



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

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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<sub>3</sub>), 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<sub>3</sub> 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<sub>3</sub> and CO can be used to quantify cloud condensation nucleus (CCN) scavenging by precipitating clouds. This is because CCN and HNO<sub>3</sub> 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<sub>3</sub>) and cloud condensation nuclei (CCN).

[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<sub>3</sub> 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

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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<sub>3</sub> 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<sub>3</sub> and CCN.

### 2.1. Chemical Transformation

[10] Nitric oxide (NO) is converted to nitrogen dioxide (NO<sub>2</sub>) through reactions with O<sub>3</sub> and peroxy radicals. NO<sub>2</sub>

is rapidly cycled back to NO through photolysis and reaction with the hydroxyl radical (OH) and O<sub>3</sub>. The principal sink of NO and NO<sub>2</sub> (NO<sub>x</sub>) during the day is the oxidation by OH of NO<sub>2</sub> to nitric acid (HNO<sub>3</sub>) with a timescale of about one day [Chatfield, 1994]. At night, NO<sub>2</sub> is converted to HNO<sub>3</sub> at a similar or faster rate, but along an oxidation pathway that includes the nitrate radical (NO<sub>3</sub>) and dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) as intermediary species [Brown et al., 2004].

[11] HNO<sub>3</sub> can also be recycled to NO<sub>x</sub>, by photolysis and reaction with OH, but this occurs on timescales of a few weeks. Thus the equilibrium between NO<sub>x</sub> (or NO<sub>2</sub>) and HNO<sub>3</sub> strongly favors HNO<sub>3</sub>, particularly at low altitudes. Measurements show that HNO<sub>3</sub> concentrations over continental North America approach two thirds of the total odd-nitrogen reservoir NO<sub>y</sub> [Parrish et al., 2004] (which includes NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, and peroxyacetyl nitrate (PAN)), and greater than 80% of NO<sub>y</sub> 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<sub>3</sub> concentrations within several hundred kilometers of source regions, at longer distances HNO<sub>3</sub> 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<sup>-1</sup> in the cleanest sites, such as Antarctica and Finland, to 16 nm h<sup>-1</sup> 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,  $\Delta\text{CO} = \text{CO} - \text{CO}^{\text{bgd}}$ , are highest near power plants, urban areas, and biomass burning. Because CO may encircle the globe before its oxidation is complete, CO<sup>bgd</sup> tends to be of similar magnitude to  $\Delta\text{CO}$ , 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  $\Delta\text{CO}$  is commonly used as a tracer for anthropogenic production and atmospheric mixing, there is no single value that can generally be applied to CO<sup>bgd</sup> as a baseline. Instead, when

calculating  $\Delta\text{CO}$ , values of  $\text{CO}^{bkgd}$  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  $\chi$  follows

$$\chi = \chi_0 e^{-\psi t} \quad (1)$$

where  $\psi$  is the linear removal rate, assumed to be constant. Dry removal of CCN and  $\text{HNO}_3$  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  $\text{HNO}_3$  and CCN may approach  $0.1 \text{ m s}^{-1}$  [Slinn, 1977; Hanson and Lindberg, 1991]. Thus, while an upper limit for  $\psi_d$  may be of order  $0.1 \text{ h}^{-1}$  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  $\text{HNO}_3$  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

$$\psi_r = \alpha \frac{p}{L} \quad (2)$$

where  $p$  and  $L$  are the column-averaged precipitation rate and amount of liquid condensate, respectively, and  $\alpha$  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 contain-

ing 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  $\tau_p$  is generally much shorter than the lifetime of the cloud itself  $\tau_c$ . 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  $\psi_r$  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]

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

where  $p$  is in  $\text{mm h}^{-1}$  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  $H = 5 \text{ km}$ ,  $p/L$  ranges from  $2 \text{ h}^{-1}$  ( $\tau_p \sim 30 \text{ min}$ ) for  $p = 1 \text{ mm h}^{-1}$  to  $10 \text{ h}^{-1}$  ( $\tau_p \sim 6 \text{ min}$ ) for  $p = 10 \text{ mm h}^{-1}$ . 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  $\alpha$  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  $\alpha$  is equal to zero.

[20] Unlike aerosol, the value of  $\alpha$  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  $\text{m}^3$  per atm [Crutzen and Lawrence, 2000]. Using a chemical transport model, Crutzen and Lawrence [2000] estimated that for typical cloud water contents,  $\alpha$  ranges from 0.1 for  $H = 10^3 \text{ mol L}^{-1} \text{ atm}^{-1}$  to near unity for  $H > 10^6 \text{ mol L}^{-1} \text{ atm}$ . In the case of gases diffusing to droplets  $\sim 10 \mu\text{m}$  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  $\text{HNO}_3$ , the value of  $H$  is about  $10^7 \text{ mol L}^{-1} \text{ atm}^{-1}$  for temperatures typical of atmospheric warm clouds [Brimblecombe and Clegg, 1988]. However, because  $\text{HNO}_3$  dissociates efficiently to nitrate ( $\text{NO}_3$ ) in the aqueous phase, the effective value of its Henry's law coefficient is much higher, and ranges between approximately  $10^{10}$  and  $10^{16} \text{ mol L}^{-1} \text{ atm}^{-1}$  for values of cloud water pH between 3 and 9 [Crutzen and Lawrence, 2000]. Effectively,  $\alpha = 1$  for  $\text{HNO}_3$ , and rainout is an effective wet scavenging process [Stohl et al., 2002].

[22] An assumption implicit in fixing  $\alpha$  at unity for both CCN and  $\text{HNO}_3$  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  $\text{HNO}_3$ . 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

$$\psi_w(\text{CCN}) \simeq \beta \frac{P}{D_m} \quad (5)$$

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

$$\psi_w(\text{CCN}) = E(d, D_m) \frac{P}{D_m}$$

In general,  $E(d, D_m)$  is small for CCN with characteristic particle sizes between approximately 0.1 and  $1 \mu\text{m}$ . In moderate rainfall with  $p = 1 \text{ mm h}^{-1}$  it is of order  $10^{-3}$ ,

increasing to  $10^{-2}$  for  $p = 10 \text{ mm h}^{-1}$  [Chate and Devara, 2005]. Compared to rainout, washout of CCN is a slow process with  $\psi_w < 0.1 \text{ h}^{-1}$ . 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  $d > 2 \mu\text{m}$  or  $d < 0.01 \mu\text{m}$ , which lies outside the size range normally associated with CCN.

