The fate of volatile chemicals during wet growth of a hailstone

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Abstract

We develop and apply a mechanistic model for the study and prediction of volatile chemical partitioning during wet growth of a hailstone. The model estimates the fraction of a chemical’s mass in the impinging drops that is retained in a two-phase hailstone. It is derived from mass and rate balances over solute and water for steady accretion conditions. We applied the model using a modified Monte Carlo ensemble simulation approach to study the impact of chemical, environmental, and hail-specific input variables on the predicted retention fraction for six atmospherically relevant volatile chemical species, sulfur dioxide, hydrogen peroxide, ammonia, nitric acid, formaldehyde, and formic acid. Individual input variables found to significantly influence retention are the ice–liquid interface supercooling, the liquid water content of the hail, and the effective Henry’s constant. The retention fraction increased with increasing values of these variables. Conversely, the ice–liquid distribution coefficient and hail diameter were found to have negligible effects on solute retention. The overall range of simulated retention fraction was from $1 \times 10^{-8}$ to 1, while ensemble mean retentions for fixed values of individual input variables ranged from $9 \times 10^{-7}$ to 0.3. No single variable was found to control the extremes; rather they are due to combinations of model input variables.

Keywords: cloud chemistry, ice chemistry, chemical partitioning, retention, hail

1. Introduction

Convective cloud systems contribute to the production and redistribution of trace chemical constituents in the troposphere. Impacts include cleansing of boundary layer pollution, scavenging, production, and deposition of acids, toxins, and nutrients, export and long-range transport of pollution over regional to global scales, and alteration of the upper-tropospheric ozone budget. Although the effects of clouds on chemistry through gas- and liquid-phase interactions has been extensively studied, recent work has begun to focus on the more poorly understood interactions with the ice phase. Volatile chemical phase partitioning during freezing and riming of supercooled drops is one such interaction. Cloud modeling studies incorporating this partitioning suggest that it may have significant impacts on chemical fate and chemistry (Cho et al. 1989, Lamb and Chen 1990, Wang and Chang 1993, Audiffren et al. 1999, Mari et al. 2000, Barth et al. 2001, 2007, Yin et al. 2002). Simulated impacts have included enhanced scavenging of intermediate to highly soluble species (Barth et al. 2001), higher amounts of H$_2$O$_2$ and sulfates in precipitation (Audiffren et al. 1999), suppression of H$_2$O$_2$ scavenging (Mari et al. 2000), and suppression of ozone precursors in convective outflows (Barth et al. 2007). Modeling results also suggest that the parameterization of partitioning can strongly affect the simulated outcome (Cho et al. 1989, Lamb and Chen 1990, Barth et al. 2001), though results may also depend on the cloud type (Yin et al. 2002) and the convection initiation representation (Salzmann et al. 2007).

To better understand and represent these effects, several laboratory and field experimental studies have studied phase partitioning during liquid-to-solid freezing and riming (Iribarne et al. 1983, Iribarne et al. 1990, Lamb and Blumenstein...
The retention fraction, or ratio of the solute mass in the icy hydrometeor particle over that in the liquid drops, is a measure of this effective chemical partitioning. Experimental studies have found retention fractions that vary widely in the range of about 0.1–1 for several species of atmospheric interest, including O₂, SO₂, H₂O₂, HNO₃, HCl, and NH₃, HCOOH, and CH₃COOH. Theoretical and drop-scale modeling studies have helped to elucidate the factors affecting this variation in retention fraction values with environmental conditions and chemical properties. In previous work (Stuart and Jacobson 2003, 2004, 2006), the retention fraction was predicted to be highly chemical specific and dependent on the Henry’s constant of the solute, the pH, temperatures, drop size, and ventilation conditions. A parameterization that compares well to experimental data was also developed. The previous work focused on non-rime drop freezing and dry growth riming conditions. In this work, we study wet rime conditions, for which theoretical and model development studies are still lacking. We develop and apply a mechanistic model for volatile chemical partitioning during steady wet hailstone growth.

2. Model development

This model considers a hailstone growing at a constant rate through collection and freezing of supercooled water drops, under conditions that lead to wet growth. Wet growth is characterized by coalescence of collected water drops, incomplete freezing of the hydrometeor, and surface temperatures of 0 °C. Under such conditions, chemical solutes dissolved in the collected drops can be retained in the water film at the surface of the hail, entrapped in water pockets within hail ice, or incorporated in the ice structure. Solutes can be removed via shed water and through evaporation. Figure 1 illustrates the microphysical processes affecting solute partitioning during wet growth.

