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Chemical and carbon isotopic evidence for the source and fate of dissolved organic matter in the northern Everglades

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Abstract. Surface waters in the Florida Everglades contain high levels of dissolved organic carbon (DOC) compounds. $\delta^{13}C$ values of DOC samples collected from the northern Everglades indicate that less than about 23% of the DOC was derived from sugarcane (the dominant agricultural crop in the area), and the amount of DOC from sugarcane was greater during the dry period. Most of the DOC (> 50%) in the northern Everglades was in the low molecular weight (< 1000 Dalton) fraction (LMW-DOC). The relative amount of high molecular weight DOC (HMW-DOC) was higher in the wet period than in the dry period. Radiocarbon ages of the DOC ranged from "> modern" to about 2400 years B.P., indicating that DOC was derived from both historic peat deposits and modern vegetation. At each site, the HMW-DOC had older radiocarbon ages than the LMW-DOC, and therefore contained a greater fraction of DOC derived from the historic peat deposits. It appears that at least some of the old DOC compounds from the historic peat deposits were decomposed during their residence in the surface water system in the northern Everglades, and the LMW-DOC was more microbially labile than the HMW-DOC. Our analysis suggests that accelerated decomposition of organic matter in the historic peat deposits (due to land-use change) could be a significant source of DOC and nutrients in the northern Everglades. Our data also suggest that the radiocarbon signature of DOC could be used as a sensitive indicator of the overall effectiveness of a wetland restoration project.

Introduction

Many surface waters in Florida contain high concentrations of dissolved organic carbon (DOC) compounds. It is generally believed that DOC is the main source of energy for heterotrophic bacteria (Williams and Carlucci 1976) and plays an important role in the cycling and transport of carbon (C), nitrogen (N), phosphorus (P), and metals (McKnight 1981; McKnight et al. 1985; Anderson and Morel 1982). The Everglades ecosystem in south Florida has historically adapted to low external nutrient loads, relying primarily on phosphorus-limited production of plant biomass and slow recycling of organic substrates by a nutrient-limited microbial pool (Reddy et al. 1999). Pristine Everglades wetlands typically consist of extensive sawgrass (*Cladium jamaicense*) marsh communities interspersed with attached and floating periphyton mats in the relatively non-vegetated sloughs. However, rapid development in South Florida during recent decades has significantly altered both the hydrology and water quality of the wetland ecosystem. Increased nutrient (particularly phosphorus) loading (from agricultural and urban runoff) into the Everglades has created a water-quality gradient that is associated with noticeable ecological changes in the marsh (Figure 1). In heavily polluted areas of the marsh, sawgrass meadows have been overtaken by dense cattails (*Typha domingensis*) which are better adapted to high nutrient conditions (McCormick and O'Dell 1996). Although the effects of nutrient loading and hydrology on plant communities are clearly evident (Figure 1), very little information is available on the influence of these factors on biogeochemical processes regulating nutrient availability and cycling in impacted and non-impacted areas (Reddy et al. 1999; Richardson 1999). Understanding the origin and cycling of DOC can help in understanding nutrient availability and the mobility and toxicity of metals.

Carbon isotopes are very useful tracers of organic substances in systems where potential sources have distinct isotopic signatures. Terrestrial plants can be divided into two major carbon isotopic groups depending on their photosynthetic pathways: C4 plants, using the C4 or Hatch-Slack photosynthetic pathway, and C3 plants, using the C3 or Calvin photosynthetic pathway (Deines 1980; O'Leary 1988; Farquhar et al. 1989). C3 plants discriminate against $^{13}CO_2$ during photosynthesis to a greater extent than C4 plants. As a result of this isotopic fractionation, C4 plants have $\delta^{13}C$ values between −9 to −17‰, with an average $\delta^{13}C$ value of −13‰; whereas C_3 plants have $\delta^{13}C$ values ranging from −23 to −34‰, with an average value of −27‰ (Deines 1980). In general, different species of plants growing in a given environment may have different stable C isotopic values, but individuals of the same species growing in the same area have similar values (Deines 1980; Faure 1986). Because organic substances (e.g., DOC, soil organic matter, etc.) have a $\delta^{13}C$ value comparable to that of the source plant material, the distinct $\delta^{13}C$ values of different photosynthetic-type plants can be used to determine the sources of dissolved, particulate and soil/sedimentary organic matter (e.g., Parker et al. (1972); Spiker and Rubin (1975); Farquhar et al. (1989); Murphy et al. (1989a, 1989b); Aravena and Wassenaar (1993); Wang et al. (1993); France-Lanord and Derry (1994)). Radioactive carbon isotope ^{14}C (with a half life of 5730 years), on the other hand, can be used to distinguish recent photosynthate (originated from modern plant material) from old soil/sedimentary organic matter.

In south Florida, the remaining Everglades is dominated by sawgrass, cattail, and a few other fresh water marsh plants, which are C3 plants. On the other hand, the Everglades Agricultural Area has been used intensively for sugarcane farming. Since sugarcane is a C4 plant, DOC compounds that originate from sugarcane are expected to carry a distinct $\delta^{13}C$ signature from those derived from marsh plants and peat deposits. Therefore, the relative contribution of sugarcane to the DOC pool in the Florida Everglades can be estimated by analyzing and comparing the stable

