Direct observations of N_2O_5 reactivity on ambient aerosol particles

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[1] N_2O_5 reactivity has been measured directly for the first time on ambient aerosol particles using an entrained aerosol flow reactor coupled to a custom-built chemical ionization mass spectrometer at two urban locations during summer. The observed N_2O_5 reactivity is a strong function of both relative humidity (RH) and particle chemical composition. We show that particulate organic mass loadings, together with ambient relative humidity, play a leading role in determining the reaction rate of N_2O_5 with particles. Our observed reactivity values are both more variable and, at times, as much as a factor of ten lower than currently implemented large-scale model parameterizations would predict. Such discrepancies have likely consequences for predictions of NO_x availability and ozone production, and the sensitivity of these quantities to aerosol particle loadings. **Citation:** Bertram, T. H., J. A. Thornton, T. P. Riedel, A. M. Middlebrook, R. Bahreini, T. S. Bates, P. K. Quinn, and D. J. Coffman (2009), Direct observations of N_2O_5 reactivity on ambient aerosol particles, *Geophys. Res. Lett.*, *36*, L19803, doi:10.1029/2009GL040248.

1.   Introduction

[2]   The production of tropospheric ozone (O_3), a criteria air pollutant and potent greenhouse gas, is a complex function of nitrogen oxides ($NO_x = NO + NO_2$), volatile organic compounds (VOC), sunlight, and trace oxidants such as the hydroxyl radical (OH). O_3 production is non-linearly dependent on NO_x abundance and thus accurate description of the processes that remove NO_x radicals is critical for predicting the down-wind influence of anthropogenic emissions on tropospheric O_3. Global modeling studies suggest that nocturnal processes involving the reactions of the nitrate radical (NO_3) and N_2O_5 account for 50% of the globally averaged annual net NO_x removal [*Dentener and Crutzen*, 1993]. However, the impact of nocturnal NO_x removal processes on the tropospheric O_3 budget continues to be limited by uncertainty in the reaction rate of N_2O_5 with aerosol particles.

[3]   The influence of N_2O_5 on the removal of atmospheric NO_x radicals is determined by the product of the probability that N_2O_5 will react on a particle given a collision, $\gamma(N_2O_5)$, and the total gas-particle collision frequency primarily set by the available particle surface area concentration (S_a). Until recently, direct measurements of $\gamma(N_2O_5)$ have been restricted to the laboratory, where simplified model particle types are probed to ascertain functional dependences. These studies have shown that N_2O_5 removal by particles and the resulting products are strongly dependent on: i) liquid water content ($H_2O(l)$) [*Thornton et al.*, 2003], ii) particle nitrate (NO_3^-), which inhibits N_2O_5 hydrolysis [*Wahner et al.*, 1998], iii) the presence of additional nucleophiles in water stressed particles [*Behnke et al.*, 1997], iv) organic coatings that have been theorized to either suppress N_2O_5 accommodation or decrease water availability at the surface [*McNeill et al.*, 2006; *Folkers et al.*, 2003], and v) particle acidity [*Mozurkewich and Calvert*, 1988]. These effects lead to measured $\gamma(N_2O_5)$ that span three orders of magnitude ($1 \times 10^{-4} < \gamma < 0.1$) depending on the chemical and physical properties of the particles employed. Consistent with this large potential variability, recent analyses of NO_3 and N_2O_5 field measurements have inferred that $\gamma(N_2O_5)$ can range from 1×10^{-3} to 0.017 and is likely dependent on particle chemical composition [*Brown et al.*, 2006].

[4]   In the context of atmospheric particle composition, the importance of the above dependences, either individually or as a whole, remains entirely unclear. Combining our direct measurements of $\gamma(N_2O_5)$ on ambient particles with co-located observations of particle chemical composition and particle S_a, gas phase precursors, and meteorological parameters, allows such evaluations and the elucidation of factors that most likely control $\gamma(N_2O_5)$ on ambient particles.

