

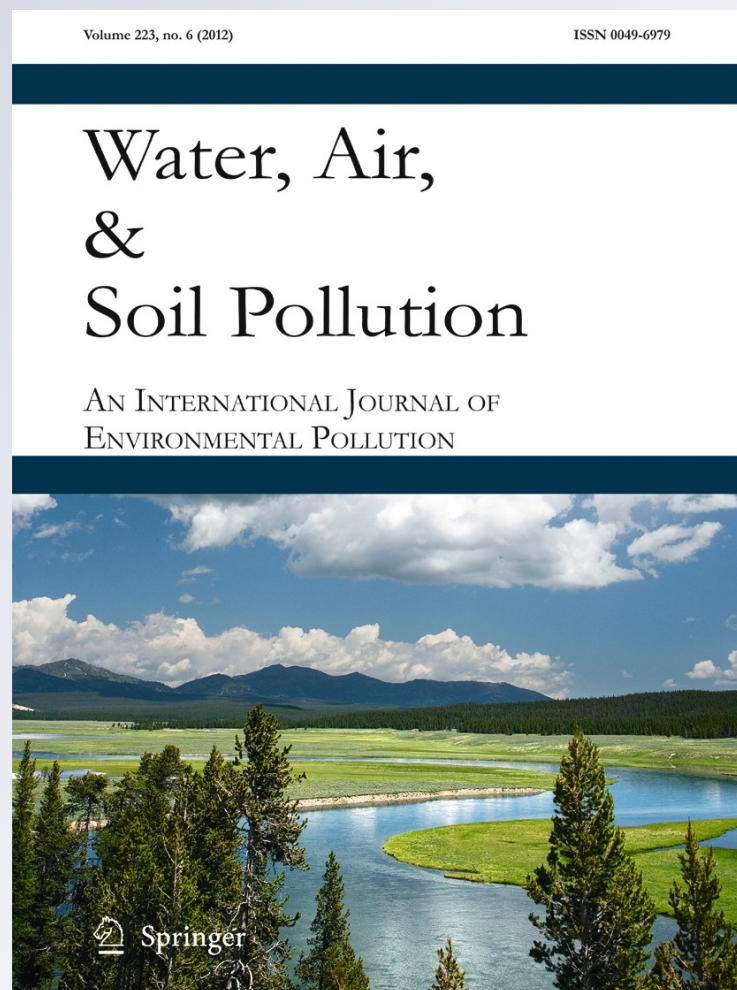
*Dissolved Organic Carbon in Association
with Water Soluble Nutrients and Metals
in Soils from Lake Okeechobee Watershed,
South Florida*

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Dissolved Organic Carbon in Association with Water Soluble Nutrients and Metals in Soils from Lake Okeechobee Watershed, South Florida

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Abstract Water quality of Lake Okeechobee has been a major environmental concern for many years. Transport of dissolved organic matter (DOM) in runoff water from watershed is critical to the increased inputs of nutrients (N and P) and metals (Cu and Zn). In this study, 124 soil samples were collected with varying soil types, land uses, and soil depths in Lake Okeechobee watershed and analyzed for water-extractable C, N, P, and metals to examine the relationship between dissolved organic carbon (DOC) and water soluble nutrients (N and P) and metals in the soils. DOC in the soils was in 27.64–400 mg kg⁻¹ (69.30 mg kg⁻¹ in average) and varied with soil types, land uses, and soil depth. The highest water-extractable DOC was found in soils collected in sugar cane and field crops (277 and 244 mg kg⁻¹ in average, respectively). Water soluble concentrations of N and P were in the range of 6.46–129 and 0.02–60.79 mg kg⁻¹, respectively. The ratios of water-extractable C/N and C/P in soils were in 0.68–12.52 (3.23 in average) and 3.19–2,329 (216 in average), and varied with land uses. The

lowest water-extractable C/N was observed in the soils from dairy (1.66), resident (1.79), and coniferous forest (4.49), whereas the lowest water-extractable C/P was with the land uses of dairy (13.1) and citrus (33.7). Therefore, N and P in the soils under these land uses may have high availability and leaching potential. The concentrations of water soluble Co, Cr, Cu, Ni, and Zn were in the ranges of <method detection limit (MDL)–0.33, <MDL–0.53, 0.04–2.42, <MDL–0.71, and 0.09–1.13 mg kg⁻¹, with corresponding mean values of 0.02, 0.01, 0.50, 0.07, and 0.37 mg kg⁻¹, respectively. The highest water soluble Co (0.10 mg kg⁻¹), Cr (0.26 mg kg⁻¹), Ni (0.31 mg kg⁻¹), and Zn (0.80 mg kg⁻¹) were observed in soils under the land use of sugar cane, whereas the highest Cu (1.50 mg kg⁻¹) was with field crop. The concentration of DOC was positively correlated with total organic carbon (TOC) ($P < 0.01$), water soluble N ($P < 0.01$), electrical conductivity (EC, $P < 0.01$), and water soluble Co, Cr, Ni, and Zn ($P < 0.01$), and Cu ($P < 0.05$), whereas water soluble N was positively correlated with water soluble P, Cu, and Zn ($P < 0.01$) in soils. These results indicate that the transport of DOC from land to water bodies may correlate with the loss of macro-nutrients (N, P), micro-nutrients (Cu, Zn, and Ni), and contaminants (Cr and Co) as well.

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1 Introduction

Dissolved organic matter is of great concern in aquatic environment since it is often associated with nutrients such as carbon, nitrogen, phosphorus, and sulfur (Michalzik et al. 2001; Wright 2009), toxic heavy metals such as Cu, Zn, and Hg (Cabaniss and Shuman 1988; Strober et al. 1995), and pesticides (Piccolo 1994). About 12–56% of DOM is bioavailable/biodegradable (Kawahigashi et al. 2004; McDowell et al. 2006); therefore, it could partially attribute to the color in water and serve as a source of carbon and energy for stream water ecosystems as well (Tipping et al. 1997; Maurice and Leff 2002). However, mobilization and transport of DOM from upland soil to downstream water is soil property-related and hydrologically mediated (Tipping et al. 2003; Kerr et al. 2008; Dawson et al. 2010). Previous studies demonstrated that upland soil texture and chemistry greatly affected the concentration and composition of DOM in downstream water (McClain et al. 1997). For example, Spodosol resulted in high DOM concentrations in river water with a consequence of black waters, whereas Oxisol the low DOM with clear waters (Leenheer 1980). Furthermore, DOM as an important source of mineralizable C, N, and P (Haynes 2000), its production is also affected by N and P status in soils, such as their chemical forms and availability (Silveira 2005).