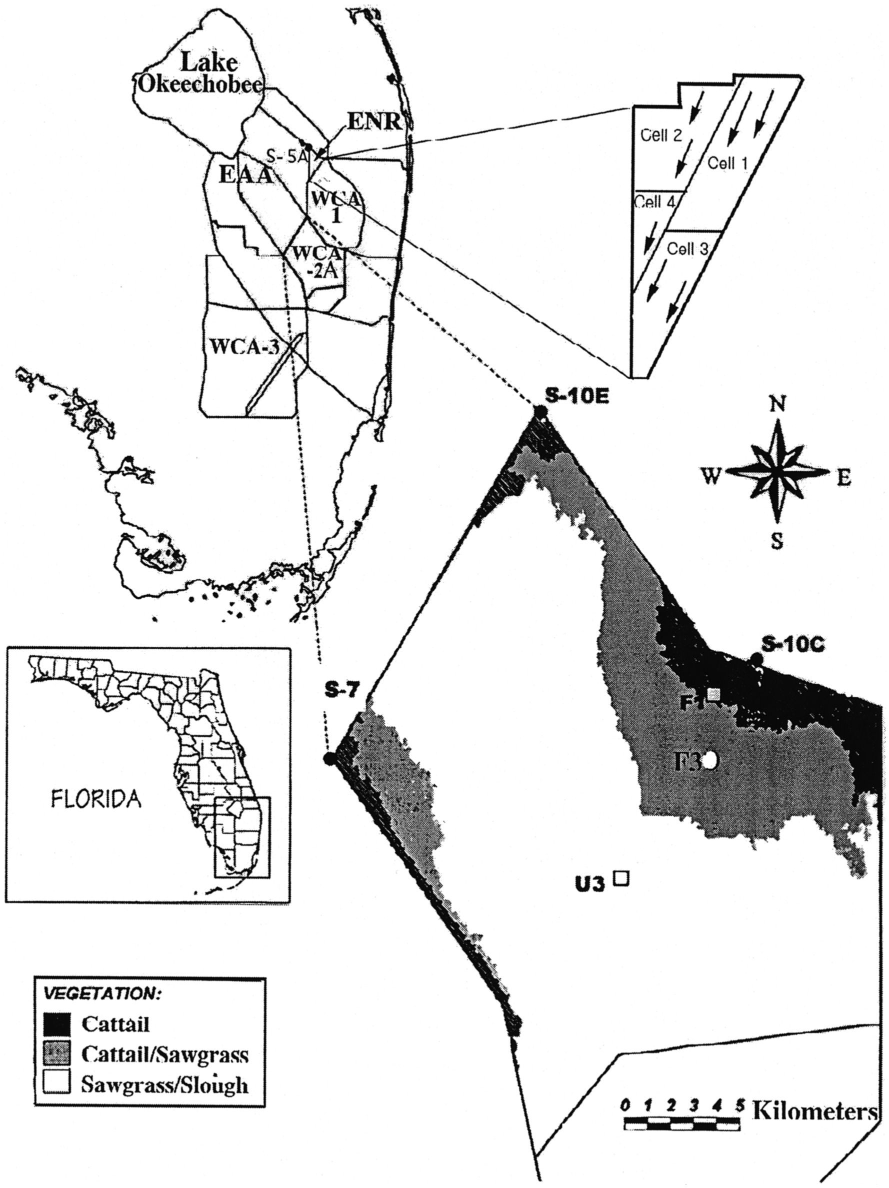

Figure 1. Locations of the study area and sampling sites

C isotopic ratios of DOC with those of potential sources (i.e., wetland plants, peat deposits, and sugarcane). While stable C isotope ratios serve to differentiate C derived from different photosynthetic-type plants, the radiocarbon signature can be used to estimate the relative contribution of the historic peat deposits to various C pools in the Everglades area, because the peat deposits were formed over thousands of years (Stephens 1984) and contain significantly less ^{14}C than modern plants (e.g., sugarcane and emergent plants).

Here we present a study on the source and fate of DOC in the northern Everglades based on natural abundances of ^{13}C and ^{14}C isotopes and the chemical characteristics of DOC, and discuss its implications concerning wetland restoration and management.

Study sites

The focus of this study is the Everglades Nutrient Removal Project (ENR) and the Water Conservation Area 2A (WCA-2A), adjacent to the Everglades Agricultural Area (EAA) in the Northern Everglades in South Florida (Figure 1).

The ENR is an artificial wetland that was constructed in 1994 on agricultural land. It consists of two parallel flow-ways: Cell 1 to Cell 3 and Cell 2 to Cell 4 (Figure 1). The plant community in each cell is manipulated to test the phosphorus removal efficiency. The goal of the ENR is to test the constructed wetland treatment methodology for reducing total nutrient loads entering the Water Conservation Areas and to gain experience for larger-scale application of the constructed wetland water treatment technique. So far the project seems to be working – the very high total phosphorus content of the inflow water (i.e., above 100 μg/L) is significantly reduced upon passing through the ENR to below the requirement (i.e., 50 μg/L) established by the Everglades Forever Act of 1994. Outflow from the ENR is combined with untreated runoff in the canals leading southward to the Water Conservation Areas. Samples for DOC analyses were collected at three locations in the ENR according to the general flow regime: supply canal ("ENR-in"), in the flow from Cell 1 to 3 ("ENR-mid"), and in the outflow ("ENR-out").

The Water Conservation Areas make up the largest remnants of the original Everglades wetland ecosystem outside the Everglades National Park. About 70% of the water input to the Water Conservation Areas is from rainfall, with the rest coming from agricultural and urban runoff, and discharges from Lake Okeechobee. Inflow into the WCA-2A is a mixture of outflow from the ENR, untreated runoff in the canal and outflow from the WCA-1. Samples were collected at four sites – S-10C, F1, F3 and U3 – in the WCA-2A in a transect along the general flow path for DOC analyses (Figure 1). Site S-10C is where canal water mixes with outflow from the WCA-1 and discharges into the WCA-2A. Site F1 is in the polluted area where native sawgrasses have been replaced by dense cattails (*Typha domingensis*), and F3 is in a mixed sawgrass (*Cladium jamaicense*)/cattail zone. Site U3 is in the relatively pristine sawgrass/slough area that is little affected by agricultural runoff. Canal discharges into the ENR and WCA-2A are controlled by the South Florida Water Management District through a series of pumping stations. The residence times of water in the study area were estimated to be about 2–4 weeks during our sampling periods.

Field and laboratory methods

We analyzed the stable C isotopic composition of various potential C sources (i.e., plants and soils/sediments) as well as DOC in the northern Everglades. Soil samples were collected with a coring apparatus (with a 2" O.D. Butyrate plastic liner) for total carbon and ^{13}C analysis. Water samples (22 liters) for DOC analyses were pre-filtered through 0.2 μm filters (Figure 3). The filtered water was then processed by cross-flow ultrafiltration using a Filtron Centrasette system holding 4 stacked 0.5 m^2 polysulfone 1,000 Dalton cutoff membrane cassettes (Powell et al. 1996; Guentzel et al. 1996; Reitmeyer et al. 1996) into two molecular weight DOC fractions – permeate and retentate (Figure 3). Permeate samples contain primarily low molecular weight DOC (< 1,000 Dalton) and retentate samples are mixtures of concentrated high molecular weight DOC (with a concentration factor of 10) and some low molecular weight DOC at the same concentration as in the permeate and the original water samples. The recovery of total DOC during ultrafiltration is always less than 100%, due primarily to adsorption of DOC on the ultrafiltration membrane, and ranged from 76 to 98% for our samples. The chemical and isotopic concentrations of low molecular weight DOC (LMW-DOC) and high molecular weight DOC (HMW-DOC) were calculated using mass balance relationships and measurements of permeate and retentate samples.

Soil samples were dried at 60 °C and then ground into powder. The powder was treated with 10% HCl to dissolve any carbonate in the sample, cleaned with distilled water, and freeze-dried. Plant samples were washed with 10% HCl, rinsed with distilled water, dried at 60 °C and then ground into powder. CO_2 was produced by combustion of the sample (i.e., soil or plant) with CuO, Cu, and silver foil in a vycor tube under vacuum at 875 °C for 2 hours, and then purified cryogenically (Minagawa et al. 1984). The stable isotope ratio of the purified CO_2 was then measured on a stable isotope ratio mass spectrometer. Weight percentage C content was determined from CO_2 yield. DOC samples were prepared following the procedure described in Peterson et al. (1994). 25 ml water samples were placed in pre-combusted 9 mm O.D. Pyrex tubes, acidified with about 50 μl of 6 N HCl and freeze-dried. The samples were then combusted with CuO, Cu and silver foil under vacuum at 550 °C for 4 hours. The CO_2 was extracted cryogenically and its stable carbon isotopic ratios were measured. We tested the procedure by processing our lab organic matter standard in the same manner as DOC samples for stable carbon isotope analysis and found that a Foreline Trap (EDWARDS International) was sufficient to prevent pump oil from contaminating the samples.

