

Nighttime chemistry at a rural site in the Lower Fraser Valley

Robert McLaren^{a,*}, Rhian A. Salmon^a, John Liggio^a, Katherine L. Hayden^b,
Kurt G. Anlauf^b, W. Richard Leitch^b

^aDepartment of Chemistry and Centre for Atmospheric Chemistry, York University 4700 Keele St., Toronto, Ont. Canada M3J 1P3

^bAir Quality Research Branch, Meteorological Service of Canada 4905 Dufferin Street, Toronto, Ont. Canada M3H 5T4

Received 16 July 2003; received in revised form 24 February 2004; accepted 10 March 2004

Abstract

NO₃ was measured at the Sumas Eagle Ridge Site during the Pacific 2001 Air Quality Study. The average maximum levels (30 min average) observed on four nights was 34 pptv. NO₃ at these levels can play a significant role in oxidation of volatile oxidation compounds (VOC), particularly biogenic monoterpenes. N₂O₅ levels were calculated on two nights presuming that the equilibrium, NO₂ + NO₃ ⇌ N₂O₅, was maintained. Peak N₂O₅ levels were 200–300 pptv. NO₃ and N₂O₅ were found to contribute 7–9% of the total gaseous NO_y on these two nights. Homogeneous and heterogeneous hydrolysis rates of N₂O₅ were calculated to estimate the nighttime production of gaseous and particulate nitric acid, respectively. Ignoring losses, the overnight total accumulated production of nitric acid was found to be 1.4–2.1 μg m⁻³. In a comparison, it was found that the calculated heterogeneous production of fine particle nitrate can account for most of that which was observed experimentally on the two nights, indicating that this process is significant. Particulate pinonaldehyde measured throughout the study showed a significant night/day enhancement, in contrast to other carbonyls, indicating that NO₃ also plays a role in formation of secondary organic aerosols at the site.

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Keywords: Differential optical absorption spectroscopy (DOAS); Nitrate radical; Particle nitrate; Pinonaldehyde; Partitioning NO_y; Dinitrogen pentoxide

1. Introduction

Since its first detection in the polluted troposphere, it has been understood that the nitrate radical, NO₃, plays a dominant role in nighttime chemistry (Platt et al., 1980). NO₃ can oxidize organic compounds at rates that compare to the role of the hydroxyl radical, OH, during the day. A recent study in which all three oxidants were measured over an extended period, concluded that the relative contributions of OH, NO₃ and O₃ initiated oxidation to total volatile organic compound (VOC)

degradation was 55%, 28% and 17%, respectively, in a rural continental area, while the relative contribution of NO₃ to total olefinic compound degradation was even higher (Geyer et al., 2001). For certain organics, NO₃ is the dominant oxidation species in the atmosphere. For example, in the North Atlantic marine boundary layer, NO₃ is believed to be a more important sink for dimethyl sulfide (DMS) at night than OH during the day (Allan et al., 2000). NO₃ reacts very rapidly with biogenic hydrocarbons, especially monoterpenes. As an example, the lifetime of α-pinene in the presence of 50 pptv of NO₃ is only 2 min.

The nitrate radical is also known to be a significant intermediate in the conversion of NO_x (NO + NO₂) to

*Corresponding author. Fax: +1-416-736-5936.

E-mail address: rmlaren@yorku.ca (R. McLaren).

nitric acid, HNO₃. Several mechanisms are known for this conversion. During the daytime, the most significant mechanism is believed to be the reaction of OH with NO₂ to produce gaseous HNO₃. At night, the most significant mechanism is believed to be the conversion of NO₃ to dinitrogen pentoxide, N₂O₅, followed by heterogeneous and homogeneous hydrolysis of N₂O₅ to give gaseous and particulate phase HNO₃, respectively. In the particle phase, HNO_{3(aq)} can further react with NH₃ to give ammonium nitrate. N₂O₅ can build up to significant levels under some conditions. It has been seen to contribute up to 30% of total NO_y at night, and early morning peaks of several ppb NO_x have been observed at sunrise as NO₃ suddenly photolyzes, depleting the pool of N₂O₅ (Brown et al., 2001). Several recent studies have attempted to quantify the nighttime losses of NO₃. In a recent study near Berlin (Geyer et al., 2001), the three most important sinks for NO₃ were found in order to be: reaction with biogenic hydrocarbons (~30–50%), the indirect loss from heterogeneous hydrolysis of N₂O₅ (→ 2HNO₃) on particulate surfaces with an estimated uptake coefficient of $\gamma_{\text{N}_2\text{O}_5} = 0.07$ (~42%), and the indirect loss from homogeneous hydrolysis of N₂O₅ (~7%). Other sources such as dry deposition of NO₃ and N₂O₅, or heterogeneous loss of NO₃ were found to be minor and negligible. A study in Helgoland (Martinez et al., 2000) showed a clear anticorrelation between the lifetime of N₂O₅ and total particulate surface area, indicating the most likely sink for NO₃ is indirect, the hydrolysis of N₂O₅ on moist aerosols. The oxidation of hydrocarbons are known to contribute to particle formation. In particular, photochemical oxidation of aromatic hydrocarbons of anthropogenic origin (Forstner et al., 1997) and monoterpenes of biogenic origin (Yokouchi and Ambe, 1985; Kavouras et al., 1999), are known to have significant yields of secondary organic aerosols. Recently, it has been shown that photooxidation of monoterpenes contributes significantly to new particle formation in forested regions (Kavouras et al., 1999). Cis-pinonic acid and other acids derived from monoterpene oxidation were the primary organic products found in the particles in that study, with a diurnal pattern that correlated with the primary daytime oxidants, OH and O₃. Pinonaldehyde and nopinone, the known oxidation products of α - and β -pinene, respectively, were also found to be present in the particle phase, although with a reverse diurnal trend compared to that of the acids. It was speculated that the increase of these carbonyls at night could result from reactions of the monoterpenes with NO₃ and/or O₃, followed by condensation onto pre-existing seed particles, aided by the lower temperatures at night.

In this paper, we present measurements of NO₃ by differential optical absorption spectroscopy (DOAS), and other gaseous and particulate species from a rural/suburban site during the Pacific 2001 Air Quality Field

Study. The main purpose of measuring NO₃ at this site was to determine the role of this radical in nighttime chemistry, including its role as an oxidant and its role in both inorganic and organic particulate formation.

