

Conversion of sea salt aerosol to NaNO_3 and the production of HCl: Analysis of temporal behavior of aerosol chloride/nitrate and gaseous HCl/ HNO_3 concentrations with AIM

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Abstract

Equilibrium modeling predicts that atmospheric sea salt can partition gas-phase HNO_3 to solid- or aqueous-phase NaNO_3 . One month of semi-continuous and simultaneous measurements of particulate chloride and nitrate and gaseous HCl and HNO_3 concentrations were made in the Tampa, Florida, as part of the Bay Region Atmospheric Chemistry Experiment (BRACE). Tampa's proximity to coastal and bay waters enriches its atmosphere with sea salt. To help explain and interpret the observed time-dependent concentration and gas-to-particle phase partitioning behavior for the NaCl – HNO_3 reaction, we applied the Aerosol Inorganics Model III (AIM) to the measurement data. Good agreement between model predictions and observations was found. Measurement and modeling results suggested that coarse-mode sea salt particles from the Atlantic Ocean arrived in the morning at the monitoring site when relative humidity (RH) was high and the nature of the equilibrium least favored the outgassing of HCl from the particles. As the RH dropped in the afternoon, the equilibrium favored outgassing of HCl and the particulate nitrate concentration increased even as the concentration of coarse particles decreased. This effect was tied to the change in the ratio of nitrate to chloride activity coefficients $\gamma_{\text{NO}_3^-}/\gamma_{\text{Cl}^-}$ with RH. AIM simulations indicated that this ratio approached unity at high RH but could take on small values (~ 0.05) at the lowest RH observed here. Thus, the particle phase slightly favored nitrate over chloride at high RH and greatly favored it at lower RH. Modeling revealed how diurnal changes in RH can rapidly shift HNO_3 concentrations from gas- to particle-phase and thus affect the distance over which nitrogen is transported.

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1. Introduction

Nitric acid (HNO_3) partitioning between gas and aerosol phases can significantly affect nitrogen transport and deposition. If HNO_3 , for example, is converted into particulate nitrate (NO_3), its atmospheric

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removal rate may decrease and the ultimate location of its nitrogen deposition may move further downwind (Pryor and Sorensen, 2000; Pryor and Barthelmie, 2000; Evans et al., 2004). Removal rates of aerosol nitrogen will depend not only on meteorology but on particle size distribution, with coarse particle NO_3 more effectively removed than fine particle NO_3 by dry (Russell et al., 2003; Evans et al., 2004) and wet deposition processes (Lee et al., 1999; Chate et al., 2003; Calderón et al., 2006). The presence of aerosolized sea salt or soil may favor the formation of coarse particle NO_3 , for example, sodium nitrate (NaNO_3) or calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), instead of fine particle ammonium nitrate (NH_4NO_3) or ammonium chloride (NH_4Cl) (Campbell et al., 2002). Sodium chloride (NaCl)—or more specifically, sea salt—is aerosolized when air bubbles entrained in waves rise to, burst, and collapse at the sea surface, or when high winds shear off the crest of a wave (Andreas, 1998; de Leeuw, 1999). Wind-dependent concentrations of sea salt Cl can vary from 1 to $100 \mu\text{g m}^{-3}$ at coastal sites (Gustafsson and Franzén, 2000), and averaged $7 \mu\text{g m}^{-3}$ in clean marine air observed at Mace Head, Ireland (Cavalli et al., 2004), for example.

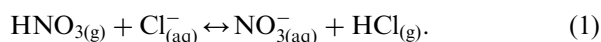
Nitric acid is produced by the reaction of nitrogen dioxide (NO_2) with the hydroxyl radical ($\text{OH}\cdot$), which is driven by daytime photochemical processing of nitrogen oxides and by nighttime reactions of NO_2 with ozone (O_3) to produce the $\text{NO}_3\cdot$ radical (Seinfeld and Pandis, 1998). The $\text{NO}_3\cdot$ radical rapidly combines with NO_2 to form N_2O_5 , which can be absorbed by condensed water to form HNO_3 (Seinfeld and Pandis, 1998).

Many investigators have observed that the depletion of chloride (Cl) and the simultaneous occurrence of NO_3 (Newberg et al., 2005) is particularly pronounced in coarse particles, typical of sea salt aerosol (Wu and Okada, 1994; Yoshizumi et al., 1996; Pakkanen, 1996; Roth and Okada, 1998; Pio and Lopes, 1998; Zhuang et al., 1999; Sellegri et al., 2001; de Leeuw et al., 2001; Bardouki et al., 2003; Topping et al., 2004; Lee et al., 2004; Bates et al., 2004; Chou et al., 2005); similar uptake of nitrogen oxides in general and HNO_3 in particular on the surface of dust/soil-derived particles have also been repeatedly observed (Wu and Okada, 1994; Pakkanen, 1996; Pakkanen et al., 1996; Zhuang et al., 1999; Jordan et al., 2000; Song and Carmichael, 2001; Topping et al., 2004; Bates et al., 2004).

As a consequence of the NaCl – HNO_3 reaction, sea salt aerosol becomes progressively depleted of

Cl as a maritime air mass is modified by anthropogenic emissions (Pio and Lopes, 1998; Niemi et al., 2005). The progress of the reaction is accompanied by the release of gaseous hydrochloric acid (HCl). Eldering et al. (1991) observed in coastal southern California that the extent of depletion of Cl in sea salt aerosol and the increase in HCl concentration was well matched.

Although the initial interest was in the reaction of atmospheric sea salt with NO_2 to form NaNO_3 (Robbins et al., 1959; Mamane and Gottlieb, 1990), Abbatt and Waschewsky (1998) have since established that the NaCl – HNO_3 reaction (1) is much faster than the NO_2 – NaCl reaction.



The NaCl – HNO_3 reaction has been studied in the laboratory by a variety of instrumental techniques, from electron microscopy (Mamane and Gottlieb, 1990; Allen et al., 1996, 1998; Krueger et al., 2003), X-ray photoelectron spectroscopy (Laux et al., 1994; Allen et al., 1996; Ghosal and Hemminger, 1999, 2004), infrared and Raman spectroscopy (Sporleder and Ewing, 2001; Zangmeister and Pemberton, 2001) to mass spectrometry (De Haan and Finlayson-Pitts, 1997; Haddrell et al., 2005), the latter even with less than a monolayer of salt particles (Hoffman et al., 2003) or with single particles (Tolocka et al., 2004). The outstanding observation that is common to all of the studies is that water present in the aerosol plays a profoundly important role.

Under completely dry conditions, reaction (1) may become self-limiting due to coating of the NaCl surface with NaNO_3 (Hemminger, 1999; Zangmeister and Pemberton, 2001), but at any realistic relative humidity (RH), even at RH levels substantially below the bulk deliquescence points of NaCl or NaNO_3 . Upon the formation of 1–2 monolayers of NaNO_3 , the reaction does not stop but rather NaNO_3 reorganizes to form microcrystallites and exposes fresh NaCl (Allen et al., 1996; Laux et al., 1996). The reaction shows no sign of stopping (Sporleder and Ewing, 2001). When investigated below the bulk deliquescence point, synthetic sea salt aerosols exhibit a HNO_3 uptake rate an order of magnitude greater than with pure NaCl (De Haan and Finlayson-Pitts, 1997); the study of Weis and Ewing (1999) have since indicated that even at low (9–30%) RH, sea salt particles contain more water than can be accounted for by the hydrates present in them. The work of Ghosal and Hemminger (1999, 2004) showed that even NaCl particles in the

1–10 μm size, where the mass mode of sea salt particles normally exists, contains water so strongly adsorbed on their surface that it cannot be removed even at 200 °C.

