Ozone in the Atlantic Ocean marine boundary layer

Patrick Boylan • Detlev Helmig • Samuel Oltmans

In situ atmospheric ozone measurements aboard the R/V Ronald H. Brown during the 2008 Gas-Ex and AMMA research cruises were compared with data from four island and coastal Global Atmospheric Watch stations in the Atlantic Ocean to examine ozone transport in the marine boundary layer (MBL). Ozone measurements made at Tudor Hill, Bermuda, were subjected to continental outflow from the east coast of the United States, which resulted in elevated ozone levels above 50 ppbv. Ozone measurements at Cape Verde, Republic of Cape Verde, approached 40 ppbv in springtime and were influenced by outflow from Northern Africa. At Ragged Point, Barbados, ozone levels were ∼21 ppbv; back trajectories showed the source region to be the middle of the Atlantic Ocean. Ozone measurements from Ushuaia, Argentina, indicated influence from the nearby city; however, the comparison of the daily maxima ozone mole fractions measured at Ushuaia and aboard the Gas-Ex cruise revealed that these were representative of background ozone in higher latitudes of the Southern Hemisphere. Diurnal ozone cycles in the shipborne data, frequently reaching 6–7 ppbv, were larger than most previous reports from coastal or island monitoring locations and simulations based on HOx photochemistry alone. However, these data show better agreement with recent ozone modeling that included ozone-halogen chemistry. The transport time between station and ship was estimated from HYSPLIT back trajectories, and the change of ozone mole fractions during transport in the MBL was estimated. Three comparisons showed declining ozone levels; in the subtropical and tropical North Atlantic Ocean the loss of ozone was <1.5 ppbv day⁻¹. Back trajectories at Ushuaia were too inconsistent to allow for this determination. Comparisons between ship and station measurements showed that ozone behavior and large-scale (∼1000 km) multi-day transport features were well retained during transport in the MBL.

1. Introduction and motivation

Over continental areas, atmospheric concentrations of ozone frequently rise above natural background levels. In urban areas the levels of nitrogen oxides and hydrocarbons are elevated, causing increasing levels of ozone during daylight hours from photochemical ozone production. The marine boundary layer (MBL) atmosphere is in general characterized by relatively low ozone levels due to the predominance of ozone sinks over ozone sources (Cooper et al., 2014). However, certain ocean environments can experience high ozone levels from the outflow of elevated ozone and by ozone production from precursors during atmospheric transport from coastal regions.

Transport of elevated ozone in the MBL has been observed on several occasions, for instance at Mace Head, Ireland (Simmonds and Derwent, 1991; Derwent et al., 2013), and at the Canary Islands (Schmitt et al., 1988; Rodriguez et al., 2004). The North Atlantic Regional Experiment (NARE) examined the distribution of ozone at four island stations in the far North Atlantic Ocean and found evidence of ozone produced from anthropogenic precursors in North America (Parrish et al., 1998). Ozone and ozone precursors from mainland Asia have been shown to travel across the Pacific Ocean and contribute to high levels of ozone in southern California (Lin et al., 2012). There have been instances of ozone pollution transported from North America.
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to Bermuda (Oltmans and Levy, 1992, 1994; Moody et al., 1995). Trend analyses have pointed out that surface ozone over both the North and South Atlantic have been increasing due to pollution outflow from the bordering continents (Lelieveld et al., 2004). Subsidence of dry air from the upper troposphere containing elevated ozone constitutes another influence on ozone levels in the North Atlantic (Oltmans and Levy, 1992; Moody et al., 1995; Val Martin et al., 2006). Parrish et al. (2013) noted that changes in tropospheric transport patterns have modified the seasonal cycle of ozone, with the occurrence of the seasonal maximum ozone at mid-latitudes shifting to earlier in the year. Despite these occurrences of elevated ozone transport, the North Atlantic atmosphere has been classified as a net ozone sink during spring and summer, demonstrating that overall ozone sinks supersede these ozone transport events (Helmig et al., 2008).