[24] Washout of  $\text{HNO}_3$  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]

$$\psi_w(\text{HNO}_3) = \frac{6Kp}{v_T D_m}$$

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

$$\psi_w(\text{HNO}_3) = ap^b$$

where  $a = 0.21$  and  $b = 0.616$  (using units of mm and h). For rain rates of  $p < 10 \text{ mm h}^{-1}$ , Asman's relation implies  $\psi_w(\text{HNO}_3) < 1 \text{ h}^{-1}$ , dropping to  $0.1 \text{ h}^{-1}$  for  $p = 1 \text{ mm h}^{-1}$ . 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  $\text{HNO}_3$  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  $\text{HNO}_3$  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  $\text{HNO}_3$  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  $\alpha$  has been removed from the atmosphere by rain

$$S = \alpha(\text{HNO}_3 / \Delta\text{CO}) / R_{\text{HNO}_3} \quad (6)$$

Here  $R_{\text{HNO}_3}$  represents the slope relating values of  $\text{HNO}_3$  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  $\text{HNO}_3$  concentrations can be considered to have reached a chemical equilibrium with respect to  $\text{NO}_x$ .  $\Delta\text{CO}$  is defined with respect to background levels (see section 2.3). Values of  $\text{HNO}_3$  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) ( $\text{HNO}_3/\Delta\text{CO}$ ) and  $R_{\text{HNO}_3}$  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  $0.1 \mu\text{m}$ . Because both CCN and  $\text{HNO}_3$  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  $\text{HNO}_3$  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  $\text{HNO}_3$  and CCN by applying the following steps. (1) Derive  $R_{\text{HNO}_3}$  in clear air unaffected by recent precipitation. (2) Assuming  $\alpha = 1$  in equation (6), derive  $S$  for  $\text{HNO}_3$  ( $S_{\text{HNO}_3}$ ) 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  $\theta_e$  to clear air samples. (4) Compare  $S_{\text{HNO}_3}$  to  $P$  to evaluate whether high precipitation production corresponds to low values of  $S_{\text{HNO}_3}$ . (5) Evaluate the value of  $S$  for accumulation mode aerosol ( $S_{\text{acc}}$ ) in an analogous fashion to the evaluation of  $S_{\text{HNO}_3}$ . (6) Compare  $S_{\text{HNO}_3}$  and  $S_{\text{acc}}$  to evaluate whether the hypothesized analogy between  $\text{HNO}_3$  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  $48 \mu\text{m}$  diameter in twenty  $2 \mu\text{m}$  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  $1500 \mu\text{m}$ , were obtained using NOAA’s PMS OAP-2DC probe, set to  $50 \mu\text{m}$  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  $\text{HNO}_3$  was measured once per second using a chemical ionization mass spectrometer (CIMS) [Neuman *et al.*, 2002] that detected  $\text{HNO}_3$  containing cluster ions formed in the selective reaction of  $\text{SiF}_5^-$  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  $\pm(15\% + 50 \text{ pptv})$ , and the measurement precision was determined from the  $1\sigma$  standard deviation on the instrument background to be  $\pm 20 \text{ pptv}$  for 1 s measurements.

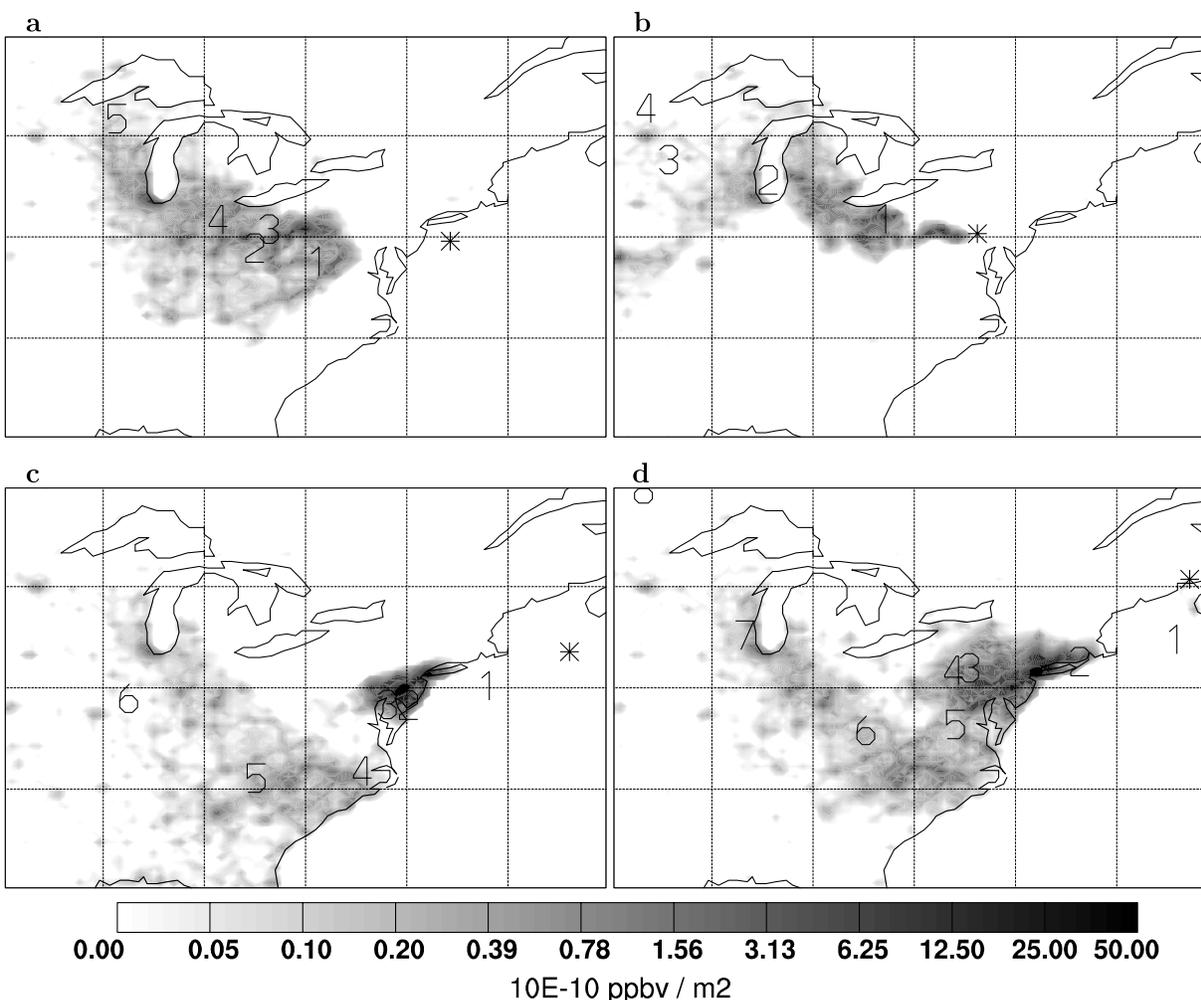
[33] Ambient mixing ratios of atmospheric carbon monoxide were determined by vacuum ultraviolet resonance fluorescence [Holloway *et al.*, 2000]. A grating filtered fluorimeter was located in a small, autonomously operated wing pod. Instrument background and sensitivity were determined in situ on a periodic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