From NO₃ and NO₂ measurements, we have calculated N₂O₅ levels for two nights, presuming that chemical equilibrium is established between these species. We then explore the contribution of these species to total NO_y measured at the site. N₂O₅ lifetimes estimated using time-dependent aerosol distributions measured on site, were used to calculate heterogeneous and homogeneous N₂O₅ hydrolysis rates and the resultant cumulative gaseous and particulate HNO₃ that would be produced overnight. The average calculated cumulative particulate nitrate is then compared to measured nighttime fine particulate nitrate. Finally, we present day and night measurements of particulate phase pinonaldehyde, a dominant product of the NO₃ + α -pinene reaction, in order to assess the potential role of NO₃ in nighttime secondary organic aerosol formation.

2. Nighttime chemistry

The most significant reactions in the formation and destruction of NO₃ are discussed below. NO₃ is initially formed from the reaction,



High production efficiencies of NO₃ are favored by high NO₂ and O₃ concentrations. High concentrations of NO₂ are seen in moderately polluted air masses that have experienced high NO_x intrusions (predominantly NO, from combustion sources), but sufficiently aged such that a significant fraction of the NO has been oxidized to NO₂; through reaction with O₃,



or through reactions with peroxy radicals, RO₂ (R = H, CH₃, ... other organics)

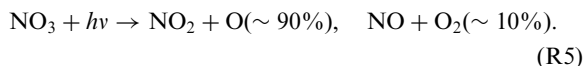


In fresh polluted air masses, NO₃ is quickly destroyed by reaction with NO



and as such, the two species do not coexist at significant levels.

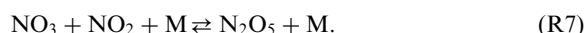
Being a radical species, a number of other loss mechanisms are known for NO₃. The most significant daytime loss, apart from reaction with NO, is photolysis at wavelengths less than 640 nm



Daytime photolysis is rapid enough such that NO_3 is usually below detection limits during the day (i.e. < 1 pptv), although under favorable conditions, measurable levels can be seen late in the day on occasion (Geyer et al., 2002). Certain organics, R, can react rapidly with NO_3 including alkenes, cresols, dimethylsulphide and monoterpenes,



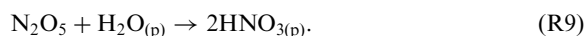
Reaction (6) yields oxygenated organic products that may be condensable, contributing to particle nucleation or condensation, and possibly heterogeneous reactions on preexisting particles (Jang and Kamens, 2001; Iraci and Tolbert, 1997; Tobias et al., 2000) for carbonyl products. Another significant loss mechanism for NO_3 is the reversible formation of nitrogen pentoxide, N_2O_5



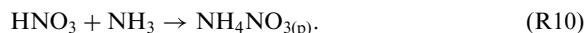
This reaction is reversible because of the thermal decomposition of N_2O_5 , yielding a highly temperature-dependent, but rapidly achieved equilibrium between NO_3 , NO_2 , and N_2O_5 . The equilibrium frequently lies to the right, allowing buildup of significant levels of N_2O_5 , which thus acts as a nighttime reservoir species for NO_3 and other nitrogen species. Because an equilibrium exists (R5), direct losses of N_2O_5 are also indirect losses of NO_3 . These direct losses include homogeneous reaction with water to form gaseous nitric acid, HNO_3



and the heterogeneous reaction on wet particulate surfaces to form particulate nitrate



Nitric acid is lost due to multiple processes including dry deposition, photolysis, and reaction with NH_3 to form particulate ammonium nitrate



3. Experimental

The NO_3 radical was measured along a 3.34 km non-returning light path using DOAS. The measurement system included a 4×100 W quartz halogen light source at the transmitter location and a light collection and measurement system at the receiver location. The receiver system was housed in a metal shed. Light was collected by a 8" Newtonian telescope and focussed onto a fiber optic coupler mounted in the eyepiece. A diffuser, to lessen the effects of atmospheric turbulence noise (Stutz and Platt, 1997), and a red filter, to reduce stray light effects, were placed in the fiber optic

coupler. A 4 m, 0.6 mm diameter single core fiber optic carried light to the spectrometer. A red optimized S2000 ocean optics spectrometer cooled to -10°C was used for collecting spectra with an optical resolution of ~ 0.6 nm and a pixel resolution of ~ 0.17 nm ($\lambda_{\text{blaze}} = 750$ nm, 1200 lines mm^{-1} , 2048 element CCD, 25 μm slit). Typically a 350 ms exposure was used, and 5000 spectra were averaged before storing to disk to give a nominal averaging time of ~ 29 min. OOIBase32 and GRAMS software were used to process the software into absorption spectra and to integrate the absorption features. Typically, an early morning spectra just after sunrise was used as a reference (when it is known that photolysis reduces NO_3 below detection limits). The presence of two significant absorption features at 623 and 662 nm were used to qualitatively identify the presence of NO_3 in each spectrum. The absorption feature centered at 662 nm was used for quantification of NO_3 concentrations, C , by integrating the differential absorption strength of the feature, $A'_e(\lambda)$, over the wavelength region of interest, and relating this to known absorption cross sections of NO_3 , and the path length, L

$$C = \frac{\int_{\lambda_1}^{\lambda_2} A'_e(\lambda) d\lambda}{L \int_{\lambda_1}^{\lambda_2} \sigma'_e(\lambda) d\lambda}. \quad (1)$$

The integrated differential cross section used in this study was $\sigma'_e(\lambda) = (5.32 \pm 1.09) \times 10^{-17}$ cm^2 molecule $^{-1}$ nm over the wavelength range, 658.9–667.0 nm, determined from NO_3 cross sections (DeMore et al., 1997). Mixing ratios of NO_3 are reported at 25°C and 1 atm. Detection limits (3σ) for NO_3 ranged from 3.9–7.6 ppt on the four nights with an average of 5.7 ppt.

Methods for measuring NO , NO_2 , NO_y , and O_3 have been described more fully elsewhere (Hayden et al., 2003), but a brief description follows. Alternating 1 min measurements of NO and NO_2 were made using an Ecophysics model CLD770 NO analyzer (based on the chemiluminescence of the $\text{NO} + \text{O}_3$ reaction) and an Ecophysics model PLC760 that photolytically converted a fraction of ambient NO_2 to NO using a 300 W high-pressure Xenon arc lamp that was filtered to 320–420 nm for high NO_2 selectivity. Uncertainty was determined to be 16% + 30 pptv for NO and 21% + 60 pptv for NO_2 (3σ , 1 min).

