NOAA R/V Ron Brown DMS Data [Huebert/Univ. of Hawaii]

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1. Overview

We report here on the atmospheric DMS concentration, sea-to-air flux, and transfer velocity measurements from the NOAA R/V *Ronald H. Brown*, on the STRATUS cruise during VOCALS-REx from 20 October to 1 December 2008. The cruise was divided to two legs. The first leg spanned from approximately 20 October to 3 November, starting from Panama and going to WHOI buoy (85°W, 20°S) and arriving in Arica, Chile. The second leg left Arica on 10 November to the Southeast Pacific and returned to Arica on 1 December. We have previously used the APIMS with isotopically labeled standard (APIMS-ILS) technique to measure atmospheric DMS (Huebert et al., 2004; Blomquist et al., 2006, Yang et al., 2009; Huebert et al., 2010). All data are presented in tab-delimited text files that should be readable by most spreadsheet programs.

2.1 Atmospheric DMS Concentration (every minute)

VOCALS_UH_DMS_1min_submit_July21_2010.txt

The inlet for the APIMS was located at 18 m above the sea surface on the foremast of the *Ronald H. Brown*. An isotopically labeled standard (d3-DMS) was added continuously to the sample air at the inlet. A high manifold flow rate (~110 LPM) was maintained, from which 4 LPM was sub-sampled by the APIMS. Protonated molecular ions at mass 63 (DMS•H+) and mass 66 (d3-DMS•H+) were monitored sequentially. Signal intensities were recorded as total ion counts in a 20 ms interval at each mass. The ambient DMS concentration was calculated from the signal ratio (mass63/mass66), the flow rate and concentration of the labeled standard, and the total sample air flow rate. DMS concentrations are condensed to minute-averages in units of parts-per-trillion by volume (pptv) or pL/L.

Instrument backgrounds (blanks) were obtained by passing ambient air through a stainless steel cylinder filled with gold-coated glass beads. As gold adsorbs DMS very efficiently, background count rates at masses 63 and 66 were typically low (~1% total signal in the atmospheric boundary layer) and subtracted from total counts before calculating the DMS concentration. Blank measurements were deleted from the data record and recorded as NaNs in the final data file. The rest of the NaNs in the data file were caused by winds coming from the stern sector of the ship and blowing exhaust into our system, which chemically interferes with our measurements.

Three cylinders of the labeled standard were used during VOCALS-REx. Their concentrations were calibrated with measurements of known amounts of DMS emitted from a permeation device at a constant temperature (50 °C), which is verified in the lab by gravimetric data. Inter-calibration between our instrument and PMEL's Gas Chromatography on standard DMS samples showed excellent agreement. Following the cruise, we found that the pressure sensor in the controller for manifold flow had failed, which likely happened after the transit from Charleston to Panama and prior to Leg 1 of the STRATUS cruise. As a result, the manifold pressure was assumed by the instrument to be 1.00 atm for the entire cruise, when at a nominal flow of 110 SLPM, the actual pressure should be about 0.75 atm. Correcting for this manifold pressure leads to an increase in DMS concentration and flux by 33%. Averaged to one minute, including uncertainties from flow rate, standard concentration, and blanks, precision of the mean DMS concentration is about ~10%.

Most associated oceanic and meteorological variables are derived from *Ronald H. Brown*'s SCS data and NOAA's flux data.

Data Format

Jday	Julian Day for 2008, UTC (1 for 0000 1 Jan)
DMS_pptv	Atmospheric mean DMS concentration, pptv
Tair_C	Air temperature, deg C
Sal	Salinity in parts per thousand
SST_C	Sea surface temperature, deg C
Lat	GPS latitude
Lon	GPS longitude

2.2 Sea-to-air DMS Flux (every hour)

VOCALS_UH_DMS_Flux_Hour_submit_July21_2010.txt

Instantaneous relative wind speeds, acceleration, and rotation in three axes were recorded at the same frequency as the DMS by a Gill Sonic anemometer and a Systron-Donner Motionpak accelerometer, respectively. Ship's motion was removed from relative winds to get true winds following Edson et al., (1998). To obtain the sea-to-air flux (*F*) via eddy covariance, DMS concentration was correlated with the motion-corrected vertical wind velocity (*w*) in the form of $F = \overline{DMS'w'}$. Flux is in units of μmole m^{-2} day^{-1}.

