

A THREE-DIMENSIONAL MODELING STUDY OF THE EFFECTS OF SOLID-PHASE HYDROMETEOR-CHEMICAL INTERACTIONS IN CUMULONIMBUS CLOUDS ON TROPOSPHERIC CHEMICAL DISTRIBUTIONS

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1. INTRODUCTION

Clouds can significantly impact trace chemical distributions in the troposphere and the chemical composition of precipitation. Clouds affect chemical distributions through convection of air and hydrometeors containing trace chemicals. They also provide a multi-phase environment for chemical phase changes and reaction. Due to the large vertical motions and turbulence of strong convective cloud systems, they can transport and mix trace chemicals between the atmospheric boundary layer and upper troposphere. If strong enough, they can also penetrate into the lower stratosphere. Hydrometeors in these clouds provide surfaces for chemical phase changes. They also act as condensed phase reactors for chemical reactions. Finally, hydrometeors serve as conduits for chemical transport from the atmosphere to the ground through scavenging and precipitation. Hence, storm clouds can impact acidic precipitation, urban pollutant dispersal, and concentrations of ozone and other atmospheric cleansing species (such as odd hydrogen radicals) in the upper troposphere and lower stratosphere,

Due to the variety of effects of convective clouds on surface and atmospheric chemistry, there has been considerable effort to understand the complex processes involved in these systems, including modeling studies. In these studies, interactions of volatile chemicals with ice- and mixed-phase hydrometeors (cloud ice, snow, graupel, and hail) are often excluded or limited due to their complexity as well as lack of theoretical understanding. Modeling studies which have included representations of interactions of ice-phase cloud hydrometeors with volatile chemicals have found that they may significantly impact chemical distribution and deposition (Audiffren et al., 1999; Chen and Lamb, 1990; Cho et al., 1989; Rutledge et al., 1986; Wang and Chang, 1993). However, the available studies use differing representations of these interactions, yield varying results, and give no consistent picture of the effects of these interactions on chemistry. A systematic investigation of the range of potential impacts of these interactions on chemical distributions and deposition is still lacking.

In this work, we discuss the state of current knowledge on the interactions between solid-phase cloud hydrometeors and chemicals. Using modeling simulations, we also investigate the effects of these interactions on tropospheric chemistry and chemical deposition for the case of a thunderstorm. We use a three-dimensional dynamical, microphysical, and chemical model. Interactions considered include sorption of chemicals from the gas phase, entrapment of chemicals in the solid-phase during liquid hydrometeor freezing, and chemical reactions in / on solid-phase hydrometeors.

2. ICE- AND MIXED-PHASE CHEMISTRY

2.1 Gas-Solid Transfer

Gas-phase chemical species can diffuse to the surface of a solid-phase hydrometeor. They may remain in that hydrometeor through adsorption at the surface, or absorption or incorporation in the bulk phase. In several laboratory studies, researchers have investigated the uptake by ice of several gas phase chemicals, including HCl, HNO₃, H₂O₂, CO₂, and SO₂, and found that uptake is dependent on the type of gas, the temperature, the crystal structure of the ice, and whether the ice phase is growing (e.g. Clapsaddle and Lamb, 1989; Valdez et al., 1989)

A few cloud modeling studies have begun to incorporate these processes and determine their potential impacts on cloud chemistry. Rutledge, et al. (1986), incorporated the adsorption of HNO₃ on snow and graupel in their 2-D numerical modeling study. Incorporating a parameterization based on a theoretical development of chemical diffusion and sticking to hydrometeors, they found the process was partially responsible for the differences in the modeled nitrate and sulfate fields. Chen and Lamb (1990) compiled three semi-theoretical parameterizations of SO₂ sorption, based on the experimental data of Valdez et al. (1989) and Clapsaddle and Lamb (1989). By incorporating these parameterizations into a Lagrangian air parcel model, they found that removal due to ice phase sorption, though significantly lower than that due to liquid removal, is potentially important. They found that the locations of removal and the temperature dependencies were different from liquid phase removal.

2.2 Retention During Riming or Freezing

During freezing of aqueous solutions, solutes may be excluded or retained in the solid phase substrate depending on the characteristics of the solute, concentration of the solute in solution, and the rate and temperature of freezing (Pruppacher and Klett, 1997). In cold clouds, riming is known to lead to the efficient retention of nonvolatile species, such as sulfate. Models of cloud chemistry usually assume full retention of these species in the solid phase during hydrometeor freezing (e.g. Rutledge et al., 1986). The degree of retention of more volatile species is less well characterized.