In soils, concentrations of DOM are dependent on climate conditions (such as temperature and rainfall) as well as vegetation coverage (Akagi and Zsolnay 2008). Anthropogenic factors, such as land-use change (Embacher et al. 2007; Aitkenhead-Peterson et al. 2009), acidification (Gauthier et al. 2010), tillage (Chantigny 2003), or application of fertilizer (Qualls and Haines 1992) and manure (Blair et al. 2006), can also affect the DOM concentrations. Practically, DOM in soils is quantified using water-extractable organic matter, comprising of dissolved organic C, N, P, and S. It is defined as the fraction of soil organic matter (SOM) extracted with deionized water that has passed through a 0.45- μm membrane filter (Zsolnay 2003) and is considered as the dissolved part of SOM in soil solution (Jones and Willet 2006). When carried in runoff water, water-extractable DOM is frequently associated with quantities of nutrients (C, N, and P)

and heavy metals. Subsequently, investigation of DOM (DOC and soluble N and P) can provide information about the state of nutrients in soils and their potential losses to the water environment.

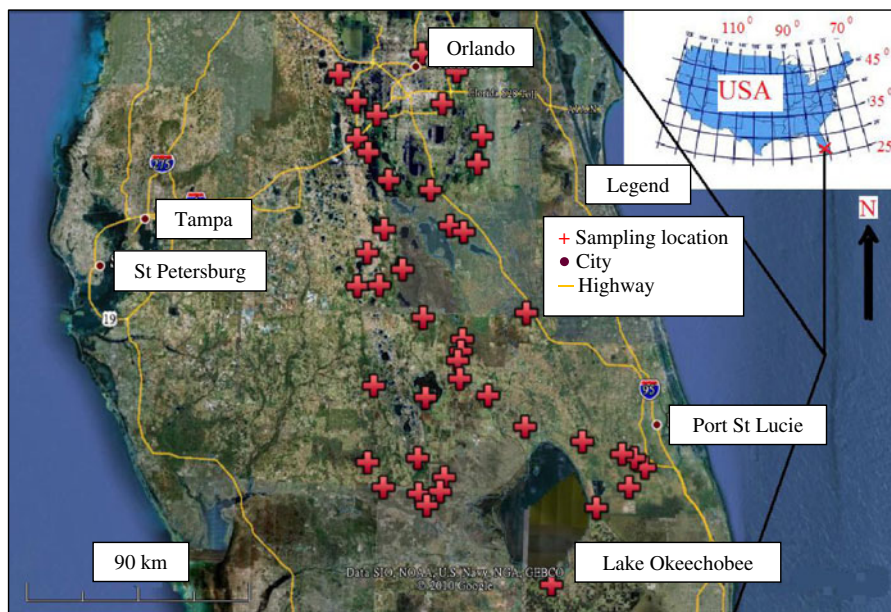
Lake Okeechobee, a 730-square-mile lake, as the headwaters of the Everglades wetland ecosystem, is the seventh largest freshwater lake in USA. Nowadays, excessive nutrient loading is one of the most adverse factors affecting the lake's ecological health. An estimated more than 656 metric tons of P was transported into the lake in 2009, and about 30,000 metric tons of P was present as legacy P in the bottom sediments (The Everglades HUB 2009). Even though a series of restoration efforts have been made to reduce nutrient loadings in the watershed, surface runoff from upland soil could potentially carry considerable amounts of C, N, and P into the lake. For instance, in 2009, about $2.58 \times 10^{10} \text{ m}^3$ of water, containing P as well as N, C, and other metals, flowed into the lake (The Everglades HUB 2009). It is hypothesized that dissolved organic matter plays an important role in the transport of nutrients and heavy metals from watershed to the Okeechobee Lake. However, minimal studies have been conducted to investigate the contribution of DOC to nutrient inputs in the lake. The objective of this study was to investigate the water-extractable DOC concentrations in soils with varying land uses and soil types in the watershed of Lake Okeechobee, Florida, and its potential correlations with water soluble nutrients and trace metals.

2 Materials and Methods

2.1 Soil Sample Collection

Soil sampling was conducted in early September, 2009. In total, 124 soil samples were collected at the depths of 0–20 cm and 20–40 cm representing upper and subsurface layers. For soils under improved and unimproved pastures, soil samples were collected at the depths of 0–20 cm, 20–40 cm, 40–70 cm, and 70–100 cm. Soil samples were collected mainly from the upland area of Lake Okeechobee watershed and included the major land uses and dominant soil types (Fig. 1). Each soil sample was duplicated with a composite of three random sampling cores at the same sampling depth.

Fig. 1 Sketch map of sampling in Okeechobee lake basin, south Florida



2.2 Preparation and Chemical Analyses of Soils

After removal of plant debris and sieved to pass a 2-mm sieve, fresh soil samples were analyzed for moisture, water-extractable dissolved organic carbon (DOC), nitrogen (N), phosphorus (P), and other macro- and micro-elements. Soil moisture was determined using a gravity method (Jones and Willet 2006). Water soluble N and DOC were determined by extracting 5.0 g of fresh soil with deionized (DI) water at a soil/solution ratio of 1:5 (w/v) for 1 h on a reciprocating shaker at a speed of 90 rpm (Jones and Willet 2006). After filtering through a 0.45- μm membrane filter, the concentrations of DOC and N in the extracts were measured using a liquid TOC analyzer (liquid TOC Trace; Elemental Analysis system GmbH, Hanau, Germany). Soils for water soluble P and other macro-elements (K, Na, Ca, Mg, Al, Fe, and Mn) and micro-elements (Cd, Co, Cr, Cu, Ni, Pb, and Zn) were extracted using DI water at a water/soil ratio of 1:10. After filtered through a 0.45- μm membrane, the filtrates were then analyzed for the concentrations of the macro- and micro-elements using an inductively coupled plasma optical emission spectrometry (ICP-OES; Ultima, JY Horiba Inc. Edison, NJ, USA).

Subsamples of the collected soils were air dried and passed through a 2-mm sieve before they were analyzed for pH, electrical conductivity (EC), and total organic carbon/total nitrogen (TOC/TN). Soil pH was

measured using a pH/conductivity meter (Model 220; Denver Instrument, Denver, CO, USA) following EPA method 150.1 at the soil/water ratio of 1:1; EC was determined at the soil/water ratio of 1:2 using the pH/conductivity meter following EPA method 120.1. Soil TOC/TN was analyzed using a C/N analyzer (Vario Max CN Macro Elemental Analyzer; Elemental Analyses system GmbH).

