J7.9 COMPARISON OF AEROSE-I AND AEROSE-II SURFACE LEVEL OZONE MEASUREMENTS AND OZONESONDE PROFILES WITHIN SAHARAN DUST AND BIOMASS BURNING PLUMES

Michelle D. Hawkins[*], Vernon R. Morris[*,**], Nicholas R. Nalli[***], Everette Joseph[*,****]

*Howard University Program in Atmospheric Sciences, Washington, DC, **Department of Chemistry, Howard University, Washington, DC, ***QSS Group, Inc., NOAA/NESDIS, Camp Springs, MD, ****Department of Physics and Astronomy, Howard University, Washington, DC

1. Introduction

As an important oxidant and the primary precursor of tropospheric OH, ozone is instrumental in regulating the atmosphere's oxidizing capacity and can influence background levels of trace chemical species. Several studies have shown that dust particles from the Sahara can impact atmospheric processes during the course of their transport by providing reactive sites for heterogeneous chemical reactions [Jacob, 2000; de Reus et al., 2000; Grassain 2002; Martin et al., 2003; Michel et al., 2003; Bauer et al., 2004; Tie et al, 2005]. These reactions can deplete gas-phase species by condensation or deposition on aerosol particles.

In addition to mineral dust, aerosol plumes off the coast of Africa may include anthropogenic aerosols and smoke from biomass burning. Biomass burning also produces chemically active atmospheric gases that serve as precursors for ozone production, including carbon monoxide, nonmethane hydrocarbons, and nitric oxide. Modeling studies suggest that biomass burning contributes 15-30% to the total tropospheric CO background concentration and more than 50% in the boundary layer near source regions [Galanter et. al., 2000]. Measurements of carbon monoxide can therefore be used as a tracer for biomass burning and an identifier of air parcels containing anthropogenic aerosols.

In-situ surface level measurements over the tropical Atlantic are sparse but still essential for understanding the regional marine boundary layer because they allow for more accurate determination of lower tropospheric ozone concentrations than current satellite observations. There have been few previous field campaigns that have collected simultaneous measurements of ozone in the Atlantic Ocean during Saharan dust events [de Reus et al., 2000; Bates et al., 2001]. During the ACE-2 campaign, vertical profiles of ozone mixing ratios measured by aircraft revealed ozone concentrations of 30ppb in the dust layer and significantly higher ozone concentrations above and below the dust layer [de Reus et al., 2000]. Several other field studies have observed a decrease in ozone concentrations in the presence of dust aerosols [Stehr et al., 1999; Bates et al., 2001, Bonasoni et al., 2004, de Reus et al., 2005]. For example, Bonasoni et al. found ozone concentrations to be 4-21% lower than monthly mean background concentrations during Saharan dust storms [Bonasoni, et al., 2004].

This study investigates the effect of the Saharan Air Layer (SAL) outflow on ozone concentrations over the tropical Atlantic Ocean through analysis of in-situ measurements. Analysis of this case study will facilitate understanding of ozone variability in the tropical marine boundary layer and will aid in validating and improving photochemical and chemical transport models. Indirectly, this study will provide insight into changes of the oxidizing capacity and photochemical properties of the marine boundary layer during Saharan dust and biomass burning events.

2. AEROSE

The trans-Atlantic Aerosol and Oceanographic Science Expeditions (AEROSE), are a series of experiments conducted aboard the NOAA research vessel, the Ronald H. Brown [Morris et al., 2006]. The primary objectives of AEROSE are to characterize the physio-chemical evolution of the SAL during its long-range transport into the eastern seaboard of the United States and the Caribbean, and to quantify the effects of the SAL on the regional environment and climate. AEROSE-I took place during the Spring of 2004, departing February 29 from Bridgetown, Barbados and concluding in San Juan, Puerto Rico on March 26. The eastward transect of the cruise was adjusted according to the location and extent of the prevailing dust plume at the time of travel.