A Thermo Environmental Instruments Inc. (TEI) model 42S instrument was used to make 3 min measurements of NO_y species (and NO). Oxides of nitrogen were reduced to NO by passing the ambient air over molybdenum heated to 325°C . The uncertainty of NO_y due to known factors was estimated to be 11% + 90 pptv (3σ , 3 min). A TEI Model 49 instrument was used to measure ozone by short path UV absorption. The instrument is calibrated against a NIST certified ozone standard. Particulate phase carbonyl compounds were measured by extraction of samples

collected on Teflon coated quartz fiber filters. Filters were collected daytime (10 a.m.–6 p.m.) and nighttime (8 p.m.–8 a.m.). The methodology for these measurements has been fully described elsewhere (Liggio and McLaren, 2003). Inorganic components of the aerosols were measured according to particulate size using a micro orifice uniform deposition impactor with Teflon filters; the filters were analyzed by ion chromatography. The MOUDI samples were collected day and night, identical to the schedule for the high volume samples. A complete description of the MOUDI methodology is given in another publication (Anlauf et al., 2004).

Measurement of all species, except NO_3 , were made at the Sumas Eagle Ridge (SER) site in the eastern end of the Lower Fraser Valley. A full description of the site is given in the overview paper (Li, 2004). The site (300 masl) was situated on a local maximum, elevated ~ 250 m above the main valley floor in a $\sim 10,000$ m² clearing in the mixed coniferous and deciduous forest. Because of the elevation, the site was often above the nocturnal boundary layer at night. The surrounding area (within 3 km radius) included significant forests at elevation, suburban areas, agricultural areas, and a major freeway in the main valley. The City of Abbotsford center was ~ 3 km west of the site. For logistical reasons, it was difficult to co-locate the DOAS measurements with the SER site. The DOAS measurement was situated in the SER site vicinity, such that the measured NO_3 levels might be typical of those experienced at SER site. The transmitter was situated on the main valley floor ~ 3.5 km southwest of the SER site (60 masl), ~ 5 m off the ground. The beam traversed upwards 3.34 km ending at the receiver location (230 masl), located on a cliff ridge approximately 600 m south of the SER site. The receiver location was also frequently above the nocturnal boundary layer at night.

4. Results and discussion

DOAS measurements were made on four nights in 2001; 15–16, 20–21, 29–30, 30–31 August. The results are shown in Fig. 1, with standard uncertainties ($\pm 1\sigma$) for each measurement. The standard uncertainties include uncertainties in the integrated differential cross section of NO_3 , the path length, and integration of absorption spectra which includes effects of instrumental and atmospheric noise. It is worth mentioning that these measurements represent the average mixing ratios of NO_3 over the length of the light path. Significant gradients are possible, due to the fact that the light beam is passing up through the nighttime inversion, and the possibility that higher levels of NO are present below the inversion, depleting the NO_3 as well as the O_3 in that lower layer. Peak levels of NO_3 on the four nights

ranged from 14–48 ppt, with a mean maximum level of 34 ppt. These levels are very typical of polluted continental air masses (Finlayson-Pitts and Pitts, 2000; Platt, 1994; Platt et al., 1984; Geyer et al., 2001).

For further analysis, there were two nights (29/30; 30/31 August) when all instruments were working, including O_3 , NO, NO_2 , NO_3 , NO_y and MOUDI impactors. The time series for O_3 , NO, NO_2 and NO_y are shown in Fig. 2(a) for these two nights. The O_3 and NO_2 levels were moderate but sufficient to sustain the formation of NO_3 by reaction (1). NO levels were very low at this elevated site, usually below detection limits, with the exception of some high levels (approaching 7 ppb) observed on the 29/30 August, with simultaneous spikes in NO_2 and NO_y , and clear titrations of O_3 . These short duration exceedances (~ 40 min) are consistent with either a breakthrough of polluted air from below the nocturnal boundary layer at the site, or impact from a very close NO_x source. A spike in NO from the detection limit, 30 ppt, to 7 ppb, would lower the lifetime of NO_3 with respect to reaction with NO from ~ 1 min to 0.2 sec, thus eliminating any NO_3 and N_2O_5 from the air mass. It is clear from the NO_3 measurements, that such an event did not happen in the DOAS path on this night. Since the DOAS path is at a slightly lower elevation than the SER site, and coupled with the fact that there was no simultaneous CO spike (not shown) correlated with the NO_x spike, it is highly unlikely that a breakthrough from below the nocturnal inversion occurred. This would suggest a local NO_x source above the nocturnal inversion. The exceedances were consistent with a wind direction of $137 \pm 4^\circ$, which is precisely the direction of the diesel generator used to provide electricity to the site at a distance of ~ 400 –500 m. Diesel combustion is known to have a much lower CO/ NO_x ratio than gasoline combustion; 0.72 vs 21.4 mol mol⁻¹, respectively (Deslauriers, 1995), which would explain the lack of a significant coincident CO peak if it were a diesel combustion source. The NO/ NO_2 ratio, is also consistent with a transit time of a few minutes given the rate of reaction of ~ 30 ppb O_3 with NO, and an assumed source that is originally rich in NO. For the above reasons, we are strongly confident that the SER site was impacted briefly on 29/30 August by a very local diesel plume for a 44 min period followed later by a 40 min period. The DOAS measurements of NO_3 , being physically separate from the SER site, were not impacted by this plume. Instead of removing these time periods from the forthcoming analysis, we have decided to interpolate NO_y and NO_2 levels for these brief periods from the appropriate levels before and after the impacts occurred.

