

Supporting Information

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SI Text

Site Location and Air Mass Trajectories

Concentration measurements of N_2O_5 and ClNO_2 were made at 10 m above sea level from the northwest boom of the 330-m Scripps Institution of Oceanography (SIO) pier (latitude $32^\circ 52.0188$ N, longitude $117^\circ 15.4350$ W) during January–February 2013. The SIO pier is located in La Jolla, CA, ~ 20 km north of downtown San Diego. At a length of 330 m, the pier extends well past the region of wave breaking. The 3D sonic anemometer (Model: HS-50; Gill Instruments Ltd.) was mounted to the NW boom, extending an additional 6.2 m off the end of the pier, this effectively eliminating flow distortion caused by the pier itself when winds are between 180° and 360° . The chemical ionization time-of-flight mass spectrometer (described in the section *N_2O_5 and ClNO_2 Concentration Measurements and Uncertainties*) was housed within an existing temperature-controlled container at the end of the pier.

Backward air trajectories for the site are computed using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model (1). As shown in Fig. S1, for the intensive sampling period discussed in this paper (February 20, 2013), backward air trajectories indicate that the air sampled at the SIO pier was primarily from the west/northwest, consistent with local measurements of true wind direction. The trajectory analysis indicates that air sampled at SIO was likely influenced by the Los Angeles plume ~ 6 – 12 h before sampling.

N_2O_5 and ClNO_2 Concentration Measurements and Uncertainties

N_2O_5 and ClNO_2 mixing ratios were measured using chemical ionization time-of-flight mass spectrometry (CI-ToFMS) discussed in detail previously (2). Here, we use Γ^- reagent ion chemistry (3), detecting N_2O_5 as the $\Gamma^-\text{N}_2\text{O}_5$ adduct and ClNO_2 as the $\Gamma^-\text{ClNO}_2$ adduct. N_2O_5 sensitivities were determined using the output of a portable N_2O_5 generation system, described previously (4), where N_2O_5 is made in situ from the dark reaction of NO_2 and O_3 , and subsequent reaction of the NO_3 product with NO_2 . ClNO_2 sensitivities were determined by passing the output of the N_2O_5 source over concentrated NaCl slurry for unit conversion of N_2O_5 to ClNO_2 (3, 5). In this study, we sample N_2O_5 and ClNO_2 through a 17-m, 3/8" o.d. perfluoroalkoxy tube. The inlet manifold is constructed of fluoropel-coated glass, closely resembling that of Ellis et al. (6). Here, air is drawn through a critical orifice, reducing the sample line pressure to 200 mbar, by a Varian TriScroll 600. The resulting mass flow rate (10 standard liters per minute) results in a laminar flow profile, with a measured gas exchange time for the inlet of 0.7 s. The hybrid inlet was primarily designed for concentration measurements and run in the laminar flow regime to minimize analyte–wall collisions. As a consequence, the laminar inlet (Reynolds number = 2000) displayed frequency attenuation above 1 Hz in laboratory tests and calculations (7). The impact of this on our flux measurements is discussed below.

N_2O_5 and ClNO_2 Flux Measurements and Uncertainties

Eddy covariance fluxes were calculated from vertical wind speed and concentration measurements similarly to those described in the literature for other time-of-flight mass spectrometers (8). Mixing ratios of N_2O_5 and ClNO_2 were determined by chemical ionization mass spectrometry during a continuous 30-min sampling period bookended by 1 min of background sampling with zero air. For both N_2O_5 and ClNO_2 , ambient count rates are