The relevance of these observations to much more hygroscopic sea salt, which is known to contain crystalline hydrates at the typical ambient RH for a coastal area, however, may be limited. In addition, the work of Ghosal and Hemminger (2004) has shown that exactly how a pure NaCl sample is prepared can profoundly affect the results.

Predictably not all observations by all groups are concordant. Ten Brink (1998) reported that a measurable reaction between HNO_3 and NaCl occurs only when the latter is in the droplet phase and furthermore, the kinetics of the overall reaction is limited by the rate at which HCl is produced. The view of Tolocka et al. (2004), who studied the reaction of HNO_3 with 100–220 nm NaCl droplets by single particle mass spectrometry, is similar. Some models (Von Salzen and Schlunzen, 1999) also indicate that there may be kinetic limitations in NaNO_3 formation. In contrast, Abbatt and Waschewsky (1998) categorically state that for NaCl droplets, the reaction is expected to be limited only by the diffusive arrival of HNO_3 to the drop.

One month of continuous collocated measurements of gas and particle concentrations made at a site near Tampa, Florida, as part of the Bay Region Atmospheric Chemistry Experiment (BRACE) provided a unique opportunity to investigate in detail an equilibrium model of the NaCl– HNO_3 reaction. In support of the BRACE goals (Atkeson and Greening, 2006), our study objectives were threefold: first, to characterize the temporal changes in the absolute and relative HNO_3 , HCl, particulate NO_3^- ($\text{NO}_{3(\text{p})}^-$), and $\text{Cl}_{(\text{p})}^-$ concentrations; second, to investigate the agreement between the equilibrium model predictions and measured concentrations; and third, to interpret the observed partitioning behavior of total NO_3^- and Cl^- with the help of the equilibrium model. Coarse particles are difficult to sample without inlet losses, so we present as well an estimate of measurement system particle losses ahead of the particle collector (PC).

2. Experimental

In May 2002, continuous and nearly simultaneous 15-min measurements of HNO_3 , HCl, $\text{NO}_{3(\text{p})}^-$, and $\text{Cl}_{(\text{p})}^-$ were made from air sampled at $\sim 4.5\text{ m}$ above a relatively open grassy property in the rural

community of Sydney (27.95°N, 82.23°W), which is on the eastern outskirts of Tampa, Florida.

2.1. Measurement of gas and particle composition

Measurements of HNO_3 and HCl were made with a parallel plate wetted denuder (Boring et al., 2002). The denuder was followed by a hydrophobic filter—mist reflux PC which collected soluble particles with high efficiency (Al-Horr et al., 2003). The ionic composition of the wet denuder effluent (the gas sample extract) and that from the PC (aerosol sample extract) were analyzed on-line by independent ion chromatographs. The design and details of field deployment of the instrument have been described by Al-Horr et al. (2003). Briefly, the entire instrument was located inside an air-conditioned trailer. The sampling arrangement involved a 15-cm i.d. polyvinyl chloride (PVC) pipe vertically traversing the shelter, extending 1 m above the rooftop with a U-joint on top to prevent precipitation ingress. Underneath the shelter, a blower fan was attached to the PVC pipe to aspirate air at 1000 l min^{-1} , sufficiently fast to minimize wall losses. This flow rate produces nearly isokinetic conditions for the secondary inlet inserted in this tube (vide infra). No size cut-off device was used. A stainless steel tube SI (10.0 mm i.d., 12.4 mm o.d., 26 cm long), lined inside with a perfluoroalkoxy (PFA) Teflon tube to minimize HNO_3 losses (Neuman et al., 1999), fashioned into an approximately semicircular shape, breaches the PVC pipe at a convenient height within the shelter such that one end of the steel tube is located at the precise center of the PVC tube, pointing upward in the direction of the incoming airflow. The stainless-steel tube directly terminated in the bottom air inlet of the denuder which had the PC connected on top. The sampling flow rate through the denuder–PC assembly was 51 l min^{-1} , maintained with the help of a downstream mass flow controller. We estimated that the particle aerodynamic diameter 50% cut point through the main PVC pipe was >30 and $\sim 12.5\text{ }\mu\text{m}$ through the denuder–PC combination. Thus, essentially “total” particle composition was measured. The denuder was strapped to the PVC pipe. All air pumps were typically located below the shelter to reduce noise in the work environment. Hydrogen peroxide, 0.5 mM in concentration, was pumped using a peristaltic pump at $\sim 0.7\text{ ml min}^{-1}$ to flow down each denuder plate. The bottom effluent from each plate was actively pumped out

peristaltically, combined and pre-concentrated on one of two alternating TAC-ULP1 anion pre-concentrator columns (5×23 mm, Dionex). The valve housing these columns switched every 15 min so that while one column was pre-concentrating the denuder effluent, the other was undergoing chromatography. The chromatographic eluent was with electrodiagnostically generated (14.75 mM KOH at 1.5 ml min^{-1}) and the separation was performed with a 4×50 mm AG11HC guard column and a 4×250 mm AS11HC separation column, followed by ASRS-Ultra 4 mm suppressor and a conductivity detection cell, all located in a LC-30 oven maintained at 30°C and all from Dionex.

2.2. Measurement of particle transmission through denuder–PC combination

Fluorescein-doped NaNO_3 particles of different aerodynamic diameters were generated by a vibrating orifice aerosol generator (VOAG, model 3450, TSI Inc. St. Paul, MN). The VOAG generates nearly monodisperse aerosols. The charge on the generated particles were brought to Boltzmann charge by a Kr-85 discharger and characterized by a laser-based optical particle counter (model A2212-01-115-1, Met-One, Grant's Pass, OR). The general experimental arrangement and details of VOAG operation have been previously described (Samanta et al., 2001). The aerosol generator feed solution was NaNO_3 doped with fluorescein; the fluorescein content was negligible relative to the NaNO_3 , except for the smallest size particles generated in this manner. After sampling for a period, the particle loss on the denuder plates and that on the denuder inlet/outlet tubes plus the PC nozzle inlet were separately measured by measuring the fluorescence of (a) the denuder effluent, and (b) combined washings of the denuder inlet/outlet tubes and the PC nozzle. The fluorescence of the PC effluent was also measured to determine the total amount of aerosol sampled. The total volumes involved in each case were measured to determine the mass in each of these cases. The fluorescence measurements were made using a spectrofluorometer (model RF 540, Shimadzu) using excitation and emission settings appropriate for fluorescein.

2.3. Data processing

The ion chromatography data were available with 15 min time resolution. These were averaged for

each hour of May 2002. If no data were available during an hour, the hourly concentration was reported as missing and thus excluded from the analyses. The benefits of this approach were to provide some data smoothing and to make easier comparison.