The stable C isotope data are reported in the standard notation relative to the PDB standard as $\delta^{13}C = [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{PDB} - 1] \times 1000$. The radiocarbon content of purified CO_2 was determined on an accelerator mass spectrometer at the NSF radiocarbon facility at the University of Arizona and the National Ocean Sciences AMS Facility at the Woods Hole Oceanographic Institution. ^{14}C data are reported as: $\Delta^{14}C = [A_{SN}/A_{ABS}-1]^{*}\ 1000‰$, where A_{SN} is the specific activity of a sample normalized to $\delta^{13}C = -25‰$ using $^{13}C/^{12}C$ ratios measured in a stable isotope ratio mass spectrometer, and A_{ABS} is the absolute international standard activity (Stuiver and Polach 1977). Analytical precision (one σ) is ± 0.1‰ for ^{13}C analysis and better than ± 9‰ for ^{14}C analysis.

DOC concentration was determined by high-temperature catalytic oxidation using a Shimadzu-5050 TOC analyzer after removal of dissolved inorganic carbon in the sample. Dissolved organic nitrogen (DON) was determined as nitrate following persulfate/autoclave oxidation. Total dissolved phosphate (TDP) and soluble reactive phosphate (SRP) which includes ortho-P and perhaps a small fraction of acid-hydrolyzable organic phosphate were determined using standard colorimetric methods (EPA 365.1). Total dissolved organic phosphorus (DOP) was calculated as the difference between TDP and soluble reactive phosphorus (SRP).

Results and discussion

Carbon isotopic characteristics of potential sources of DOC

In the surface waters in the northern Everglades, DOC can come from various potential sources, including the historic peat deposits, modern wetland vegetation, algae, and sugarcane (the dominant agricultural crop in the EAA). In order to determine the sources of DOC in surface waters in the Everglades Area, we analyzed the stable C isotopic compositions of soils, sediments and plants collected from the ENR, WCA-2A and EAA (Table 1). Our data show that the major plants in the WCA-2A and ENR have $\delta^{13}C$ values ranging from −24.3 to −29.3‰ with an average of −27.0 ± 1.6‰ (Table 1), which are, as expected, within the $\delta^{13}C$ range of C3 plants. On the other hand, the dominant agricultural crop in the area, the sugarcane (a C4 plant), has an average $\delta^{13}C$ of −11.4 ± 0.4‰ (Table 1). Although it is difficult to determine the amounts of DOC derived from different plant species, various potential DOC sources in the area can be grouped into two broad categories with distinct $\delta^{13}C$ values: (1) sugarcane and (2) wetland vegetation and peat (Figure 2). The large stable C isotopic difference of about 16‰ between these two source groups thus allows us to assess the relative importance of sugarcane in contributing to the soil organic C and DOC pools and place an upper limit on the amount of DOC originating from sugarcane.

$\delta^{13}C$ values of peat deposits (0-5 cm) in the WCA-2A range from −27.3 to −29.9‰, with an average of −28.5 ± 1.0‰, which is slightly lower than the $\delta^{13}C$ values of major plants (i.e., sawgrass, periphyton and cattail, with an average $\delta^{13}C$ = −27.0 ± 1.6‰) contributing to the peat. It is known that lipids, lignin and cellulose have lower $\delta^{13}C$ values than bulk plant tissue, whereas sugars, amino acids, hemicellulose and pectin are more enriched in ^{13}C than bulk plant tissue (Deines 1980). Therefore, the slight isotopic difference between the peat and plants in the WCA-2A could be caused by preferential preservation of different plant biochemical fractions such as lignin and/or lipids and/or cellulose. This preferential preservation has been observed in some other wetlands (Benner et al. 1987). However, studies have shown that preferential preservation does not appear to lower the $\delta^{13}C$

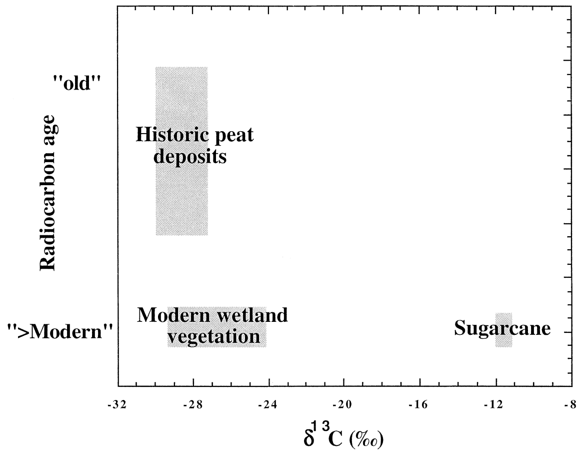

Figure 2. Carbon isotopic characteristics of potential sources of DOC in the Everglades area, showing that stable and radioactive carbon isotopes can be used to differentiate DOC derived from various sources

values of either residual litter or the associated soil organic matter in well-drained terrestrial environments (see review by Boutton (1996)). Soils collected from various locations in the EAA displayed similar $\delta^{13}C$ (soil organic matter)-depth profiles, with $\delta^{13}C$ values becoming slightly more negative with increasing depth (Table 1). This $\delta^{13}C$-depth trend is opposite to what has been observed in many well-drained soils. Many studies (e.g., Rosenfeld and Silverman (1959); Kaplan and Rittenberg (1964); Goh et al. (1976, 1977); O'Brien and Stout (1978); Schleser and Bertram (1981); Schleser and Pohling (1980); Boutton (1996); Dzurec et al. (1985); Gulliet et al. (1988)) show that organic matter is generally enriched in ^{13}C by about 1-3‰ with age and increasing depth probably because of fractionation during respiration of soil decomposer organisms. Therefore, the decreasing $\delta^{13}C$ values with depth in agricultural soils in the northern Everglades can not be explained by isotopic fractionation during decomposition, but rather reflects the decreasing contribution of sugarcane crop to the soil organic C pool with depth as one would expect. This is because most of the sugarcane-C input is from litter/crop residue and from root growth and decay, which decreases with depth. Agriculture began in the area after the drainage projects of the 1906-27 era and intensified after the water control projects of the early 1950s (Snyder and Davidson 1994). If we assume that the historic peat deposits in the EAA have the same $\delta^{13}C$ value (of about −28‰) as the preserved peats in the WCA-2A wetland, the relative amount of organic matter derived from sugarcane can be estimated (Table 1) using a mass balance relationship (i.e., $\delta^{13}C_{soil} = \delta^{13}C_{old\ peat}\ {}^{*}(1\text{-}X) + \delta^{13}C_{sugarcane}\ {}^{*}X$, where X is the fraction of organic C from sugarcane). However, if we assume that the "old" peat in the EAA has a $\delta^{13}C$ value of −27‰ (i.e., the average $\delta^{13}C$ of wetland plants in the area), the relative amounts of sugarcane-derived soil organic C would be about 5% lower than those presented in Table 1. Thus, our C isotope data suggest that sugarcane contributed about 10 to 20% of the total soil organic C in the upper 50 cm

