7363 \pm 18,073a	311 \pm 837b	33.1 \pm 118a	50.7 \pm 161a	11.0 \pm 39.0a
Cumulative loads in runoff water							
Year	TS (kg ha ⁻¹)	TP (g ha ⁻¹)	DOC (g ha ⁻¹)	TN (g ha ⁻¹)	Cu (g ha ⁻¹)	Fe (g ha ⁻¹)	Zn (g ha ⁻¹)
2008	3358	9190	120,707	57,110	330	1132	372
2009	7248	13,208	311,685	39,167	690	841	357
2010	1217	3396	184,072	7768	828	1268	276

Data are presented as mean \pm standard deviation. DOC: dissolved organic carbon; Cu: copper; Fe: iron; Zn: zinc.

^a Average was calculated from each rainfall events.

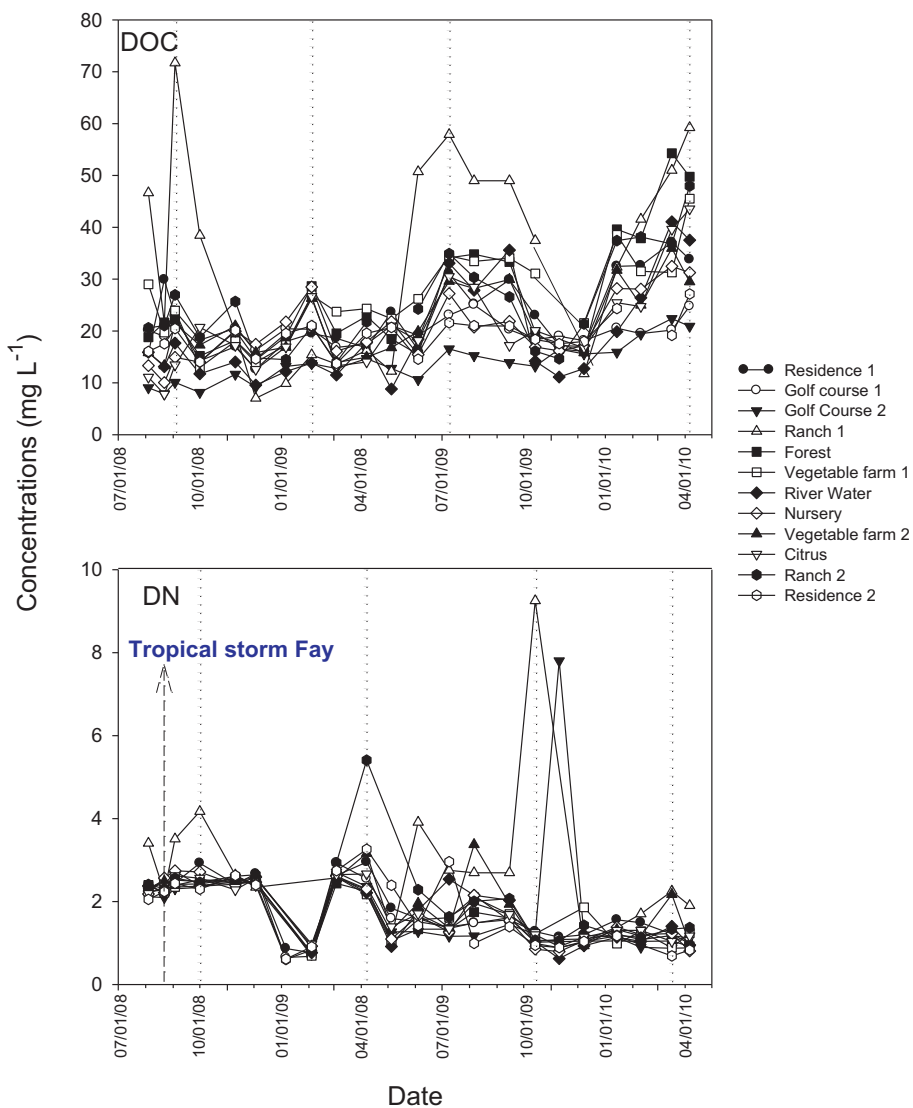


Fig. 2. Concentrations of DOC and DN in the water of grabbing samples in relation to sampling date. DOC: dissolved organic carbon; DN: dissolved nitrogen.

