

# Undersaturation of inert gases at the ocean surface: A thermal pumping mechanism

Craig L. McNeil

Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island, USA

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[1] A diurnal ‘thermal pumping’ mechanism is proposed to explain why undersaturation of inert gases may develop at the sea surface during extended periods of low wind speed and net warming. A simple two-layer model of the upper ocean with parameterized air-sea gas exchange is used to explain the process. The model predicts maximum undersaturations of 0.25% for Ne, 0.75% for N<sub>2</sub>, 0.88% for Ar, and 1.12% for Kr for an assumed diurnal warming signal of 2°C, a gas transfer rate appropriate to a wind speed of 4 ms<sup>-1</sup>, and the simplifying assumption of no net warming over the day. The model results depend on the air-sea gas transfer rate and the details of the upper ocean heating and mixing cycle. Observations of N<sub>2</sub> undersaturation from the tropical Atlantic provide supporting experimental evidence. **Citation:** McNeil, C. L. (2006), Undersaturation of inert gases at the ocean surface: A thermal pumping mechanism, *Geophys. Res. Lett.*, 33, L01607, doi:10.1029/2005GL024752.

## 1. Introduction

[2] A warm layer of surface water, typically a few meters in depth, is known to develop during the daytime over large regions of the world’s oceans. This phenomenon is mostly confined to areas with strong solar heating and low wind speeds, such as the tropics and certain midlatitude regions [Donlon *et al.*, 2002; Stuart-Menteth *et al.*, 2003]. Diurnal warm layers form because approximately 50% of the total solar radiation heat entering the ocean is absorbed by seawater at depths less than 2 m. Exceptionally strong warming of more than 3°C has been observed in the western equatorial Pacific during calm conditions [Soloviev and Lukas, 1997].

[3] Processes that contribute to anomalies in the saturation levels of dissolved gases at the ocean surface are important to identify and understand, because they ultimately control the net regional air-sea gas fluxes. Prior work considered the influence of diurnal warm layers on high-frequency time series measurements of dissolved O<sub>2</sub> [McNeil and Farmer, 1995] and net air-sea CO<sub>2</sub> fluxes [McNeil and Merlivat, 1996]. More detailed experimental studies related to air-sea fluxes of CO<sub>2</sub> included the influence of the ‘cool-skin’ effect [Ward *et al.*, 2004].

[4] Temporal and spatial variability in inert gas distributions at the ocean surface provide a useful measure of the state and rate of gas equilibration between the ocean and the atmosphere. This information is necessary to better understand biogeochemical cycling of biologically active gases

such as O<sub>2</sub> and CO<sub>2</sub>. In addition, inert gases can be used as conservative tracers for water masses that move from the ocean surface to the deep ocean. In this study, I investigate the influence of a persistent diurnal warm layer of ocean surface waters on inert gas distributions to explain why gas undersaturation can develop even during periods of net warming.

## 2. Observations

[5] Although large data sets on pCO<sub>2</sub> distributions at the ocean surface have been collected by research vessels and ships of opportunity [Takahashi *et al.*, 2002], relatively little data on ocean surface inert, or bioinactive, gases exist. The dissolved N<sub>2</sub> data presented here were collected by the R/V *Brown* during the A16N transit from Iceland to the equatorial Atlantic. The data presented in Figure 1 were collected between 19 July 2003 and 8 August 2003, and cover the latitudes 30°N to approximately 5°S at longitudes 25–30°W. Dissolved N<sub>2</sub> levels were estimated using the gas tension (total dissolved gas pressure) method as described by McNeil *et al.* [2005]. For this procedure, gas tension, dissolved O<sub>2</sub>, seawater temperature, and salinity measurements at approximately every 0.5° latitude were used. Seawater samples were collected mostly at 5–10 m depth by hydrocast, and analyzed for dissolved O<sub>2</sub> content by the Winkler titration method. The ship’s CTD profiler provided water temperature and salinity measurements. As described by McNeil *et al.* [2005], dissolved Ar and N<sub>2</sub> are assumed to be saturated to the same level. Data on O<sub>2</sub> solubility are taken from Garcia and Gordon [1992] and data on N<sub>2</sub> and Ar solubility are taken from Hamme and Emerson [2004]. Dissolved gases are expressed with respect to local atmospheric pressure, assuming 100% relative humidity in the atmospheric marine boundary layer, and assuming standard dry air mole fractions of 0.78084 for N<sub>2</sub>, 0.20946 for O<sub>2</sub>, 0.00934 for Ar, and 0.000365 for CO<sub>2</sub>.

[6] The variability in O<sub>2</sub> measurements between duplicate samples was ±0.2%. The overall accuracy was estimated at ±0.5%. The accuracy of the GTD pressure sensor was ±0.02%. The overall accuracy of gas tension measurements was estimated at ±0.07%. A conservative estimate of overall accuracy of dissolved N<sub>2</sub> was ±0.7% [McNeil *et al.*, 1995, 2005].

[7] As shown in Figure 1, N<sub>2</sub> was mostly undersaturated from 10°N to 5°S except near the equator, where N<sub>2</sub> was close to saturation and O<sub>2</sub> was anomalously low compared to other waters in the region. These equatorial waters had likely upwelled just prior to sampling. However, the general undersaturation of N<sub>2</sub> was unexpected in light of seasonal warming effects during the sampling period. Warming