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Rapid accretion of dissolved organic carbon in the Springs of Florida: the most organic-poor natural waters

C. M. Duarte[1], R. Martínez[1], Y. T. Prairie[2], T. K. Frazer[3], M. V. Hoyer[3], S. K. Notestein[3], and D. E. Canfield[3]

[1]Department of Global Change Research, IMEDEA (CSIC-UIB), C/ Miquel Marqués 21, 07190 Esporles (Illes Balears), Spain
[2]Département des sciences biologiques, Université du Québec à Montréal, Case postale 8888, succ. Centre-Ville, Montréal, H3C 3P8, Canada
[3]University of Florida, School of Forest Resources and Conservation, Fisheries and Aquatic Sciences Program, 7922 NW 71st Street, Gainesville, Florida 32653-3071, USA

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Correspondence to: C. M. Duarte (carlosduarte@imedea.uib-csic.es)

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Abstract

The concentration of dissolved organic carbon (DOC) in groundwater emanating as spring discharge at several locations in Florida, USA, and the net rate of DOC increase in the downstream receiving waters were measured as part of a larger investigation of carbon dynamics in flowing waters. Springs with high discharge (>2.8 $m^3 s^{-1}$) were found to be the most organic-poor natural waters yet reported (13 ± 1.6 µmol C L^{-1}), while springs with lesser discharge exhibited somewhat higher DOC concentrations (values ranging from 30 to 77 µmol C L^{-1}). DOC concentrations increased rapidly downstream from the point of spring discharge, with the calculated net areal input rate of DOC ranging from 0.04 to 1.64 mol C $m^{-2} d^{-1}$ across springs. Rates of DOC increase were generally greater in those springs with high discharge rates. These input rates compare favorably with values reported for gross primary production in these macrophyte-dominated spring systems, assuming that 17% of macrophyte primary production is lost, on average, as DOC. The measures reported here are possible only because of the remarkably low DOC levels in the up-surging groundwaters and the short residency times of the water in the spring-runs themselves.

1 Introduction

The global pool of dissolved organic carbon (DOC) in the biosphere is substantial (Mulholland, 2003). However, DOC concentrations reported for individual ecosystems can range widely, and some natural waters can be quite depleted in DOC. For example, Sommaruga (2001) reported DOC concentrations as low as 17 µmol C L^{-1} in ultraoligotrophic alpine lakes, and Arístegui et al. (2002) reported a concentration of 42 µmol C L^{-1} in the deep ocean. These values are believed to render these the fresh- and marine waters with the lowest DOC concentrations. However, most aquatic ecosystems have DOC concentrations well in excess of these lower thresholds. Freshwater ecosystems, in particular, tend to exhibit high DOC concentrations, often

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in excess of 1000 µmol C L^{-1} (Kortelainen, 1993; Enache and Prairie, 2002). The high DOC concentration in most natural waters is a rather stable property. In fact, DOC concentrations in most aquatic systems exhibit only modest temporal variability (typically 10% of the mean, Prairie, unpub. data; Williams, 1995), suggesting, at first glance, a slow turnover of this material. However, DOC is certainly a highly dynamic pool, as it is subject to a number of removal processes (e.g., bacterial metabolism, photochemical egradation and flocculation, e.g. del Giorgio and Davis, 2003) as well as inputs (e.g., atmospheric deposition and autochthonous inputs, especially through the release of dissolved primary production from algae and macrophytes; cf. Bertilsson and Jones, 2003). Hence, the relative uniformity of DOC concentrations within a wide variety of aquatic systems noted above must occur as a result of a close balance between inputs and outputs, which, in turn, conceal the dynamic nature of DOC. Further insights into DOC dynamics must therefore be gained through experimental and budgeting approaches. Florida contains a large number (>700) of springs, including 33 ranked as first magnitude springs (discharge >2.8 $m^3 s^{-1}$), and is arguably the most important regional spring complex worldwide (Scott et al.,2002). Springs serve as the origin of flow for many of Florida's streams and rivers (Scott et al., 2002), in which lush and highly productive ecosystems develop (Odum, 1956, 1958; Duarte and Canfield, 1990a). The groundwaters upwelling at Florida springs are extremely transparent and have been claimed to rank amongst the clearest natural waters (Duarte and Canfield, 1990b), thereby suggesting that DOC, which is a major source of light absorption in the UV and blue wavelengths (Kirk, 1983), occurs at very low concentrations. Herein, we provide data that corroborate this suggestion, but also demonstrate a very rapid increase of DOC in spring runs that can be accounted for by autochthonous sources; submersed aquatic vegetation in particular.