The dynamic equilibrium between NO_2 , NO_3 and N_2O_5 has been shown to be maintained to a large extent in the atmosphere, except for periods of rapid air mass change (close to sources) or during periods close to

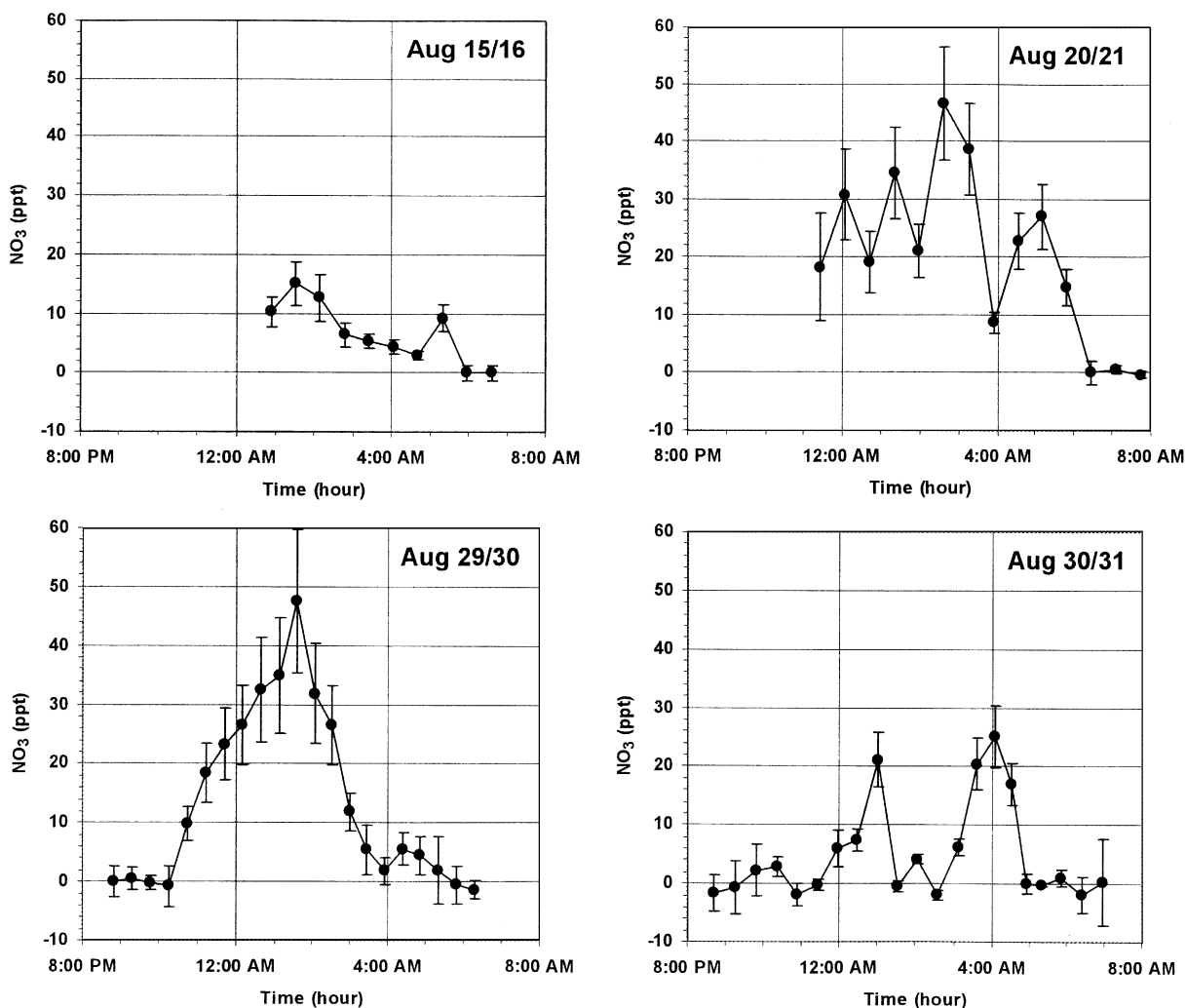


Fig. 1. Measured NO₃ levels at the DOAS site. Error bars indicate the estimated uncertainty ($\pm 1\sigma$). Sunset (pm)/Sunrise (am): 15/16-8:26/6:02; 20/21-8:16/6:09; 29/30-7:58/6:22; 30/31-7:56/6:24.

sunrise and sunset (Brown et al., 2001). In this study, we estimate the concentrations of N₂O₅ at the SER site by assuming that equilibrium is maintained and that the measured NO₃ levels in the DOAS path are typical of the levels experienced at the SER site. The long averaging times for NO₃ (~30–40 min) aid us for the first approximation. The second approximation may not be valid due to the possible positive vertical gradient in NO₃. As such, the measured NO₃ is likely a lower estimate of that experienced at the SER site, due to the higher elevation of the SER site and the gradient of the light beam. Likewise the calculated N₂O₅ is a lower estimate of that at the SER site. The value of the equilibrium constant used here was $K_7 = 5.5 \times 10^{-27} \exp((10724 \pm 75) T^{-1})$ (Wängberg et al., 1997), which is valid for the range 7–21°C. Temperature measured at

the site varied from 15 to 20°C on the two nights. Calculated N₂O₅ levels are shown in Fig. 2(b), with peak values from 200 to 300 ppt.

The fractional contribution of N₂O₅ and NO₃ to the total gaseous NO_y is illustrated in Fig. 3(a) with peak values on the two nights of 0.07–0.09 (7–9%). These are lower limits for reasons discussed previously. Brown et al. (2001) have reported fractional contributions as high as 30% on some nights at a rural site outside Boulder Colorado. A more complete discussion of the NO_y budget measured at this site is given elsewhere (Hayden et al., 2004). This may be compared to the NO_y partitioning measured at another elevated forest site in Quebec (Hayden et al., 2003).

