Evidence of O₂ consumption in underway seawater lines: Implications for air-sea O₂ and CO₂ fluxes

Lauren W. Juranek,¹ Roberta C. Hamme,² Jan Kaiser,³ Rik Wanninkhof,⁴ and Paul D. Quay⁵

Received 20 August 2009; revised 4 November 2009; accepted 17 November 2009; published 6 January 2010.

We observed O₂ deficits of 0.5 to 2.0% (1 to 4 μmol/kg) in the underway seawater lines of three different ships. Deficits in O₂/Ar and isotopic enrichments in dissolved O₂ observed in underway seawater lines indicate a respiratory removal process. A 1% respiratory bias in underway lines would lead to a 2.5–5 μatm (2.5–5 μbar) enhancement in surface water pCO₂. If an underway pCO₂ bias of this magnitude affected all measurements, the global oceanic carbon uptake based on pCO₂ climatologies would be 0.5–0.8 Pg/yr higher than the present estimate of 1.6 Pg/yr.

Treatment of underway lines with bleach for several hours and thorough flushing appeared to minimize O₂ loss. Given the increasing interest in underway seawater measurements for the determination of surface CO₂ and O₂ fluxes, respiratory consumption in underway seawater lines must be identified and eliminated on all observing ships to ensure unbiased data. Citation: Juranek, L. W., R. C. Hamme, J. Kaiser, R. Wanninkhof, and P. D. Quay (2010), Evidence of O₂ consumption in underway seawater lines: Implications for air-sea O₂ and CO₂ fluxes, Geophys. Res. Lett., 37, L01601, doi:10.1029/2009GL040423.

1. Introduction

Determination of dissolved gas concentrations in ship underway surface seawater lines is becoming a valued approach to increase the spatial and temporal resolution of biogeochemical parameters in surface waters. Underway measurements are critical to the continually-expanding database of surface ocean pCO₂ observations used to calculate CO₂ uptake [Takahashi et al., 2002, 2009; International Ocean Carbon Coordination Project, 2009]; increased use of underway sampling to improve the space and time resolution of surface ocean pCO₂ observations is a priority for future ocean carbon cycle research [Doney et al., 2009]. Observations of the surface dissolved O₂/Ar ratio in underway surface seawater lines have recently been used to estimate net community production (NCP) in the equatorial Pacific [Kaiser et al., 2005], coastal environments [Nemcek et al., 2008], and across frontal boundaries in the Southern Ocean [Tortell and Long, 2009]. Ongoing improvements to continuous O₂/Ar methods [Kaiser et al., 2005; Tortell, 2005; Cassar et al., 2009] invite an expanded use of these observations to broaden understanding of NCP and controls on surface ocean carbon cycling.

3 However, here we show that samples from underway seawater lines on research and commercial ships can have O₂ deficits of up to 2% compared to traditional Niskin bottles. If the O₂ removal is due to respiration in underway lines, as oxygen isotope and O₂/Ar data indicate, CO₂ measurements from surface seawater lines would be impacted. A respiratory O₂ consumption of 1% or ≈2 μmol/kg, for example, would result in a ≈1% (≈4 μatm, equivalent to about 4 μbar) change in pCO₂ as discussed below. These observations of O₂ consumption therefore have significant implications for calculations of oceanic carbon uptake from air-sea pCO₂ gradients [Takahashi et al., 2009].

4 Given trends toward lower-cost, high-resolution oceanographic data collection through the use of underway lines on a variety of ships, several questions must be answered: Is respiration in underway lines widespread? If so, how large is the potential impact on global carbon cycle observations? And how can these problems be remedied? Here we present the evidence for respiration in underway seawater lines, discuss implications, and present potential treatment options. Our goal is to raise awareness and a community response to the issue so that future measurements are not impacted.

