Ship-borne Ozone Flux Measurements during TexAQS 2006

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1. Introduction

The NOAA ESRL/Physical Science Division (PSD) in collaboration with the INSTAAR laboratory, University of Colorado, have used a newly developed fast ozone instrument aboard the R/V Ronald H. Brown during the 2006 Texas Air Quality Study (TexAQS). This sensor, based on the chemiluminescence principle, is used to measure the ozone flux over the ocean by direct eddy correlation (EC). The study area of the Gulf of Mexico represents an interesting data set for both ocean and land footprints. This poster presents the technique used to do ozone flux measurements, and the recent progress made in the data analysis.

2. Goals

In the literature, past experiments show a wide range of ozone deposition rate (Table 1). The values for ocean water range from v_d ~ 0.01 to 0.15 cm/s. In contrary, the global atmospheric chemistry models present a single value for ozone deposition velocity to ocean surfaces (Figure 1). To improve these models, and to have better knowledge of the biological, chemical and physical processes involved in the ozone destruction into the oceans, some recent progress and studies have been made:

1.Parameterization of oceanic turbulence dependency (Fairall et al., 2007).

2. Investigation of chemistry for ozone reactions in ocean water due to I- and DOM (Dissolved organic carbon) chemistry (Figure 2) (Ganzeveld et al., 2007).

3. Development of ship-borne eddy correlation flux system; TexAQS 2006 was the first deployment of this fast ozone sensor.

Location	Technique	Deposition Velocity cm s	Reference
Sea Water Fresh Water	Box Enclosure Decay Box Enclosure Decay	0.03 - 0.06 0.1	Aldaz, 1969
Sea Water	Profile Method	0.08 - 0.15	Tiefenau and Fabian, 1972*
Sea Water	Wind Tunnel	0.04	Garland and Penkett, 1976
Sea Water Fresh Water	Laboratory Laboratory	0.025 - 0.09 0.015 - 0.1	Galbally and Roy, 1980
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 Fresh Water	Literature Review	0.01 - 0.05 0.01	Wesely and Hicks, 2000
Coastal Region North Sea	Tower Eddy Correlation	0.11	Gallagher et al., 2001

*referenced in McKay et al., 1992

Table 1. Previous estimates and measurements of oceanic ozone deposition over ocean and lakes. Obviously, a large range of deposition velocities is reported with values ranging from v_d ~ 0.006 to 0.15 cm/s. None of the literature gives specific details on the chemical, biological and physical water properties during the experiment.

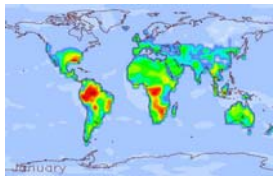

Figure 1. Global map of the ozone deposition velocity over land and oceans during January, as previously described in ECHAM4/MATCH (European Center Hamburg Model / Model for Atmospheric Transport and Chemistry). The mean oceanic value for v_d is 0.05 cm/s.

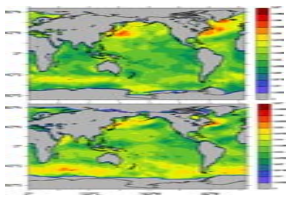

Figure 2. January and July mean simulated oceanic ozone dry deposition velocity [cm/s] after incorporating the influence of oceanic turbulence enhancement and I^- chemistry on the ozone deposition .

3. Instrumentation

• The principle for determining ozone mixing ratio relies on the chemiluminescence reaction (Stedman et al., 1972; Schiff et al., 1974; Ridley and Grahek, 1990) : NO + O3 → NO2 + O2 + photon

• The sampling inlet of the sensor is located on the jackstaff, near the sonic anemometer (Figure 3). The air is pulled through a Teflon line to a reaction chamber where the ozone reacts with the NO (Figure 4). A photomultiplier tube is used to count the number of photons during the reaction.

Figure 3. Configuration of the experiment during TexAQS 2006. Left: the inlet is located with a particle filter near the sonic anemometer, and the sampling line runs from the foremast to the sensor. Right: The fast ozone instrument was deployed on the third deck. The gray box contains the sensors, and the white box the pump system.