2.3 Data Processing

Statistical analyses were performed using SPSS 10.0 software (SPSS Inc., Richmond, CA, USA). One-way analysis of variance (ANOVA) and a post hoc multiple comparison procedure (MCP) using Duncan's test were performed to compare the difference of DOC, DOC/TOC, soluble N, soluble N/TN, soluble P and trace metals, and water-extractable ratios of C/N and C/P among varying land uses and soil types at a significance level of $P < 0.05$. Bivariate correlation analyses were performed to distinguish relationships of DOC, soluble N and P with soil chemical parameters, and then a stepwise multiple regression analysis was conducted to determine the major contributions of soil chemical parameters to water-extractable DOC in soils. All raw data sets were pooled for a standard transformation prior to principal component analysis (PCA) for dimension reduction. Resultant data sets were subject to canonical variate analysis (CVA) to

discriminate the combinations among land use, soil type, and chemical properties. Data of nutrients C, N, and P were also pooled to perform PCA analysis to discriminate their associations in soils. All figures were obtained using SigmaPlot 10.0 (SPSS Inc.).

3 Results

3.1 Concentrations of DOC and Soluble N and P in Soils

Of the studied soils, water-extractable DOC, soluble N and P varied in 27.64–400, 6.46–129, and 0.02–60.80 mg kg⁻¹, with their averages of 69.30, 26.40, and 4.13 mg kg⁻¹, and standard deviations of 62.70, 22.15, and 7.95, respectively. Their median concentrations were 50.85, 18.93, and 1.52 mg kg⁻¹, with their respective 90th percentile concentrations of 102, 44.0, and 9.28 mg kg⁻¹. In comparison, the average concentration of DOC in soils was two and 15 times as much as those of soluble N and P (Table 1).

Water-extractable concentrations of DOC and soluble N were soil type dependent. The highest concentrations of DOC and soluble N were observed in Histosol, with their averages being two to three times as much as those in other soil types (Table 1). Low in DOC and soluble N concentrations, with the highest percentages of DOC/TOC (3.40%) and soluble N/TN (12.7%), Ultisol demonstrated a larger quantity of soil organic matter (SOM) being soluble than other soil types (Table 1). However, it is not the case for soluble P (Table 1).

DOC, soluble N and P in soils varied with landuse class. Soils under sugar cane and field crop had the greatest mean DOC (244 and 272 mg kg⁻¹), whereas soils under field crop had the greatest mean soluble N (83.99 mg kg⁻¹) and dairy the greatest mean soluble P (13.91 mg kg⁻¹) (Table 1). The lowest DOC was measured in soils under the land uses of citrus, forest, cypress, dairy, deciduous, improved and unimproved pasture, mixshrub, oak, ornamentals, resident, row crop, and tree crop (with their averages in 37.88–78.72 mg kg⁻¹). However, the lowest soluble N was under ornamentals (12.36 mg kg⁻¹ in average) and tree crop (12.88 mg kg⁻¹ in average) (Table 1). Even though soils under field crop had the greatest concentrations of DOC and soluble N, and sugar cane the greatest concentrations of DOC, they had the lowest

percentages of DOC/TOC (0.28–0.32%) and soluble N/TN (0.52–1.57%) (Table 1). Furthermore, improved pasture demonstrated no significant difference from unimproved pasture in soil DOC and soluble N, DOC/TOC, and soluble N/TN (Table 1).

Variation of DOC and soluble P with soil depth was complicated. Most soils had greater concentrations of DOC and soluble P in upper layer (0–20 cm) than in subsurface layers (20–40 cm), but few soils had a reverse situation (Fig. 2a, c). Most soils had DOC and soluble P below their respective average concentrations (69.30 and 4.13 mg kg⁻¹), especially in subsurface layer (Fig. 2a, c). For soluble N, higher concentration in soils was measured in upper layer (0–20 cm) than in deeper layers (>20 cm). Only one exception was observed in Histosol under field crop, where subsurface layer (20–40cm) had higher soluble N (129 mg kg⁻¹) than upper layer (0–20 cm) (Fig. 2b). Other than DOC and soluble P, soluble N in most upper soils was above its average concentration of 26.40 mg kg⁻¹ (Fig. 2b).

3.2 Variation of Water-Extractable C/N and C/P Ratios in Soils

Water-extractable C/N and C/P in the soils varied in 0.68–12.5 and 3.19–2,329, with their averages of 3.23 and 216, and standard deviations of 2.04 and 368, respectively. No statistically significant differences in C/N ratios were observed among different soil types (Fig. 3). However, greater C/P ratios were observed in Histosol (360 in average) than in Mollisol (89.7 in average) or Inceptisol (31.6 in average), whereas Alfisol, Entisol, Spodosol, and Ultisol had similar C/P ratios (Fig. 3).

Ratios of C/N and C/P varied with land use class as well. The greatest C/N ratios were in the soils under hardwood (8.09) and sugar cane (8.62), whereas the lowest under the land use of dairy (1.66). Soils under other land uses (citrus, coniferous forest, cypress, deciduous, field crop, improved pasture, mixshrub, oak, ornamentals, resident, row crop, tree crop, and unimproved pasture) had similar C/N ratios (1.79–3.78) (Fig. 4). The highest C/P was in soils under hardwood (908), whereas the lowest C/P with land uses of citrus (33.7), dairy (13.1), improved pasture (58.4), and resident (42.8) (Fig. 4). Furthermore, soils under cypress and unimproved pasture had average C/

Table 1 Concentrations of dissolved organic carbon (DOC) and soluble N and P, and percentages of DOC/TOC and soluble N/TN in soils with varying soil types and land uses

		DOC (mg kg ⁻¹)	DOC/TOC (%)	Soluble N (mg kg ⁻¹)	Soluble N/TN (%)	Soluble P (mg kg ⁻¹)
Soil type	Alfisol	51.31±13.69b	0.84±0.50b	24.23±8.49ab	5.44±2.66bc	2.10±2.17a
	Entisol	60.58±33.83b	1.00±0.71b	19.29±12.84ab	4.59±2.17bc	2.91±3.16a
	Histosol	150±141a	0.46±0.45b	41.95±38.94a	2.35±2.30c	3.16±5.02a
	Inceptisol	43.52±5.45b	0.99±0.67b	21.03±10.11ab	6.14±2.43b	4.69±3.03a
	Mollisol	53.97±17.35b	0.73±0.44b	30.60±24.08ab	4.84±1.13bc	1.57±0.50a
	Spodosol	59.99±24.23b	1.03±0.78b	25.69±19.88ab	6.00±3.14b	5.74±10.8a
	Ultisol	39.80±6.89b	3.40±2.94a	13.82±4.62b	12.7±10.91a	1.07±1.20a
Land use	Citrus	41.19±6.10c	1.20±0.78b	15.36±6.39bc	5.57±1.93abcd	4.00±2.44ab
	Coniferous forest	78.72±29.03c	0.73±0.38b	21.13±11.11bc	4.43±1.72abcd	1.71±0.46b
	Cypress	61.98±14.72c	0.37±0.28b	22.06±11.34bc	2.98±1.60bcd	1.07±1.57b
	Dairy	61.76±13.39c	0.45±0.28b	45.61±32.12b	3.86±1.19bcd	13.91±9.28a
	Deciduous	56.55±20.07c	0.64±0.40b	29.10±24.69bc	4.37±2.28abcd	1.39±1.23b
	Field crop	244±151a	0.28±0.13b	83.99±43.11a	1.57±0.92cd	5.37±5.34ab
	Hardwood/coniferous mixed	134±14.29b	0.56±0.08b	19.11±9.43bc	2.27±0.96bcd	0.79±0.83b
	Improved pasture	52.87±13.75c	1.08±0.85b	30.11±23.72bc	6.31±2.56abc	9.37±13.82ab
	Mixshrub	43.00±8.75c	0.97±0.57b	17.57±7.23bc	5.48±2.53abcd	0.62±0.46b
	Oak	65.40±14.15c	0.85±0.42b	26.65±9.32bc	4.43±0.68abcd	1.26±1.00b
	Ornamentals	41.84±10.64c	0.70±0.28b	12.36±3.99c	4.46±1.24abcd	0.93±0.27b
	Resident	41.01±7.85c	0.42±0.13b	26.97±12.82bc	4.11±0.56bcd	2.92±1.59ab
	Row crop	67.19±13.78c	1.38±0.90ab	34.19±35.12bc	4.40±1.08abcd	1.46±0.87b
	Sugar cane	272±123a	0.32±0.16b	37.63±30.14bc	0.52±0.46d	5.94±7.83ab
	Tree crop	37.88±7.33c	2.47±2.70a	12.88±4.26c	9.55±9.84a	4.01±4.65ab
	Unimproved pasture	56.18±18.89c	1.12±0.84b	22.11±12.09bc	7.35±4.33ab	0.96±1.02b