Table 1. Carbon isotopic composition of soils, sediments and plants

Sample type	Sampling location	$\delta^{13}C$ (‰)	Carbon content (%)	Estimated sugarcane content (%)
Peat soils:				
0-5 cm	EAA	−24.91±0.18 (3)*	56.8±1.8 (3)	19±1 (3)
5-10 cm	EAA	−25.01±0.05 (3)	56.7±1.1 (3)	18±0.3 (3)
10-20 cm	EAA	−25.17±0.04 (3)	57.1±0.8 (3)	17±0.3 (3)
20-30 cm	EAA	−25.38±0.02 (3)	57.4±1.8 (3)	16±0.1 (3)
30-40 cm	EAA	−25.3 (1)	65.9	16.2
Sediments:				
0-5 cm (peat)	ENR	−25.52±0.16 (3)	61.3±2.4 (3)	
0-5 cm (peat)	WCA-2A	−28.53±0.95 (5)	55.2±1.9 (5)	
15-0 cm (detritus)	WCA-2A	−28.90±0.06 (2)	47.7±2.0 (2)	
Plants:				
Typha domingensis (cattail)	ENR	−27.2		
Eichhornia crassipes (water hyacinth)	ENR	−27.6		
Pistia stratiotes (water lettuce)	ENR	−27.6		
Ceratophyllum demersum (Coontail)	ENR	−28.6		
Najas quadalupensis (southern naiad)	ENR	−24.5		
Sagitaria latifolia (arrowhead)	ENR	−25.4		
Eleocharis interstincta (spikerush)	ENR	−28.5		
Sugarcane	EAA	−11.4±0.4 (2)		
Typha domingensis (Cattail)	WCA-2A	−27.3		
Cladium jamaicense (sawgrass)	WCA-2A	−26.4		
Nymphaea odorata (Water lily)	WCA-2A	−24.0±0.4 (2)		
Periphyton mat	WCA-2A	−27.2±2.1 (2)		
Utricularia macrorhiza (bladderwort)	WCA-2A	−29.3		
Utricularia Chara	WCA-2A	−27.8		
Eleocharis interstincta	WCA-2A	−25.4		

* Values are averages ± standard deviation. The numbers in brackets indicate the number of samples analyzed.

of the soil in the EAA after 40-50 years of intensive cultivation. While the fraction of sugarcane-derived soil organic C seems low, its amount (3600–8600 gC/m^2) is well within the range of normal upland soils. The parent material for the agricultural soil in the EAA is peat that formed under previous wetland conditions and contained many times more C than most upland soils. Conversion of wetland to agricultural land in the EAA has accelerated the decomposition of the historic peat, resulting in subsidence of the soil surface as if the peat was "evaporated" (Stephens 1984). The modern soil organic C (derived from sugarcane) is accumulated within the historic peat matrix. The low proportion of sugarcane-derived C in the total soil organic C pool reflects the difference in the rates of soil organic C accumulation

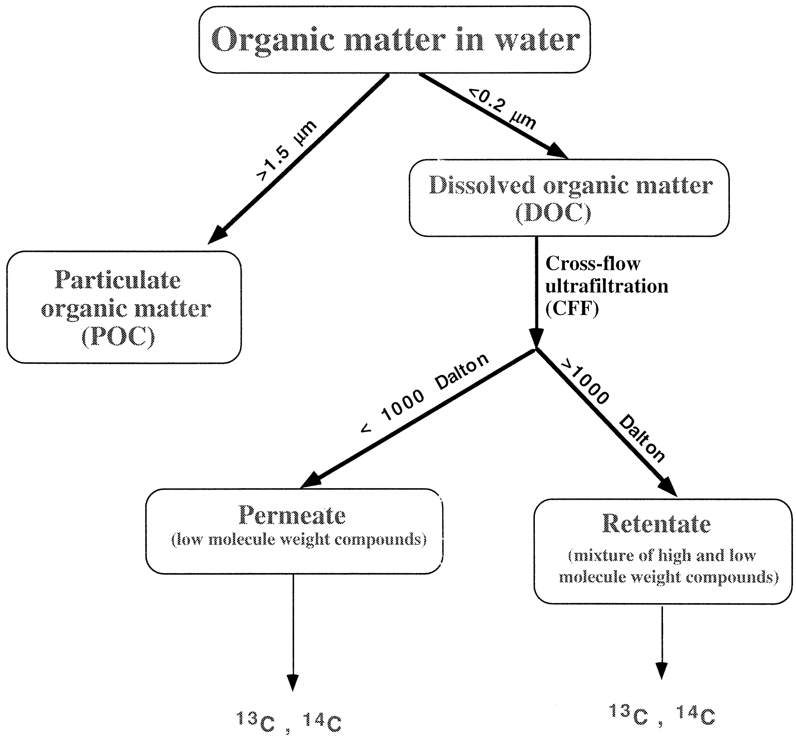

Figure 3. Schematic diagram showing the separation of the various organic carbon fractions in water for isotopic analyses

between two very different soil environments: previous wetland vs. present drained agricultural land.

Concentration and Distribution of DOC

A major fraction of the organic matter in surface waters is present in dissolved form as DOC. DOC consists of a wide spectrum of organic compounds, ranging from low molecular weight short-chain acids to high molecular weight molecules such as humic acids, and may influence water acidity, nutrient availability, and the mobility and toxicity of metals (Thurman 1985; McKnight et al. 1985). The DOC concentrations in surface waters in the northern Everglades varied significantly among sites and with season (Figure 4a). The average concentration of DOC for samples collected from our study sites in December 1997 and May 1998 was 32 mg C/L, with a range from 13 to 61 mg C/L. In the inflow waters to the ENR and WCA-2A, the highest concentration was found in the supply canal at the inlet of the ENR in December 1997. The concentration of DOC decreased from December 1997 to May 1998, mostly notably at the inlet of the ENR. The amount of nitrogen and phosphorus associated with DOC (i.e., DON – dissolved organic nitrogen, and

DOP – dissolved organic phosphorus) also varied among sites (Figure 4b, 4c). In May 1998, which was unexpectedly drier than December 1997, both DOC and DON increased as water passed through the ENR and WCA-2A due to production of DOC and DON within the wetlands. Our data show (Figure 4) that the amounts of DOC and DOP (and perhaps DON although we have no DON data from December 1997 for comparison), as well as soluble reactive phosphorus (SRP), were significantly higher in the inflow waters in the wet period (December 1997) than in the dry period (May 1998). The higher concentration of DOC and nutrients in inflows in the wet period is likely caused by higher runoff, which resulted in higher erosion and leaching of soil C and nutrients from the EAA. Most of the phosphorus in the inflow waters to the ENR and WCA-2A was in the low molecular weight fraction (Schaefer 2000). In both the ENR and WCA-2A, the amount of SRP decreased along the general flow regime except site F1 (Figure 4d), which suggests rapid consumption of SRP related to the P loading from the canals. Whereas, the concentration of DOP increased as water moved through the ENR and then decreased to detection limit levels (< 3 ppb) from site F1 to site U3 in the WCA-2A (Figure 4c). The higher concentrations of DOP and DOC at site F1, where native vegetation (sawgrass) has been overtaken by dense cattails, suggest a higher rate of decomposition of organic matter in the cattail area, resulting in a higher production of DOC and DOP at the site.

