



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

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[1] 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, respiration 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

[2] 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 central 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 surface 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

[5] 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 potentiometric (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).

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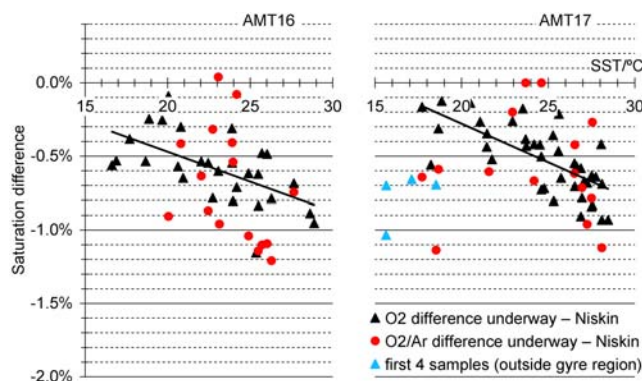


Figure 1. Comparisons of dissolved O_2 and $\Delta O_2/Ar$ saturation difference between underway and surface Niskin samples during AMT16 and AMT17. O_2 concentrations had a precision of $0.08 \mu\text{mol/kg}$ and $0.17 \mu\text{mol/kg}$ (0.04 and 0.09% of saturation), respectively. O_2/Ar ratios were collected and analyzed using procedures described by Kaiser *et al.* [2005] with a precision of 0.1%. Linear least squares fits are highly significant: $r^2 = 0.35$ ($p < 0.001$) and $r^2 = 0.45$ ($p < 0.00001$) 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).

[6] An O_2 deficit was also evident in the dissolved O_2/Ar ratio observed on AMT16 and AMT17 (Figure 1). The measured O_2/Ar ratio, when normalized to the ratio expected from solubility equilibrium [Hamme and Emerson, 2004], yields a measure of the changes in O_2 saturation solely due to biological activity, $\Delta O_2/Ar = ([O_2]/[Ar])_{\text{meas}} / ([O_2]/[Ar])_{\text{sat}} - 1$. Because Ar has solubility and diffusion characteristics similar to O_2 , $\Delta O_2/Ar$ is insensitive to physical processes such as warming or bubble injection that could occur as seawater flows through an underway system. The observed offset in $\Delta O_2/Ar$ therefore indicates that a biological O_2 -consuming process is the cause of the O_2 saturation decrease in underway seawater lines. Together, these AMT $\Delta O_2/Ar$ and O_2 observations indicate that biological O_2 removal occurs in underway systems, and the removal rate is variable, and possibly influenced by temperature.

2.2. Underway O_2/Ar and $^{18}O/^{16}O$ Ratios on Trans-Pacific Container Ship Crossings

[7] Additional evidence of respiration in underway lines comes from a series of $\Delta O_2/Ar$ and oxygen isotope observations collected from the underway surface seawater line of a commercial cargo ship, *M/V Columbus Waikato*, in 2004–2005 [Juraneck and Quay, 2009]. Approximately 65 discrete samples were drawn from the line supplying an automated pCO_2 system (<http://www.pmel.noaa.gov/co2/uwpc2>) on each of four crossings between the US west coast and Australia or New Zealand. On all four trans-Pacific cruises, O_2/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

Pacific in all seasons is unexpected and contradicts previous $\Delta O_2/Ar$ 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 $^{18}O/^{16}O$ isotope ratio enrichments of the cross-Pacific transit samples relative to Niskin-collected samples in the same region (Figure 2). Respiration enriches the heavy ^{18}O isotope in the remaining dissolved O_2 . A 0.4‰ enrichment in $^{18}O/^{16}O$ corresponds to a 2% decrease in $\Delta O_2/Ar$ if the removal process has an isotopic fractionation similar to that observed for respiration ($\epsilon = 18\text{--}22\text{‰}$) [Kiddon *et al.*, 1993; Hendricks *et al.*, 2005]. If the underway data are corrected by +2% for $\Delta O_2/Ar$ and -0.4‰ for $^{18}O/^{16}O$, they show better agreement with the Niskin observations from $152^\circ W$ (Figure 2). Furthermore, the corrected $\Delta O_2/Ar$ data become slightly positive ($1.0 \pm 0.6\%$) between $3^\circ\text{--}30^\circ$ 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 $^{18}O/^{16}O$ and O_2/Ar ratios in the tropical and subtropical Pacific make it difficult to absolutely determine the degree of O_2 consumption from the cross-Pacific transit $\Delta O_2/Ar$ observations. However, the