Data are presented as mean±1 standard deviation (STDEV). Different letters under the same classification are statistically different ($P < 0.05$)

P ratios of 507 and 490, whereas those with other land uses had C/P ratios in 112–320 (Fig. 4).

3.3 Concentrations of Soluble Metals in Soils

The concentrations of water soluble Co, Cr, Cu, Ni, and Zn were in the ranges of <method detection limit (MDL)–0.33 mg kg⁻¹, <MDL–0.53 mg kg⁻¹, 0.04–2.42 mg kg⁻¹, <MDL–0.71 mg kg⁻¹, and 0.09–1.13 mg kg⁻¹, respectively, with their respective average values of 0.02, 0.01, 0.50, 0.07, and 0.37 mg kg⁻¹. Such variations were dependent on soil types and land use class as well. Mollisol had the greatest water soluble Co (0.05 mg kg⁻¹) and Ni (0.12 mg kg⁻¹), whereas Alfisol, Inceptisol, and Ultisol the smallest Co and Ni. Histosol had the highest water soluble Cr

(0.07 mg kg⁻¹) and Zn (0.56 mg kg⁻¹) (Table 2). However, water soluble Cu was not different among soil types (Table 2). The highest water soluble Co (0.10 mg kg⁻¹), Cr (0.26 mg kg⁻¹), Ni (0.31 mg kg⁻¹), and Zn (0.81 mg kg⁻¹) were observed in the soils under sugar cane, whereas the highest Cu (1.50 mg kg⁻¹) under field crop (Table 2).

3.4 DOC and soluble N and P in Association with Soluble Metals and Soil Chemical Parameters

Soil DOC and soluble N did not have a clear relationship with soil pH, but they demonstrated positive correlations with EC ($P < 0.01$). Soil soluble P was positively correlated with soil pH ($P < 0.01$), but not with soil EC (Table 3). Both soil DOC and soluble N

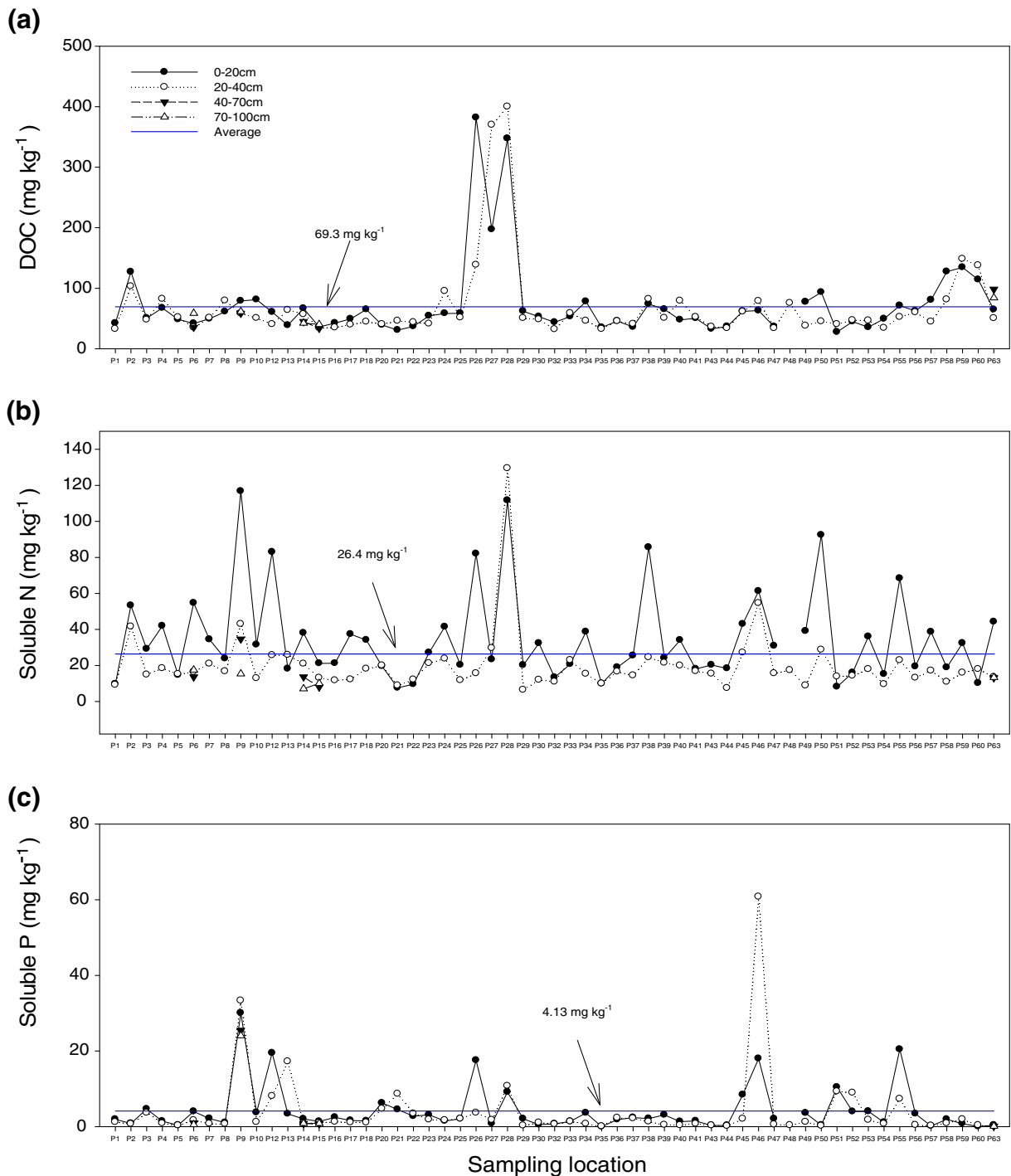


Fig. 2 Variation of DOC (a), soluble N (b), and soluble P (c) in soils with sampling location and depth

showed positive relations with water-extractable K, Na, Ca, Mg, and Mn ($P < 0.01$), and soluble Co, Ni, and Zn ($P < 0.01$) in soils (Table 3). DOC was

positively correlated with soluble N ($P < 0.01$), water-extractable Al, Fe, $\text{NH}_4\text{-N}$ ($P < 0.01$), and soluble heavy metal Cr ($P < 0.01$), whereas soluble N was

