Dominance of solubility over speciation in thermodynamic water uptake model: a sensitivity study for Barrow, Alaska particle hygroscopic growth

The ability of aerosol particles to take up water before supersaturated activation is defined as hygroscopic growth. The particle hygroscopic growth factor (HGF) is required for calculations of aerosol optical properties. To represent HGF in real environments, it is desirable to initialize a thermodynamic water uptake model with ambient aerosol measurements. The assumptions needed to adapt measurements - especially those of the organic fraction - into the necessary model inputs are tested here. Before HGF could be calculated, measured concentrations of three organic functional groups (alcohol, alkane and acid) were apportioned among five organic compounds (n-nonadecane, adipic acid, oxalic acid, citric acid and levoglucosan) by balancing the moles of each group between compounds. The same method was performed on inorganic ions to obtain electrolyte compositions required by the model. To test the sensitivity of HGF calculations on actual measurements, a subset of submicron particle filter observations from Barrow, Alaska was used to constrain an organic-electrolyte water uptake model. Model results showed larger changes in HGF around the base case (range = 1.34 - 1.45) when levoglucosan was varied. Smaller magnitude change was observed when citric acid and adipic acid were varied (range = 1.37 - 1.40). The range in HGF was much smaller when changing individual organic compounds compared to changing the ratio of inorganic to total organic fraction (range = 1.25 - 1.55). Every sensitivity experiment varied the test fraction in the same increment, allowing for as fair a comparison as possible among experiments. The model appeared to be twice as sensitive to the ratio of organic fraction to inorganic fraction than to changes in the individual organic compounds. Because known solubility is implicitly included in the model, HGF calculations are controlled more by the total soluble fraction than by organic speciation when testing a range centered on average filter concentrations.

1. Introduction

The Arctic is proving to be especially sensitive to recent climate change (Hansen et al., 2007) and a key atmospheric property to understand is how aerosol particles influence local radiative forcing. From January 2008 to April 2009, near-continuous submicron filter measurements were collected at Barrow, Alaska at the NOAA CMDL observatory. The subset of filters used for this modeling study sampled for 24 hours under sector controlled inlet flow. Two filters sampled in tandem; one taken to perform Fourier transform infrared (FTIR) spectroscopy for organic functional group concentration (Maria et al., 2003), the other taken to perform ion chromatography (IC) for inorganic concentration.

Direct light scattering is controlled by size and refractive index, which are controlled in part by the amount of water taken up by particles (also known as hygroscopic growth). The hygroscopic growth factor (HGF) is the ratio of the wet diameter to dry diameter at a specified RH. The HGF of multi-component mixtures can be predicted with thermodynamic theory. The equation for Gibbs free energy of a particle with given chemical constituents is minimized when (Seinfeld and Pandis, 2006):

\[ \Delta G = -(4\pi R^3 kT/3\nu)\ln(S) + \sigma 4\pi R^2 = 0 \] (1)

R is the radius of the dry particle, \( \sigma \) is its surface tension, \( n \) is the concentration of the constituent. The free energy is optimized for a given temperature and saturation (S, essentially the ambient RH) by varying liquid volume (v) until \( \Delta G = 0 \). The resulting \( v_c \) with the associated density of water, is used to calculate the new wet diameter, which defines HGF.

Many thermodynamic chemical models calculate HGF for inorganic species (Tang and Munkelwitz, 1993; Wexler and Clegg, 2002). Ming and Russell (2001) developed an organic-electrolyte model (herein called MR01) using an iterative genetic algorithm to minimize Eq. 1 for multiple organic and inorganic compounds with known interactions and solubilities. MR01 requires a priori knowledge of the particle composition at the compound level. FTIR and IC do not measure compounds per se. In practice, only the components of whole compounds are measured. For electrolytes, the cations and anions are measured (e.g. Na\(^+\) and Cl\(^-\) are measured ionic components of the electrolyte compound NaCl). For organics, the functional groups are measured (e.g. alcohols, alkanes and acids are functional groups of organic compound citric acid). A method was developed to apportion component measurements into compounds (Takahama et al. 2009, in preparation). A molar balance is used to minimize the difference in measured component mass and the apportioned compound mass. Component measurements and their corresponding compounds are listed in Table 1.

One important question to answer is how important is the apportionment of the measurements into the compounds compared to the magnitudes of the measurements themselves? Since it is well known that increasing soluble inorganic compounds increases HGF (Tang and Munkelwitz, 1993; Wexler and Clegg, 2002), this study examines how sensitive modeled HGF values as calculated by MR01 are to the choice and fractions of the organic compounds.

