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Quantifying wet scavenging processes in aircraft observations of nitric acid and cloud condensation nuclei

T. J. Garrett,[1] L. Avey,[1] P. I. Palmer,[2] A. Stohl,[3] J. A. Neuman,[4,5] C. A. Brock,[5] T. B. Ryerson,[5] and J. S. Holloway[4,5]

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[1] Wet scavenging is an important sink term for many atmospheric constituents. However, production of precipitation in clouds is poorly understood, and pollutant removal through wet scavenging is difficult to separate from removal through dry scavenging, atmospheric mixing, or chemical transformations. Here we use airborne data from the International Consortium for Atmospheric Research on Transport and Transformation project to show that measured ratios of soluble and insoluble trace gases provide a useful indicator for quantifying wet scavenging. Specifically, nitric acid (HNO_3), produced as a by-product of combustion, is highly soluble and removed efficiently from clouds by rain. Regional carbon monoxide (CO), which is also an indicator of anthropogenic activity, is insoluble and has a lifetime against oxidation of about a month. We find that relative concentrations of HNO_3 to regional CO observed in clear air are negatively correlated with precipitation production rates in nearby cloudy air (r^2 = 0.85). Also, we show that relative concentrations of HNO_3 and CO can be used to quantify cloud condensation nucleus (CCN) scavenging by precipitating clouds. This is because CCN and HNO_3 molecules are both fully soluble in cloud water and hence can be treated as analogous species insofar as wet scavenging is concerned. While approximate, the practical advantage of this approach to scavenging studies is that it requires only measurement in clear air and no a priori knowledge of the cloud or aerosol properties involved.

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1. Introduction

[2] Polluted air is rapidly cleaned by clouds and rain. With the passage of a storm, the air clears, and raindrops leave a silty residue on plants and windows. No other aspect of pollution-cloud interactions can be as easily appreciated by the casual observer. The goal of this paper is to provide an approach for quantifying this process, by focusing on atmospheric pollution by-products that are highly soluble in cloud water and efficiently removed by precipitation. In particular, we address removal of the most cloud soluble of these species: nitric acid (HNO_3) and cloud condensation nuclei (CCN).

[1]Meteorology Department, University of Utah, Salt Lake City, Utah, USA.
[2]School of Earth and Environment, University of Leeds, Leeds, UK.
[3]Norsk Institute for Luftforskning, Kjeller, Norway.
[4]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, USA.
[5]Chemical Sciences Division, Earth System Research Laboratory, NOAA, Boulder, Colorado, USA.

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[3] While the Earth's atmosphere is dominated by non-reactive nitrogen, reactive nitrogen, a trace by-product of fossil-fuel combustion, plays a central role in much of atmospheric chemistry in the troposphere. Of reactive nitrogen species, HNO_3 is particularly notable because it represents nitrogen's final oxidized state [*Stohl et al.*, 2002; *Parrish et al.*, 2004; *Brown et al.*, 2004]. Therefore its sinks are physical rather than chemical, and arise from either contact with the ground or from cloud precipitation. This physical deposition is significant for it introduces anthropogenic reactive nitrogen to terrestrial and aquatic ecosystems where it may significantly alter their biology [*Galloway and Cowling*, 2002].

[4] CCN are aerosol particles that serve as nuclei for warm cloud droplet formation. They have received considerable attention for their role in modifying regional and global climate [*Intergovernmental Panel on Climate Change*, 2001]. By making cloud droplets more numerous and smaller, CCN may increase both cloud shortwave reflection [*Twomey*, 1977] and longwave emission [*Garrett and Zhao*, 2006]. Additionally, smaller droplet sizes inhibit the collision-coalescence mechanism for rain formation, and thereby lead to cloud moistening through lowered precipitation [*Albrecht*, 1989]. A feedback mechanism has been

suggested whereby equilibrium concentrations of anthropogenic CCN are amplified because CCN inhibit precipitation production in clouds, and as a result reduce their primary sink without affecting their sources [*Baker and Charlson*, 1990; *Ackerman et al.*, 1994; *Rosenfeld et al.*, 2001].