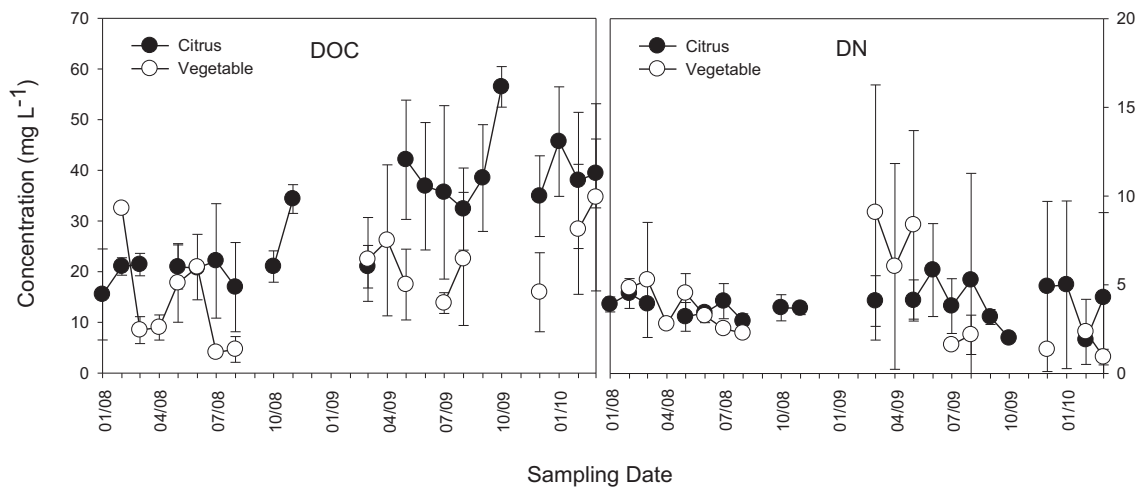


Fig. 3. Concentrations of DOC and DN in runoff water (captured by autosamplers) from two traditional agricultural practice lands as varied with sampling date (monthly) in 2008–2010. DOC: dissolved organic carbon; DN: dissolved nitrogen; data are presented as mean ± standard deviation.

Table 5
Correlations of DOC, DN, and C/N in runoff water with water chemical and physical properties.

Runoff water from autosampler sampling (N = 397)									
	pH	EC	Total solid	Turbidity	Total P	Cu	Fe	Zn	
DOC	-0.01	0.38**	0.13**	-0.17**	0.17**	0.32**	0.42**	0.26**	
DN	-0.02	0.19**	0.12*	0.01	0.34**	0.22**	0.13**	0.30**	
C/N	0.00	0.21**	0.11*	-0.22**	0.15**	0.24**	0.21**	0.22**	
Runoff water from grab sampling (N = 261)									
	pH	EC	Total solid	DO	Turbidity	Total P	Cu	Fe	Zn
DOC	-0.07	-0.10	0.22**	-0.17*	0.13*	0.48**	0.43**	0.52**	0.18**
DN	-0.07	-0.08	0.16*	-0.13	0.44**	0.19*	-0.23**	0.18**	-0.08
C/N	-0.01	-0.03	0.21**	0.06	-0.06	0.06	0.46**	0.11	0.18*

Sample numbers are 397 and 261 for autosampler and grab samples, respectively in 2008–2010. EC: electrical conductivity; DO: dissolved oxygen; DOC: dissolved organic carbon; DN: dissolved nitrogen; Cu: copper; Fe: iron; Zn: zinc.

