Variability of ozone in the marine boundary layer of the equatorial Pacific Ocean

Xiao-Ming Hu¹, Jeffrey M. Sigler², and Jose D. Fuentes¹*

¹Department of Meteorology, Pennsylvania State University, University Park, Pennsylvania, USA

²Department of Environmental Sciences, Tulane University, New Orleans, Louisiana, USA

Manuscript submitted to the Journal of Atmospheric Chemistry

On December 29, 2010

Revised on May 20, 2011

*Corresponding author address: Jose D Fuentes, Department of Meteorology, The Pennsylvania State University, University Park, PA, USA 16802.

Email: jdfuentes@psu.edu
Abstract

This study examines the processes controlling the diurnal variability of ozone (O\textsubscript{3}) in the marine boundary layer of the Kwajalein Atoll, Republic of the Marshall Islands (latitude 8° 43’ N, longitude 167° 44’ E), during July to September 1999. At the study site, situated in the equatorial Pacific Ocean, O\textsubscript{3} mixing ratios remained low, with an overall average of 9-10 parts per billion on a volume basis (ppbv) and a standard deviation of 2.5 ppbv. In the absence of convective storms, daily O\textsubscript{3} mixing ratios decreased after sunrise and reached minimum during the afternoon in response to photochemical reactions. The peak-to-peak amplitude of O\textsubscript{3} diurnal variation was approximately 1-3 ppbv. During the daytime, O\textsubscript{3} photolysis, hydroperoxyl radicals, hydroxyl radicals, and bromine atoms contributed to the destruction of O\textsubscript{3}, which explained the observed minimum O\textsubscript{3} levels observed in the afternoon. The entrainment of O\textsubscript{3}-richer air from the free troposphere to the local marine boundary layer provided a recovery mechanism of surface O\textsubscript{3} mixing ratio with a transport rate of 0.04 to 0.2 ppbv per hour during nighttime. In the presence of convection, downward transport of O\textsubscript{3}-richer tropospheric air increased surface O\textsubscript{3} mixing ratios by 3-12 ppbv. The magnitude of O\textsubscript{3} increase due to moist convection was lower than that observed over the continent (as high as 20-30 ppbv). Differences were ascribed to the higher O\textsubscript{3} levels in the continental troposphere and weaker convection over the ocean. Present results suggest that moist convection plays a role in surface-level O\textsubscript{3} dynamics in the tropical marine boundary layer.

Keywords: Ozone, marine boundary layer, tropical meteorology, deep convection.
1. Introduction

Ozone ($O_3$) is an important constituent in the Earth’s troposphere due to its role as a greenhouse gas, secondary pollutant, and contribution to influencing atmospheric chemical cycles. In the moist atmospheric boundary layer $O_3$ is an important precursor of the hydroxyl radical (OH) which drives a plethora of atmospheric chemical cycles. Hydroxyl radicals are formed when $O_3$ undergoes photolysis to produce atomic oxygen in the electronically excited state ($O(1^D)$) that readily combines with water vapor to produce OH. While $O_3$ sinks and sources are relatively well established in the continental boundary layer (CBL), the processes that drive $O_3$ dynamics remain poorly understood in the remote marine boundary layer (MBL) (Galbally et al., 2000; Read et al., 2008; von Glasow, 2008). Compared to continental regions, the chemistry governing $O_3$ formation and destruction is different over the oceans. Therefore, in the MBL mechanisms of $O_3$ production and destruction must be understood and quantified so that the tropospheric $O_3$ budget can be constrained (Galbally et al., 2000; Horowitz et al., 2003; Yang et al., 2005; von Glasow, 2008). Due to logistical challenges, atmospheric measurements of reactive trace gases are rarely reported for the remote MBL. To improve estimates of the global $O_3$ budget, long-term studies over the open ocean are essential (Lelieveld et al., 2004; von Glasow, 2008).

Because of low concentrations of nitrogen oxides, photochemical destruction and reactions with halogens (especially bromine) represent the major $O_3$ sinks in the MBL (Johnson et al., 1990; Lee et al., 2009). Deep moist convection, associated with upward and downward transport of air masses, can also influence the spatio-temporal distribution of $O_3$ in the lower tropical atmosphere (Betts et al., 2001; Grant et al., 2008; Sahu and Lal, 2006; Hu et al., 2010b). Over the open oceans, previous studies (Solomon et al., 2005; Kley et al., 1996; Takashima et al., 2008) indicated that due to upward transport of low-$O_3$ air masses associated with convection, upper air layers can be at times devoid of $O_3$. To date, little information exists on the $O_3$ transport associated with downdrafts of mesoscale convective systems in the oceanic marine boundary layer. Thus, the present study investigates the meteorological conditions governing the diurnal patterns of $O_3$ in the open central Pacific Ocean. An additional goal of this study is to estimate the downward $O_3$ transport associated with moist convection and define the $O_3$ changes in the MBL as a function of the propagation velocity of convective storms. The
results reported herein provide insights to advance the current understanding of O$_3$ sinks and sources in the marine atmosphere.