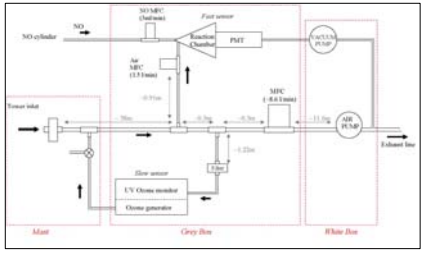

Figure 4. Fast ozone instrument schematics during TexAQS 2006. The UV Ozone monitor is used as a reference standard for the calibration of the sensor.

4. Methodology

• Due to the length of the sampling line (38 m), the ozone signal is slightly delayed compared to the instantaneous sonic anemometer's measurement. Cross-correlation is used for computing the lag time (Figure 5).

• The anemometer 3-component velocities are rotated to fixed earth coordinates and corrected for ship motion (Edson et al., 1998).

• Quality control and flow distortion correction are applied to the flux data set. The quality criteria consist of relative wind direction (to avoid data from the back of the ship), ship maneuvers, and reasonable limits on certain variables. More filters have been added for the ozone fluxes. For instance, the standard deviation of the 10 Hz data within the ten minute averaging period is used to determine the change in ozone concentration over this time.

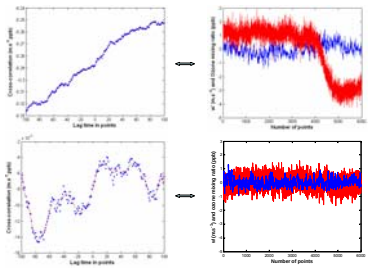

Figure 5. Examples of the cross-correlation technique. The two figures on the right side show the detrended turbulent vertical wind component (blue) and the ozone mixing ratio (red) for a ten minute period. The figures on the left side are the corresponding cross-correlation plots from these two data series. The upper part shows an example where the technique fails, while the lower part shows a good detection of the lag time by this technique.

5. Results

After obtaining data that met the filter criteria, variation in the time series of the ozone deposition velocity was observed (Figure 6). This is due to the fact that the TexAQS cruise had the unique advantage of collecting measurements in waters with both land and marine controls (Figure 7). To separate these two regimes, a simple location filter was used with all the data obtained more than 8km offshore were considered as ocean data. The histograms of the two groups of data are shown in Figures 8 and 9. A median deposition velocity of about 0.05 cm/s was determined for the ocean footprint (Figure 8). In contrast, values obtained for mixed land/ocean footprint (<8 km from the coast) are much more scattered and higher (Figure 9). The median is about 0.2 cm/s, and some values are 40 times higher than over the ocean.

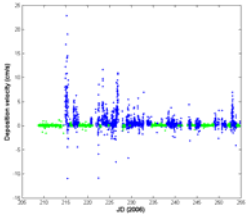

Figure 6. Time series of the ozone deposition velocity (cm/s) during Texaqs06. Green dots are data for the open ocean, and the blue dots are data for the mixed ocean-land footprint.

Figure 7. Ship track of the Ronald H. Brown during TexAQS06. The cruise started in Charleston in July 27, and ended in Galveston in September 11, 2006.

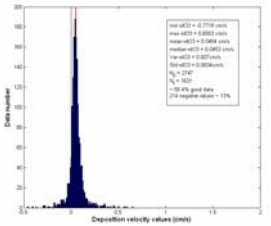

Figure 8. Histogram of ozone deposition velocity for open ocean data only (>8km offshore). This footprint represents ~42% of the cruise time.

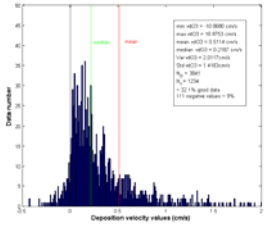

Figure 9. Histogram of ozone deposition velocity measurements with variable land effect (<8km offshore).

6. Summary & Future Work

The preliminary results show a median value for the ozone deposition in the Gulf of Mexico of about 0.05 cm/s. On the other hand, higher values were found when the ship was near land, indicating the expected higher ozone deposition rates for land footprints.

Regarding the quality control of the ozone fluxes, new filters are being used to test for the change in ozone over the flux integration period, such as the slope of the ozone signal rather than the standard deviation. In addition, corrections are needed to the ozone signal for instance high frequency loss due to the sampling line effect (~10%) and atmospheric humidity effects (quenching, Webb Correction (~ 10-20%)). Future studies will also include the dependence of ozone deposition rates on oceanic conditions, such as the wave heights, the surface wind speeds...

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