The remote marine atmosphere is a net ozone sink with ozone being removed by a series of chemical reactions and deposition to the ocean surface. The primary chemical ozone sinks are photochemical pathways, with direct photolysis being the dominant sink followed by ozone reacting with the HO and OH radicals (Monks et al., 1998, 2000; Monks, 2005; Conley et al., 2011). It has been noted that HO, chemistry alone cannot account for the observed diurnal ozone dynamics in the marine boundary layer; consequently, ozone-halogen chemistry has been suggested as an additional ozone destruction pathway in the MBL (Dickerson et al., 1999; Watanabe et al., 2005; Read et al., 2008; Saiz-Lopez et al., 2012). Dry deposition, with surface deposition rates on the order of 0.01–0.02 cm s⁻¹ over the open ocean, is another contributing sink (Conley et al., 2011; Helmig et al., 2012). Approximately 1010 Tg yr⁻¹ of ozone is lost to the Earth's surface through dry deposition (Stevenson et al., 2006). Ganzeveld et al. (2009) estimated that oceanic ozone dry deposition accounts for approximately one-third of the global ozone deposition sink, roughly 335 Tg yr⁻¹.

The net ozone loss over the remote ocean varies by latitude and time of year. These loss terms result in ozone destruction rates to be higher during the day, and diurnal ozone cycles that show declining ambient air ozone mole fractions during the day and partial to full recovery at night from entrainment of free tropospheric air and advection into the MBL. Earlier publications reported ozone diurnal cycle amplitudes in the MBL on the order of 1–3 ppbv (Oltmans and Levy, 1992, 1994; Monks et al., 1998, 2000). Due to the predominance of the photochemical loss term, surface ozone declines towards the summer, resulting in a seasonal cycle with up to an ~ 25 ppbv amplitude at some MBL locations (Oltmans and Levy, 1992, 1994).

In this study we used atmospheric ozone measurements acquired during ocean ozone flux experiments onboard the research vessel (R/V) Ronald H. Brown to investigate the long range transport of ozone over the ocean. These data were analyzed in relation to long-term surface ozone observations conducted within the World Meteorological Organization (WMO) Global Atmospheric Watch (GAW) program at four island and coastal stations. The comparison of these unique shipboard and station data allows for the investigation of how ozone is transported in the MBL and ozone loss by photochemical destruction and deposition to the ocean surface.

2. Study methodology

2.1 Land-based stations

Four stationary atmospheric GAW observatories in the Atlantic Ocean provided surface ozone measurements. The observations from these stations were chosen due to their proximity to the available shipborne ozone measurements. The station data were obtained from the World Data Centre for Greenhouse Gases (WDCGG, 2014) and are summarized in Table 1. Data are available in hourly, daily, and monthly means.

The Tudor Hill site (32.27° N, 64.87° W, 30 m) is located in Bermuda and operated by the Bermuda Biological Station (Tudor Hill, 2014). Ozone measurements are managed by the Global Monitoring Division (GMD) of the Earth Systems Research Laboratory (ESRL) of the National Oceanic and Atmospheric Administration (NOAA). Continuous ozone measurements were made using an ozone UV absorption monitor. Ozone data are available from October 1988 to May 1998, using a DASIBI instrument, and from February 2003 to July 2013, using a Thermo Environmental Corp. (TEI) Model 49C monitor. The instrument was calibrated to a standard at the National Institute of Standards and Technology (NIST).

Table 1. Ozone monitoring station information and ozone records used in this study

| Station name                  | Station location          | Ozone record               |
|-------------------------------|---------------------------|----------------------------|
| Tudor Hill, Bermuda           | 32.27° N, 64.87° W, 30 m  | 1988-10-01 to 2013-07-31, TEI 49C |
| Cape Verde, Republic of Cape  | 16.85° N, 24.87° W, 10 m  | 2006-10-01 to 2012-03-13, TEI 49C |
| Point, Barbados               | 13.17° N, 59.43° W, 45 m | 1989-04-01 to 2013-07-31, TEI 49C |
| Ushuaia, Argentina            | 54.83° S, 68.30° W, 18 m | 1994-11-25 to 2009-03-31, TEI 49 |

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The Ragged Point site (13.17° N, 59.43° W, 45 m) is located in Barbados, operated by the University of Miami, and the ozone monitoring is managed by GMD/ESRL/NOAA (Ragged Point, 2014). Continuous ozone measurements are available from January 1989 to December 1995, using a DASIBI ozone monitor, and from August 2006 to July 2013, using a TEI Model 49C. These instruments were calibrated to the NIST instrument.