* Significance levels of $P < 0.05$.

** Significance levels of $P < 0.01$.

or DN. Correlation could be a reflection of such mechanism. As shown in Table 6, soil TON and TOC had significantly positive correlations with soil Mehlich 3 extractable Cu, Fe, and Zn ($P < 0.01$); however, soil C/N ratio demonstrated negative correlations with Mehlich 3 extractable Cu ($P < 0.01$), P ($P < 0.01$), Fe ($P < 0.05$), and Zn ($P < 0.01$) (Table 6). Whereas, 0.5 M K_2SO_4 solution extractable DN showed significantly positive relations with M3 extractable P and Zn ($P < 0.05$), negative correlations were observed between C/N

ratios in 0.5 M K_2SO_4 extracts and Mehlich 3 extractable Cu, P, and Zn concentrations (Table 6).

The C/N ratio in the surface runoff water (15.2 ± 9.68) was lower than that in soils (21.7 ± 10.0 , $P < 0.01$). However, 0.5 M K_2SO_4 solution extractable C/N ratio in soils (5.38 ± 3.64) were far smaller than those in surface runoff water ($P < 0.01$). This suggested that N in soils was more readily subjected to leaching loss, resulting in a lower C/N ratio in the runoff water.

4. Discussion

4.1. Impact of rainfall events on temporal variation of DOC and DN in runoff water

Temporal variation of concentrations of DOC and DN concentrations in the two sets of runoff water was evident (Figs. 2 and 3) and the fluctuation in the loads of DOC, nutrients, and metals was closely related to rainfall events (Fig. 4). Previous studies reported an increase in DOC concentrations in water of streams and lakes throughout the UK in the last decades (Evans and Monteith, 2001), and changes in climate (Christ and David, 1996; Freeman et al., 2001, 2004; Worrall et al., 2003), nitrogen deposition (Findlay, 2005) or changes in land use (Garnett et al., 2000) are regarded as important responsible factors. Hejzlar et al. (2003) confirmed that seasonal hydrological pattern was the influential factor of DOC in the Malse River. Reynolds and Edwards (1995) also confirmed nitrogen deposition as one of the major factors contributing to the increase of DN

