Ship-borne Ozone Flux Measurements during Southern Ocean GasEx-2008

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1. Introduction

CIRES, NOAA ESRL/PSD and INSTAAR have collaborated to develop and deploy a fast ozone instrument on the *Ronald H. Brown* during the SO-GasEx cruise. This sensor, based on the chemiluminescence principle, combined with other turbulence instrumentation, is used to measure the air-sea flux of ozone by direct eddy correlation. This instrument has been previously deployed on 2006-07 cruises in the Gulf of Mexico (TexAQS / GOMECC) and in the Eastern Pacific Ocean (Stratus). Here, we present the measurement technique and recent progress made in the GasEx-2008 data analysis.

2. Goals

Past experimental efforts provide a wide range of ozone deposition rates (***Table 1***), with over-water values ranging from v_d ~ 0.006 to 0.15 cm/s. Atmospheric chemistry models typically use a single value for ozone deposition velocity to ocean surfaces (***Figure 1***). To improve these models, and to develop a deeper understanding of the biological, chemical and physical processes involved in the ozone destruction into the oceans, several recent studies have been conducted:

1. Improved parameterization of air-sea ozone transfer by oceanic turbulence (Fairall et al., 2007).
2. A global scale analysis of ozone chemical destruction with a new modeling study (***Figure 2***; Ganzeveld et al., 2009).
3. The development of ship-borne ozone instrumentation (Bariteau et al., 2009; Lang et al., 2009).

Location	Technique	Deposition Velocity cm s^{-1}	Reference
Sea Water	Box Enclosure Decay	0.03 - 0.06	Aldaz, 1969
Fresh Water	Box Enclosure Decay	0.1	
Sea Water	Profile Method	0.08 - 0.15	Tiefenau and Fabian, 1972*
Sea Water	Wind Tunnel	0.04	Garland and Penkett, 1976
Sea Water	Laboratory	0.025 - 0.09	Galbally and Roy, 1980
Fresh Water	Laboratory	0.015 - 0.1	
Lake Water	Tower Eddy Correlation	0.01	Wesely et al., 1981
Gulf of Mexico, North Pacific	Aircraft Eddy Correlation	0.056	Lenschow et al., 1982
Sea Water, off Southern California	Aircraft Eddy Correlation	0.02	Kawa and Pearson, 1989
Sea Water and Saline Solutions	Static Chamber Technique	0.006 - 0.014	McKay et al., 1992
South Atlantic	Budget	0.03	Heikes et al., 1996
Sea Water	Literature Review	0.01 - 0.05	Wesely and Hicks, 2000
Fresh Water		0.01	
Coastal Region North Sea	Tower Eddy Correlation	0.11	Gallagher et al., 2001

*referenced in McKay et al., 1992

Gulf of Mexico (TexAQS 2006)	Ship-based Eddy Correlation	0.045	Bariteau et al., 2008
Coastal regions (TexAQS 2006)	Ship-based Eddy Correlation	0.23	Bariteau et al., 2008
Eastern Pacific (STRATUS 2006)	Ship-based Eddy Correlation	0.027	Bariteau et al., 2008
Atlantic Ocean (GOMECC 2007)	Ship-based Eddy Correlation	0.016	Lang et al., 2008
Gulf of Mexico (GOMECC 2007)	Ship-based Eddy Correlation	0.017	Lang et al., 2008

Table 1
Top: **Previous estimates and measurements of oceanic O_3 deposition over ocean and lakes. A large range of deposition velocities are reported.**

***Bottom*: Mean values from previous shipboard deployments of the ozone covariance flux system.**

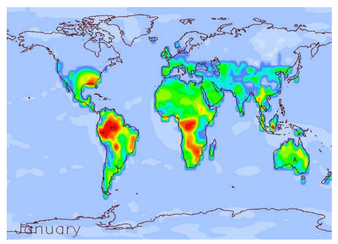

Figure 1. **Global map of the ozone deposition velocity over land and oceans during January, as previously described for the European Center Hamburg Model / Model for Atmospheric Transport and Chemistry. The mean oceanic value for v_d is 0.05 cm/s.**