2.4. AIM modeling

To model reaction (1), we applied to our BRACE May 2002 data set the Aerosol Inorganic Model III (AIM) (Clegg et al., 1998, see also <http://www.mae.ucdavis.edu/wexler/aim.htm>). The application of AIM to the present data set has the following limitations:

- (1) In its present form, AIM is limited to temperatures of 298.15 K. The data reported here span an ambient temperature range of 288 to 308 K.
- (2) AIM considers only aerosols comprised of Na^+ , NH_4^+ , H_3O^+ , Cl^- , SO_4^{2-} , and NO_3^- ions. Micro-orifice impactor measurements made during this study showed that Ca^{2+} , K^+ , and Mg^{2+} were also present in significant amounts.
- (3) The data obtained here were not size resolved and did not include measurement of sodium ion concentrations.

While it may be difficult to obtain quantitative agreement between modeled and measured gas and particle phase compositions because of these reasons, even a qualitative agreement between model and experiment will provide some insight into the observed trends in partitioning of NO_3^- and Cl^- and the role of the thermodynamic variables in driving the mass transfer between the phases.

3. Results and discussion

3.1. Particle loss through the measurement system

The measurement system must accurately measure the particle composition without major losses of the large particles. Fig. 1 shows that these conditions were attained, with a particle aerodynamic diameter 50% cut point of $12.5 \mu\text{m}$. For the particle size distributions shown in Fig. 2, the measurement system particle loss characteristics would cause a negative bias of $\sim 7\%$ and $\sim 12\%$ in the $\text{NO}_{3(\text{p})}^-$ and $\text{Cl}_{(\text{p})}^-$ concentrations, respectively. If NaCl accumulated in the inlet tubing, RH-dependent sorptive losses of HNO_3 could occur resulting

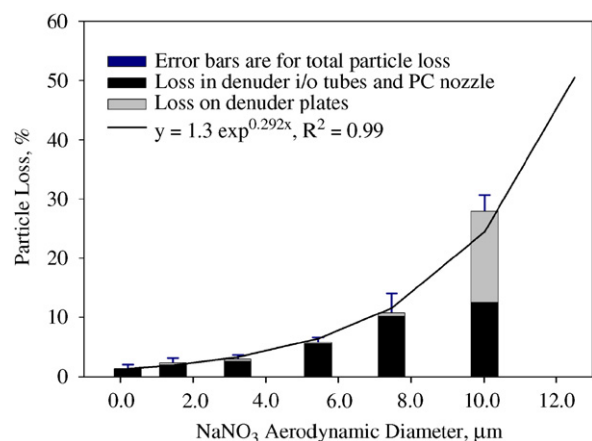


Fig. 1. Particle loss from inlet tubing through denuder to particle collector (PC); D_{50} is $\sim 12.5 \mu\text{m}$.

in HNO_3 measurements that were biased low (Li-Jones et al., 2001). Substantial differences in HNO_3 concentrations were seen across three collocated methods (continuous parallel plate denuder and chemiluminescence methods and an integrated annular denuder method) at our monitoring site in May 2002, for example, and were thought to be related both to inlet configuration and sampling height (Arnold et al., 2006). The present system used a minimum of denuder inlet line ($\sim 15 \text{ cm}$) and the HNO_3 loss is presumably minimal.

3.2. Size distributions of aerosol constituents

Figs. 2(A) and (B), respectively, show the average size distribution of NO_3^- , SO_4^{2-} , NH_4^+ , H_3O^+ , and crustal or sea salt derived ions, namely Na^+ , Ca^{2+} , Mg^{2+} , and Cl^- , at the experimental site, obtained with a 10-stage micro-orifice impactor (Evans et al., 2004). The SO_4^{2-} and H_3O^+ mass peaks were in the submicron particle size fraction (SO_4^{2-} has a smaller peak also at a higher particle size fraction), but the largest amount of NO_3^- was found in the $4.2 \mu\text{m}$ size bin, the same as all the sea salt derived ions. The adjacent bin is geometrically centered at $2.4 \mu\text{m}$; the distribution for NO_3^- in Fig. 2(A) strongly suggests that measurement of $\text{PM}_{2.5}$ will dramatically underestimate the total NO_3^- present.

Fig. 3 shows comparative NO_3 measurements made with the above instrument with its $\text{PM}_{12.5}$ inlet, and measurements obtained with a similar collocated instrument, except with a $\text{PM}_{2.5}$ inlet. This comparison supports the conclusion from the micro-orifice impactor measurements that during

our measurement campaign atmospheric NO_3^- was present predominantly as a coarse particle. Anlauf et al. (2006) compared daytime and nighttime particle NO_3 size distributions for monitoring sites in or near Vancouver, Canada. They reported a shift in particle size distribution from a daytime coarse mode toward a nighttime accumulation mode, and suggested that lower temperatures or production of N_2O_5 could favor the formation of NH_4NO_3 . Interestingly, we observed a 6 AM pulse of fine particle NO_3^- that recurred several times during the 2-week span of available total and fine particle NO_3 measurements (Fig. 3).

For this measurement campaign, on the average NH_4^+ was less than SO_4^{2-} on an equivalents basis, indicating an ammonia-poor atmosphere for NH_4NO_3 formation (Seinfeld and Pandis, 1998). Average pre-dawn (5 AM) concentrations of O_3 and NO_2 were 57 and 17 ppb, respectively, and RH typically 90% (Fig. 6). On some days early morning winds from the south brought a plume of NH_3 over the site. Thus, the recurring fine particle NO_3 pulse could be explained as postulated by Anlauf et al. (2006): a result of regional HNO_3 production from O_3 – NO_x – NO_3 – N_2O_5 reactions achieving equilibrium with elevated morning levels of NH_3 to form NH_4NO_3 .

3.3. Trends in $\text{HNO}_{3(g)}$, $\text{HCl}_{(g)}$, NO_3 , and Cl

Mean concentrations of $\text{HNO}_{3(g)}$, $\text{HCl}_{(g)}$ (subscripts indicating the gas phase for these acids are not used henceforth for simplicity), NO_3^- , and Cl^- were 0.91, 1.08, 1.48, and $1.22 \mu\text{g m}^{-3}$, respectively; and concentration distributions were significantly asymmetric about their mean (Table 1). Observed HNO_3 , HCl , and NO_3^- concentrations are typical of those seen at atmospheric monitoring sites with low to moderate air pollution (Eldering et al., 1991; Mehlmann and Warneck, 1995; Olszyna et al., 2005; Kasper and Puxbaum, 1998; Harrison et al., 1999; Redington and Derwent, 2002; Gao, 2002), while Cl^- concentrations indicate a marine influence but are not as high as those seen aboard a ship or at a coastline, for example (Ottley and Harrison, 1992; Gustafsson and Franzén, 2000).

