High Precision $^{13}C/^{12}C$ Measurement of Dissolved Carbon Using a Transportable Cavity Ring-Down Spectrophotometer System

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Significance of Inorganic Carbon in Rivers

- Studies of major rivers often show that CO_2 concentrations are about 10-15 times greater than expected for an equilibrium with atmosphere
- Thus, rivers are actively degassing CO_2 into the atmosphere and affecting the natural carbon cycle
- Therefore, there's an increased interest in analyzing freshwater systems for their $\delta^{13}C$ values

Relevance of Inorganic Carbon in Oceans to GHG

- Half of the 1015 g of the annual combusted fossil fuel-derived CO_2 emitted into the atmosphere is absorbed into the oceans and the terrestrial biosphere
- Is the ocean sink large enough for the entire absorption?
- Can the terrestrial biosphere be a large carbon sink?
- $\delta^{13}C$ measurement can be used to estimate the relative contributions and sink processes

Environmental Significance of Dissolved Organic Carbon

- DOC is the largest pool of reduced carbon in aquatic ecosystems
- The ^{13}C stable isotope is an excellent environmental tracer for natural and anthropogenic carbon species
- ^{13}C can be used to characterize DOC in landfill leachates and interpret origin of DOC in ground water

DOC: Analytical Challenges

Despite the prominence of DOC as a carbon reservoir, it remains difficult to chemically characterize:

- Heterogeneous mixture of largely unidentified species
- Low concentration in fresh water

Isotopic analysis of freshwater DOC is quite difficult:

- Low concentration
- Lack of available sample preparation instrumentation

Tool of Choice for $\delta^{13}C$ Analysis of DIC/DOC

Until the introduction of the iTOC-CRDS instrumentation described here, Isotope Ratio Mass Spectrometry (IRMS) has been the only choice:

IRMS	*i*TOC-CRDS
Bulky ▸ lab-restricted	Small footprint ▸ field deployable
Complex, high maintenance	Simple, turnkey, robust, reliable
High Capital Cost	Low upfront cost, minimal operating cost
Expert operator ▸ High operational cost	Easy to use, low cost of ownership

Cavity Ring Down Spectroscopy (CRDS) – Principle of operation

- The CO_2 gas generated from the oxidation of aqueous samples is first collected in a gas sampling bag. Then, the flow from the bag is diverted to the isotopic analyzer as a continuous gas stream.
- Light from a tunable semiconductor diode laser (1.63 μm) is directed into an optical resonator cavity containing the analyte gas.
- When the optical frequency matches the resonance frequency of the cavity, energy builds up in the cavity.
- When the build-up is complete, the laser is shut off.
- The energy decays from the cavity exponentially in time, or "rings down," with a characteristic decay time. This energy decay is measured, as a function of time, on a photodiode.
- The ring down time measurement is continuously repeated at several different well-controlled points in wavelength as the laser is tuned across the spectral features of the isotopomers of the analyte gas.
- CRDS is a measurement of time not of absorbance. When the laser is at a wavelength where the gas in the cavity is strongly absorbing, the ring down time is short; when the wavelength is such that the gas does not absorb, the ring down time is long.
- Each isotopomer concentration is determined by a multi-parameter fit to its lineshape (Fig 2) and is proportional to the area under the curve. The vertical axis is loss (or absorption, measured with cavity ring down); the horizontal axis is wavelength (measured with Picarro's patented Wavelength monitor)

The Difference Between Dissolved Inorganic Carbon and Dissolved Organic Carbon Chemistry

- Inorganic carbon is mainly controlled by acid-base reactions
- Inorganic Carbon species are: Dissolved CO_2, HCO^{3-}, CO_3^{2-}
- The ratio of these species depends on the pH of the solution
- Organic Carbon originates from chemical and physical changes in soil organic material that becomes soluble
- Carbon transformations are linked via acid/base and redox reactions
- The basis of carbon cycle studies are the analyses of DOC & DIC