Adapting the development of Makkonen (1987) for determining the salinity of sea spray ice, we can write a rate balance on solute mass during steady wet growth of a hailstone as:

\[ X_d F = X_l G + X_e E + X_1 S. \]  

(1)

\( F \) is the rate of drop collection, \( G \) is the rate of hailstone growth, \( E \) is the rate of evaporation, and \( S \) is the rate of shedding (each having units of aqueous solution mass per time). \( X_d, X_l, X_e, \) and \( X_1 \) are the solute mass fractions (mass of solute per mass of solution) for the drops, hailstone, evaporate, and shed (and surface) liquid, respectively. Rearrangement results in:

\[ \frac{X_d G}{X_d F} = \frac{(X_b/X_l)G}{(X_b/X_l)G + (X_e/X_1)E + S}. \]  

(2)

\( X_e/X_1 \) is a mass fraction air–water distribution coefficient. In terms of a more traditional dimensionless effective Henry’s constant \( (H^*) \), it is \( X_e/X_1 = (1/H^*)(\rho_i/\rho_v) \), where \( \rho_i \) is the density of the liquid solution, and \( \rho_v \) is the saturation vapor density over the liquid solution. \( X_b/X_1 \) can be determined by a solute mass balance on the hailstone:

\[ X_b M_b = X_1 M_1 + X_l M_l, \]  

(3)

\( M_b, M_l, \) and \( M_l \) are the total mass, liquid-phase mass, and ice-phase mass of the hailstone, respectively. Rearrangement gives \( X_b/X_1 = \eta + k_e(1 - \eta) \), where \( \eta \) is the mass fraction liquid water content of the hailstone (\( M_l/M_b \)), and \( k_e \) is the effective ice–liquid interfacial distribution coefficient \( (X_e/X_1) \), which includes the effects of dendritic trapping (non-equilibrium partitioning) of solute in ice (Hobbs 1974, pp 600–6).

The left-hand side of equation (2) provides the rate of solute accumulation in the hailstone over that collected in liquid drops. For any period of steady growth, it is equal to the previously defined retention fraction, \( \Gamma \). Substitution of the above definitions into equation (2) results in the following model expression for the retention fraction:

\[ \Gamma = \frac{G[\eta + k_e(1 - \eta)]}{G[\eta + k_e(1 - \eta)] + E[(1/H^*)(\rho_i/\rho_v)] + S}. \]  

(4)

To determine the retention fraction, rates of the microphysical processes, \( E, G, \) and \( S \) must be calculated based on environmental conditions. Evaporation is estimated as a first order mass transfer rate process for a spherical particle in an open system, as \( E = 4\pi r D\Phi (P_v^s/R, T_h) \) (Pruppacher and Klett 1998), where \( r \) is the hailstone radius, \( D \) is the diffusivity of water vapor in air, \( \Phi \) is the ventilation coefficient, \( P_v^s \) is the saturation vapor pressure over liquid water, \( R_v \) is gas constant for water vapor, and \( T_h \) is the hailstone surface temperature. We note that the representation of solute vapor in equation (1) \( (X_e E) \) approximates evaporation rates for solute and water as proportional. This approximation assumes an open system (low concentrations of water vapor and solute in surrounding air compared with those near the hailstone surface), similar diffusivities of water vapor and solute in air, and similar ventilation coefficients. Equilibrium chemical partitioning at the liquid–gas interface (but not between the bulk phases) is also assumed. These are reasonably good assumptions for the conditions here, but will be less applicable as cloud supercooling decreases, for lower cloud liquid water contents, and for chemicals or conditions resulting in significant interfacial transfer resistances.
Table 1. Model parameters and methods.