The Cape Verde Observatory (16.85° N, 24.87° W, 10 m) is located in the Republic of Cape Verde and is operated by the Instituto Nacional de Meteorologia e Geofisica (Cape Verde, 2014). Ozone monitoring is provided by the University of York Wolfson Atmospheric Chemistry Laboratories, UK. Continuous ozone measurements are available from January 2006, to January 2012, using a TEI Model 49C. The instrument was calibrated to a standard traceable to NIST in 2007 and again in May 2010. Zero air was added into the ozone inlet once a month and external calibrations using a photometer standard were applied every 6 months.

The Ushuaia station (54.83° S, 68.30° W, 18 m) is located at the southern tip of Argentina and is operated and managed by the Gobierno de Tierra del Fuego - Servicio Meteorologico Nacional (Ushuaia, 2014). Continuous ozone measurements are available from November 1994 to January 2009 from two TEI Model 49 analyzers running in parallel using the same inlet. System and performance audits were performed in 1994, 1997, 1998, and 2003, in addition to daily zero checks. The metadata associated with this dataset define background conditions for a wind direction sector of 220° to 270° with wind velocity ≥ 5 m s⁻¹; however, wind measurements were not available in the database for the period of the 2008 experiment, and therefore the unfiltered ozone record was used.

2.2 Open ocean ozone data

A ship-based eddy covariance ozone flux system (Figure 1 in Bariteau et al., 2010) was deployed to investigate ambient ozone mole fractions and the magnitude and variability of ozone surface fluxes over the open ocean. The core of the eddy covariance ozone flux system is a fast response ozone instrument (FROI) based on the chemiluminescence reaction of ozone with nitric oxide (NO). Sample air was pulled at 10 L min⁻¹ through 30 m of 9.5 mm o.d. Teflon-PFA line from an inlet at 18 m height above the ocean surface on the jackstaff onboard the ship. From this sample line, two 6.4 mm o.d. Teflon-PFA tubes were connected; one ran to an UV absorption O₃ monitor, a Monitor Lab 8810 (Measurement Controls Corp. Englewood, CO, USA) and the other to the FROI. The mass flow-controlled sampling rate to the FROI was set at 1.5 L min⁻¹ and the NO flow rate was set at 3 ml min⁻¹ (99.995% NO). Sample air was dried using a Nafton drying membrane which has been shown to be permeable to water vapor but not to ozone (Boylan et al., 2014). FROI calibrations were carried out with the laboratory-calibrated Monitor Lab 8890 and showed a sensitivity of ~ 2800 counts s⁻¹ ppbv⁻¹. The system response time was 0.3 seconds. Data from the FROI were collected at 10 Hz and averaged to 10 min. The flux experiments were conducted on board the NOAA Research Vessel (R/V) Ronald H. Brown (Helmig et al., 2012). Data from two cruises, AMMA and Gas-Ex, were used in

Figure 1
Cruise tracks and location of island and coastal ozone monitoring stations considered in this study.

The AMMA cruise track is shown in red; the Gas-Ex in green.
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this study. The AMMA cruise departed Montevideo, Uruguay, on 27 April 2008 and arrived in Charleston, SC, USA on 18 May 2008. The Gas-Ex cruise steamed from Punta Arenas, Chile to Montevideo, Uruguay between 29 February and 11 April 2008. A cruise map is shown in Figure 1.

2.3 Measurement uncertainties

The measurement uncertainties in the two independent data sets need to be considered when evaluating differences between data from these independent measurements. The manufacturer of the TEI 49C reports an accuracy of 0.5 ppbv under laboratory conditions; however, the accuracy error in the field is expected to be somewhat larger. The error in the ozone measurement at Cape Verde is reported as 0.9 ppbv, and at Ragged Point as 2%, which, at ozone levels of 35 ppbv, equates to an error of 0.7 ppbv. The measurement error of the FROI is dependent on operating conditions and is ≤ 1.0 ppbv. The comparisons of absolute ozone levels need to consider the accuracy of the measurements at both points. Consequently, differences between the two data sets need to be on the order of ≥ 2 ppbv to be considered significant.