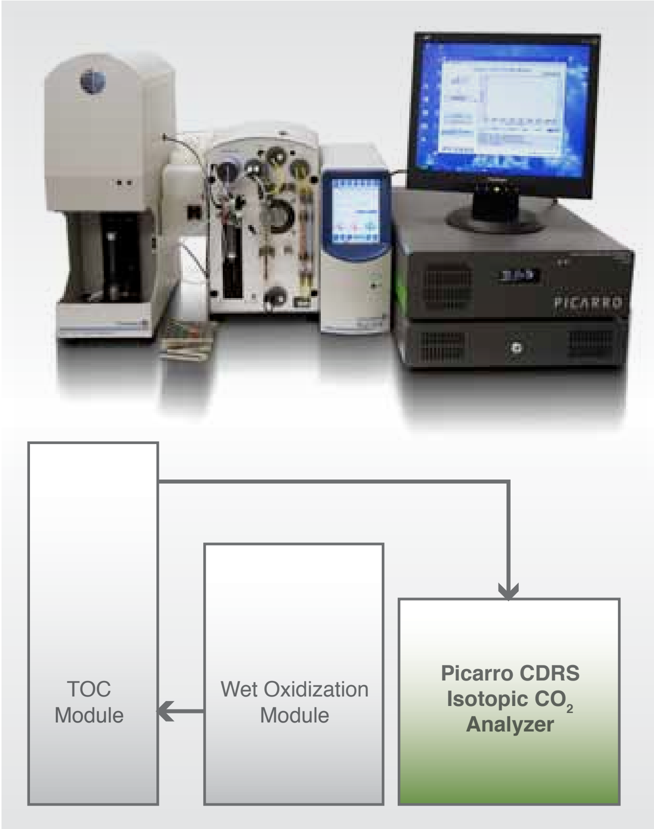

Fig. 1. iTOC-CRDS photo and schematic. CO_2 from combustion in the TOC solids module or from a wet oxidation process is analyzed for total carbon and then analyzed for isotopic content by the CRDS analyzer.

