

## RESEARCH ARTICLE

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## Key Points:

- We present the first meridional transects of atmospheric O<sub>2</sub>, CO<sub>2</sub>, and atmospheric potential oxygen (APO) over the Atlantic Ocean
- In contrast to the Pacific Ocean, our Atlantic data do not show a significant equatorial APO bulge
- Our Atlantic APO data are in disagreement with existing oceanic oxygen data products and models

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# In situ measurements of atmospheric O<sub>2</sub> and CO<sub>2</sub> reveal an unexpected O<sub>2</sub> signal over the tropical Atlantic Ocean

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**Abstract** We present the first meridional transects of atmospheric O<sub>2</sub> and CO<sub>2</sub> over the Atlantic Ocean. We combine these measurements into the tracer atmospheric potential oxygen (APO), which is a measure of the oceanic contribution to atmospheric O<sub>2</sub> variations. Our new in situ measurement system, deployed on board a commercial container ship during 2015, performs as well as or better than existing similar measurement systems. The data show small short-term variability (hours to days), a step-change corresponding to the position of the Intertropical Convergence Zone (ITCZ), and seasonal cycles that vary with latitude. In contrast to data from the Pacific Ocean and to previous modeling studies, our Atlantic Ocean APO data show no significant bulge in the tropics. This difference cannot be accounted for by interannual variability in the position of the ITCZ or the Atlantic Meridional Mode Index and appears to be a persistent feature of the Atlantic Ocean system. Modeled APO using the TM3 atmospheric transport model does exhibit a significant bulge over the Atlantic and overestimates the interhemispheric gradient in APO over the Atlantic Ocean. These results indicate that either there are inaccuracies in the oceanic flux data products in the equatorial Atlantic Ocean region, or that there are atmospheric transport inaccuracies in the model, or a combination of both. Our shipboard O<sub>2</sub> and CO<sub>2</sub> measurements are ongoing and will reveal the long-term nature of equatorial APO outgassing over the Atlantic as more data become available.

## 1. Introduction

The global ocean is a major long-term sink for anthropogenic carbon dioxide (CO<sub>2</sub>) [Le Quéré *et al.*, 2016], and yet the spatial and temporal variability of the oceanic CO<sub>2</sub> sink has large uncertainties [Landschützer *et al.*, 2014; Rödenbeck *et al.*, 2015]. High precision atmospheric oxygen (O<sub>2</sub>) and CO<sub>2</sub> data can be combined to isolate the ocean influences on atmospheric O<sub>2</sub> variability, by removing the influence of the terrestrial biosphere on O<sub>2</sub>. This is done using the tracer atmospheric potential oxygen (APO) which is defined as  $APO \approx O_2 + 1.1 \times CO_2$  [Stephens *et al.*, 1998]. The value of 1.1 denotes the mean -O<sub>2</sub>:CO<sub>2</sub> ratio of terrestrial biosphere-atmosphere exchange [Severinghaus, 1995]. APO is thus conservative with respect to terrestrial biosphere processes and mainly reflects seasonal and long-term air-sea exchange of O<sub>2</sub> and CO<sub>2</sub>, with a minor influence from fossil fuel combustion.

Early studies used atmospheric O<sub>2</sub> and CO<sub>2</sub> data to calculate ocean biological productivity [Keeling and Shertz, 1992], constrain the open ocean gas exchange velocity for O<sub>2</sub> [Keeling *et al.*, 1998b], test ocean model parametrizations of interhemispheric transport of O<sub>2</sub> and CO<sub>2</sub> in the oceans [Stephens *et al.*, 1998], and calculate the global land and ocean carbon sinks [Keeling and Shertz, 1992; Keeling and Manning, 2014]. More recently, atmospheric O<sub>2</sub> and CO<sub>2</sub> measurements have been used to determine spatial and temporal features in air-sea O<sub>2</sub> fluxes [Rödenbeck *et al.*, 2008], test oceanic net primary productivity and ventilation fluxes in Earth system models [Nevison *et al.*, 2015], and detect CO<sub>2</sub> leaks from carbon capture and storage sites [Van Leeuwen, 2015].

In addition to CO<sub>2</sub> uptake resulting from increased CO<sub>2</sub> in the atmosphere, air-sea fluxes of O<sub>2</sub> and CO<sub>2</sub> on regional scales are caused by three main oceanic processes: changes in solubility from temperature and salinity changes, biological primary productivity and respiration, and upwelling of deep ocean waters, which are depleted in O<sub>2</sub> and enriched in CO<sub>2</sub> [Bender and Battle, 1999]. The effects of O<sub>2</sub> and CO<sub>2</sub> fluxes from these three processes on APO is complicated, partly because biological and upwelling fluxes affect air-sea exchange of O<sub>2</sub> and CO<sub>2</sub> in opposite directions, whereas solubility affects air-sea fluxes of O<sub>2</sub> and CO<sub>2</sub> in the same direction [Stephens *et al.*, 1998]. Furthermore, the air-sea equilibration time for CO<sub>2</sub>

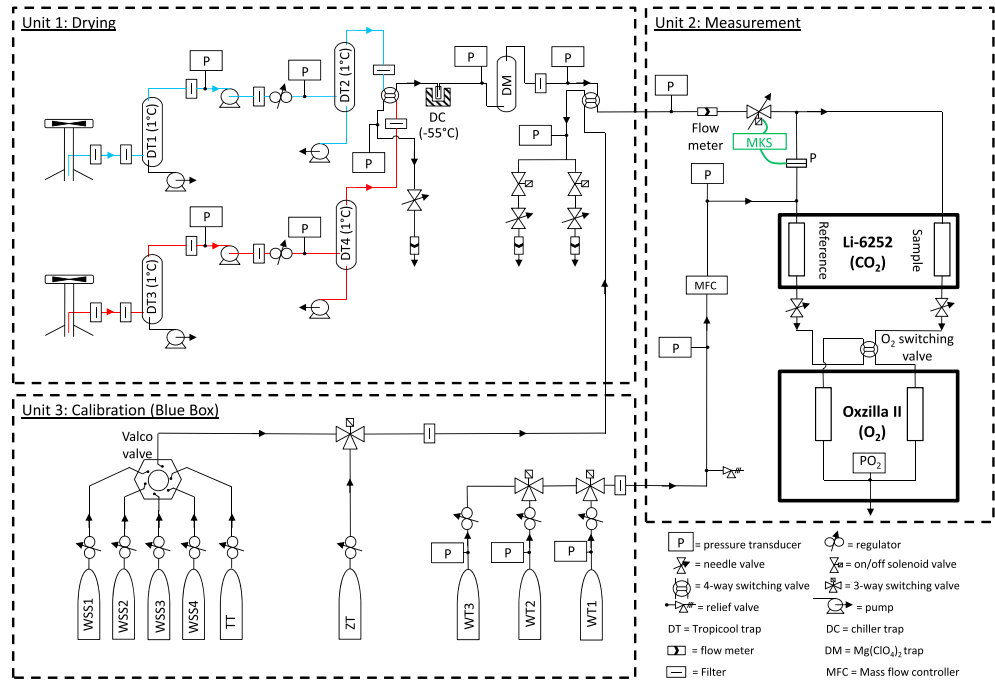
(~1 year) is much longer than for  $O_2$  (a few weeks) [Keeling and Shertz, 1992]. Overall, regional variations in APO are dominated by solubility effects, because ventilation and biological  $O_2$  and  $CO_2$  fluxes largely cancel out [Stephens *et al.*, 1998].

Large-scale features in APO, such as the APO latitudinal gradient, can be used to examine ocean circulation and air-sea interactions in climate models. For example, Stephens *et al.* [1998] found that model-generated latitudinal gradients in annual-mean APO over the Pacific Ocean significantly underestimated the observed interhemispheric gradient in APO, suggesting that the models were underestimating the net southward transport of oceanic potential oxygen (the oceanic equivalent of APO [see Resplandy *et al.*, 2016]) in the oceans. A later study by Gruber *et al.* [2001] also found that modeled APO underestimated the observed APO interhemispheric gradient, particularly at southern hemisphere high-latitude stations. However, these authors found that robustly constraining oceanic transport of  $O_2$  and  $CO_2$  using APO data was not possible. This was owing to large uncertainties in the modeled APO, which stemmed from a combination of the seasonal  $O_2$  rectifier effect (caused by the seasonal covariation of atmospheric mixing processes and surface ocean fluxes) and a lack of APO observations.

Both studies by Stephens *et al.* [1998] and Gruber *et al.* [2001] found a significant equatorial APO bulge (between 5 and 15 per meg in magnitude) in modeled APO over the Pacific Ocean, caused largely by  $O_2$  and  $CO_2$  solubility-driven outgassing from the equatorial Pacific Ocean. Subsequent shipboard measurements confirmed the existence of this bulge, which occurred just south of the equator [Battle *et al.*, 2006]. More recently, the long  $O_2$  and  $CO_2$  data set of Tohjima *et al.* [2015] over the western Pacific Ocean showed that the amplitude of the western Pacific equatorial APO bulge in this region was anticorrelated to El Niño–Southern Oscillation (ENSO), with a suppressed APO bulge over the western Pacific during El Niño conditions, which is mostly attributed to changes in atmospheric circulation associated with meridional shifts in the ITCZ (Intertropical Convergence Zone). The results of Tohjima *et al.* [2015] are contradictory to those of a previous modeling study by Rödenbeck *et al.* [2008], who found a significant positive correlation between APO anomalies over the tropical Pacific Ocean and ENSO variability; however, this discrepancy has recently been reconciled by Eddebbar *et al.* [2017], who showed that the response of APO to ENSO variability differs significantly between the western and central/eastern Pacific. Model simulations suggest that an APO bulge of comparable shape and magnitude should exist over the Atlantic [Gruber *et al.*, 2001], but these predictions have never been verified with observational data until now.