2. Research methods

2.1 In-situ measurements

The field study took place during July to September 1999 at Kwajalein Atoll in the Republic of the Marshall Islands (Figure 1a) and was part of the NASA-funded KWAJEX (Kwajalein Experiment) ground validation campaign (Yuter et al., 2005). The KWAJEX campaign was designed to validate radar observations made by the Tropical Rainfall Measurement Mission (TRMM) satellite. A 12-m flux tower, located 3 m from the high tide line of Meck Island (latitude 8° 43’ N, longitude 167° 44’ E), served as a platform to deploy sensors and thus define the state of the lower atmosphere. Air temperature (at 1.5, 3.0, 5.0, 7.0, and 8.5 m above ground), water vapor mixing ratio (at 5.0, and 9.0 m above ground), wind speed (WSP) and direction (at 10.0 m above the ground), and atmosphere pressure (at 1.5 m above ground) were acquired every 2 seconds. Sensors were connected to and resulting information was stored on a data logger (model CR7, Campbell Scientific Inc., Logan, UT). Components of the surface energy balance were measured, including the incoming and outgoing solar and thermal energy fluxes (model CNR1, Kipp and Zonen, Delft, Netherlands). An eddy covariance system comprised of a sonic anemometer (model WindMaster Pro, Gill Instruments Ltd., Hampshire, England) and a water vapor/carbon dioxide infrared gas analyzer (model LI-6262, LiCor Inc., Lincoln, NB) made fast-response measurements at 9.5 m above the ground. A tethered sonde system consisting of balloon, hydraulic winch, instrumented sonde, and on-board data acquisition system was deployed. One complete ascending and descending profile was made every three hours at 03:00, 06:00, 09:00, 12:00, 15:00, 18:00, 21:00, and 2400 UTC (Universal Time Coordinate), weather permitting. Data were logged onboard and transferred to a computer after each sounding. With a constant rate of rise and descent of 1 m s$^{-1}$, a 30-m$^3$ tethered balloon was used to lift a single sonde to a maximum altitude of 1500 m. The sonde was equipped with sensors to measure horizontal wind speed and direction, atmospheric pressure, air temperature, and relative humidity every 2 seconds, corresponding to 2-m vertical resolution. Such information was necessary to estimate the vertical profiles of variables such as specific humidity,
wind speed, and virtual potential temperature.

Ozone mixing ratios were measured at 2 m above the surface. Air was drawn through Teflon tubing and into a TECO gas analyzer (model TECO 49C, Thermal Environmental Instruments, Franklin, MA). The air-sampling inlet had a filter holder with a filter membrane (1 micron in pore size) to keep the tubing free of dust and sea salt particles. The O₃ gas analyzer (the instrument has a quoted response time of 20 seconds) made measurements every second and 1-minute O₃ averages were generated and stored on a logger (model 21X, Campbell Scientific, Logan, UT). Before and after the field campaign, the O₃ gas analyzer was calibrated. Instrument span was verified once a week.

### 2.2 Zero-dimensional simulations

To investigate the destruction of O₃ due to gas phase reactions, simulations were conducted using a zero-dimensional version of the model of Regional Atmospheric Chemistry Mechanism (RACM) photochemical mechanism (Stockwell et al., 1997). The RACM mechanism was intended to be valid for remote to polluted conditions; however, the original mechanism did not include the bromide chemistry. To estimate the contribution of bromide chemistry to the destruction of O₃ during daytime in the MBL, the RACM model was extended to include the bromide chemistry. Simulations were also conducted using the extended RACM model to quantify the impact of bromide chemistry.

### 3. Results

During summer of 1999, the Kwajalein Island was located at or near the northern edge of the western Pacific Ocean inter-tropical convergence zone (ITCZ), which was centered between 5° and 10° N (Sobel et al., 2004; Yuter et al., 2005). In the Kwajalein region, weather conditions were dominated by westward-propagating synoptic scale disturbances, punctuated by mesoscale convective storms (Sobel et al., 2004). For example, on August 14, 1999 the geopotential height map at 800 hPa (Figure 1a) showed a westward-propagating synoptic system near Kwajalein. In the absence of regional convection, equivalent potential temperature (Θₑ) increased with height (Figure 1b), implying that the lower atmosphere over the ocean was mostly stable. Water vapor
was mostly confined in the lower atmosphere (Figure 1c). At higher altitude (>3 km), specific humidity was less than 6 g kg\(^{-1}\).