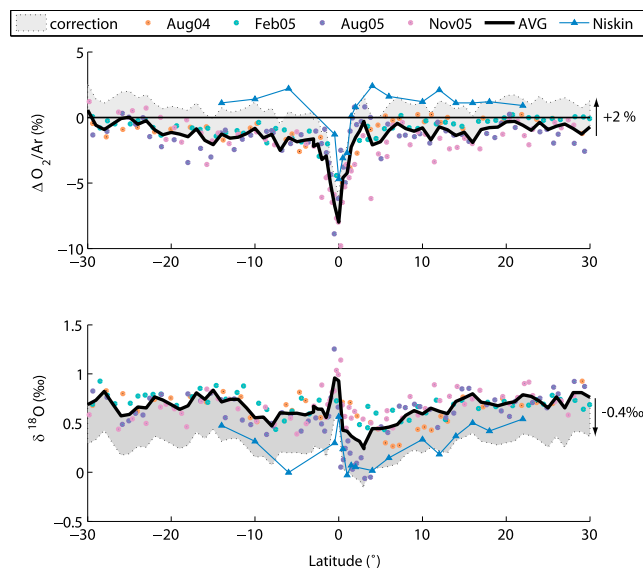


Figure 2. $\Delta O_2/Ar$ and $\delta^{18}O$ of O_2 ($\delta^{18}O = R_{\text{sample}}/R_{\text{std}} - 1$, where R_{sample} and R_{std} represents the $^{18}O/^{16}O$ of sample and an air standard, respectively) of dissolved O_2 samples collected from the underway system on individual Pacific transits (colored dots), and taken from Niskin bottles on the CLIVAR P16N cruise along $152^\circ W$ in February 2006 [Juraneck, 2007] (blue triangles). Also shown is the 4-cruise average (heavy black line) and the effect of a +2% $\Delta O_2/Ar$ and -0.4‰ $\delta^{18}O$ correction on the observations (dotted edge of grey shaded region). Dissolved gas samples were collected and analyzed as described by Juraneck and Quay (submitted manuscript, 2009), with typical $\delta^{18}O$ and O_2/Ar precision of 0.05‰ and 0.1% , respectively, based on analysis of duplicate samples.

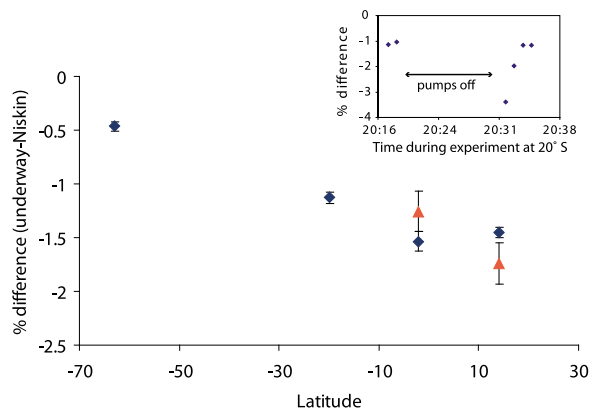


Figure 3. Observed differences between underway surface seawater samples and surface Niskin O_2 saturations on CLIVAR P18. Water samples collected downstream of a vortex debubbler (red triangles) are comparable to those collected without debubbling (blue diamonds). Inset shows saturation changes observed after seawater pumps supplying the underway system were turned off for ≈ 10 minutes. A bleach rinse was performed in Easter Island ($\approx 27^\circ S$). All O_2 concentrations were determined by Winkler titration with amperometric detection of the endpoint [Culbertson and Huang, 1987] with typical precision of $0.15 \mu\text{mol/kg}$ ($\approx 0.06\%$ of saturation) based on 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 ($14.5^\circ N$ $110^\circ W$ and $2^\circ S$ $110^\circ W$), 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 deficits in samples collected from the underway line were 3–4 $\mu\text{mol/kg}$ (1–2%) compared to Niskin samples, with no difference between samples collected before or after debubbling. At a third location ($20.5^\circ S$ $103^\circ W$), pumps for the underway line were shut down for approximately 10 minutes; two samples were drawn immediately prior to pump shutdown, and four samples were drawn during the four minutes following the pump restart. The O_2 concentration deficit in samples collected after the 10 minutes of pump inactivity (8 $\mu\text{mol/kg}$, 3.5%) was roughly twice that experienced under normal flow conditions, but approached the previous 3–4 $\mu\text{mol/kg}$ deficit within a few minutes of pump restart (Figure 3). A sulfide smell was also noted by observers immediately following pump initiation, suggesting that there may have been pockets in the underway line that were anoxic.