To date, most of the in situ atmospheric  $O_2$  and  $CO_2$  measurements made over the ocean have focused on the Pacific and Southern Ocean regions. In addition, the majority of measurements have been from research vessels, which tend to have limited deployment periods of only a few weeks or months [e.g., Patecki and Manning, 2007; Stephens *et al.*, 2003; Thompson *et al.*, 2007, 2008]. The longest in situ atmospheric  $O_2$  and  $CO_2$  data set from a research vessel is measured from the Laurence M. Gould, which travels semicontinuously between Chile and Antarctica across the Drake Passage, and has been collecting  $O_2$  and  $CO_2$  data since 2012 [Stephens, 2017]. In contrast to research vessels, there have also been several atmospheric  $O_2$  and  $CO_2$  data sets collected from commercial container ships, including flask samples collected over the Pacific Ocean from 1996 to 2001 [Battle *et al.*, 2006], and ongoing flask samples (2001 to present) and in situ  $O_2$  and  $CO_2$  measurements (2007 to present) from over the western and northern Pacific [Tohjima *et al.*, 2005b, 2015]. The key advantage of deploying an in situ system on a commercial container ship, in contrast to both fixed stations and most research ships, is that multiple measurements can be combined into discrete latitude or longitude bands, thus forming time series from several virtual stations collected from a single measurement system. This avoids common technical problems arising from potential calibration offsets between different measurement systems (which are particularly important when investigating relatively small latitudinal gradients) and reduces costs.

We present and interpret the first meridional atmospheric  $O_2$ ,  $CO_2$ , and APO data over the Atlantic Ocean, providing new insights into latitudinal  $O_2$ ,  $CO_2$ , and APO variability and distribution over the Atlantic Ocean. Section 2 presents the in situ measurement system design and data analysis methodology. Section 3 presents the performance of the measurement system, as well as seasonal cycle variability and annual mean distribution in  $O_2$ ,  $CO_2$ , and APO from the meridional transect data. Section 4 discusses the results in the context of interannual variability, compares our results to modeled APO data, and outlines the future potential of the shipboard atmospheric  $O_2$ ,  $CO_2$ , and APO data set.



**Figure 1.** Gas handling diagram of the shipboard O<sub>2</sub> and CO<sub>2</sub> measurement system. The three units of drying, measurement, and calibration are shown in separate boxes. The “red” and “blue” inlet lines are colored accordingly in Unit 1, and the green coloring in Unit 2 denotes electrical components.

## 2. Methods

### 2.1. The Cap San Lorenzo Container Ship

The Cap San Lorenzo (CSL) is a 333 m long commercial container ship operated by Hamburg Süd Group, which travels continuously between Hamburg, Germany (53.57°N, 10.00°E) and Buenos Aires, Argentina (34.60°S, 58.38°W), stopping in the UK at the London Gateway port in Essex. A complete Europe-South America-Europe rotation takes exactly 8 weeks. The northward and southward routes are identical, with the exception that during the northward voyage, the ship stops at Tangier, Morocco (~36°N), before continuing to Europe.

### 2.2. O<sub>2</sub> and CO<sub>2</sub> Measurement

The shipboard O<sub>2</sub> and CO<sub>2</sub> atmospheric measurement system is composed of three units: drying, measurement, and calibration (Figure 1). The drying unit is where sample air is drawn into the system and dried to less than 1 ppm water vapor content using a three-stage drying system. The measurement unit comprises of a Li-6252 CO<sub>2</sub> analyzer (Li-Cor Inc.) and an Oxzilla II O<sub>2</sub> analyzer (Sable Systems International Inc.) in series. The calibration unit comprises of a thermally insulated “Blue Box,” containing a suite of high-pressure calibration standards filled with air of known O<sub>2</sub> and CO<sub>2</sub> mole fractions, as well as three high-pressure reference air cylinders, known as Working Tanks (WTs). Our shipboard O<sub>2</sub> and CO<sub>2</sub> measurement system is described in full in Pickers [2016] and is similar in design to the measurement systems described in Stephens *et al.* [2007] and Thompson *et al.* [2007], with some key exceptions, which are described in the following sections.

Atmospheric O<sub>2</sub> mole fraction is measured using an Oxzilla II analyzer, which employs two MAX-250 lead fuel cell O<sub>2</sub> sensors (Maxtec Inc.), and is described in more detail in Thompson *et al.* [2007] and Stephens *et al.* [2007]. The MAX-250 O<sub>2</sub> sensors are sensitive to both temperature and pressure changes. These effects are largely mitigated by employing active temperature control of the Oxzilla housing, correcting the O<sub>2</sub> signal for pressure changes [Thompson *et al.*, 2007] and placing the SenSym SCX-Series pressure sensor (Sensortech GmbH; “PO<sub>2</sub>” in Figure 1) in-line according to Stephens *et al.* [2007], as well as measuring the O<sub>2</sub> mole fraction differentially, i.e., the difference between the sample air O<sub>2</sub> and the WT gas O<sub>2</sub> (denoted as ΔO<sub>2</sub>). Atmospheric CO<sub>2</sub> mole fraction is measured using a Li-6252 analyzer operated in differential mode,

which uses nondispersive infrared (NDIR) sensor technology. The Li-6252 and Oxzilla internal plastic tubing was replaced with steam-cleaned stainless steel 1/16th inch and 1/8th inch (outside diameter; OD) tubing (VICI Valco Instruments Co. Inc.), because plastics are known to be semipermeable to CO<sub>2</sub> and differentially permeable to O<sub>2</sub> and N<sub>2</sub>. Atmospheric O<sub>2</sub> measurements are reported as δ(O<sub>2</sub>/N<sub>2</sub>) ratios in per meg units, rather than mole fractions, because O<sub>2</sub> is not a trace gas and its mole fraction is therefore affected by small changes in other gases, such as CO<sub>2</sub> [Keeling *et al.*, 1998a]. We calculate δ(O<sub>2</sub>/N<sub>2</sub>) ratios from the Oxzilla and Li-6252 output using equation (1) taken from Kozlova *et al.* [2008]:

$$\delta(\text{O}_2/\text{N}_2)(\text{per meg}) = \frac{\delta\text{O}_2(\text{ppm}) + S_{\text{O}_2}([\text{CO}_2] - 363.29)}{S_{\text{O}_2}(1 - S_{\text{O}_2})} \quad (1)$$

where  $S_{\text{O}_2}$  is the standard mole fraction of O<sub>2</sub> in dry air (we use 0.2094, based on Tohjima *et al.* [2005a]), [CO<sub>2</sub>] is the measured CO<sub>2</sub> mole fraction from the Li-6252 (in ppm), and 363.29 is an arbitrary reference value for CO<sub>2</sub> in ppm, based on the CO<sub>2</sub> mole fraction of cylinders that define zero on the Scripps Institution of Oceanography (SIO) O<sub>2</sub> calibration scale.

The δO<sub>2</sub> (ppm) value is calculated from three ΔO<sub>2</sub> values as follows. To further increase the precision and stability of the O<sub>2</sub> measurements, a four-way valve (composed of two miniature three-way solenoid valves mounted on a manifold; Numatics, TM series) immediately upstream of the Oxzilla analyzer (“O<sub>2</sub> switching valve” in Figure 1) switches the sample air and WT gas between each fuel cell every 30 s (see Pickers [2016] and Stephens *et al.* [2007] for more details). Thus, a so-called “double differential O<sub>2</sub>” (ΔΔO<sub>2</sub>) is calculated from the mole fraction difference between the three successive 30 s periods and is effectively twice the difference between sample air and WT gas. The δO<sub>2</sub> (ppm) is therefore roughly half of the mean ΔΔO<sub>2</sub> from the three switching periods. We employ a faster sample-WT switching frequency than Stephens *et al.* [2007] and Thompson *et al.* [2007], because we found that faster switching improves the short-term O<sub>2</sub> precision (see section 2.4).

### 2.3. Sample Air Drying, Gas Handling, and Calibration

Air is sampled from the roof of the CSL bridge (~40 m above sea level) using two aspirated air inlets (AAIs), which prevent the differential fractionation of O<sub>2</sub> molecules relative to N<sub>2</sub> molecules [Blaine *et al.*, 2006] and are electrically isolated and grounded to the ship to protect the measurement system in the event of a lightning strike. As shown in Figure 1, two identical inlet lines (1/4 inch OD Synflex 1300 tubing; ~25 m in length) are used, denoted as “red line” and “blue line,” which alternately pass sample air to the analyzers once per hour. Duplicate inlet lines are used to diagnose leaks and faults in the inlet system, such as blockages in the first stage of the drying system, failed AAI blowers, or leaking pump diaphragms. Air is drawn down the inlet lines using two diaphragm pumps (KNF Neuberger Inc. N05-AT1 pumps), which are oriented upside-down to prevent water collecting inside the pump heads and tubing.