[5] While equilibrium pollutant concentrations may vary, their sources and sinks must exist in approximate balance. Past studies devoted to assessing distributions of anthropogenic emissions have thus far tended to devote detail to the sources, while heavily parameterizing such physical sinks as precipitation [e.g., *Mari et al.*, 2000; *Adams and Seinfeld*, 2002]. Ostensibly, the physics associated with the precipitation, or "wet scavenging," sink is relatively simple. Raindrops fall, and if they do not evaporate entirely, soluble species are removed from the atmosphere in linear proportion to the quantity of cloud water converted to precipitate.

[6] Unfortunately, these parameterizations do not reflect the highly nonlinear and poorly understood nature of precipitation production. A long-standing problem is that even the most explicit precipitation models fail to reproduce the short times observed to produce rain in natural clouds. The collision-coalescence mechanism is by nature both turbulent and stochastic, and governed by spatial scales ranging from micrometers to a kilometer. Even the microphysical details of cloud formation itself are poorly constrained in models, particularly those whose spatial resolution is coarser than individual cloud and precipitating elements.

[7] Finally, it is not clear how to adequately constrain model wet scavenging through observations. For example, while a sampled air mass may seem pristine, and this may indeed be due to wet scavenging, mixing with unpolluted air, dry deposition, or chemical transformations may also all play important roles. Moreover, ground-based measurements neither follow an air parcel, nor do they easily entail measurement of the relevant clouds. Thus there are considerable practical difficulties associated with observationally separating scavenging mechanisms within a moving parcel of air.

[8] The goal of this paper is to develop an experimental method for simplifying quantification of the scavenging of soluble pollutants by rain. We outline first the basic principles controlling sources and sinks of HNO_3 and CCN, and develop a parameter for evaluating in clear air their removal by wet scavenging from liquid clouds. We then evaluate this parameter with measurements obtained aboard the NOAA WP-3D aircraft during the summer 2004 International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) experiment based from Portsmouth, New Hampshire.

2. Theory and Background

[9] Following emission, the primary mechanisms controlling concentrations of anthropogenic pollutants are the chemical reactions, condensation, dilution, and wet and dry deposition. We examine these components separately in an effort to assess the primary processes responsible for removal of HNO_3 and CCN.

2.1. Chemical Transformation

[10] Nitric oxide (NO) is converted to nitrogen dioxide (NO_2) through reactions with O_3 and peroxy radicals. NO_2 is rapidly cycled back to NO through photolysis and reaction with the hydroxyl radical (OH) and O_3. The principal sink of NO and NO_2 (NO_x) during the day is the oxidation by OH of NO_2 to nitric acid (HNO_3) with a timescale of about one day [*Chatfield*, 1994]. At night, NO_2 is converted to HNO_3 at a similar or faster rate, but along an oxidation pathway that includes the nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5) as intermediary species [*Brown et al.*, 2004].

[11] HNO_3 can also be recycled to NO_x, by photolysis and reaction with OH, but this occurs on timescales of a few weeks. Thus the equilibrium between NO_x (or NO_2) and HNO_3 strongly favors HNO_3, particularly at low altitudes. Measurements show that HNO_3 concentrations over continental North America approach two thirds of the total odd-nitrogen reservoir NO_y [*Parrish et al.*, 2004] (which includes NO, NO_2, NO_3, N_2O_5, HNO_3, and peroxyacetyl nitrate (PAN)), and greater than 80% of NO_y in aged plumes downwind of the North American northeast urban corridor [*Neuman et al.*, 2006]. While gas-phase chemical reactions play an active role in HNO_3 concentrations within several hundred kilometers of source regions, at longer distances HNO_3 concentrations are determined more by physical removal through cloud precipitation and dry deposition.

