7.5 THE ROLE OF ADSORPTION OF CHEMICAL SPECIES ONTO ICE AND SNOW IN DEEP CONVECTION

Mary C. Barth*

National Center for Atmospheric Research, Boulder, Colorado, USA

1. INTRODUCTION

The adsorption of gas-phase species onto ice and snow has been documented as an important process for nitric acid in both laboratory (Zondlo et al., 1997) and field studies (Popp et al., 2004). Recent modeling studies (von Kuhlmann and Lawrence, 2006) have indicated that the adsorption of gas-phase nitric acid onto ice reduces the gas-phase concentration of nitric acid in the upper troposphere by 40-60%. Wang (2005) also shows significant nitric acid uptake on ice in the anvil region of a tropical deep convective storm, but only small to negligible amounts of uptake of formaldehyde onto ice.

In this study, numerical model simulations using the Weather Research and Forecast model coupled with gas and aqueous chemistry are analyzed to examine the importance of adsorption of gas species onto ice for a summertime, midlatitude thunderstorm. The analysis focuses on nitric acid (HNO_3), formaldehyde (CH_2O), hydrogen peroxide (H_2O_2), and sulfur dioxide (SO_2), species that are adsorbed onto ice in varying degrees.

2. MODEL DESCRIPTION

The Weather Research and Forecasting (WRF) model is the meteorological model in which the chemistry modules reside. The WRF model solves the conservative (flux-form), nonhydrostatic compressible equations (Skamarock et al., 2001) using a split explicit time-integration method based on a 3rd order Runge-Kutta scheme (Wicker and Skamarock, 2002). Scalar transport is integrated with the Runge-Kutta scheme using 5th order (horizontal) and 3rd order (vertical) upwind-biased advection operators. Transported scalars include water vapor, cloud water, rain, cloud ice, snow, graupel (or hail), and chemical species. The ice microphysics parameterization is that described by Lin et al. (1983). For the simulations performed here, hail hydrometeor characteristics (ρ_h = 917 kg m^{-3}, N$_o$ = 4 x10^4 m^{-4}) are used.

The model is configured to a 160 x 160 x 20 km domain with 161 grid points in each horizontal direction (1 km resolution) and 51 grid points in the vertical direction with a variable resolution beginning at 50 m at the surface and stretching to 750 m at the top of the domain. A description of the meteorological scenario and transport of passive tracers is found in Skamarock et al. (2000) for the 10 July 1996 STERAO storm. We initialize the model environment and the initiation of convection in the same manner as Skamarock et al..

The chemical module is described in Barth et al. (2000, 2006). The gas chemistry represents daytime chemistry of 15 chemical species. The aqueous chemistry is computed for the cloud water and rain reservoirs. The pH of the cloud water and rain is calculated via a charge balance at each time step and grid point containing liquid water. Most chemical species are initialized with values measured in the inflow region of the storm; other species are estimated from values found in the literature or from the July monthly-mean mixing ratio for northeastern Colorado calculated by the 3-dimensional global transport model, MOZART (Brasseur et al., 1998). The chemical mechanism is solved with an Euler backward iterative approximation using a Gauss-Seidel method with variable iterations. A convergence criterion of 0.01% is used for all the species.

The adsorption of gas-phase HNO_3, CH_2O, H_2O_2, and SO_2 occurs where ice and snow mass mixing ratios are greater than 1x10^{-12} kg and T < -35°C. These cold temperatures were chosen because laboratory data is available for T < -35°C and because at warmer temperatures liquid layers on the ice surface alter the adsorption mechanism. The adsorption of species follows the methodology of Tabazadeh (1999), that is Langmuir equilibrium is assumed. By calculating the equilibrium surface coverage, θ, the partial pressure of the species in the ice or snow can be determined as follows.