The sample air makes two passes through the first stage drying, which is a Peltier element thermo-electric cooler (Tropicool XC3000A; “DT1-DT4” in Figure 1), set at about 1°C. The Tropicool traps (filled with 4 mm glass beads to enhance the surface area for moisture condensation) are drained by peristaltic pumping units (Masterflex model, Cole Parmer Instrument Co. Ltd.), with a 1 rpm rotation speed. The diaphragm pumps are located between the first and second passes of the air through the Tropicool for two reasons: first, the initial pass prevents excess water from collecting in the diaphragm pump heads, and second, the overpressure of the air in the second pass results in additional water vapor removal. Swagelok Company 2 μm FW Series filters are placed in-line throughout the measurement system to prevent particulate matter generated by the diaphragm pumps or the glass beads in the drying traps from traveling through the tubing to the analyzers.

The second stage of drying employs an FTS VT255D cryogenic cooler (SP Scientific), referred to here as a chiller (“DC” in Figure 1), which can achieve a dew point of about –50 to –55°C. The chiller has a 2 L bath, filled with a nonflammable coolant (Halden ZT130, from Solvay Solexis Inc.) to comply with Hamburg Süd health and safety regulations, into which a tapered trap is placed. The chiller trap is also filled with 4 mm diameter glass beads, in this case to reduce the internal volume of the trap in order to reduce the effects of transient O<sub>2</sub> spikes caused by O<sub>2</sub> accumulation in the coldest part of the trap, as discussed in Manning [2001]. The VT255D

chiller in the second drying stage was chosen specifically for the ship system because it is much smaller and lighter than the VT490 and VT890 models (which are typically used in other O<sub>2</sub> and CO<sub>2</sub> measurement systems). This, however, meant that a third stage of drying was required, since the –55°C level of drying achieved by the VT255D is not sufficient for high precision O<sub>2</sub> measurement.

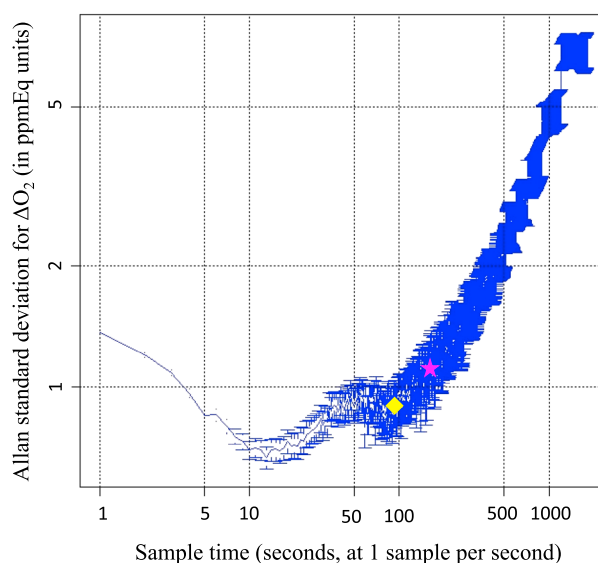
For the third drying stage, a magnesium perchlorate trap is used (“DM” in Figure 1). Magnesium perchlorate, Mg(ClO<sub>4</sub>)<sub>2</sub>, is an oxidizing agent and therefore might introduce O<sub>2</sub> artifacts when the magnesium perchlorate reacts with water [Langenfelts, 2002]. Under conditions of strict pressure control, however, Mg(ClO<sub>4</sub>)<sub>2</sub> has been shown to be a stable drying agent for O<sub>2</sub> and CO<sub>2</sub>, with negligible effects on the sample air [Langenfelts, 2002]. The water content of the sample air after passing through all three drying stages was checked using a Meeco Inc. Accupoint 2 moisture transmitter and shown to have <1 ppm water, which is sufficient to prevent dilution effects significantly biasing the O<sub>2</sub> measurements [Stephens *et al.*, 2007]. After increasing the pressure inside the first stage drying traps, we found that both the second and third stage drying traps were able to function without requiring any maintenance for at least 8 weeks.

Model A-10 (Wika Instruments Ltd.) pressure transmitters (“P” in Figure 1) placed throughout the system ensure that incoming pressures can be well matched (e.g., between red and blue inlet lines) and also help to diagnose problems, such as a blockage in the chiller trap. The pressure of the sample air and WT gas that passes through the analyzers is balanced (to within  $0.00 \pm 0.06$  mbar for sustained periods of a week or more) using the same setup described in Stephens *et al.* [2007] and Thompson *et al.* [2007], and the same equipment from MKS Instruments Inc. A mass flow controller on the reference side of the system (MKS Instruments Inc., Type 1179A; “MFC” in Figure 1) maintains the flow rate of the WT gas at  $100 \text{ mL min}^{-1}$ , and a mass flowmeter on the sample side of the system (McMillan Company Inc., model 50 K; “Flow meter” in Figure 1) is used to check that the flow rate of the sample side is matched with the reference side. Two needle valves (Brooks Instrument Co., model 8504) downstream of the Li-6252 analyzer are used to ensure that the flows and pressures between the sample and reference sides are well matched. Flowmeters (Honeywell International Inc. AWM3000 Series) and needle valves (Swagelok Company S Series metering valves) on the three purging lines prevent flow and pressure disruptions when either switching between the red and blue inlet lines or between sample air and calibration cylinder gas.

One final consideration in the gas handling procedure of the measurement system is to avoid the use of tee junctions, where the airflow is divided into two streams. Tee junctions cause O<sub>2</sub>/N<sub>2</sub> fractionation, because O<sub>2</sub> molecules will preferentially flow through one branch of the tee compared to the other branch, even when pressure changes (e.g., caused by diaphragm pump pulsations) and temperature changes in the airstream are mitigated [Manning, 2001].

All diagnostic parameters are recorded by a custom-built electronics box, and, together with analyzer data, are passed to the measurement system computer (Shuttle XH61V Intel System, Ambros Direct UK Ltd.) via a USB serial adapter (Quatech Inc.). All of the power supplied to the measurement system passes through a PowerGem Pro (British Power Conversion Company) 1000 W uninterruptible power supply that converts the CSL power frequency of 60 Hz to 50 Hz. Our sophisticated, custom software, written in-house using C#, can run the shipboard measurement system without the need for human intervention (including via an internet connection) for at least 8 weeks, by calling calibration procedures at predefined time intervals, switching valves at predetermined intervals or pressures (such as switching to the next WT when the current WT pressure falls below a predetermined user-defined threshold), setting the system flow rate, re-starting the measurements if they are temporarily interrupted by a fault, and automatically flagging suspect data based on the examination of approximately 30 diagnostic parameters.

The shipboard measurement system is calibrated every 23 h, using a suite of four Working Secondary Standards (WSSes), composed of 20 L aluminum alloy cylinders (Luxfer Gas Cylinders Ltd., model P3056Z) filled with dry air to ~200 bar. The WSSes are assigned CO<sub>2</sub> and O<sub>2</sub> values by measuring them repeatedly in our laboratory at the University of East Anglia (UEA) against a suite of eight CO<sub>2</sub> Primary Secondary Standards (PSSes) [Manning, 2005] purchased from NOAA (National Oceanic and Atmospheric Administration, USA) and a suite of six O<sub>2</sub> PSSes received from SIO. We employ an O<sub>2</sub> and CO<sub>2</sub> WSS calibration routine similar to that described in Kozlova and Manning [2009]. A Target Tank (TT) is also periodically measured (typically every 10 h) as a quality control check for both the O<sub>2</sub> and CO<sub>2</sub> measurements [Kozlova and Manning, 2009], while a Zero Tank (ZT) is measured (typically every 3 h) to



**Figure 2.** Allan standard deviation plot showing the potential improvements in short-term precision for the Oxzilla. Optimizing the trade-off between improved precision from averaging the signal noise and reduced precision owing to the inclusion of short-term drift in the  $\Delta O_2$  signal is important for achieving the best possible short-term precision from the Oxzilla. The pink star shows the Allan standard deviation at 180 s (equivalent to  $\sim 1.1$  ppmEq  $O_2$ ), corresponding to a 60 s sample-WT switching scheme frequently cited in the literature, whereas the yellow diamond shows the Allan standard deviation at 90 s (equivalent to  $\sim 0.6$  ppmEq  $O_2$ ), corresponding to a 30 s sample-WT switching scheme, which was employed by our system. One ppmEq is comparable to  $\sim 6$  per meg [Kozlova and Manning, 2009].

#### 2.4. Faster Sample-WT Switching

The sample-WT switching frequency for fuel cell  $O_2$  measurement systems has typically been set to between 60 and 120 s [Patecki and Manning, 2007; Popa, 2008; Stephens et al., 2007; Wilson, 2013]. We found, however, that Allan standard deviation analyses of  $\Delta O_2$  on our measurement system (without sample-WT switching) suggest that a shorter averaging time improves the short-term  $O_2$  precision, owing to the exclusion of short-term drift in the  $O_2$  signal (Figure 2). Each  $\delta(O_2/N_2)$  measurement consists of three sample-WT switches (in order to calculate  $\Delta\Delta O_2$ ); thus, it is not possible to obtain the optimum precision from the fuel cells, because the response time of the fuel cells to any change in  $O_2$  mole fraction (e.g., after each sample-WT valve switch) is 15 s (for a 90% response). Figure 2 demonstrates, however, that any feasible reduction in the frequency of the sample-WT switching should translate into an improvement in short-term  $O_2$  measurement precision.

