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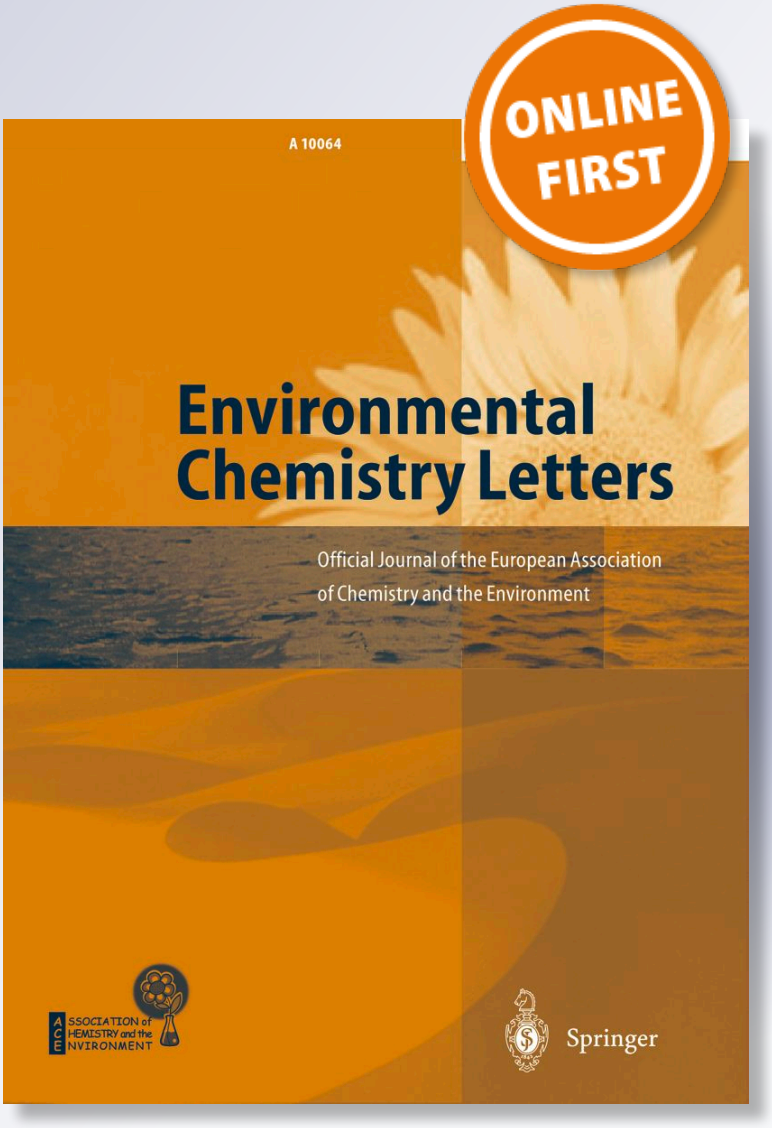

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ORIGINAL PAPER

Measuring dissolved organic carbon $\delta^{13}C$ in freshwaters using total organic carbon cavity ring-down spectroscopy (TOC-CRDS)

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Abstract This article reports the first application of coupled total organic carbon cavity ring-down spectroscopy (TOC-CRDS) for the analysis of the $\delta^{13}C$ signature of dissolved organic carbon (DOC) in freshwater samples. DOC represents a major, dynamic component of the global carbon cycle. The export of DOC from soils into rivers and groundwaters may be highly climate sensitive, and much of this export may occur in ephemeral fluxes. Thus, a robust, simple and inexpensive method for the continuous determination of DOC concentration and quality is urgently needed. We detail recent advances made in the analysis of the $\delta^{13}C$ signature of DOC using a TOC-CRDS system optimised for the analysis of DOC with natural abundances greater than 2.5 mg L^{-1} with no sample pre-concentration required and sample volumes of 40 mL. Precision between replicated samples was comparable to conventional analysis by gas-source isotope ratio mass spectrometry, yielding $\delta^{13}C$ values with standard deviations of $\pm$ 0.5 ‰ for DOC concentrations higher than 1.5 mg L^{-1}. The utility of this technique for the analysis of DOC in samples with a broad range of compositions and concentrations (2.5–25 mg L^{-1} DOC) is demonstrated. Since DOC $\delta^{13}C$ can be measured continuously, ca. 45 min per measurement, this method enables the online monitoring of DOC in river water, water intakes and treated waters, allowing changes in DOC fluxes to be monitored in real time.