2.   Experimental Design

[5]   The pseudo-first order rate coefficient for N_2O_5 loss to aerosol particles (k_{het}) was measured directly using an entrained aerosol flow reactor coupled to a chemical ionization mass spectrometer (CIMS) [*Kercher et al.*, 2009]. The experimental technique is described in detail elsewhere [*Bertram et al.*, 2009]. Observations of $\gamma(N_2O_5)$ were made at two urban sampling locations during the summer of 2008. Between July 3rd and 21st, observations were made from a 10 m tower adjacent to the NOAA Earth System Research Laboratory in Boulder, CO. Particle size distributions (65 nm to 1 μm) were measured by an ultra-high sensitivity aerosol spectrometer and particle composition measured by an Aerodyne compact time-of-flight aerosol mass spectrometer [*DeCarlo et al.*, 2006; *Drewnick et al.*, 2005]. Coincident measurements of gas-phase precursors (e.g., O_3 and NO) and basic meteorological parameters were also made during the sampling period. Between August 6th and 16th, observations were made from a 5 m sampling mast extending above an instrument sea container located at the NOAA

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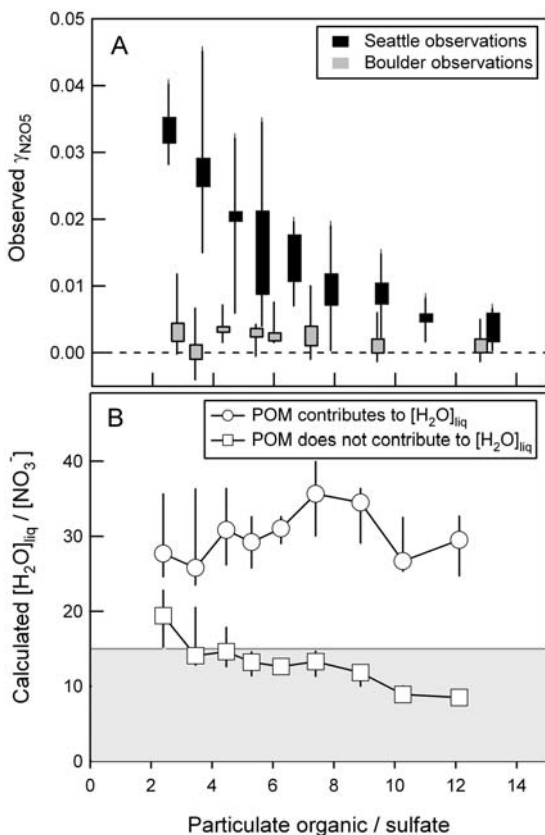[6]Pacific Marine Environmental Laboratory, NOAA, Seattle, Washington, USA.

Figure 1. (a) Observed dependence of $\gamma(N_2O_5)$ on the mass ratio of POM to SO_4^{2-} for measurements made in Seattle (black) and Boulder (gray). (b) Calculated dependence of the molar ratio of $H_2O(l)$ to NO_3^- on the mass ratio of POM to SO_4^{2-} for measurements made in Seattle, assuming that POM does (circles) and does not (squares) contribute to $H_2O(l)$ uptake. Data points are equal population binned medians, where the bar corresponds to the interquartile range of the calculations. The shaded region (in panel b) represents values of $[H_2O(l)]/[NO_3^-]$ where laboratory measurements predict suppression in $\gamma(N_2O_5)$ due to the NO_3^- effect.

Pacific Marine Environmental Laboratory, 10 km NE of downtown Seattle, WA. Particle size distributions (10 nm to 10 μm) were measured with two differential mobility particle sizing instruments and aerodynamic particle sizer. Sub-micron particle composition was measured by an Aerodyne quadrupole aerosol mass spectrometer [*Jayne et al.*, 2000].

[6] We interpret these results using a newly developed parameterization of $\gamma(N_2O_5)$ [*Bertram and Thornton*, 2009] that is driven by observations of particle composition and RH, and calculations of $H_2O(l)$ as determined by the aerosol inorganics model (AIM Model II) [*Carslaw et al.*, 1995]. This approach permits us to directly assess the dependence of the observed $\gamma(N_2O_5)$ on the factors outlined in section 1.