The improvements in short-term  $O_2$  precision gained by reducing the sample-WT switching frequency from 60 s to 30 s were determined from a test comprising of seven ZT analyses (12 min of  $O_2$  measurements per ZT run), which can be used to cross check instrument precision and repeatability in addition to correcting baseline  $CO_2$  drift. The means of the  $\pm 1\sigma$  standard deviations of the seven ZT analyses, reported with  $\pm 1\sigma$  standard deviation were found to be  $\pm 6.3 \pm 4.3$  ppmEq and  $\pm 2.3 \pm 0.4$  ppmEq for 60 s and 30 s sample-WT switching frequencies, respectively. For the 30 second sample-WT switching frequency, the period of data that were not used after the switch was reduced from 30 s to 15 s, so that only the latter 15 s of data from each switching period were used to calculate the  $\Delta\Delta O_2$  values. It is important to ensure that the accuracy of the  $O_2$  measurement is not compromised when reducing the amount of excluded data after the switch, because of possible incomplete sweep-out of the tubing, or incomplete fuel cell response. The  $O_2$  accuracy was tested and verified by comparing the calibrated  $O_2$  mean value and  $\pm 1\sigma$  standard deviations using a 60 s switching scheme and by varying the period of excluded data after the switch from 5 to 50 s. Reducing the period of excluded data to as low as 15 s did not compromise

correct baseline drift in the Li-6252 analyzer response, using a procedure similar to that described by Andrews et al. [2014]. In contrast to Stephens et al. [2007] and Thompson et al. [2007], we employ three WTs using 10 L carbon fiber hoop wrap composite cylinders (Luxfer Gas Cylinders Ltd., model BFC 124–136-002), which can be filled with up to 300 bar of pressure to ensure that the measurement system has enough WT gas for a full ship cycle (i.e., 8 weeks). Our 23 h calibration frequency was chosen to minimize potential bias in the  $O_2$  data caused by WT gas  $O_2$  depletion as the cylinder pressure reduces. Calibrating at the more common frequency of 47 h [e.g., Wilson, 2013] caused a measurable bias in the TT  $O_2$  data [Pickers, 2016]. All high-pressure cylinders are stored horizontally in a thermally insulated Blue Box enclosure to prevent thermal and gravitational fractionation of  $O_2$  relative to  $N_2$  [Keeling et al., 1998a].

the accuracy of the measured O<sub>2</sub> values (to within  $\pm 0.3$  ppmEq), but 10 s resulted in an O<sub>2</sub> measurement bias, with  $\Delta O_2$  values noticeably lower.

## 2.5. Data Analyses and Modeling

Seasonal variability in O<sub>2</sub>, CO<sub>2</sub>, and APO over the Atlantic Ocean at different latitudes was examined by binning the open ocean meridional transect data into nineteen 5° latitude bands. A small amount of data influenced by atmospheric transport short-term events, which may be representative of a different latitude band, were excluded manually prior to binning. O<sub>2</sub>, CO<sub>2</sub>, and APO seasonal cycles were determined by fitting curves to the binned data using the HPspline parametric curve fitting program (see *Pickers and Manning* [2015] for more details). Since the CSL data set is currently only  $\sim 1$  year in duration, the data set for each latitude band was artificially extended by a year at each end prior to curve fitting, so that the HPspline curve fits would not be unduly biased by end effects. The curve fit results from the artificially extended data were subsequently discarded and are not included in our seasonal analysis. The long-term trends were prescribed in the curve fitting process (again, owing to the short duration of the CSL data set) using long-term trend values calculated by *Wilson* [2013], from  $\sim 3$  years of atmospheric O<sub>2</sub>, CO<sub>2</sub>, and APO data from Weybourne Atmospheric Observatory, UK. These prescribed trends are not the most suitable for our data set, but since our purpose is only to quantify the seasonal characteristics and annual means at each latitude and not to quantify the long-term trend, or growth rate of the long-term trend, it is appropriate to use them in this way, as the impact on the seasonal cycle and annual mean determination is minimal. Ideally, more than one single curve fitting program should be used when interpreting time series data to ensure that the subsequent analyses are not biased by the choice of curve fitting program [*Pickers and Manning*, 2015]. However, owing to the sparsity of the latitudinally binned data, it was not possible to employ the other two curve fitting programs commonly utilized in our community: NOAA's Carbon Cycle Group Curve fitting program [see *Thoning et al.*, 1989] and Seasonal and Trend decomposition using LOESS [see *Cleveland et al.*, 1990]. Varying the stiffness of the cubic spline component of the HPspline fitting procedure had a negligible effect on the curve fit results, which provides confidence in the curve fitting procedure.

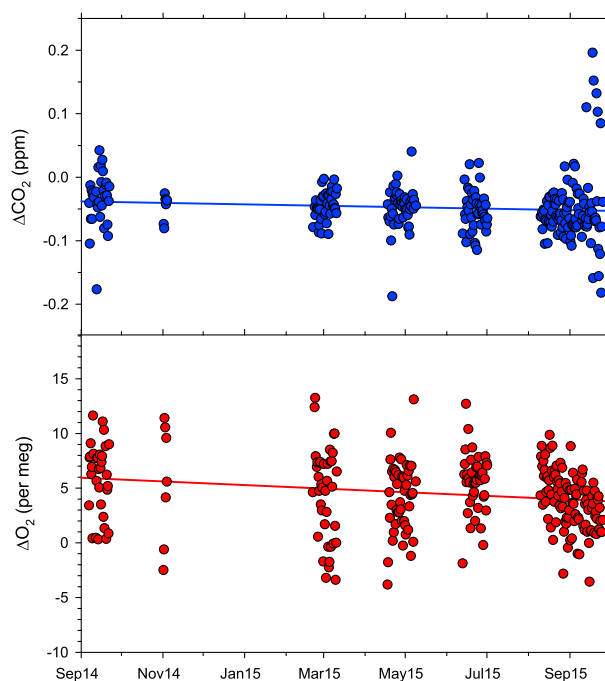
The UK Met Office NAME (Numerical Atmospheric-dispersion Modelling Environment) model [*Jones et al.*, 2007] was used to produce 3 day atmospheric footprints in order to investigate the origin of some short-term variations in the CSL O<sub>2</sub>, CO<sub>2</sub>, and APO data. The 3 day footprints were produced by releasing 10,000 inert particles into the model domain at the ship's location and running the model backward at 3 hourly time stamps, using the UK Met Office Unified Model meteorological fields.

We also compared our APO data with model-generated APO (produced for the same Atlantic route as the CSL) using the TM3 atmospheric tracer transport model [*Heimann and Körner*, 2003], which is driven off-line using the National Centers for Environmental Prediction reanalysis climatological wind fields from 1997 to 2013 [*Kalnay et al.*, 1996]. The flux inputs to TM3 are as follows: fossil fuel emissions are from the Carbon Dioxide Information Analysis Center; annual ocean O<sub>2</sub> and N<sub>2</sub> fluxes are from *Gruber et al.* [2001] and *Gloor et al.* [2001], respectively; ocean seasonal O<sub>2</sub> and N<sub>2</sub> variabilities are from the climatologies of *Garcia and Keeling* [2001]; and ocean seasonal CO<sub>2</sub> variability is from the climatology of *Takahashi et al.* [2009]. The contribution to modeled APO from the seasonal covariance of O<sub>2</sub>, N<sub>2</sub>, and atmospheric transport and mixing, also known as the "seasonal rectifier effect" (shown in Figure 6d), was simulated from the O<sub>2</sub> and N<sub>2</sub> climatological fluxes as explained in *Gruber et al.* [2001]. The fluxes used in our model-generated APO are the same as those used to produce the model-generated APO presented in *Gruber et al.* [2001] and in *Battle et al.* [2006]; hence, one can directly compare our Atlantic results to those from these two previous studies over the Pacific.

## 3. Results

### 3.1. Measurement System Performance

In terms of measurement system reliability, the main loss of data was caused by premature blocking of the chiller trap with ice, most likely caused by the first stage drying traps being overloaded. This resulted from excess water breakthrough caused by high water vapor present as the CSL passes through the tropics. This problem mainly affected the northward transects and prevented data collection at the most southerly latitudes during the first half of 2015. In late 2016 we increased the pressure inside the first stage drying traps, which increased the removal of water vapor and enabled the downstream drying traps to last the full 8 week



**Figure 3.** (top) CO<sub>2</sub> and (bottom) O<sub>2</sub> measurements of the Target Tank (TT) on board the Cap San Lorenzo (CSL). Data are shown as differences from the UEA laboratory measurements of these TT cylinders. TT measurements that were made when the measurement system was experiencing known technical difficulties have been excluded (a total of 7.6% excluded). Each TT measurement shown is the mean of 13 consecutive 1 min averages of O<sub>2</sub> and CO<sub>2</sub>.

route. In addition to data loss from technical issues, many shipboard O<sub>2</sub> and CO<sub>2</sub> data sets require extensive flagging to remove pollution from the ship’s exhaust. However, data contamination from the CSL exhaust was very rare in our system owing to the unusual design of the ship, with the engine exhaust stack and bridge separated by about 150 m.