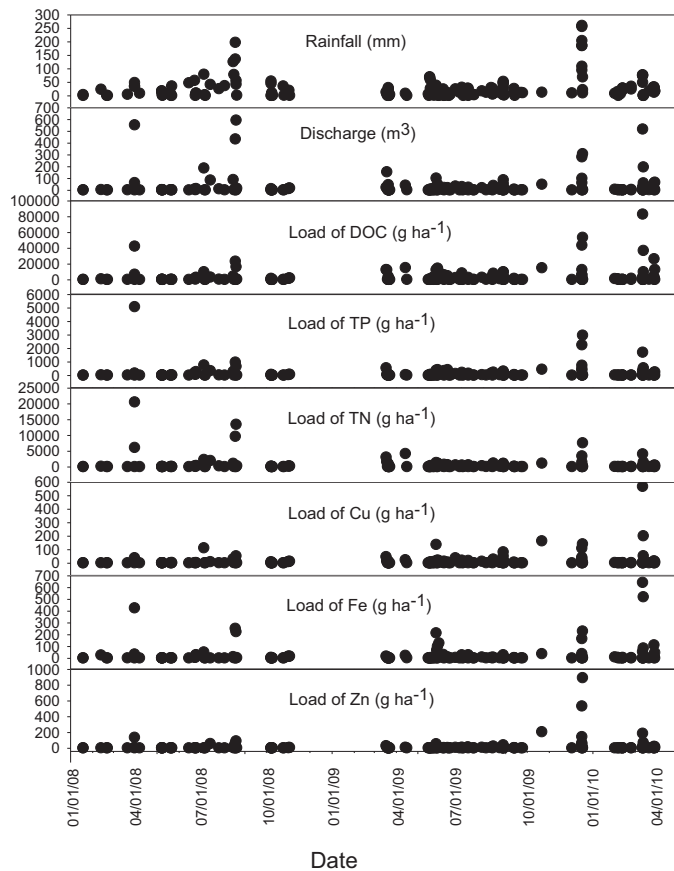


Fig. 4. Loads of DOC, TN, TP, Cu, Fe, and Zn in the runoff water from two traditional agricultural practice lands as varied with sampling date in 2008–2010. DOC: dissolved organic carbon; DN: dissolved nitrogen; TP: total phosphorus; TN: total nitrogen; Cu: copper; Fe: iron; Zn: zinc.

Table 6
Correlations of soil extractable DOC and DN, and soil TOC and TN with Mehlich 3 extractable concentrations of Cu, P, Fe, and Zn in soils.

	Mehlich 3 extractable			
	Cu	P	Fe	Zn
K_2SO_4 -DN	0.11	0.58**	-0.07	0.21*
K_2SO_4 -DOC	-0.14	-0.16	0.07	0.08
K_2SO_4 -C/N	-0.28**	-0.57**	-0.08	-0.31**
Soil TN	0.50**	0.11	0.31**	0.42**
Soil TOC	0.33**	-0.01	0.23*	0.27**
Soil C/N	-0.29**	-0.34**	-0.20*	-0.29**

K_2SO_4 -DN, K_2SO_4 -DOC, and K_2SO_4 -C/N represent 0.5 M K_2SO_4 solution extractable soil DN, DOC, and C/N molar ratio; soil TN, soil TOC, and soil C/N are soil total N, soil total organic carbon, and C/N molar ratio, respectively.

* Significance levels of $P < 0.05$ ($N = 96$).