2.4 Back trajectories

Local wind direction is useful for obtaining a short term picture of the variation of air masses but is not accurate enough to determine synoptic scale transport (Fleming et al., 2012). Modelled back trajectories are estimations of the transport pathway of an air mass. The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model was utilized to compute air parcel back trajectories (Draxler and Hess, 1997, 1998; Draxler, 1999; Draxler and Rolph, 2013; Rolph, 2013). Back trajectories were used to estimate the centerline of an advected air mass that is subjected to vertical and horizontal dispersion. A back trajectory does not provide any information pertaining to ozone concentration or air parcel dispersion, i.e. width or depth, but can provide a path of an air mass backwards in time. Back trajectories were computed twice daily at ship locations along the cruise track and at the height of the inlet on the ship. The model output was set to the location of an air parcel for the previous 144 h before arriving at the location of the ship. The meteorology was based on Global Data Assimilation System (GDAS) 1° data, which provide global coverage, including remote areas of the Atlantic Ocean. The HYSPLIT model was used to compute trajectories along the AMMA and Gas-Ex cruise tracks.

3. Results and discussion

Open ocean ozone data from the ship were compared to measurements from the four nearby island and coastal surface ozone stations. Ozone measurements were taken on the AMMA cruise from 29 April through 18 May 2008. During this period, the ship sailed within ~ 1000 km of three island stations in the North Atlantic Ocean. One coastal station, Ushuaia, was located in the proximity of the Gas-Ex cruise and allowed for the comparison of ozone measurements in the Southern Hemisphere.

During the AMMA cruise, ozone was in the 10–30 ppbv range off the coast of South America, while higher values of 40–60 ppbv were measured when the ship sailed towards South Carolina. The lowest ozone mole fractions were measured in the Southern Atlantic during the Gas-Ex cruise, with levels consistently between 15–25 ppbv.

3.1 Tudor Hill

Tudor Hill is the closest of the four stations to the North American continent. Monthly ozone mole fraction averages from 1988 to 2010 are shown in Figure 2A. The monthly means range between 34 and 50 ppbv, with relatively large seasonal changes of ozone occurring during May, the time of the cruise. The comparison between ozone measured on the AMMA cruise and hourly Tudor Hill data is shown in the upper pane of Figure 3, with ozone measurements made aboard the ship color-coded to represent the distance between the ship and the station during the time of the measurements. Remarkably, ozone measured onboard the ship was ~ 30 ppbv lower from day 132 to 136 than at Tudor Hill. During this period, a clear diurnal cycle was observed in the ship data that was not observed at Tudor Hill. The shipborne ozone dramatically increased on day 136 when the ship was within 1200 km of the station. Between days 137 to 139 the ship was less than 1000 km distance from the station. During this period the ship ozone measurements were ~ 8 ppbv lower than ozone measured at the station; however, there was good agreement in the day to day variability of ozone measurements.

A map of the back trajectories every 12 h along the AMMA cruise track for days 135 to 139 is shown in Figure 3. The solid red line is the cruise track, the maroon stars are the island ozone monitoring stations, and the black, green, blue, and pink lines are the back trajectories. Markers along the back trajectories represent the location of the air parcel every 12 h from the start. The four colors are only used to visually differentiate between the back trajectories. The ~ 25 ppbv increase of ozone between days 136 and 137 was investigated further to identify the source of this ozone transport. Unfortunately, no other chemical tracers that would
be beneficial to identifying the history of the air mass were measured on the cruise. Figure 3 shows that there was a significant change in the air masses that were measured onboard the ship around day 136.5. Trajectories before that period showed air parcels transported directly from the open ocean in the North Atlantic. After this time, measured air parcels were transported near the North American continent before arriving at Tudor Hill and the ship. For further analysis, the back trajectories in Figure 3 were extended to 240 h (not shown). Trajectories between days 135 and 136.5 continued to originate in the North Atlantic; however, trajectories between 137 and 139 extended northward to the Labrador Sea and Baffin Bay. At Summit Station, Greenland, ozone during this period was approximately 10–20 ppbv higher than typical background ozone levels during this time of year (Helmig et al., 2007) with values between 54.1 and 60.9 ppbv during days 136 and 137 (Kramer et al., 2014). This analysis suggests that during this event high ozone observed in the Arctic springtime was transported and observed as far south as the Tudor Hill station.

Based on the back trajectories, there was a transport time between ~ 36 and 48 h between measurements made at Tudor Hill and aboard the ship. Shifting the cruise data backwards by 44 h (day 138 becomes 136) reveals that the pattern seen in the station observations closely resembles the ship data. The shifted ship data between days 135 and 136.5 (unshifted days 137 to 138.5) are ~ 2 ppbv lower than the station data. Based on the 44-h transport time, this difference corresponds to a ~ 1.0 ppbv day$^{-1}$ loss of ozone, which is within the uncertainty window of the data comparison.