Figure 3 shows all Target Tank (TT) O<sub>2</sub> and CO<sub>2</sub> measurements from on board the CSL, plotted as differences from the UEA laboratory measurements of these TT cylinders. Both the O<sub>2</sub> and CO<sub>2</sub> measurements show slight downward drift of about 1.1 meg<sup>-1</sup> yr<sup>-1</sup> and 0.02 ppm yr<sup>-1</sup>, respectively. These drifts are not significant because the WSSes have a lifetime of only ~15 months.

For CO<sub>2</sub>, the measurement system repeatability and compatibility meet the World Meteorological Organization (WMO) goals (for both hemispheres), and in the case of repeatability, the system is significantly better than the WMO goals (see Table 1). For O<sub>2</sub>, the measurement system repeatability and compatibility are both within the extended WMO goals but do not meet the more ambitious scientifically desirable WMO goals. The scientifically desirable WMO O<sub>2</sub> goals, however, are not currently routinely achievable by the O<sub>2</sub> measurement community. For example, the best current O<sub>2</sub> compatibility between international laboratories is

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**Table 1.** Repeatability and Compatibility of the CSL O<sub>2</sub> and CO<sub>2</sub> Measurement System

Gas Species	Repeatability			Compatibility	
	WMO Goal <sup>a</sup>	From TT <sup>b</sup>	From Air Lines <sup>c</sup>	WMO Goal <sup>a</sup>	From TT <sup>d</sup>
CO <sub>2</sub> (ppm)	±0.05 (±0.025)	±0.0065 ± 0.0049	±0.02	±0.1 (±0.05)	-0.05 ± 0.04
O <sub>2</sub> (per meg)	±1 (±5)	±3.0 ± 4.6	±3.2	±2 (±10)	4.6 ± 3.3

<sup>a</sup>WMO repeatability and compatibility goals, where the repeatability of a measurement system should be at most half of the value of the compatibility goal [Tans and Zellweger, 2013]. For CO<sub>2</sub>, the WMO goals are for northern hemisphere measurements, with southern hemisphere measurement goals shown in parentheses. For O<sub>2</sub>, the WMO goals are the same for northern and southern hemisphere measurements, but are very ambitious, and are not currently achievable by the O<sub>2</sub> measurement community; hence, the so-called “extended” O<sub>2</sub> goals, which are suitable for many O<sub>2</sub> measurement applications, are shown in parentheses.

<sup>b</sup>Values are calculated using the same method as Kozlova and Manning [2009], from the mean 1σ standard deviations of the average of two consecutive 1 min TT measurements, determined from 275 TT analyses during the period September 2014 to September 2015. TT repeatability is reported with ±1σ uncertainty, which recognizes the fact that the measurement system repeatability varies over time.

<sup>c</sup>Values are calculated from two successive 1 min sample air measurements during periods with little variability in ambient air O<sub>2</sub> and CO<sub>2</sub>, from August 2015 (a total of 275 pairs of measurements). These values, which represent the repeatability of the whole measurement system, are used to validate the TT repeatability values, because the TT gas does not pass through the air inlet lines, diaphragm pumps, or drying traps of the measurement system.

<sup>d</sup>Compatibility is determined from the mean difference in TT CO<sub>2</sub> and O<sub>2</sub> between the shipboard TT measurements, and the UEA laboratory TT measurements, which were determined using the NOAA and Scripps PSSes. Compatibility values are calculated from the same 275 TT measurements mentioned in footnote <sup>b</sup>. Uncertainties are the ±1σ standard deviations of the CSL-UEA mean differences.



estimated to be  $\pm 5$  per meg, compared to the WMO goal of  $\pm 2$  per meg [Tans and Zellweger, 2013]. The repeatability of the  $O_2$  measurement system from the air lines and from the TT analyses are very similar, providing confidence that no additional analytical  $O_2$  imprecision is introduced by the inlet lines, diaphragm pumps, or drying traps. For  $CO_2$ , the repeatability from the inlet lines is much worse than that from the TT analyses (but still within the northern hemisphere WMO goal). However, we suspect that this is not caused by imprecision introduced by the inlet lines or pumps, but rather because ambient  $CO_2$  variability is much greater than the achievable  $CO_2$  analytical precision, even when atmospheric conditions are extremely stable.

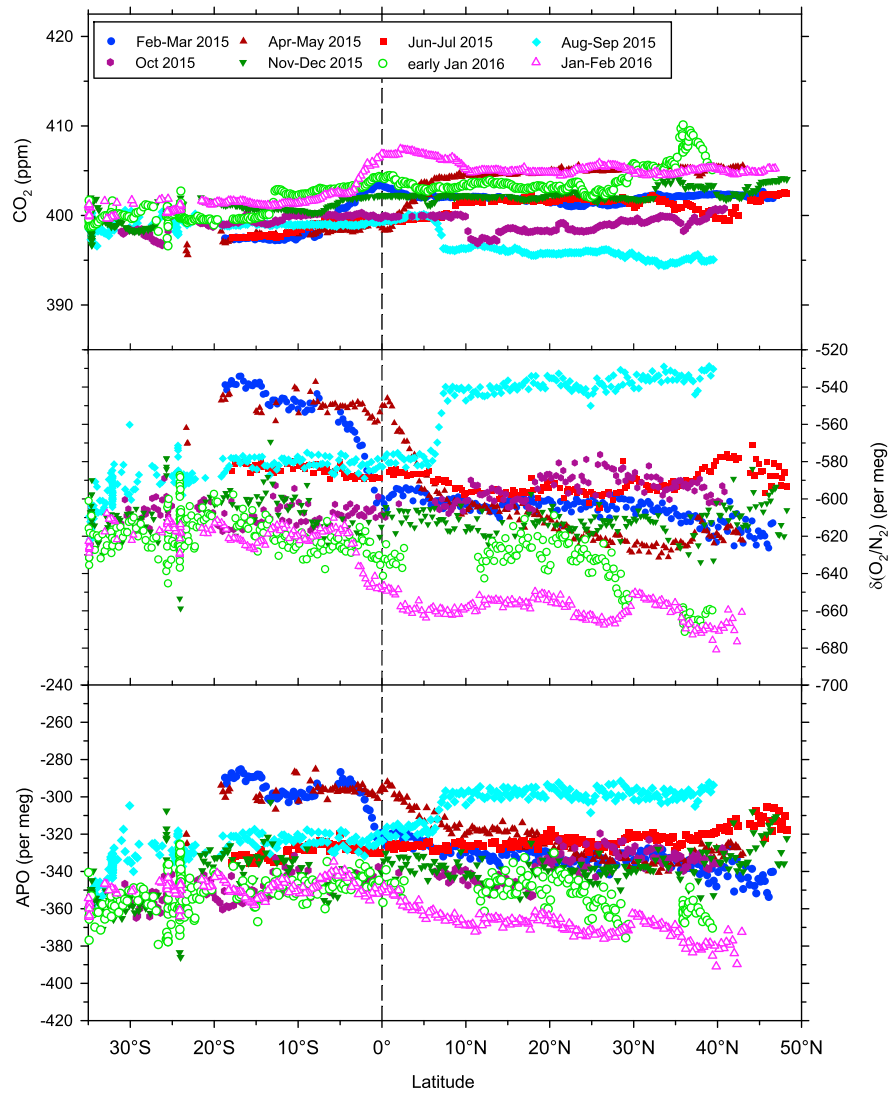
Overall, the measurement system  $O_2$  results shown in Table 1 are comparable to or better than other measurement systems using the fuel cell analytical technique. For example, on short timescales our  $\pm 1\sigma$   $O_2$  precision over 6 min is typically  $\pm 2.7$  per meg but can be as low as  $\pm 0.8$  per meg, compared to the 6 min  $\pm 1\sigma$   $O_2$  precisions reported by Stephens *et al.* [2007] ( $\pm 1.4$  per meg) and Thompson *et al.* [2007] ( $\pm 7$  per meg).

### 3.2. Meridional Transects

Hourly-averaged atmospheric  $O_2$ ,  $CO_2$ , and APO data from the CSL meridional transects between January 2015 and March 2016 (see Figure 4) show several significant features: first, the short-term variability in all three species is significantly smaller than typically seen from land or coastal measurement stations; second, the main feature in most of the transects is a step change close to the equator caused by seasonal differences between northern and southern hemisphere air, and thus is representative of the position of the ITCZ; and third, the data display both seasonal and long-term changes in all three species. For example,  $CO_2$  is higher (and  $O_2$  is lower) in the northern hemisphere in April–May 2015 compared to June–July 2015 as expected from the strong drawdown of  $CO_2$  (and release of  $O_2$ ) in the summer months by the land biosphere. APO is also lower in the northern hemisphere in April–May 2015 compared to June–July 2015 because of  $O_2$  outgassing from ocean warming in the spring and summer.  $CO_2$  is also co-emitted with  $O_2$  to the atmosphere as the ocean warms, but seasonal variability is not observed in atmospheric  $CO_2$  data because the air-sea equilibration time for  $CO_2$  is relatively slow ( $\sim 1$  year) compared to atmospheric mixing times ( $\sim 1$  month) [Keeling and Shertz, 1992], and because biological and ventilation-related  $CO_2$  fluxes counteract solubility-related air-sea  $CO_2$  fluxes [Stephens *et al.*, 1998]. Long-term changes in  $O_2$ ,  $CO_2$ , and APO are also apparent from the atmospheric data collected over two successive years, such as February 2015 and February 2016, which show that  $CO_2$  is increasing, while  $O_2$  and APO are decreasing, primarily owing to fossil fuel combustion.