Time series plots of measured concentrations of Cl^- , NO_3^- , HNO_3 and HCl are shown in Fig. 4. While there are some day-to-day variations, the general trend is that NO_3^- , HNO_3 and HCl peak during the early afternoon while Cl^- peaks twice each day, in the morning and at midnight. In particular, the behavior of Cl^- is curious and is

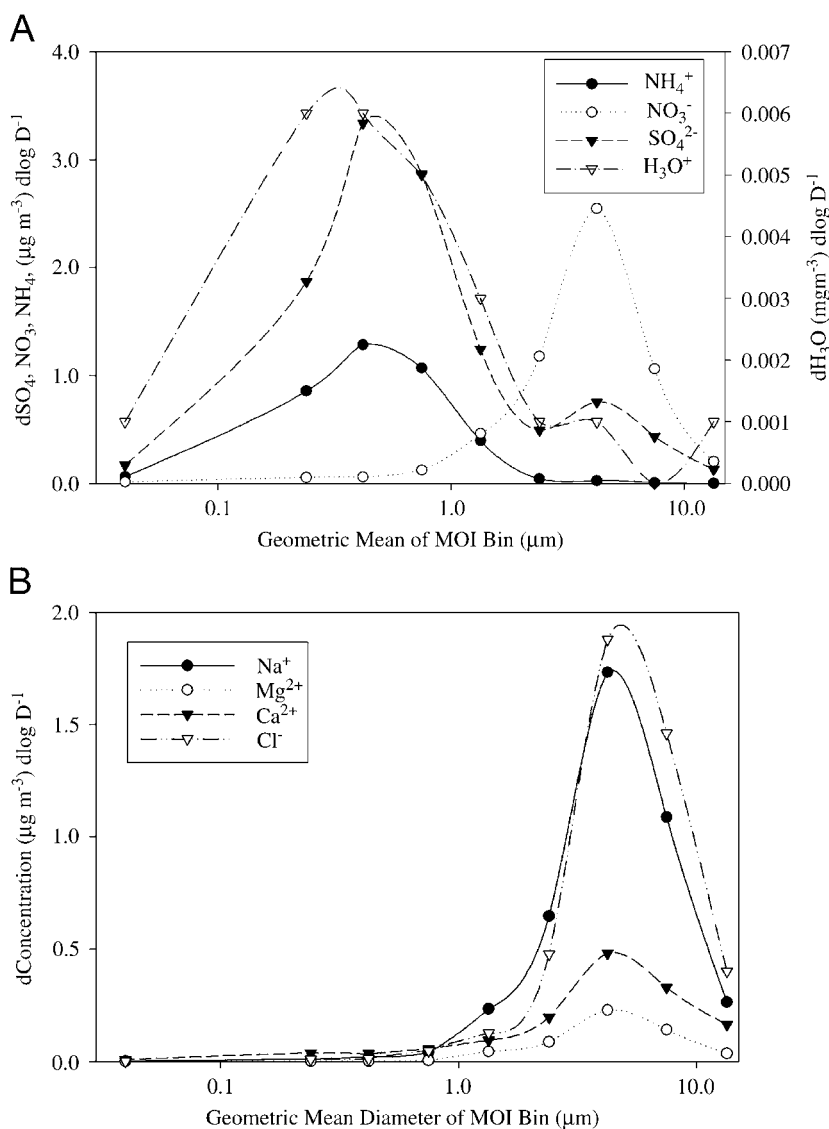


Fig. 2. Average size distribution of atmospheric (A) NH_4^+ , NO_3^- , SO_4^{2-} , and H_3O^+ (A), and (B) Na^+ , Mg^{2+} , Ca^{2+} , and Cl^- obtained from micro-orifice impactor (MOI) measurements.

undoubtedly related to the partitioning behavior of NO_3^- and Cl^- between the particle and gas phases. The analysis is complicated by the fact that source strengths for NO_3^- and Cl^- (both particle and gas) may vary with time. In Section 3.6, we examine the different temporal behaviors of $\text{Cl}_{(\text{p})}^-$ and $\text{NO}_{3(\text{p})}^-$ peaks by considering both sources and partitioning behavior.

3.4. AIM applied to BRACE 2002 data

Application of AIM requires specifications of RH and total (gas + particle) concentrations of

$\text{NH}_{4(\text{p})}^+/\text{NH}_3$, Na^+ , $\text{NO}_3^-/\text{HNO}_3$, Cl^-/HCl and $\text{SO}_{4(\text{p})}^{2-}$. Hydrogen ion concentrations are chosen to satisfy charge balances. The algorithm partitions NH_3 , HNO_3 , and HCl into the gas phase such that thermodynamic equilibrium with the particle phase is achieved. Outputs are gas-phase concentrations of HNO_3 , NH_3 and HCl , and particle phase concentrations of the ions listed above. If the RH is low enough that solid phases are favored, the algorithm calculates the amount of each such solid as well.

As applied here, the inputs of total NO_3 and Cl are obtained by summing the respective measured gas and particle phase compositions. As a result, the

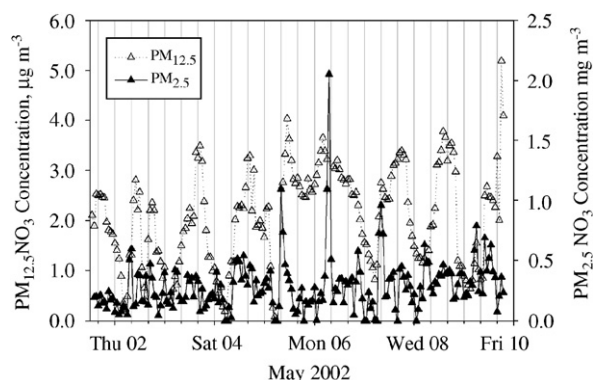


Fig. 3. Total ($\sim$ PM_{12.5}) and PM_{2.5} NO_{3(p)} concentrations versus time.

Table 1

Concentration statistics for OLE_LINK3atmospheric HNO₃, HCl, nitrate (NO₃) and chloride (Cl)OLE_LINK3

Statistic	HNO ₃ (µg m ⁻³)	HCl (µg m ⁻³)	NO ₃ (µg m ⁻³)	Cl (µg m ⁻³)
Count (<i>N</i> cases)	719	719	705	703
Minimum	0.04	0.02	0.08	0.02
Maximum	8.54	9.07	5.20	4.29
Median	0.63	0.64	1.28	1.04
Mean	0.91	1.08	1.48	1.22
Standard error (SE)	0.03	0.04	0.03	0.03
Standard dev.	0.82	1.16	0.85	0.91
Skewness	3.04	2.61	0.91	0.71
SE skewness	0.09	0.09	0.09	0.09

calculations are constrained to yield the observed *total* concentrations. Specification of NH_{4(p)}⁺, SO_{4(p)}²⁻, and Na_(p)⁺ required additional assumptions.

Initial tests indicated much better results were obtained when SO_{4(p)}²⁻ and NH_{4(p)}⁺ were neglected, even though they were present in significant amounts. This can be explained by examining the size distributions shown in Fig. 2, which were obtained by averaging micro-orifice impactor measurements taken at the same site over the same time period. As is evident in the figure, SO_{4(p)}²⁻ and NH_{4(p)}⁺ were primarily in the fine mode, while Na_(p)⁺, NO_{3(p)}⁻, and Cl_(p)⁻ were mainly in the coarse mode. The calculations made here assume all particles were of the same size and were internally mixed. The inclusion of SO_{4(p)}²⁻ and NH_{4(p)}⁺ would lump fine and coarse particles into an unrealistic mixture that did not in fact exist. By neglecting SO_{4(p)}²⁻ and

NH_{4(p)}⁺, we are essentially examining equilibrium only between coarse particles and the gas phase.