** Significance levels of $P < 0.01$ ($N = 96$).

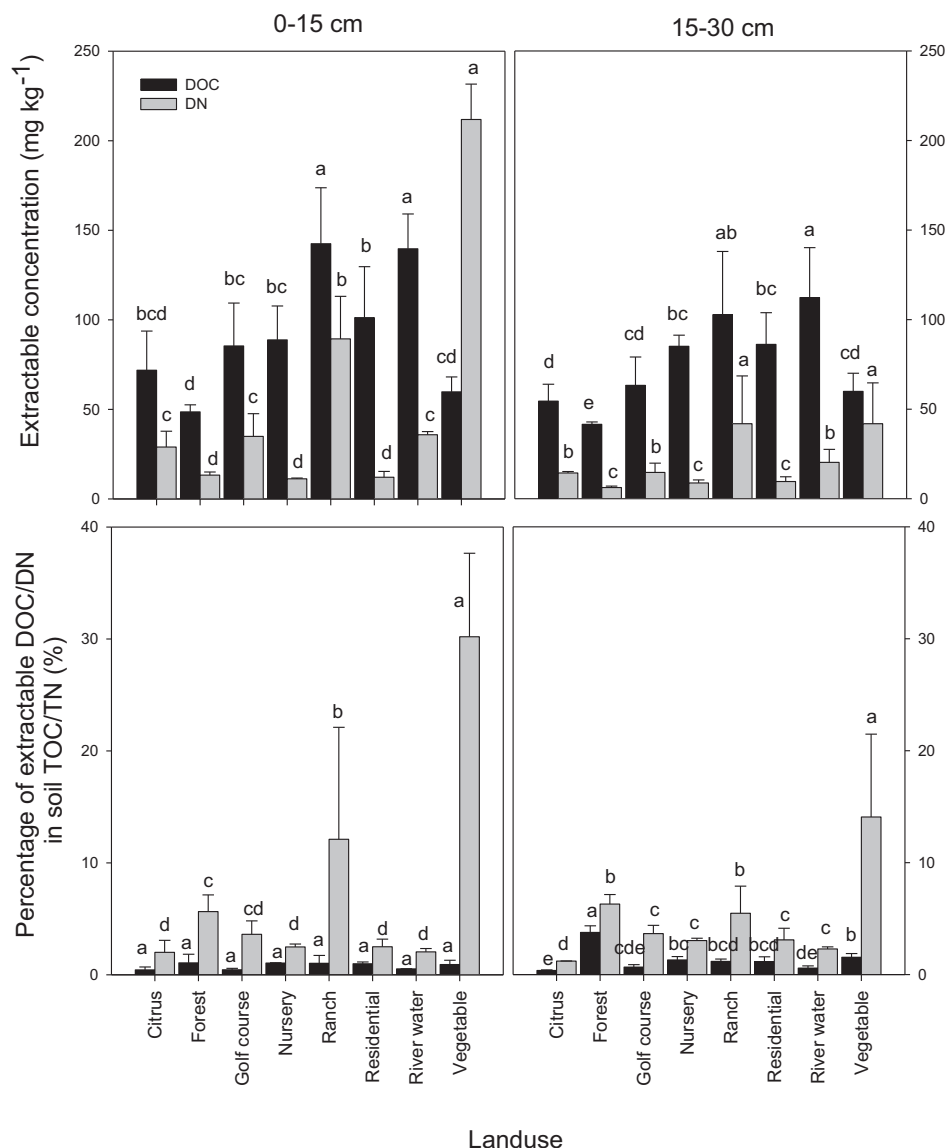


Fig. 5. 0.5 M K_2SO_4 solution extractable DOC and DN concentrations in soils with different land uses and their percentages as of soil TOC and TN. DOC: dissolved organic carbon; DN: dissolved nitrogen; TOC: total organic carbon; TN: total nitrogen. Data are presented as mean \pm standard deviation. Different letters represent differences at a significance level of $P < 0.05$.

concentrations in upland streams in UK. In this study, sampling region is located in south Florida, where seasonal hydrological patterns are profoundly affected by frequent tropical storm activities. Therefore, temporal fluctuation of DOC and DN in runoff water can be observed (Figs. 2–4). Evidences show that wet deposition can alter the solubility of soil organic matter by affecting the acidity of soils or ionic strength of soil solutions (Monteith et al., 2007). Therefore, flushing away of ions such as Ca, Mg, Al, Cl^- and SO_4^{2-} from frequent rainfall events is supposed to be accompanied by an increase of DOC and DN in runoff water. This is evidenced by the close correlations of DOC/DN with total solids, turbidity, and total P in runoff water (Table 5). The results in Figs. 2–4 showed the variation of DOC and DN in runoff water with varying hydrological conditions.

Concentration of DOC and DN in the runoff water in this study averaged 24.5 and 2.99 $mg L^{-1}$ with its fluctuation range in 2.04–71.7 and 0.605–17.4 $mg L^{-1}$, respectively. The mean DOC in this study was two times over that in runoff water (12.7 $mg L^{-1}$

in average) from meadow land in Canada (Royer et al., 2007). It is reported that the concentrations of DOC in streams are generally in the range of 2–50 $mg L^{-1}$ (Spiteller, 1987; Moore and Dalva, 2001). The average concentration of DOC in water in this study fell within this range; but the 90 percentile was above 50 $mg L^{-1}$ (Figs. 2 and 3). Furthermore, DOC in runoff water in Year 2008 was within this range, but the 90 percentiles of DOC in runoff water in Year 2009 and 2010 were above 50 $mg L^{-1}$. Also three peaks (71.7, 57.9, and 59.2 $mg L^{-1}$) of DOC concentration were above 50 $mg L^{-1}$ (Fig. 2), which coincidentally agreed with the rainfall events (Fig. 4). The reference levels of DN in U.S. streams in 1992–2001 were in the range of 0.12–2.2 $mg L^{-1}$ (Mueller and Spahr, 2005), which is lower than the average (2.99 $mg L^{-1}$) in this study. The highest concentration of DN (17.4 $mg L^{-1}$) in runoff water in this study was eight times the highest value (2.2 $mg L^{-1}$) in the reference levels, but was similar to the reported maximum (18.2 $mg L^{-1}$) in drainage water from an improved upland pasture (Roberts et al., 1986). Apparently, both agricultural management practices and climatic condition are

influential to the fluctuation of the DOC and DN concentrations in runoff water.