[34] Aerosol particle size distributions from  $0.004$  to  $8.3 \mu\text{m}$  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  $0.12 \mu\text{m}$  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  $1^\circ \times 1^\circ$  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. $\text{HNO}_3$ Wet Scavenging

[36] The first step toward assessing the extent of wet scavenging of  $\text{HNO}_3$  is to establish a baseline value for

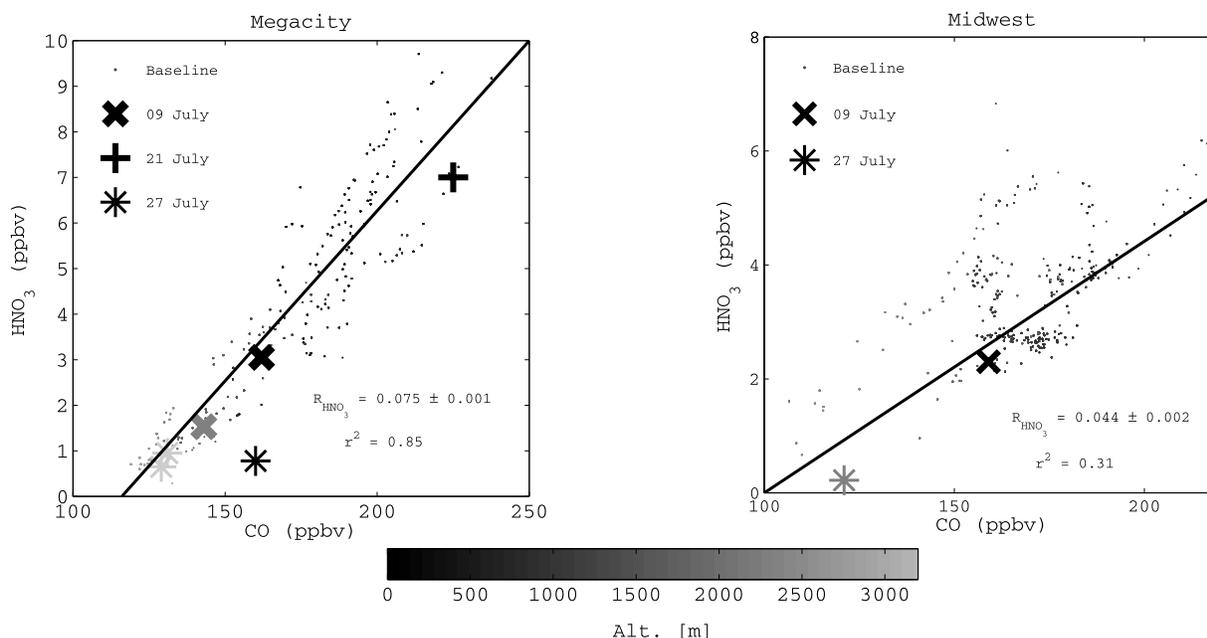


**Figure 1.** Regional contributions of CO to air sampled by the WP-3D research aircraft (location denoted by an asterisk) for the baseline cases chosen for this study: “Midwest” cases sampled on (a) 20 July and (b) 9 August and “megacity” cases sampled on (c) 21 July and (d) 22 July. Numbers indicate the centroid location of the sampled air at the numbered day prior to sampling.

$R_{\text{HNO}_3}$ , representative of aged air masses unperturbed by recent precipitation. To this end, cases were identified that (1) FLEXPART indicated were derived from pollution sources primarily from either the Ohio River Valley (“Midwest”) or the northeast urban corridor (“megacity”), (2) GOES-E infrared satellite imagery indicated were not in the vicinity of clouds (3) NOAA Air Resource Laboratory (ARL) HYSPLIT model back trajectories indicated that the air mass relative humidity had not exceeded 80% since emission from primary source regions (showing an absence of recent precipitation), and (4) FLEXPART indicated the air was sufficiently aged that chemical transformations affecting  $\text{HNO}_3$  concentrations had mostly ceased (i.e., >1 day). Portions of four flights on four separate days satisfied these criteria, two each from “megacity” and “Midwest” sources (Figure 1). The megacity cases were sampled over ocean near Nova Scotia, and were associated with air more than one day out from anthropogenic source regions. The Midwest samples, having been taken over or near the continental United States, were also aged but also

partly influenced by more recent contamination. In each case, examination of satellite imagery indicated that there had been no precipitation along the primary pollution back trajectory (indicated by numbers in Figure 1) in the three days prior to sampling. Moreover, in order to constrain the chemistry involved [Brown *et al.*, 2004], the emissions sampled originated primarily during the daylight hours.

