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Analysis of δ18O and δD values of environmental waters at high temporal and spatial resolution by continuous diffusion sampling cavity ring-down spectrometry

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A novel sampling device utilises diffusion through porous PTFE tubing to deliver water vapour continuously from a liquid water source for analysis of δ18O and δD values by Cavity Ring-Down Spectrometry (CRDS). Comparison of isotopic data for a range of water samples analysed by Diffusion Sampling-CRDS (DS-CRDS) and Isotope Ratio Mass Spectrometry (IRMS) shows significant linear correlations between the two methods allowing for accurate standardisation of DS-CRDS data. The internal precision for an integration period of 3 min (standard deviation = 0.1 ‰ and 0.3 ‰ for δ18O and δD values, respectively) is similar to analysis of water by injection/evaporation CRDS of discrete water samples. The isotopic effects of variable air and water temperature, water vapour concentration and water pumping rate were found to be either negligible or correctable by analysis of water standards. Separation of the analysed water vapour from non-volatile dissolved and particulate contaminants in the liquid sample minimises interferences associated with CRDS analyses of many aqueous samples. Coupling of the DS-CRDS instrument to an auto sampler enables rapid analysis (10 min) of discrete water samples.

The DS-CRDS system was used in the first continuous shipboard measurement of δ18O and δD of water. Combined with continuous salinity recordings, a data set of nearly 6,000 isotope measurements was made at 30-s intervals during a 3-day voyage through the Great Barrier Reef Lagoon. Precise identification of river plumes within the Great Barrier Reef Lagoon was possible because unique δ18O/δD–salinity relationships of individual plumes were measured at high spatial and temporal resolution. Continuous shipboard measurement of δ18O/δD values by DS-CRDS provides additional discriminatory power for assessing water mass formation processes and histories at a small fraction of the cost of traditional isotope analysis of discrete samples.

In a second application of DS-CRDS, continuous real-time analysis, at 30-s intervals, of precipitation at an Australian tropical location revealed extreme and rapidly changing δ18O and δD values related to variations in moisture source areas, transport paths and precipitation histories. The range of δ18O (-19.6 ‰ to +2.6 ‰ and δD (-140 ‰ to +13 ‰ values from almost 6,000 measurements of nine rain events over 15 days during an 8-month period at a single location was comparable with the range measured in 1532 monthly samples from all seven Australian Global Network of Isotopes in Precipitation stations from 1962 to 2002. Extreme variations in δ18O (-8.7 ‰ to -19.6 ‰ and δD (-54 ‰ to -140 ‰ were recorded within a single 4-h period.

Real-time stable isotope monitoring of environmental waters at high temporal and spatial resolution enables new and powerful tracer applications in climatology, hydrology, eco-physiology and palaeo-climatology.