

# ATMOSPHERIC AR/N<sub>2</sub> MEASUREMENTS AS A TRACER FOR AIR-SEA HEAT FLUX

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## ABSTRACT

We present 16 months of semi-continuous Ar/N<sub>2</sub> data measured at the Scripps Pier in La Jolla, CA. The concentration of atmospheric Ar/N<sub>2</sub> depends on air-sea heat flux. As the ocean takes up heat, both argon and nitrogen are degassed to the atmosphere; as the ocean cools, they are taken up. This record is the beginning of a long-term monitoring program that will parallel the O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub> measurement programs at Scripps and may help resolve the oceanic contribution to atmospheric CO<sub>2</sub> variability.

## RATIONALE OF THE MEASUREMENT PROGRAM

High-precision mass spectrometer measurements of the argon to nitrogen (Ar/N<sub>2</sub>) can be used as a tracer for air-sea heat flux. Because argon and nitrogen are, in effect, inert gases in the atmosphere, their concentrations depend significantly on changes in seawater gas solubility at the ocean surface. As water temperature rises, the solubility of each gas drops, and more gas is released to the atmosphere. The reverse happens as heat is released from the ocean and water temperatures cool. Ar/N<sub>2</sub> measurements allow us to address questions of how air-sea heat flux varies on seasonal and interannual time scales. Such issues are important to climatological questions on both local and global levels. As part of a long-term monitoring program, Ar/N<sub>2</sub> measurements will provide an independent estimate of the amount of heat taken up by the ocean due to global warming. Ocean warming and cooling also influence the CO<sub>2</sub> cycle, such that measurements of changes in the Ar/N<sub>2</sub> ratio may also help resolve the oceanic contribution to atmospheric CO<sub>2</sub> variability.

The Ar/N<sub>2</sub> ratio, assessed concurrently with other atmospheric species such as O<sub>2</sub> and CO<sub>2</sub>, will also allow such questions to be addressed as the partitioning of the seasonal O<sub>2</sub> flux between ocean biology and gas exchange associated with air-sea heat flux. As the ocean warms due to climate change, O<sub>2</sub> is being degassed to the atmosphere; present estimates of the amount are based through indirect methods on the heat storage change estimated by *S. Levitus et al.* [2000] and may have significant interannual variability [*G. Plattner et al.*, 2002]. Natural changes such as ENSO and wintertime convection in the north Atlantic are already known to be important for understanding interannual variability in air-sea O<sub>2</sub> flux [*McKinley et al.*, 2003]. Model results also suggest that ocean warming will also lead to changes in stratification, impacting ventilation and biological productivity [*L. Bopp et al.*, 2002]. Correcting the partitioning of contributions of land and ocean production in the overall O<sub>2</sub> and CO<sub>2</sub> budgets requires more information on the size of physical and biological processes on O<sub>2</sub> air-sea fluxes. This information may also help to constrain the interannual changes in air-sea CO<sub>2</sub> flux, which are presently poorly known [*C. Le Quéré et al.*, 2000].

## RESULTS

We now have 16 months of semi-continuous atmospheric Ar/N<sub>2</sub> data from the Scripps Pier, La Jolla, CA (Fig. 1). Air is pumped directly from the pier into a magnetic sector mass spectrometer with eight collectors, allowing for simultaneous measurements of the Ar/N<sub>2</sub> ratio, the O<sub>2</sub>/N<sub>2</sub> ratio, and CO<sub>2</sub>. With an hourly precision of 2-3 per meg, we have observed an annual cycle in the Ar/N<sub>2</sub> ratio of 7-8 per meg. A measurable diurnal cycle of 1 per meg provides a bound on the size of potential laboratory problems associated with regular changes in pressure or temperature or sampling bias associated with local air mass origins. The data show significant synoptic variability imposed on top of the seasonal cycle that is most likely related to regional changes in air-sea heat flux and/or atmospheric transport; however, they may also be a sign that there may still be significant instrumental problems that we do not yet understand.

Measurements of changes in the Ar/N<sub>2</sub> ratio can also establish the contribution of air-sea heat exchange on the composition of a given air parcel, including the contributions to other constituents such as CO<sub>2</sub> and O<sub>2</sub>.

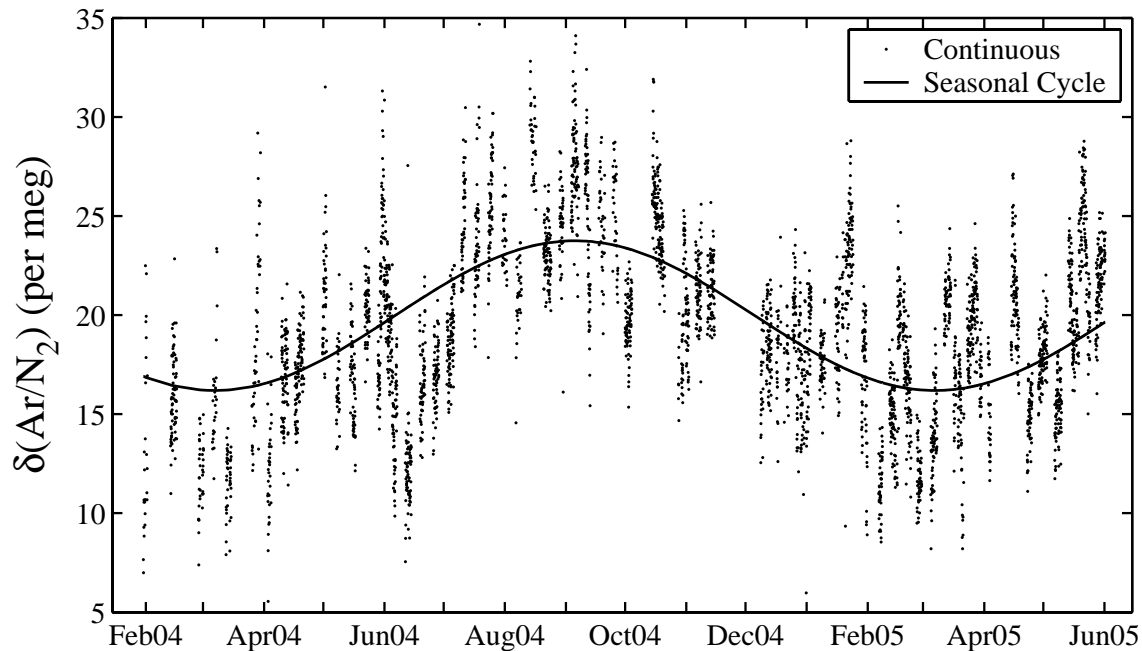


Fig. 1. Semi-continuous measurements taken at the Scripps Pier in La Jolla, CA, between February 2004 and June 2005. The seasonal cycle (fit as the first harmonic to the data) is clearly visible.

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