2.2. Condensation on Aerosol

[12] Anthropogenic CCN are formed primarily from the condensation of soluble material onto recently nucleated particles produced by combustion [*Adams and Seinfeld*, 2003]. Aerosol diameter increases from 0.01 μm to 0.1 μm, providing sufficient solute that haze droplets activate to form cloud in a supersaturated environment. Growth rates appear to be correlated with pollution levels. Measurements show growth rates ranging from <1 nm h^{-1} in the cleanest sites, such as Antarctica and Finland, to 16 nm h^{-1} in highly polluted locations such as New Delhi [*Kulmala et al.*, 2005]. In Mexico City, *Baumgardner et al.* [2004] noted a diurnal cycle in aerosol concentrations of all sizes, but that concentrations of CCN peaked 3 to 4 hours later than those of nucleation mode aerosol. These results indicate that CCN concentrations do not stabilize instantaneously following emission, but rather they appear to increase over several hours to one day. The adjustment period is shortest in heavily polluted areas.

2.3. Dynamic Mixing of Pollutants

[13] All by-products of anthropogenic combustion are affected by dilution through mixing with cleaner air. Among these is carbon monoxide (CO), which is often used as a tracer for anthropogenic emissions for its long atmospheric lifetime under oxidative processes and its extremely low solubility in cloud water. Compared to background levels, regional CO perturbations, $\Delta CO = CO - CO^{bkgd}$, are highest near power plants, urban areas, and biomass burning. Because CO may encircle the globe before its oxidation is complete, CO^{bkgd} tends to be of similar magnitude to ΔCO, and it is seasonally and regionally variable, ranging between 70 and 130 ppbv over North America [*Stohl et al.*, 2002; *Parrish et al.*, 2004]. Thus, although ΔCO is commonly used as a tracer for anthropogenic production and atmospheric mixing, there is no single value that can generally be applied to CO^{bkgd} as a baseline. Instead, when

calculating ΔCO, values of CO^{bkgd} are determined specific to the time and place.

2.4. Dry Scavenging

[14] In a well-mixed layer, the scavenging of a species with concentration χ follows

$$\chi = \chi_0 e^{-\psi t} \tag{1}$$

where ψ is the linear removal rate, assumed to be constant. Dry removal of CCN and HNO_3 is an important component of the concentration budget, although of relatively minor significance when wet-removal processes are concurrent. For a well-mixed boundary layer of depth h_{bl}, the dry scavenging rate can be parameterized through

$$\psi_d = \frac{v_D}{h_{bl}}$$

where v_D is the velocity for deposition to the surface. In general, dry scavenging rates are poorly quantified. They are most rapid over forest canopies, where v_D for HNO_3 and CCN may approach 0.1 m s^{-1} [*Slinn*, 1977; *Hanson and Lindberg*, 1991]. Thus, while an upper limit for ψ_d may be of order 0.1 h^{-1} over continents, typical removal rates will be slower, particularly to the ocean or during the night when the atmosphere is less turbulent. Of course, removal is zero in air that is decoupled from the surface, for example in air advected over the ocean downwind of the northeast urban corridor [*Neuman et al.*, 2006]. However, while dry scavenging is slow compared to wet scavenging (section 2.5), wet scavenging is episodic while dry scavenging is, on average, continuous provided contact is maintained with the ground. Under some circumstances the two processes may make comparable contributions to pollutant removal.

2.5. Wet Scavenging

[15] The irreversible wet scavenging of gases and particles from the atmosphere is often divided into rainout and washout. In warm clouds, soluble species are taken up by cloud droplets and converted to raindrops through the collision-coalescence process. Rainout occurs when precipitation removes the dissolved species to the ground in proportion to the number of cloud droplets transformed to raindrops. Washout involves the scavenging of a species through diffusion or impaction to falling raindrops. We focus here on these two processes individually, and argue that, to a good approximation, rainout is the primary process responsible for removal of HNO_3 and CCN.