corrected by subtracting interpolated baseline count rates between zero air sampling periods. The flux is determined as the covariance of vertical wind speed and baseline-corrected mass spectrometer signal over a continuous 29.8-min time period. We note that throughout the flux calculation, the mass spectrometer signal is in units of cps, and the calculated half-hour flux is initially in units of cps-m/s. This half-hour flux is converted to mixing ratio by applying an N_2O_5 and ClNO_2 sensitivity factor determined by laboratory experiments described previously. We note that this is mathematically identical to calculating the flux in units of concentration. The temporal difference between the sonic anemometer sampling an air mass and the CI-ToFMS measurement (i.e., the time taken for air to flow through the sampling line and into the mass spectrometer) is considered in the flux calculations by applying a time lag to the anemometer data. The lag time is calculated by autocorrelation analysis (9). Average lag times during significant (nocturnal) flux periods were 1.7 s, similar to the 0.7-s lag time calculated from inlet residence time (Fig. S3). The error for each half-hour flux was determined empirically from baseline fluctuations in the cross-correlation function by calculating the covariance between vertical wind speed and mass spectrometer signal at lag times of 90–120 s, significantly longer than the calculated lag time (10). Based on this calculated error (σ_{flux}), we determine a detection limit for each half-hour flux measurement period as σ_{flux} (8). A flux detection limit was computed from the mean covariance during the same extended lag periods. Detection limits ranged from 0.0026 to 4.9 ppt m/s. To test the stationarity criterion for eddy covariance calculations, we compared the half-hour flux measurement with the mean of six consecutive 5-min fluxes (11). If the overall flux and mean of the 5-min periods do not agree within 30%, 12 N_2O_5 and 9 ClNO_2 half-hour flux periods are rejected out of the total 43 flux periods. We note that all of the rejected flux periods have small or near-zero fluxes. If the rejection criterion is raised to 35%, 8 of the N_2O_5 and 9 of the ClNO_2 flux periods are rejected. For the data reported here, a 30% rejection criterion was applied.

Comparison of power spectra and cospectra between the sensible heat flux and the N_2O_5 and ClNO_2 fluxes demonstrates the validity of applying eddy covariance flux calculations to the trace gas datasets (Figs. S4 and S5). The cumulative flux contributions as a function of frequency (ogive, Fig. S4) demonstrate the similarity in frequency dependence for all three scalars, with eddies with frequencies between 0.02 and 0.3 Hz carrying the majority of the turbulent flux. Little or no attenuation is observed for N_2O_5 , whereas cospectra and ogives of ClNO_2 suggest some loss of flux at the high frequencies (>3 Hz). This attenuation is expected as the laminar flow in the sampling lines will cause smearing of high-frequency fluctuations. However, comparison with the sensible heat flux shows that 86% to 96% (ClNO_2 and N_2O_5 , respectively) of the total flux occurs at frequencies less than 1 Hz, confirming that while present, attenuation introduces only a small systematic bias (i.e., underestimation of flux) to the flux data. Due to this small error and the difficulties in predicting spectra for reactive trace gases, we do not apply a correction to the fluxes. The frequency-multiplied cospectra (e.g., Fig. S5) demonstrate the clearly distinguishable flux signal. The negative cospectral power density in Fig. S5 indicates that the N_2O_5 is depositing from the atmosphere to the ocean surface. Similar to the ogive plots, the cospectra show that the bulk of the flux signal is carried by eddies in the 0.02- to 0.3-Hz range. For a wind speed of 10 m/s, this corresponds to eddies in the nocturnal boundary layer on the order of 50–500 m.

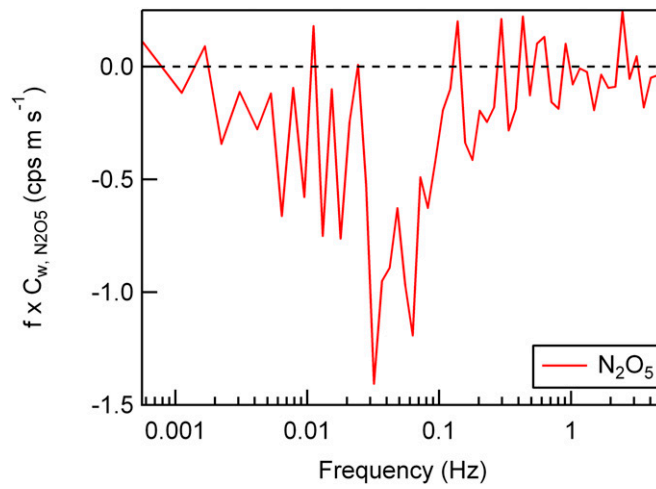


Fig. 55. Cospectral density of N_2O_5 and vertical wind speed for the flux period between 2157 and 2227 on February 20, 2013 as a function of frequency demonstrates that the deposition of N_2O_5 , with the majority of the flux signal carried by eddies in the 0.02- to 0.3-Hz range and negligible contribution of white noise.