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2 Materials and methods

2.1 Sample collection

We sampled 9 Florida springs spanning a broad rangeof discharges, from modest to large (range 1.5 to 27.6 $m^3 s^{-1}$, Table 1). At each spring, divers used acid-washed polycarbonate Nalgene bottles to collect a sample of the upwelling groundwater at the spring boil, i.e. the point of highest discharge. We then collected and additional 2 to 5 water samples (ca. 0.5 m depth) at stations along the spring run downstream from the initial collection point. Water to be used for DOC analysis was processed immediately, while that used for other chemical analyses (see below) was stored on ice and transported to the laboratory. The distance between the spring boil and downstream sampling stations as well as the mean channel widths were computed from GPS coordinates and digital maps using GIS software (ArcView 3.1).

2.2 Sample preparation and analyses

At each sampling station, duplicate water samples for DOC analysis (10 ml) were immediately filtered through a pre-combusted (450 °C for a minimum of 4 h) GF/F filter and the filtrate transferred to an acid-washed glass ampoule. All samples were preserved with the addition of 100 µl of 2N HCl before flame-sealing the ampoules. DOC analysis was performed using Pt-catalyzed high-temperature combustion on a Shimadzu TOC-5000A analyzer (Qian and Mopper, 1996). Distilled UV-radiated water from a Millipore Simplicity Ultrapure DI water system was used to prepare blanks. Standard curves were prepared with potassium biphthalate (range: 0 to 400 µmol C L^{-1}). The instrument blank, ca. 3 µmol C L^{-1}, was assessed using 2 external standards (44–45 µM and 2 µM) provided by Dennis A. Hansell and Wenhao Chen (University of Miami) and all reported measurements were appropriately corrected for accuracy. The precision of the measurements, which were derived from the standard curves, was ±1 µmol C L^{-1}. The accuracy and detection limit, derived from the external standards used, was better

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than 3 µmol C L^{-1} (average 2.83 µmol C L^{-1}). Hence, the analytical techniques and procedures allowed us to accurately estimate DOC in DOC-depleted waters, such as those examined here.

At the laboratory, total phosphorus concentrations were determined using the procedures of Murphy and Riley (1962) with a persulfate digestion (Menzel and Corwin, 1965). Total nitrogen concentrations were determined by oxidizing water samples with persulfate and determining nitrate-nitrogen with second derivative spectroscopy (D'Elia et al., 1977; Simal et al., 1985; Wollin, 1987). Specific conductance (µS cm^{-1} at 25 °C) was measured using a Yellow Springs Instrument Model 35 conductance meter. An Accumet model 10 pH meter calibrated with buffers of pH 4.0 and 7.0 was used to measure pH. Total alkalinity (mg L^{-1} as $CaCO_3$) was determined by titration with 0.02 N sulfuric acid (Method 2320 B; APHA, 1992).

The rate of accretion of DOC along the rivers (DOC_{acc}, µmol C m^{-4}) was calculated as the linear slope of the increase in concentration with distance from the spring origin (boil). Net areal DOC input rates (mol C m^{-2} d^{-1}) along the spring surface were then calculated from the equation:

$$\text{Net DOC input} = \frac{0.086\, Q\, \text{DOC}_{\text{acc}}}{W} \tag{1}$$

where Q is the spring discharge (m^3 s^{-1}, Table 1), W is the mean channel width (m) along the length of the spring run and 0.086 is a factor to convert the units to mol C added per day. These calculations could not be applied to Kings' Bay, the configuration of which is more akin to a lagoon than a river. Estimates of net DOC areal input are conservative as they assume no water inputs along the channel, which do occur in some springs. Increased water inputs either from surface waters or groundwater (as diffuse seepage, for example) would result in an increase in Q, and, as a consequence, an increase in the estimate of the net areal DOC input.