| Parameter | Method references and assumptions |
|-----------|-----------------------------------|
| Hail temperature ($T_{hi}$) | Assumed equal to 0 °C |
| Latent heat of water melting ($L_m$) | J, p 40, equation 2.55 |
| Latent heat of water sublimation($L_i$) | J, p 40, equation 2.56 |
| Latent heat of water evaporation | $L_r - L_m$, J, p 40, equation 2.56 |
| Saturation vapor pressure over liquid water ($P_{vL}$) | J, p 41, equation 2.62 |
| Saturation vapor density over liquid water ($\rho_{vL}$) | J, p 31, equation 2.25 |
| Saturation vapor density over ice | J, p 43, equation 2.64 |
| Water–air surface tension | J, 2005, p 485, equation 14.19 |
| Dynamic viscosity of dry air | J, p 102, equation 4.54 |
| Heat capacity of dry air at constant pressure | (Smith and Van Ness 2001), p 109 |
| Partial pressure of water vapor in air | J, p 21, equation 2.27 |
| Mass mixing ratio of water vapor in air | J, p 32, equation 2.31 |
| Thermal conductivity of dry air | J, p 20, equation 2.5 |
| Gas constant for water vapor ($R_v$) | J, p 712 |
| Gas constant for moist air | J, p 33, equation 2.37 |
| Molecular weight of moist air | J, p 31, equation 2.26 |
| Density of moist air ($\rho_i$) | J, p 33, equation 2.36 |
| Kinematic viscosity of moist air | J, p 102, equation 4.55 |
| Mean free path of moist air | J, p 506, equation 15.24 |
| Effective Henry’s constant ($H^*$) | SP, p 340–50, |
| Heat capacity of moist air at constant pressure | J, p 20, equation 2.5 |
| Diffusivity of water vapor in air ($D$) | PK, p 503, equation 13-3 |
| Heat capacity of (supercooled) water | PK, p 93, equation 3-16 |
| Density of (supercooled) liquid water ($\rho_l$) | PK, p 87, equation 3-14 |
| Density of ice ($\rho_i$) | PK, p 9, equation 3-2 |
| Density of hailstone | $\varepsilon = [\eta/\rho_i + (1 - \eta)/\rho_d]^{-1}$ |
| Drop terminal fall velocity | J, p 664, equation 20.9 |
| Hailstone fall velocity | PK, p 441,SP, p 467 |
| Impact speed of droplets and hailstone ($v$) | Assumed equal to $v_d - v_h$ |
| Reynolds number for flow around drops | J, p 664, equation 20.6 |
| Reynolds number for flow around hailstone | SP, p 460 |
| Prandtl number | J, p 532, equation 16.32 |
| Schmidt number | J, p 531, equation 16.25 |
| Stokes, Russelt, and Sherwood numbers | SJ, section 2.3 |
| Ventilation coefficient ($\Phi$) | PK, p 537, equation 13-52 |
| Critical liquid water content ($\omega_i$) | SJ, equation 14 |

* Symbols are provided for parameters used elsewhere in the text.
* a Method references and assumptions used to calculate chemical and physical parameter properties in the above equations are provided in table 1.
* b We assume the air is saturated with respect to liquid water at the air temperature.
* c Weighted reciprocal average of ice and liquid water.

The hailstone growth rate, $G$, was determined as the sum of the ice growth rate ($G_i$) and the rate of change of liquid water mass of the hydrometeor ($G_w$). Ice growth was estimated as $G_i = 4\pi r^2 b(\Delta T)^c \rho_i$, where $\rho_i$ is the ice density and $\Delta T$ is the ice–liquid interface supercooling ($T_{0} - T_{int}$). $T_{0}$ is the equilibrium freezing temperature of water, 0 °C, and $T_{int}$ is interface temperature. $b(\Delta T)^c$ is the intrinsic crystal interface growth speed (Pruppacher and Klett 1998, pp 668–74). As the interface temperature during wet growth is expected to be very close to zero, we use $b$ of 0.3 and $c$ of 2 for the classical growth regime (Bolling and Tiller 1961). The rate of change of hailstone water mass can be determined as $G_w = G_i \eta/(1 - \eta)$, for the case of constant hailstone liquid water content. The shedding rate is determined, by water mass conservation, as $S = F - G - E$, with the rate of drop collection by a falling hailstone estimated as $F = \varepsilon \pi r^2 \omega_i \rho_d$ (Pruppacher and Klett 1998, pp 568–70).

Here, $\varepsilon$ is the fall speed of the hailstone relative to the drop, $\rho_d$ is the density of air, $\omega$ is the cloud liquid water content, and $\varepsilon$ is the collection efficiency. References, expressions, and assumptions used to calculate chemical and physical parameter properties in the above equations are provided in table 1.