3. Observed Dependence of $\gamma(N_2O_5)$ on Particle Chemical Composition

[7] In Boulder, the ambient RH was low (30 ± 15%), particle loadings were rather uniform (mean S_a = 108 ± 35,

total mass = 5.3 ± 1.5 μg m^{-3}), and particles contained high organic mass fractions (mean organic/sulfate mass ratio = 6.1 ± 3.9). The median $\gamma(N_2O_5)$ observed in Boulder was 0.003 (interquartile range of $0.9-1.2 \times 10^{-3}$). In contrast, in Seattle, the ambient RH was higher (74 ± 13%), particle loadings were enhanced and more variable (mean S_a = 190 ± 115, total mass = 7.2 ± 4.1 μg m^{-3}), but particles had similar bulk particle chemical composition as in Boulder (mean organic/sulfate = 7.1 ± 4.8). The median $\gamma(N_2O_5)$ observed in Seattle was 0.009 (interquartile range of $0.26-2.9 \times 10^{-2}$), a factor of three larger than measured in Boulder.

[8] These differences in the median $\gamma(N_2O_5)$ are grossly consistent with the difference in RH between the two locations leading to lower $H_2O(l)$ in Boulder relative to Seattle. But, RH alone is not sufficient for describing either the observed variability in, or the level of suppression of $\gamma(N_2O_5)$ relative to that expected on aqueous solution particles. For example, the strongly decreasing trend of $\gamma(N_2O_5)$ with the increasing mass ratio of particulate organic matter (POM) to sulfate (SO_4^{2-}) observed in the Seattle data, and the lack of such a correlation in the Boulder data (Figure 1a), provide insights into the particle characteristics that exert control over $\gamma(N_2O_5)$. In what follows, we investigate the dependence of $\gamma(N_2O_5)$ on POM, making the reasonable assumption that the aerosol particles are largely internal mixtures [*Murphy et al.*, 2006] (see auxiliary material).[1]

[9] In the absence of POM, $\gamma(N_2O_5)$ should be controlled by the RH-dependent liquid water content and the molarity of nucleophiles such as NO_3^- and chloride (Cl^-) [*Bertram and Thornton*, 2009; *Griffiths et al.*, 2009; *Wahner et al.*, 1998; *Behnke et al.*, 1997]. In both locations studied, when POM/SO_4^{2-} was lowest, the non-refractory particle composition was mainly ammonium sulfate (AS) with trace NO_3^- and Cl^- (Figure S1), and our observations of $\gamma(N_2O_5)$ are in good agreement with both laboratory measurements and the parameterization of *Bertram and Thornton* [2009]. Probing the response of $\gamma(N_2O_5)$ to an increasing mass fraction of POM, in both Boulder and Seattle, permits us to assess the potential affects of POM on $\gamma(N_2O_5)$. POM has been suggested to influence $\gamma(N_2O_5)$ via: i) altering $H_2O(l)$, which has been shown to influence $\gamma(N_2O_5)$ either through a direct $H_2O(l)$ limitation [*Thornton et al.*, 2003] or by changing particle $[H_2O(l)]/[NO_3^-]$ [*Mentel et al.*, 1999], and/or ii) the formation of organic coatings on aqueous cores that inhibit the accommodation or reaction of N_2O_5 [*Badger et al.*, 2006; *McNeill et al.*, 2006; *Folkers et al.*, 2003].