In the absence of moist convection, during the period of observations daily O\(_3\) mixing ratios exhibited diurnal variations amounting to 1-3 ppbv (around the mean). Ozone mixing ratios decreased after sunrise, reached minimum in the afternoon, and increased during nighttime (Figure 2). Mean O\(_3\) mixing ratio during nighttime and morning was approximately 10 ppbv. During the afternoon hours, the O\(_3\) mixing ratio decreased and reached minimum values of 9 ppbv by 16:00 and 19:00 hours (local time, LT) likely in response to photochemical sinks. Based on sonde and aircraft measurements in remote oceanic environments, other studies (Kley et al., 1996; Singh et al., 1996; Takashima et al., 2008) also reported similar O\(_3\) patterns in the lower atmosphere. The observed diurnal O\(_3\) patterns reflect the reduced contribution of precursors such as nitrogen oxides and volatile organic compounds.

During calm days without disturbance of convective weather systems, the O\(_3\) mixing ratios in the afternoon were lower by about 3 ppbv than those levels observed during nighttime or early morning. Figure 3 shows two examples for July 28 and August 15, 1999. Throughout the course of these days, the zonal wind speed exhibited little variability and stayed around 3-5 m s\(^{-1}\). Previous studies (e.g., Oltmans, 1981; Johnson et al., 1990; Thompson et al., 1993; Rhoads et al, 1997; Lal et al., 1998; Dickerson et al., 1999; Nagao et al., 1999b; Bhugwant and Bremaud, 2001; Bhugwant et al., 2001; Watanabe et al., 2005) also documented similar diurnal variations of O\(_3\) mixing ratio in the MBL. As shown below, chemical reactions and turbulent transport explained the diurnal patterns of O\(_3\) levels.

Diurnal variations of surface O\(_3\) mixing ratios over the Pacific Ocean are different from those ordinarily observed in the CBL where sufficient precursors prevail to form O\(_3\) via photochemical processes. The O\(_3\) minimum in the afternoon over the ocean can be related to chemical sinks that are different from those associated with continental photochemical processes (Johnson et al., 1990; Ayers et al., 1992; Dickerson et al., 1999). The conventional chemistry for tropospheric O\(_3\) destruction can be summarized via reactions R1 to R5:

\[
\begin{align*}
O_3 + hv & \rightarrow O_2 + O(^1D) \\
O(^1D) + H_2O & \rightarrow OH + OH \\
OH + O_3 & \rightarrow O_2 + HO_2
\end{align*}
\]

R1  
R2  
R3
Over the ocean, the mixing ratio of nitrogen oxides is low (Torres and Thompson, 1993). Under such conditions, the OH radical cannot recycle O₃ and thus photochemical reactions destroy O₃ in the MBL (Liu et al., 1983; Thompson and Lenschow, 1984; Thompson et al., 1993; Singh et al., 1996; Stickler et al., 2007). A zero-dimensional model, based on the RACM photochemical mechanism (Stockwell et al., 1997), was applied to estimate O₃ depletion rate due to photolysis of O₃ and reactions with OH and HO₂. The zero-dimensional RACM model was applied to a clear day in Kwajelein. The initial mixing ratio values for O₃, NO, NO₂ were set as 10 ppbv, 5 pptv, 10 pptv. The model was integrated from 5:00 LT to 19:00 LT. In addition to a control simulation, two other sensitivity simulations were conducted to estimate the contribution to the destruction of O₃ from the photolysis reaction and reactions with OH and HO₂. The configuration of the simulations is summarized in Table 1. These simulations implied photolysis of O₃ (O₃+hv=O(¹D)+O₂) and its reactions with OH and HO₂ decreased O₃ mixing ratios by 1 ppbv (i.e, 10.4-9.4 ppbv) during the daytime. The reactions with OH and HO₂ accounted for 0.3 ppbv (i.e., 9.7-9.4 ppbv).

Hydrogen oxides (HOₓ = OH + HO₂) alone could not account for the observed amplitude of O₃ diurnal variation over the ocean (de Laat et al., 1999; Dickerson et al., 1999; Nagao et al., 1999a; Galbally et al., 2000; von Glasow et al., 2002). Sea-salt particles can release reactive bromine (Br) through heterogeneous reactions (Sander et al., 2003; Hunt et al., 2004; Simpson et al., 2007) and then lead to surface O₃ destruction during daytime (Fan and Jacob, 1992; Vogt et al., 1996; Jacob, 2000; Hara et al., 2010). Bromine can provide an additional photochemical O₃ sink through reactions R6 to R9 (Dickerson et al., 1999; Jacob, 2000; Foster et al., 2001; Hara et al., 2010):

\[
\begin{align*}
\text{Br}_2 + \text{hv} & \rightarrow 2\text{Br} & \text{R6} \\
\text{Br} + \text{O}_3 & \rightarrow \text{BrO} + \text{O}_2 & \text{R7} \\
\text{BrO} + \text{HO}_2 & \rightarrow \text{HOBr} + \text{O}_2 & \text{R8} \\
\text{HOBr} + \text{hv} & \rightarrow \text{OH} + \text{Br} & \text{R9}
\end{align*}
\]