3. Application

To investigate the dependence of partitioning on forcing variables, retention fractions were calculated for several chemicals of atmospheric interest. Six trace chemicals were considered, SO$_2$, H$_2$O$_2$, NH$_3$, HNO$_3$, CH$_2$O, and HCOOH. Input variables defining environmental conditions, hailstone characteristics, and chemical-specific properties are listed in table 2, along with the range of values considered. Ranges are based on literature values for conditions applicable to
wet growth and calculated effective Henry’s constants for the chemicals studied. A modified Monte Carlo ensemble modeling approach was used. For each input variable a series of ensemble simulations was run for which the focus variable was held constant at discrete values spaced over the range listed in table 2. For each of these values, a 100-member ensemble was assembled by allowing all other variables to vary randomly over a continuous uniform distribution also defined by the ranges listed in the table. Log transformed ranges were used for the effective Henry’s constant. Only those results meeting model constraints were retained in the analysis. Two constraint conditions were applied. First, the cloud liquid water content had to exceed the calculated Schumann–Ludlam limit critical liquid water content, \( \omega_c \), to ensure only wet growth conditions are considered. (The expression used to calculated \( \omega_c \) is provided in table 1.) Second, only input condition cases resulting in hailstone growth that did not violate mass conservation (i.e., more growth than available accreted water) were allowed. Model calculations were performed using microsoft excel with Oracle’s crystal ball software for ensemble generation and statistical calculations. Testing of the model included comparison of derived intermediate model parameters with published data and overall mass conservation calculations for both water and solute. (Further discussion of the constraint calculations and model testing is provided in Michael (2008).)

### Table 2. Input variables and ranges.

| Name and symbol                     | Units | Range | References and assumptions |
|-------------------------------------|-------|-------|----------------------------|
| Cloud liquid water content (\( \omega \)) | g m\(^{-3} \) | 0.2–5 | Pruppacher and Klett (1998, p 23)\(^b\) |
| Drop radius (\( \alpha \))          | \( \mu m \) | 5–100 | Jacobson (2005, p 447) |
| Atmospheric pressure (\( P \))      | mb    | 200–1013 | Tropospheric pressures |
| Air temperature (\( T_a \))         | °C    | 0–30  | Observed wet growth regime limits Pruppacher and Klett (1998, p 682) |
| Hailstone diameter (\( D_h \))      | mm    | 1–50  | Pruppacher and Klett (1998, p 71) |
| Hailstone liquid water content (\( \eta \)) |         | \( 10^{-4}–0.5 \) | Max observed water fraction (Lesins and List 1986) |
| Ice interface supercooling (\( \Delta T \)) | °C | \( 10^{-4}–0.1 \) | Close to zero, due to the heat released during freezing\(^a\) |
| Hailstone shape factor (\( f \))    |       | 3.14–4 | Macklin and Payne (1967), Jayaratne (1993)\(^d\) |
| Collection efficiency (\( \varepsilon \)) |       | 0.5–1 | Assumed close to 1 (Lin et al 1983) |
| Effective Henry’s constant (\( H^* \)) |       | \( 10^{-5}–10^{4.5} \) | Calculated for pH range (Seinfeld and Pandis 1998, pp 340–85)\(^e\) |
| pH                                  |       | 2–8   | Approximate range observed in experimental retention studies |
| Effective ice–liquid distribution coefficient (\( k_e \)) |       | \( 10^{-5}–10^{-3} \) | Experimental data and theory (Hobbs 1974, pp 600–6)\(^f\) |

\(^a\) The input ranges used were based on the references provided, given the listed assumptions. They were chosen to span the natural ranges observed in clouds. See individual parameter notes for those ranges that were effectively further limited by the model constraint conditions. Michael (2008) also provides some further discussion of the input and resultant ranges.

\(^b\) Values below 2 resulted in a large percentage of member runs that did not meet the constraint conditions (e.g. wet growth). Hence, no results are provided for these values in figure 2(a) (the \( \omega \) dependence plot).

\(^c\) Values up to 10 (for classical growth, Pruppacher and Klett (1998, p 668)) were initially considered, but larger values resulted in violation of the constraint conditions (discussed in the text), and hence the range was limited to values below 0.1.

