

Sampling and Analytical Procedures Summary

For dataset "ContinuousNobleGasData" <https://www.bco-dmo.org/dataset/869295>

A full description of the sample collection and analysis is in Stanley et al., "Gas Fluxes and Steady State Saturation Anomalies at Very High Wind Speeds" Submitted to JGR-Oceans in Dec. 2021. Here are the relevant paragraphs from that paper:

The noble gas ratios and concentrations of the seawater within the SUSTAIN tank were analyzed continuously using the portable Gas Equilibrator Mass Spectrometer (GEMS) for Ne, Ar, Kr and Xe ratios (Manning et al., 2016) and an Equilibrator Inlet Mass Spectrometer (EIMS) for O₂/Ar ratios (Cassar et al., 2009). For both systems, water was pumped from a level of 28.75 cm above the bottom of the SUSTAIN tank, just down-fetch from the bubble imager into a 4 L beaker set up on the level right above the tank (a distance of approximately 2 meters) using an in situ fountain pump (Smart Pond 500-Gph), a type of pump that leads to less gas distortion than pumps that pull the water from the top. The beaker was temperature-controlled by outflowing water, and then the outflowing water was circulated back into the tank so that the total volume of water in the tank did not change appreciably.

For the GEMS: a microgear pump, equipped with tygon tubing, brought the water from the bucket through a polyester filter bag (14 cm OD, 38 cm long, 25 μm pore size) and a filter sock (3.8 cm wide, 30 cm long, 5 μm inner and 100 μm outer pore size) into a Membrana Liqui-Cell ExtraFlow Equilibrating Cartridge. The headspace in that cartridge was swept through a nafion box and drierite tubing for drying and then through a 0.05 μm capillary to a gettering system constructed of SAES STS-2001 getters at 350 °C and at room temperature for removal of active gases, and finally into a Hiden RGA HAL 3F Quadrupole Mass Spectrometer (for details, see Manning et al. 2016). Precision of the gases, based on laboratory experiments of equilibrated water, conducted immediately before the work at SUSTAIN, suggest that the ratios of noble gases are quantified with precisions better than 0.5% for Ne/Xe, and Ar/Kr and better than 0.8% for Ne/Ar, Ar/Kr and Ar/Xe. The e-folding equilibration time of the cartridge is several minutes, with ratios being measured every 60 seconds. Thus this method, though powerful, may average over the first few minutes of intense gas exchange.

For the EIMS: a second Liquicel ExtraFlow Equilibration cartridge, complete with its own filters, gear pump, and air circulation loop (all similar to the ones for the GEMS), was set up and gas from that cartridge was fed into a Pfeiffer PrismaPlus Quadrupole Mass Spectrometer for analysis of O₂/Ar. Notably, this second system was similar to the first but it did not have getters, allowing analysis of O₂ (which is removed by the getters). Measurements were collected every 15 seconds and e-folding equilibration time of the cartridge is similarly several minutes.

Both the GEMS and the EIMS contained Vici valves that allowed switching between the capillary connected to the cartridges that were sampling the gas content of water in the SUSTAIN tank and the capillaries that were measuring laboratory air which was used for standardization of gas ratios since the gas content of oxygen and noble gases in air is constant and well-known. Before and after each experiment, the GEMS and the EIMS sampled laboratory air. These frequent calibrations were necessary because the humidity and temperature of the SUSTAIN lab building increased during the day as hot Miami air was blown through the system. Frequent air calibrations allowed us to correct for these humidity and temperature effects on the mass spectrometers. Additionally, experiments were conducted where the GEMS sampled air that was within the SUSTAIN tank itself to confirm that the SUSTAIN tank air (i.e air directly overlying the water) was the same as the general laboratory air. However, due to the risk of salt spray getting into the air capillary and subsequently into the mass spectrometer, most of the air calibrations were performed using laboratory air.

Ratios of gases in either the GEMS (e.g. Ne/Xe, Ar/Kr, or any combination thereof) or the EIMS (O₂/Ar) were calculated according to Manning et al., 2016 with the gas ratios in air interpolated between the start and end of

each experiment (roughly 1 hour interval) and then the measured gas ratios in water related to the air ratios according to:

$$\Delta \left(\frac{Ne}{Xe} \right) = \left[\frac{\left(\frac{Ne}{Xe} \right)_{hs}}{\left(\frac{Ne}{Xe} \right)_{air}} - 1 \right] \times 100$$

where *hs* refers to the gas ratio in the headspace of the cartridge and *air* refers to the gas ratio as measured in laboratory air.

Oxygen concentrations were measured every 5 seconds using an Anderra optode deployed directly in the tank, affixed 35 cm above the tank bottom to the main mast from which the water was pumped. The optode was calibrated with oxygen samples measured using the Winkler method by F. Millero's laboratory at the University of Miami.

The GEMS furnishes ratios of noble gases in seawater. These ratios are informative, since for example, bubbles impact the saturation anomaly of Ne much more than they affect X due to Ne's lower solubility and thus the Ne/Xe ratio can be used as a diagnostic for the influence of bubble processes. However, for flux calculations, concentrations of the gases are necessary. Thus we calculated noble gas concentrations from the continuous GEMS record by combining the optode O₂ concentrations, the EIMS O₂/Ar ratios, and the GEMS Ne/Ar, Kr/Ar and Xe/Ar ratios, according to the equation (given for Xe but analogous equations can be written for other gases):

$$[Xe] = O_{2_{optode}} \times \left(\frac{Ar}{O_2} \right)_{EIMS} \times \left(\frac{Xe}{Ar} \right)_{GEMS}$$

where Ar/O₂ is the air-calibrated ratio of ion currents of Ar and O₂ as measured in the headspace by the EIMS and Xe/Ar is air-calibrated ratio of the ion currents of Xe and Ar as measured in the headspace by the GEMS.

Temperature was interpolated from in situ measurements of temperature made by an Anderra optode located next to the in situ pump that brought water to the copper tubes. Salinity measurements were made at the beginning and end of most experiments and then interpolated to the time of noble gas data collection to obtain an appropriate salinity. The salinity in the SUSTAIN tank changed slowly for the most part since typically it was a closed system and thus evaporation was the only cause for change. However, at certain points within the experiment, new water was added to the tank and at those times, salinity samples were also taken. Thus the salinity data is usually smoothly changing but with some jumps.