2.5.1. Rainout

[16] A general expression for the instantaneous rate of rainout from a column of air swept out by precipitation is

$$\psi_r = \alpha \frac{p}{L} \tag{2}$$

where p and L are the column-averaged precipitation rate and amount of liquid condensate, respectively, and α the proportion of a gaseous or particulate species that is partitioned to the aqueous phase in cloud. It might be considered that equation (2) should contain a term containing the depth of the cloud relative to the column depth, the rainout removal occurring only within the fraction of the air column the cloud occupies. However, we have assumed here that cloud water is replenished in approximate balance with precipitation. While rain can contribute to the ultimate dissipation of a cloud, the lifetime of cloud water under precipitation τ_p is generally much shorter than the lifetime of the cloud itself τ_c. Clouds are efficient "processors" of air. For a cloud to survive beyond the characteristic cloud water removal time, it must continually pump fresh, water (and pollutant) laden air through its volume. The implication is that the volume of air affected by the cloud is much larger than the volume of the cloud itself.

[17] For illustration, we can estimate the value of p/L (and hence ψ_r for a soluble pollutant) using an approximation that has been applied to space-borne Special Sensor Microwave/Imager (SSM/I) retrievals [*Wentz and Spencer*, 1998]

$$L(\mathrm{mm}) = 0.18\left(1 + \sqrt{Hp}\right) \tag{3}$$

where p is in mm h^{-1} and H is the rain column height, assumed to be equal to the atmospheric freezing level (in km) for locations outside the tropics. Assuming a characteristic value of H = 5 km, p/L ranges from 2 h^{-1} ($\tau_p \sim 30$ min) for p = 1 mm h^{-1} to 10 h^{-1} ($\tau_p \sim 6$ min) for p = 10 mm h^{-1}. Thus cloud processing is fast, emphasizing that equation (2) should be a reasonable approximation of pollutant removal independent of the depth occupied by the cloud. Using measurements and a more detailed regional model for the eastern United States, *Andronache* [2004] obtained similar rain removal rates for soluble pollutants.

[18] In the case of CCN particles, however, considerable uncertainties are often associated with removal by rainout. The relationship between aerosol activation in clouds to their size and composition and to cloud dynamics remains poorly understood [*Lance et al.*, 2004]. Where there has been success in finding a "closed" relationship between aerosol and cloud droplet concentrations [e.g., *Conant et al.*, 2004], assumptions are still required. First, closure requires a match between particles of known size and composition, and the concentrations $N(s)$ of the fraction of particles that activate at water vapor supersaturation s. Second, this "CCN spectrum" must match measured concentrations of droplets N_d for the actual value of s in a cloud. Unfortunately, in a current absence of techniques for the measurement of s in clouds, actual CCN activation can only be inferred from very simplified expressions relating s to measured cloud updraft velocities. Even here, vertical velocity measurements from aircraft tend to be much more precise than accurate, and clouds contain turbulent eddies covering many orders of magnitude in their range of scales and speeds.

[19] To simplify the problem, our approach in this study is to prescribe that, insofar as clouds are concerned, aerosol solubility is binary. All particles that activate to form a cloud droplet are by definition CCN, such that the solubility α equals unity regardless of their composition or the cloudy air dynamics. The remainder of particles entering cloud are insoluble insofar as droplet activation is concerned, such that α is equal to zero.