Na_(p)⁺ concentrations were not measured but must be specified. The Na_(p)⁺ concentration was assumed to be the sum (on a molar basis) of the observed concentrations of NO_{3(p)}⁻ and Cl_(p)⁻. Measurements from the micro-orifice impactor data indicated that the molar ratio of Na_(p)⁺ to NO_{3(p)}⁻ + Cl_(p)⁻ was about 0.8. AIM, however, does not include other non-volatile ions such as Ca²⁺, Mg²⁺, K⁺, and HPO₄²⁻. If one treats the effects of these other species in terms of Na⁺ equivalents (adding for cations and subtracting for anions), the ratio is slightly greater than 1.0. Assuming Na_(p)⁺ = NO_{3(p)}⁻ and Cl_(p)⁻ does not overspecify the system. The calculations are constrained to yield *total* NO₃⁻/HNO₃ and Cl⁻/HCl concentrations that are in agreement with the measured values. Because there is relatively little H₃O_(p)⁺, the *sum* of NO_{3(p)}⁻ and Cl_(p)⁻ will be close to the experimental values. The *ratios* NO_{3(p)}⁻/Cl_(p)⁻ and HNO₃/HCl are, however, unconstrained and the equilibrium calculation are free to predict results quite different from the measured values.

To examine our assumption about the Na_(p)⁺ to (NO_{3(p)}⁻ + Cl_(p)⁻) ratio further, we carried out simulations in which gas-phase concentrations were calculated from the observed particle concentrations and where Na_(p)⁺ was not constrained to be equal to NO_{3(p)}⁻ and Cl_(p)⁻ was not assumed. The values of HCl and HNO₃ were very sensitive to the Na_(p)⁺/(NO_{3(p)}⁻ + Cl_(p)⁻) ratio and Na_(p)⁺ = NO_{3(p)}⁻ and Cl_(p)⁻ in fact produced the best agreement with the observed values of HCl and HNO₃. In fact, in an unconstrained calculation even small departures of this ratio from unity can result in calculated gas phase concentrations that differ from measured values by orders of magnitude. This is not surprising since constrained equilibrium calculations for this system invariably partition the vast majority of hydrogen into the gas phase.

3.5. The metastable model

Rood et al. (1989) found that metastable aqueous droplets existed more than 50% of the time for RH between 45% and 75% for both urban and rural sites. Therefore, AIM was applied here both in equilibrium mode and in metastable mode. In the latter mode, we assume that solids do not form and separate in the aerosol particles. The results from the calculations in these two modes were not far apart but results from the calculations assuming a

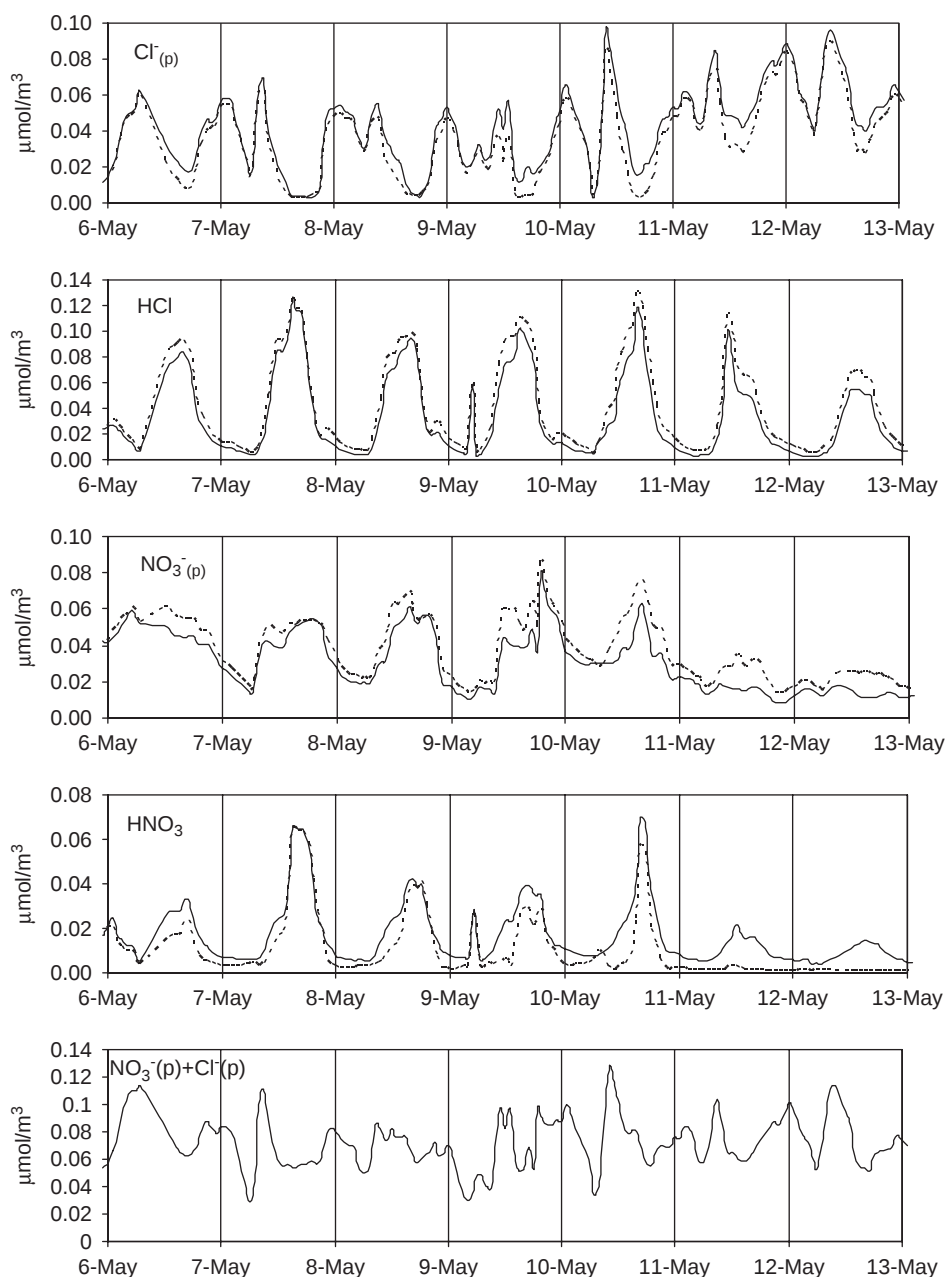


Fig. 4. Time series plots for $\text{Cl}^-_{(\text{p})}$, HCl , $\text{NO}_3^-_{(\text{p})}$, HNO_3 , and $(\text{NO}_3^-_{(\text{p})} + \text{Cl}^-_{(\text{p})})$ for 1 week in May 2002. Solid lines are measured values and dashed lines are those calculated from AIM.

metastable mode were slightly closer to the experimental values. It is the calculation results from the metastable mode that are reported here.