Previous studies (von Glasow et al., 2002; Read et al., 2008) indicated that bromine reactions accounted for 30-47 % of the total chemical O₃ destruction in the MBL. Thus, the O₃
minimum in the afternoon is likely due to the chemical reactions involving both HOx and bromine. Nagao et al. (1999a) studied a three-year O3 record obtained at an island in the subtropical northwestern Pacific Ocean and found that HOx and bromine played different roles in destroying O3 during different times of day. The HOx-O3 destruction mechanism mainly results from ultraviolet photolysis of O3 and subsequent catalytic reaction with HOx (R2 and R3). Therefore, the HOx-O3 destruction mechanism plays a dominant role around midday while reactive bromine-containing gases accumulate in the MBL during nighttime (Hunt et al., 2004). Shortly after sunrise, bromine compounds can be rapidly photolyzed to produce bromine atoms (von Glasow, 2008). Bromine chemistry plays a dominant role in destroying O3 in the morning (Nagao et al., 1999a; Galbally et al., 2000; Saiz-Lopez et al., 2004). In order to demonstrate the O3 temporal tendency, mean diurnal variations of the time derivative of O3 mixing ratio (δ[O3]/δt) are plotted in Figure 4, in which negative values of δ[O3]/δt indicate O3 destruction. During 06:00 to 18:00 LT O3 was destroyed, except 10:00 LT. Nagao et al. (1999a) reported a similar pattern of δ[O3]/δt for the subtropical northwestern Pacific Ocean during August. In the present study, the O3 destruction during the early morning and the rest of the daytime can be ascribed to bromine and HOx reactions.

To investigate the role of bromide chemistry in the daytime O3 depletion in Kwajalein, an extended zero-dimensional RACM model was developed to include the bromide chemistry (see Table 2). Same as the simulations summarized in Table 1, the extended RACM model was integrated from 5:00 LT to 19:00 LT. The initial Br2 mixing ratio was set as 10 pptv based on results reported by Hunt et al. (2004). Shortly after the sunrise around 6:00 LT, photolysis (R6) converted all Br2 to bromide atom and O3 was depleted through R7. Because R6 and R7 occurred so quickly after sunrise, BrO showed a peak right after sunrise (Figure 5). Ozone was depleted to 8.9 ppbv at 19:00 LT. The zero-dimensional model results were consistent with those reported in Saiz-Lopez et al. (2006) in terms of the diurnal pattern of O3, BrO and Br2. Compared with the control simulation (Table 1), the exclusion of bromide chemistry caused an underestimation of O3 loss by 0.5 ppbv (45%). Such estimation was close to that estimated in Read et al. (2008). The simulated O3 destruction rate during the daytime with and without bromide chemistry is compared in Figure 6. When the bromide chemistry was excluded, the change of O3 destruction rate followed the change of photolysis rate (also change of OH mixing
ratio) and reached peak value during the middle of the day. When the bromide chemistry was included, the O₃ destruction rate almost doubled during the daytime and it showed a spike in the early morning. The simulated spike of O₃ destruction rate in the early morning is consistent with the observations shown in Figure 4. The time of the spike of O₃ destruction rate matches that of the spike of the BrO values shown in Figure 5. Thus, the zero-dimensional model simulation confirmed that the spike of O₃ destruction in the early morning occurred because the accumulated Br₂ during nighttime in the MBL was photolyzed rapidly after sunrise and the following bromide catalytic reactions destroyed O₃.

Chemical reactions alone cannot explain the observed O₃ temporal patterns. Ozone mixing ratios increased during the nighttime in response to the lack of photolytic reactions (Figures 2 and 3). Transport of O₃-richer air from the free troposphere to the surface likely explained the O₃ increases observed during the nighttime (Ayers et al., 1997; Bremaud et al., 1998; Monks et al., 2000; Chand et al., 2003; Sigler et al., 2002). Skewness of specific humidity, \( q', (S_q = \frac{\overline{q'^3}}{\overline{q''^2}})^{1/2} \), \( q' \) represents the specific humidity perturbation from the mean) can be used as a proxy to investigate the O₃ vertical transport process (Deardorff, 1974; Lambert et al., 1999). Tethered balloon measurements of q profiles and associated S_q values were estimated for the month of August 1999 to determine the influence of vertical transport on the O₃ temporal variability (in the absence of storms, the height of the mixed layer (z_i) ranged from 400 to 450 m and average q values in the mixed layer reach 20 g kg⁻¹, Figure 7). Positive S_q values were estimated for the lower part of the MBL (below 280 m) whereas negative S_q values were observed in the upper part of the MBL. Negative S_q values in the upper part of the MBL indicated that the dry air entrained from the free troposphere became stretched into narrow downward streamers. This finding indicated that vertical transport contributed to the replenishment of O₃ in the upper MBL as reported in previous studies (Lambert et al., 1999). The low S_q values below 280 m indicated that more symmetric turbulence was likely responsible for vertical mixing in the lower part of the MBL.