Several laboratory and field observational studies have measured retention efficiencies of gases in freezing substrates for a limited number of chemical species found in clouds, including H₂O₂, SO₂, O₂, HCl, NH₃, HNO₃ (e.g. Lamb and Blumenstein, 1987; Snider et al., 1992). (The retention efficiency represents the concentration of solute in the solid phase versus that in the original liquid hydrometeor). These studies have resulted in varying estimates of retention efficiencies

(sometimes for the same gas), ranging from 0.01 to 1. Although these differences may be due to different experimental (freezing) conditions, there is currently little theoretical analysis to explain the variations.

Cloud chemistry modeling studies have begun to include the freezing transport mechanism for a limited number of volatile chemical species using representative retention efficiencies. In a 2-D modeling study, Rutledge et al. (1986) assumed full retention of H_2O_2 , S(IV) , nitrate, and non-volatile sulfate during freezing. Chen and Lamb (1990) used a temperature dependent retention coefficient for SO_2 , based on Lamb and Blumenstein (1987) data, in a Lagrangian air parcel model. Kreidenweis et al. (1997) and Audiffren et al. (1999) used a similar retention parameterization for SO_2 in their 2-D modeling studies. Kreidenweis et al. further assumed 24% retention of H_2O_2 , based on data from Snider et al. (1992). Wang and Chang (1993), in their 3-D cloud modeling study, assumed all processes that convert liquid hydrometeors to the solid phase also transfer the solutes contained.

A few of these studies have explicitly examined the effects of including these processes on chemical distributions in clouds or precipitation. Both Chen and Lamb (1990) and Wang and Chang (1993), found that the ice phase chemical transfer mechanisms impacted the pollutant distributions and their time evolution. Cho et al. (1989), through a test of the sensitivity of their 1-D cloud model to including full solid retention of SO_2 and H_2O_2 , found 37% less deposition of sulfate when solid retention was excluded. Audiffren et al. (1999) found that the dependence of the chemistry on the ice-phase is strongly non-linear and chemical dependent, among other results.

2.3 Chemical Reaction

Solid phase hydrometeors may also impact the chemistry occurring in clouds by providing appropriate conditions for chemical reactions. Many types of chemical reactions are known to proceed at significant rates in the ice phase or partially frozen ice phase, including hydrolysis, dehydration, oxidation, and peroxide decomposition reactions (Grant and Alburn, 1965). For some reactions, studies have shown an accelerated reaction rate when ice is present over the reaction rate in liquid solution (e.g. Grant and Alburn, 1965; Sato et al., 1996; Takenaka et al., 1996). Experimental studies of reactions in / on ice that are potentially important to cloud chemistry have primarily focused on the oxidation of sulfur dioxide and nitrite (e.g. Iribarne and Barrie, 1995; Sato et al., 1996; Takenaka et al., 1996). No modeling studies of convective cloud chemistry to date have included ice-phase reactions.

3. DESCRIPTION OF MODEL SIMULATIONS

We use the COllaborative Model for Multiscale Atmospheric Simulation (COMMAS), a 3-D non-hydrostatic convective cloud model (Wicker and Wilhelmson, 1995; Wicker and Skamarock, 1998) for this work. The model contains a bulk parameterization of microphysics, described by Tao and Simpson (1993), which includes three glaciated hydrometeor species (cloud ice, snow, and hail). The model includes gas-

liquid inter-phase transfer of chemical species and their advective transport in the gas and hydrometeor phases (Barth et al., 2000; Skamarock et al., 2000). The base chemical mechanism, representing daytime nitrogen and ozone chemistry in the troposphere, includes 15 chemical species undergoing 27 gas-phase and 15 aqueous-phase reactions.

We apply the COMMAS model to the July 10, 1996 STERAO thunderstorm observed in northeastern Colorado for the simulations in this work. The model domain is 120 x 120 x 20 km with 1 km horizontal resolution and variable vertical resolution (stretching from 50 m at the surface to 750 m at the domain top). Detailed discussion of the initialization and modeling of the storm dynamics and insoluble tracer transport can be found in Skamarock et al., (2000). Barth et al. (2000) include discussion of the effects of gas-liquid transfer on tracer fate. For the purposes of the work here, it is important to note that species mixing ratios are initially highest (135 ppbm) in the boundary layer, and decrease to 70 ppbm by 9.5 km above the ground (11 km MSL).