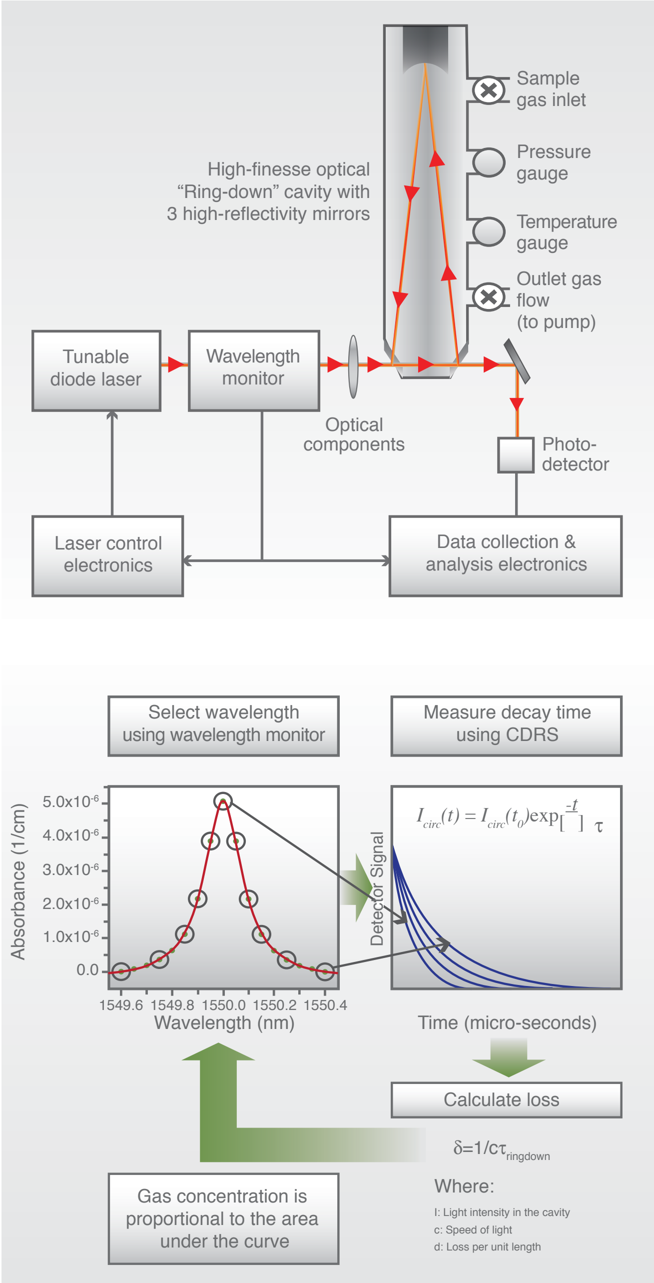

Fig. 2. CRDS analyzer schematic

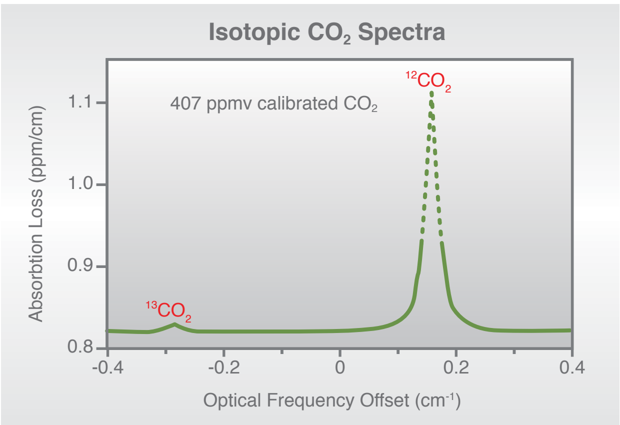

Fig. 3. Shown here are the two spectral features used in the CRDS analyzer to measure the isotopic ratio of carbon in CO_2

Materials and Methods

Measurement of $\delta^{13}C$ from total dissolved inorganic carbon (DIC) and was made using a sample preparation system coupled to a small footprint Cavity Ring-Down Spectrometer (CRDS). This system is capable of applying a 5 % H_3PO_4 solution or a Sodium persulfate oxidation process to a water sample in an exetainer vial, thereby liberating gaseous CO_2 and permitting stable carbon isotope measurement in DIC and DOC, respectively. The isotopic carbon signature determination can then be used to trace the origin of carbonates or organic carbon compounds. In a first phase, a manual process was employed in which DIC containing samples were acidified and the evolved CO_2 was collected inside gas pillows. The gas pillows were then connected to the inlet of the isotopic CRDS instrument for carbon ratio measurement. In a second phase, the CO_2 liberation processes were automated in an integrated analyzer enabling software control of a sample preparation system directly connected to the gas inlet of the isotopic CRDS instrument.

Water Sample Source Locations

Water Sample Collection

- Stream water samples were collected from three different watersheds in SF Bay Area:
- East Laurel Creek: feeds into the Seal Creek watershed (San Mateo Hills)
- Coyote Creek: main river of the Coyote Creek watershed (Diablo range)
- San Francisquito Creek: part of the San Francisquito watershed (El Corte Madera range)

Stream water samples analysis: Concentration & Isotopic determination of DIC/DOC

Stream	DIC, ppm	$\delta^{13}C$, ‰ DIC	DOC, ppm	$\delta^{13}C$, ‰ DOC
San Francisquito Creek	33.7 ± 0.3	-1.8 ± 0.5	16.3 ± 0.3	-21.1 ± 0.9
Coyote Creek	46.1 ± 0.5	-0.8 ± 0.4	10.11 ± 0.05	-18.0 ± 0.8
E. Laurel Creek	93.1 ± 0.2	-1.8 ± 0.3	10.72 ± 0.09	-17.3 ± 0.6

Conclusions

The world's first continuous flow isotopic TIC/DOC-CRDS measurements are reported here with remarkable achieved precisions. A measurement precision of the isotopic ratio in the range of 0.2 ‰ to 0.4 ‰ was achieved in minutes of measurement time. Such precision readily distinguishes the isotopic DIC and DOC signatures from a set of three different streamwater samples collected from various sites in Northern California. The current TIC/DOC-CRDS setup will enable shipboard measurement and presents a rugged, portable and inexpensive analytical instrumentation alternative to the traditional use of methods based on the more complex and lab-confined isotope ratio mass spectrometry technique.