The homogeneous and heterogeneous hydrolysis rates of N₂O₅, reactions (R8) and (R9) respectively, were

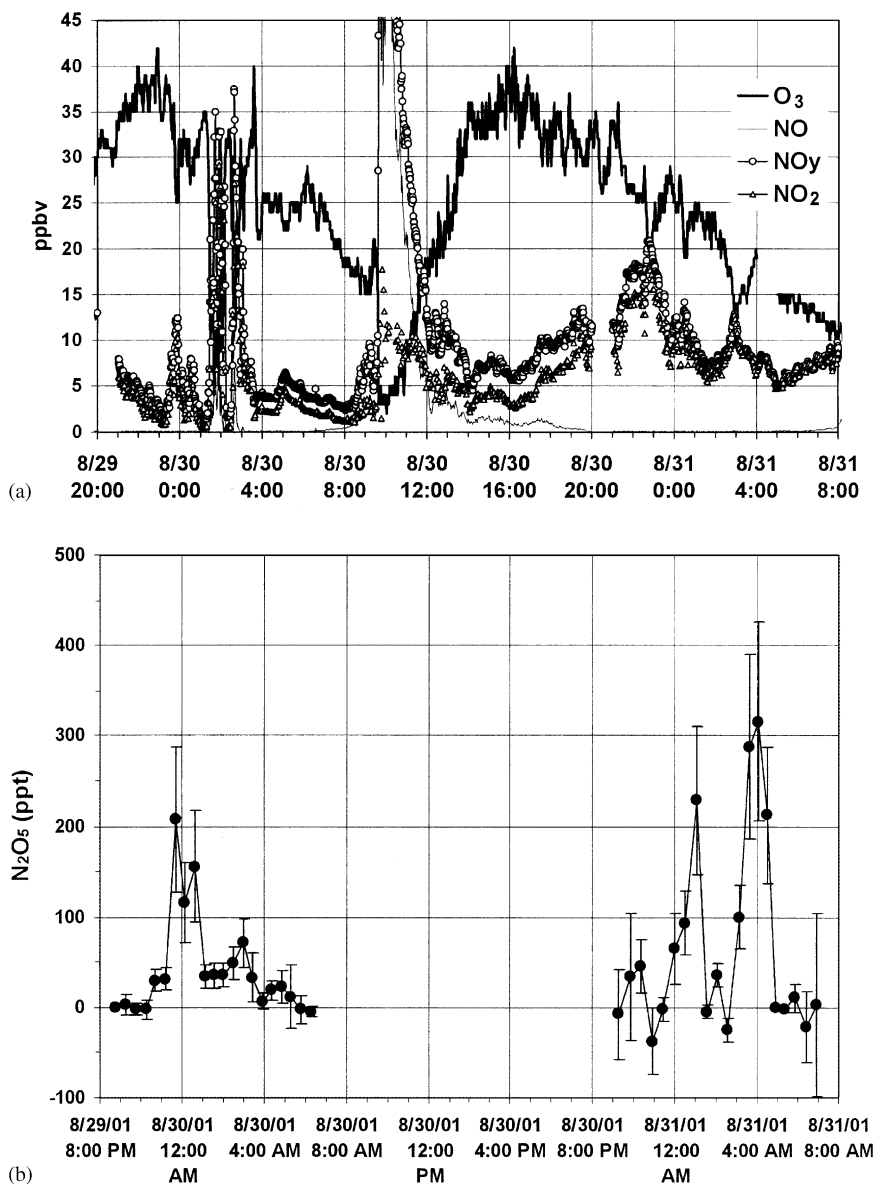


Fig. 2. (a) gaseous measurements of O₃, NO₂, NO and NO_y at the Sumas site. (b) calculated N₂O₅ levels at the Sumas site using measured NO₃ and NO₂ levels and assuming equilibrium $K = [\text{N}_2\text{O}_5]/[\text{NO}_2][\text{NO}_3]$.

calculated over the course of the two nights. For the homogeneous reaction, R8, time-dependent H₂O concentrations measured at the SER site were used, falling in the range $3.3\text{--}4.3 \times 10^{17}$ molecules cm⁻³. Similar to the study by Geyer et al. (2001), we have used the recommended homogeneous rate constant proposed by Dimitroulopoulou and Marsh (1997), adapted from the binary component only, of the rate constant measured by Mentel et al. (1996). The temperature-dependent rate constant varied between 2.1 and 3.8×10^{-22} molecules⁻¹ cm³ s⁻¹ on the two nights. For the

heterogeneous hydrolysis of N₂O₅ on aerosols, the N₂O₅ lifetimes were estimated using the aerosol size distributions measured at 5 min intervals (Mozurkewich et al., 2004). The uptake by particles in each size bin were calculated using the Fuchs-Sutugin equation (Fuchs and Sutugin, 1971) with a reaction probability of $\gamma_{\text{N}_2\text{O}_5} = 0.07$, summed over all size bins ($d_m < 650 \mu\text{m}$). The value of $\gamma_{\text{N}_2\text{O}_5}$ is variable and uncertain. The chosen value for these calculations lies between the uptake coefficient on H₂O; $\gamma_{\text{N}_2\text{O}_5} \sim 0.01\text{--}0.06$ (Finlayson-Pitts and Pitts, 2000), and those on aqueous H₂SO₄ solutions;