Keywords Organic matter · Quality · Characterisation · Stable isotopes · Mass spectrometry · Monitoring

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Introduction

Stable isotope analysis is a useful tool for the characterisation of dissolved organic carbon (DOC), which provides a signature of its environmental origin and, in temporal studies, may provide information on DOC breakdown through natural and anthropogenic action. In hydrology, carbon isotopes in DOC can provide a tracer of water movement and provenance (Dalzell et al. 2007; Amiotte-suchet et al. 2007), and in studies of heterotrophic food webs (e.g. interstitial fauna in groundwaters), DOC $\delta^{13}C$ represents the isotopic baseline against which C fractionation by microbes and higher consumers is evaluated (Hartland et al. 2011).

The stable isotopes of carbon ($^{13}C/^{12}C$) fractionate across a dynamic range, encompassing highly negative, methanogenic signatures (ca. −80 ‰, Orphan et al., 2001) and less negative values between −34 and −10 ‰,

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encompassing plant-based carbon derived from the C_3 and C_4 photosynthetic pathways (O'Leary 1988). Therefore, the $\delta^{13}C$ value of DOC can provide insights into the sources and sinks of DOC in a catchment that may become active at different times, and enabling the knock-on effects of DOC assimilation by ecosystems to be assessed (Craft et al. 2002; Findlay et al. 2003). This is especially pertinent in groundwaters; although traditionally considered to be food-poor, because of the often-observed decline in the DOC concentration with depth (Pabich et al. 2001), the evolving understanding of the DOC dynamics is that carbon can be stored for long periods and then released in transient pulses, or 'hot moments' (Andrews et al. 2011). The evidence from studies of interstitial fauna and microbes suggests that these pulses of DOC and other nutrients can be used with a high degree of efficiency by in situ communities (Baker et al. 2000; Craft et al. 2002), implying tight C cycling and high retention in alluvial groundwaters. Isotopic studies offer perhaps the best way to assess the response of interstitial communities to changes in DOC delivery, but first, the isotopic composition of DOC must be determined before assimilation by microbial biofilms (Foreman and Covert 2003; Findlay et al. 2003) and higher consumers (Hartland et al. 2011) can be assessed.

Carbon isotopes are also useful for assessing C turnover in soils through the mass-dependent fractionation of organic carbon by microbes (Rasmussen et al. 2006). Indeed, how soil carbon stocks will respond to climate warming is an area of active debate (Arneth et al. 2010). In addition to increased respiration by soil microbes, the release of DOC from soils and peats may show strong climate sensitivity, possibly indicated by the secular increase in DOC in UK Rivers over recent decades (Roulet and Moore 2006). What is clear is that mobilisation of DOC, colloids and particles into receiving waters is not controlled purely by hydrology (Sen and Khilar 2006). Most mobilisation occurs during the upward and downward limbs of the infiltration hydrograph rather than at peak flow (El-Farhan et al. 2000), but initial soil moisture content (Rousseau et al. 2004) and the extent of delays between infiltration events (Schelde et al. 2002) also play a role. Perhaps most importantly, DOC release is favoured when the energy barrier on detachment is overcome by an increase in the charge of surfaces caused by a change in solution chemistry (Sen and Khilar 2006). Clearly a method for the continuous assessment of the DOC concentration and quality is needed that is both rapid, field-portable, simple and accurately determines DOC $\delta^{13}C$ at a range of natural abundances.