[37] Figure 2 shows  $\text{HNO}_3$  versus CO, categorized by altitude, in the megacity and Midwest samples illustrated in Figure 1. A bisquare linear regression for the megacity measurements indicates a slope  $R_{\text{HNO}_3}$  of  $0.081 \pm 0.001$  ( $r^2 = 0.85$ ). The CO intercept, where  $\text{HNO}_3$  equals zero, is 116 ppbv, which we interpret to be a nominal value of  $\text{CO}^{\text{bkgd}}$ . For the Midwest case, the correlation is less well defined. We define the value of  $\text{CO}^{\text{bkgd}}$  for these samples as 100 ppbv, based on the lowest value measured from the WP-3D over the Midwest region during ICARTT between  $38^\circ \text{N}$  and  $45^\circ \text{N}$  and  $-95^\circ \text{W}$  and  $-78^\circ \text{W}$ . The corresponding value of  $R_{\text{HNO}_3}$  was  $0.044 \pm 0.002$  ( $r^2 = 0.31$ ).



**Figure 2.**  $\text{HNO}_3$  and CO sampled by the WP-3D in air unaffected (dots) and affected (symbols) by recent exposure to clouds in megacity and Midwest air. Dots are 10-s averages representing “baseline” values sampled at the locations shown in Figure 1. Symbols represent averages of 60- to 200-s averages. Dots and symbols are shaded according to the altitude at which they were sampled.

[38] Without knowing the exact nature of the respective chemical emissions, it is difficult to ascertain why  $R_{\text{HNO}_3}$  was lower in the Midwest samples. However, we note that the mean  $\Delta\text{CO}/\text{NO}_y$  and  $\text{HNO}_3/\text{NO}_x$  ratios were 20 and 7.43, respectively, in the Midwest baseline samples, and 8.6 and 44, respectively, in the megacity samples. *Neuman et al.* [2006] showed that fresh plumes (i.e., those with minimal conversion of  $\text{NO}_x$  to  $\text{HNO}_3$ ) are characterized by  $\Delta\text{CO}/\text{NO}_y$  ratios that are on average about 5, but with significant scatter (about  $\pm 3$ ). The implication appears to be that, while there had been sufficient aging to nearly completely convert  $\text{NO}_x$  to  $\text{HNO}_3$  in both regional samples, unlike the megacity samples, the Midwest samples may have been depleted in  $\text{NO}_y$  (and hence  $\text{HNO}_3$ ) through dry scavenging. This would be consistent with greater exposure of Midwest air to forest canopies during advection downwind from pollutant source regions. megacity air was transported principally over the ocean, where it was decoupled from the surface marine boundary layer [*Neuman et al.*, 2006].

[39] The second step of the evaluation process involved pairing samples of clear and cloudy air in the airborne measurements. The primary requirement for pairing air masses was that, in the clear air periods identified, the air had been processed by cloud with properties similar to those measured during the cloudy air periods. Within the entire WP-3D data set during ICARTT, we looked for flight periods representing an average of between 60 and 200 seconds of continuous flight time, provided that they had aged at least 1 day from their primary sources, the emissions sampled had originated primarily during daylight, cloudy and clear samples were located within 50 km of each other (although for one Midwest case, the separation was

$\sim 140$  km due to CIMS instrument failure), the cloudy air samples had temperatures above freezing, and the paired samples of the quasi-conserved tracers equivalent potential temperature  $\theta_e$  and CO were similar (to within  $\pm 2$  K and 10 ppbv, respectively). With the aforementioned constraints, and taking into account periods of instrument failures and diagnostics, the cloudy/clear air pairs available for study were limited to just 8, shown in Table 1.

[40] Symbols in Figure 2 show the chosen paired samples of measurements of  $\text{HNO}_3$  and CO in clear air (Table 1) that had potentially been affected by wet scavenging. The paired samples are matched with the “baseline” data points according to the region of primary pollutant origin, either Midwest or megacity. By comparing the paired samples to a baseline measured in a different (non-cloudy) air mass, we are assuming that the baseline relationship between  $\text{HNO}_3$  and CO that was measured is approximately characteristic of the specific regional sources in general. This caveat aside, in each case, the samples lie below the baseline fit  $R_{\text{HNO}_3}$ , although most are within the noise of baseline variability, and therefore do not distinguishably differ from baseline values known not to have been scavenged by precipitation (i.e.,  $S_{\text{HNO}_3} \simeq 1$ ). However, several samples, for example, on 27 July, represent significant departures from  $R_{\text{HNO}_3}$  (i.e.,  $S_{\text{HNO}_3} < 1$ ), and therefore are plausibly characterized by  $\text{HNO}_3$  removal through rainout.

[41] To determine whether these clear air samples are associated with wet scavenging, we evaluate the degree of precipitation production in the paired cloudy air samples. From measurements of droplet size distributions in cloudy air, we quantify the “autoconversion” rate  $P$  with which the cloud water  $W$  (i.e., the fraction of the cloud with droplets

**Table 1.** Locations and Thermodynamic and Chemical Conserved Quantities in Paired Cloudy and Clear Air Masses Sampled by the WP-3D<sup>a</sup>

Date	Location		$\theta_e$ , K		CO, ppbv		$P$ , $10^{-6} \text{ g m}^{-3} \text{ s}^{-1}$
	Cloudy	Clear	Cloudy	Clear	Cloudy	Clear	
9 Jul	43.59 N–66.40 W	43.63 N–66.43 W	331.8	330.6	149	143	0.65
9 Jul	42.73 N–66.99 W	42.78 N–66.94 W	332.1	332.5	160	157	0.31
9 Jul	42.84 N–68.33 W	41.81 N–68.82 W	331.3	329.8	158	163	0.66
21 Jul	44.00 N–65.75 W	43.82 N–65.92 W	334.2	334.8	218	225	0.26
27 Jul	40.48 N–76.84 W	40.54 N–76.34 W	341.0	339.6	131	129	2.96
27 Jul	40.80 N–75.44 W	40.77 N–75.66 W	341.3	340.4	121	122	9.67
27 Jul	40.49 N–76.78 W	40.64 N–76.34 W	340.3	338.6	128	129	1.25
27 Jul	40.33 N–75.43 W	40.33 N–75.64 W	344.2	342.9	153	160	65.1

<sup>a</sup> $P$  is the precipitation production rate determined from the cloudy measurements.