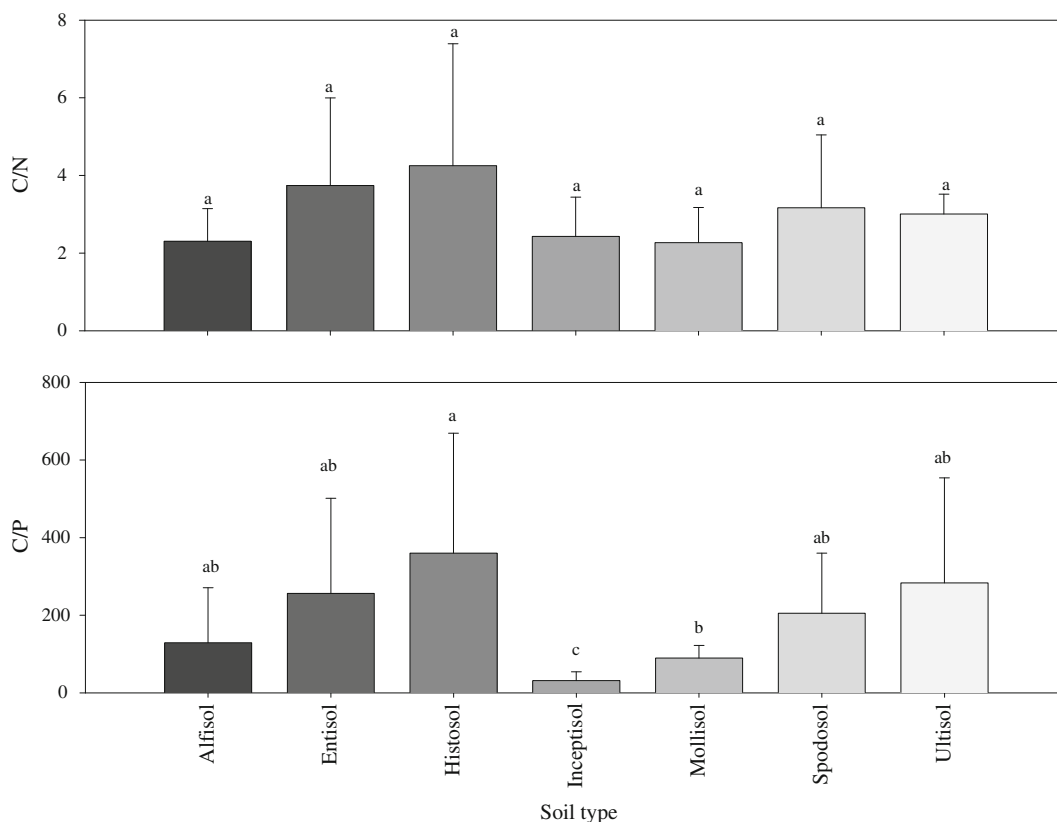


Fig. 3 Variation of water-extractable C/N and C/P with soil type

positively correlated with soluble P ($P < 0.01$) and soluble Cu ($P < 0.01$) (Table 3). Soil soluble P had positive relations with soluble N ($P < 0.01$), extractable Al, K, and Ca ($P < 0.01$), and soluble heavy metals Cr, Ni, and Zn ($P < 0.05$) (Table 3). However, no significant correlations were observed in soluble Pb and Cd with DOC or soluble N and P (Table 3). Therefore, heavy metals such as Co, Cr, Ni, and Zn were probably more associated with DOC, whereas Cu and P were more associated with soluble N. A stepwise linear regression was therefore executed, and the following equation was obtained:

$$\begin{aligned} \text{DOC} = & 44.903 + 0.808\text{Mg} + 1.939\text{TOC} \\ & + 1.733\text{NH}_4 - \text{N} - 26.161\text{TN} - 0.0537\text{EC} \\ & + 0.121\text{Ca} \end{aligned}$$

$$(F = 158, N = 124, P < 0.001)$$

The most influential factors on DOC can be observed in sequence as water-extractable Mg, TOC,

water-extractable $\text{NH}_4\text{-N}$, soil total N, EC, and water-extractable Ca.

Principal component analysis was performed for three data sets (chemical parameters, land uses, and soil types) and followed by canonical variate analysis. In the combined loading plot of CV1 vs. CV2 (Fig. 5), soil chemical parameters formed four separate clusters (I–IV) with negative CV1 loadings. Cluster I contained water-extractable Ca, Na, and K, soluble N and Cu, and soil EC, TOC, and TN. Cluster IV consisted of water-extractable Fe, Al, and Mn, and soluble Cd, Pb, Cr, Co, and Ni. Clusters I and IV were distinguishable by soil type and land use class on the CV2 loadings. Clusters II included extractable Mg and Zn, and DOC, and was overlapped by the land use of dairy (cluster 6). It was close to cluster c (soil type Histosol), demonstrating a close relationship of DOC with water-extractable Mg and Zn, soil type Histosol, and land use dairy (Fig. 5). Cluster III was comprised of soil pH, soluble P, and water-extractable $\text{NH}_4\text{-N}$. It was overlapped by cluster 4 (land uses of citrus, mixshrub,