Although Figure 4 shows only open ocean data, there is still some land influence apparent in the short-term variability (hours to days) in  $CO_2$  and  $O_2$ , which is often larger in magnitude than the short-term APO variability. Several transects also display short-term variability in the  $O_2$ ,  $CO_2$ , and APO data close to the ITCZ step changes; for example, in April–May 2015 there is a small positive excursion in  $CO_2$  and corresponding negative excursions in  $O_2$  and APO, just south of the equator, after the ship crossed the ITCZ. These excursions are most likely caused by transient changes in atmospheric transport that bring air to the ship from a different latitude, hemisphere, or altitude, and not by equatorial upwelling fluxes local to the ship. A dominant upwelling contribution is unlikely because the equatorial excursions are only apparent in two of the eight meridional transects (February–March 2015 and April–May 2015), which is inconsistent with typical intra-annual variability of equatorial upwelling in the Atlantic [Weingartner and Weisberg, 1991]. Furthermore, the different air-sea gas equilibration times for  $O_2$  and  $CO_2$  preclude a simultaneous signal with similar magnitudes (on a mole per mole basis).

We have found that much of the short-term  $O_2$ ,  $CO_2$ , and APO variability over the North Atlantic and close to the ITCZ corresponds to changes in air mass origin, as indicated by the NAME atmospheric footprints (not shown). The sharp transition of the ITCZ for  $O_2$ ,  $CO_2$ , and APO can also be explained using the NAME footprints: we find that sharp changes correspond to rapid changes in air mass origin from northern hemisphere easterlies to southern hemisphere easterlies, while more gradual changes across the ITCZ correspond to short periods of mixed air that originate from both hemispheres. In contrast to many previous shipboard and coastal APO analyses [e.g., Ishidoya *et al.*, 2016; Lueker, 2004; Lueker *et al.*, 2003; Patecki and Manning, 2007; Thompson *et al.*, 2007, 2008; van der Laan-Luijkx, 2010; Yamagishi *et al.*, 2008], we do not observe any significant ( $> 10$  per meg) short-term variability (hours to days) in our CSL APO data set (currently  $\sim 14$  months in duration) that can be attributed to specific ocean related  $O_2$  or  $CO_2$  variability (i.e., from phytoplankton blooms or upwelling of subsurface waters; see Pickers [2016] for more details).

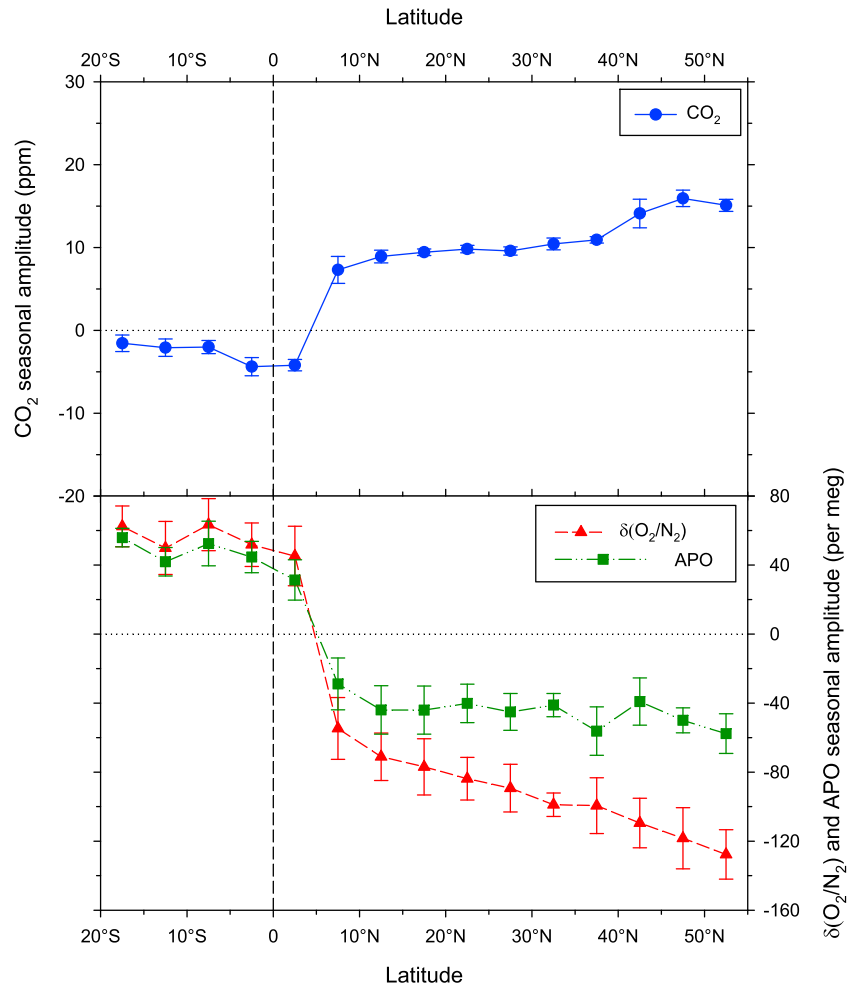


**Figure 4.** Meridional transects from February 2015 to February 2016 of hourly averaged atmospheric CO<sub>2</sub>, δ(O<sub>2</sub>/N<sub>2</sub>), and APO over the Atlantic Ocean, excluding polluted data from when the ship was in port or very close to land. The y axes have been scaled so that variability in all three species is visually comparable on a mole per mole basis.

### 3.3. Seasonal Variability

As expected, the seasonality of the CSL O<sub>2</sub>, CO<sub>2</sub>, and APO changes with latitude similarly to the data presented by *Tohjima et al.* [2012]. There is a distinct change in the phasing of the seasonal cycle at about 5°N for all three species (see Figure 5, denoted by the change in the sign of the amplitude values), which coincides with the mean position of the ITCZ in the Atlantic Ocean and is significantly larger than the seasonal amplitude uncertainty (indicated by the error bars in Figure 5). The atmospheric O<sub>2</sub> and CO<sub>2</sub> seasonal amplitudes decrease from pole to equator in the northern hemisphere. For CO<sub>2</sub>, the amplitude of the seasonal cycle in the southern hemisphere is significantly less than at corresponding latitudes in the northern hemisphere. For O<sub>2</sub>, the amplitudes are similar in magnitude at corresponding latitudes in both the northern and southern hemisphere up to 20°. For APO, there is no significant change in seasonal cycle amplitude with latitude, and northern and southern hemisphere seasonal cycle amplitudes are of similar magnitudes.

At ~50°N, the APO seasonal cycle amplitude is about half of the O<sub>2</sub> seasonal cycle amplitude, which indicates that about half of the O<sub>2</sub> seasonal cycle can be attributed to ocean processes, and half to land processes. At ~15°S, the seasonal cycle of APO seasonal is ~82% of that of O<sub>2</sub>, suggesting that most the O<sub>2</sub> seasonal cycle