3.6. Model vs. observations

Comparisons of measured concentrations of HNO_3 , HCl , $\text{NO}_3^-_{(\text{p})}$, and $\text{Cl}^-_{(\text{p})}$ to those obtained

from AIM are shown in Fig. 5. Agreement is quite good considering the number of assumptions made in the calculation. It is evident, however, that $\text{NO}_3^-_{(\text{p})}$ and $\text{Cl}^-_{(\text{p})}$ concentrations in the particles are, respectively, over-predicted and under-predicted by the model with the reverse being true for the respective gas-phase concentrations. In terms of $\text{Cl}^-_{(\text{p})}$ depletion, it may appear at first sight

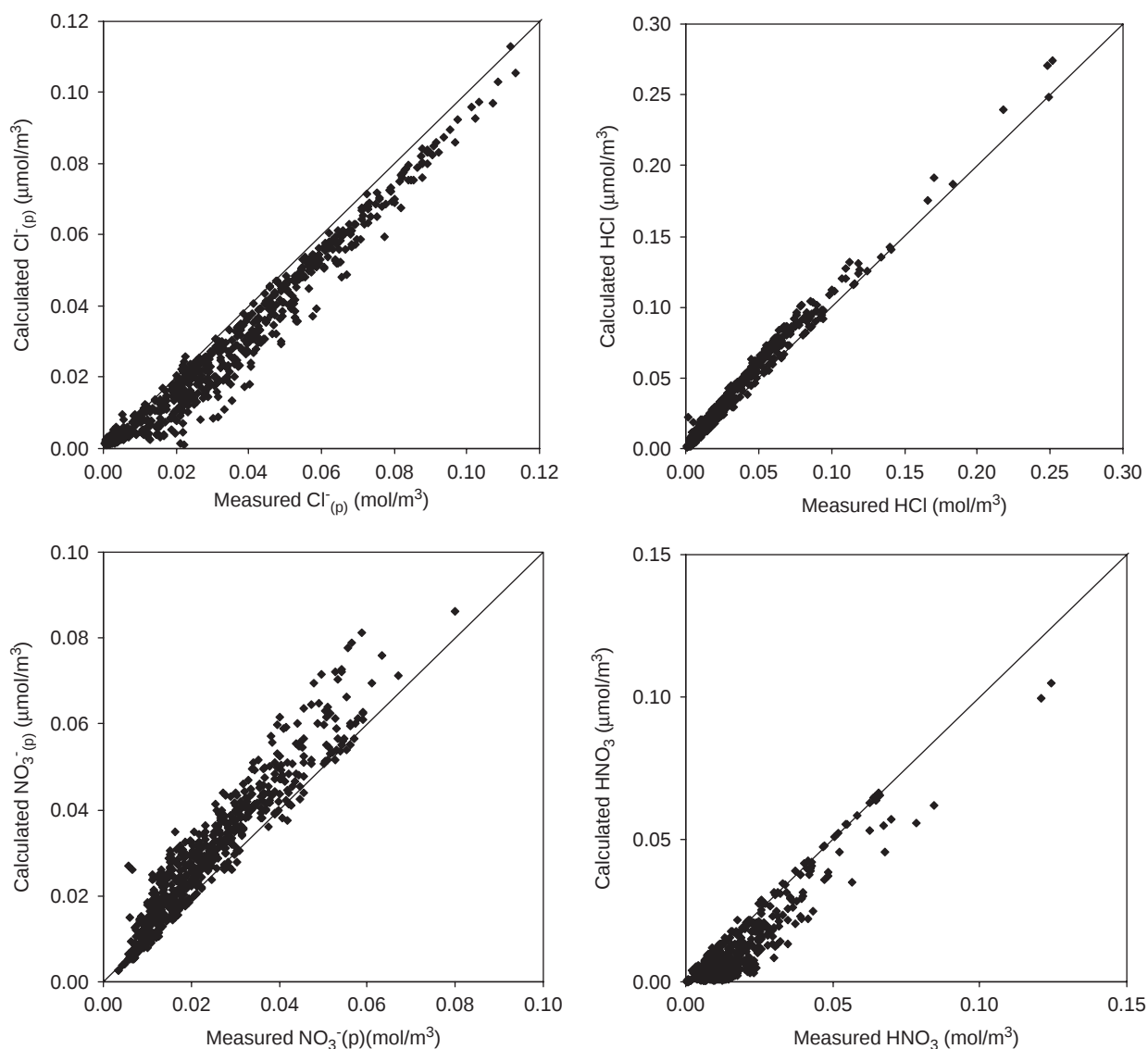


Fig. 5. Comparison of measured concentrations of particles Cl and NO_3 , and gas-phase HCl and HNO_3 , to those calculated from AIM.

gas-particle equilibrium has not been fully attained. It will be seen shortly, however, that there are daytime periods when HCl is being converted to $\text{Cl}^-_{(p)}$ and other periods where the transfer is in the reverse direction. An explanation of the data in Fig. 5 by incomplete equilibrium is inconsistent with these changes in the direction of mass transfer. The biases between the modeled and the measured values are more likely due to the limitations of the assumptions that were made in applying the model.

Fig. 4 shows a time series comparison of measured concentrations of $\text{Cl}^-_{(p)}$, HCl, $\text{NO}_3^-_{(p)}$ and

HNO_3 to those calculated by AIM for a 1-week period. Again, it is apparent from this figure that $\text{NO}_3^-_{(p)}$ tends to reach its maximum value in the afternoon while $\text{Cl}^-_{(p)}$ peaks in the morning and at midnight. As Fig. 5 would predict, the model captures the structure of the time series well and thus suggests that this behavior is indeed driven by partitioning but provides no clue about the timing of the peaks.

A time series plot of $\text{NO}_3^-_{(p)} + \text{Cl}^-_{(p)}$, which is a surrogate for $\text{Na}^+_{(p)}$ or coarse particles in general, is shown in the bottom of Fig. 4. This graph suggests

that the temporal advection of coarse particles to the site is somewhat similar to the temporal profile of $\text{Cl}_{(\text{p})}^-$ (which is the dominant component of the sum), with peaks during the night and morning. CSIRO Atmospheric Research (2001) and Keywood et al. (2003) have attributed nighttime and early morning peaks of PM_{10} to the trapping of pollutants in the shallow nighttime boundary layer. It is logical to deduce that the daily peak in NO_x between 5 and 8 AM on weekdays at our monitoring site originates from traffic emissions. The surrogate $\text{Na}_{(\text{p})}^+$ peak, however, begins at about 7 AM and lasts until the early afternoon. We propose that this morning $\text{Na}_{(\text{p})}^+$ peak was caused by the longer-range transport of sea salt particles from the Atlantic.

Wind patterns for the time period shown in Fig. 4 were similar from day to day. In Fig. 6 an air mass back trajectory from the NOAA HYSPLIT model (Draxler and Rolph, 2003) is shown for a typical day; the trajectory is for a 24 h backward projection in time from 9 AM EST at the monitoring site. Trajectories at other ending times show substantially similar behavior. They indicate for this time

period that particles reaching the monitoring site throughout the morning hours were advected from the Atlantic Ocean.