To determine the range of potential effects of solid-phase hydrometeor-chemical interactions on tropospheric chemical distributions and deposition, we follow the fate of chemicals during model simulations in which several distinct parameterizations of these solid-phase hydrometeor-chemical interactions are implemented.

4. MODELING RESULTS

As discussed by Skamarock et al. (2000) the simulated storm evolved from a Northeast to Southwest multicellular convective line to supercellular after about two hours. During the simulated storm lifetime, the largest heights reached by the convective cells was approximately 15 km, with the storm anvil above approximately 8 km. The simulated storm anvil consisted primarily of snow and ice, while liquid and frozen hydrometeors coexisted in the storm core (Barth et al., 2000). Rain precipitated below cloud level to reach the ground surface. Analyses of passive tracer fate and parcel trajectories indicate that the storm transported air from the boundary layer, between 0.5 – 2 km above ground, to the anvil, with some entrainment and dilution in the convective updrafts and anvil (Skamarock et al., 2000).

To begin our investigation of the effects of interactions between chemicals and solid hydrometeors on chemical fate, here we will compare and discuss results of two simulations with distinct representations of chemical transfer during riming and freezing. For the first simulation, we assume that all dissolved species degas when a hydrometeor freezes. For the second, dissolved species are retained in the frozen hydrometeor and are transported throughout the storm with the parent hydrometeor. We investigate the effects on species of varying solubilities by considering pseudo-species with a range of solubilities. Results shown are for simulations in which chemical reactions were not activated.

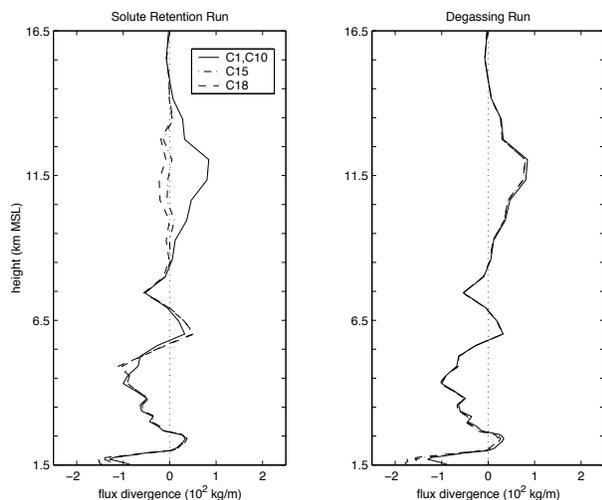


Figure 1. Time and horizontally integrated vertical flux divergence (a measure of mass accumulation) versus height after 3 hours of storm simulation for four pseudo-species of varying solubility. C1 is a passive tracer (only transported in air). C10, C15, and C18 have increasing solubilities, with Henry's constants (K_h) of 100, 10^5 , 10^{12} M atm⁻¹, respectively. (a) results for the simulation in which solutes are retained during hydrometeor freezing. (b) gives results for the simulation in which solutes are degassed.

The effect of retention of solutes during hydrometeor freezing on species mass transport due to the storm is shown in Figure 1. The figure shows a measure of mass accumulation versus height after 3 hours of storm simulation for pseudo-species of varying solubilities (Henry's constants, K_h , of 0, 100, 10^5 , and 10^{12} M atm⁻¹ for C1, C10, C15, and C18, respectively). For the simulation in which solutes are degassed during hydrometeor freezing, Figure 1b, shows that, over the storm lifetime, species of all solubilities are generally lost from lower levels (below 6 km MSL) and gained in the anvil region (above 8 km MSL). In other words, overall mass transport is mainly due to advection of species in air. The simulation allowing species to remain in the frozen hydrometeor, Figure 1a, leads to less accumulation of species in the anvil as species solubility increases. For highly soluble species ($K_h \geq 10^5$ M atm⁻¹), solute retention during freezing reverses the trend of species transport from lower to higher levels. As species are carried with their parent frozen hydrometeor, mass in the anvil outflow air is instead depleted and more is transported to the ground in precipitation. Table 1 lists the total mass of the most soluble species, C18, deposited to the ground and accumulated in the anvil.

Simulation	Accumulation in Anvil (kg)	Surface Deposition (kg)
Solute retention	-5.59×10^4	2.82×10^5
Degassing	2.13×10^5	5.79×10^4

Table 1. Total mass accumulation in the storm anvil (8 to 15 km MSL) and deposited to the ground, of C18 after 3 hours of storm simulation (kg).