[11] During a port stop in Easter Island ($\approx 27^\circ S$) the underway line was treated with approximately 0.5 L of common household bleach (3% sodium hypochlorite solution). Five samples drawn from the underway seawater line

at a fourth location ($63.2^\circ S$ $103^\circ W$) one month later were offset from Niskin-collected samples by roughly half the amount observed during the first three comparisons ($-1.5 \mu\text{mol/kg}$, -0.5%).

[12] Prior to the Southern Ocean GasEx (SOGasEx) cruise in March 2008 the underway system underwent a more extensive bleach treatment. Briefly, 4 L of bleach was added to the sea chest with pumps off. After a few hours, pumps were briefly turned on to distribute the bleach into the lines, then turned off again for several hours. During SOGasEx, dissolved O_2 samples drawn from the underway surface seawater line in duplicate or triplicate had no significant offset relative to samples collected from mixed layer Niskin bottles at 22 stations (underway-Niskin average = $-0.07 \pm 0.17 \mu\text{mol/kg}$, average standard deviation of duplicates $0.15 \mu\text{mol/kg}$).

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 or 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% ($\approx 2 \mu\text{mol/kg}$) would result in a surface seawater dissolved inorganic carbon (DIC) change of 1.5–2 $\mu\text{mol/kg}$ or 0.07–0.10% (for an $O_2:C$ of 1.0–1.34, a range that includes typical respiratory quotients [Rodrigues and Williams, 2002] and revised Redfield stoichiometry [Körtzinger et al., 2001]). This results in a ≈ 0.6 –1.3% (2.5 – $5 \mu\text{atm}$) enhancement in pCO_2 for Revelle buffer factor ($\frac{dpCO_2/dDIC}{pCO_2/DIC}$) values of 9–13. While 2.5 – $5 \mu\text{atm}$ is small compared to seasonal changes in seawater pCO_2 it is comparable to the global mean air-sea pCO_2 gradient ($3.9 \mu\text{atm}$) [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 $4 \mu\text{atm}$ ($\approx 1\%$) due to in-line respiratory effects. The additional oceanic carbon uptake calculated if this bias were accounted for (i.e., subtracted from observations) would be 0.8 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 $2.5 \mu\text{atm}$ 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 CO_2 uptake calculations. However, this simple calculation demonstrates that the issue is significant, and needs to be documented and addressed throughout the observing fleet. The observations presented here suggest that the degree of O_2 consumption can vary from ship to ship, and may also be influenced by temperature (Figure 1). In similar comparisons of underway/Niskin $\Delta\text{O}_2/\text{Ar}$ on the *R/V Thomas G. Thompson* in the subarctic North Pacific no significant O_2 effect was observed [Juraneck, 2007] (see also Table S1 of the auxiliary material).¹ When the above $4 \mu\text{atm}$ offset calculation is repeated only for climatological boxes with temperatures $>10^\circ\text{C}$ 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 $2 \mu\text{mol/kg}$ decrease: $0.7 \mu\text{mol kg}^{-1} \text{ min}^{-1}$, or $1000 \text{ mmol m}^{-3} \text{ d}^{-1}$), 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) O_2 levels, with considerable spatial heterogeneity [Costerton *et al.*, 1994]. The H_2S 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 O_2 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 O_2 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 O_2 offset observed at 63°S on P18 (0.5% or $1.5 \mu\text{mol/kg}$, 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 O_2 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 O_2 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 O_2 consumption in research ships, and a comparison of the maintenance procedures accompanying these results, may elucidate a standard protocol for minimizing O_2 consumption in underway lines.

5. Conclusions

[20] Observations of respiratory O_2 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 $p\text{CO}_2$ 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 CO_2 exchange and ocean carbon export rates based on CO_2 and O_2 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.

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¹Auxiliary materials are available in the HTML. doi:10.1029/2009GL040423.

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