DOC analysis of permeate and retentate samples show that a large fraction of the DOC in water samples collected from the ENR and WCA-2A was in the LMW-DOC fraction with molecular weight less than 1000 Dalton (Figure 5). During the wet period (i.e., December 1997), HMW-DOC accounted for ∼22% of the total DOC in the inflow waters to both the ENR and WCA-2A. However, under the drier conditions in May 1998, the relative amount of HMW-DOC increased, making up 27% to 48% of the total DOC. The C/N ratio of the LMW-DOC ranged from 12 to 20, whereas the C/N ratio of the HMW-DOC varied from 22 to 37 in our samples. High C/N ratios are characteristic of non-proteinaceous material (e.g., lignin, cellulose, carbohydrate and lipid compounds). Therefore, the lower C/N ratios of the LMW-DOC in the ENR and WCA-2A suggest that the LMW-DOC contains a larger fraction of "high quality" organic matter and is probably more bioavailable.

Carbon isotopic composition of DOC

$\delta^{13}C$ values of DOC in water samples collected from the supply canals to the ENR and WCA-2A ranged from −24 to −28‰, indicating that less than 23% of the DOC was derived from sugarcane (Figure 6). The relative amount of sugarcane-derived DOC was estimated using a mass balance relationship, assuming that the DOC originated from peat and wetland vegetation has a $\delta^{13}C$ value of about −28‰ which is the average $\delta^{13}C$ value for the peat in the preserved wetland in the WCA-2A. The amount of DOC from sugarcane was greater in the May 1998 samples than in the December 1997 samples (Figure 6). This is probably because the low water level in May 1998 widened the unsaturated zone and increased the aerobic oxidation of crop residues tilled into the subsurface.

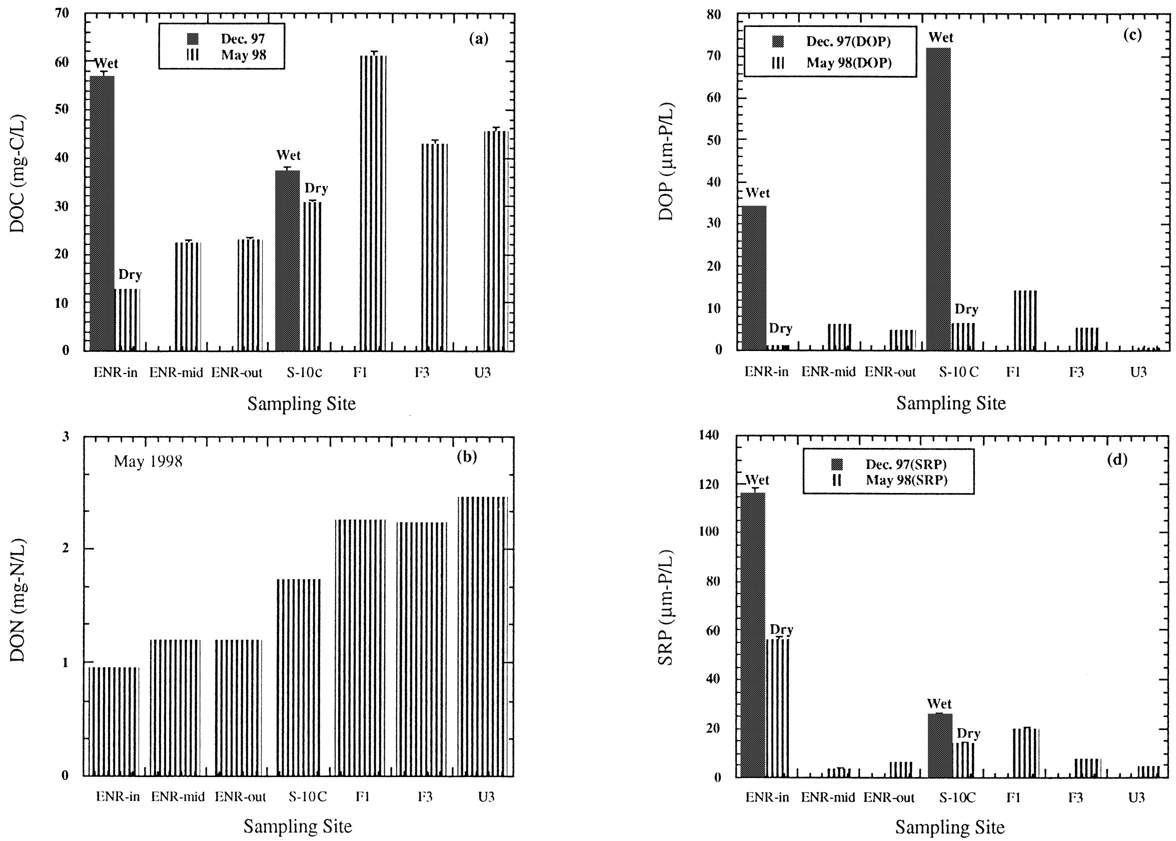

Figure 4. Concentrations of (a) dissolved organic carbon (DOC), (b) dissolved organic nitrogen (DON), (c) dissolved organic phosphorus (DOP), and (d) soluble reactive phosphorus (SRP) in Everglades waters sampled in December 1997 and May 1998.