4.2. Impact of land use on DOC and DN in soil and runoff water

Fluctuation of DOC in runoff water not only varied with rainfall events, but widely with land use types (Table 2 and Fig. 1); however, variation of DN in runoff water with land uses was not so apparent (Fig. 1). The dominant origin of DOM in terrestrial catchments, such as headwater of streams, is leaching from soils (Hejzlar et al., 2003), therefore, land use poses an important impact on DOC concentration in runoff water (Garnett et al., 2000). Kindler et al. (2011) observed that DOC loss from forest was much less than from grassland or cropland, and Saviozzi et al. (1994) reported higher extractable DOC in grassland soils than in arable (corn cropping) soils. This can be supported from this study (Fig. 5), whereas, extractable DN did not follow the same trend for arable soil (vegetable soil) and grassland (ranch soil), which may be explained by seasonal applications of N fertilizers in vegetable fields. However, plastic mulching practice might hinder much DOC and DN loss into the runoff water from vegetable fields as compared with those from forest or ranch (Table 2 and Fig. 1). Furthermore, a change in land uses would also affect soil DOM concentrations: for example, clear cutting of forests leads to an increase in DOC concentrations in soils (Hughes et al., 1990); while a change from grassland to arable cropping can result in a decrease in DOC (Chantigny, 2003).

Accordingly, availability of SOM in soils with varying land uses plays an important role in the export of DOC and DN into runoff water. Most soils with varying land uses in this study had less than 1% of extractable DOC in the soil TOC at the 0–15 cm and <2% at the 15–30 cm depth (Fig. 5). In comparison, larger portions of extractable DN were observed in soils, especially, up to 30% in vegetable soils at the 0–15 cm (Fig. 5). This agreed with the statement that DOC accounts for only a small proportion (<1%) of total soil organic carbon (Zsolnay, 2003); however, larger extractable portions of DN in soils, especially in arable soils, were evident, possibly due to the application of N fertilizers (Reynolds and Edwards, 1995). Thus, differences in solubility of soil organic matter can lead to varying DOC concentrations in runoff water (Garnett et al., 2000). Tillage management in vegetable farms could alter the availability of soil organic matter due to frequent tillage or cropping rotation; therefore, could affect the amounts of DOC and DN subjected to leaching (Christou et al., 2005; Franzluebbers, 2005). Surface soil (0–15 cm) with citrus and ranch had more extractable DOC than the subsoil (15–30 cm, Fig. 5), which agrees with the result of Kindler et al. (2011). However, no significant difference in extractable DOC in soils was observed between citrus and vegetable, which contrasts with extractable DN (Fig. 5). More DOC and DN were measured in runoff water from citrus groves than vegetable farm (Table 2), even though the soils from the vegetable farm contained more TOC (not TN) (Table 3). This may be attributed to the plastic mulching practices in the vegetable farms, which reduce soil leaching. Extractable DOM in soils was reported to vary in the sequence of forest soil > grassland > arable soil (Chantigny, 2003). However, in this study, ranch soil and river bank soil had the greatest extractable DOC concentrations at both 0–15 cm and 15–30 cm; and vegetable soil and ranch soil had the highest extractable DN (Fig. 5). These results agree with the high organic matter content in the soils from river banks (Table 3) and the extra organic matter input from animal feces in ranches (Table 3), and high N fertilizer application rate may be responsible for high extractable DN in vegetable soils. Even though concentrations of extractable DOM in forest soil were not among the highest levels, forest soil did have greater availability of carbon (>1%) and nitrogen (>5%), especially at the 15–30 cm depth (Fig. 5), which could be due to tree canopies containing a greater proportion of organic substances such as tannins and phenolic acids