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3 Results

The groundwater emanating as spring discharge ranged broadly in chemical properties (Table 1). For example, conductivity measurements differed by nearly 50 fold among the systems, and nutrient (total N) concentrations differed by as much 25 fold (Table 1). This observed variability in water chemistry could be explained largely by differences in spring discharge; conductivity decreased exponentially ($R^2 = 0.76$, $P < 0.01$) and total N concentration increased linearly ($R^2 = 0.36$, $P < 0.05$) with increasing discharge. Spring waters, at the point of highest discharge, were undersaturated in oxygen (mean ± SE, 110 ± 17 µmol O_2 L^{-1}), and supported relatively high DIC concentrations (mean ± SE, 2410 ± 226 µmol C L^{-1}). DOC concentrations in the spring boils were generally low to very low, but also ranged broadly, from exceedingly low values (<10 µmol C L^{-1} in Silver Spring) to moderate concentrations (76.8 µmol C L^{-1} in Homosassa Spring). DOC concentrations declined with increasing spring discharge (Fig. 1). First magnitude springs, i.e. springs with high (>2.8 m^3 s^{-1}) discharge, maintained very low DOC concentrations (mean ± SE, 13.1 ± 1.6 µmol C L^{-1}), likely representing that of the Floridian aquifer. These findings render these, to the best of our knowledge, the most organic-depleted natural waters yet examined. DOC concentrations also declined with increasing total nitrogen concentration (Fig. 1).

DOC concentrations increased rapidly downstream from the origin of the springs to reach rather high values at distances of a few kilometers from the spring boil in some springs (Fig. 2). The rates of accretion in DOC ranged broadly from 2.7 to 72.5 µmol C m^{-4} (Fig. 2). DOC values remained relatively uniform downstream in some springs (e.g., Rainbow Springs, Table 2), whereas they increased sharply downstream in others (e.g., Silver Springs, Fig. 2, Table 2). The calculated net areal input rate of DOC ranged from 0.04 to 1.64 mol C m^{-2} d^{-1} across all sampled springs (Table 2).

4 Discussion

The data presented here suggest that there are two groundwater masses contributing to the discharge of the Florida springs: (1) a water mass highly depleted in dissolved organic carbon with high nitrogen concentrations and low conductivity, and (2) a water mass with higher DOC concentrations, higher conductivity and lower total nitrogen concentrations. This is in accord with the presence of two distinct groundwater masses in Florida, a superficial aquifer and the Upper Floridian Aquifer system (Miller, 1986), representing a recent water mass with high DOC and moderate total nitrogen levels and an older (residence time 20 y, Scott, 2002) water mass depleted in DOC and enriched in total nitrogen, respectively. The low O_2 and high DIC concentrations of the spring waters indicate that loss of DOC in both the superficial aquifer and Upper Floridian Aquifer occurs through microbial respiration of the organic matter during the process of groundwater recharge, which likely involves anaerobic pathways. Microbial respiration over the long residence time of the waters in the Upper Floridan Aquifer system renders these the most organic-depleted waters yet reported in the biosphere.

Whereas the downstream receiving waters of some springs such as Rainbow Springs remain DOC-poor at considerable distances from their sources, others such as Silver Springs rapidly accumulate high concentrations of DOC. There are two likely sources for the rapid increase of DOC in the spring runs: (1) net inputs from within the spring ecosystems, presumably derived from the lush and highly productive macrophyte communities and associated epiphytes (Odum, 1956, 1958; Duarte and Canfield, 1990a), and (2) inputs from the adjacent terrestrial ecosystem, which include in some cases (e.g., Silver Springs), swamps. The upper limit to the autochthonous contribution to DOC inputs is set by the net community production (NCP) of the spring ecosystems, which has been investigated in the past (Odum, 1956, 1958; Duarte and Canfield, 1990a). Comparison of the net input rates with previously reported primary production rates for the springs investigated (Table 2, Odum, 1958; Duarte and Canfield, 1990a) indicate that autochthonous production is sufficient (in all springs except

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Silver Springs) to account for the calculated rate of net DOC increase, as the median net DOC excretion represents 14% of primary production (Table 2). This estimate is very crude and should be considered an order-of-magnitude approximation alone, as the primary production values were separated in time from the DOC measurements reported here (Table 2). Nevertheless, the 14% of primary production required to yield the observed DOC changes is well within the range of reported percent primary production released as DOC by aquatic macrophytes (Bertilsson and Jones, 2003) in all springs except Silver Springs, where net DOC increase exceeds primary production and allochthonous, land-derived DOC inputs must contribute at least half of the net DOC inputs (Table 2). This area is surrounded by swamps that deliver significant amounts of DOC to the spring channel. However, the high primary production of Florida springs, which rank amongst the most productive freshwater ecosystems, is generally attributable to the lush submerged macrophyte communities that they support (Odum, 1956, 1958; Duarte and Canfield, 1990a). The lush macrophyte communities of most of Florida's spring-fed streams and rivers render them strongly autotrophic (Odum, 1956), yet the macrophyte communities likely release much of their excess production as dissolved organic carbon.