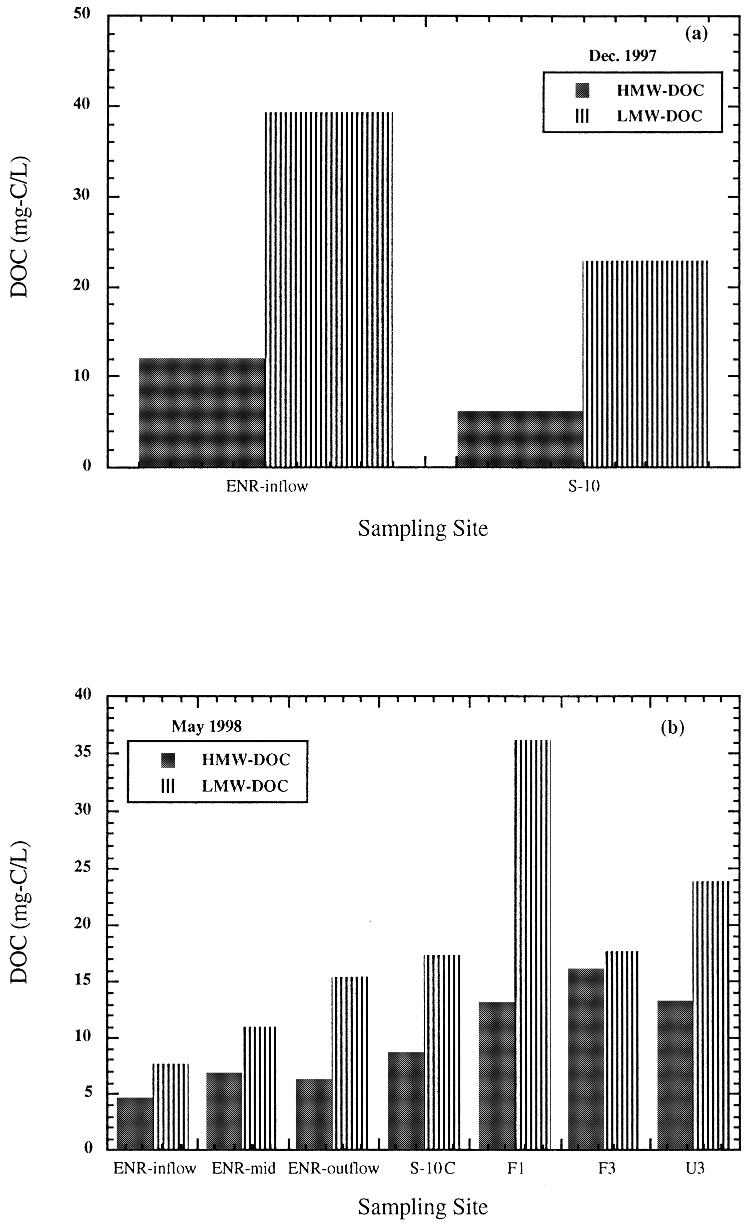

Figure 5. Distribution of DOC in Everglades waters sampled in December 1997 (a) and May 1998 (b), showing that the majority of the DOC was in the low molecular weight fraction.

The $\delta^{13}C$ values of DOC in the ENR outflow and in the inflow to the WCA-2A were more negative than those observed in the ENR inflow (Figure 7). This indicates that the relative amount of sugarcane-derived DOC decreased as water passed

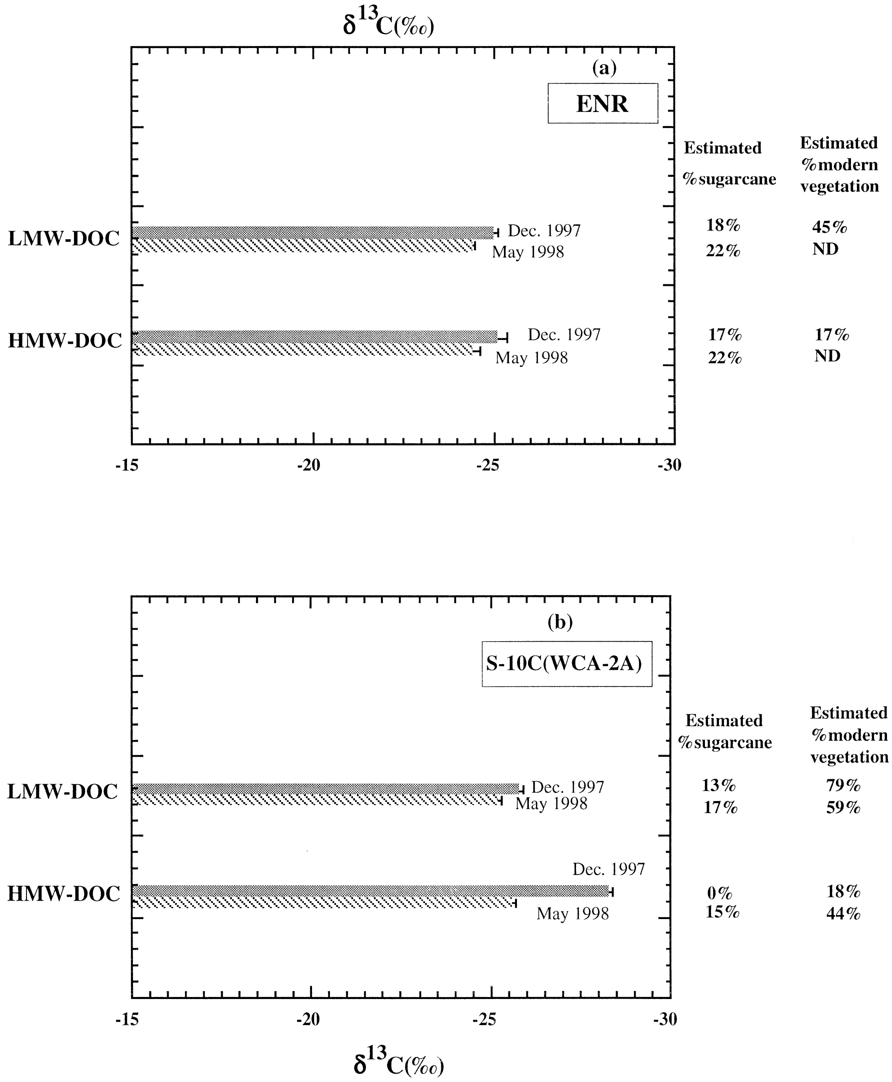

Figure 6. Comparison of stable C isotopic compositions of DOC in the inflow waters to ENR (a) and WCA-2A (b) between wet period (December 1997) and dry period (May 1998). The relative amounts of DOC originating from sugarcane and modern vegetation were estimated from the ^{13}C and ^{14}C data, respectively, based on assumptions discussed in the text.

through the ENR and also as canal water traveled south from the ENR to the WCA-2A. This implies that sugarcane-derived DOC compounds were being decomposed and/or diluted during their residence in the canal and in the ENR.

Radiocarbon ages of DOC in the northern Everglades ranged from "> modern" to about 2400 years BP (Figure 8), indicating that DOC compounds were derived from both historic peat deposits and modern plants. Before 1950, the $\Delta^{14}C$ values

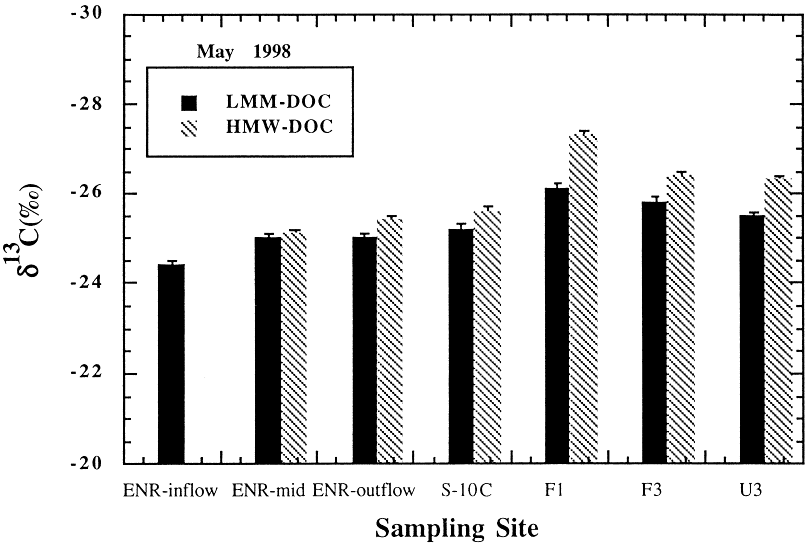

Figure 7. δ^{13}C of DOC in water samples collected in May 1998 from the ENR and WCA-2A.