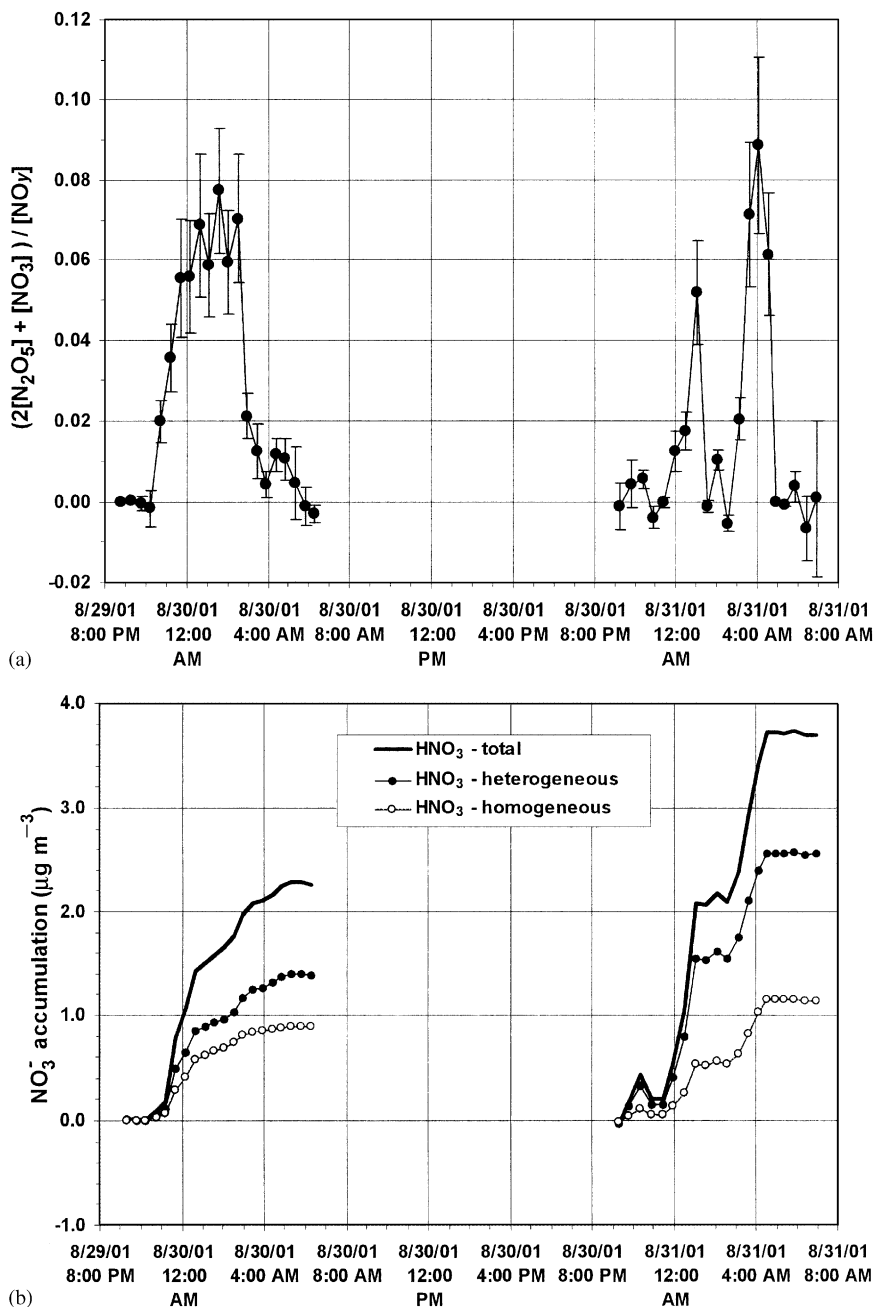


Fig. 3. Results for two nights: (a) fraction of gaseous NO_y accounted for by measured NO_3 and N_2O_5 (b) calculated cumulative formation of gaseous HNO_3 (homogeneous reaction), particulate nitrate (heterogeneous reaction) and the total nitrate from N_2O_5 hydrolysis.

$\gamma_{\text{N}_2\text{O}_5} \sim 0.05\text{--}0.16$ (DeMore et al., 1997). It is larger than those measured on H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ particles which decrease from 0.05 to 0.02 as relative humidity decreases (Hu and Abbatt, 1997) and larger than the uptake coefficients measured on NaNO_3 particles, $\gamma_{\text{N}_2\text{O}_5} \sim 0.002\text{--}0.003$, with a reported nitrate effect

(Mentel et al., 1999). The value of $\gamma_{\text{N}_2\text{O}_5} = 0.07$ was ultimately chosen to be most similar to that estimated in the continental boundary layer in a field study near Berlin, $\gamma_{\text{N}_2\text{O}_5} = 0.07$ (Geyer et al., 2001) and those estimated in another field study relevant to the marine boundary layer where the estimated coefficient was

found to lie most frequently in the range, $\gamma_{\text{N}_2\text{O}_5} = 0.04\text{--}0.10$ (Allan et al., 2000).

Instantaneous rates of production of particulate HNO_3 were calculated from the N_2O_5 lifetimes. It should be noted that the heterogeneous hydrolysis reaction may occur on coarse particles as well, the calculation here was limited to $d_m < 650$ nm since this was the limitation of the DMA-CNC measurement system used at the site. Fig. 3(b) shows the cumulative buildup of HNO_3 each night from these two hydrolysis channels starting from zero and assuming no losses occur overnight. The data are summarized in Table 1. The homogeneous production of gaseous HNO_3 produces a cumulative total (from sunset to sunrise) of 0.89 and $1.14 \mu\text{g m}^{-3}$ on 29/30 August and 30/31 August respectively, while the overnight cumulative total heterogeneous production of HNO_3 is 1.38 and $2.56 \mu\text{g m}^{-3}$ respectively. Also shown in the table are the appropriate average cumulative values calculated for the overnight period, which are more appropriate for comparison to 12 h filter samples, such as those collected on the MOUDI. There are uncertainties in this comparison, since the filter sampling is performed in a Eulerian framework (point measurement), while the average cumulative particulate nitrate calculation is pseudo-Lagrangian, requiring either a static air mass, or a completely homogeneous air mass within 12 h transport distance from the SER site, to be strictly comparable in a quantitative sense. This distance would be ~ 120 km for a 10 km h^{-1} wind speed.

Fig. 4 presents the results for day and night samples collected by the MOUDI at the SER site for three 24 h periods. For clarity and discussion, only five ions are presented. A more complete discussion of MOUDI results collected at this and other sites is presented elsewhere (Anlauf et al., 2004). The results are presented as nanoequivalents m^{-3} , as a function of the mid-point diameter of each stage, to facilitate comparison of the chemical balancing of the inorganic constituents in the particle phase. The daytime samples show very little fine particle nitrate; the inorganic constituents of the fine particles appears to be composed primarily of $(\text{NH}_4)_2\text{SO}_4$. The daytime coarse particles are sometimes

composed of aged sea salt particles, NaNO_3 , with Cl^- replaced by NO_3^- due to the reaction (see 27 August-daytime),