AEROSE-II took place during the Summer of 2006, departing San Juan, Puerto Rico on May 28

* *Corresponding author address*: Michelle D. Hawkins, Howard University Program in Atmospheric Sciences, HURB-1, 1840 7th St. NW, Washington, DC 20059; email: hawkins.michelle@gmail.com

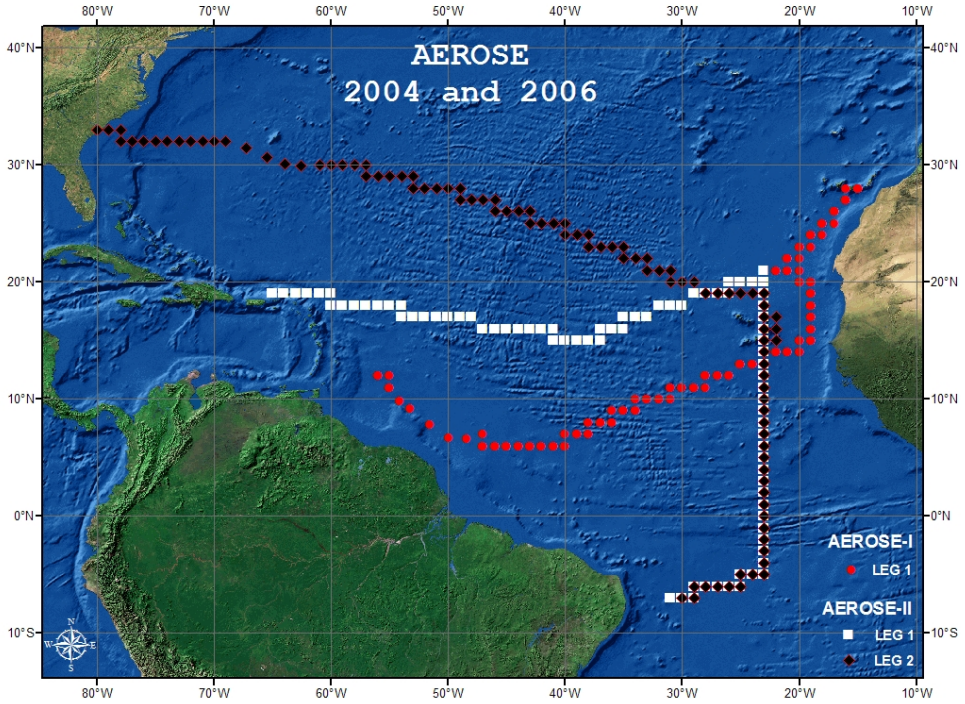

Figure 1. AEROSE-I and AEROSE-II cruise tracks.

and concluding in Charleston, SC on July 16 (Fig. 1). AEROSE-II was conducted in conjunction with the African Monsoon Multidisciplinary Analysis (AMMA) which is a coordinated international project to improve the ability to predict and monitor the weather and climate of West Africa and downstream tropical Atlantic.

3. Measurements

CO and O_3 concentrations were measured continuously using a Thermo Environmental Instruments (TEI) model 48C non-dispersive infrared gas filter correlation instrument and a TEI model 49C UV photometer, respectively throughout the duration of AEROSE-I and AEROSE-II. The instruments were located forward port side of the ship. Air samples were collected through ¼ inch diameter Teflon tubing that was connected from the back of the instruments to a shrouded intake approximately 57 feet above sea level during AEROSE-I and approximately 50 feet above sea level during AEROSE-II.

In addition to surface level ozone measurements, ozonesondes provided vertical measurements of ozone during AEROSE-II. The ozone sounding consisted of a Vaisala Radiosonde RS92 connected to a Science Pump Corporation model ECC-6A ozone sensor via a Vaisala OIF92 ozone interface card. This package measured pressure, temperature, humidity, geopotential height, and the vertical distribution of ozone. Throughout the duration of AEROSE-II, a total of sixteen ozonesondes were launched along the 23ºW longitudinal transect. Six ozonesondes were launched along the southward transect of Leg 1 and ten during the northward transect of Leg 2.

4. Meteorology

Since AEROSE-I and AEROSE-II occurred during different seasons and along different pathways, the dominant meteorological features were considerably different for each cruise. AEROSE-I took place during March of 2004. March 1-6 the Azores High remained stationary over the north-central Atlantic. Dominant flow was westerly and the ship encountered a major Saharan dust storm on March 6. Satellite imagery confirmed massive amounts of dust loading beginning on March 3 that was subsequently transported across the Atlantic. During March 7-9, a strong jet propagated along an upper level trough and caused the Azores High to be pushed eastward, closer to the northwestern coast of Africa. Streamline analysis showed dominant flow directly from the Saharan Desert and Sahel region

of West Africa. This displacement of the Azores High also allowed aged anthropogenic aerosols from Southern Europe to intersect the cruise track.