Entrainment of free tropospheric air into the mixed layer and surface deposition can contribute to O₃ temporal patterns. Under steady state and homogeneous (non-advective) conditions, the amount of O₃ entrained into the MBL can be estimated from (1)
\[
\frac{[O_3]_{\text{Ent}}}{z_i} = \frac{w_e([O_3]_{\text{FT}} - [O_3]_{\text{BL}})}{z_i}
\]  

(1)

where \([O_3]_{\text{Ent}}\) is the average change rate of the O\(_3\) mixing ratio in the MBL due to the entrainment, \(w_e\) is the entrainment velocity, \([O_3]_{\text{FT}}\) is the O\(_3\) mixing ratio in the free troposphere, \([O_3]_{\text{BL}}\) is the O\(_3\) mixing ratio in the MBL and \(z_i\) is the mixed layer height (Monks et al., 2000). Since no O\(_3\) profile data were available for MBL over Kawjalein, the \([O_3]_{\text{BL}}\) and \([O_3]_{\text{FT}}\) values needed to apply equation (1) were obtained from ozonesondes obtained in the American Samoa (14.23° S, 170.56° W) during April and May of 1999. The \([O_3]_{\text{FT}}\) was normally larger than \([O_3]_{\text{BL}}\) (Thompson et al., 2003). The average \([O_3]_{\text{FT}}-\text{[O}_3]\text{BL}\) over the equatorial Pacific Ocean in summer was about 2 ppbv. The value of \(w_e\) over the ocean was reported to be 4-14 mm s\(^{-1}\) (Boers et al., 1998; Bremaud and Taupin, 1998; Bremaud et al., 1998; Stevens et al., 2003).

Using the tethered balloon data (Figure 7), the average \(z_i\) ranged from 500 to 800 m. Therefore, the estimated \([O_3]_{\text{Ent}}\) varied from 0.04 to 0.2 ppbv hr\(^{-1}\). With this increasing rate, due to the entrainment process, the nighttime surface O\(_3\) mixing ratio increased after sunset to the O\(_3\) levels observed at sunrise (Figures 2 and 3). Thus, the photochemical reactions and the recovery mechanism during nighttime contributed to the diurnal variation of surface O\(_3\) mixing ratio shown in Figure 2. In addition to the enhanced O\(_3\) destructive reactions in the afternoon, dry deposition was another process contributing to reductions in surface O\(_3\) mixing ratios (Singh et al., 1996; Fairall et al., 2007). Dry deposition was estimated to account for 13% of total O\(_3\) loss in summer in the remote MBL when bromine chemistry was neglected (Monks et al., 2000; Ganzeveld et al., 2009).

Thermodynamic conditions of the MBL exerted control on the O\(_3\) temporal variability. For example, Figures 8 and 9 illustrate examples of O\(_3\) levels on August 13 and 19, 1999 exhibiting little diurnal variation (and associated meteorological conditions: equivalent potential temperature, wind vector, solar irradiance, and specific humidity). During the daytime, O\(_3\) mixing ratios slowly decreased with time. However, after sunset O\(_3\) levels did not increase to reach the mixing ratios observed around sunrise. This may be because the downward O\(_3\) transport due to entrainment was not as strong as that on days such as July 28 and August 15, 1999. The thermodynamic attributes of the MBL on August 13, 15 and 19, 1999 were investigated from the tethersonde data (data were not available on July 28, 1999) (Figure 10).
The 1.5-theta-increase method (Nielsen-Gammon et al. 2008; Hu et al., 2010a) was used to diagnose mixed layer height from the potential temperature profile. The 1.5-theta-increase method defined the mixed layer height as the level at which the potential temperature first exceeded the minimum potential temperature within the boundary layer by 1.5 K. Inferred from the tethersonde data, the mixed layer height was greater at 22:00 LT on August 13 (713 m) and August 19 (773 m) than that on August 15 (698 m). In addition, specific humidity and wind speed across the MBL top exhibited little gradients on August 13 and August 19, 1999 (Figure 10). These MBL dynamic conditions (Figure 10) likely became ineffective in downwardly transporting O$_3$-richer air to the surface. Also, for both days (Figure 8 and 9) the friction velocity (u*) was low (< 0.2 m s$^{-1}$) in response to weaker mechanical turbulence. Weaker turbulence and reduced vertical mixing combined with higher MBL height implied less increase of surface O$_3$ due to entrainment.