Recent technological advances have led to the first generation of infrared spectroscopy instruments based on cavity ring-down spectroscopy (CRDS) for the measurement of $\delta^{2}H$ and $\delta^{18}O$ in waters (Munksgaard et al. 2011) and $\delta^{13}C$ in gaseous CO_2 (Berryman et al. 2011). Coupled TOC-CRDS instruments are now commercially available and offer precision of $\delta^{13}C$ ($\pm$ 0.5 ‰) approaching that of more expensive and involved analyses by gas-source isotope ratio mass spectrometry (Gandhi et al. 2004) with the simplicity of total organic carbon (TOC) and CRDS measurements. However, such instruments are configured for, and tested against, highly concentrated (i.e. 50,000 mg L^{-1} C) samples (Picarro 2010), and so their suitability for analysis of DOC in the range encountered in natural waters (e.g. $<$ 1–15 mg L^{-1}) remains unproven. This paper presents the results of the optimisation, calibration and testing of a commercially available, coupled TOC-CRDS system for the analysis freshwater samples in the concentration range of 1.5–15 mg L^{-1}.

Experimental

Instrument structure and optimisation

We optimised $\delta^{13}C$ measurements of DOC using an Aurora 1030 wet oxidation TOC analyser (OI Analytical, College Station, TX, USA) coupled to a G1111-i CO_2 isotope cavity ring-down spectrometer (Picarro Instruments, Sunnyvale, CA, United States). The iTOC-CRDS system first measures the TOC (Non-Purgable Organic Carbon method) concentration in the sample by high-temperature oxidation via reaction with sodium persulphate [$Na_2S_2O_8$], following removal of dissolved inorganic carbon (DIC) by the addition of phosphoric acid [H_3PO_4] and sparging in a stream of inert gas for 2 min. Carbon dioxide is generated and measured by infrared absorption (non-dispersive infrared (NDIR)) on the iTOC and is then collected in a gas-tight bag. Following the injection of the final aliquot on the iTOC, the accumulated CO_2 (plus pure air carrier gas) is transferred to the CRDS. The iTOC analyser attached to a 1088 rotary auto-sampler (OI Analytical, College Station, TX, United States) is compatible with 40-mL sample vials and comes equipped with a 10-mL syringe for sample injection, the volume of which cannot be increased due to the dimensions of the syringe housing. Thus, the off-the-shelf iTOC-CRDS system cannot be modified to inject greater than a total sample volume of 30 mL, meaning that for many environmental samples (e.g. groundwaters, 0.1–1 mg L^{-1} organic carbon), the total mass of CO_2 available for analysis on the CRDS is negligible (0.01–0.1 mg CO_2). Thus, optimisation of the iTOC-CRDS system is limited to:

1. Volume of sample injected;

2. Sample dilution in the TOC analyser by the aqueous reagents; and
3. $CO_{2(g)}$ dilution by the iTOC purified-air carrier gas.

In order to improve the system performance for low concentration samples, we firstly maximised the sample injection volume on the iTOC from 2 mL (system pre-set) to 9 mL. The concentration of wet reagents was then increased to their maximum safe level, thereby reducing the volume required in the analysis and minimising sample dilution. The sodium persulphate concentration was increased from 10 to 30 %, and the phosphoric acid concentration was increased from 5 to 25 %. These changes enabled the maximum mass of organic carbon to be reacted with the smallest volume of reagents. Further optimisation was then achieved by reducing the pressure of the carrier gas phase from 25 to 15 psi and by modification of the system peak detection parameters to minimise $CO_{2(g)}$ dilution with the carrier gas. Reduction in system carrier gas pressure and fine-tuning of the peak detection parameters resulted in a further doubling of CO_2 signal strength on the CRDS (Fig. 1).

Sample collection and preparation

Samples were taken in pre-cleaned glass bottles and kept in the dark at ≤ 5 °C during transport to the laboratory. Samples were then filtered at 0.45 µm prior to analysis on the iTOC-CRDS system. All samples were analysed within 1 week of collection, and all glassware was rigorously cleaned using 10 % HCl and deionised water.