2. Evidence for O₂ Consumption

2.1. Underway and Discrete O₂ and ΔO₂/Ar on Atlantic Meridional Transect Cruises

Direct evidence for O₂ consumption comes from a series of observations collected on the Atlantic Meridional Transect cruises 16 and 17 (AMT16 and AMT17) between the UK and South Africa on the RRS Discovery in 2005. Discrete samples for O₂ concentration determined by automated Winkler titration with photometric (AMT16) or photometric (AMT17) endpoint detection were collected from the underway surface seawater line and surface Niskin bottles. In over 70 comparisons, underway samples had O₂ deficits of 0.6 ± 0.2% (1.2 ± 0.4 μmol/kg) compared to Niskin samples, with variable but predominantly negative offsets during both cruises (Figure 1). A trend toward greater deficit at warmer temperatures was apparent. The average deficit was significant relative to the measurement precision (0.08 μmol/kg on AMT16 and 0.17 μmol/kg on AMT17, based on the standard deviation of duplicates).
Pacific in all seasons is unexpected and contradicts previous ΔO2/Ar and NCP observations [Kaiser et al., 2005; Hamme and Emerson, 2006; Quay et al., 2009].

[8] Further evidence for respiration in the underway seawater line of the M/V Columbus Waikato comes from observed 18O/16O isotope ratio enrichments of the cross-Pacific transit samples relative to Niskin-collected samples in the same region (Figure 2). Respiration enriches the heavy 18O isotope in the remaining dissolved O2. A 0.4‰ enrichment in 18O/16O corresponds to a 2% decrease in ΔO2/Ar if the removal process has an isotopic fractionation similar to that observed for respiration (ε = 18 ≈ 22‰ [Kiddon et al., 1993; Hendricks et al., 2005]). If the underway data are corrected by +2% for ΔO2/Ar and −0.4‰ for 18O/16O, they show better agreement with the Niskin observations from 152°W (Figure 2). Furthermore, the corrected ΔO2/Ar data become slightly positive (1.0 ± 0.6‰) between 3°–30° north and south of the equator, indicating net autotrophy throughout the transect. This brings the observations into better agreement with previous work [e.g., Quay et al., 2009].

[9] Limited data availability of Niskin-collected samples, and the variability of 18O/16O and O2/Ar ratios in the tropical and subtropical Pacific make it difficult to absolutely determine the degree of O2 consumption from the cross-Pacific transit ΔO2/Ar observations. However, the

Figure 1. Comparisons of dissolved O2 and ΔO2/Ar saturation difference between underway and surface Niskin samples during AMT16 and AMT17. O2 concentrations had a precision of 0.08 μmol/kg and 0.17 μmol/kg (0.04 and 0.09% of saturation), respectively. O2/Ar ratios were collected and analyzed using procedures described by Kaiser et al. [2005] with a precision of 0.1%. Linear least squares fits are highly significant: r² = 0.35 (p < 0.001) and r² = 0.45 (p < 0.00001) for AMT16/17, respectively (the first four samples after cruise departure have been omitted). The temperature trend is also present when plotted versus concentration (i.e., observed trends are not due to solubility alone).

2.2. Underway O2/Ar and 18O/16O Ratios on Trans-Pacific Container Ship Crossings

[7] Additional evidence of respiration in underway lines comes from a series of ΔO2/Ar and oxygen isotope observations collected from the underway surface seawater line of a commercial cargo ship, M/V Columbus Waikato, in 2004–2005 [Juraneke and Quay, 2009]. Approximately 65 discrete samples were drawn from the line supplying an automated pCO2 system (http://www.pmel.noaa.gov/co2/uwpc02) on each of four crossings between the US west coast and Australia or New Zealand. On all four trans-Pacific cruises, O2/Ar was consistently below saturation throughout the subtropics and tropics (Figure 2). Although undersaturation at the equator is expected [Hendricks et al., 2005; Kaiser et al., 2005], undersaturation across the entire