2. Methodology

Several assumptions were made for all tests using MR01. All cases assume spherical, internally mixed particles. The initial dry diameter (the R term in Eq.1) was set to 100 nm. In previous tests (not shown) HGF was not observed...
to change appreciably above this diameter. Surface tension affects particles below 50 nm differently, making the MR01 model insufficient to predict HGF at this size range. The initial relative humidity was set at 75 % to represent a mid-point on the deliquescence curve. The model is designed to calculate in a RH range of 60-95 %, below which particle efflorescence cannot be predicted and above which the deliquescence curve evolves into Kohler theory.

Table 1. MR01 input compounds apportioned from corresponding measured components

<table>
<thead>
<tr>
<th>MR01 input compounds</th>
<th>Measured species</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>NH₄⁺; NO₃⁻</td>
<td>IC</td>
</tr>
<tr>
<td>NH₄HSO₄</td>
<td>NH₄⁺; (SO₄)²⁻</td>
<td>IC</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>NH₄⁺; (SO₄)²⁻</td>
<td>IC</td>
</tr>
<tr>
<td>NaCl</td>
<td>Na⁺; Cl⁻</td>
<td>IC</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>Na⁺; (SO₄)²⁻</td>
<td>IC</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>Mg²⁺; (SO₄)²⁻</td>
<td>IC</td>
</tr>
<tr>
<td>oxalic acid</td>
<td>oxalate</td>
<td>IC</td>
</tr>
<tr>
<td>citric acid</td>
<td>alkane; acid; alcohol</td>
<td>FTIR</td>
</tr>
<tr>
<td>adipic acid</td>
<td>alkane; acid</td>
<td>FTIR</td>
</tr>
<tr>
<td>n-nonadecane</td>
<td>alkane</td>
<td>FTIR</td>
</tr>
<tr>
<td>levoglucosan</td>
<td>alkane; acid; alcohol</td>
<td>FTIR</td>
</tr>
</tbody>
</table>

Five experiments were conducted, each calculating 16 different HGF values that were interpolated into surface plots. The first four experiments tested the apportionment of organics. Each experiment varied a pair of compounds - one against the other - while holding constant all others (including electrolytes) at the set size and RH.

A reasonable range was determined by first taking the mean concentration of each measured component of the Barrow filter subset and then using the apportionment method to make an average concentration of input compounds. It was determined that the organic compound concentrations generally did not vary by more than a factor of two. Each experiment then simulated values of +50 %, +25 %, -25 %, -50 % around the mean of each compound. Mean concentrations and ranges for measured components and apportioned compounds are shown in Fig 1.

An additional experiment varied the initial concentration of total organics and total inorganics separately. The functional group concentrations were simultaneously varied in +50 %, +25 %, -25 %, -50 % increments around the subset mean, thereby keeping the same compound fractions but changing the total amount of functional groups measurements in the same proportions. The same was done for the ion measurements, which were previously held constant. This particular experiment essentially tested different fractions of organics to total and inorganics to total in order to test the sensitivity of solubility rather than apportionment.

3. Results

The surface plots in Fig. 3 show how HGF changed when two compounds were varied against each other. This was intended to assess how HGF would change if the apportionment method made, for example, 50 % more levoglucosan than citric acid, or 25 % more adipic acid and 25 % less n-nonadecane. The red dot in the center of each panel indicates the HGF calculated for the mean case. It is the same value in each plot (HGF$_{mean}$ = 1.385).

Each levoglucosan experiment showed HGF slightly increasing with larger fractions of levoglucosan. The opposite was true for n-nonadecane. The range of HGF as predicted for the range of organics was largest when levoglucosan was changed. When varied with n-nonadecane, the range of levoglucosan was slightly smaller (0.11) than with citric acid (HGF = 0.13). When adipic acid and citric acid were tested against each other, the range of HGF was small (0.02) from the mean value. The range for n-nonadecane versus citric acid was only slightly larger (0.03). The experiment that varied total organic and total inorganic fractions had a much larger effect (HGF range = 0.3) and markedly different pattern in the iso-HGF lines. Whereas HGF grew slightly larger to the upper right corners of the plots when adding single organic compounds, HGF was highest in the second experiment when the fraction of organics was smallest and fraction of inorganics the largest.

Figure 1. Summary of measured component concentrations used in sensitivity tests. Components are apportioned into compounds.
4. Discussion

It was shown that varying pairs of organics through mass apportionment had a weak effect on HGF compared to the change in total fraction of organics and inorganics. Changes in levoglucosan had the largest effect among organics as seen in the only real dramatic change in shading and gradient in contours. Subtle variation in HGF occurred for adipic acid-citric acid changes, indicating that there is little sensitivity in how measurements are apportioned between diacids. In an overall sense, the apportioning of organics is still relatively insignificant.