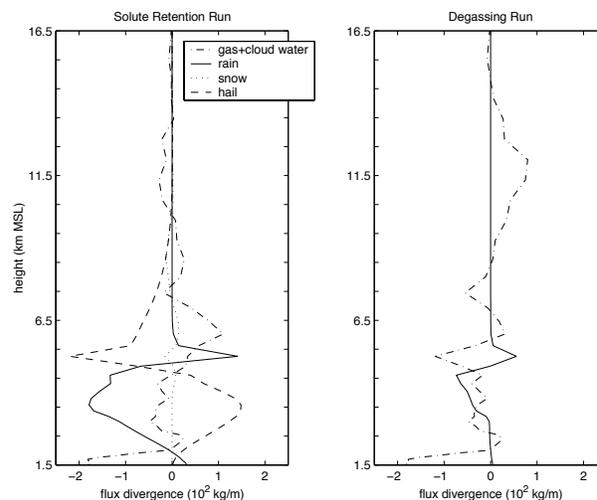


Figure 2. Hydrometeor specific time and horizontally integrated vertical flux divergence versus height after 3 hours of storm simulation for a highly soluble species, C18 ($K_h = 10^{12}$ M atm⁻¹). (a) gives results for the solute retention simulation. (b) gives results for solute degassing simulation.

The impact of specific hydrometeor motion on the fate of a highly soluble species, C18 ($K_h = 10^{12}$ M atm⁻¹), is shown in Figure 2. For the solute retention simulation Figure 2a, we see that chemical transport in ice and snow play a very minor role compared to that in rain and hail. Transport in rain plays a more significant role for the solute retention run than for the degassing run. Transport in gas and cloud water together also play a less significant role in chemical redistribution in the solute retention run than the degassing run. Though not shown, for less soluble species, transport in hydrometeors becomes insignificant compared to that in air.

5. DISCUSSION AND CONCLUSIONS

Despite their potential impact on chemical fate, interactions of chemicals with solid phase hydrometeors, including gas-solid transfer, liquid-solid transfer, and chemical reaction, are not represented in many cloud models. A thorough understanding of the effects of these interactions on chemical distributions, in order to ensure that relevant processes are included in models used to represent larger scale phenomena (e.g. acid rain and upper tropospheric ozone) is lacking. Available studies including limited representation of these interactions indicated that the impacts may be significant, but yield varying results.

In a first step toward a systematic investigation of the range of potential impacts of these interactions on chemical distributions and deposition, we compare 3-D modeling simulations of chemical tracer transport in the July 10, 1996 STERAO thunderstorm. We compare fates of species for simulations including two representations of liquid-solid chemical transfer during hydrometeor freezing, in order to investigate the effects of these representations on tracers of varying solubilities. We find that allowing species to be retained in solid hydrometeors during freezing, rather than being

re-emitted to the gas phase, may have significant impacts on the fate of highly soluble species ($K_h \geq 10^5 \text{ M atm}^{-1}$). Relevant natural species falling within that range of solubilities include hydrogen peroxide and nitric acid. For the simulation in which solutes are retained during freezing, increasing solubility of pseudo-species leads to less transport of species mass upward into the anvil outflow air and more transport to the ground, as compared to a passive tracer transported in air only, and as compared to the transport of tracers which undergo degassing during hydrometeor freezing. For highly soluble pseudo-species ($K_h \geq 10^5 \text{ M atm}^{-1}$), overall depletion of species mass at some levels of the anvil outflow area occurs due to the storm. Analysis of the hydrometeor specific transport reveals that precipitation of hail and rain are largely responsible for this trend reversal. With retention of species in frozen hydrometeors at lower levels of the storm, less species mass is made available for transport upward in air. Instead species mass is transported in hail, and in rain formed by melting hail. Ice and snow are likely insignificant contributors to the chemical fate because less species mass is available for partitioning to these species at upper levels, where ice and snow hydrometeors reside.

The results discussed here are a first step, using a necessary 3-dimensional model framework, towards understanding the potentially significant impacts of chemical interactions with solid-phase hydrometeors on trace species fate during and after a convective storm. Much further work is needed to understand the breadth of effects of these types of interactions, through systematic analysis and comparison of results from simulations including several representations of chemical / solid-phase hydrometeor interaction and chemical transformations.

6. ACKNOWLEDGEMENTS

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