sufficiently small to stay in suspension) is converted to precipitation using a parameterization defined by *Liu and Daum* [2004] and *Liu et al.* [2004]

$$P = \left( \frac{3}{4\pi\rho} \right)^2 \frac{\kappa_2 \beta_6^6}{N} W^3 H(r_6 - r_{6c})$$

where  $\kappa_2 = 1.9 \times 10^{11} \text{ cm}^3 \text{ s}^{-1}$ ,  $N$  is the cloud droplet number concentration,  $\beta_6$  parameterizes the width of the cloud droplet size distribution through the ratio of its sixth to its third moment  $r_6/r_3$ , and  $H(r_6 - r_{6c})$  represents a Heaviside step function with respect to the critical droplet radius  $r_{6c}$  required to initiate the collision-coalescence mechanism for producing rain:

$$r_{6c} = 4.09 \times 10^{-4} \beta_{con}^{1/6} \frac{N^{1/6}}{W^{1/3}}$$

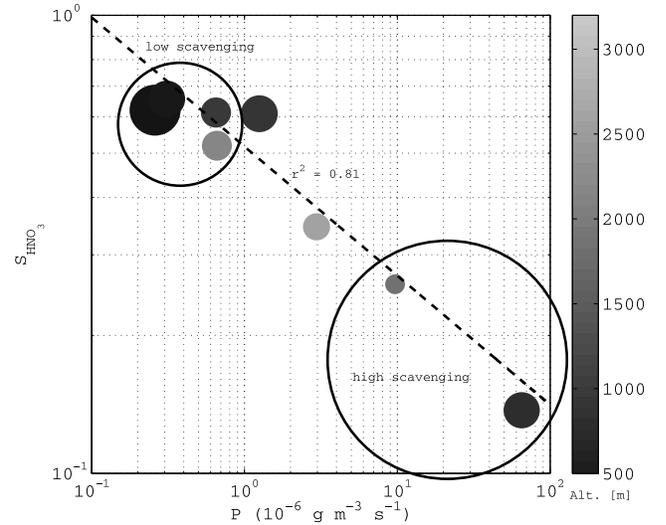
where  $r_{6c}$  is in  $\mu\text{m}$ ,  $W$  in  $\text{g m}^{-3}$ ,  $N$  in  $\text{cm}^{-3}$ , and  $\beta_{con} = 1.15 \times 10^{23} \text{ s}^{-1}$ .

[42] Figure 3 shows that clear air values of the scavenging parameter  $S_{\text{HNO}_3}$  are highly correlated with values of  $P$  in paired cloudy air masses ( $r^2 = 0.85$ ). In particular, the lowest values of  $S_{\text{HNO}_3}$ , with values near 0.1, were found within two air masses that were associated with intense frontal activity sampled during a flight on 27 July 2004. Peak precipitation rates measured in situ during this flight reached  $25 \text{ mm h}^{-1}$ . Low values of  $P$ , less than  $1 \times 10^{-6} \text{ g m}^{-3} \text{ s}^{-1}$ , were associated with no scavenging of  $\text{HNO}_3$ , outside of the expected range of variability. The lack of any apparent correlation between the value of  $S_{\text{HNO}_3}$  and either the sample height or pollution level (as estimated from regional CO concentrations) is suggestive the observed variability in  $S_{\text{HNO}_3}$  was due primarily to variations in  $P$ .

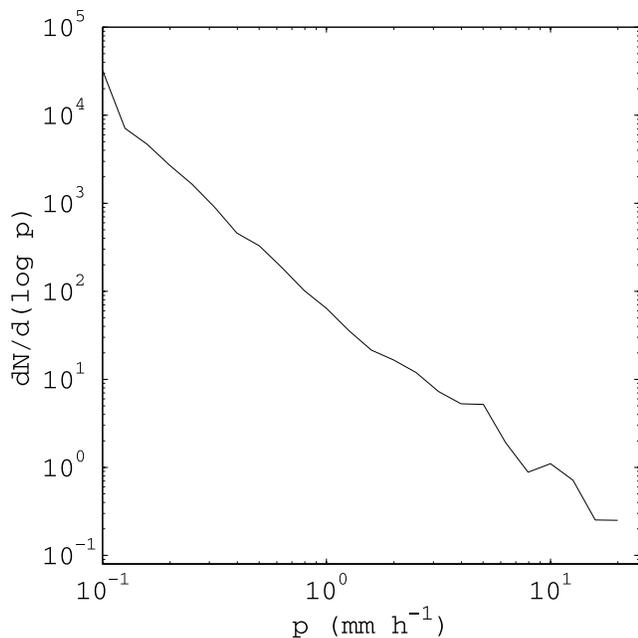
[43] Notably, the exponential slope relationship between  $S_{\text{HNO}_3}$  and  $P$  was only approximately  $-0.28$  rather than linear, as might be expected from equation (2). We speculate that this was because  $S_{\text{HNO}_3}$  is controlled not by rainfall production rate  $P$ , but rather total rainfall, expressible as  $P$  times the duration an air mass is exposed to  $P$ . Of course, it is not obvious how to observationally estimate total rainfall along a Lagrangian trajectory. However, we note that intense precipitation events tend to be shorter duration than broad, long-lasting, but less intense events. To show this, we use precipitation measurements from the SSM/I on the F13 Sun-synchronous polar orbiting satellite that is part of

the Defense Meteorological Satellite Program (DMSP). During ICARTT, precipitation signatures over ocean (retrievals were not obtained over land) downwind of the northeastern megacity corridor show that the exponential slope relationship between incidence and rainfall rate  $p$  is approximately  $\sim -2$  (Figure 4). For example, it could be expected that at any given location, convective precipitation, with a nominal precipitation rate of  $10 \text{ mm h}^{-1}$ , would be 100 times less frequent than stratiform precipitation with a rate of  $1 \text{ mm h}^{-1}$ . Thus heavy rain has a smaller impact on calculated values of  $S_{\text{HNO}_3}$  (equation (6)) than would be expected from the value of  $P$  alone.

[44] Therefore our observations, while based on a limited data set, suggest that rainfall produces a distinguishable signature in the measured concentrations of  $\text{HNO}_3$  when they are factored against measured concentrations of CO and compared to a baseline value of an air mass unaffected by precipitation.