Because of the remarkably low DOC concentrations in groundwater emanating as spring discharge, Florida springs are ideal systems to study organic carbon dynamics in flowing waters; dynamics which are typically masked in other ecosystems by the natural coupling of input and removal processes. Florida springs are the aquatic ecosystems with the lowest DOC load yet reported. These results show that aquifers with long residence times, such as the Upper Floridian Aquifer, can be highly depleted in DOC, affecting the DOC dynamics of the rivers and streams these groundwaters feed. The very low DOC concentration in the groundwater feeding the Florida springs allowed the net DOC input rates to be calculated across significance lengths of the rivers. The remarkably low DOC values of spring waters may provide an opportunity to produce low-DOC reference matterials, to be used, similar to available Deep Ocean seawater standards, to test the precision, detection limit and accuracy of DOC measurements in freshwaters, a practice that is lagging behind the use of reference materials for DOC analyses in oceanography.

5 Conclusions

These results add new and unexpected value to H. T. Odum's statement from nearly half a century ago (Odum, 1958) that the springs of Florida represent a *"giant laboratory for the study of natural communities".* In addition to the remarkably low DOC levels that rendered measurements of DOC increase rates possible, individual springs in Florida are highly uniform with regard to many of their physical and chemical properties (e.g., temperature, chemistry, discharge) both seasonally and in the long-term (cf. Odum, 1958; Scott, 2002), and approach nearly true steady-state conditions. The results reported for the Florida springs highlight the significant inputs of DOC to aquatic ecosystems from a combination of internal and external sources, which renders DOC the dominant C pool supporting carbon flux and metabolism in freshwater ecosystems.

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Interactive Discussion

Table 1. pH, alkalinity, conductivity, DOC concentration, total N and total P concentrations and dissolved oxygen, of the water upwelling at the boils of the Florida springs studied. Water discharges are the most recent values reported in Scott et al. (2002) and Rosenau et al. (1977). Water chemistry for Ichetucknee Spring was taken from Scott et al. (2002).

Spring	pH	mg/LT ALK	Conductivity µmhos	DOC µmol C L^{-1}	Total P µmol P L^{-1}	Total N µmol N L^{-1}	O_2 µmol O_2 L^{-1}
Alexander	7.8	81	1110	60.3	1.39	7.9	47
Chassahowitzka	7.5	151	4520	30.0	0.65	37.1	118
Homosassa	7.7	113	4210	76.8	1.39	27.9	150
Ichetucknee	7.54	154	310	14.3	1.6	74.5	62
Kings Bay	8.0	82	355	18.2	0.74	25.0	173
Rainbow	8.0	53	133	11.0	0.87	70.0	184
Salt	7.7	65	5310	38.6	0.35	15.0	99
Silver	7.5	183	466	9.8	1.29	211.4	83
Weeki Wachee	7.8	142	313	12.4	0.19	49.3	70

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Table 2. Water discharge, mean channel width, net rate of DOC increase (mean ± SE), calculated net input rate of DOC and gross primary production for Florida springs. Salt Springs calculations are based on two points only and have, therefore, no error estimate. Water discharge are the most recent values reported in Scott et al. (2002) and Rosenau et al. (1977). Net primary production from (1) Odum (1957) and (2) Duarte and Canfield (1990a).

Spring	Discharge ($m^3 s^{-1}$)	Channel width (m)	DOC accretion (µmol DOC m^{-4})	Net DOC input (mol C $m^{-2} d^{-1}$)	Net Primary Production (mol C $m^{-2} d^{-1}$)
Alexander	2.7	42.2	54.7 ± 28	0.30	0.51 (2)
Homosassa	2.5	79.6	16.4 ± 5.4	0.04	7.91 (2)
Ichetucknee	5.3	23.4	3.4 ± 0.7	0.07	0.46
Rainbow	17.9	43.6	2.7 ± 3.7	0.10	1.5 (1)–2.66 (2)
Salt	2.2	108.3	72.5	0.13	1.35 (2)
Silver	15.7	34.4	41.5 ± 7.5	1.64	0.58 (2)–1.45 (1)
Weeki Wachee	4.6	19.1	4.8 ± 0.6	0.10	0.60 (2)–0.78 (1)

