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A Real-time Monitoring System of Dissolved Nitrous Oxide, Methane and other Gases and their Isotopes in Aquatic Ecosystems

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Coastal ecosystems are dynamic regions especially rich in diverse biological and geochemical interactions. However, major gaps exist in our knowledge of the primary biogeochemical processes and the factors regulating their relative importance. The study of the biogeochemical cycles of nitrogen and carbon in aquatic systems is important for understanding the fate of nutrients and other chemical components present there. Nitrous oxide (N_2O) and methane (CH_4), have important roles in these nitrogen and carbon biogeochemical processes as they are produced and cycled within coastal and ocean environments. They are also significant greenhouse gases with major roles in climate change. The gaps in our understanding of the distribution and dynamics of the underlying processes controlling their fluxes can be filled with the development and deployment of high-resolution spatial-temporal measurement methods.

We have developed a field deployable, real-time, *in situ* system to quantify dissolved greenhouse gases (N_2O and CH_4 and their isotopologues) in aquatic ecosystems including coastal wetlands. This measurement system consists of i) an array of permeable, hydrophobic probes that can be brought under a partial vacuum without intrusion of liquid water; ii) a collection protocol for efficiently drawing dissolved gases into the sampling system without isotopic fractionation; and iii) an interface of the probe array and the extraction and sampling system with real time analytical instrumentation. By integrating an Aerodyne tunable infrared laser direct absorption spectrometer (TILDAS) into the measurement system, we can achieve real time determination of concentration and isotopic abundances of N_2O and CH_4.

We have compared dissolved gases extracted from a variety of collected water samples including different tap water sources, ocean water, and wetland "swamp" water. We observed higher N_2O in the tap water samples compared to the ocean waters. Swamp water collected from two areas of the wetland (i.e., still and moving water zones) had elevated CH_4 and N_2O, with the still water having higher methane and lower N_2O than observed in water from area with movement. We also compared dissolved N_2O isotopologues with headspace in dosing experiments, achieving excellent comparisons of the $^{15}N_2O$ isotopic ratios (δ456, δ546) and site preference (SP = δ456- δ546) of dissolved N_2O with the headspace. Laboratory results as well as plans for field demonstrations in coastal areas will be discussed.