System maintenance and pre-run checks

The iTOC-CRDS system requires a series of pre-analysis checks to be performed before sample analysis can commence. We briefly detail these checks here for the benefit of future users of this system. Following preparation of the system reagents (deionised water, sodium persulphate and phosphoric acid), the system must be 'woken up' and the furnace 'solids temp' must reach ca. 900 °C (ca. 10 min). Following this, the NDIR detector is reset to 2,500 absorbance units (maintenance tab in the OI analytical software) and a system clean-up (repeated analysis of deionised water) is run until a stable baseline (CO_2 absorbance) is reached. Before the beginning of each run, the 'data buffer' in the iTOC-CRDS software window must be emptied and a new data log is started. The system reports the identity and location of the CRDS data file corresponding to the new run.

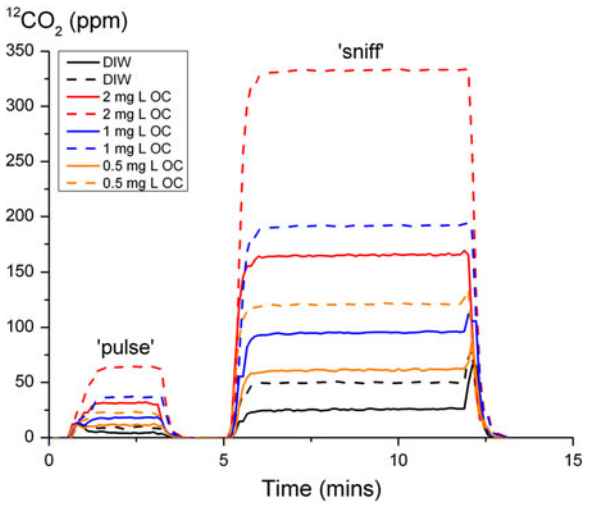

Fig. 1 Doubling of the $^{12}CO_2$ signal on the cavity ring-down spectroscopy system as a result of the reduction of the total organic carbon analyser carrier gas pressure from 25 (*solid lines*) to 15 (*dashed lines*) psi. *DIW* deionised water, *OC* organic carbon

Postprocessing of $\delta^{13}C$ data

The G1111-i CRDS system produces time-integrated data and detailed information on system performance metrics, most of which can be disregarded for the purposes of routine standard isotope analysis. We reduced the data extracted to the time-step, ^{12}C absorbance, the 30 s integrated $\delta^{13}C$ ratio and the H_2O signal. We used the 'user.dat' data file exported by the CRDS since this contained the most concise report of the system data generated. The raw CO_2 ($^{12}CO_2$) data for a given run of samples and standards describe a series of peaks corresponding to each analysis. Each analysis is composed of two peaks, a short and small 'sniff' and then a larger and longer 'pulse' (Fig. 1). The absolute values of CO_2 in the pulse vary with the DOC concentration in the sample being analysed. The timing of the start and end of each 'pulse' were noted. The raw (uncalibrated) $\delta^{13}C$ data show an internal structure within each peak. For the first part of the pulse, the $\delta^{13}C$ value (delta_30 s) is unstable, but this gives way to a stable series of measurements (flat part of the peak), the mean and standard deviation of which are reported here. This part of the analysis of raw $\delta^{13}C$ values introduces an element of subjectivity, but it is most important to be consistent in the determination of the 'stable' region of values within each peak. Following the measurement of the raw $\delta^{13}C$ values on the iTOC-CRDS, we used the known $\delta^{13}C$ composition of USGS standards and an in-house urea standard to derive the linear calibration equation of the instrument.

Results and discussion

Analytical precision, accuracy and uncertainty of $\delta^{13}C$ measurement

Modification of iTOC wet chemistry methods (increased injection volume and minimised dilution by reagents)