[20] Unlike aerosol, the value of α for gases applies equally to all molecules, and depends on the density of

cloud water in air W and the gas solubility, typically represented by the Henry's law coefficient H

$$\alpha = \frac{HW}{N_{air}} \quad (4)$$

where N_{air} is the density of air in units of moles per m^3 per atm [*Crutzen and Lawrence*, 2000]. Using a chemical transport model, *Crutzen and Lawrence* [2000] estimated that for typical cloud water contents, α ranges from 0.1 for $H = 10^3$ mol L^{-1} atm^{-1} to near unity for $H > 10^6$ mol L^{-1} atm. In the case of gases diffusing to droplets $\sim$10 μm across, the timescale to establish equilibrium between the concentrations in solution and the vapor phase is fast compared to timescales of dynamic motions in clouds [*Pruppacher and Klett*, 1997]. Therefore kinetic effects associated with gas dissolution are usually ignored.

[21] For HNO_3, the value of H is about 10^7 mol L^{-1} atm^{-1} for temperatures typical of atmospheric warm clouds [*Brimblecombe and Clegg*, 1988]. However, because HNO_3 dissociates efficiently to nitrate (NO_3) in the aqueous phase, the effective value of its Henry's law coefficient is much higher, and ranges between approximately 10^{10} and 10^{16} mol L^{-1} atm^{-1} for values of cloud water pH between 3 and 9 [*Crutzen and Lawrence*, 2000]. Effectively, α = 1 for HNO_3, and rainout is an effective wet scavenging process [*Stohl et al.*, 2002].

[22] An assumption implicit in fixing α at unity for both CCN and HNO_3 is that both species are returned to their original state when cloud droplets fully evaporate. Under the high acidification associated with evaporation, nitrate and hydrogen ions recombine and are desorbed as HNO_3. A fraction of nitrate may be irreversibly sequestered as particulate mass, but this usually represents a negligible fraction of total nitrogen [*Neuman et al.*, 2006]. Also, CCN may be irreversibly processed by clouds through aqueous phase production of aerosol mass inside droplets. However, the effect on CCN concentrations should be minor because, following evaporation, subsequent cycling through cloudy air does not necessarily make the CCN particle more likely to activate, only more likely to activate at a supersaturation lower than the peak supersaturations normally attained in a particular cloud field.

2.5.2. Washout

[23] Washout of CCN is generally negligible compared to rainout. A general form for the removal of CCN by washout is

$$\psi_w(\mathrm{CCN}) \simeq \beta \frac{p}{D_m} \quad (5)$$

where D_m is the volume mean diameter of the raindrops, and β is the collection efficiency $E(d, D_m)$ of CCN with diameter d due to collisions with falling raindrops [*Slinn*, 1977]

$$\psi_w(\mathrm{CCN}) = E(d, D_m) \frac{p}{D_m}$$

In general, $E(d, D_m)$ is small for CCN with characteristic particle sizes between approximately 0.1 and 1 μm. In moderate rainfall with p = 1 mm h^{-1} it is of order 10^{-3}, increasing to 10^{-2} for p = 10 mm h^{-1} [*Chate and Devara*, 2005]. Compared to rainout, washout of CCN is a slow process with $\psi_w < 0.1$ h^{-1}. *Radke et al.* [1980] noted an order of magnitude discrepancy between observations of precipitation removal of submicron aerosol in industrial plumes, and those expected from Brownian and phoretic washout below cloud base alone, a discrepancy attributed to removal of CCN through rainout. Detailed simulations by *Andronache* [2003] show washout contributing to total aerosol removal only for particles with $d > 2$ μm or $d < 0.01$ μm, which lies outside the size range normally associated with CCN.

[24] Washout of HNO_3 by falling raindrops is typically more efficient than washout of CCN. It is limited by its rate of uptake through diffusion relative to the raindrop terminal fall speed v_T. Assuming droplet sphericity, $\beta = 6K/v_T$, where K is the effective ventilated mass transfer coefficient for diffusion of a gas to a falling drop [*Pruppacher and Klett*, 1997; *Seinfeld and Pandis*, 1998]

$$\psi_w(\mathrm{HNO_3}) = \frac{6Kp}{v_T D_m}$$

From these considerations, *Asman* [1995] derived a parameterized expression

$$\psi_w(\mathrm{HNO_3}) = ap^b$$

where a = 0.21 and b = 0.616 (using units of mm and h). For rain rates of p < 10 mm h^{-1}, Asman's relation implies $\psi_w(\mathrm{HNO_3}) < 1$ h^{-1}, dropping to 0.1 h^{-1} for p = 1 mm h^{-1}. However, because Asman's derivation ignores the resistance of molecular transport across the vapor-liquid barrier, their calculated rate should be considered an upper limit. Regardless, the implication is that washout of HNO_3 is at least 1 order of magnitude slower than rainout.