The daytime coarse particles also have some components of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$. On each night, there is a large increase in the fine particle nitrate. The daytime fine particle nitrate on 27, 29, 30 August were: 0.08, 0.14, $0.09 \mu\text{g m}^{-3}$; the nighttime values were 2.50, 0.99, $1.48 \mu\text{g m}^{-3}$ correspondingly. The fine particles have a composition that is mixed, NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$. There appears to be an increase in the coarse particle nitrate at night as well, although not as dramatic as the fine particle nitrate. The daytime coarse particle nitrate on 27, 29, 30 August were: 1.54, 0.39, $0.13 \mu\text{g m}^{-3}$; the nighttime values were 2.85, 0.62, $0.41 \mu\text{g m}^{-3}$ correspondingly. The increase in fine particle nitrate, from day to night, is shown in Table 1 for 29/30 and 30/31 August, for comparison to the average overnight cumulative fine particle nitrate calculated from the heterogeneous reaction of N_2O_5 with fine particle surfaces. These two results agree to within 10% each night, suggesting that most of the measured fine particle nitrate does indeed originate from the heterogeneous N_2O_5 hydrolysis source. The agreement may be somewhat fortuitous though, considering the significant uncertainties and assumptions that exist in the calculated value. The following uncertainties are identified, all having a positive correlation with calculated particle nitrate and all expected to be random: (i) measured NO_3 , $\pm 25\%$, (ii) estimated $\gamma_{\text{N}_2\text{O}_5}$, $\pm 43\%$, (iii) K_7 , $\pm 20\%$, (iv) measured NO_3^- , $\pm 20\%$. These contribute to an estimated random uncertainty of $\pm 57\%$ in the calculated fine particle nitrate values. In addition to this, a considerable biased uncertainty exists in the assumption that the measured NO_3 along the DOAS path is representative of that experienced at the SER site. Because of the expected positive gradient with height in NO_3 , the calculated N_2O_5 is a lower limit with an estimated negative biased uncertainty of 0–100%. Since the particulate nitrate is roughly proportional to N_2O_5 , the calculated particulate nitrate would have this same

Table 1

Comparison of calculated overnight cumulative and average cumulative HNO_3 from homogeneous (gas) and heterogeneous (particle) hydrolysis of N_2O_5 , with measured nighttime buildup of fine particle nitrate from analysis of MOUDI samples

Date	Calculated						Measured Nighttime filter accumulation ($\mu\text{g m}^{-3}$)
	Cumulative HNO_3 ($\mu\text{g m}^{-3}$)			Avg cumulative HNO_3 ($\mu\text{g m}^{-3}$)			
	Gas	Particle	Total	Gas	Particle	Total	Fine particulate
29/30 August	0.89	1.38	2.27	0.55	0.82	1.37	0.85
30/31 August	1.14	2.56	3.7	0.61	1.49	2.1	1.39

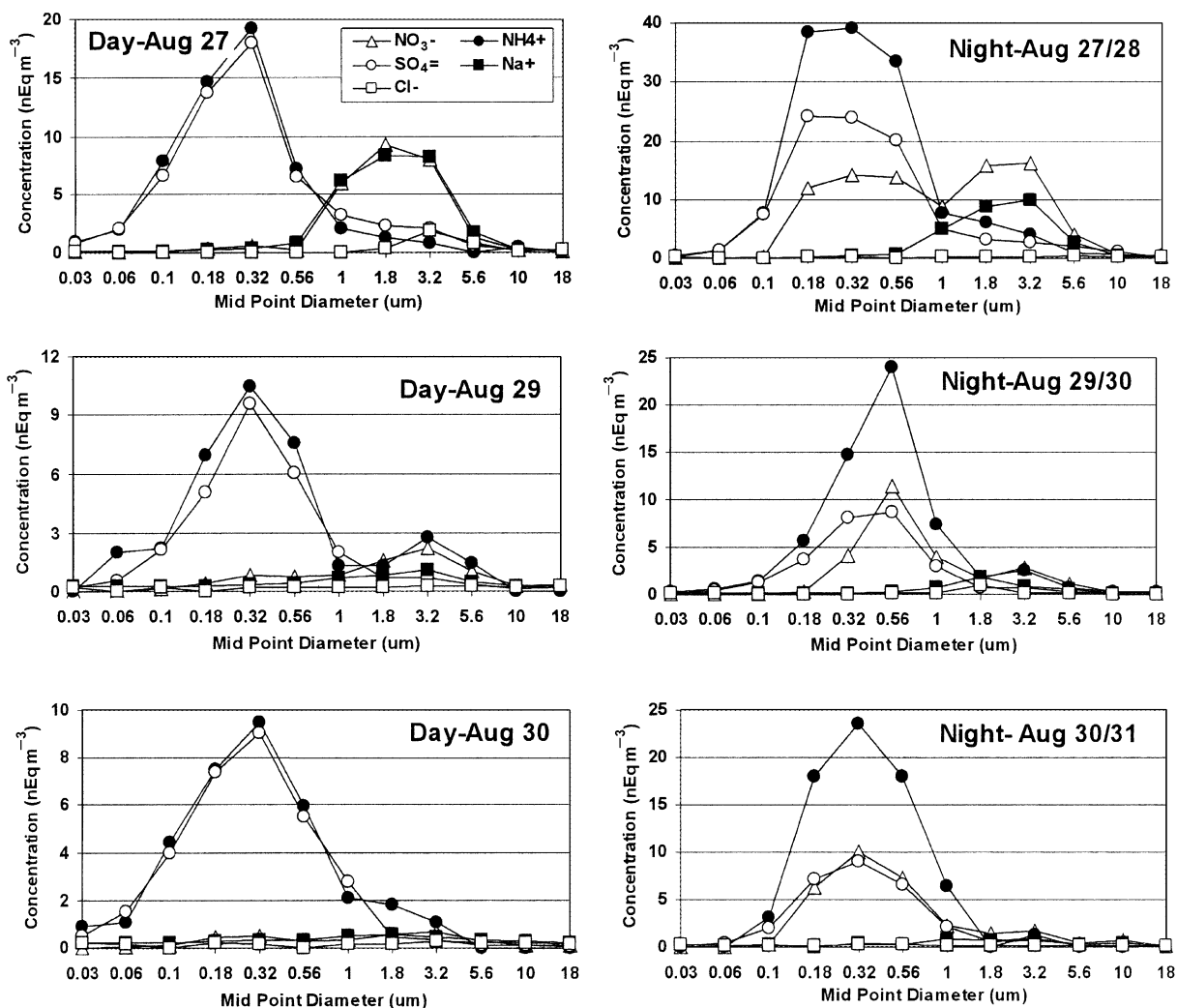


Fig. 4. Results of ion analysis of daytime and nighttime MOUDI samples as a function of particle size for 3 days.

negatively biased uncertainty. Despite these uncertainties, the results show that a significant fraction, likely a majority fraction, of the fine particle nitrate is formed from the heterogeneous hydrolysis of N_2O_5 on particulate surfaces. It is likely that this process is occurring on coarse particles as well, although a quantitative comparison is not possible here due to the lack of surface area data for the coarse particles. There is also undoubtedly some particle nitrate, both fine and coarse, that results from deposition of gaseous HNO_3 , both residual from the daytime source ($\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$) and other nighttime sources (R6, R8, R10 for example), on particles.