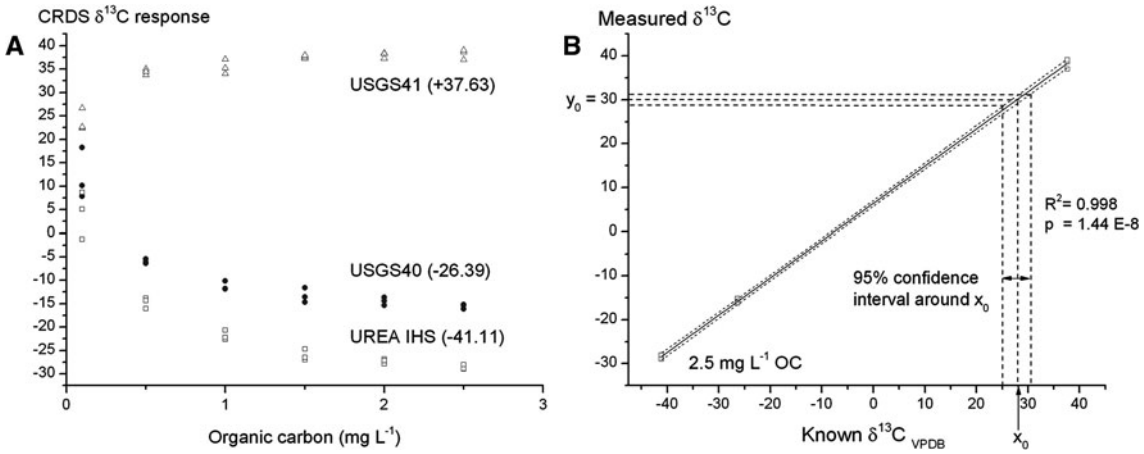

Fig. 2 Results of system calibration at organic carbon (OC) concentrations in the range 0.1–2.5 mg L^{-1} (**a**) and **b** the confidence interval on a $\delta^{13}C$ value (x_0) estimated from a CRDS response (y_0) of +30.0 ± 1.0 ‰ based on 2.5 mg L^{-1} OC concentration. $\delta^{13}C$ x_0 = 28.0 ± 2.5 ‰

resulted in a reduction of pre-analysis sample dilution by a factor of 5.5. With the system configured for non-purgable organic carbon analysis with three 9-mL injections, we achieved good within-peak precision of $\delta^{13}C$ (± ca. 1 ‰) for concentrations in excess of 3 mg L^{-1} of organic carbon. For many environmental applications (e.g. measurement of river and waste waters), the iTOC-CRDS system performance was sufficiently improved. But because many natural waters have DOC concentrations below 3 mg L^{-1}, the system was further optimised by reducing the carrier gas pressure to 15 psi and by modifying the CO_2 peak detection settings on the iTOC. Peak detection on the iTOC at lower system pressure resulted, predictably, in the attenuation of the CO_2 peak start, but did not substantively affect the overall duration of the CO_2 peak. Thus, by increasing the delay (ca. 30 s) between sample oxidation and the start of the peak detection window, we effectively minimised the dilution of the CO_2 signal with the carrier gas.

This further refinement enabled $\delta^{13}C$ values from single analyses (within-peak variance) to be obtained to within ± 1 and ± 2.5 ‰ for DOC concentrations > 1 and < 1 mg L^{-1}, respectively. When considering the variance (standard deviation) of the $\delta^{13}C$ values of three replicated analyses, analytical precision was better than ± 0.5 and 1 ‰ for DOC concentrations of > 1 and < 1 mg L^{-1}, respectively. This compares with a quoted system precision of ± 0.5 ‰ for carbon concentrations of 50,000 mg L^{-1}.

Improvements in precision at low concentrations enable accurate carbon isotope analysis at the full range of ambient concentrations encountered in freshwaters. Although the CRDS system showed non-linearity (Fig. 2a) at decreasing DOC concentrations below 2 mg L^{-1}, accurate $\delta^{13}C$ values are obtainable, albeit with separate (concentration-specific) calibration in this range. The observed non-linearity in the CRDS system was most probably a reflection of the relative increase in the C signal from the deionised water $\delta^{13}C$ blank, therefore explaining the convergence of CRDS $\delta^{13}C$ values (Fig. 2a).

Further improvements could be achieved using a pre-concentration step, such as ultrafiltration or rotary evaporation, by further purification of the deionised water, or by deriving calibration curves for specific concentrations below 2 mg L^{-1}. The methodology presented here uses 0.4 mL of 25 % H_3PO_4 and 0.7 mL of 30 % $Na_2S_2O_8$. Close to saturation, sodium persulphate crystallizes easily ($Na_2S_2O_8$ has a solubility of 55.6 g/100 mL water), which can cause blockage of the lines and it is also risky to pump concentrated H_3PO_4 through the system. Thus, further increases in reagent concentrations are not recommended.