Figure 2. ΔO2/Ar and δ18O of O2 (δ18O = Rsamp/Rstd − 1, where Rsamp and Rstd represents the 18O/16O of sample and an air standard, respectively) of dissolved O2 samples collected from the underway system on individual Pacific transits (colored dots), and taken from Niskin bottles on the CLIVAR P16N cruise along 152°W in February 2006 [Juraneke, 2007] (blue triangles). Also shown is the 4-cruise average (heavy black line) and the effect of a +2% ΔO2/Ar and −0.4‰ δ18O correction on the observations (dotted edge of grey shaded region). Dissolved gas samples were collected and analyzed as described by Juraneke and Quay (submitted manuscript, 2009), with typical δ18O and O2/Ar precision of 0.05‰ and 0.1%, respectively, based on analysis of duplicate samples.
available data suggest a respiratory removal of $O_2$ on the order of 2%.

2.3. Underway and Discrete $O_2$ Comparisons on CLIVAR P18 and Southern Ocean GasEx

[10] Comparable $O_2$ deficits to those already described were observed on the CLIVAR P18 repeat hydrography cruise (San Diego, CA to Punta Arenas, Chile) on the R/V Ronald H. Brown in 2007–2008 (Figure 3). At the first two stations where comparisons were made (14.5°N 110°W and 2°S 110°W), two sets of triplicate samples were drawn from the underway line during the last half hour of the CTD upcast, one set from water that had passed through a vortex debubbler and one set that had not been debubbled. Apparent $O_2$ concentrations determined by Winkler titration with amperometric detection of the endpoint [Culberson and Huang, 1987] with typical precision of $0.15 \mu mol/kg$ ($\approx0.06\%$ of saturation) based on duplicate samples. Observations (3.6 mol m$^{-2}$ C25 m yr$^{-1}$ of export fluxes [e.g., Tortell and Long, 2006]) values of 9–13.

$\text{m}_d$ measurements and calculated air-sea consumption of $1\%$ ([ie., subtracted from observations) would be $0.8 \text{Pg yr}^{-1}$, thereby increasing the global uptake estimate of $1.6 \pm 0.9 \text{Pg yr}^{-1}$ [Takahashi et al., 2009] by $50\%$. Using a value

Figure 3. Observed differences between underway surface seawater samples and surface Niskin $O_2$ saturations on CLIVAR P18. Water samples collected downstream of a vortex debubbler (red triangles) are comparable to those collected without debubbling (blue diamonds). Inset shows saturation changes observed after seawater pumps supplying the underway system were turned off for $\approx 10$ minutes. A bleach rinse was performed in Easter Island ($\approx 27°$S). All $O_2$ concentrations were determined by Winkler titration with amperometric detection of the endpoint [Culberson and Huang, 1987] with typical precision of $0.15 \mu mol/kg$ ($\approx0.06\%$ of saturation) based on duplicate samples.

3. Implications for Interpretation of $O_2/Ar$ and $pCO_2$ Observations

[13] Evidence of respiration in surface seawater supply lines of research and commercial ships has significant consequences for studies which rely on unbiased measurements of $O_2$ and $CO_2$. Underway measurements of the dissolved $O_2/Ar$ ratio can be used for monitoring the spatial and temporal variability of organic carbon export and provide a basis to construct better models of export production from remotely-sensed climatologies [Kaiser et al., 2005; Tortell and Long, 2009]. However, to fully exploit this potential even small biases in underway measurements must be eliminated. For example, a $1\%$ bias in $\Delta O_2/Ar$ in the subtropical ocean is equivalent to an approximate $10 \text{mmol m}^{-2} \text{d}^{-1}$ ($3.6 \text{mol m}^{-2} \text{yr}^{-1}$) bias in NCP determined from a mixed layer $O_2$ budget. This bias is roughly equal to estimates of NCP in the subtropical N. Pacific [e.g., Hamme and Emerson, 2006].