To further test this hypothesis, we simulated the intrastate transport of $\text{Na}_{(\text{p})}^+$ using the CALMET/CALPUFF modeling system. The computational modeling domain was 325×325 km centered over peninsular Florida, with a 5-km grid scale and 12 vertical layers. CALMET files for May 2002 were prepared by SESSCO, Inc. (now Wind Logics, St. Paul, MN) as described in Park et al. (2005). Sodium was presumed to be present as a coarse particle, (geometric mean mass diameter of $4 \mu\text{m}$, and $\sigma_g = 3 \mu\text{m}$, same as the experimental data from our monitoring site (Fig. 2)). Fig. 7 bottom shows the results of this simulation, for an average day beginning with an arbitrarily chosen input of $10 \mu\text{g m}^{-3}$ $\text{Na}_{(\text{p})}^+$ at the eastern boundary of our modeling domain over the Atlantic Ocean. Fig. 7 top shows the surrogate $\text{Na}_{(\text{p})}^+$ concentration measured at the monitoring site is shown for the average day. Although the experimentally observed peak falls off faster than the model-simulated peak, the similar starting times of the peaks in the model and

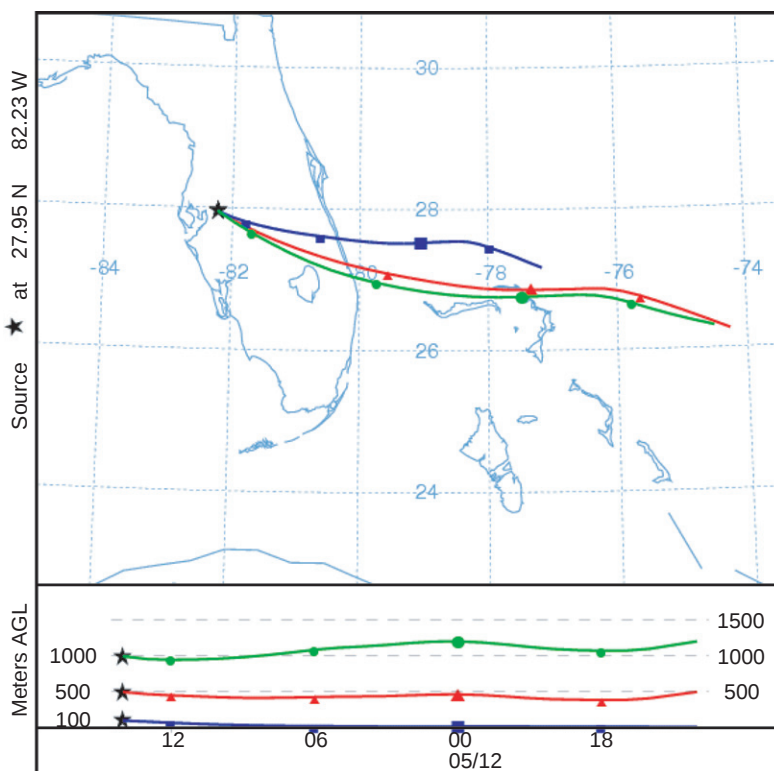


Fig. 6. Back trajectories (24 h) from the monitoring site ending at 9 AM for May 12, 2002. Shown are trajectory heights of 100 (■), 500 (▲) and 1000 (●) m.

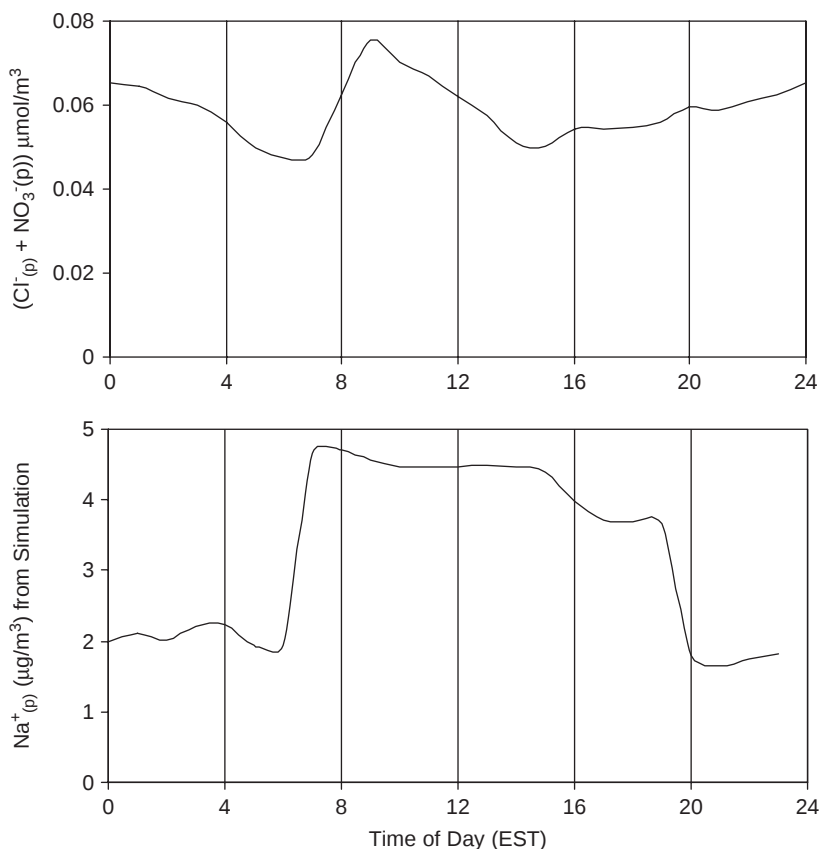


Fig. 7. $\text{NO}_3^-(\text{p}) + \text{Cl}^-(\text{p})$ (top) and simulated $\text{Na}^+(\text{p})$ (bottom) concentrations at the monitoring site versus time of day for an average day during the May 2002 campaign.

the simulation strongly supports the hypothesis that the coarse particles that arrived in the morning were advected from the Atlantic Ocean.

Finally, before interpreting the temporal behavior of the chloride and nitrate concentrations, it is useful to consider an important feature of the chloride and nitrate partitioning relationship. At 298.15 K, the equilibrium constant K for reaction (1) has the value of 1.27 (Zhang et al., 2000), indicating that outgassing of HCl and formation of $\text{NO}_3^-(\text{p})$ would be slightly favored over the reactants $\text{HNO}_3(\text{g})$ and $\text{Cl}^-(\text{p})$. Further, the relationship between species concentrations and the equilibrium constant for this reaction is given by

$$K = \frac{\gamma_{\text{NO}_3^-} [\text{NO}_3^-] p_{\text{HCl}}}{\gamma_{\text{Cl}^-} [\text{Cl}^-] p_{\text{HNO}_3}}, \quad (2)$$

where $\gamma_{\text{NO}_3^-}$ and γ_{Cl^-} are activity coefficients of NO_3^- and Cl^- in the droplet, the parenthetical quantities

are the aqueous concentrations and p_{HX} denote the partial pressures of the gaseous acids. AIM simulations indicate that the ratio $\gamma_{\text{NO}_3^-} / \gamma_{\text{Cl}^-}$ approaches unity at high RH but can approach very low values (~ 0.05) at the lowest RH levels encountered during this study. This suggests that the outgassing of HCl is slightly favored at high humidity and greatly favored at lower humidity.