**Figure 3.** For the cloudy and clear air masses shown in Table 1, the scavenging parameter  $S_{\text{HNO}_3}$  obtained in clear air versus the precipitation production rate  $P$  in nearby cloudy air. Circles are shaded according to altitude, and their area is proportional to regional CO concentrations. Nominal “low scavenging” and “high scavenging” cases are encircled.



**Figure 4.** Frequency distribution ( $dN/d\log p$ ) of precipitation rates  $p$  sampled over ocean between ( $38^\circ$ ,  $48^\circ$ )N and ( $-80^\circ$ ,  $-55^\circ$ )W during the ICARTT time period using retrievals from the Special Sensor Microwave/Imager (SSM/I) aboard the DMSP F13 satellite [Wentz and Spencer, 1998].

### 3.3. CCN Scavenging

[45] We proposed in section 2.5 that, because,  $\alpha = 1$  for both  $\text{HNO}_3$  and cloud-activated CCN, and washout makes a relatively small portion to wet scavenging, the two should be scavenged from clouds in a nearly equivalent fashion. Here we evaluate this hypothesis.

[46] No direct measurements of CCN were made aboard the WP-3D during ICARTT. Even if such measurements were obtained, intrinsic ambiguities would remain in evaluating their concentrations because of an absence of simultaneous measurements of supersaturation in liquid clouds. No such instrumental capability currently exists.

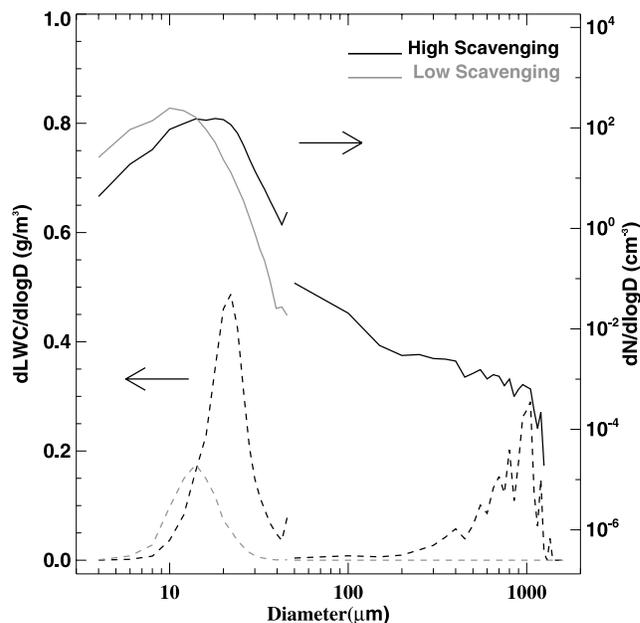
[47] Instead, we are constrained to measurements of aerosol size distributions, and estimate approximate size range normally subsumed by CCN aerosol. While crude, because a purely a size-based criterion ignores chemical contributions to aerosol activation, Dusek *et al.* [2006] have shown that particle size accounts for 84 to 96% of observed variability in CCN concentrations. Moreover, for a wide range of clean and polluted air masses, the supersaturation for which one half of particles of fixed size act as CCN varies by only 0.1% about a mean value of 0.6%, and for increasing supersaturation, the 50% cutoff size increases only gradually. Therefore, on the basis of observations by Covert *et al.* [1998], we assume that all accumulation mode aerosol with diameters larger than  $0.08 \mu\text{m}$  contain sufficient solute to be activated in clouds (equivalent to about 0.5% supersaturation [Dusek *et al.*, 2006]). Applying this size criterion, concentrations of these nominal CCN ( $N_{acc}$ ) are depleted by rainout according to

$$S_{acc} = (N_{acc}/\Delta\text{CO})/R_{acc}$$

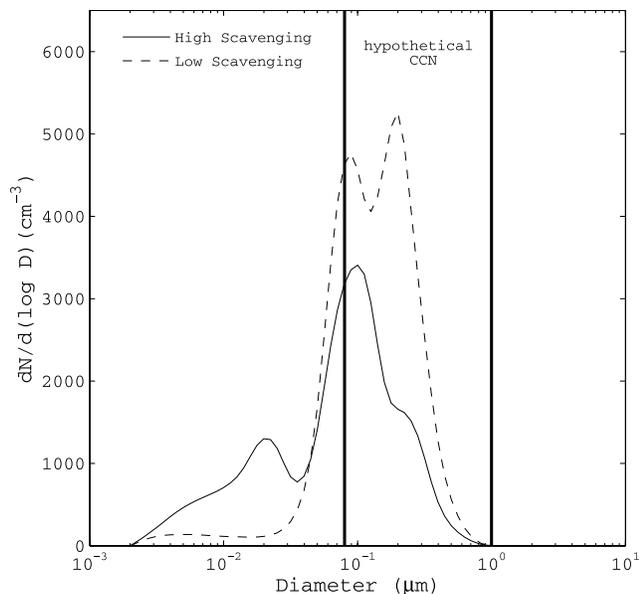
where, as with  $R_{\text{HNO}_3}$  in equation (6),  $R_{acc}$  represents a baseline ratio based on measurements in an air mass not recently perturbed by precipitation.

[48] For example, in Figure 3, we highlight two “high scavenging” cases associated with high values of  $P$  and low values of  $S_{\text{HNO}_3}$ , and four “low scavenging cases” associated with little or no precipitation and values of  $S_{\text{HNO}_3}$  close to unity. The average cloud particle size distributions for these two cases are shown in Figure 5. The high scavenging size distributions have concentrations of coalescence sized droplets ( $>40 \mu\text{m}$  diameter) nearly 2 orders of magnitude higher than in the low scavenging case, and a pronounced precipitation mode at about  $1 \text{ mm}$  diameter. For comparison, no precipitation sized particles were measured within the low scavenging case. Measured aerosol particle size distributions in paired clear air samples for these cases (Figure 6) show that, consistent with removal by wet scavenging, aerosol particles hypothetically associated with CCN have the lowest concentrations  $N_{acc}$  in the high scavenging cases.