AEROSE-II took place during June and July 2006. The Tropical Prediction Center surface analysis showed dominant flow from a region in south-western Africa where satellite images confirmed active and intense biomass burning. Above 12ºN, the local meteorology and transport was strongly influenced by the Azores High which remained stationary over the central northern Atlantic Ocean. The Azores High was very pronounced and streamline analysis obtained from the NOAA global forecasting system model showed that circulation about the high introduced aged air from southern Europe directly into the ship's pathway. During Leg 2 of the 23ºW transect, the ITCZ moved northward along with the cruise track so that the ship traveled well within the ITCZ for about 4 days, between about 3ºN and 12ºN.

This paper focuses on observations obtained during Leg 1 of AEROSE-I and Legs 1 and 2 of AEROSE-II.

5. Observations

During AEROSE-I, surface level O_3 concentrations decreased as the ship sailed into pristine marine conditions and remained significantly low at 7-12ppb before encountering the March 6 Saharan dust storm (Fig. 2). During the intense dust there was a distinct absence of a diurnal cycle in the O_3 time series. Ozone concentrations were observed to increase as the ship traveled eastward along the cruise track and continued to increase after approaching air masses influenced by biomass burning. CO concentrations continued to increase along the cruise track eastward toward the west coast of Africa (Fig. 3).

During AEROSE-II, ozone concentrations decreased slightly along the east-west transect of Leg 1 but consistently remained between 30-40ppb, which was typically higher than that encountered during AEROSE-I. There was also a clear diurnal cycle in ozone. CO concentrations slightly increased along the cruise track and also did not vary much (σ=2.5ppb). CO concentrations consistently remained between 132-140ppb (Fig. 4).

Along the 23ºW transect of Leg 1, O_3 concentrations remained between 30-40ppb. However, during Leg 2 of the 23ºW transect, O_3 concentrations reached as high as 168ppb (Fig. 5). There was also a significant increase in the average concentrations of CO during the 23ºW transect of Leg 2 (Fig. 6).

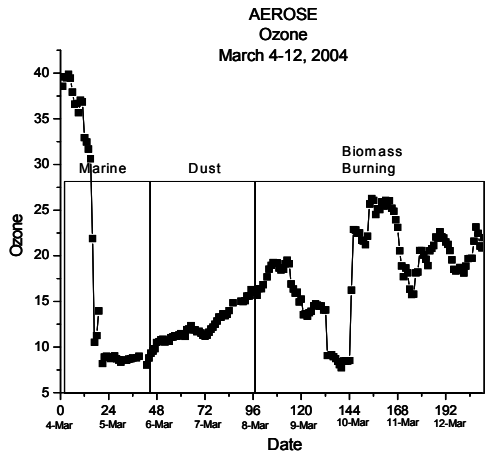

Figure 2. O_3 concentrations during AEROSE-I.

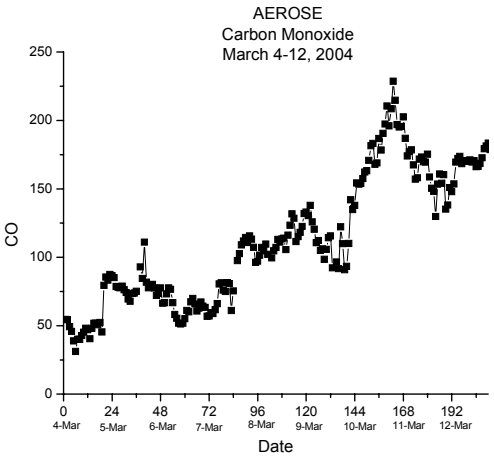

Figure 3. CO concentrations during AEROSE-I.

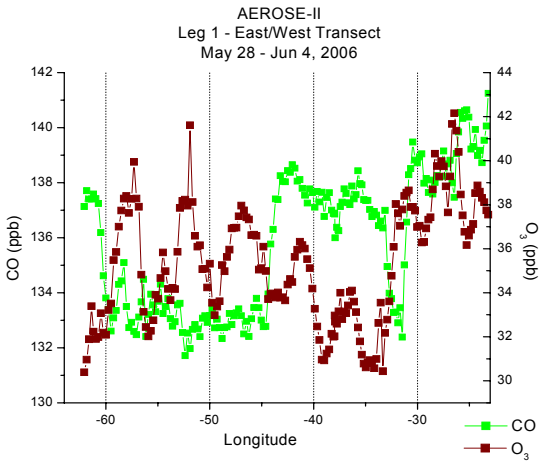

Figure 4. O_3 and CO along the east-west transect of AEROSE-II.