of the atmosphere were relatively constant and were around 0‰. In the 1950s and early 1960s, the ^{14}C content of the atmosphere was elevated by several orders of magnitude by thermonuclear weapons testing. This pulse of ^{14}C or "bomb" ^{14}C has been declining towards pre-bomb levels since the test-ban treaty in 1963 (Suess 1955; Stuiver 1965; Levin et al. 1985; Manning et al. 1990; Wang et al. 1997). The "bomb" ^{14}C has tagged all contemporary organic matter produced by photosynthesis. Therefore, positive Δ^{14}C values indicate significant amounts of "bomb" ^{14}C and thus a "young" source. Negative Δ^{14}C values indicate that the C is derived from an "old" source (such as peat) that has a mean residence time long enough to reflect radioactive decay of cosmogenic ^{14}C. The very negative Δ^{14}C values of DOC in the inflows to the ENR and WCA-2A (except for the LMW-DOC sample collected at S-10C in Dec. 1997) indicate that the historic peat deposits were a significant source of DOC in these samples – an effect of accelerated decomposition of "old" peats due to the agricultural practices (Figure 8). On the other hand, the positive Δ^{14}C values of DOC at sites F3 and U3 in the WCA-2A indicate that the DOC was mainly derived from organic matter photosynthesized over the past 30-40 years. Available evidence suggests that the historic peat deposits in the Everglades were accumulated over the past several thousands of years (Stephens 1984). If we assume that the average age of the historic peat deposits in the EAA is 3200 years (equivalent to a Δ^{14}C value of −329‰) and that DOC derived from modern vegetation has a Δ^{14}C value of 100‰ (close to the present-day atmospheric value), the Δ^{14}C values of DOC in our samples would suggest that $\sim$17 to 45% of the DOC in the inflows to the ENR and WCA-2A was derived from modern vegetation (including sugarcane and macrophytes) except the LMW-DOC samples from S-10C (Figure 6). Under the same assumptions, mass balance calculations suggest that

~ 59 to 79% of the LMW-DOC in the samples from S-10C originated from modern vegetation. Therefore, the ^{14}C data support the conclusions drawn from the ^{13}C data concerning the contributions of sugarcane to the DOC pool (Figure 6).

The "very old" radiocarbon ages of DOC (i.e., very negative $\Delta^{14}C$ values) at the inlets of both the ENR and WCA-2A seem to be characteristic of disturbed wetlands. Our hypothesis is that in undisturbed/pristine wetlands most DOC compounds originate, directly or indirectly, from the modern primary production in the wetland system and should not be much older than a few years. Our limited ^{14}C data from the WCA-2A show that the $\Delta^{14}C$ values of DOC increased (became younger) along the water quality gradient from S-10C to F3 to U3 (Figure 8), which seem to support this hypothesis. If this is true, the older radiocarbon signature of DOC could be used as a sensitive indicator of the degree of disturbance of a wetland ecosystem from its natural state as a result of hydrological alterations. In turn, restoration of the natural hydro-geochemical processes in a disturbed wetland should result in the "rejuvenation" of the DOC radiocarbon age back towards more "modern" values. However, more data are needed before reaching any definitive conclusion.

As shown in Figure 8, the DOC collected from the inlet of the ENR had older radiocarbon ages (or more negative $\Delta^{14}C$ values) than the DOC collected from the inlet of the WCA-2A (i.e., S-10C site) and also the $\Delta^{14}C$ values of DOC became more positive along the water quality gradient (from S-10C to U3) in the WCA-2A. This indicates a decreased contribution from the old peat deposits to the total DOC pool as water traveled farther down the canal and also down the water quality gradient in the WCA-2A. These data suggest that at least some of the DOC derived from the historic peat deposits in the EAA was decomposed by sunlight and microorganisms during its residence in the canal and in the WCA-2A, implying that the "old" and young DOC may not be very different biologically. The decreasing trend in radiocarbon age of DOC along the general flow regime also suggests that there was no significant contribution to the DOC pool from upward movement of "old" groundwater. Although the relative importance of photochemical vs. microbial degradation of DOC at our sites can not be evaluated in this study, other studies in estuarine and riverine environments (e.g., Kieber et al. (1990); Mopper et al. (1991); Miller and Moran (1997); Moran et al. (2000)) have demonstrated that photochemical processes can decompose DOC into dissolved inorganic C and more biologically-labile compounds that can be utilized by microbes, thereby playing an important role in the cycling of DOC in surface waters. Recent incubation studies show that photochemical degradation of DOC tends to enrich the remaining DOC in ^{13}C by about 1–2‰ (Opsahl and Zepp 2001). However, our data show a slight decreasing trend in the ^{13}C values of DOC related to the general flow regime (Figure 7), suggesting that the effect of photochemical degradation on the $\delta^{13}C$ of DOC is overwhelmed by DOC production within the system. A study in Alaskan tundra (Schell 1983) also showed that C derived from old peat could be utilized by organisms. Analysis of the ^{14}C content of dissolved inorganic C, plants and peat/soil samples should allow assessment of the role of the historic peat de-

