A General Framework for Predicting CCN Activity of Organic Molecules from Functional Group Data

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Motivation: 0.4 W m$^{-2}$ in indirect forcing

How important is organic aerosol hygroscopicity to aerosol indirect forcing?

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“The simulation results show that the uncertainty in organics aerosol hygroscopicity, based on current understanding and our model formulation, may lead to an uncertainty of about 0.4 W m$^{-2}$ ... . This uncertainty is comparable to or even larger than those due to autoconversion parameterization and tuning parameters related to entrainment, drizzle and snow formation.”
Levels of representation of organic aerosol

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<td>product schemes</td>
<td>principle components HOA/OOA/LV-OOA ...</td>
<td>functional group composition</td>
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Can we predict the water uptake/CCN properties of a substance from molecular composition? 

Hydrophobic and insoluble

Hydrophilic and water soluble
We can represent this molecule as

\[ \nu = 115 \frac{cm^{-3}}{mol}, \ 6 \times (C), \ 5 \times (-OH), \ 1 \times (= O), \ 1 \times (CH_2) \]

molar volume, # carbon, #hydroxyl, #carbonyl, #CH_2

Our objective is to find a relationship for

CCN activity = function(molar volume, #carbons, sum[#moiety(i)])

Why do we need such a relationship?

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1. Parameterization of CCN activity example for SOA for monoterpene + $O_3$

$k=0.1$

(Prenni et al., 2007, JGR)
2. For sufficiently water soluble compounds, $\kappa$ is controlled by molar volume.

There are a number of compounds with lower $\kappa$ values that behave non-ideally because they are not sufficiently functionalized – Need to understand this part of the state space.

Upper limit $\kappa$ is $\sim 0.3$.
Seek an equation that works also for less soluble compounds

\[ \kappa = f(\text{size of molecule}) \times f(\text{functional groups}) \]

- Term between 0 and 1
- 1 for “soluble” compounds
- Account for different types of functional groups (e.g. “acid”, “nitrate”, “hydroxyl”...)
- Need experimental framework to constrain this term
3. Use model SOA systems to synthesize molecules with known moieties

Example system: linear 1-alkene + $O_3$ +

\[
\text{HOO}(\text{GO})\text{CH} \rightarrow (\text{CH}_2)_R \rightarrow \text{CH}_3
\]

- $\text{H}_2\text{O}$
- Methanol
- Propanol

oxidized tail with functionality reflecting the SCI reactant
Number of $\text{CH}_2$ groups depends on precursor chain length

(Tobias and Ziemann, ES&T, 2001)
3. Empirical relationship between # of CH$_x$ groups and the hygroscopicity parameter

\[
\frac{\Delta \ln \kappa}{\Delta n_{\text{CH}_x}} \sim -0.35 \pm 0.15
\]
3. Second example: synthesize molecules with different # of OH groups

2-methyl-1alkene + OH/NO$_x$

(Matsunaga et al., PNAS, 2010)

β-hydroxynitrates  dihydroxynitrates  trihydroxynitrates

Use offline HPLC-CCN technique to measure CCN activity of individual compounds: See poster *Hygroscopicity frequency distributions of secondary organic aerosols* by Sarah Suda
3. Empirical relationship between # of OH groups and the hygroscopicity parameter

Hygroscopicity parameter

\[ \frac{\Delta \ln \kappa}{\Delta n_{OH}} \approx 0.35 \pm 0.15 \]

\( \beta \)-hydroxynitrates  dihydroxynitrates  trihydroxynitrates
4. The empirical relationships can be used to construct the following framework

\[ \kappa = \kappa_{\text{Flory Huggins}} \exp(cn_e) \]

\[ n_e = n_c - \sum \alpha_i n_i \]

- detrimental effect of CH\(_x\) on kappa
- number of effective CH\(_x\) groups (≥0)
- number of carbon atoms
- ability of functional group to negate CH\(_x\)
- number of that group type
4. Test of fidelity with current parameters against CCN data from pure compounds
Conclusions

• For sufficiently functionalized molecules Flory-Huggins theory presents a reasonable baseline.

• Developed a simple mathematical framework to compute kappa from
  – number of carbon atoms/molar volume
  – number of functional groups of type i
  – a functional group dependent interaction parameter

• Experiments with model SOA systems can be used to populate the parameter space of the relationship.