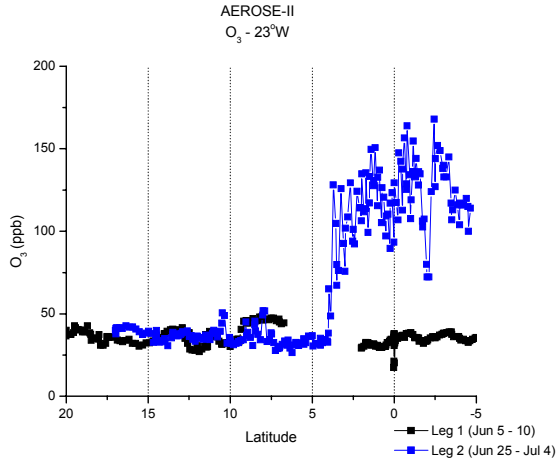

Figure 5. O_3 concentrations along 23ºW transect.

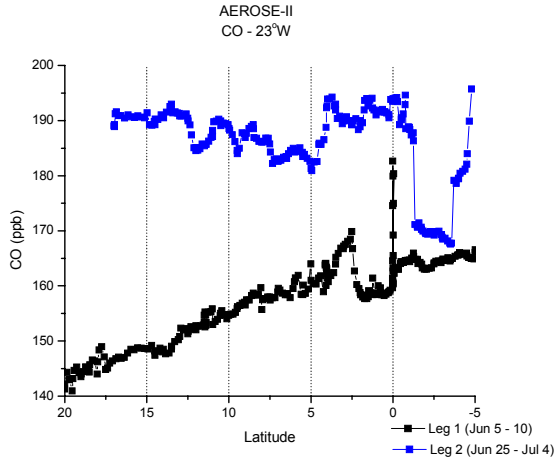

Figure 6. CO concentrations along 23ºW transect.

Ozonesondes launched during AEROSE-II provided vertical profiles of ozone along the 23ºW transect of the cruise (Fig. 7). In the mid-troposphere ozone concentrations were observed in the range of 60-80ppb on average during Leg 1. Significantly higher O_3 concentrations in the range of 80-100ppb were observed during Leg 2. Beginning on July 2 during Leg 2, significant drying of the mid-to-upper troposphere was observed, indicating the presence of the SAL as the ship approached dust impacted areas.

Analysis of the entire ozonesonde dataset revealed heterogeneity of ozone along the cruise track, however when separated by meteorological regimes similarities in the behavior of ozone become apparent. Figure 8 shows four ozonesondes that were launched along the 23ºW transect of the cruise. The dust and biomass burning columns show two ozonesondes that were launched at nearly the same latitude and longitude during each leg of the cruise, within each respective regime. Sondes launched while traveling through dust (Fig. 8a and 8c) reveal two distinct dry layers: one close to the surface and another beginning at about 6km and extending through the upper troposphere. Sondes launched during biomass burning conditions (Fig. 8b and 8d) show a deep moist layer extending 3-4km above the surface which correlates well with a nearly constant mixing ratio of ozone. During both regimes, ozone concentrations were higher during Leg 2.

6. Discussion

A combination of chemical and microphysical analyses together with analyses of satellite images, surface weather maps, back trajectories, and aerosol datasets revealed four distinct air mass regimes for both AEROSE-I and AEROSE-II: Marine Background, Dust, Mixed Biomass Burning and Dust, and Biomass Burning.

Particulate matter mass and number density concentrations were obtained using a suite of quartz-crystal microbalance cascade impactors, high volume filter impactors, and Climet models CI-500 and CI-550 laser particle counters. During AEROSE-I, Anderson high-volume aerosol samplers, models RAAS 400 and RASS 200, were used to measure PM2.5 and PM10 respectively. During AEROSE-I, the ship encountered three distinct dust events. Figure 9 shows the daily averaged PM10 and PM2.5 values obtained from the cascade impactors during AEROSE-I. The first pulse in PM concentrations indicates the first dust front. Satellite images, surface weather maps, back trajectories, and chemical and microphysical analyses revealed that this storm was primarily dust that originated from the Sahara. Satellite imagery showed active fires burning in western Africa in areas such as Guinea, Sierra Leone, and Liberia. Figure 10 shows the black carbon aerosol data obtained from a Thermo Environmental Instruments multi-angle absorption photometer (MAAP) which was deployed during AEROSE-I. Additional analyses of the CO and black carbon datasets revealed that the second and third aerosol events included air masses with significant amounts of biomass burning aerosols.