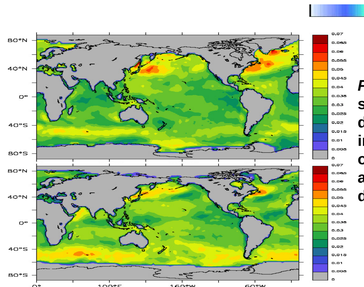

Figure 2. **January and July mean simulated oceanic ozone dry deposition velocity [cm/s] after incorporating the influence of oceanic turbulence enhancement and I^- chemistry on the ozone deposition .**

3. Instrumentation

• Determination of ozone volume mixing ratio from the chemiluminescence reaction: $NO + O_3 \rightarrow NO_2 + O_2 + h\nu$

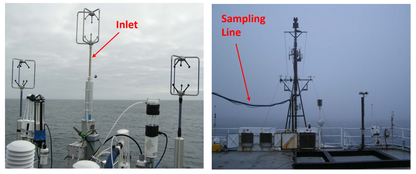

Figure 3. **The sampling inlet of the sensor is located on the jackstaff, at the sonic anemometer. Air is pulled through a Teflon line to a reaction chamber where O_3 reacts with the NO (see *Figure 4*). A photomultiplier tube (PMT) used to count the resulting photons.**

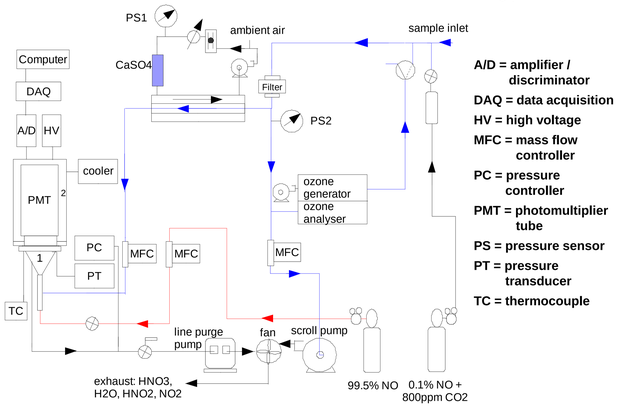

Figure 4. **Fast ozone instrument schematics. The UV Ozone monitor is used as a reference standard for the calibration of the sensor.**

4. Methodology

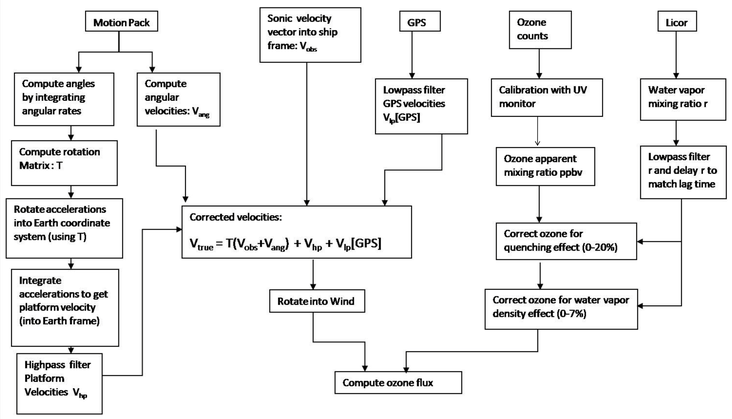

Figure 5. **A flowchart of the method used to compute the ozone flux. Here the corrections for quenching due to water vapor and Webb effect are shown but are not applied for SO-GasEx data set due to the use of a nafion membrane.**

• The sonic anemometer velocities are rotated to fixed earth coordinates and corrected for ship motion (Edson et al., 1998).

• The ozone signal is delayed relative to the sonic anemometer measurement, and the lag time is estimated using a puff system (***Figure 6***).