Mesoscale convective storms modulated the diurnal O$_3$ patterns. For example, between 21:00 and 22:00 LT on August 13, 1999, O$_3$ mixing ratios suddenly increased (2-3 ppbv) in response of a storm that caused rapid decreases in $\Theta_E$ and increases in wind speed (Figure 8). Two additional cases (Figures 11 and 12) showed greater increases of O$_3$ (amounting to 6-12 ppb on July 25 and August 10, 1999). On July 25, 1999 the O$_3$ increase occurred during the nighttime (around 19:00 LT) while that on August 10 happened during the daytime (around 11:00 LT). The O$_3$ increases near the surface occurred in response to the downward transport associated with convection that brought air from the upper air layers down to the surface with lower $\Theta_E$ and specific humidity. The surface $\Theta_E$ decreased in response to the evaporative cooling associated with rainfall. At times the reduction in surface $\Theta_E$ exceeded 4 K which agreed with previously reported findings in tropical maritime environments (Schumacher et al., 2007). For the case of July 25, 1999 there was a rapid increase of wind speed during convection while the change of wind speed for the case of August 10, 1999 was not substantial. Rainfall was associated with the case of July 25, 1999 while no rainfall occurred during the convective case of August 10, 1999 (data not shown). Previous studies (Betts et al., 2001; Grant et al., 2008; Hu et al., 2010b) reported that downdrafts associated with moist convection over continental regions increased the ground-level O$_3$ by 10-30 ppb and lasted for a few hours (> 2 hours). In contrast, over the ocean the elevated O$_3$ levels after convection decreased to the level before convection in a short time.
period (less than 1 hour) (Figures 11 and 12). These differences likely resulted due to the
different O₃ distribution patterns in the free troposphere (Thompson et al., 1984), different
strength of convective storms (Zipser and Lutz, 1994), and different air chemistry (Kley et al.,
1996). Over the equatorial Pacific Ocean marine boundary layer, the O₃ mixing ratio in the free
troposphere is relatively low (e.g., < 20 ppbv, Kley et al., 1996). Thus, the free tropospheric air
masses over the ocean brought down to the surface by convection contained low-O₃ air.
Convective systems over tropical oceans have weaker vertical velocities than those observed
over continents (Del Genio et al., 2007; Zipser and Lutz, 1994). A summary of the influences of
convection and storm propagating velocities on the transport of O₃ and changes in Θₑ is provided
in Table 3.

During the field campaign, as documented by Sobel et al. (2004) and Yuter et al. (2005),
one of the largest rainfall events occurred on August 12, 1999. Radar reflectivity values showed
that the study region became cloudy during most of August 12, 1999. The incoming solar
radiation reaching the surface was less than 100 W m⁻² (Figure 13). Under such conditions, the
photolytic reactions and subsequent HOₓ and bromine reactions were suppressed. This was the
likely reason why the O₃ decreases during the daytime (Figures 2 and 3) did not occur on August
12, 1999. During August 12, 1999 the mixed layer height decreased in response to the
disturbance caused by the storm. Diagnosed from the profiles of virtual potential temperature
(Figure 14), the mixed layer height changed from about 800 m at 01:00 LT on August 12 to
about 300 m at 04:00 LT on August 13, 1999. The presence of clouds enhanced turbulence in
the MBL relative to clear conditions (Betts and Boers, 1990), which entrained more O₃-richer air
into the MBL and augmented the air mass transport to the lower MBL. Elevated friction velocity
(>0.4 m s⁻¹) on August 12, 1999 (data not shown) implied greater turbulent transport. Surface
specific humidity decreased between 15:00 LT to 21:00 LT (Figure 13) in response to the
downward transport of free tropospheric air, which contained less water vapor. Enhanced
turbulence and reduced depth of the MBL likely enhanced downward O₃ transport to the surface
from the free troposphere; thus, the surface O₃ mixing ratio increased during the daytime of
August 12, 1999.

The relationship between mixed layer height and surface O₃ mixing ratio was further
investigated. The mixed layer varied between 250 and 850 m. Estimated mixed layer heights
and measured O$_3$ mixing ratios exhibited a linear relationship (Figure 15), with a correlation coefficient of -0.43. The relatively low correlation coefficient (-0.43) implied that the boundary layer height was only one of the factors that affected surface O$_3$ mixing ratios. Higher O$_3$ mixing ratios were associated with shallower mixed layers. Conversely, lower O$_3$ mixing ratios occurred when the mixed layer became deep.

4. Summary and Conclusions

Over the equatorial Pacific Ocean O$_3$ mixing ratios exhibited minimal diurnal variation, with an average of 9-10±2.5 ppbv. Following sunrise, O$_3$ mixing ratios decreased, reached minimum in the afternoon, and increased in the evening. Peak-to-peak amplitudes of O$_3$ diurnal variation ranged from 1 to 3 ppbv. Diurnal variations of O$_3$ in the marine mixed layer were ascribed to a combination of chemistry, entrainment of free-tropospheric air into the mixed layer, and downward transport associated with moist convection.

The present results provide evidence that reactions of O$_3$ with bromine and HO$_x$ exerted control on the diurnal variation of O$_3$ in the marine boundary layer, leading to an O$_3$ minimum in the afternoon. Under undisturbed conditions (i.e., no rain events), the mixed layer reached heights ranging from 500 to 800 m and remained largely invariant with time. Additionally, the top of the mixed layer exhibited a well-defined temperature discontinuity, which defined the “capping” temperature inversion and separated MBL air from free tropospheric air. Due to entrainment of air from the free troposphere to the mixed layer, O$_3$ was transported down to the surface. This transport process increased O$_3$ by as much as 0.04 to 0.2 ppbv per hour, thereby influencing the observed diurnal O$_3$ patterns. During the nighttime, due to reduced chemical sinks, the transport of O$_3$-richer air from the free troposphere to the surface became more evident and partly explained the increases in surface O$_3$.