The decrease observed in O_3 concentrations after March 4 correlates well with the increase in Saharan dust aerosols. Ozone concentrations remained significantly low but began to increase after encountering air masses that included biomass burning aerosols and precursors for

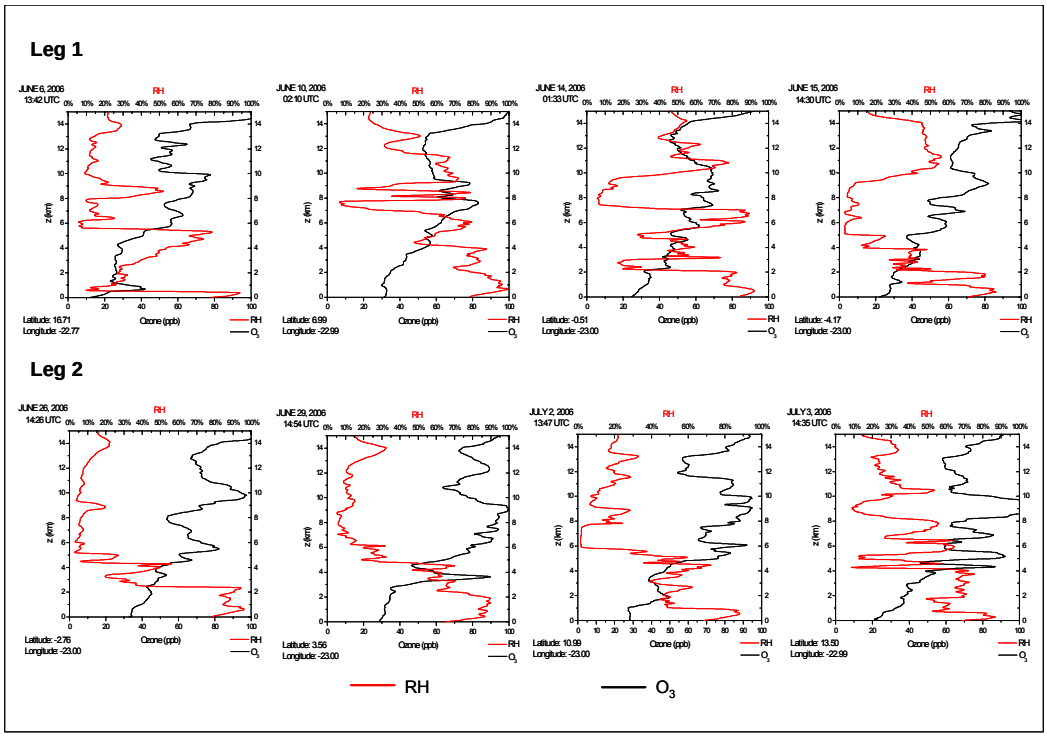

Figure 7. Sample selection of ozonesondes launched during AEROSE-II along 23°W. All bottom x-axes are O_3 (0-100ppb), all top x-axes are RH (0-100%) and all y-axes are z (0-15km).