[14] Underway seawater line respiration will also impact surface seawater $pCO_2$ measurements and calculated air-sea $CO_2$ fluxes [e.g., Takahashi et al., 2002, 2009]. For example, a respiratory $O_2$ consumption of $1\%$ ($\approx2 \mu mol/kg$) would result in a surface seawater dissolved inorganic carbon (DIC) change of $1.5–2 \mu mol/kg$ or $0.07–0.10\%$ for an $O_2/C$ of $1.0–1.34$, a range that includes typical respiratory quotients [Rodriguez and Williams, 2002] and revised Redfield stoichiometry [Körtzinger et al., 2001]. This results in a $0.6–1.3\%$ ($2.5–5 \mu atm$) enhancement in $pCO_2$ for Revelle buffer factor ($pCO_2/dIC$) values of 9–13. While 2.5–5 $\mu atm$ is small compared to seasonal changes in seawater $pCO_2$ it is comparable to the global mean air-sea $pCO_2$ gradient (3.9 $\mu atm$ [Takahashi et al., 2009] and larger than the reported accuracy of underway systems [Pierrot et al., 2009].

[15] To demonstrate the potential impact of these artifacts, consider a case in which all $pCO_2$ measurements in the latest climatology [Takahashi et al., 2009] were collected from underway lines and were biased high by 4 $\mu atm$ ($\approx1\%$) due to in-line respiratory effects. The additional oceanic carbon uptake calculated if this bias were accounted for would be $0.8 \text{Pg yr}^{-1}$, thereby increasing the global uptake estimate of $1.6 \pm 0.9 \text{Pg yr}^{-1}$ [Takahashi et al., 2009] by $50\%$. Using a value...
of 2.5 μatm decreases the calculated bias by 40%, to 0.5 Pg yr⁻¹.

[16] Since not all climatological data are from underway observations and not all ships are likely to have this bias, 0.8 Pg yr⁻¹ is likely an upper limit of the potential artifact on CO₂ uptake calculations. However, this simple calculation demonstrates that the degree of O₂ consumption can vary from ship to ship, and may also be influenced by temperature (Figure 1). In similar comparisons of underway/Niskin ΔO₂/Ar on the R/V Thomas G. Thompson in the subarctic North Pacific no significant O₂ effect was observed [Juranek, 2007] (see also Table S1 of the auxiliary material).¹ When the above 4 μatm offset calculation is repeated only for climatological boxes with temperatures >10°C the resulting bias is lower, but still significant (0.5 Pg yr⁻¹).

4. Causes, Tests and Remedies

[17] A possible explanation for these in-line respiratory effects comes from literature on bacterial biofilms in industrial and seawater supply pipes and municipal drinking water pipes (summarized by Costerton et al. [1987, 1994]). Biofilms can colonize any surface in contact with water under any type of flow regime. Their organic secretions in aggregate can concentrate nutrients in nutrient deplete environments, protect them from biocides (e.g., bleach), and cause zones of enhanced metabolic activity. Given typical residence times for water in the plumbing lines of ships (<3 min), the respiration rate required to achieve observed deficits is huge (e.g., for a 2 μmol/kg decrease: 0.7 μmol kg⁻¹ min⁻¹, or 1000 mmol m⁻³ d⁻¹), roughly 1000 times typical rates observed in the subtropics [e.g., Williams et al., 2004]. Such intense activity could only be achieved by colonization of a large surface area in underway seawater supply lines and receiving tanks (sea chests). Microelectrode studies show the centers of biofilm microcolonies can have extremely low (near-anoxic) O₂ levels, with considerable spatial heterogeneity [Costerton et al., 1994]. The H₂S odor following the 10 minute pump shutdown on CLIVAR P18 provides anecdotal evidence that anoxic zones were present in the underway line on the R/V Ronald H. Brown. The presence or absence of O₂ consumption in ships may therefore reflect severity of biofilm colonization, which in turn may reflect differences in plumbing configurations, surface area or type, and cleaning protocols of underway seawater systems from ship to ship. Research ships in particular, with their extensively branched plumbing systems, may have “dead spots” for organic matter accumulation, which may enhance colonization. The tendency toward lower O₂ deficits in cold water regions (Figures 1 and 3 and Table S1) may also indicate that biofilm activity is influenced by temperature, as has been demonstrated in laboratory experiments [e.g., Gamby et al., 2008].