### 3.2 Cape Verde

Monthly mean ozone mole fractions from Cape Verde shown in Figure 2B reveal that springtime is a transition period between ozone maxima in the winter and minima in the summer. Figure 4 shows the comparison of ozone measurements between Cape Verde and the AMMA cruise. Ozone values at Cape Verde were 20 ppbv lower than observations at Tudor Hill. A diurnal cycle similar to that seen at Tudor Hill is evident. The synoptic flow around Cape Verde was primarily determined by northeast trade winds. These winds may include dust, sand, and pollution outflow from Saharan Africa. Between days 129 and 135 air parcels came from the northeast while between 127 and 128.5 air originated from the South Atlantic Ocean. Between days 130.5 and 131.5, air was transported near Cape Verde before arriving at the ship location. The lag time of an air parcel from Cape Verde to the ship location on day 130.5 was between 48 and 60 h and on days 131 and 131.5 was 50 h. Shifting the ship ozone data in Figure 4 by 50 h (day 130 becomes day 128) results in a nearly perfect match in the absolute levels and variability of the station data between days 128 and 130.5.
**Figure 3**
Comparison of ozone data from Tudor Hill and the AMMA cruise with back trajectories.

Top plot: Hourly ozone data from the Tudor Hill station (black squares) are plotted with the 15-min shipborne ozone data (colored circles) from 11 May 2008 to 21 May 2008. The color-coding of the shipborne ozone measurements represents the distance between the ship and station. The purple ellipses correspond to the ship data (right) and the matching station data (left) shifted by 48 h, the approximate transport time between both measurement sites. Bottom plot: Back-trajectories every 12 h are shown along the cruise track near Tudor Hill. The solid red line is the AMMA cruise track. The 144-h back trajectories are the black, blue, pink, and green lines. The colors and symbols are used to differentiate various trajectories for ease of viewing. Symbols are placed on the trajectory lines every 12 h. Day of year is labeled next to each second trajectory.

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**Figure 4**
Comparison of ozone data from Cape Verde and the AMMA cruise with back trajectories.

Top plot: Hourly ozone data from the Cape Verde station (black squares) are plotted with the 15-min shipborne ozone data (colored circles) from 6 May 2008 to 16 May 2008. The color-coding of the shipborne ozone measurements represents the distance between the ship and station. The purple ellipses correspond to the ship data (right) and the matching station data (left) shifted by 48 h, the approximate transport time between both measurement sites. Bottom plot: Back-trajectories every 12 h are shown along the cruise track near Cape Verde. The solid red line is the AMMA cruise track. The 144-h back trajectories are the black, blue, pink, and green lines. The colors and symbols are used to differentiate various trajectories for ease of viewing. Symbols are placed on the trajectory lines every 12 h. Day of year is labeled next to each second trajectory.

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The data comparison shows a less than 1 ppbv difference, indicating little loss of ozone during the MBL during the 50 h of transport.

### 3.3 Ragged Point

Monthly ozone measurements from Ragged Point station, shown in Figure 2C, display a smaller annual variability than Tudor Hill. The hourly ozone data in Figure 5 show a diurnal cycle of 3–6 ppbv. Since Ragged Point was downwind of the cruise track, back trajectories were started from Ragged Point and show the synoptic air parcel transport from upwind where they crossed the ship track to Ragged Point, with red markers for day of year corresponding to the day that the ship was at each point. Tick marks are placed on the back trajectories every 24 h. The northeast trade winds carried air parcels over the location of the ship to Ragged Point.

Since the back trajectories originated from Ragged Point and not the ship, the transport time was determined by finding the back trajectory that crossed the ship track at the same time that the ship was at that position. This finding corresponded to the day 135 back trajectory crossing the ship path at ship day 133.6, which is confirmed with a back trajectory lag of 33 h, meaning that air measured aboard the ship on day 133.6 was measured at Ragged Point on day 135. After shifting the time series by 33 h, shown by the purple ellipses in Figure 5, the diurnal variability in the ozone measurements agree, although the ozone measured on the ship was ~ 2–3 ppbv higher than at Ragged Point. This analysis corresponds to an ozone loss rate of 1.0–1.5 ppbv day$^{-1}$, which is the highest seen in the ship-station comparisons that were available for this study. However, it should be noted that this ozone difference and derived loss rate are just slightly outside the uncertainty bounds for the determination.