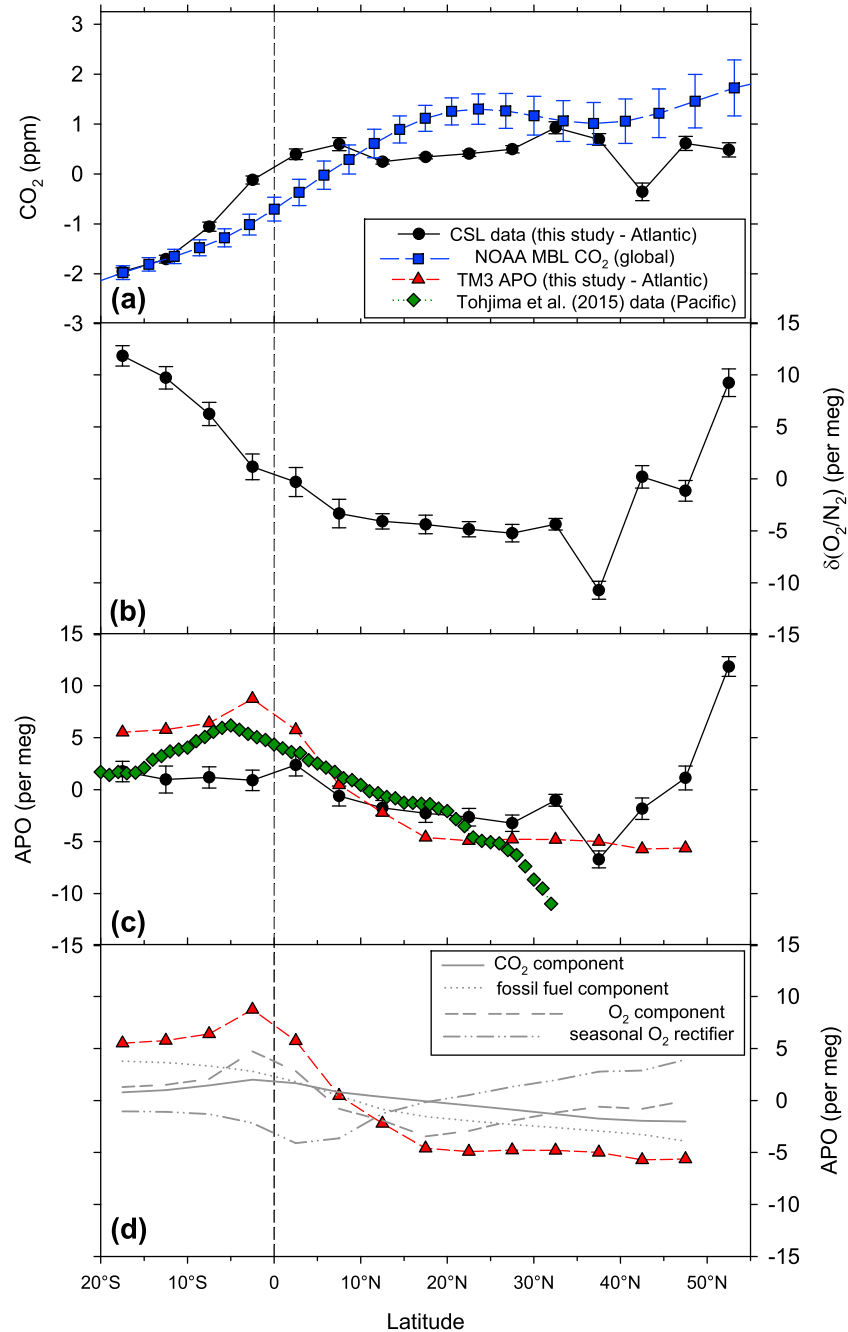


**Figure 5.** Amplitude of the seasonal cycle as a function of latitude. Data are (top) CO<sub>2</sub> (blue circles and solid lines), (bottom)  $\delta(\text{O}_2/\text{N}_2)$  (red triangles and dashed lines), and (bottom) APO (green squares and dash-dotted lines). Positive CO<sub>2</sub> values (negative  $\delta(\text{O}_2/\text{N}_2)$  and APO values) indicate amplitudes where the seasonal maxima (minima) occur during the boreal winter months, while negative (positive) values indicate amplitudes where the seasonal maxima (minima) occur during the austral winter months. The error bars show the uncertainty in the seasonal amplitude calculated for each species, which was determined from the mean magnitude of the HPspline curve fit residuals at the seasonal inflection points. The y axes have been scaled so that changes are visually comparable on a mole per mole basis. The horizontal dotted lines when the seasonal amplitude is zero are shown to emphasize the changes in the seasonal cycle phasing, and the vertical dashed line indicates the equator.

can be attributed to ocean processes. Additionally, the seasonal cycles in APO and O<sub>2</sub> differ by ~10 per meg, equivalent to a 2.1 ppm change in CO<sub>2</sub>, which is very similar to the magnitude of the CO<sub>2</sub> seasonal cycle at this latitude.

### 3.4. Annual Mean Latitudinal Distribution

Latitudinal distribution in annual mean O<sub>2</sub>, CO<sub>2</sub>, and APO over the Atlantic Ocean is shown in Figure 6. Annual mean CO<sub>2</sub> is ~2 ppm lower in our southern hemisphere data compared to the northern hemisphere (comparing 20°S with 55°N) owing to greater fossil fuel emissions in the north. The CSL CO<sub>2</sub> data presented here are more variable and generally lower than the NOAA Marine Boundary Layer (MBL) reference CO<sub>2</sub> data [Dlugokencky *et al.*, 2015] in the northern hemisphere (by up to ~1 ppm) and exhibit a steeper cross-equatorial change than the NOAA data (Figure 6a). These differences are likely due to different representation and averaging: the CSL data presented here represent the atmosphere over the Atlantic Ocean only, while the NOAA MBL CO<sub>2</sub> data represent a meridional global average, and have been smoothed and interpolated from measurements in the NOAA global network.



**Figure 6.** (a) Latitudinal distribution in annual mean CO<sub>2</sub> from the CSL over the Atlantic Ocean (black circles). Also shown is the latitudinal distribution in global annual mean CO<sub>2</sub> from the NOAA Marine Boundary Layer (MBL) reference product, estimated for 2015 (blue squares). (b) Latitudinal distribution in annual mean  $\delta(\text{O}_2/\text{N}_2)$  from the CSL over the Atlantic Ocean (black circles). (c) Latitudinal distribution in annual mean APO from the CSL (black circles) and in modeled APO data (red triangles) over the Atlantic Ocean. Also shown is the latitudinal distribution in annual mean APO over the western Pacific from *Tohjima et al.* [2015], averaged over the years 2008–2012 (green diamonds). (d) Modeled APO data over the Atlantic (red triangles) alongside the simulated APO components. All y axes have been scaled so that changes are visually comparable on a mole per mole basis. Uncertainty in the CSL data is denoted by the error bars, which represent the mean standard error calculated from the HPspline curve fit residuals for each latitude band.

O<sub>2</sub> and APO generally have an inverse latitudinal distribution compared to CO<sub>2</sub> (Figures 6b and 6c, black circles). This is largely caused by greater atmospheric O<sub>2</sub> uptake in the northern hemisphere from fossil fuel burning compared to the southern hemisphere [Gruber *et al.*, 2001]. Both the annual mean O<sub>2</sub> and APO data exhibit similar variability in the northern hemisphere midlatitudes, with a slight positive excursion between 30 and 35°N, followed by a significant negative excursion between 35 and 40°N, and then a relatively large increase between 45 and 55°N. This northern hemisphere latitudinal variability in annual mean O<sub>2</sub> and APO is very similar to the latitudinal APO variability produced by Gruber *et al.* [2001].

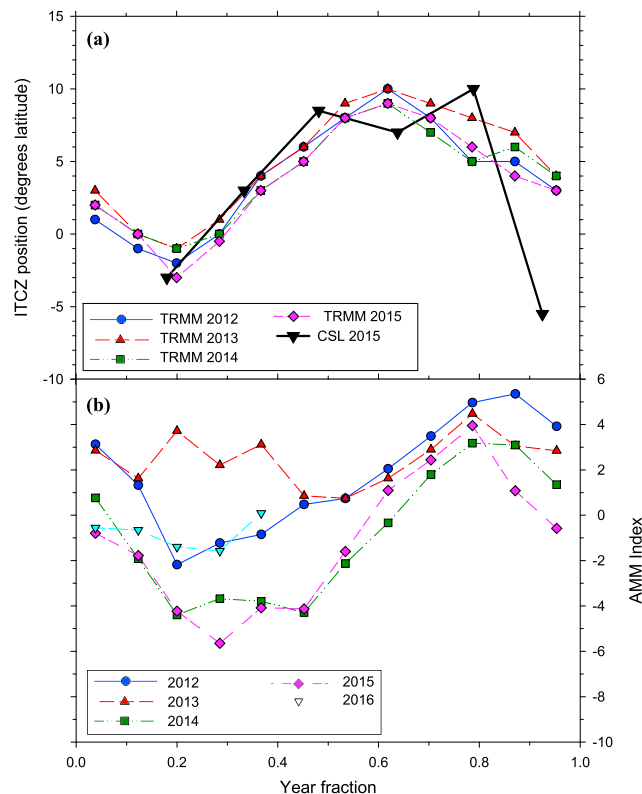
The CSL annual mean APO data do not exhibit a significant equatorial bulge, as observed over the Pacific Ocean [e.g., Battle *et al.*, 2006; Tohjima *et al.*, 2015] (Figure 6c). Although there is a small bulge in the CSL APO data at ~2.5°N, it is not significant, given the uncertainty of the equatorial annual mean APO values, and because the bulge consists of only a single data point. In contrast, the Pacific Ocean equatorial APO bulge covers a latitudinal range of ~20° (Figure 6c, green diamonds). No equatorial APO bulge is found when the CSL APO data is binned with a higher resolution of 2.5° latitude bands (not shown), which indicates that the small equatorial bulge in the CSL APO data is not significant.

Our results are compared with model-generated APO using TM3 as described in section 2.5 and shown by the red symbols in Figures 6c and 6d, with the main contributing components shown in Figure 6d. The model exhibits a larger interhemispheric gradient (between 20°S and 55°N) than the CSL APO data, generally overestimating the southern hemisphere and underestimating the northern hemisphere APO annual means. This contrasts with the previous studies of Stephens *et al.* [1998] and Gruber *et al.* [2001], who found that the model generated APO significantly underestimated the interhemispheric gradient over the Pacific Ocean. In addition, the modeled APO does not reproduce the variability that is apparent in the CSL APO data between 30 and 55°N, the latter of which is very similar to the northern hemisphere APO variability reported in Gruber *et al.* [2001], who found that this northern hemisphere APO variability is caused by a combination of a latitudinal minimum in fossil fuel emissions and the seasonal O<sub>2</sub> rectifier effect. We find, however, that the CSL northern hemisphere APO variability cannot be adequately explained by the latitudinal variability in the fossil fuel and seasonal O<sub>2</sub> rectifier components of our TM3-modeled APO over the Atlantic (Figure 6d). Most significantly, the modeled APO does exhibit a significant equatorial bulge, centered around ~2.5°S, which is ~5 per meg in magnitude. This modeled Atlantic Ocean equatorial APO bulge is of a similar magnitude to that found in APO observations over the western Pacific (averaged over 2008–2012) by Tohjima *et al.* [2015] but is not supported by the CSL Atlantic APO data. Figure 6d demonstrates that the modeled APO bulge over the Atlantic is mostly driven by the O<sub>2</sub> component, with a significantly more minor contribution from the CO<sub>2</sub> component.