In the presence of convection, downward transport of O$_3$-richer free tropospheric air increased surface O$_3$ mixing ratio, while surface equivalent potential temperature and specific humidity concurrently decreased in response to evaporative cooling and transport of dry air from the free troposphere. Compared to continental regions, where the increased O$_3$ due to convection could be maintained for several hours following the storms, over the ocean the elevated O$_3$ mixing ratios after convection was relatively short lived, lasting less than 1 hour. The magnitude
of the sudden increase of surface O₃ due to convection over the ocean was smaller (3-12 ppbv) than that observed over the continent regions (as high as 20-30 ppbv). The differences can be ascribed to the distribution of O₃ in the lower troposphere. Over the ocean, the free troposphere has lower O₃ mixing ratios (< 20 ppbv) than those observed over the continent (> 40 ppbv). Moreover, convection is stronger and deeper over continent regions than over oceans.

The current findings indicate that both entrainment of relatively O₃-richer air from the free troposphere as well as storm-related convective activity play dominant roles in surface-level O₃ dynamics over tropical oceans, just as they do over continental surfaces. The observations reported in this study were conducted in the remote ocean, which is devoid of continental pollution. Results apply to the open ocean, a major sink region for tropospheric O₃. Thus, the O₃ levels and source/sink mechanisms reported in this study may be necessary to develop a more complete understanding of the global O₃ budget and therefore the role played by O₃ in atmospheric chemistry and climate.

**Acknowledgements**

NASA provided funding for the field research related to the KWJEX project (grants NAG5-9768). Authors are grateful to Michael Garstang, John Deary, Ryan Heitz, and Oliver W. Frauenfeld for their collaboration with the field research. Discussions with Tianle Yuan were helpful.
References


Table 1. Configurations for the simulations with the zero-dimensional model.

<table>
<thead>
<tr>
<th>Simulations</th>
<th>Configuration</th>
<th>O$_3$ mixing ratios at 19:00 LT, ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control simulation</td>
<td>Default reactions included in RACM</td>
<td>9.4</td>
</tr>
<tr>
<td>Sensitivity simulation 1</td>
<td>Turn off O$_3$+hv → O($^1$D)+O$_2$</td>
<td>10.4</td>
</tr>
<tr>
<td>Sensitivity simulation 2</td>
<td>Turn off O$_3$+HO → HO$_2$+O$_2$ and O$_3$+HO$_2$ → HO+2.0O$_2$</td>
<td>9.7</td>
</tr>
</tbody>
</table>

Table 2. Kinetic data related to bromine used in the extended zero-dimensional model.

<table>
<thead>
<tr>
<th>Photolysis reaction</th>
<th>Photolysis frequency, s$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOBr+hv =Br+HO</td>
<td>7.9×10$^{-4}$</td>
<td>Michalowski et al. (2000)</td>
</tr>
<tr>
<td>Br$_2$+hv → 2 Br</td>
<td>3.02×10$^{-2}$</td>
<td>Jacobson (2005)</td>
</tr>
<tr>
<td>BrO+hv → Br+O$_3$P</td>
<td>3.82×10$^{-3}$</td>
<td>Jacobson (2005)</td>
</tr>
<tr>
<td>Bimolecular reaction</td>
<td>Reaction rate constant, cm molecule$^{-1}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Br+O$_3$ → BrO+O$_2$</td>
<td>1.7×10$^{-11}$ e$^{(-800/1)}$</td>
<td>Jacobson (2005)</td>
</tr>
<tr>
<td>BrO+O$_3$ → Br+O$_2$</td>
<td>1.0×10$^{-12}$ e$^{(-5200/1)}$</td>
<td>Jacobson (2005)</td>
</tr>
<tr>
<td>BrO+HO$_2$ → HOBr+O$_2$</td>
<td>3.4×10$^{-12}$ e$^{(-5400/1)}$</td>
<td>Jacobson (2005)</td>
</tr>
<tr>
<td>Br+HO$_2$ → HBr+O$_2$</td>
<td>1.5×10$^{-11}$ e$^{(-6000/1)}$</td>
<td>Jacobson (2005)</td>
</tr>
<tr>
<td>HBr+HO → Br+H$_2$O</td>
<td>1.1×10$^{-11}$</td>
<td></td>
</tr>
<tr>
<td>BrO+NO → Br+NO$_2$</td>
<td>8.8×10$^{-12}$ e$^{(-2600/1)}$</td>
<td>Read et al. (2008)</td>
</tr>
<tr>
<td>BrO+BrO → 2 Br+O$_2$</td>
<td>2.4×10$^{-12}$ e$^{(-400/1)}$</td>
<td>Jacobson (2005)</td>
</tr>
<tr>
<td>BrO+BrO → Br$_2$+O$_2$</td>
<td>2.8×10$^{-14}$ e$^{(-8600/1)}$</td>
<td>Jacobson (2005)</td>
</tr>
<tr>
<td>Br+HCHO → HBr+CO+HO$_2$</td>
<td>1.7×10$^{-11}$ e$^{(-8000/1)}$</td>
<td>Jacobson (2005)</td>
</tr>
</tbody>
</table>