[18] Comparison of the O₂ offset observed at 63°S on P18 (0.5% or 1.5 μmol/kg, Figure 3) with the absence of an offset during SOGasEx, which sampled at similar temperatures, suggests that the bleach treatment, and not temperature, was the cause of the reduction in the underway bias between the two cruises. This indicates that underway biases may be mitigated with a relatively minor time and resource investment. Based on the apparent success of the bleach treatment new cleaning protocols were developed for the underway line on the R/V Ronald H. Brown. These include flushing the sea-chest and all underway lines with bleach at regular intervals. Other options could be tested, such as backfilling the underway seawater system with freshwater while in port. From O₂ comparisons, the bleach cleaning proved to be effective for at least 45 days following the treatment. However, longer-term observations are necessary to determine an appropriate time interval for treatment. Biofilms are resilient to biocide treatments; their activity may temporarily decrease following a treatment but they will recolonize given enough time [Costerton et al., 1987]. The effectiveness of bleach treatments at a range of temperatures should also be tested.

[19] Calibrating underway data from cargo ships is problematic because it is difficult to obtain Niskin-type samples for calibration at the speeds at which these ships typically operate. However, tests of O₂ uptake in sections of the underway line, by turning off the pumps for several minutes and sampling immediately after restarting them, may help to identify problems. Calibration with available Niskin-collected data from similar regions/timeframes will also be useful. Further assessment of the prevalence of underway O₂ consumption in research ships, and a comparison of the maintenance procedures accompanying these results, may elucidate a standard protocol for minimizing O₂ consumption in underway lines.

5. Conclusions

[20] Observations of respiratory O₂ consumption in underway lines of merchant and scientific vessels have important implications for global carbon cycle investigations. Given the attractiveness of ships of opportunity as a low-cost means to obtain ocean-wide coverage of surface conditions, and the continued development of new sensor methodologies that are well-suited for deployment on these platforms, increasing use of underway lines is expected. The time and space scales necessary to resolve regional carbon fluxes from pCO₂ in the oceans necessitate underway measurements as an observing component [Doney et al., 2009]. However, our ability to constrain key carbon cycle fluxes, such as air-sea CO₂ exchange and ocean carbon export rates based on CO₂ and O₂ saturation levels, depends on identifying and eliminating underway measurement biases. Awareness and routine checks in the underway observing community are essential to identifying the extent of these underway biases and resolving them in a timely manner.

[21] Acknowledgments. We thank the captains and crews of all of the ships mentioned for their support of this work. We especially thank J. Shannahoff, who helped to test for and minimize O₂ effects on the R/V Brown. We also thank B. Castle, G. Berberian, C. Langdon, N. Gist and B. Barnett for help with analyses. JK was supported by a NERC grant (NE/C51484X/1) to C. Robinson and M. Bender. This is contribution 183 of the AMT program.
References


---

R. C. Hamre, School of Earth and Ocean Sciences, University of Victoria, Victoria, BC V8W 3P6, Canada.

L. W. Juranek, Pacific Marine Environmental Laboratory, NOAA, 7600 Sand Point Way NE, Seattle, WA 98115, USA. (laurie.juranek@noaa.gov)

J. Kaiser, School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK.

P. D. Quay, School of Oceanography, University of Washington, P.O. Box 355351, Seattle, WA 98195, USA.

R. Wanninkhof, Atlantic Oceanographic and Meteorological Laboratory, NOAA, 4301 Rickenbacker Cswy., Miami, FL 33149, USA.

5 of 5