[49] For the same data set shown in Figure 2, the baseline slope  $R_{acc}$  relating  $N_{acc}$  and CO is derived for dry megacity and Midwest air masses (Figure 7). In general there is high correlation between  $N_{acc}$  and CO in the megacity and Midwest air, with fitted slopes of  $28.8 \pm 0.3 \text{ cm}^{-3} \text{ ppbv}^{-1}$  and  $41.8 \pm 0.7 \text{ cm}^{-3} \text{ ppbv}^{-1}$ , respectively. The CO intercepts are 104 and 100 ppbv, respectively. As with  $\text{HNO}_3$ , all paired samples associated with clouds (Table 1) lie below the least squares best fit line to the baseline data set, although many of the points lie within the range of variability. A few data points, however, are suggestive of significant scavenging by precipitation. On the basis of the results shown in Figure 8, a similar linear relationship



**Figure 5.** Average cloudy air measurements of cloud number (top curves, log scale) and liquid water (bottom curves, linear scale) size distributions in the paired air masses (Table 1) highlighted as “high scavenging” and “low scavenging” in Figure 3.



**Figure 6.** Average clear air measurements of aerosol size distributions in the paired air masses (Table 1) highlighted as “high scavenging” and “low scavenging” in Figure 3. A hypothetical size range for the nominal CCN in this study is bounded by the vertical lines.

( $r^2 = 0.79$ ) can be seen between  $S_{acc}$  and  $P$  as was observed between  $S_{HNO_3}$  and  $P$  (Figure 3), although the slope is somewhat steeper (about  $-0.33$ ).

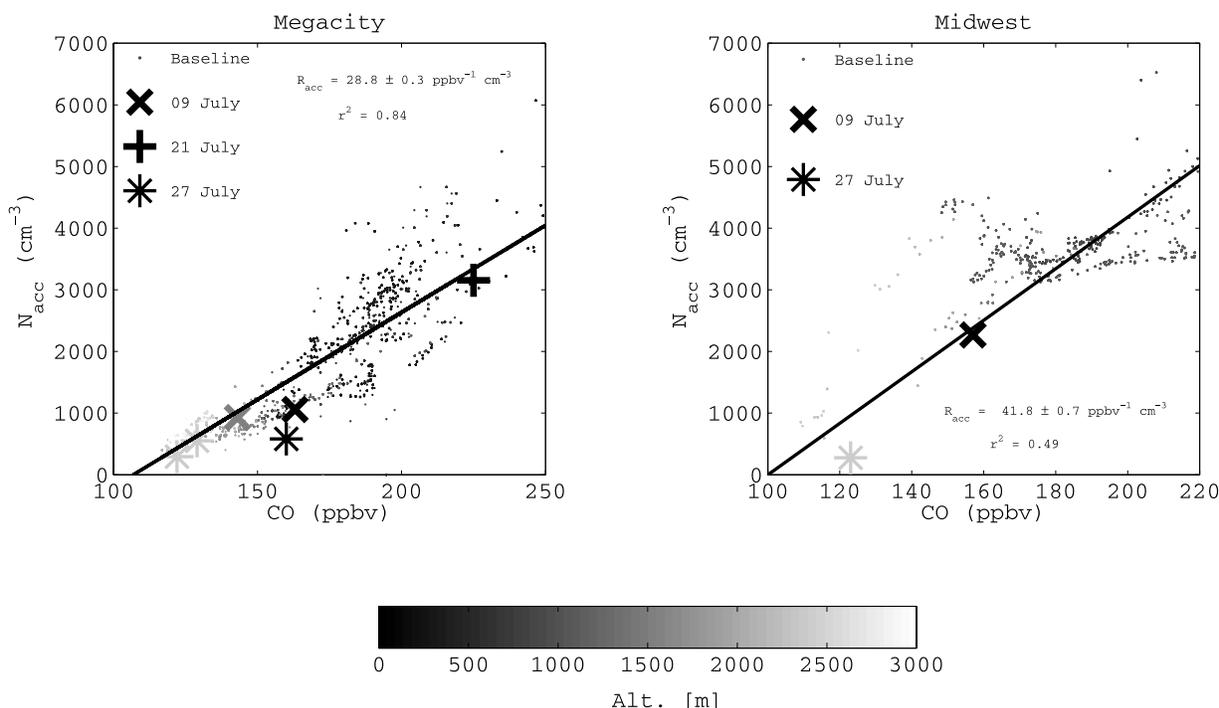
[50] The correlation between  $S_{acc}$  and  $S_{HNO_3}$  is shown in Figure 9. Although the agreement is not perfect, the two

parameters apparently follow a 1:1 slope with a high degree of correlation ( $r^2 = 0.84$ ). There is no apparent correlation between the values of  $S$  and the magnitude of the regional CO concentrations. The results suggest that, for both  $HNO_3$  and  $N_{acc}$ ,  $S$  is indicative of wet scavenging, independent of the diluting effects on concentrations from mixing. To the extent that  $N_{acc}$  is representative of aerosol that activated in cloud, CCN and  $HNO_3$  appear to be scavenged by precipitation in an analogous fashion, in qualitative confirmation of the hypothesis we proposed.

#### 4. Discussion and Conclusions

[51] We have provided a framework for the observational quantification of wet scavenging of soluble species anthropogenic pollution. We have focused on measurements of  $HNO_3$  and CCN, on the basis that both are entirely soluble in cloud water, and both are scavenged primarily by rainout (removal of cloud water to the surface) rather than washout (scavenging by falling precipitation drops). We have argued that, with certain important restrictions, it may be possible to assess the fractional extent to which anthropogenic  $HNO_3$  and CCN have been removed from the atmosphere, without requiring any a priori knowledge of the clouds and precipitation involved.