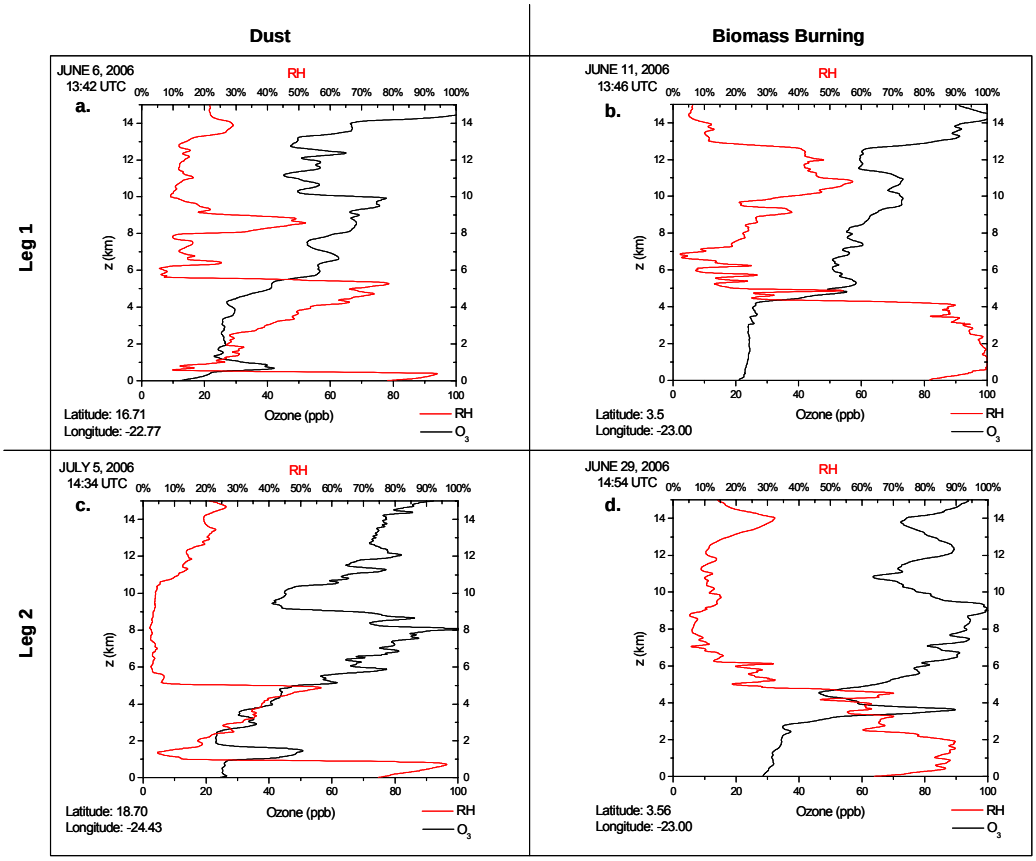

Figure 8.Ozonesondes during Leg 1 and Leg 2 dust and biomass burning regimes.

ozone production.

During Leg 2 of the 23ºW transect of AEROSE-II significantly higher O_3 and CO concentrations were observed. Analyses of air mass history, surface weather maps, and aerosol datasets revealed that Leg 2 of the cruise encountered more biomass burning aerosols than Leg 1. Satellite imagery further confirmed the presence of intense biomass burning in south-western Africa. Back trajectories showed that aerosols from this region could have been transported as far over the Atlantic as 23ºW. Ozone concentrations were observed to decrease at 4ºN and throughout the ITCZ transit. The mean concentration in this region was 36ppb. Ozone began to increase again after turning west at about 17ºN. This increase could be partly attributed to the influence of aged European air that was entrained in the Azores High and transported southward. In addition, wildfires in the Iberian Peninsula were extensive during this time and also in the proper region for introducing biomass smoke and byproducts in the ship's path due to the location and strength of the Azores High.

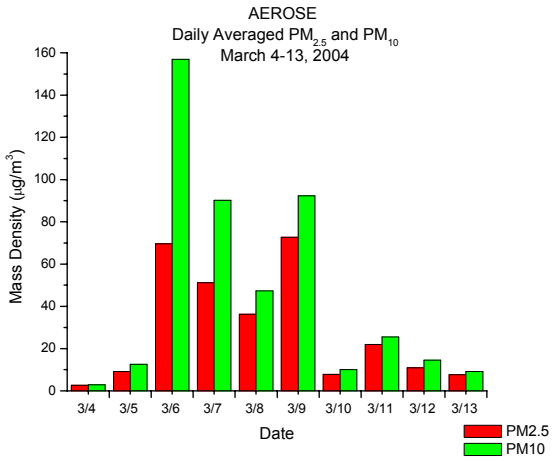

Figure 9. PM concentrations during AEROSE-I.