### 3.4 Ushuaia

Ushuaia is the only station that allowed for a southern hemisphere data comparison. Monthly averages of ozone measured at Ushuaia between 1994 and 2009 are shown in Figure 2D. The noise in the hourly station data is most likely an indication of local influences from the nearby city of Ushuaia on these ozone measure-
ments, with the drops in ambient ozone probably caused by titration of ozone by nitric oxide in polluted air (Figure 6). As stated in the experimental section, these ozone observations could not be filtered due to the lack of wind data. Furthermore, there were no other chemical tracers, for instance carbon monoxide measurements, available during the comparison period for further evaluation; however, high values of carbon monoxide, indicative of local pollution issues, are evident for other periods that we investigated. The monthly variability in ozone ranges between 12 and 27 ppbv in the available data. This amplitude is primarily due to the seasonal change of ozone that occurs between March and April. The ozone annual cycle is reversed, as expected, due to the role of the solar cycle in determining the seasonal photochemical ozone sinks. Data from this station were compared against ozone data from the Gas-Ex cruise. Ozone measurements were made on the ship from 2 March to 6 April 2008 (Figure 6). The frequent drops in ambient ozone, as seen by the spikes in the Ushuaia station data, were not observed in the open ocean data. Despite the noise in the Ushuaia station data, the ozone measurements from the Gas-Ex cruise matched up reasonably well with the daily maxima of the station data. A seasonal increase in ozone, consistent with the monthly data, was also seen in the hourly observations from the ship. Interestingly, when the distance between the ship and station was at a minimum, the ozone measurements deviated the most.

Figure 6 shows 6-day back trajectories from the Gas-Ex cruise. Air masses generally came from the west and only briefly traveled over the southern tip of South America. This region is known for high winds and turbulent seas, which keeps the atmosphere well mixed and the day-to-day variations in ozone to a minimum. Even though there is not a consistent pattern in the back trajectories, the data comparison suggests that the ozone measured aboard the ship and at the station were subjected to similar synoptic scale ozone patterns. However, the high degree of scatter in the station data point out that the record from the station does not represent the background ozone mole fraction for the large-scale area during a significant fraction of time.

3.5 Diurnal ozone cycles
A daytime decline of ozone mole fractions and nighttime increase was evident in most of the open ocean observations. This behavior indicates that the ocean regions surveyed by the cruise were predominantly an
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this cruise. Of the four stations investigated, the ozone measurements at Tudor Hill had the highest annual behavior is an indication of the variable influence of continental and arctic outflow that was sampled during the cruise and previously reported amplitudes of < 2–3 ppbv at these stations (Oltmans and Levy, 1992, 1994). Diurnal cycles of < 1 to 4 ppbv have been observed at other coastal and open ocean locations in the Pacific (Ayers et al., 1992, 1997; Oltmans, 1981; Johnson et al., 1990; Monks et al., 1998; Monks et al., 2000) and Indian Oceans (Bremaud et al., 1998; de Laat and Lelieveld, 2000). Watanabe et al. (2005) reported similar values (2–4 ppbv) for the diurnal amplitude in the northern North Pacific Ocean during summer and winter; however, they observed diurnal changes of 7–8 ppbv in the springtime, comparable to what was observed aboard the AMMA cruise. Diurnal amplitudes in the Atlantic Ocean (3–4 ppbv, autumn) were slightly larger than those of the Pacific and Indian Oceans (Piotrowicz et al., 1989; Slemr and Tremmel, 1994).

The higher time resolution of the ship (i.e. 10 min) data, compared to the station (1 h) data retrieved from the archive, results in a finer resolved diurnal cycle for the ship observations. The hourly averaging dampens some of the maxima and minima, resulting in a slightly smaller diurnal amplitude. This difference in the data resolution possibly accounts for some of the dampened diurnal cycle in the station record, but this effect is too small to account for all of it. Consequently, the larger diurnal cycles that were seen in the ship measurements raise the question if hitherto undiscovered effects may dampen diurnal cycles at coastal sites in comparison to open ocean ozone measurements.