The uncertainty of the measurement of the $\delta^{13}C$ composition of an unknown sample with a concentration ≥ 2.5 mg L^{-1} was estimated by calculation of the standard deviation of the unknown, s_0, following methods given in AMCTB (2006). The uncertainty, s_0, was estimated at 1.13 ‰ for DOC concentrations > 2 mg L^{-1}. In Fig. 2b, we present the results of the iTOC-CRDS calibration with organic carbon standards a concentration of 2.5 mg L^{-1}. Details of the standards used are given in Table 1. In Fig. 2b, the confidence interval for a CRDS $\delta^{13}C$ response of 30.0 ± 1.0 ‰ is estimated for the DOC concentration of 2.5 mg L^{-1}. In this example, the 95 % confidence limits for x_0 are estimated at 28.0 ± 2.5 ‰. The standard deviation of the unknown (s_0) and the confidence interval of x_0 can be minimised when the line is well determined, that is, through the use of multiple calibration standards. For the majority of environmental applications, the optimised iTOC-CRDS system provides sufficiently precise $\delta^{13}C$ analyses of DOC and has the advantage of allowing high sample throughput at low cost,

Table 1 Composition of system blanks and reference isotope standards (2.5 mg L^{-1} OC) and the measured, uncalibrated signal from the cavity ring-down spectrometer (CRDS)

Standard	Composition	Known isotope composition (x) ($\delta^{13}C$ ‰ relative to VPDB)	CRDS response (y)
UREA50	Urea (in-house)	−41.11 ± 0.18	−28.63 ± 0.53
USGS40	L-Glutamic acid	−26.39 ± 0.04	−15.59 ± 0.52
USGS41	L-Glutamic acid	+37.63 ± 0.05	+38.22 ± 1.09
DIW	N/a	N/a	−10.97 ± 0.00

Deionised water (DIW) used in the preparation of reference standards had an average organic carbon content of 0.1 mg L^{-1}

making the prospect of routine $\delta^{13}C$ analysis by iTOC-CRDS a realistic option.

Assessment of performance for different sample compositions and concentrations

Samples were taken from a range of river waters and drinking water treatment works. The results of these analyses revealed no systematic bias with sample type or concentration, demonstrating that the iTOC-CRDS system performs well with a range of samples with appropriate calibration. The within-run stability of the iTOC-CRDS system was generally excellent with 1 mg L^{-1} check standards varying by ± 1 ‰.

River waters were obtained from the Namoi region of New South Wales, Australia. Data from samples collected and analysed in January 2012 demonstrate that the $\delta^{13}C$ compositions of river waters were in the expected range for DOC originating from the C^3 photosynthetic pathway (O'Leary 1988). Samples were also obtained from water treatment plants (WTP) and were found to occupy a similar range of isotope values. No systematic bias in delta values was identified as a function of sample type or DOC concentration in the 2–10 mg L^{-1} range (Fig. 3).

The methods outlined here for iTOC-CRDS analysis at low concentrations are applicable for DOC concentrations up to 25 mg L^{-1}. Separate calibration curves derived using higher carrier gas pressures would be necessary for samples with concentrations exceeding 25 mg L^{-1} because of linearity issues on the iTOC. Data obtained from the iTOC-CRDS system at 25 psi carrier gas pressure and a calibrated DOC range of 1–100 mg L^{-1} showed good precision (within-peak variance) with standard deviations of 0.61 ‰ for samples with concentrations in excess of 3.5 mg L^{-1}. Thus, the iTOC-CRDS approach is highly adaptable and may reliably measure the isotopic composition of DOC in a range of concentrations given sufficient prior knowledge of sample concentration provided by a suitable technique, such as UV–Vis spectrometry, which is both rapid (analysis time < 1 min) and sensitive to humic-like DOC concentration at 254 nm.

