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# Continuous measurements of nitrous oxide, carbon monoxide, methane and carbon dioxide in the surface ocean with novel laser-absorption analysers

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In recent years, improvements in spectroscopic technology have revolutionised atmospheric trace gas research. In particular, cavity-based optical absorption analysers allow determination of gas concentrations with high frequency, repeatability, reproducibility and long-term stability. These qualities make them particularly suitable for autonomous measurements on voluntary observing ships (VOS). Here, we present results from three of the first deployments of such analysers on research ships, as a first step towards VOS installations.

Los Gatos off-axis ICOS (Integrated Cavity Output Spectroscopy) analysers were used to measure nitrous oxide ($N_2O$), carbon monoxide (CO), methane ($CH_4$) and carbon dioxide ($CO_2$) mixing ratios in ocean surface water during research cruises in 2010, 2011 and 2012. The analysers were coupled to an equilibrator fed by the scientific seawater supply in the ship's laboratories. The equilibrator measurements were alternated with regular measurements of marine air and calibrated standard gases.

Short-term precision for 10 s-average N2O mole fractions at an acquisition rate of 1 Hz was better than 0.2 nmol $mol^{-1}$. The same value was achieved for duplicate measurements of a standard gas analysed within 1 hour of each other. The response time to concentration changes in water was 142-203 s, depending on the headspace flow rate.

During the first deployment on the AMT20 cruise (Atlantic Meridional Transect, Southampton to Punta Arenas, 12 October to 25 November 2010), we unexpectedly found the subtropical gyres to be slightly undersaturated in $N_2O$, implying that this region acted as a sink for this greenhouse gas. In contrast, the equatorial region was supersaturated and a source of nitrous oxide to the atmosphere. Mean sea-to-air fluxes were overall small and ranged between $-1.6$ and 0.11 $\mu$mol $m^{-2}$ $d^{-1}$ (negative fluxes imply an net uptake by the ocean). Despite the good short-term repeatability, significant calibration drift occurred between the six-hourly calibration intervals. We have therefore repeated the observations during the AMT22 cruise (Southampton to Punta Arenas, 10 October to 24 November 2012) and will present the results together with the 2010 data.

The second deployment during the D366 Round Britain ocean acidification cruise (6 June to 9 July 2011) showed virtually no day-to-day drift, based on the calibration gases and marine air analyses. Preliminary analyses of the data show that $CH_4$ and $N_2O$ were supersaturated in the Skagerrak region, presumably due to the influence of Baltic Sea water, and in coastal areas. Phytoplankton blooms show evidence of $CO_2$ draw-down. CO is extremely supersaturated (up to 50 times), which can be attributed to photochemical breakdown of dissolved organic carbon compounds.

For the more recent deployments, a $CO_2$/$CH_4$ and an $N_2O$/CO analyser were successfully operated in series, off of a single equilibrator feed. No leaks or other problems occurred during these deployments, which shows that such a configuration would be ideal for VOS installations as part of the ICOS observational network.