[52] To achieve this, a comparison was made between measurements of  $HNO_3$  and CO obtained within an air mass nominally affected by precipitation, and a “baseline” air mass representative of the primary pollution source regions but demonstrably unaffected by recent precipitation. Because the approximate time required for  $HNO_3$  to reach a chemical equilibrium with respect to primary emissions of  $NO_x$  is about one day, measurements of the scavenged and



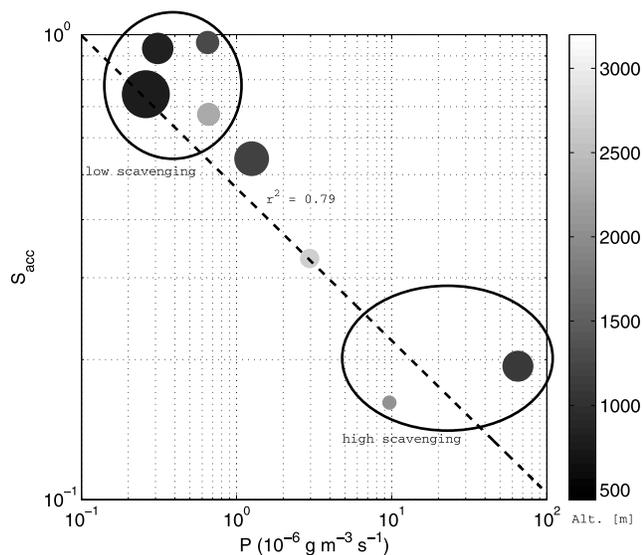
**Figure 7.** As for Figure 2 except for  $N_{acc}$ , the concentration of accumulation mode aerosol with sizes between  $0.08$  and  $1.0 \mu m$ .

baseline air masses were generally restricted to plumes at least this old.  $\text{HNO}_3$  concentrations were ratioed to CO, a respective tracer for mixing because of its insolubility and its long lifetime under atmospheric oxidation. By comparing  $\text{HNO}_3$  and CO concentrations in scavenged and baseline air, a wet scavenging parameter  $S$  was obtained that we hypothesized can be used to isolate the effects of precipitation on a soluble species, separate from influence from dilution or chemical transformations. Measurements from the WP-3D during the ICARTT field experiment showed, in apparent confirmation of this hypothesis, that the value of  $S$  for  $\text{HNO}_3$ ,  $S_{\text{HNO}_3}$ , was strongly negatively correlated with the precipitation production rate  $P$  in nearby clouds.

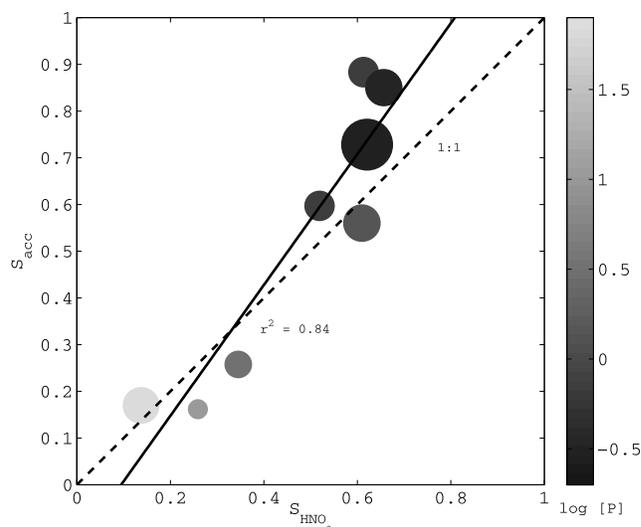
[53] A second hypothesis examined was whether the wet scavenging parameter  $S$  could also be applied to quantify cloud removal of CCN, the motivation being that the primary physical mechanism for the removal of  $\text{HNO}_3$  and CCN, rainout, acts on both species in a similar fashion. No direct measurements were obtained of CCN, so their concentrations were instead estimated from measured concentrations of accumulation mode aerosol larger than  $0.08 \mu\text{m}$  ( $N_{\text{acc}}$ ). It was found that the scavenging of  $N_{\text{acc}}$  relative to CO ( $S_{\text{acc}}$ ) corresponded closely with the scavenging of  $\text{HNO}_3$  relative to CO ( $S_{\text{HNO}_3}$ ), in apparent confirmation of the stated hypothesis.

[54] Thus we have provided a measurement technique for assessing the extent to which concentrations of  $\text{HNO}_3$  and CCN are reduced by precipitation, distinct from dilution, dry deposition, or chemical transformation sinks. An important advantage of the technique is that it does not require any detailed knowledge of the aerosol, cloud or precipitation properties involved, only the concentrations of  $\text{HNO}_3$  and CO in clear air. Thus derived values for  $S$  may provide a simplified approach for the observational validation of chemical and aerosol sinks parameterized in transport models.

[55] A possible added consideration is that  $\text{HNO}_3$  and CCN have reservoirs that are not efficiently removed by precipitation and can act as a source following a rain event.



**Figure 8.** As for Figure 3 except for accumulation mode aerosol concentrations  $N_{\text{acc}}$  with sizes larger than  $0.08 \mu\text{m}$ .



**Figure 9.** Derived values of  $S_{\text{acc}}$  and  $S_{\text{HNO}_3}$  from Figures 3 and 8 for the paired air mass samples in Table 1. Values are shaded according to the precipitation production rate  $P$  (units  $\mu\text{g m}^{-3} \text{s}^{-1}$ ), and circle area is proportional to the regional CO concentration. A 1:1 line is shown for comparison.

For example, once a steady state with respect to  $\text{NO}_x$  is reached, a small portion of total  $\text{NO}_y$  resides as PAN [Parrish et al., 2004; Neuman et al., 2006]. Following complete wet scavenging of  $\text{HNO}_3$ , thermal decomposition of the PAN reservoir leads to  $\text{NO}_x$  restoration over several hours, which may be subsequently converted to  $\text{HNO}_3$  in about one day. There is also a reservoir for CCN, from the coagulation of, or condensation onto, nucleation mode aerosol. Thus there may be a weak time dependence to  $S$ , such that  $S$  increases (erroneously indicating less scavenging) with time from the most recent precipitation event.

[56] Finally, we were restricted in our analysis of the ICARTT data set by the limited number of time periods that were suitable for comparing clean and cloudy air samples. We look to future airborne field missions to verify the approach we proposed, in which case measurement will be necessary in both clear air and nearby precipitating clouds downwind of major pollutant source regions. The technique may plausibly be extended to include removal by ice-phase precipitation, and of partially soluble species (e.g., sulfur dioxide,  $\text{SO}_2$ ) for which  $\alpha < 1$ .

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