AN014

Stable Isotope Ratio Measurement of Dissolved Inorganic Carbon (DIC)

WS-CRDS provides simple $\delta^{13}C$ measurements of DIC, enabling the source type of these compounds to be determined.

Keywords:

Material: Water, dissolved inorganic carbon (DIC), carbonates, bicarbonates, water analysis, water quality, water purity, water hardness, carbon cycle, coral, sediments.

Summary and Relevance:

There is an established need and methodology to measure dissolved inorganic carbon (carbonate and bicarbonate) concentrations in aqueous samples[1]. Carbon/water cycle studies use this technique to aid in assessment of the capture/storage capacity of seawater and its role in stabilizing atmospheric CO_2 levels. Another such application is monitoring the performance of man-made sequestration projects where captured CO_2 is stored in deep saline aquifers. A powerful additional metric that has been underexploited is the stable isotope ratio of the DIC i.e. $\delta^{13}C$. Since different sources of CO_2, from plant respiration to fossil fuel combustion, have a characteristic $\delta^{13}C$ value, measuring $\delta^{13}C$ can provide important sourcing/tracing information about the origins of the DIC found in samples.

The limiting factors to the more frequent and diversified measurement of $\delta^{13}C$ in DIC have been the complexity of measurements, the high cost of instrumentation and the level of expertise required for the traditional IRMS (isotope ratio mass spectrometry) methods. This has now completely changed with the advent of simple-to-use, turnkey and field-portable instruments based on a technique called wavelength scanned cavity ring down spectroscopy (WS-CRDS), well-proven in high-precision greenhouse gas (GHG) monitoring applications. These instruments can quickly provide $\delta^{13}C$ in just a few minutes, and for a fraction of the hardware cost and operation expertise. These factors enable the measurement of isotopic DIC in the field and at sea. Thus, scientists are able to make measurements in real-time rather than send samples back to a lab and await results. This has several major benefits: samples are not at risk from prolonged storage and travel, nor from poisoning or free/thaw processes used to prevent microbial contamination. In addition, field or ship based studies can be positioned and repositioned based on real-time data, saving time and expense.

This application note demonstrates the simplicity of the method by comparing water samples collected from three different locations in the San Francisco Bay Area.

Analyzer Used:

Picarro G1101-*i* with AutoMate system from AutoMate FX, Inc.

Process:

Three water samples from three different locations in the San Francisco Bay Area (Redwood City harbor, Shoreline Park Lake, and Half Moon Bay) were collected between Dec. 08 and Jan. 09. Aliquots (4ml) of these water samples were pipetted into 5 Exetainer vials. An automated DIC sample preparation system (AutoMate) was used to inject a 10% phosphoric acid solution into each sealed vial to liberate CO_2 from inorganics. In addition, a stream of dry, CO_2 free nitrogen was bubbled through the acidified solution to flush the released CO_2 from the vial headspace. The released CO_2 was captured into a standard gas sampling bag using a manually operated two-position 4-port rotary valve. The outlet of the gas pillows is connected via a manually controlled three-way solenoid valve to the gas inlet of the Picarro isotopic CO_2 WS-CRDS analyzer, which measures the stable isotope ratio, $\delta^{13}C$. The instrument and the gas sampling bag were purged with fully dry, CO_2 free nitrogen between successive DIC/$\delta^{13}C$ measurements.

Results:

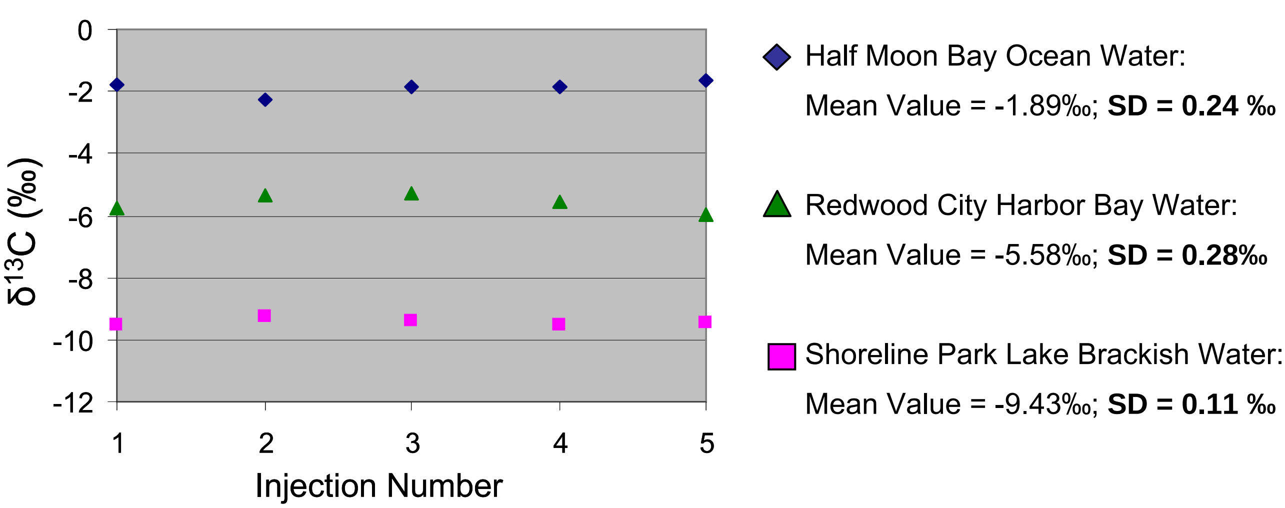

Figure 1. DIC $\delta^{13}C$ ratios. Raw data from three water samples (n=5) from various sites in the SF Bay Area. Notice the excellent repeatability. With only 4-5 minutes of sample analysis time for each vial, this application yielded data that exceeded the published, guaranteed precision for the Picarro G1101-*i* WS-CRDS isotopic CO_2 analyzer.

As shown in figure 1, the isotopic analysis of DIC in the SF Bay Area water samples yielded three distinguishable $\delta^{13}C$ values. The data also show the excellent precision for this method. The observed differences in the delta values presumably indicate the degree of inclusion of the sampled water system and the degree of mixing of sea and river water.

Comments:

Better understanding of DIC can benefit researchers and engineers in many different fields from carbon cycle science, to geology and sequestration. For example, precipitation and dissolution behavior of carbonates plays a major role in the formation of sediments, sedimentary rocks and in man-made constructions, and is also closely associated with coral reef vitality. The ability to now rapidly measure $\delta^{13}C$ ratios provides scientists with important information that was previously rarely exploited.

References:

[1] See for example Kroopnick, P. *Earth and Planetary Science Letters* Volume 49, Issue 2, September 1980, Pages 469-484