Putting the temporal behavior of the $\text{Cl}^-(\text{p})$ source together with the partitioning behavior above allows an interpretation of the observed temporal behavior of the relevant species. In Fig. 8, (A) the RH, (B) the ratio $\text{NO}_3^-(\text{p}) / (\text{NO}_3^-(\text{p}) + \text{Cl}^-(\text{p}))$ (C), the surrogate $\text{Na}^+(\text{p})$, (D) $\text{NO}_3^-(\text{p})$ and (E) $\text{Cl}^-(\text{p})$ are plotted versus time of day for an average day. Plot (C) shows that the coarse particle concentration has a broad peak during the night and a sharper peak during the morning. Plot (A) shows the variation of RH during the day and, consistent with the discussion following Eq. (2), plot (B) illustrates that $\text{NO}_3^-(\text{p})$ is favored over $\text{Cl}^-(\text{p})$ during the afternoon

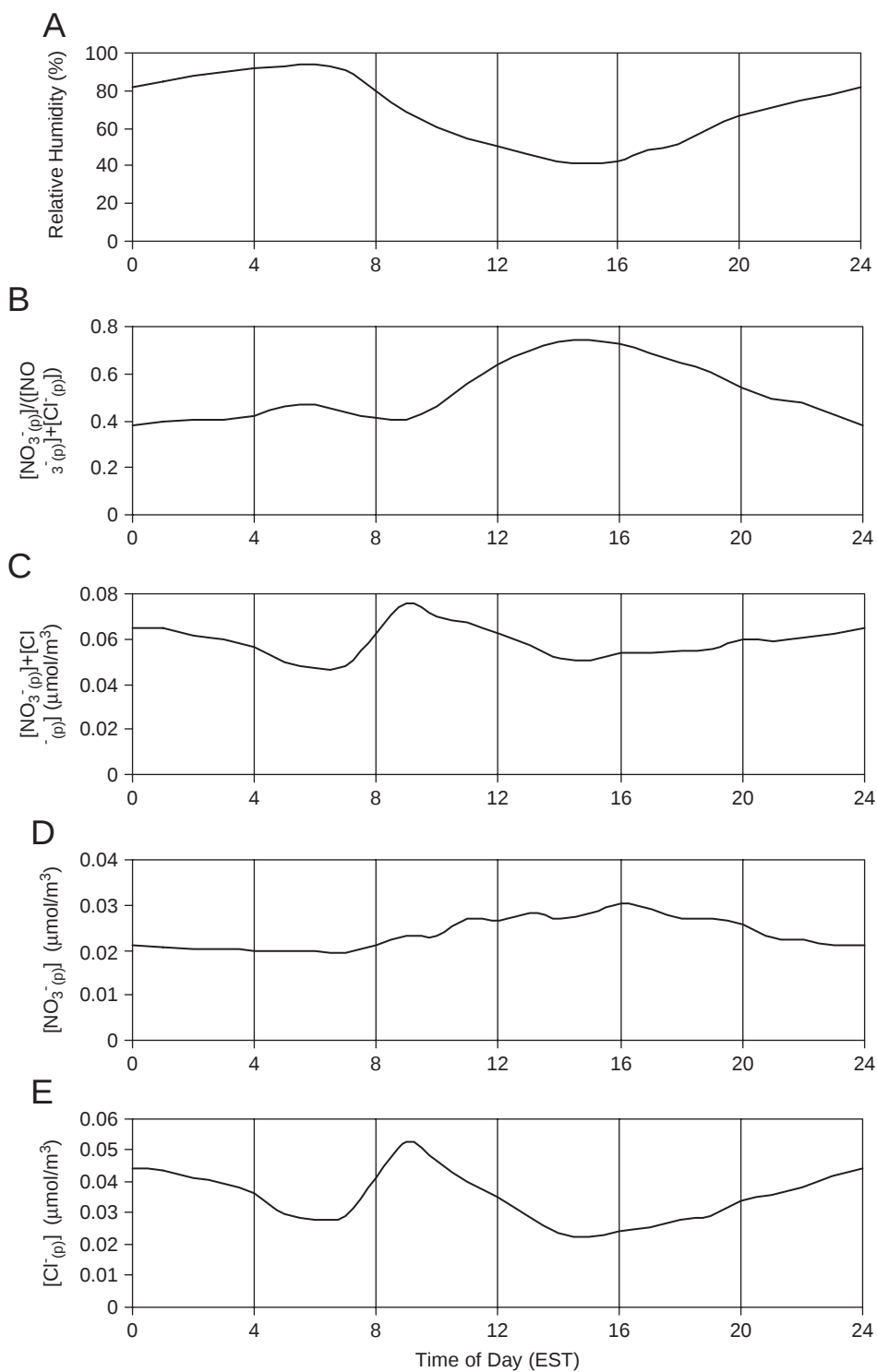


Fig. 8. (A) Relative humidity, (B) $\text{NO}_3^-/(\text{NO}_3^- + \text{Cl}^-)$, (C) $\text{NO}_3^- + \text{Cl}^-$, (D) NO_3^- , and (E) Cl^- versus time for an average day.

hours. The start of the morning coarse particle peak (plot (C)) happens to coincide with the maximum in RH (plot (A)) and therefore these particles arrive when outgassing of HCl is least likely. The coarse particle concentration (plot (C)) begins to decrease after 9 AM but as the RH (plot (A)) drops, the likelihood of HCl outgassing and formation of $\text{NO}_3^-_{(\text{p})}$ increases (plot (D)), even though the total coarse particle concentration is decreasing.

While the concentrations of HCl do show the expected patterns, we have deliberately not focused the discussion on p_{HCl} and p_{HNO_3} . The nature of this equilibrium places the major portion of the net acidity in the gas phase. Because Na^+ is nonvolatile, the only way for Cl^- to outgas as HCl is for an equivalent number of moles of $\text{NO}_3^-_{(\text{p})}$ to be formed. As a result, $\text{NO}_3^-_{(\text{p})} + \text{Cl}^-_{(\text{p})}$ is effectively independent of $p_{\text{HCl}} + p_{\text{HNO}_3}$. Since at this site total NO_3^- and total Cl^- are well correlated, it is interesting that the primary driving force for any change in the partitioning behavior is the RH, with the exception that spikes from local sources in any of the four participants in reaction (1) can of course also change the observed distribution.

4. Conclusions

In Tampa, Florida, atmospheric $\text{NO}_3^-_{(\text{p})}$ was predominantly present as a coarse particle, with a log normal coarse particle size distribution and mode of $\sim 4 \mu\text{m}$, similar to that seen for sea salt constituents. To quantitatively capture coarse $\text{NO}_3^-_{(\text{p})}$, measurement techniques need to have an inlet cut point of at least $10 \mu\text{m}$.

With highly time resolved and simultaneous gas and particle measurements, the diurnal changes in the position of the equilibrium in the NaCl – HNO_3 reaction to form NaNO_3 and HCl was readily observable. Model simulations with AIM explained the measurement data well, and reinforced the observed strong sensitivity of the particle chloride/nitrate ratio to RH. Obviously the development of accurate activity coefficient models for multi-component concentrated electrolyte systems is of paramount importance in accurately predicting the behavior of coastal urban areas like Tampa. Modeling revealed how diurnal changes in RH can rapidly shift HNO_3 concentrations from gas- to particle-phase and thus affect the distance over which nitrogen is transported. Finally, the time resolution of the measurements suggested that assumptions inherent in the modeling rather than

reaction kinetics likely explained biases between predictions and observations.

In summary, although our input data set was not complete and the model itself had limitations (e.g., temperature fixed at 298 K), equilibrium models like AIM can still provide remarkable insights when highly time resolved data sets are available for gas and particle composition measurement.

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