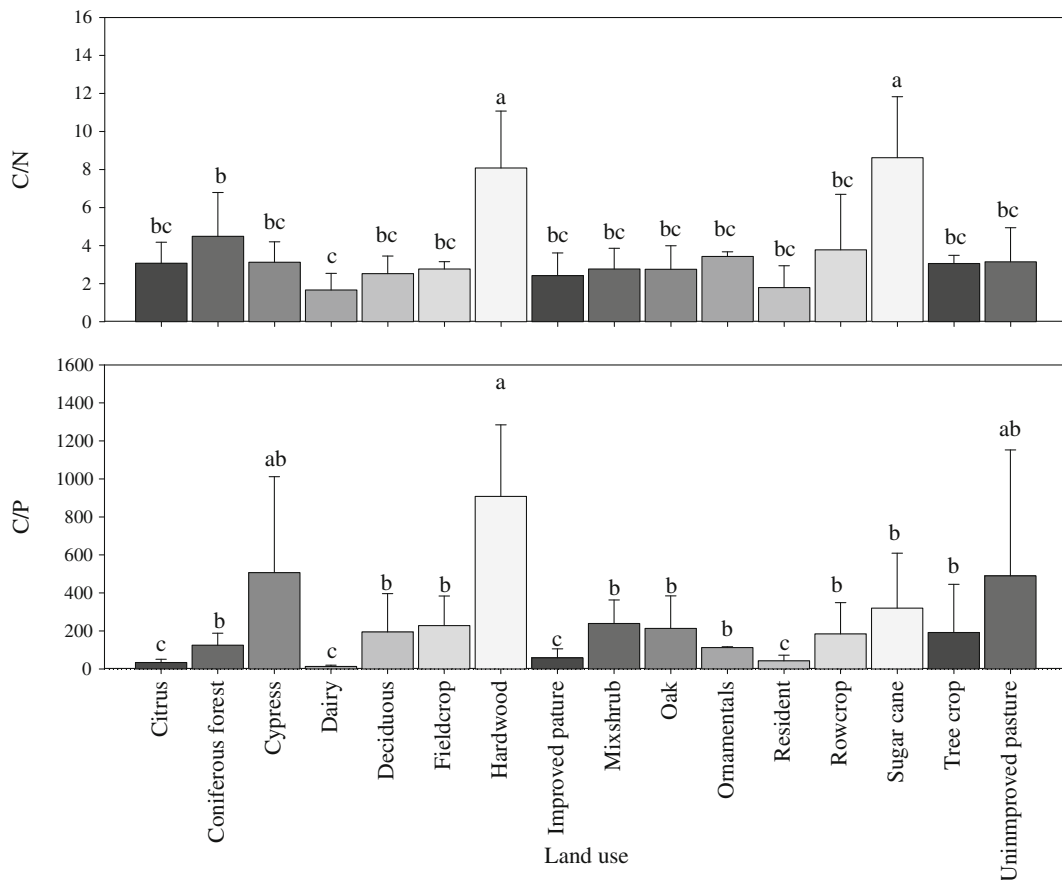


Fig. 4 Variation of water-extractable C/N and C/P with land use

ornamentals, tree crop, unimproved pasture, and resident) and cluster 5 (land uses of coniferous forest, improved pasture, and cypress). It was also close to cluster 3 (land uses of deciduous and oak) (Fig. 5). Cluster 1 (land uses of hardwood and sugar cane) and cluster a (soil types of Alfisol, Inceptisol, and Spodosol) were close together, but they were anti-correlative to cluster IV (water-extractable Fe, Al, and Mn and soluble Cd, Pb, Cr, Co, and Ni) (Fig. 5). Furthermore, cluster 2 (land uses of field crop and row crop) and cluster b (soil types of Entisol, Mollisol, and Ultisol) were together. They had positive CV1 loadings and negative CV2 loadings, being anti-correlative to cluster I (water-extractable Ca Na, K, soil EC, TOC, and TN, and soluble N and Cu) (Fig. 5).

Concentrations of nutrients C, N, and P in soils were also pooled together for PCA analysis. It was observed that DOC and soil TOC and TN were clustered together (Fig. 6), which explained the close relationship of DOC to soil organic matter. Soluble

N and P had positive PC2 loadings, whereas DOC, extractable $\text{NH}_4\text{-N}$, and soil TOC and TN had negative PC2 loadings (Fig. 6). This provided the information of a close relationship of soluble P to soluble N other than DOC.

4 Discussion

4.1 DOC and Soluble N Concentrations as Affected by Land Uses and Soil Properties

Soil leaching is the predominant origin of dissolved organic matter in terrestrial catchments (Hejzlar et al. 2003); therefore, land use is influential on the export of DOM from soils to runoff water (Garnett et al. 2000). Previous studies stressed the importance of land use in controlling DOM export from soils (Nemeth et al. 1988; Huges et al. 1990; Saviozzi et al. 1994). In this study, two important land uses, sugar cane and field

Table 2 Soluble heavy metals in soils with varying soil types and land uses

		Co (mg kg ⁻¹)	Cr	Cu	Ni	Zn
Soil type	Alfisol	<MDL b	0.01±0.02b	0.39±0.20a	<MDL c	0.33±0.06b
	Entisol	0.02±0.04ab	0.01±0.02b	0.51±0.32a	0.06±0.08abc	0.29±0.13b
	Histosol	0.04±0.09ab	0.07±0.15a	0.72±0.76a	0.11±0.19ab	0.56±0.32a
	Inceptisol	<MDL b	0.01±0.02b	0.61±0.18a	0.01±0.02bc	0.41±0.09ab
	Mollisol	0.05±0.03a	<MDL b	0.46±0.29a	0.12±0.08a	0.28±0.05b
	Spodosol	0.02±0.03ab	<MDL b	0.47±0.36a	0.07±0.08abc	0.37±0.16b
	Ultisol	<MDL b	<MDL b	0.38±0.24a	<MDL c	0.29±0.09b
Land use	Citrus	0.05±0.04bc	0.02±0.02b	0.56±0.25b	0.12±0.10bc	0.38±0.09bcd
	Coniferous forest	0.08±0.06ab	0.01±0.01b	0.48±0.45b	0.18±0.14b	0.44±0.10bc
	Cypress	<MDL c	<MDL b	0.56±0.55b	<MDL c	0.37±0.12bcd
	Dairy	<MDL c	<MDL b	0.56±0.49b	<MDL c	0.47±0.33bc
	Deciduous	<MDL c	<MDL b	0.54±0.51b	<MDL c	0.35±0.20bcd
	Field crop	0.07±0.03ab	<MDL b	1.50±0.95a	0.18±0.10b	0.59±0.49b
	Hardwood/coniferous mixed	<MDL c	<MDL b	0.26±0.22b	<MDL c	0.30±0.14cd
	Improved pasture	0.03±0.02bc	0.01±0.02b	0.54±0.40b	0.10±0.06bc	0.33±0.10cd
	Mixshrub	<MDL c	<MDL b	0.43±0.32b	<MDL c	0.28±0.08cd
	Oak	<MDL c	<MDL b	0.44±0.13b	0.01±0.01c	0.30±0.10cd
	Ornamentals	<MDL c	<MDL b	0.07±0.02b	<MDL c	0.18±0.05d
	Residential	<MDL c	<MDL b	0.47±0.07b	<MDL c	0.35±0.07bcd
	Row crop	<MDL c	<MDL b	0.23±0.24b	<MDL c	0.17±0.10d
	Sugar cane	0.10±0.16a	0.26±0.20a	0.32±0.22b	0.31±0.28a	0.80±0.25a
	Tree crop	<MDL c	0.01±0.02b	0.52±0.32b	0.01±0.01c	0.36±0.13bcd
	Unimproved pasture	<MDL c	<MDL b	0.40±0.20b	0.02±0.02c	0.42±0.19bcd