Table 3. Maximum wind speed (WSP), magnitude of O$_3$ change (Δ[O$_3$]), magnitude of θ$_E$ change (Δ[θ$_E$]), duration (τ) of O$_3$ enhancement, and occurrence of precipitation associated with four representative convective storms observed in Kwajalein on July 25, August 10, 12, 13, 1999

<table>
<thead>
<tr>
<th>Cases</th>
<th>Maximum WSP, m s$^{-1}$</th>
<th>Δ[O$_3$], ppbv</th>
<th>Δ[θ$_E$], °C</th>
<th>τ, minutes</th>
<th>Precipitation occurred?</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 25</td>
<td>17.3</td>
<td>12</td>
<td>3.0</td>
<td>45</td>
<td>Yes</td>
</tr>
<tr>
<td>August 10</td>
<td>12.2</td>
<td>6</td>
<td>1.2</td>
<td>45</td>
<td>No</td>
</tr>
<tr>
<td>August 12</td>
<td>15.3</td>
<td>3</td>
<td>3.9</td>
<td>30</td>
<td>Yes</td>
</tr>
<tr>
<td>August 13</td>
<td>13.4</td>
<td>3</td>
<td>1.6</td>
<td>50</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Figure 1. (a) Map of geopotential heights and wind vectors at 800 hPa over Kwajalein, (b) equivalent potential temperature ($\Theta_E$), and (c) specific humidity for the south-north cross section through Kwajalein on August 14, 1999 obtained from the National Centers for Environmental Prediction (NCEP) global forecast system (GFS) final (FNL) operational global analysis data. Reference wind vector of 8 m s$^{-1}$ is provided in the up-right corner of Figure 1a.

Figure 2. Mean diurnal variation of O$_3$ mixing ratio and standard deviation at Kwajalein during July, August and September 1999.

Figure 3. Ozone mixing ratio, equivalent potential temperature ($\Theta_E$), wind vector, incoming solar radiation, and specific humidity (SH) at Kwajalein on (left to right) July 28 and August 15, 1999.

Figure 4. Average diurnal variation of ozone change rate ($\delta$[O$_3$]/$\delta$t) and standard deviation at Kwajalein during the summer of 1999.

Figure 5. Simulated time series of ozone (O$_3$), bromine atoms (Br), hydroxyl radical (OH), and bromine monoxide (BrO) mixing ratios during the daytime using the extended zero-dimensional model.

Figure 6. Simulated destruction rate of ozone (O$_3$) during the daytime in the MBL using the zero-dimensional model (without bromide chemistry) and the extended zero-dimensional model (with bromide chemistry).

Figure 7. Profiles of (a) mean specific humidity during August 1999 in Kwajalein, (b) skewness of specific humidity, (c) mean virtual potential temperature, and (d) mean wind speed. One standard deviations of specific humidity, virtual potential temperature and wind speed are shown with the dashed lines in (a), (c) and (d).

Figure 8. Ozone mixing ratio, equivalent potential temperature ($\Theta_E$), wind vector, incoming solar radiation, and specific humidity (SH) at Kwajalein for the case of ozone decreasing with time (during August 13, 1999).

Figure 9. Ozone mixing ratio, equivalent potential temperature ($\Theta_E$), wind vector, incoming solar radiation, and specific humidity (SH) at Kwajalein for the case of ozone decreasing with time (during August 19, 1999).

Figure 10. Profiles of (left) virtual potential temperature, (middle) specific humidity, and (right) wind speed (WSP) during nighttime on August 13, 15, and 19, 1999 in Kwajalein.

Figure 11. Ozone mixing ratio, equivalent potential temperature ($\Theta_E$), wind vector, incoming solar radiation, and specific humidity (SH) at Kwajalein for storm case on July 25, 1999.
Figure 12. Ozone mixing ratio, equivalent potential temperature (Θ_E), wind vector, incoming solar radiation, and specific humidity (SH) at Kwajalein for storm case on August 10, 1999.

Figure 13. Ozone mixing ratio, equivalent potential temperature (Θ_E), wind vector, incoming solar radiation, and specific humidity (SH) at Kwajalein for the case with increasing O_3 on August 12, 1999.

Figure 14. Profiles of (left) virtual potential temperature and (right) specific humidity on August 12 and 13, 1999 in Kwajalein.

Figure 15. Correlation between observed MBL height and O_3 during the summer of 1999. The correlation coefficient is -0.43. The blue line represents the linear regression of all data points.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8
Figure 9
Figure 10
Figure 11
Figure 12
Figure 13
Figure 14
Figure 15