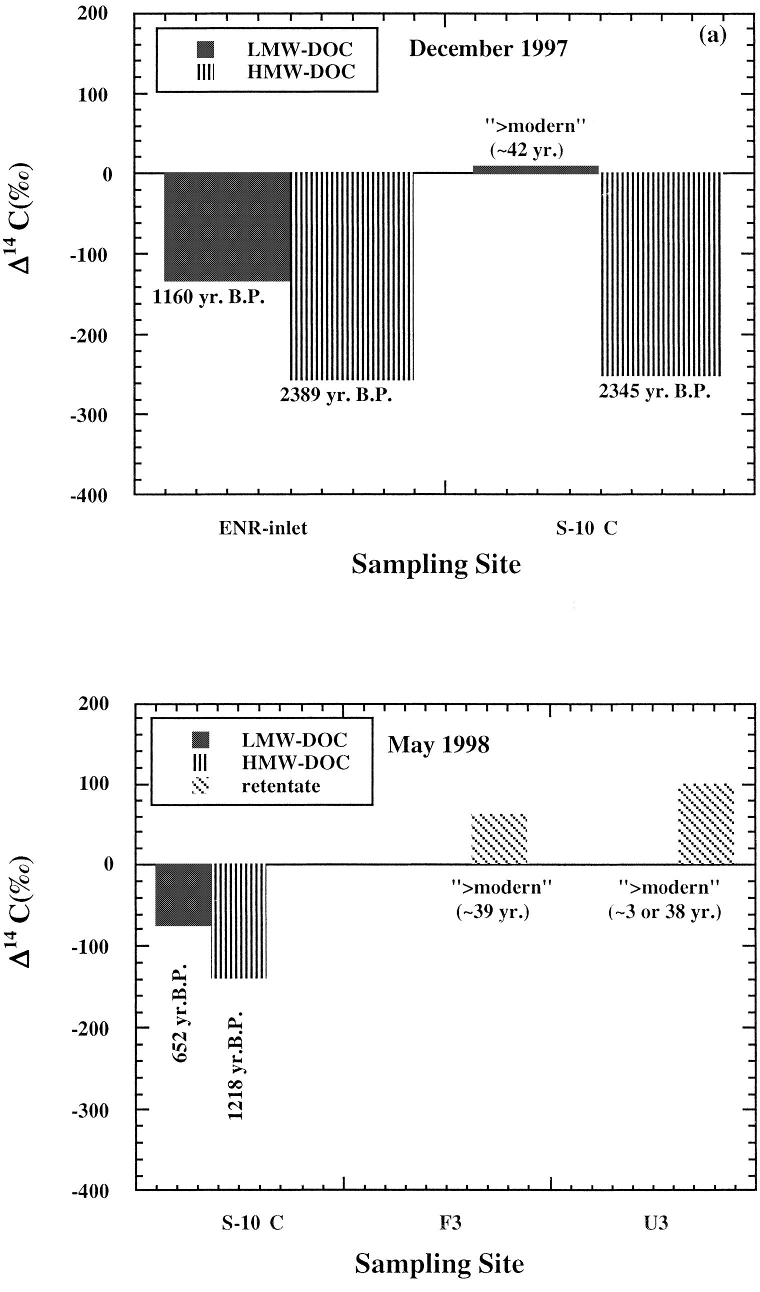

Figure 8. $\Delta^{14}C$ values of DOC in water samples collected in December 1997 (a) and May 1998 (b) from ENR and WCA-2A. $\Delta^{14}C$ values of LMW-DOC = $\Delta^{14}C$ of permeate. $\Delta^{14}C$ of HMW-DOC was calculated from the C and ^{14}C measurements of both permeate and retentate (mixture of HMW-DOC and LMW-DOC). Also shown in the diagram are the radiocarbon ages of the DOC (*The mean ages were determined from the "bomb" ^{14}C curve).

posits and the production of submerged plants (which are taking up CO_2 from water rather than the atmosphere) in supporting the food web in the Everglades.

Our ^{14}C data (Figure 8) also show that the HMW-DOC had older radiocarbon ages than the LMW-DOC at each site, indicating that a greater fraction of the HMW-DOC was derived from the historic peat deposits. It is interesting to note that the radiocarbon age of the LMW-DOC decreased more drastically than that of the HMW-DOC as water traveled down the canal from the ENR inlet to the WCA-2A. This suggests that the LMW-DOC compounds have a shorter turnover time and are more microbially labile than the HMW-DOC. The higher lability of the LMW-DOC may be related to their lower C/N ratios as discussed in previous section. Outflow from the WCA-1 can also affect the ^{14}C content of DOC at the inlet of the WCA-2A, particularly in the wet season. However, we did not have samples from the WCA-1 and can not evaluate the extent to which the chemical and isotopic characteristics of DOC in the supply canal were modified by mixing with outflow from the WCA-1.

These results have several important implications concerning the C and nutrient cycles and the restoration/management of wetland ecosystems. Our results demonstrate that the organic C previously preserved in peats in the northern Everglades is now being released into the aquatic system due to the agricultural practices on drained peat deposits. As the "old" C is mobilized, so are the nutrients and metals (such as mercury) that were previously preserved in peats. In south Florida, the average annual rainfall is about 60 inches and annual runoff $\sim$ 12 inches (Duever et al. 1994). The EAA consists of 3059 km^2 of peat soils (Light and Dineen 1994). Assuming that the average DOC concentration in the runoff from the agricultural land is 34 mg-C/L as measured in the inflow waters to the ENR and WCA-2A in December 1997 and May 1998, the amount of DOC released from peat soils is estimated to be about 32 billion g-C/year. Using the average C/N and C/P ratios of DOC in inflow waters to the ENR and WCA-2A in December 1997 and May 1998 (i.e., C/N=18 and C/P=4170), we estimated the amount of DON and DOP mobilized from peat soils to be about 2 billion g-N/year and about 8 million g-P/year, respectively! Clearly, accelerated decomposition of organic matter in the historic peat deposits could provide a significant source of DOC, nutrients and perhaps toxic metals for aquatic organisms. Although DOP only accounts for a small fraction of the TDP in the inflow waters to the ENR and WCA-2A, our data show that some of the SRP was converted to DOP as water passed through the ENR and down the canal (Schaefer 2000), providing an additional source of DOP. Microbiological and enzymatic analyses of the water samples from the ENR and WCA-2A (Proctor et al. 2001) suggest that the DOP pool is currently bioavailable to native bacteria at all sites regardless of the level of inorganic phosphorus. These C and nutrient releases from peat deposits associated with land-use change may stimulate production in the Everglades wetland ecosystems. Although our data suggest that there is a seasonal or hydrologic variation in the source and cycling of DOC, more studies are needed to reveal the underlying factors and processes controlling the production, transport and transformation of C and nutrients through the landscape in the Everglades.

Conclusions

In our chemical and C isotopic study of the organic matter in the northern Everglades, we have determined that the historic peat deposits in the agricultural area were a major source of DOC in the inflow waters to the ENR and WCA-2A and sugarcane contributed less than 23% of the DOC pool. We have also shown that there is a seasonal variation in the source/production and cycling of DOC, DON and DOP at our sites. The relative amounts of sugarcane-derived DOC were greater in the dry period (May 1998) than in the wet period (December 1997) at the inlets of both the ENR and the WCA-2A. Radiocarbon measurements of DOC suggest that not only "young" DOC derived from sugarcane and modern wetland vegetation but also "old" DOC derived from historic peat deposits can be decomposed by microbes and sunlight during their residence in the canal as well as in the ENR and WCA-2A. However, the LMW-DOC (< 1000 Dalton), which accounted for more than 50% of the total DOC, appeared to be more microbially labile than the HMW-DOC (> 1000 Dalton). Mobilization of "old" C in peat deposits in the northern Everglades is indicated by old radiocarbon ages of DOC in canal discharges and in disturbed areas of the wetland. On the other hand, DOC in relatively pristine areas in the WCA-2A had much younger radiocarbon signatures. We therefore propose that the radiocarbon signature of DOC could be used as a sensitive indicator of the overall effectiveness of an ecosystem restoration project. As a restored wetland ecosystem moves towards its original/natural state, the ^{14}C content of DOC should approach that of the "modern" atmosphere. However, more data are needed to test this hypothesis. Our data also suggest that accelerated decomposition of organic matter in the historic peat deposits (due to land-use change) could provide a significant source of DOC, nutrients and perhaps metals (including toxic metals) for aquatic organisms.

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