[10] The small $\gamma(N_2O_5)$ values and lack of correlation with POM observed in Boulder indicates that the particles sampled were either solid (independent of POM mass fraction) or that increases in POM did not lead to the associated increase in $H_2O(l)$ required to enhance $\gamma(N_2O_5)$. Interestingly, our observed $\gamma(N_2O_5)$ values are consistent with that predicted by the *Bertram and Thornton* [2009] parameterization regardless of the AS phase state. Laboratory measurements of $\gamma(N_2O_5)$ are <0.005 on crystalline AS [*Mozurkewich and Calvert*, 1988], similar to the median of 0.003 observed in Boulder. If AS crystallization was inhibited by the available POM [*Parsons et al.*, 2004] and we treat POM as hygroscopic (i.e. malonic acid like),
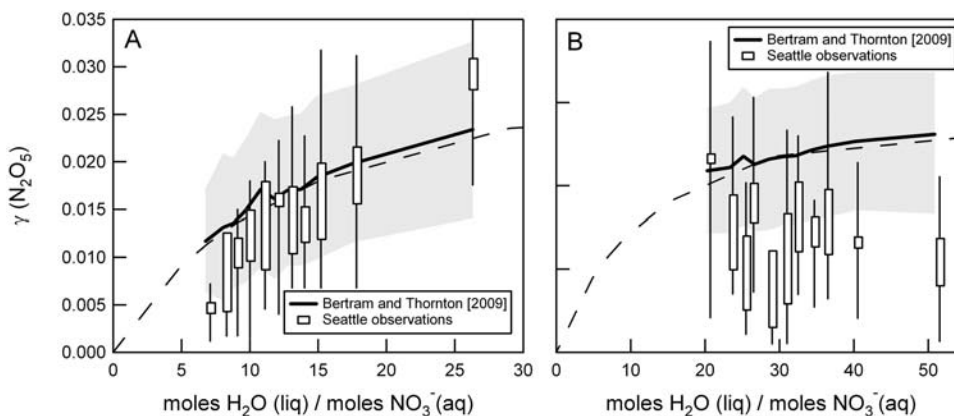
Figure 2. Comparison of parameterized [*Bertram and Thornton*, 2009] and observed $\gamma(N_2O_5)$ as a function of the molar ratio of $H_2O(l)$ to NO_3^- assuming (a) that POM does not contribute to $H_2O(l)$ uptake and (b) that POM contributes to $H_2O(l)$ uptake. Data points are separated into equal population bins, where the bar and whiskers correspond to the median to mean range and the interquartile range of the observations, respectively. The parameterized $\gamma(N_2O_5)$, derived from the observed particle chemical composition and RH, is shown with black solid lines and the shaded region represents the propagated uncertainty in its determination. The dashed black line depicts $\gamma(N_2O_5)$ as parameterized for regions where direct measurements of $\gamma(N_2O_5)$ were not available.

calculations made using the *Bertram and Thornton* [2009] parameterization show that at the low RH sampled, $[H_2O(l)]/[NO_3^-]$ is low enough to significantly suppress $\gamma(N_2O_5)$ to <0.005 across the entire range of POM/SO_4^{2-} observed in Boulder. Co-located measurements of $\gamma(N_2O_5)$ and particle phase state [*Martin et al.*, 2008] will clearly allow such distinctions to be made in the future.

[11] The behavior of $\gamma(N_2O_5)$ observed in Seattle, at higher RH, more clearly illustrates the importance of understanding POM in order to assess the factors controlling $\gamma(N_2O_5)$. The dependence of $\gamma(N_2O_5)$ on POM/SO_4^{2-} was observed during a stagnation episode in which most of the POM mass growth was likely due to SOA formation as indicated by the fraction of POM that is measured to be highly oxidized (see Figure S4). In light of the above expectations, the decreasing $\gamma(N_2O_5)$ with increasing POM/SO_4^{2-} can be hypothesized to be a result of: i) a relative decrease in the particulate water mass fraction, following increased partitioning of organics that are less hygroscopic than AS (i.e. $\Delta H_2O(l)/\Delta POM \sim 0$), leading to both an increased nitrate effect [*Wahner et al.*, 1998] and a possible $H_2O(l)$ limitation [*Thornton et al.*, 2003], and/or ii) an increasing role of organic coatings that limit either N_2O_5 surface accommodation or N_2O_5 accessibility to $H_2O(l)$.