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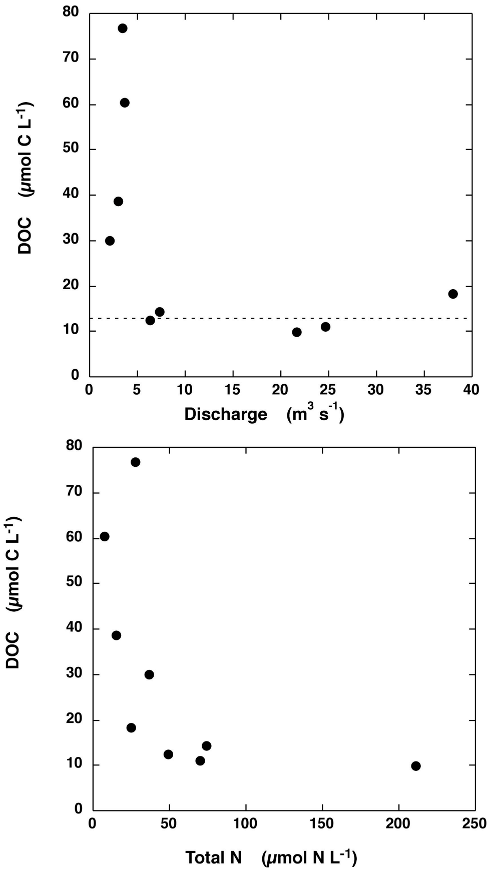

Fig. 1. The relationship between dissolved organic carbon (DOC) concentration and the discharge and total nitrogen concentration in the main surgences (boils) of nine Florida springs. The dotted line shows the mean DOC concentration in springs with discharge $>5\,m^3\,s^{-1}$, $13.1 \pm 1.6\,\mu mol\,C\,L^{-1}$, probably representing the DOC concentration in the Floridian aquifer.

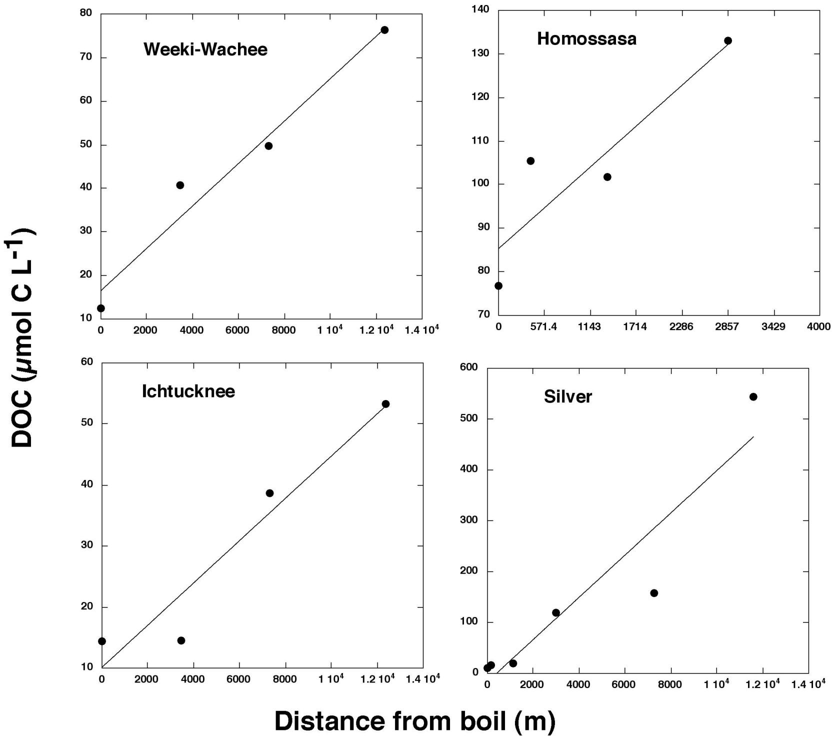

Fig. 2. The relationship between dissolved organic carbon (DOC) concentrations and distance from the point of surgence of groundwater in Weeki Wachee, Homosassa, Ichetucknee, and Silver springs. The solid lines show the fitted least squares regression equations; Weeki Wachee: DOC (μmol C L^{-1}) = 16.5 + 0.0048 Distance (m), $R^2 = 0.96$; Homosassa: DOC (μmol C L^{-1}) = 85.3 + 0.0016 Distance (m), $R^2 = 0.81$; Ichetucknee: DOC (μmol C L^{-1}) = 10.1 + 0.0034 Distance (m), $R^2 = 0.92$; Silver: DOC (μmol C L^{-1}) = 15.6 + 0.041 Distance (m), $R^2 = 0.85$.

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