[25] We note that a more rigorous and general estimate of the relative importance of HNO_3 rainout to washout may be given by the dimensionless quantity $\alpha D_m/\beta L$. However, for our purposes, it appears reasonably accurate to assume for simplicity that the depletion of both HNO_3 and CCN through wet scavenging is controlled by rainout alone.

2.6. A Wet Scavenging Parameter

[26] On the basis of the above considerations, we propose a wet scavenging parameter that can be used to observationally estimate the extent to which a species with solubility α has been removed from the atmosphere by rain

$$S = \alpha(\mathrm{HNO_3}/\Delta\mathrm{CO})/R_{\mathrm{HNO_3}} \quad (6)$$

Here $R_{\mathrm{HNO_3}}$ represents the slope relating values of HNO_3 and CO sampled within "baseline" air not recently affected by precipitation [e.g., *Stohl et al.*, 2002], and that is sufficiently far removed from pollution sources (e.g., >1 day) that HNO_3 concentrations can be considered to have reached a chemical equilibrium with respect to NO_y. ΔCO is defined with respect to background levels (see section 2.3). Values of HNO_3 and CO in the numerator of equation (6) can be derived from measurements taken in clear air that are also more than 1 day old, but have recently been exposed to clouds and possibly also to rainout. For any species that is effectively completely soluble, i.e., $\alpha \simeq 1$, the value of S in an air mass unaffected by recent precipitation should be near unity, independent of the pollution level and degree of atmospheric mixing; S is expected to be less than unity only in approximate proportion to the extent the species is depleted from being processed through raining clouds.

[27] As noted, washout is generally of secondary importance to rainout. The effect of dry scavenging on calculation of S is constrained by the extent to which it is (1) second order in the presence of precipitation, and (2) ($HNO_3/\Delta CO$) and R_{HNO_3} are affected equally. While dry scavenging of individual plumes can be episodic and rapid, assumption of slow linear removal may be warranted if S is applied to air samples well downwind of pollution sources: mixing will tend to "blend out" the more highly episodic dry scavenging events.

[28] CCN and CO are both associated with fossil fuel combustion. In urban areas, *Longley et al.* [2005] found generally good correlation ($r^2 = 0.78$) between concentrations of CO and aerosol characteristic of CCN with diameters greater than 0.1 μm. Because both CCN and HNO_3 have $\alpha = 1$ and behave similarly insofar as wet scavenging is concerned, and because CCN and CO are correlated, we hypothesize that measured values of S for the wet scavenging of HNO_3 are equally applicable to the measurement of wet scavenging of CCN. The advantage of this approach is that it requires only measurements in clear air, and no a priori knowledge of either the related precipitating clouds or aerosols.

3. Evaluation

[29] We evaluate the merit of using equation (6) to quantify wet scavenging of HNO_3 and CCN by applying the following steps. (1) Derive R_{HNO_3}in clear air unaffected by recent precipitation. (2) Assuming $\alpha = 1$ in equation (6), derive S for HNO_3 (S_{HNO_3}) in clear air affected by clouds. (3) Derive cloud precipitation production rates P in samples of above-freezing cloudy air, paired according to their values of CO and equivalent potential temperature θ_e to clear air samples. (4) Compare S_{HNO_3} to P to evaluate whether high precipitation production corresponds to low values of S_{HNO_3}. (5) Evaluate the value of S for accumulation mode aerosol (S_{acc}) in an analogous fashion to the evaluation of S_{HNO_3}. (6) Compare S_{HNO_3} and S_{acc} to evaluate whether the hypothesized analogy between HNO_3 and CCN applies to wet scavenging.