\(^d\) Values between a cylindrical and spherical geometry.

\(^e\) The effective Henry’s constant was first calculated for all studied chemicals over the range of pH considered. The overall range of \( H^* \) used in simulations was chosen to span the range of calculated values (as discussed in the text).

\(^f\) The effective ice–liquid distribution coefficient is not very chemical specific.

### 4. Results

Figure 2 shows the simulated response of the ensemble mean retention fraction and other distribution parameters to changes in each of the environmental input variables (cloud liquid water content, drop radius, atmospheric pressure, and air temperature). Of the environmental input variables, the mean retention fraction varies the most with cloud liquid water content, ranging between 0.1 and 0.2 over the range of \( \omega \). However, the relationship is nonmonotonic and very small. We also see nonmonotonic relationships for the other distribution parameters. However, the number of valid member runs in each ensemble increases as cloud liquid water content increases (i.e, more members met the model constraints of wet growth and mass conserving hail growth). The other environmental variables had no apparent effect individually on the retention fraction, though the number of valid members increases as the air temperature increases and pressure decreases.

Figure 3 shows the simulated response of retention fraction to increasing values of each of the hail input variables (hail diameter, hail liquid water content, ice–liquid interface supercooling, hail shape factor, and collection efficiency). Changes in the hail liquid water content (\( \eta \)) and interface supercooling (\( \Delta T \)) led to discernible trends in the ensemble mean retention fraction. Mean retention fraction increased with increasing values of both these parameters. For the
interface supercooling, mean $\Gamma$ increased from $9 \times 10^{-7}$ to 0.3 as $\Delta T$ increased from $1 \times 10^{-4}$ to 0.08°C. The trend was monotonic, though retention increases appear to level off at higher values of $\Delta T$. For hail liquid water content, mean $\Gamma$ ranged from $8 \times 10^{-3}$ to 0.3 as $\eta$ increased from $1 \times 10^{-4}$ to 0.5. The spread of the simulated retention fraction also increased with these variables. For $\Delta T$, the spread increased despite a decreasing trend in the number of valid member runs at higher interface supercooling. Detailed analysis of constraint results (not shown) indicate that this trend is primarily due to the growth rate mass balance constraint, i.e. ice growth rates that would result from higher supercooling would outstrip the mass available for growth under many conditions. No clear trend was observed for the response of retention fraction to hail diameter, hail shape factor, or collection efficiency individually. However, increasing hail diameter did result in an increase in valid runs, due to an increase in the number of runs meeting both constraints (not shown).

Figure 2 shows the simulated response of retention fraction to increasing values of each of the chemical input variables (effective Henry’s constant and effective ice–liquid distribution coefficient). The ensemble mean retention fraction increased from $2 \times 10^{-3}$ to 0.2 for dimensionless effective Henry’s constant increasing from 300 to $3 \times 10^{18}$. However, the response is not uniform; almost all the increase in retention fraction occurs at low values of effective Henry’s constant (from 300 to $3 \times 10^{18}$), with retention values leveling off at higher $H^*$. Retention is therefore predicted to be somewhat greater for higher solubility, lower volatility chemicals and conditions resulting in higher effective Henry’s constants. Specifically, the pH is known to be an important determinant of effective water–air partitioning for many chemicals of atmospheric interest, due to changes in dissociation amounts. Figure 4(c) shows the simulated effect of pH conditions on the effective Henry’s constant for the chemicals studied here. Only SO$_2$ and NH$_3$ have effective Henry’s constants that change with pH over the range for which impacts on retention are predicted. Hence, we expect that for these chemicals, pH conditions will impact retention (with retention increasing with pH for SO$_2$ and decreasing with pH for NH$_3$). No clear trend in retention fraction was observed with the effective ice–liquid distribution coefficient.

Table 3 provides a synthesis of the results obtained. A description of the relationship between each variable and retention fraction, the range of ensemble mean retention fractions for each constant value of that variable, and the overall range of retention fraction for all values of that variable are provided. The table is sorted from largest effect to smallest (approximately). The table shows that the single variable with the largest effect on retention was the interface supercooling, followed by hail liquid water content, and effective Henry’s constant. All other input variables were found to have very small or no effects on retention individually.