To quantify the sensitivity $\lambda$ of HGF to change in each group:

$$\lambda_x = \frac{\Delta HGF}{\Delta [\% X]}$$  \hspace{1cm} (2)  

$$\lambda_y = \frac{\Delta HGF}{\Delta [\% Y]}$$  \hspace{1cm} (3)  

$$\lambda_{xy} = sqrt(\lambda_x^2 + \lambda_y^2)$$  \hspace{1cm} (4)

Table 2 summarizes the calculated model sensitivity for given pairings. Even for the largest range for levoglucosan, the sensitivity was approximately $\lambda = 0.13/(150 - 50) = 0.0013$. Adding n-nonadecane slightly decreased HGF. This implies that choice of organics may matter, as n-nonadecane (a hydrophobic hydrocarbon) and levoglucosan (a more soluble sugar) have
different effects. But it is shown here that the sensitivity is small in a reasonable range from observations. If enough alkanes are present in functional group component measurements to apportion a large amount of n-nonadecane, it would be possible to decrease HGF.

Table 2. Sensitivity parameters of different test pairings

<table>
<thead>
<tr>
<th>Pairing</th>
<th>$\lambda_x$</th>
<th>$\lambda_y$</th>
<th>$\lambda_{xy}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>citric acid vs. adipic acid</td>
<td>0.0004</td>
<td>0.0008</td>
<td>0.00089</td>
</tr>
<tr>
<td>citric acid vs. levoglucosan</td>
<td>0.00003</td>
<td>0.0013</td>
<td>0.0013</td>
</tr>
<tr>
<td>n-nonadecane vs. levoglucosan</td>
<td>0.0002</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>n-nonadecane vs. citric acid</td>
<td>0.00025</td>
<td>0.00005</td>
<td>0.000255</td>
</tr>
<tr>
<td>total inorganic vs. total organic</td>
<td>0.002</td>
<td>0.001</td>
<td>0.00024</td>
</tr>
</tbody>
</table>

The dominant factor in HGF calculation is less how the organics vary between themselves and more how the total fraction of organics compares to the total fraction of inorganics. This reaffirms the findings of the previously mentioned studies. Fig. 2 showed the $\lambda$ for change in HGF with respect to change in inorganic fraction was $+0.003$. This is approximately the same magnitude for change in HGF with respect to change in inorganic fraction was $+0.00089$. The sign is reversed. HGF decreased when the organic fraction dominated, and increased when the inorganic fraction dominated.

\[
\text{Fraction}_i = \frac{\sum \text{total}_i}{\sum \text{organics} + \sum \text{inorganics}} \quad (5)
\]

The solubilities of each fraction are specified into the model as so-called interaction parameters. This dependence of HGF on fraction is thus deemed to be solubility effect. The results show modeled organic fraction was less soluble than the inorganic fraction. The overall solubility of the organic fraction is more important than the individual amounts of organic compounds in calculating HGF. In this case, the total organic fraction contained enough alkanes to apportion an appreciable amount of growth limiting n-nonadecane and citric acid to reduce HGF. It is possible that higher concentration measurements of alkanes and acids could make the organic fraction less soluble than this simple test case. More rigorous tests are needed to determine sensitivity to all components and compounds that go into the model.

Hundreds to thousands of unknown organic compounds exist in ambient aerosol (Cass, 2000; Rogge et al., 1993). If it is safe to assume that apportionment is not as important for average conditions, as the findings in this study suggest, it may not be necessary to specify all possible compounds as long as a suitable organic fraction with known solubility is used.

5. Conclusions

Concentrations from a subset of submicron particle filter measurements from Barrow, Alaska were used to constrain a thermodynamic water uptake model. The underlying uncertainty existed in how measurements were apportioned into model input compounds. A suitable range of test values was obtained by taking averages of the filter measurements. By varying individual organic input compounds at discrete intervals around their mean value, the sensitivity of HGF to changes in apportionment were tested. The sensitivity in HGF to organics was more than a factor of two smaller compared to the sensitivity to the overall soluble fraction. HGF was reduced most with small inorganic fraction and largest organic fraction, illustrating the importance of both IC and FTIR filter measurements towards a better understanding of the aerosol radiative effects in the Arctic. If indeed the organic fraction in Arctic haze composes as much aerosol mass as suggested, future particle growth and light scattering calculations for these events will be strongly influenced by both ambient IC and FTIR measurements.

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References