#### 4. Discussion

Although there is a lack of an equatorial APO bulge over the Atlantic Ocean during 2015 in our observations, the CSL data set is currently only ~1 year in duration. Tohjima *et al.* [2015] found that equatorial APO outgassing over the western Pacific Ocean was suppressed during 2010 owing to the development of El Niño conditions. Thus, it is possible that the lack of an Atlantic APO bulge is a transient feature caused by the development of strong El Niño conditions during 2015. Alternatively, the lack of an equatorial APO bulge, as observed by the CSL, may be a persistent feature over the Atlantic Ocean. Tohjima *et al.* [2015] largely attribute the suppression of western Pacific equatorial APO bulge to changes in atmospheric transport, whereby an equatorward shift in the ITCZ position during the 2009/2010 El Niño event enhanced the transport of wintertime northern hemisphere air into the tropics, reducing annual mean APO values near the equator. They also found, however, that up to ~25% of the equatorial annual mean APO interannual variability might be caused by changes in equatorial APO outgassing fluxes in the western Pacific, which are also associated with the ENSO cycle. The modeling study by Rödenbeck *et al.* [2008] also found a significant correlation between ENSO variability and APO anomalies, albeit in the opposite direction to that found by Tohjima *et al.* [2015], and more recently, Eddebbbar *et al.* [2017] showed that the response of APO to ENSO variability differs between the western and central/eastern Pacific and confirmed that the suppression of the APO bulge over the western Pacific is mainly dominated by the weakening of trade winds.

To assess whether atmospheric transport patterns over the Atlantic Ocean were unusual during 2015, we have compared the ITCZ position during 2015 to the position during 2012–2014. The ITCZ position is



**Figure 7.** (a) Seasonal migration in the position of the ITCZ in the Atlantic Ocean, determined from the CSL atmospheric CO<sub>2</sub> and O<sub>2</sub> data (black triangles) and from rainfall maxima using NASA's Tropical Rainfall Measuring Mission (TRMM) satellite from 2012 to 2015 (coloured symbols). Note that the CSL data are discrete measurements, whereas the TRMM data are monthly averages. (b) Seasonal and interannual variability in the Atlantic Meridional Mode (AMM) index from sea surface temperatures from 2012 to mid-2016.

found that an equatorial APO bulge was present in all years and was not suppressed during years with prevailing El Niño conditions (data not shown).

We also examined the role of interannual and seasonal variability in the Atlantic Meridional Mode (AMM) index [Foltz and McPhaden, 2010] between 2012 and mid-2016, determined from sea surface temperatures [Chiang and Vimont, 2004] (see Figure 7b). Most of the interannual variability in the AMM occurs during the first half of the year, and 2015 was not characterized by unusual AMM sea surface temperatures compared to previous years.

Finally, we have examined interannual variability in equatorial Atlantic air-sea O<sub>2</sub> fluxes from the Plankton Types Ocean Model (PlankTOM; version 5.3) embedded within the Nucleus for European Modeling of the Ocean (NEMO; version 2.3) framework [Buitenhuis et al., 2013], which we refer to as the NEMO-PlankTOM model, between 2012 and 2015 (data not shown). The NEMO-PlankTOM air-sea O<sub>2</sub> fluxes show interannual variability that is mostly confined to the extratropical Atlantic, with less interannual variability apparent in the equatorial region, suggesting that equatorial APO outgassing in 2015 was not unusually reduced compared to previous years in the model.

The four lines of evidence discussed above suggest that the lack of equatorial APO bulge is unlikely to be a transient feature caused by the 2015/2016 El Niño event and is more likely to be a persistent characteristic over the Atlantic Ocean. This result is perhaps not surprising, as the suppression of equatorial APO outgassing during El Niño events in the western Pacific is unlikely to manifest in the same way in the Atlantic.

determined from the observed step changes in the equatorial atmospheric O<sub>2</sub> and CO<sub>2</sub> data and using monthly mean precipitation data from NASA's (National Aeronautics and Space Administration) Tropical Rainfall Measuring Mission (TRMM) satellite (see Figure 7a). The ITCZ migrates seasonally toward the warming hemisphere, owing to cross equatorial atmospheric and surface ocean energy fluxes from the warming hemisphere into the cooling hemisphere [Schneider et al., 2014]. The ITCZ position in the Atlantic determined from the CSL data agrees with the TRMM 2015 values except at the end of the year, which indicates that step changes in atmospheric O<sub>2</sub> and CO<sub>2</sub> time series are generally a good proxy for the ITCZ position. Figure 7a shows that the position of the ITCZ during 2015 was not unusual compared to the previous 3 years. These data indicate that the lack of equatorial APO bulge in the CSL data is unlikely to be caused by an unusual change in the ITCZ position. In addition, we reproduced the TM3-modeled APO using nonclimatological winds from 2001 to 2010 and

We have found that the modeled APO is overestimated in the equatorial Atlantic and that the modeled APO overestimates the observed interhemispheric APO gradient. These model-observation discrepancies are most likely either caused by inaccuracies in the air-sea flux data used in TM3, and/or by inaccuracies in the atmospheric transport model itself, the latter of which were found by *Battle et al.* [2006] to dominate differences in modeled and measured APO.

Comparing our results with those from previous studies indicates that the model overestimation of the Atlantic equatorial APO bulge is likely to be dominated by inaccuracies in the O<sub>2</sub> flux data product. For example, the modeled APO data presented in *Tohjima et al.* [2012] and *Tohjima et al.* [2015] also predict a significant equatorial APO bulge over the Atlantic Ocean. These results are based on the same ocean O<sub>2</sub> fluxes used to produce our modeled APO shown in Figures 6c and 6d, but transported using the NIES transport model (version 99), where we have used TM3. This suggests that either both the NIES and TM3 transport models (which are driven by different meteorological fields) are inaccurate or that the ocean O<sub>2</sub> outgassing fluxes are overestimated in the equatorial Atlantic. Conversely, the model overestimation of the interhemispheric APO gradient is more likely to be caused by meridional atmospheric transport inaccuracies in the TM3 model, as found by *Battle et al.* [2006]. Conclusively determining the influences of atmospheric transport and oceanic fluxes on the model-data APO discrepancy over the Atlantic Ocean requires further analyses; however, our CSL data potentially have significant implications, both for our current understanding of air-sea O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> fluxes in the Atlantic Ocean and also for our understanding of how Atlantic Ocean carbon uptake may change in a warmer climate.

## 5. Conclusions

We have presented the first meridional transects of atmospheric O<sub>2</sub>, CO<sub>2</sub>, and APO over the Atlantic Ocean from a new, automated shipboard measurement system deployed on a commercial container ship traveling continuously between Europe and South America. For CO<sub>2</sub>, the measurement system performs well within the WMO repeatability and compatibility goals for both hemispheres, while for O<sub>2</sub>, the measurements compare well to other O<sub>2</sub> measurement systems that employ the fuel cell technique and are at the limit of what is currently achievable using a fuel cell analyzer. Our in situ measurement system provides new insights into short term, seasonal and annual mean variability in O<sub>2</sub>, CO<sub>2</sub>, and APO over the Atlantic Ocean.

The Pacific Ocean equatorial APO bulge predicted by *Stephens et al.* [1998] and *Gruber et al.* [2001], and later confirmed from observations by *Battle et al.* [2006] and *Tohjima et al.* [2005b], is not apparent in our Atlantic APO data in 2015. Owing to the development of strong El Niño conditions during 2015, it is possible that the equatorial APO bulge was suppressed by ENSO-related changes in ITCZ position and atmospheric transport, as was found to be the case in the western Pacific Ocean during 2010 [*Tohjima et al.*, 2015]. However, our analysis indicates that neither the ITCZ position, sea surface temperatures, or equatorial ocean O<sub>2</sub> fluxes were unusual during 2015 compared to previous years, and our TM3-modeled APO bulge was not suppressed during periods with prevailing El Niño conditions between 2001–2010. Thus, we conclude that the lack of an equatorial APO bulge is most likely a persistent feature over the Atlantic Ocean.

In contrast to the observational data, model simulated annual mean APO data exhibit a significant Atlantic Ocean equatorial bulge. Assuming that the lack of an Atlantic Ocean equatorial APO bulge is indeed a persistent feature, we infer that the ocean flux data products used in the model may be inaccurate in the equatorial Atlantic Ocean, based on previous studies using these data, but with different atmospheric transport models. Additionally, we find that the modeled APO overestimates the observed APO interhemispheric gradient over the Atlantic (between 20°S and 50°N), which also alludes to possible inaccuracies in the atmospheric transport model.

The shipboard O<sub>2</sub>, CO<sub>2</sub>, and APO measurements are ongoing; thus, as the time series increases in duration, the nature and persistence of the Atlantic equatorial APO bulge will become clearer. Potential future applications of Atlantic Ocean APO data include constraining Atlantic Ocean O<sub>2</sub>, CO<sub>2</sub>, and heat transport in ocean models and examining how the Atlantic Ocean carbon sink is changing over time. Recent advances in atmospheric transport model resolution and more sophisticated ocean model simulations [e.g., *Resplandy et al.*, 2015], combined with new APO observations, including the CSL data presented here and pole-to-pole aircraft APO observations [e.g., *Bent*, 2014], mean that ocean model validation using APO is a viable and powerful tool for both global and regional studies [e.g., *Nevison et al.*, 2015, 2016].

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