[12] To examine these suppositions, we first calculate $[H_2O(l)]$ and $[H_2O(l)]/[NO_3^-]$ using AIM for the two extremes of POM hygroscopicity: i) POM does not contribute to $H_2O(l)$ uptake, and ii) POM is highly hygroscopic, contributing significantly to $H_2O(l)$ (POM treated as malonic acid) (Figure 1b). In both cases $[H_2O(l)]$ is sufficiently high (>20M), so as not to suppress $\gamma(N_2O_5)$ directly. The molar ratio of $H_2O(l)$ to NO_3^- remains nearly constant when POM is allowed to contribute to $H_2O(l)$, but decreases with increasing POM/SO_4^{-2} when POM is prohibited from contributing to $H_2O(l)$. To determine whether the calculated changes in $[H_2O(l)]/[NO_3^-]$ are sufficient for describing the observed changes in $\gamma(N_2O_5)$, we use the parameterization for $\gamma(N_2O_5)$ described by *Bertram and Thornton* [2009].

[13] Figure 2 depicts the parameterization-observation comparison for both cases as a function of the molar ratio of $H_2O(l)$ to NO_3^-. The strong parameterization-observation agreement, shown in panel A, lends support to the conclusion that POM sampled in Seattle did not contribute significantly to $H_2O(l)$. Such a notion would be generally consistent with the findings of *Mochida et al.* [2008] and *Quinn et al.* [2005], where ambient observations revealed decreases in RH-dependent particle growth factors or scattering efficiency in the presence of large organic mass fractions. Based on our observations alone, we cannot rule out the possibility that organic coatings may act to offset the effects of hygroscopic organics (Figure 2b). Nonetheless, it is clear that the presence and chemical properties of POM play a decisive role in setting $\gamma(N_2O_5)$ in the troposphere. Further measurements of $\gamma(N_2O_5)$ downwind of source regions, where POM is likely more oxidized [*Zhang et al.*, 2007], and more hygroscopic [*Kondo et al.*, 2007], and/ or alongside co-located observations of particle hygroscopic growth will be strong tests of this hypothesis and the applicability of these first results to regional and global models.

4. Implications for NO_x Processing Rates

[14] Quantifying the absolute magnitude of $\gamma(N_2O_5)$ and ultimately the loss rate of N_2O_5 to particles is necessary for reliable model representations of NO_x, OH, O_3, and particle abundances and the couplings between them. The sensitivity of the NO_x budget to $\gamma(N_2O_5)$ is a strong function of the NO_3 and N_2O_5 production rates, S_a, temperature, and NO_3 reactivity. To assess the importance of $\gamma(N_2O_5)$ we examine the fraction of NO_x present at sunset, $[NO_x]_{sunset}$, that is lost at night as a function of $\gamma(N_2O_5)$.

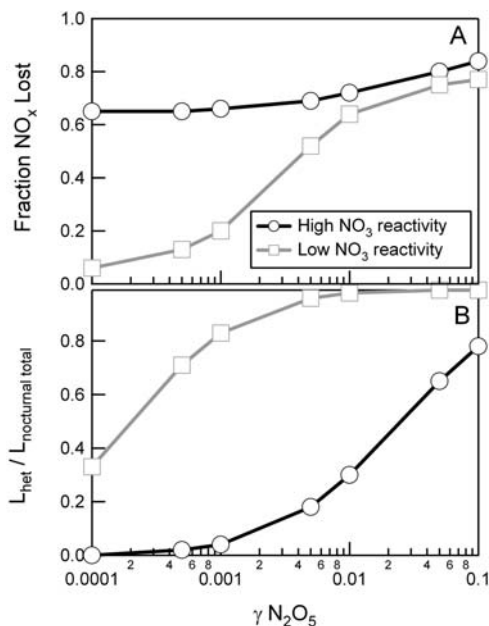$$F_{lost} = \frac{[NO_x]_{Sunset} - [NO_x]_{Sunrise}}{[NO_x]_{Sunset}} \quad \text{E1}$$

Figure 3. (a) Fraction of available NO_x ($[NO_x]_{sunset}$) lost during a 12-hr night as a function of $\gamma(N_2O_5)$ for low NO_3 reactivity (T = 278°K and NO_3 reactivity = 0.01 min^{-1}, gray squares) and high NO_3 reactivity (T = 298°K and NO_3 reactivity = 0.1 min^{-1}, black circles) conditions. Values were calculated using a time-dependent chemical box model, with the following initial conditions: $[O_3]$ = 50 ppbv, $[NO_2]$ = 5 ppbv, and S_a = 200 $\mu m^2 cm^{-3}$. (b) Fraction of total nocturnal NO_x loss *via* N_2O_5 for summer and winter conditions.