Earlier box model calculations estimated a < 1–2 ppbv diurnal change in ozone for the MBL (Ayers et al., 1992; Bremaud et al., 1998), underestimating the values found by previous researchers and the work presented here. Other research has reported rapid decrease in the ozone mole fraction immediately after sunrise (Nagao et al., 1999; Galbally et al., 2000; Watanabe et al., 2005). Due to low concentrations of HOx and limited UV radiation, this ozone decline in the early morning cannot solely be due to these mechanisms. Nagao et al. (1999) postulated that halogen species are responsible for the early morning ozone destruction. Subsequent numerical modeling has supported this hypothesis (von Glasow et al., 2004). Von Glasow et al. (2002) proposed that bromine gases are released from sea-salt particles that accumulate during the night and photolyze to form atomic bromine at sunrise, which results in early morning rapid ozone destruction, whereas during the day ozone loss primarily occurs due to UV photolysis and reactions with HOx. Read et al. (2008) compared the daytime loss of ozone at Cape Verde to three chemistry and box model results, with and without bromine and iodine halogen chemistry included. They found that a box model for the month of May (time of the AMMA cruise) without halogen chemistry estimated a ∼ 3.9 ppbv daily decrease in ozone, while the box model including halogens yielded an average daily ozone loss of ∼ 5.6 ppbv (values interpolated from Figure 2b in Read et al., 2008). These values compared to measured mean May 2007 values at Cape Verde of ∼ 4.9 ppbv (value interpolated from Figure 2b in Read et al., 2008). Saiz-Lopez et al. (2012) modified the Community Atmosphere Model (CAM) to include interactive chemistry (CAM-Chem) to further investigate the diurnal ozone loss at Cape Verde, and ran the model both with and without halogen chemistry included. The model predicted an annually averaged 2.6 ppbv diurnal MBL ozone loss without halogen chemistry, and a 3.2 ppbv loss with inclusion of halogen chemistry (values interpolated from Figure 5 in Saiz-Lopez et al., 2012). The latter value, including halogen chemistry, is in closer agreement with the measured annually averaged diurnal ozone loss (∼ 3.4 ppbv, derived from averaging the monthly values shown in Figure 2b in Read et al., 2008). The data presented in our manuscript provide another set of observations that supports the consideration of halogen chemistry in the diurnal cycles of ozone in the MBL. It is also noteworthy that the Read et al. (2008) May 2007 monthly mean value measured at Cape Verde and the box model including halogen chemistry are at the lower end of the range of daytime ozone loss seen in the shipborne diurnal ozone amplitudes (∼ 5–8 ppbv), while air was being sampled that originated from the Cape Verde Archipelago region (DOY 129–135), which raises the question if halogen chemistry may even be more pronounced over the open ocean compared to island and coastal environments.

3.6 Site comparison

The considered ozone measurements from the cruise and coastal and island locations both near and far from the American continent revealed large differences in the ozone mole fractions at this range of locations. MBL ozone mole fractions measured on board the AMMA cruise increased from ∼ 20 ppbv when the ship sailed around South America to over 50 ppbv as the ship approached the East Coast of the United States. This behavior is an indication of the variable influence of continental and arctic outflow that was sampled during this cruise. Of the four stations investigated, the ozone measurements at Tudor Hill had the highest annual
average and the largest seasonal variability. Even though Tudor Hill is located ~ 1000 km from the coast of the United States, ozone at this site appears to be largely affected by pollution outflow. Back trajectories indicated that during the study period, air masses measured at Tudor Hill originated over the east north American continent extending far into the Arctic.

Ozone measured at Cape Verde was more than 20 ppbv lower than ozone measured at Tudor Hill, indicating that elevated ozone transport had a smaller contribution at Cape Verde despite air masses originating off the western coast of Northern Africa, which can be a source region for elevated levels of trace gases and aerosols transported to the site (Lee et al., 2009; Read et al., 2009; Carpenter et al., 2010). Ozone measured at Ragged Point had the lowest average mole fractions of ~ 21 ppbv, similar to previously reported background levels in the Caribbean (Vingarzan, 2004). Back trajectories indicated transport from over the mid-Atlantic ocean, void of anthropogenic influence. Measurements at Ushuaia appear to be strongly influenced by the nearby city. Back trajectories from the Gas-Ex cruise showed an inconsistent behavior of surface layer transport from strong winds through the Drake Passage. Available measurements did not allow deciphering a correlation between large-scale air mass origin and ozone levels.