3.1. Measurements

[30] All measurements described in this study were obtained aboard the National Oceanographic and Atmospheric Administration (NOAA) WP-3D Orion research aircraft, based from Portsmouth, New Hampshire during the summer 2004 ICARTT field program.

[31] Cloud droplet size distributions were obtained with a Particle Measurement Systems (PMS) FSSP-100, set to measure droplets between 2 and 48 μm diameter in twenty 2 μm bins. Prior to the project, the FSSP-100 was calibrated and its electronics were updated with the Droplet Measurement Technologies (DMT) SPP-100 signal processing package. Faster electronics eliminate artificially broadened size distributions normally associated with older FSSP-100 probes. During the field project, the probe performance was regularly monitored with glass beads of known sizes and the instrument optics cleaned. Measurements of raindrops, with sizes between 50 and 1500 μm, were obtained using NOAA's PMS OAP-2DC probe, set to 50 μm size resolution. The data were analyzed using particle acceptance and rejection criteria outlined by *Heymsfield and Parrish* [1978]. The NOAA OAP-2DC was overhauled by DMT before ICARTT. Data in clouds below freezing that may have contained ice crystals or snow were excluded from analysis in this study.

[32] Gas phase HNO_3 was measured once per second using a chemical ionization mass spectrometer (CIMS) [*Neuman et al.*, 2002] that detected HNO_3 containing cluster ions formed in the selective reaction of SiF_5^- reagent ions with ambient air. Particulate nitrate was not detected [*Neuman et al.*, 2003], and measurements in cloud were ignored because, occasionally, water droplets were ingested when the aircraft flew through clouds, which caused brief (tens of seconds) measurement artifacts. Measurement accuracy for the 1 s data was ±(15% +50 pptv), and the measurement precision was determined from the 1σ standard deviation on the instrument background to be ±20 pptv for 1 s measurements.

[33] Ambient mixing ratios of atmospheric carbon monoxide were determined by vacuum ultraviolet resonance fluorescence [*Holloway et al.*, 2000]. A grating filtered fluorimeter was located in a small, autonomously operated wing pod. Instrument background and sensitivity were determined in situ on a periodic basis. Overall, for the ICARTT 2004 campaign, the instrument demonstrated a 1 s detection limit of <1 ppbv, with an estimated accuracy of about 2.5%.

[34] Aerosol particle size distributions from 0.004 to 8.3 μm diameter were measured with one second resolution using three instruments coupled using a nonlinear inversion algorithm [*Brock et al.*, 2004]. The portion of the size distribution larger than 0.12 μm was measured at a relative humidity of 40% downstream of a low-turbulence inlet with quantified small sampling losses [*Wilson et al.*, 2004]. Uncertainties were dependent upon particle size and concentration statistics, but were typically <12% for integrated particle number and <45% for particle volume, accounting for expected variations in particle refractive index and other systematic and random errors.

[35] The relative contributions of regional CO emissions to measurements along the aircraft flight path were estimated using the FLEXPART model [*Stohl et al.*, 2005]. FLEXPART advects tracer particles within 1° × 1° European Centre for Medium-Range Weather Forecasts (ECMWF) meteorological fields, subject to large-scale winds, turbulence and convection, ignoring wet and dry deposition. Pollutant source functions are based on the Environmental Protection Agency (EPA) 1999 National Emissions Inventory (NEI 99) with a base resolution of 4 km in urban areas, and with large point sources such as power plants treated as points [*Frost et al.*, 2006].

3.2. HNO_3 Wet Scavenging

[36] The first step toward assessing the extent of wet scavenging of HNO_3 is to establish a baseline value for