Development of a CRDS method for methane determination on discrete water samples: Application to the study of CH_4 dynamics in a shallow sub-tropical estuary

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Methane is the third most abundant greenhouse gas (GHG) but is understudied in comparison to carbon dioxide. Sources and sinks to the atmosphere vary considerably in estimation, including sources such as freshwater and marine systems. We examined the seasonal variability of methane fluxes within St. Louis Bay, Mississippi, a shallow sub-tropical estuary. As part of this work, we also tested a new method for discrete sample methane determination utilizing cavity ring-down spectroscopy (CRDS).

The new method for methane determination involves equilibration of water samples with a zero air headspace. Generally, the equilibration is done in 140-mL syringes with equal volumes of water and gas. The gas is then transferred to a dry syringe and drawn into the CRDS analyzer (Picarro G2301) by the instrument's pump. We show that this instrument holds a linear calibration into the sub-ppm methane concentration range and holds a stable calibration at least two years.

The new method for methane determination has been applied to a variety of natural waters ranging from rivers to estuaries to the open ocean as well as a hypersaline basin. In particular, we are examining methane dynamics in a shallow bay in the northern Gulf of Mexico. St. Louis Bay, Mississippi, is a shallow subtropical estuary having an area of 4000 ha with a mean depth of 1.3 m. Ongoing surveys of methane in the bay began in August 2013. Methane inventories for the bay have varied from 700 – 5000 mol. The sediments appear to be the main source of methane and air-water evasion the main sink. Residence times of water column methane with respect to atmospheric evasion range from 1 - 14 hrs. Overall evasion rates from the bay are 0.02 – 2 mmol m^{-2} day^{-1}, similar to other determinations of estuarine methane fluxes to the atmosphere. While there are hints in the data that temperature and wind speed are important factors in determining the bay's methane inventory, our currently limited dataset does not yet allow us to definitively state which controlling factors are most important.