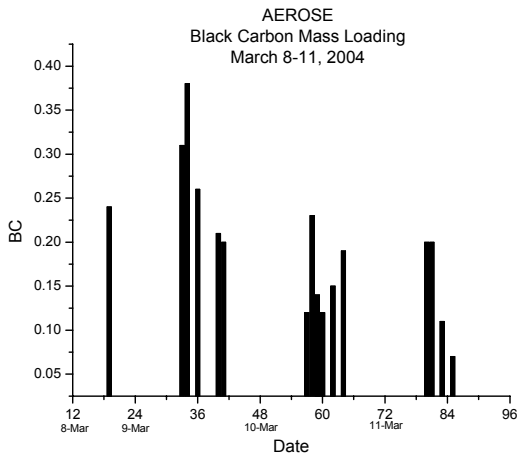

Figure 10. Black carbon concentration during AEROSE-I

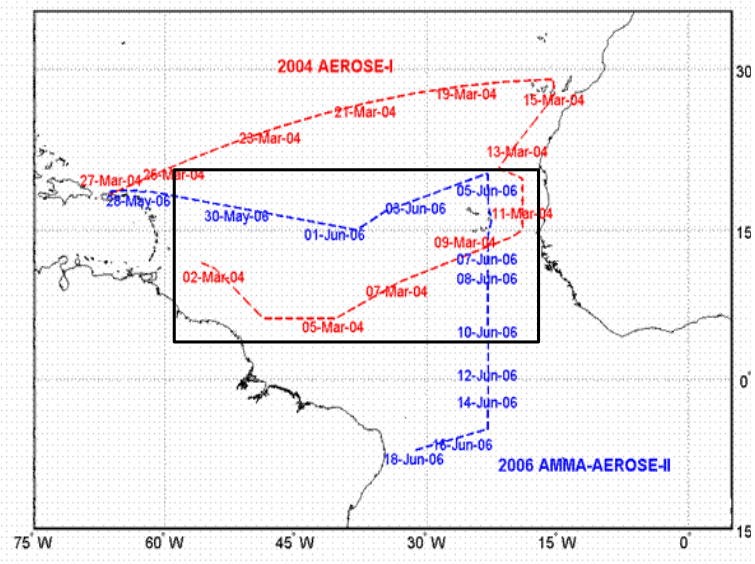

Figure 11. Comparison of O_3 concentrations for AEROSE-I and AEROSE-II along east-west transect only (cruise tracks in rectangle on map).

A comparison of the 2004 and 2006 surface O_3 data along the Leg 1 east-west transect only (see rectangle on map in Fig. 11) is shown in Fig. 12. Though the cruises were at different times of the year (2004-Spring, 2006-Summer) this comparison is useful because the intensity of the dust storms the ship encountered were significantly different (Fig. 13). Thus, a comparison can be made between the behavior of ozone during intense and during less intense dust loading conditions. Analyses of these two datasets revealed the suppression of ozone and its diurnal cycle during high dust loading episodes. It is apparent that O_3 concentrations are significantly lower under heavy Saharan dust loading conditions.

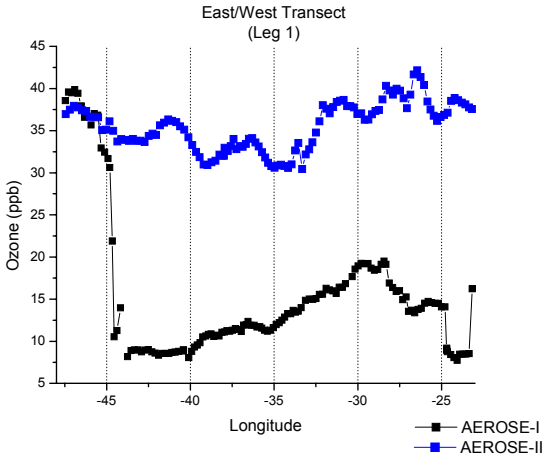

Figure 12. Comparison of AEROSE-I and AEROSE-II O_3 concentrations.

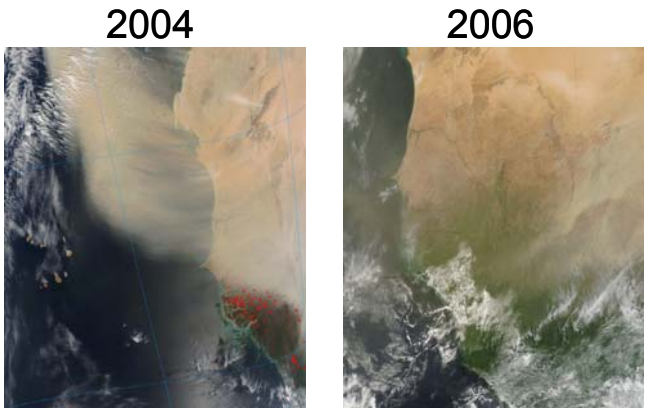

Figure 13. MODIS images of Saharan dust for March 2004 and June 2006.