From the Lagrangian comparison between ozone measured at Tudor Hill and the ship, the observed 24-h ozone loss was ~ 1 ppbv day$^{-1}$. The distance between Cape Verde and the ship was further than for the other two northern hemisphere stations, and a 24-h averaged ozone loss of 0.5 ppbv day$^{-1}$ was calculated during the MBL transport. Ozone measurements between the ship and Ragged Point showed a 2–3 ppbv drop in ozone, corresponding to a loss rate of 1.5 ppbv day$^{-1}$. It should be noted that these estimates of the ozone loss rate during transport in the MBL between the two reference points are highly uncertain as the ozone change falls within the uncertainty of the calculated difference between the ship and station ozone measurements.

4. Conclusions

Three monitoring stations in the North Atlantic Ocean showed a seasonal ozone cycle that was stronger in the mid-latitudes and less pronounced in the tropics. Ozone mole fractions measured at Tudor Hill were the highest, approaching 60 ppbv. During the AMMA cruise, the research vessel sailed within 1000 km of three northern hemisphere stations. Back trajectories showed that air transport originating from the northeastern portion of the North American continent resulted in an increase of background ozone. The ozone mole fractions measured at island monitoring stations and aboard the R/V Brown provided the basis for an analysis of the transport of ozone over the open ocean. The large scale behavior of continental outflow is a major determining effect downwind over the ocean, even after several days of transport in the MBL. The source of ozone that passed over the Cape Verde and Ragged Point stations was from the north central Atlantic Ocean, following the regional trade winds. Agreement in ozone measurements between Ragged Point and the ship was often better than 3 ppbv, even when the ship was over 1000 km away, suggesting that both were measuring the clean background levels of ozone. Measurements of ozone mole fractions in the Southern Hemisphere were between 15 and 20 ppbv and the ship and Ushuaia daily ozone maxima agreed within 3 ppbv.

The amplitude of the diurnal cycle of ozone recorded aboard the ship was about twice as large as values observed at the stations and most reports in the literature. Similarly high diurnal amplitudes have previously only been observed in the open ocean of the North Pacific during springtime. The large diurnal cycles agree with predictions from chemistry models that include halogen chemistry and support the notion that halogen chemistry, in addition to HO$_x$ chemistry, photochemical destruction, and deposition, plays a role in the diurnal ozone loss over the open ocean.

The transport time of an air mass between the ship and station was determined using HYSPLIT. The minimum transport time between the AMMA cruise and Tudor Hill was 36–48 h and in that time the ship reported ozone mole fractions ~ 2 ppbv less than at the station. There was no difference in ozone mole fractions after accounting for the 50-h transport time between Cape Verde and the ship, and there was good agreement in the variability in the two ozone measurements. The transport time between the ship and Ragged Point was 33 h, with a difference in ozone of ~ 3 ppbv. Complex flows around Ushuaia prevented determination of transport times.

These data comparisons show that large-scale signatures in ozone variations are maintained during transport over scales of 100s to 1000–2000 km in the MBL over multiple days. This finding opens the door for using a Lagrangian approach for investigating the change in ozone from photochemistry and deposition along the air mass transport path. Differences seen in the data comparisons between the shipboard and island measurements were on the order of < 1 to 3 ppbv for 36–48 h of transport. The data quality objective for current ozone monitoring within the World Meteorological Organization Global Atmospheric Watch Program is 1.0 ppbv (2 sigma) (Galbally and Schultz, 2013), which can be achieved by most stations using ozone monitoring by UV absorption and following stringent data quality objectives, including flagging
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contaminated measurements. This accuracy is sufficient for site comparisons and deciphering diurnal cycles and long-term trends; however, determination of the change in ozone during transport in the MBL from these two point measurements would require higher measurement accuracy than what is currently defined by WMO and that is obtained by these routine surface ozone monitoring programs.

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Contributions
- Contributed to conception and design: PB, DH
- Contributed to acquisition of data: DH, SO
- Contributed to analysis and interpretation of data: PB, DH, SO
- Drafted and/or revised the article: PB, DH
- Approved the submitted version for publication: PB, DH, SO

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Competing interests
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Data accessibility statement
Ozone data from the AMMA and Gas-Ex cruises are available on the NOAA-ESRL-PSD Research Cruise website (ftp://ftp1.esrl.noaa.gov/psd3/cruises/). The station ozone data are available on the WMO World Data Centre for Greenhouse Gases, operated by the Japan Meteorological Agency, website (http://ds.data.jma.go.jp/gmd/wdcgg/).

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