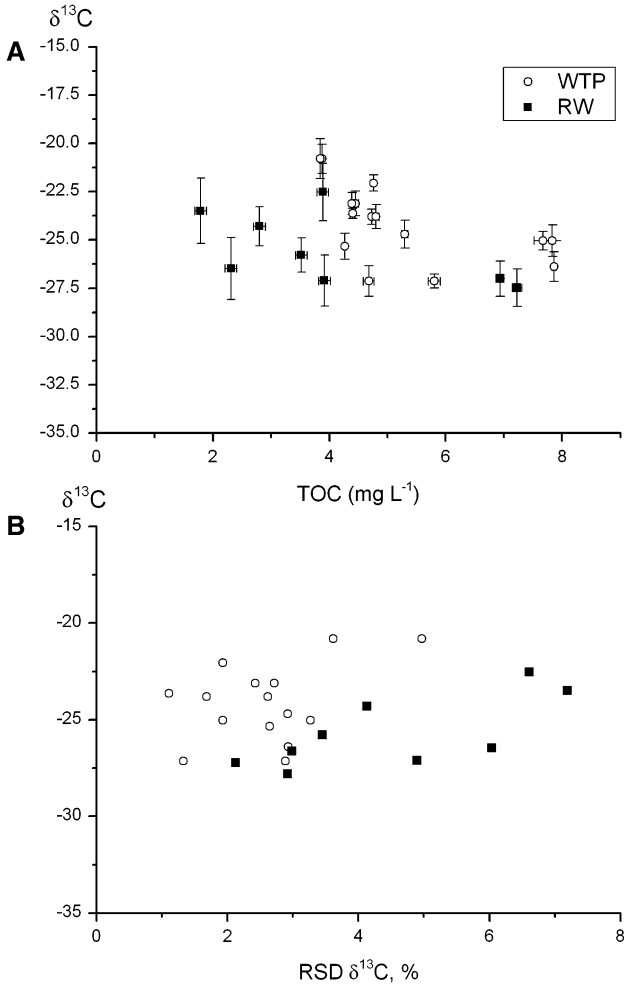

Fig. 3 Analysis of the effect of organic carbon concentration on the $\delta^{13}C$ value of environmental samples measured on the optimised iTOC-CRDS system. Using the new method, $\delta^{13}C$ values showed no systematic bias with organic carbon concentration (above 2 mg L^{-1}) or composition. *RW* river water, *WTP* waste water treatment plant water. Errors are the standard deviation (within-peak variability) for single analyses with the exception of WTP analyses that are the mean and standard deviations of three replicate analyses

Our results demonstrate that coupled TOC-CRDS systems are capable of precision equivalent to that achievable through conventional isotope ratio mass spectrometry (Gandhi et al. 2004), whilst using small sample volumes

(40 mL) and concentrations in the natural range encountered in surface waters. Thus, given the low per-analysis cost, high throughput (ca. 45 min/analysis) and simplicity of operation, TOC-CRDS offers a viable alternative to conventional DOC analysis by isotope ratio mass spectrometry.

Conclusions

In this study, we have made the first measurements of carbon isotope ratios in DOC using TOC-CRDS. The system showed comparable performance (analytical precision) to traditional isotope ratio mass spectrometry whilst analysing samples with low DOC concentration (i.e. ca. 2 mg L^{-1}), using low sample volumes (40 mL) and without any sample pre-treatment. Thus, the optimised iTOC-CRDS system is capable of DOC $\delta^{13}C$ analysis with high precision, low cost and high throughput and should be suitable for long-term field deployment, for example, in a portable laboratory.

It should be noted that the TOC-CRDS system is also suitable for the analysis of $\delta^{13}C$ of dissolved inorganic carbon (DIC). Although natural samples typically have higher DIC concentrations than DOC (Baker et al. 2008), there are some applications where low DIC analyses are needed (e.g. non-calcareous groundwater, snow and glacier samples, rain, etc.). Recent developments in CRDS analysis of DIC in the field (Bass et al. 2012) address this need but do not combine $\delta^{13}C$ measurements of both DIC and DOC. Therefore, the system refinements reported here may have broader applications than simply for the analysis of DOC.

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