(Chantigny, 2003). This suggested that DOM (especially DOC) in forest soils is readily subjected to leaching, which is evidenced by the greater DOC concentrations in the runoff water (Fig. 1). In addition, plants could also be a contributor to DOC and DN in forest and agricultural soils (Chantigny et al., 1997; van Kessel et al., 2009), and up to ~40% of soil total carbon were produced from plants (Whipps, 1990). For example, coniferous forests resulted in more DOC in soils than deciduous forests (Yano et al., 2000); and soils under legumes had more DOC than those under gramineae (Chantigny, 2003). Soils with fruit trees and maize/soy bean contained more leachable dissolved organic nitrogen than soils with cereals (van Kessel et al., 2009). A recent study reported that plant-derived DOC mainly consisted of soluble carbohydrates, organic acids, amino acids/peptides, and phenolic compounds (He et al., 2009), and is more readily subject to leaching. Therefore, the variety in plant species in the seven different land use types could also be relevant to the DOC and DN in soils subjected to surface runoff.

Manuring and grazing management can result in more SOC sequestration than forest land uses (Ussiri and Lal, 2005). Besides the contribution of root biomass to the soil organic matter pool (Eriksen et al., 2004), beef cattle feces offer additional organic matter sources in pasture soils (McTiernan et al., 2001). Under the condition of high temperature and humidity in south Florida, animal manures could be quickly decomposed by soil microorganisms and become a part of DOC and DN in pasture soils. Furthermore, grass coverage was heavy in the pasture and river bank soils, and grass roots may exude more soluble molecules, contributing to the greater DOC and DN in these soils (~140 mg kg⁻¹ and ~50 mg kg⁻¹, Fig. 5). These values were above the reported range of extractable organic N (2.5–10 mg kg⁻¹) in agricultural soils (Murphy et al., 2000).

Golf course was uniformly covered by turfgrass. DOC concentrations in the runoff water were mainly affected by turfgrass type (*Cynodon dactylon*), management (such as mowing and fertilization), and soil conditions (Aitkenhead-Peterson et al., 2009). Previous studies reported more than 25 mg L⁻¹ of DOC in watershed water from turfgrass land and 250–500 mg kg⁻¹ of DOC from turfgrass soils (Wright et al., 2008; Aitkenhead-Peterson et al., 2009), which is higher than that from this study (Figs. 1 and 5). Barton et al. (2006) observed 0.6–27 and 0.1–69 mg L⁻¹ of DN in leachate at high irrigation and low irrigation from a turfgrass sandy soil, which was also higher than that measured in this study (0.652–7.80 mg L⁻¹). In addition, no colored runoff water from turfgrass land was observed in this study, which is similar to the description of Aitkenhead-Peterson et al. (2009). Such information might suggest a SOC sequestration in golf courses, resulting in lower DOC and DN concentrations in the runoff water. Soil carbon acting as energy for denitrifying microorganisms may enhance the denitrification and therefore, restrain N (especially NO₃-N) from leaching in golf courses (Vinther et al., 2006).

5. Conclusions

Temporal fluctuation of DOC and DN, and loads of DOC, TP, TN, and metals in runoff water from agricultural fields were strongly associated with rainfall events. Of the eight land uses investigated, Ranch 1 had the greatest DOC and DN concentrations in runoff water, followed by vegetable farm and forest, and golf course usually had the lowest DOC in runoff water. Soil total carbon pool and its availability varied among the land uses, consequently, posed an important effect on DOC and DN concentrations in runoff water as well. Loss of DOC from soils would result in the transport of nutrients P and N, and metals Fe, Cu, and Zn into the studied watershed.

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