### 5. Discussion

The ice–liquid interface supercooling was found to be the most important forcing variable for solute retention during wet growth of hail. Experimental studies have found a direct relationship between retention and supercooling under mixed wet and dry growth conditions (Lamb and Blumenstein 1987, Iribarne et al 1990, Snider et al 1992). In this study,
Figure 3. The effect of individual hail input variables on retention fraction. The box plots characterize the ensemble distribution of simulated results with the abscissa variable held constant and other parameters varied randomly. The italicized value above each box plot provides the number of ensemble member runs that met model constraints.

Table 3. Dependence of simulated retention fraction on input variables.

| Input variable                              | Effect description                  | Range of ensemble means | Overall range          |
|---------------------------------------------|-------------------------------------|-------------------------|------------------------|
| Interface supercooling, $\Delta T$         | Large, direct, monotonic            | $9.0 \times 10^{-7} - 0.30$ | $1.1 \times 10^{-8} - 0.99$ |
| Mass fraction hail liquid water content, $\eta$ | Large, direct                       | $7.5 \times 10^{-3} - 0.27$ | $6.0 \times 10^{-8} - 0.99$ |
| Chemical’s effective Henry’s constant, $H^*$ | Large, direct, but levels off       | $1.6 \times 10^{-3} - 0.17$ | $1.4 \times 10^{-4} - 0.79$ |
| Cloud liquid water content, $\omega$       | Very small, nonmonotonic            | $0.11 - 0.21$           | $1.1 \times 10^{-6} - 0.96$ |
| Hail shape factor, $f$                      | Very small, nonmonotonic            | $0.091 - 0.19$          | $1.3 \times 10^{-6} - 0.95$ |
| Hail diameter, $D_h$                        | Very small, nonmonotonic            | $0.068 - 0.15$          | $5.1 \times 10^{-6} - 0.88$ |
| Collection efficiency, $\varepsilon$       | Very small, nonmonotonic            | $0.10 - 0.17$           | $2.8 \times 10^{-6} - 0.97$ |
| Effective ice–liquid distribution coefficient, $k_e$ | None                                | $0.087 - 0.14$          | $6.2 \times 10^{-6} - 0.95$ |
| Air temperature, $T_a$                      | None                                | $0.12 - 0.16$           | $5.6 \times 10^{-6} - 0.93$ |
| Atmospheric pressure, $P$                  | None                                | $0.11 - 0.15$           | $1.3 \times 10^{-3} - 0.88$ |
| Drop radius, $a$                            | None                                | $0.12 - 0.15$           | $4.9 \times 10^{-3} - 0.92$ |
retention was found to increase as interface supercooling increased (lower interface temperatures). Conversely, air temperatures, and hence drop (and cloud) supercooling, had no effect. This difference in the simulated dependence of retention on independently varied temperature variables, in light of experimental evidence, supports the idea that temperatures are primarily important to retention due to their effects on ice–liquid interface supercooling, and hence, on ice growth rates and solute trapping. However, we must note that co-dependence of these temperature variables is not currently represented in this model, though cloud supercooling (air and drop temperatures) will likely impact interface supercooling in nature.

The liquid water content of the hail was also found to be an important forcing variable for solute retention during wet growth of hail. With higher liquid water content, more solute can be retained in the liquid water portion of the hail. Related to this finding, simulated mean retention values are all relatively low, even for highly soluble chemicals. This contrasts with values predicted for dry growth conditions (Stuart and Jacobson 2003, 2004, 2006), for which trapping of solute by dendritically growing ice and surface ice was found to be important to retaining high concentrations of solute, particularly for highly soluble chemicals. During wet growth, we find here that the liquid-phase solute concentrations (rather than trapping) dominate retention, with solute loss processes (evaporation and shedding) remaining important. This leads to lower retention fraction values. However, an overall hail particle can often contain layers formed during alternating wet and dry growth (Pruppacher and Klett 1998, p 73). Since much of the solute is found to be retained in the liquid during wet growth, we expect that rate of formation of a surface ice layer during the transition to dry growth will be important to final retention in the wet grown layers. Nonetheless, our findings indicate the importance of considering and quantifying hail liquid water content in future theoretical and experimental work to understand retention. Although the dependence of $\eta$ on environment conditions was not represented here, its importance to the retention fraction suggests that this dependence should also be studied and represented.