The dependence of F_{lost} on $\gamma(N_2O_5)$ and NO_3 reactivity, as calculated using a time-dependent chemical box model (see SI) for characteristic summer and winter conditions, is shown in Figure 3. We chose conditions (e.g., temperature and NO_3 reactivity) in order to bracket the range of possible sensitivities to $\gamma(N_2O_5)$. In our summer calculations, F_{lost} is primarily limited by the NO_3 production rate and nearly independent of $\gamma(N_2O_5)$ due to assuming high loadings of biogenic volatile organic compounds (BVOC), which increase NO_3 reactivity, and warmer temperatures, which shift the N_2O_5-NO_3 equilibrium in favor of NO_3. The result is that at high NO_3 reactivity the nocturnal loss of NO_x is independent of $\gamma(N_2O_5)$. During winter, BVOC emissions are significantly smaller, and lower temperatures shift the N_2O_5-NO_3 equilibrium in favor of N_2O_5. As a result, F_{lost} is far more sensitive to $\gamma(N_2O_5)$ during winter than in summer. These calculations illustrate the acute sensitivity of the NO_x budget to changes in $\gamma(N_2O_5)$ between 1×10^{-4} and 0.1 and imply that the NO_x lifetime is strongly dependent on NO_3 reactivity at low $\gamma(N_2O_5)$.

[15] In addition to accurate predictions of the total nocturnal NO_x loss, models must also correctly attribute that loss between the N_2O_5 and NO_3 channels to achieve a realistic sensitivity of the NO_x budget to changes in VOC, temperature, and particle loadings. Our modeling shows this branching is sensitive to $\gamma(N_2O_5)$ for the majority of likely conditions. The reaction products for the two channels have different effects on oxidant concentrations and particle mass loadings: the products of NO_3 homogeneous reactions can

lead to the formation of secondary organic aerosol [*Ng et al.*, 2008] and the heterogeneous reaction of N_2O_5 can lead to halogen activation [*Finlayson-Pitts et al.*, 1989] or increased particulate nitrate mass [*Riemer et al.*, 2003].

[16] When compared to predictions of $\gamma(N_2O_5)$ made using two currently implemented large-scale model parameterizations [*Davis et al.*, 2008; *Evans and Jacob*, 2005], our directly observed reactivity values are both more variable and as much as a factor of ten lower, consistent with reactivity values inferred from aircraft observations of NO_3 and N_2O_5 [*Brown et al.*, 2009]. If our observations described herein are representative of other urban/suburban locations, then incorporating the observed $\gamma(N_2O_5)$ into current models would likely lead to increases in predicted O_3 and OH, and an increased sensitivity of NO_x loss to both NO_3 reactivity and particle loadings.

5. Conclusions

[17] We present an analysis of the first direct measurements of $\gamma(N_2O_5)$ on ambient aerosol particles. At the limit of low POM, our observations confirm RH as a primary control and particulate nitrate as a secondary control in regulating $\gamma(N_2O_5)$. Observations at high RH illustrate a strong dependence of $\gamma(N_2O_5)$ on particle POM/SO_4^{2-}. Our recent parameterization [*Bertram and Thornton*, 2009] can adequately capture the trend and variability in the observed $\gamma(N_2O_5)$ if we make the assumption that the increasing POM mass fractions do not contribute significantly to additional particulate water uptake at the same RH. In such a case, the nitrate effect is sufficient to explain our results. If POM does contribute to $H_2O(l)$ uptake, then our results suggest an additional means of suppressing $\gamma(N_2O_5)$ that is correlated with oxidized POM such as organic coatings. Regardless, these results clearly indicate that regional and global modeling efforts need to consider the effects of particulate organic loadings and hygroscopicity in parameterizing the rate of nocturnal NO_x loss *via* N_2O_5 reactions on particles.

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