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* Correspoding author address: Mary C. Barth, NCAR, P. O. Box 3000, Boulder, CO 80307-3000. Email: barthm@ucar.edu

$$\theta = \frac{(K_{eq} P_g)^b}{1 + (K_{eq} P_g)^b} \qquad (1)$$

$$P_a = \frac{\theta\, A_{ice}}{\sigma\, \beta} \qquad (2)$$

$$P_g = P_{tot} - P_a \qquad (3)$$

where K_{eq} is the equilibrium adsorption constant, P_g, P_a, and P_{tot} are the partial pressures of the species in the gas phase, the ice phase, and both phases, respectively, A_{ice} is the surface area of the ice and snow, $\sigma = 10^{-19}$ m^2 is the surface area of a site on the crystals available for adsorption, and $\beta = 9.656 \times 10^{18}/T$ (cm^{-3} torr^{-1}) is a conversion factor. The constant b is either equal to 0.5 or 1 depending on whether the species will dissociate when it is adsorbed. HNO_3 and SO_2 will dissociate, thus $b = 0.5$; H_2O_2 and CH_2O do not dissociate and $b = 1$. The equilibrium adsorption constant K_{eq} (Table 1) is taken from laboratory studies. Because of the co-dependence of equations 1-3 on each other, the solution is found after several iterations (~5).

Table 1. Equilibrium adsorption coefficients

	K_{eq} (Pa^{-1})
HNO_3	$3.3195 \times 10^{-9}\ T^{-0.5} \exp(-\Delta H/RT)$
SO_2	$3.2935 \times 10^{-9}\ T^{-0.5} \exp(-\Delta H/RT)$
H_2O_2	$4.5186 \times 10^{-9}\ T^{-0.5} \exp(-\Delta H/RT)$
CH_2O	$50.7\ T^{-1}$

Pre-exponential factors follow Popp et al. (2004). ΔH = -44.0, -33.5, -39.75 kJ mol^{-1} for HNO_3, SO_2, H_2O_2, respectively. For HNO_3 K_{eq} follows Bartels-Rausch et al. (2005). For H_2O_2 and SO_2, K_{eq} follows laboratory studies of Clegg and Abbatt (2001). For CH_2O K_{eq} follows Winkler et al. (2002).

3. RESULTS

As a test of the adsorption of gas species onto ice, a simulation without the adsorption was computed. The ice and snow mass mixing ratios and the HNO_3 mixing ratios were obtained from the model results at 1 hour of integration. These mixing ratios were used to determine the surface area of the ice and the potential for nitric acid uptake.

The surface area of the ice and snow is calculated based on mean diameters of the ice and snow. Ice in the model is assumed to be monodispersed with a 45 μm diameter and a density of 917 kg m^{-3}. Snow in the model is described with a size distribution in the form of an exponential decay (ρ_s = 100 kg m^{-3}, $N_o = 3 \times 10^6$ m^{-4}). At t = 1 h the sum of the surface area for ice and snow is quite large at the top of the updraft cores (Figure 1). Regions where T < -35°C are shown. Ice (Figure 1, middle panels) and snow (bottom panels) contribute equally to the total ice surface area.

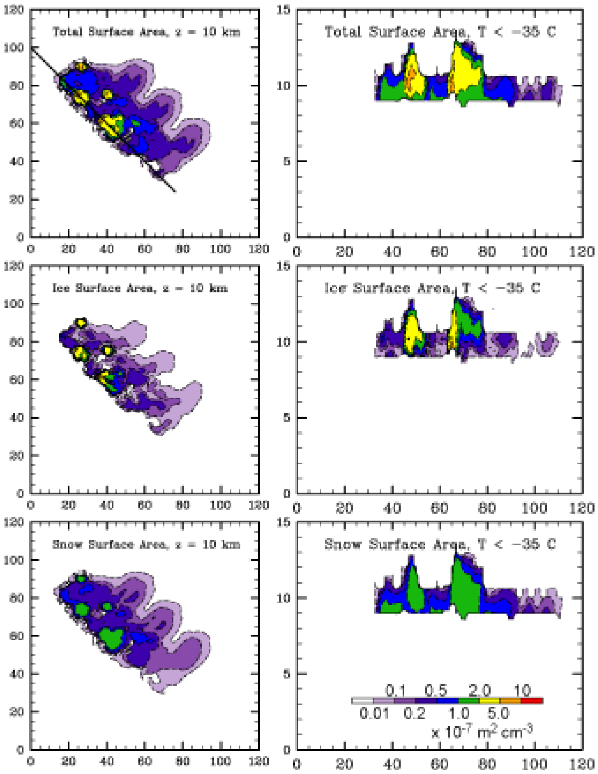

Figure 1. Horizontal (left panels) and vertical (right panels) of the total surface area (ice + snow, top panels), ice surface area (middle panels), snow surface area (bottom panels). Color scale is in m^2 cm^{-3}.