Overall, the issue of co-dependence and indirect effects on retention through independently varied hail parameters decreases our confidence in findings for the environmental variables (cloud liquid water content, air temperature, atmospheric pressure, and drop radius). The environmental variables may affect the hail liquid water content and/or the interface supercooling temperature, which were found to significantly force retention. Hence, to better understand the impacts of environmental variables, it will be important to calculate these two hail variables within the model, rather than set them independently as input variables. This will require heat balance calculations to determine temperatures and calculation of the shedding rate independent of the water mass balance. For the other hail-related parameters (collection efficiency, hail shape factor, and hail diameter) and for the effective ice–liquid chemical distribution coefficient, no clear effect was observed on retention. Hence, it is less important to represent their dependence on environmental conditions or
consider their effects on retention. As collection efficiency, hail shape factor, and the ice–liquid distribution coefficient are poorly understood themselves and would be difficult to calculate from physical (non-empirical) principles, this result is helpful to future micro- and cloud-scale modeling. Also, the very small impact of hail diameter on retention is important to the applicability of this model. Since hail diameter has no effect on retention, the assumption of a constant value is appropriate.

Chemical Henry’s constant was found to be the third important determinant of retention fractions, with higher fractions observed for higher effective Henry’s constants (more soluble, less volatile chemicals). This is consistent with previous findings for dry growth conditions and experiment fractions observed for higher effective Henry’s constants (more important determinant of retention fractions, with higher appropriate).

Finally, despite high predicted maximum values for all ensemble simulations (of 0.9–1), the means for all ensembles were much lower, with the highest mean predicted at 0.3. Hence, no single variable was found to be responsible for simulated maximum values of retention. Rather, combinations of favorable input conditions were needed to generate retention fractions greater that 0.3. Further investigation of variable combinations that lead to the high observed values is needed.

In this work, we explore the physical relationships between environmental, hail, and chemical parameters that impact retention of volatile chemicals during steady wet growth of hail. Findings provide results on the dependence of retention fraction on these parameters, which can be used to inform development of better cloud modeling parameterizations. Important findings include that the retention fraction of chemicals is somewhat dependent on the effective Henry’s constant for wet growth conditions, as was found previously (and more strongly) for dry growth and non-rime freezing conditions. Hence, Henry’s constant (and pH for dissociating species) should likely be included in any future cloud modeling parameterizations of chemical retention. However, retention is likely to be small during steady wet growth, even for highly soluble chemicals, since most of the retention under these conditions is occurring in the liquid phase, allowing significant loss through shedding and evaporation. Also, since the retention fraction is likely to be different under wet and dry growth conditions, robust parameterization in cloud models may require representation of the changing regimes and allow for dynamic retention calculations, rather than using a single retention value for a given species (or simple temperature dependent expressions). Finally, the retention fraction in wet growing hail is likely highly dependent on the hail liquid water content and ice water interface supercooling. Hence, these should be considered (measured or calculated) in future experimental and modeling studies of chemical partitioning during cloud freezing.