The measured amounts of particle phase pinonaldehyde at the SER site, is shown in Fig. 5, along with the same values measured at the Langley site (rural agricultural) and the Slocan Park site (urban) through-

out the field study. The most striking observation is the obvious increase in particulate pinonaldehyde at night compared to the day samples at all sites. Highest values were seen at the SER site, which had the most significant local forests. One can define a night preference ratio (NPR), the ratio of nighttime to daytime particulate organic concentration. The NPRs were calculated for each nighttime/day sample pair. For comparison, the median NPRs ($n = 12$) for all species at the SER site were: formaldehyde—0.63; acetaldehyde—0.94; acetone—0.85; glyoxal—1.14, methylglyoxal—0.81; nonanal—0.46, pinonaldehyde—2.49. The median NPR for pinonaldehyde, 2.49, with an average of 3.24 ($n = 12$), indicates a much higher preference for pinonaldehyde in the particle phase at night, the only species of all those listed that has a statistically significant nighttime preference. We believe this preference is related to the

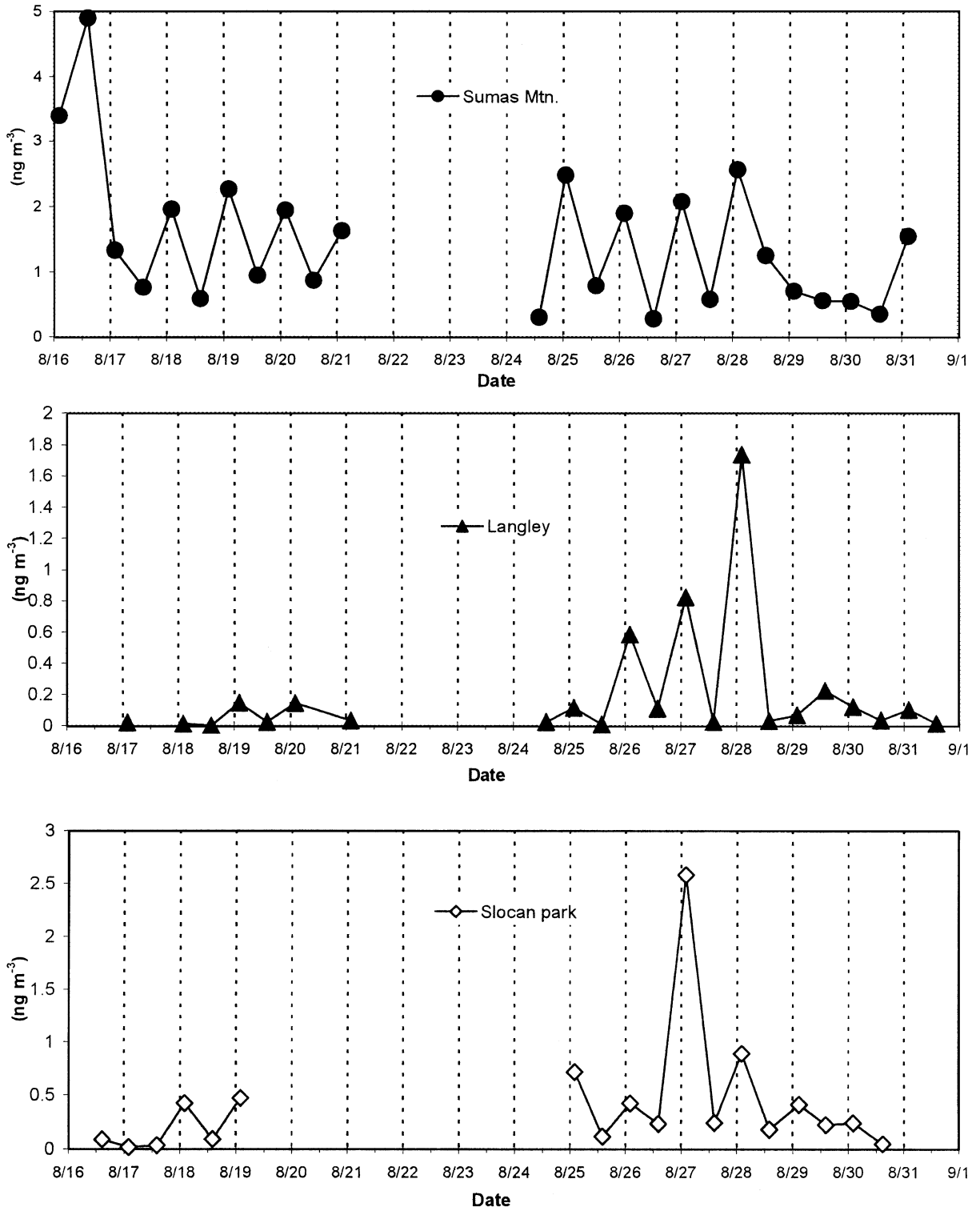


Fig. 5. Particulate pinonaldehyde measurements at the Sumas site for daytime and nighttime filter samples.

high nighttime preference for the NO₃ radical, which oxidizes α -pinene at night, coupled with low OH levels, that normally would react quickly with pinonaldehyde during the day. The particulate phase pinonic acids, believed to be derived from OH initiated oxidation of α -pinene, were found to have a high daytime preference in the Pacific 2001 field study (Shantz et al., 2004; Cheng et al., 2004). A more complete analysis of the biogenic contribution to secondary organic aerosols at the SER site, including both daytime and nighttime processes will be the focus of another study in the near future.

Acknowledgements

We would like to acknowledge the National Science and Engineering Research Council, and the Canadian Foundation for Climate and Atmospheric Science for funding. We thank Wayne Belzer, Bruce Thomson, staff at Eagle Mountain Homes and staff at University College of the Lower Fraser Valley for logistical support and technical assistance. Calculations of N₂O₅ lifetimes were performed by Michael Mozurkewich. Ken Stubbs and staff at the GVRD supplied trace gas and meteorological data from their MAMU unit deployed at the Sumas site, as well as technical support. We thank Mauro Aiello, Daniel Aubin, Nina Ivanis, Desiree Toom-Sauntry, Al Wiebe and Heng Yao for technical support and Joy McCourt for assistance in manuscript preparation.

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