• Quality control filters, tube smoothing, and flow distortion corrections are applied to the flux data set. A Nafion membrane in the flow was used in order to avoid the corrections due to the presence of water vapor.

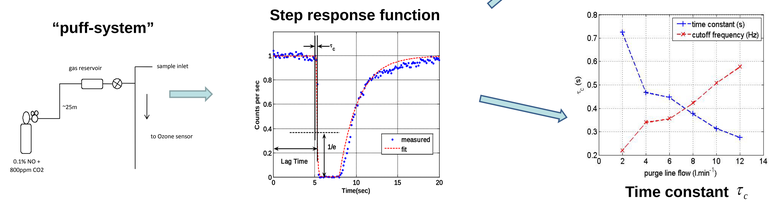

Figure 6. **Determination of the sampling line delay; a lag time of 5.3 sec is used for processing the SO-GasEx results.**

5. Results

The SO-GasEx time series of mean ozone and ozone deposition velocity are shown in **Figure 7**. Deposition velocity is computed from the observed covariance flux from v_d = Flux / [O_3] (Lang et al, 2009). Note the relative magnitude of deposition velocity, in comparison to **Table 1**. The variability in the deposition velocities is significant in comparison to the nominal magnitude. In **Figure 8**, we show the histogram of ozone deposition velocity, along with relevant statistics of the observations. **Figure 9** presents the ozone deposition velocity in wind-speed averaged bins, compared to the NOAA/COARE model with and without the oceanic turbulence routine (Fairall et al, 2007). Also present on this figure are some previous expeditions done in 2006.

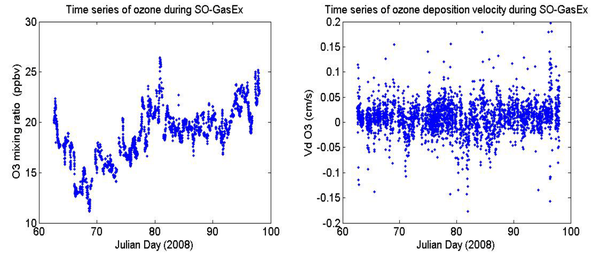

Figure 7. **Time series of the ozone mixing ratio (ppbv; left) and deposition velocity (cm/s;right) computed from the covariance flux observations during SO-GasEx.**

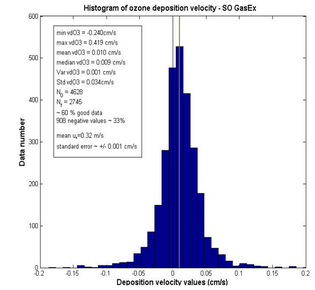

Figure 8. **Histogram and statistics of O_3 deposition velocities.**

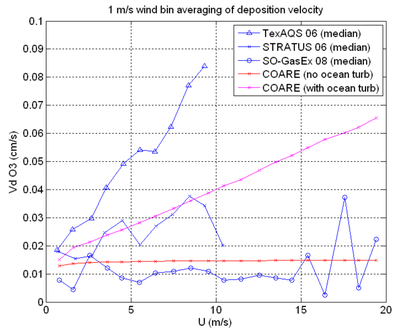

Figure 9. **Wind speed bin averaged observed ozone deposition velocities, including NOAA/COARE model results (solubility of 0.3, reactivity of 100 s^{-1}, Schmidt number of 500).**

6. Summary & Future Work

The preliminary results show a relatively low median value for the ozone deposition in the Southern Ocean of about 0.01 cm/s. The deposition velocity is shown to be nearly independent of wind speed, which contradicts results from some previous expeditions. The NOAA/COARE ozone parameterization appears to fit the observations only when the water-side turbulence is not activated.

We speculate that the preliminary results in Figure 9 may be a result of wind-speed dependent reactivity and/or due to changes in the distribution of total stress among its components (molecular, turbulent, and wave-correlated) in the unique Southern Ocean environment. Future studies include investigation of the dependencies of ozone deposition rates on oceanic conditions, such as the wave state, chemistry, etc.

References

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