Fluxes were computed in ten-minute segments that overlap by 50% (11 segments/hr) and reduced to hourly averages. Only segments with relative wind directions within 60 degrees from either side of the bow were included in the hourly averages. Ten-minute segments with the gyro heading varying by more than 10 degrees were excluded. Every valid hourly value contains at least three ten-minute segments that passed the aforementioned criteria (minimum of 20 minutes). The wind direction and gyro filtering criteria were necessary because turbulent eddies were more likely to be distorted by the ship's superstructure when the winds were coming from the stern or when the ship was turning sharply; either can result in an inadequate motion correction on the relative winds and a lack of correlation between DMS and *w*.

We consider the uncertainty in eddy covariance to be $\Delta F \approx \frac{\sigma_{DMS}\sigma_w}{(T/\tau_i)^{1/2}}$ (Fairall et al., 2000; Blomquist et al., 2010), where σ denotes standard deviation, T is the integration time, and $\tau_i \approx 12z/\bar{u}$ is the integral timescale (z and $\bar{u}$ are sensor height and mean horizontal wind speed, respectively). Relative uncertainty in the flux, accounting for error in DMS concentration, is likely to be on the order of ~30% for an integration time of an hour, and increases with shorter integration times. Uncertainty in the flux (and hence transfer velocity) is likely higher at times when the marine boundary layer is statically stable (positive Z/L).

Overlapping with atmospheric measurements, discrete sea water DMS (DMS_w) samples were taken from ship's non-toxic water supply, at 5.5 m depth, and determined by PMEL's gas chromatography every 15~30 minutes. The transfer velocity of DMS (k_{DMS}) was calculated by dividing the flux by the air-sea concentration difference in DMS, with the atmospheric DMS concentration adjusted by the dimensionless solubility factor. In units of cm/hr, k_{DMS} is presented at ambient temperatures and salinities (i.e. not normalized to a reference Schmidt number); k_{600} is k_{DMS} normalized to a reference Schmidt number of 660. NaNs in k_{DMS} correspond to when we had DMS flux, but no DMS_w measurement.

Data Format

Jday	Julian Day for 2008, UTC (1 for 0000 1 Jan), start of hour for hourly flux measurement
DMS_pptv	Atmospheric mean DMS concentration, pptv
DMSflux_uM_m2_d	DMS flux in μmole m^{-2} day^{-1} at ambient conditions
DMSflux_error	Flux error in μmole m^{-2} day^{-1} computed following Blomquist et al., 2010
kDMS_cm_hr	DMS transfer velocity for ambient conditions in units of cm/hr (not Sc normalized)
k660_cm_hr	DMS transfer velocity at Sc=660 in units of cm/hr, assuming a $Sc^{-0.5}$ relationship
k660_Error_cm_hr	Error for k660_cm_hr in cm/hr, propagated from DMS flux error
RWdir_deg	Relative wind direction, zero degrees on bow, starboard positive

RWspd_m_s	Relative wind speed in m/s at anemometer height (18 m above surface)
TWdir_deg	True wind direction, zero degrees North, 90 degrees East
U10N_m_s	10 m neutral wind speed in m/s from COARE 3.0 bulk flux model
Ustar_COARE_m_s	Friction velocity in m/s from COARE 3.0
Sc_DMS	DMS Schmidt number at ambient sea surface temperature and salinity
swDMS_nM	Sea water DMS concentration in nM (or uMoles m^{-3})
swDMS_RSEM	Relative standard error of the mean for hourly Sea water DMS concentration
Tair_C	Air temperature, deg C
SST_C	Sea surface temperature, deg C
Sal	Salinity in parts per thousand
Lat	GPS latitude
Lon	GPS longitude
ZoverL	Stability parameter z/L; z is sampling height and L is the Monin Obukhov length from COARE 3.0

3. References

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