Data are presented as mean±1 STDEV. Different letters under the same classification are statistically different (*P* <0.05). Elements below MDL were given a value of zero in the calculation

MDL method detection limit

crop (totally accounting for 15% in this region), contributed the highest DOC in soils (Table 1). This is probably

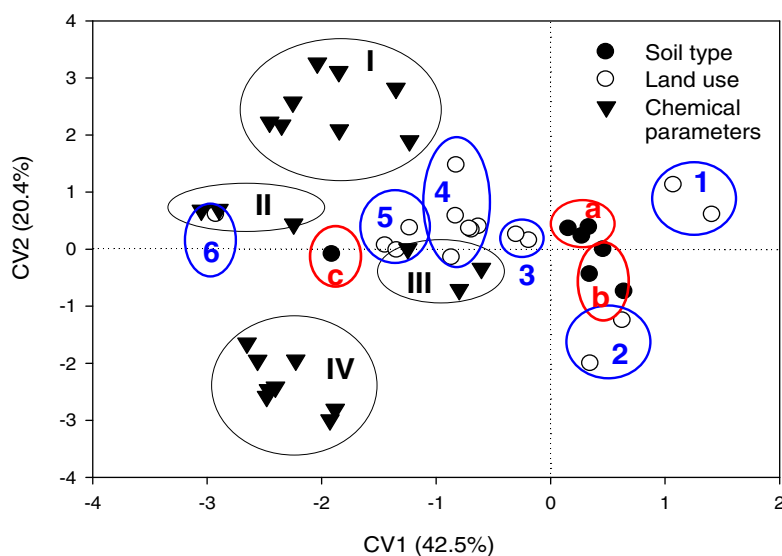
due to their cultivation on Histosol or the extra addition of organic matters from the burning or decay of crop

Table 3 Correlations among DOC, soluble N and P, and soil pH, EC, and DI water-extractable cations

	pH	EC	Al	Fe	K	Na	Ca	Mg	Mn	Cd
DOC	0.09	0.63**	0.54**	0.65**	0.66**	0.45**	0.69**	0.92**	0.60**	0.14
Soluble N	0.12	0.56**	0.09	0.14	0.74**	0.50**	0.69**	0.54**	0.27**	0.02
Soluble P	0.27**	0.09	0.28**	0.12	0.30**	0.10	0.21*	0.15	0.14	0.05
	Co	Cr	Cu	Ni	Pb	Zn	NH ₄ -N	Soluble P	Soluble N	DOC
DOC	0.45**	0.61**	0.36	0.49**	0.16	0.62**	0.48**	0.14	0.56**	1.00**
Soluble N	0.26**	0.17	0.53**	0.25**	0.04	0.51**	0.06	0.44**	1.00**	0.56**
Soluble P	0.14	0.22*	0.17	0.19*	0.14	0.18*	-0.05	1.00**	0.44**	0.14

* and ** represent significance levels of *P* <0.05, and 0.01, respectively. *N*=124

Fig. 5 Combined plots of canonical variate analysis loadings on CV1–CV2 for soil type, land use, and chemical parameter in sampled soils



- | | |
|---|---|
| a. Alfisol, Inceptisol, Spodosol | 1. Hardwood, Sugar cane |
| b. Entisol, Mollisol, Ultisol | 2. Field crop, Row crop |
| c. Histosol | 3. Deciduous, Oak |
| I. Ca, EC, Na, TOC, TN, K, Soluble N, Cu | 4. Citrus, Mixshrub, Ornamentals
Tree crop, Unimproved pasture,
Resident |
| II. Mg, DOC, Zn | 5. Coniferous forest, Improved pasture,
Cypress |
| III. Soluble P, pH, NH ₄ -N | 6. Dairy |
| IV. Cd, Pb, Cr, Fe, Al, Co, Mn, Ni | |

straws. It is reported that buried straw had faster decay rate than pine needles or maple leaves (Ellert and Gregorich 1995). No significant differences in DOC and soluble N were observed under other land uses (Table 1), which supported previous reports (Deluca and Keeney 1993; Corre et al. 1999).

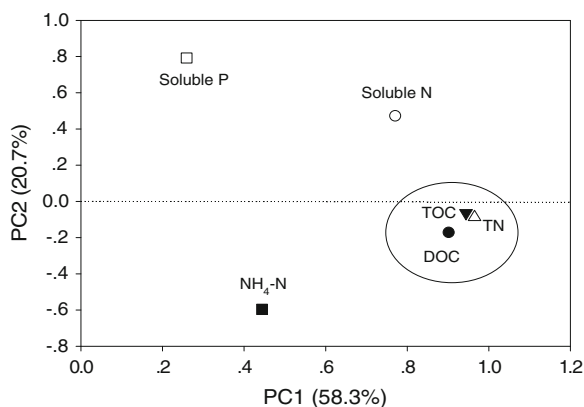


Fig. 6 Plots of PCA loadings on PC1–PC2 for the relationships of C, N, and P in sampled soils

Soils under pasture and grassland can result in more SOC sequestration than under forest (Ussiri and Lal 2005); therefore, DOC concentration in forest soils is generally higher than that in pasture/grassland soils (Haynes 2000; Chantigny 2003). However, DOC was not significantly different between forest soils and pasture soils in this study (Table 1), probably suggesting that beef cattle feces could offer additional dissolved organic carbon sources for pasture soils (Mctiernan et al. 2001). Improved and non-improved pastures had similar concentrations of DOC and soluble N in soils, indicating that dissolved organic matter was not apparently N-fertilizer dependent under the management practice of forage grazing. This agreed with the study of Rochette and Gregorich (1998). McDowell et al. (1998) suggested a possible consumption of dissolved organic carbon by soil microorganisms with N application; however, Yano et al. (2000) regarded no biodegradable DOC decline with long-term N addition in forest soil as abiotic N retention.

The dissolved fraction of organic carbon normally constitutes less than 1% of soil total organic carbon

(Zsolnay 2003), and water-extractable organic C from “root-free fresh” organic layers comprised of roughly 0.25% of soil TOC (Hagedorn et al. 2008). However, soils under citrus, unimproved and improved pasture, row crop, and tree crops had a DOC/TOC percentage greater than 1%, and soils with varying land uses had a soluble N/TN percentage >1% (Table 1). This suggested that application of N fertilizer could result in a larger proportion of DOM in SOM (Liu et al. 1995). The highest DOC in soils under sugar cane and field crop and the highest soluble N under field crop were not proportional to their smallest percentages of DOC/TOC and soluble N/TN (Table 1). This complied with the statement that the quantities of organic matter in soils prevailed in the production of dissolved organic matters (Kalbitz et al. 2000).