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References

Audiffren N, Cautenet S and Chaumerliac N 1999 A modeling study of the influence of ice scavenging on the chemical composition of liquid-phase precipitation of a cumulonimbus cloud J. Appl. Meteorol. 38 1148–60 Barth M C, Kim S-W, Skamarock W C, Stuart A L, Pickering K E and Ort L E 2007 Simulations of the redistribution of formaldehyde, formic acid, and peroxides in the 10 July 1996 stratospheric-tropospheric experiment: radiation, aerosols, and ozone deep convection storm J. Geophys. Res. 112 D13310 Barth M C, Stuart A L and Skamarock W C 2001 Numerical simulations of the July 10, 1996, stratospheric–tropospheric experiment: radiation, aerosols, and ozone (STERAO)-deep convection experiment storm: redistribution of soluble tracers J. Geophys. Res. 106 12381–400 Bolling G F and Tiller W A 1961 Growth from the melt III dendirct growth J. Appl. Phys. 32 2587–605 Cho H R, Niewiadomski M, Iribarne J V and Melo O 1989 A model of the effect of cumulus clouds on the redistribution and transformation of pollutants J. Geophys. Res. 94 12895–910 Hobbs P V 1974 Ice Physics (Oxford: Oxford University Press) Iribarne J V and Barrie L A 1995 The oxidation of S(IV) during riming by cloud droplets J. Atmos. Chem. 21 97–114 Iribarne J V, Barrie L A and Iribarne A 1983 Effect of freezing on sulfur dioxide dissolved in supercooled droplets Atmos. Environ. 17 1047–50 Iribarne J V and Pyshnov T 1990 The effect of freezing on the composition of supercooled droplets–I. Retention of HCl, HNO3, NH3 and H2O2 Atmos. Environ. A 24 383–87 Iribarne J V, Pyshnov T and Naik B 1990 The effect of freezing on the composition of supercooled droplets–II. Retention of S(IV) Atmos. Environ. A 24 389–98 Jacobson M Z 2005 Fundamentals of Atmospheric Modeling 2nd edn (New York: Cambridge University Press) Jayaratne E R 1993 The heat balance of a riming graupel pellet and the charge separation during ice–ice collisions J. Atmos. Sci. 50 3185–93 Lamb D and Blumenstein R 1987 Measurement of the entrainment of sulfur dioxide by rime ice Atmos. Environ. 21 1765–72 Lamb D and Chen J P 1990 A modeling study of the effects of ice-phase microphysical processes on trace chemical removal efficiencies Atmos. Res. 25 31–51 Lesins G B and List R 1986 Sponginess and drop shedding of gyrating hailstones in a pressure-controlled icing wind tunnel J. Atmos. Sci. 43 2813–25 Lin Y L, Farley R D and Orville H D 1983 Bulk parameterization of the snow field in a cloud model J. Clim. Appl. Meteorol. 22 1065–92 Macklin W C and Payne G S 1967 A theoretical study of the ice accretion process Q. J. R. Meteorol. Soc. 93 195–213 Makkonen L 1987 Salinity and growth rate of ice formed by sea spray Cold Reg. Sci. Technol. 14 163–71 Mari C, Jacob D J and Bechhold P 2000 Transport and scavenging of soluble gases in a deep convective cloud J. Geophys. Res. 105 22255–67 Michael R A 2008 Factors influencing volatile chemical fate during accretion on wet-growing hail MS Thesis University of South Florida Pruppacher H R and Klett J D 1998 Microphysics of Clouds and Precipitation 2nd edn (Dordrecht: Kluwer Academic) Salzmann M, Lawrence M G, Phillips V T J and Donner L J 2007 Model sensitivity studies regarding the role of retention
coefficient for the scavenging and redistribution of highly soluble trace gases by deep convective cloud systems Atmos. Chem. Phys. 7 2027–45
Seinfeld J H and Pandis S N 1998 Atmospheric Chemistry and Physics: From Pollution to Climate Change (New York: Wiley)
Smith J M and Van Ness H C 2001 Introduction to Chemical Engineering Thermodynamics 6th edn (New York: Wiley)
Snider J R and Huang J 1998 Factors influencing the retention of hydrogen peroxide and molecular oxygen in rime ice J. Geophys. Res. 103 1405–16
Snider J R, Montague D C and Vali G 1992 Hydrogen peroxide retention in rime ice J. Geophys. Res. 97 7569–78
Stuart A L and Jacobson M Z 2003 A timescale investigation of volatile chemical retention during hydrometeor freezing: nonrime freezing and dry growth riming without spreading J. Geophys. Res. 108 4187
Stuart A L and Jacobson M Z 2004 Chemical retention during dry growth riming J. Geophys. Res. 109 D07305
Stuart A L and Jacobson M Z 2006 A numerical model of the partitioning of trace chemical solutes during drop freezing J. Atmos. Chem. 53 13–42
Voisin D, Legrand M and Chaumerliac N 2000 Scavenging of acidic gases (HCOOH, CH₃COOH, HNO₃, HCl, and SO₂) and ammonia in mixed liquid–solid water clouds at the Puy de Dome mountain (France) J. Geophys. Res. 105 6817–35
Wang C and Chang J S 1993 A three-dimensional numerical model of cloud dynamics, microphysics, and chemistry 4. Cloud chemistry and precipitation chemistry J. Geophys. Res. 98 16799–808
Yin Y, Carslaw K S and Parker D J 2002 Redistribution of trace gases by convective clouds-mixed-phase processes Atmos. Chem. Phys. 2 293–306