7. Summary and Conclusions

Two shipboard experiments were conducted to determine the influence of Saharan dust on ozone concentrations over the remote tropical Atlantic Ocean. AEROSE-I took place during Spring 2004 while AEROSE-II took place during Summer 2006. AEROSE-I encountered air masses with significant Saharan dust loading early in the cruise and mixed dust and biomass burning aerosols later along the cruise track. AEROSE-II also traveled through a Saharan dust regime but encountered significantly more biomass burning plumes than AEROSE-I. An increase in O_3 concentrations was observed while traveling through air masses with large amounts of biomass burning aerosols while a significant decrease in O_3 concentrations was observed while traveling through intense dust regimes.

The NCAR Community Atmosphere Model with chemistry is currently being used to compare AEROSE-I and AEROSE-II shipboard observations with model output. Model comparisons and sensitivity studies will provide some insight to help identify the most important factors contributing to the behavior of ozone during intense dust loading and biomass burning events.

8. References

Bates, T.S., P.K. Quinn, D.J. Coffman, J.E. Johnson, T.L. Miller, D.S. Covert, A. Wiedensohler, S. Leinert, A. Nowak, C. Neususs, 2001. Regional physical and chemical properties of the marine boundary layer aerosol across the Atlantic during Aerosols 99: An overview. *J. Geophys. Res*., **106(D18)**, 20,767-20,782

Bauer, S.E., Y. Balkanski, M. Schulz, D.A. Hauglustaine, F. Dentener, 2004. Global modeling of heterogeneous chemistry on mineral aerosol surfaces: Influence on tropospheric ozone chemistry and comparison to observations. *J. Geophys. Res*., **109(D02304)**, doi:10.1029/2003JD003868

Bonasoni, P., P. Cristofanelli, F. Calzolari, U. Bonafe, F. Evangelisti, A. Stohl, S. Zauli Sajani, R. Van Dingenen, T. Colombo, Y. Balkanski, 2004. Aerosol-ozone correlations during dust transport episodes. *Atmos. Chem. and Phys.*, **4**, 1201-1215

De Reus, M. H. Fischer, R. Sander, V. Gros, R. Kormann, G. Salisbury, R. Van Dingenen, J. Williams, M. Zöllner, J. Lelieveld, 2005. Observations and model calculations of trace gas scavenging in a dense Saharan dust plume during MINATROC. *Atmos. Chem. and Phys.*, **5**, 1787-1803

De Reus, M., F. Dentener, A. Thomas, S. Borrmann, J. Strom, J. Lelieveld, 2000. Airborne

observations of dust aerosol over the North Atlantic Ocean during ACE 2: Indications for heterogeneous ozone destruction. *J. Geophys. Res*., **105(D12)**, 15,263-15,275

Galanter, M., H. Levy, G. R. Carmichael, 2000. Impacts of biomass burning on tropospheric CO, NO_x, and O_3. *J. Geophys. Res*., **105**, 6633–6653

Grassian, V. H., 2002. Chemical reactions of nitrogen oxides on the surface of oxide, carbonate, soot, and mineral dust particles: Implications for the chemical balance of the troposphere. *J. Phys. Chem. A*, **106**, 860-877

Jacob, D., 2000. Heterogeneous chemistry and tropospheric ozone. *Atmospheric Environment*, **34**, 2131-2159

Martin, R., D. Jacob, R. Yantosca, 2003. Global and regional decreases in tropospheric oxidants from photochemical effects of aerosols. *J. Geophys. Res.*, **108(D3)**, 4097, 10.1029/2002JD002622

Michel, A.E., C.R. Usher, V.H. Grassain, 2003. Reactive uptake of ozone on mineral oxides and mineral dusts. *Atmospheric Environment*, **37**, 3201-3211

Morris, V., P. Clemente-Colon, N.R. Nalli, E. Joseph, R.A. Armstrong, Y. Detres, M.D. Goldberg, P.J. Minnett, R. Lumpkin, 2006. AEROSE science team conducts ongoing investigations of downwind transport from Saharan and sub-Saharan Africa in the tropical Atlantic. *EOS*

Stehr, J.W., W.P. Ball, R.R. Dickerson, B.G. Doddridge, C.A. Piety, J.E. Johnson, 2002. Latitudinal gradients in O_3 and CO during INDOEX 1999. *J. Geophys. Res.*, **107(D19)**, 8015, 10.1029/2001JD000446

Tie, X., S. Madronich, S. Walters, D. P. Edwards, P. Ginoux, N. Mahowald, R. Zhang, C. Lou, and G. Brasseur, 2005. Assessment of the global impact of aerosols on tropospheric oxidants, *J. Geophys. Res*., **110**, D03204, doi:10.1029/2004JD005359