Soil properties, such as Al and Fe oxides and clay minerals, can influence dissolved organic matter in soils (Chantigny 2003). Significant correlations of DOC and soluble N with water extractable K, Na, Ca, and Mg, and soil EC (Table 3, Fig. 5) gave the information that in the studied soils, DOC and soluble N were closely associated with soluble mineral cations. Such correlations were also observed in water-extractable Al, Fe, and Mn with DOC (Table 3). These results may offer an indirect evidence for the importance of adsorption mechanism for DOC in soils. Jardine et al. (1989) suggested the dominate mechanism for DOC retention in soil as physical adsorption, which is pH dependent. Soil pH elevation was reported to increase DOC in soils (Hartikainen and Yli-Halla 1996). However, no significant correlations between DOC and soil pH were observed in this study (Table 3), which might suggest a possible adsorption diminishing mechanism for dissolve organic matters by pH in the studied soils (Kaiser and Zech 1998). The significant correlation between DOC and water extractable $\text{NH}_4\text{-N}$ (Table 3) supported the result from a previous laboratory experiment (Myers and Thien 1988).

Soil type (soil category) affecting the variation of DOC or soluble N was seldom reported, probably due to the complexity of vegetation. In the studied soils, Histosol was rich in organic matters (77.3 g kg^{-1} of TOC); therefore, the highest DOC was expected from Histosol (Table 1). This supported the statement that soil total organic matter is important in controlling the production of dissolved organic matter in soils (Kalbitz et al. 2000). High DOC concentration in Spodosol was also reported (Christ and David 1996).

Variations of dissolved organic matters in soil horizons are controlled by hydrologic variability and mineral compositions in soil profiles (Kalbitz et al. 2000). Even though a decreased tendency of DOC and soluble N with soil depth was noticed, the reverse did occur (Fig. 2). This may be attributed to the strong adsorption of dissolved organic matter onto mineral surface, which is indirectly supported by the significant correlations among DOC and soluble N with water-extractable K, Na, Ca, and Mg (Table 3). But microbial activity may be critical in the upper layer (Kalbitz et al. 2000), resulting in greater soluble N in the upper soil (0–20 cm). This agreed with the observation of Clarke et al. (2005) who noticed the highest DOC in Spodosol profile being within the upper layer (organic layer). Kalbitz et al. (2000) reported a sharp decrease of DOC in soil profiles from $20\text{--}75 \text{ mg L}^{-1}$ in horizon A to $\sim 1.2 \text{ mg L}^{-1}$ in horizon C. Physical adsorption and ligand exchange are two dominant mechanisms for variations of dissolved organic matters in soil profile (Jardine et al. 1989; Edwards et al. 1996). However, greater DOC/TOC and soluble N/TN in the deeper layer (40–100 cm) could be related to the less total organic matter.

4.2 Variations of Water-Extractable C/N and C/P Ratios in Soils

Dissolved organic matter in soil is mainly originated from plant litter, soil humus, microbial biomass, or root exudates (Kalbitz et al. 2000); therefore, DOC is highly dependent on plant species that produce litters, which varied greatly with land uses. The C/N ratio was previously applied to predict the potential loss of dissolved inorganic N from leaching under various land uses (Kortelainen et al. 1997; Cairns et al. 2010). Dissolved organic N usually comprised a substantial fraction in the N loss in forest ecosystems (Hedin et al. 1995); therefore, a close relationship between water-extractable C/N ratios and soil total organic C/N ratios can be expected (Neff et al. 2000). In the studied soils, water-extractable C/N ratios were generally less than 15 (the critical limit in soil for N release), regardless of the land use class, soil type, or soil depth (Figs. 3 and 4). Our values were lower than those reported by Neff et al. (2000) for either tree trimmings (C/N \sim 16) or hardwood barks (C/N=100–400). Such difference could be attributed to the difference in geographical location and long-term N fertilization (Neff et al. 2000). For example, in the Lake Okeechobee watershed, it is estimated that 998,614 tons

of TN were preserved in the 0–20 cm of Spodosol in a 458,531-ha area, suggesting a potential release of N into runoff water.

Water-extractable C/P ratios ranged in 3.19–2328 and the lowest C/P ratios were from soils under the land uses of dairy, citrus, improved pasture and resident area (13.1–58.4) (Fig. 4). The lowest values were smaller than the report value in soils (186) (Cleveland and Liptzin 2007) or the Redfield ratio (106) (Sterner and Elser 2002). This hints a highly potential release of P from soils under these land uses. However, the water-extractable C/P ratios in soils under hardwood (908), cypress (507), and unimproved pasture (490) were far greater than 186, but lower than those in tree foliage (1,334) and tree litter (3,144) (McGroddy et al. 2004). This result suggested that the addition of vegetation debris in soils could elevate their water-extractable C/P ratios. This process is beneficial to the resistance of P from leaching loss. The water-extractable C/P ratios in Inceptisol (31.6 in average) and Mollisol (89.7 in average) (Fig. 3) were less than the Redfield ratio (106) and the report value (186) by Cleveland and Liptzin (2007); however, the C/P ratios were >200 in other soil types (Fig. 3). The average C/P ratio in the upper soil (0–20 cm) was 179, which is greater than the Redfield ratio (106). However, its variation range (6.47–2,151) was wider than the range (40–800) reported by Neff et al (2000). Chemical factor, such as P bound to Ca forming an oxidation-resistant Ca-bound fraction under sugar cane cultivation in Florida (Wright 2009), might explain the high water-extractable C/P ratios in these soils. The variation range of C/P is strongly geographical location dependent and could be related to long-term P fertilization (Neff et al. 2000).

Water-extractable C, N, and P approximately represent soluble amounts of C, N, and P in soil solution (Jones and Willet 2006); therefore, lower water-extractable C/N and C/P ratios in some soils (Figs. 3 and 4) indicated a potential movement of N and P from soil solution to runoff water when subjected to rainfall events. This result suggested a potential N and P loss from some upper soils into the watershed of Lake Okeechobee.

5 Conclusions

Dissolved organic carbon and soluble N in soils from the Lake Okeechobee watershed were in close relations

to land uses as well as soil chemical properties other than pH. Water-extractable C/N and C/P ratios varied greatly with land uses. Land uses by dairy, resident, or coniferous forest could result in potential loss of N, whereas dairy or citrus the loss of P if subjected to leaching or surface runoff. Dissolved organic carbon in soils was closely associated with soluble heavy metals Co, Cr, Ni, and Zn, whereas water soluble N with soluble Cu and P. Export of dissolved organic carbon into water bodies could be accompanied with the export of N, P, and heavy metals. But this process is significantly affected by land use, soil type, or some soil chemical properties.

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