Gas-phase HNO_3 mixing ratios show a large depletion in the convective cores (Figure 2, top panels) where liquid water has absorbed the HNO_3. Depletion of HNO_3 is also seen in ice, snow and hail regions where these frozen hydrometeors have gained HNO_3 via riming of cloud water. When the adsorption of gas-phase HNO_3 is calculated, its mixing ratios appear to have hardly changed (Figure 2, middle panels). The difference between the top and middle panels shows that HNO_3 adsorption is occurring mostly at the top of the convective cores (over 150 pptv lost from the gas phase). Less than 50 pptv of gas-phase HNO_3 is depleted just downwind of the convective cores. In relation to the HNO_3 mixing ratios, adsorption of HNO_3 onto ice and snow accounts for depletion of 10-20% near the top of the convective cores.

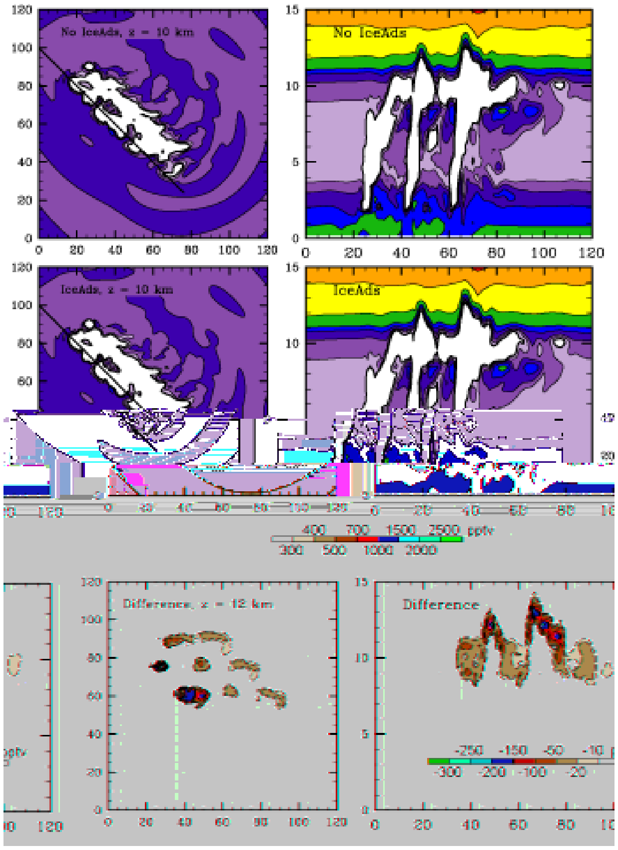

Figure 2. Horizontal (left panels) and vertical (right panels) of gas-phase HNO_3 volume mixing ratios for when HNO_3 is not adsorbed by ice (top panels) and for when that HNO_3 field is adsorbed by ice (middle panels). The bottom panels show the difference between the two HNO_3 fields. The vertical cross-section is denoted by the black line in the horizontal cross-sections.

4. DISCUSSION

The results shown here indicate that HNO_3 adsorption by ice and snow crystals could further deplete HNO_3 gas phase mixing ratios, but that it is not an ubiquitous process throughout the anvil. Results for SO_2, H_2O_2, and CH_2O are smaller in magnitude because of their smaller equilibrium adsorption coefficients (Table 1).

Several assumptions were used for these calculations. Firstly, the assumption that the adsorption is an equilibrium process may be incorrect. Kärcher and Basko (2004) point out that this process is better described as a kinetic process. Secondly, the assumed diameter (especially for ice) is very uncertain. The 45 μm diameter is based on the calculation of the total number of ice crystals which is evaluated with observations from the University of North Dakota Citation aircraft, which flew in the anvil of this storm. This diameter gave the best ice number concentration comparison with the observations. Other assumptions, such as the burial of the species in the ice, also contribute to the uncertainties in the results shown. Sensitivities to some of these uncertainties will be shown in the oral presentation.

5. ACKNOWLEDGMENTS

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