Assessing aerosol mixing state and diversity

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Overview

- Background on aerosol mixing state
- The Aerosol Time-of-Flight Mass Spectrometer
- Quantifying aerosol mixing state
- Conclusions and future directions
Aerosol mixing state

- Externally mixed
- Internally mixed
- ????

- Organic aerosol
- Black carbon
- Sulphate
- Nitrate
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Single particle sampling - online: ATOFMS
Single particle sampling- online: ATOFMS

- Single particle information retained
- Enables source identification and investigation of chemical processing
- Data typically **qualitative** only

Data output:
Single particle mixing state (qualitative)
Quantitative approach

- Derived ATOFMS mass spectral relative sensitivity factors (RSF) for OA, BC, NH$_4$, NO$_3$ and SO$_4$

- Calculated quantitative chemical composition estimates for each single particle

Quantitative approach

- Chemical composition of each particle in the population can also be summed to produce size-resolved bulk composition information
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Quantifying aerosol mixing state with entropy and diversity measures

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Abstract. This paper presents the first quantitative metric for aerosol population mixing state, defined as the distribution of per-particle chemical species composition. This new metric, the mixing state index $\chi$, is an affine ratio of the average per-particle species diversity $D_a$ and the bulk population species diversity $D_P$, both of which are based on information-theoretic entropy measures. The mixing state index $\chi$ enables the first rigorous definition of the spectrum by processes that occur on the particle-scale, and these microscale processes are difficult to represent in large-scale models (Ghan and Schwartz, 2007).

An important quantity in this context is the so-called mixing state of the aerosol population, which we define as the distribution of the per-particle chemical species compositions. Recent observations made in the laboratory and in the field using single-particle measurement techniques have re-
Parameterisation of particle mixing state

- To what extent is each chemical species represented in a particle?

- Shannon entropy is used to determine this representation, similar to applications in biodiversity and ecology

- For a single particle \((i)\)…

Shannon entropy

\[
H_i = \sum_{a=1}^{A} -p_i^a \ln p_i^a
\]

Mass fraction of species \(a\) (for example SO\(_4\)) in particle \(i\)
Single particle diversity \( (D_i) \) examples

- Example 1: **2 species**, equal proportions

\[
H_i = (-0.5\ln(0.5)) + (-0.5\ln(0.5)) = 0.69
\]

The single particle *diversity* \( (D_i) \), defined as \( e^{(H_i)} = 2.0 \)
Single particle diversity ($D_i$) examples

- Example 2: 2 species, unequal proportions

Typical fresh combustion particle

Single particle diversity ($D_i$) = 1.8
Single particle diversity ($D_i$) examples

- Example 4: 5 species, unequal proportions

![Pie chart showing typical aged particle](image)

Typical aged particle

Single particle *diversity* ($D_i$) = 4.2
Paris single particle example 1

$D_i = 2.0$

*Healy et al. Atmos. Chem. Phys. 2014*
Paris single particle example 2

$m/z$

\[\text{Relative peak area (arbitrary units)}\]

\[\begin{align*}
\text{C}^+ & \quad \text{NH}_4^+ \\
\text{C}_3^+ & \quad \text{C}_2\text{H}_3\text{O}^+ \\
\text{C}_5^+ & \quad \text{NO}_3^- \\
\text{NO}_2^- & \quad \text{HSO}_4^- \\
\end{align*}\]

$D_i = 3.0$

Diversity : Paris

Single particle diversity ($D_i$) vs size

Average single particle composition vs size
Whole dataset: Paris

- We can average $D_i$ across all particles for every hour of the measurement period

- This average value is termed $D_\alpha$, and represents how well mixed chemical species are at the single particle level only

- What about the bulk aerosol?
Bulk aerosol diversity ($D_y$)

- Bulk diversity is easier to calculate for each hour

- Shannon entropy calculated from the mass fractions of each species present in the bulk aerosol

Bulk aerosol diversity $D_y = 4.5$
Quantifying aerosol mixing state ($\chi$) in Paris

- Relating $D_\alpha$ and $D_\gamma$ gives the quantitative mixing state index ($\chi$)
- Expressed as a percentage
- Average value for Paris $\chi = 59\%$
Mixing state ($\chi$) as a function of time
Dependence of $\chi$ on air mass origin

**Continental**

26. Jan 2010 18:00 to 21:00

Bulk population mass fraction

Date

[NH$_4$, NO$_3$, SO$_4$, OA, BC]

$\chi$ (%)
Dependence of $\chi$ on air mass origin

Marine
Quantifying aerosol mixing state ($\chi$) in Paris

Marine $\chi = 55$
Continental $\chi = 60$

[Diagram showing $D_1$ vs $D_0$ with data points and lines indicating marine and continental mixing states]
Conclusions

• ATOFMS data can be used to estimate single particle composition

• Calculating single particle diversity and bulk aerosol diversity enables an assessment of aerosol mixing state ($\chi$)

• Aerosol detected in Paris is 59% internally mixed on average

• Aerosol mixing state depends on local emissions, chemical processing and regional transport
Future Directions

• Query single particle datasets from other global locations for $\chi$

• Investigate mixing state in fresh vs aged urban plumes

• Evaluate error introduced in climate models when full internal mixing assumed
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Assumptions

• All particles are spherical with a density of 1.5 g cm\(^{-3}\) for aerodynamic diameter to mobility diameter conversions prior to scaling

• All particles are composed exclusively of NH\(_4\), SO\(_4\), NO\(_3\), OA and BC

• ATOFMS ‘sees’ all particle types with equal efficiency at a given size
Why do we need $D_\alpha$ and $D_\gamma$? Example 1

$D_\alpha = 2.0$

$D_\gamma = 4.0$
Why do we need $D_\alpha$ and $D_\nu$? Example 2

$D_\alpha = 4.0$

$D_\nu = 4.0$
Diurnal dependence of $D_\alpha$, $D_\gamma$ and $\chi$
Diurnal dependence of $D_{\alpha}$ $D_{\gamma}$ and $\chi$
Size-dependent number scaling factors

Box-plot of hourly size-dependent scaling factors for the entire measurement period (n = 624). Median, 75th percentile and 90th percentile are denoted by the solid line, box and whisker respectively.
Relative sensitivity factors by species

Box-plot of hourly mass spectral relative sensitivity factors (n = 610). Median, 75th percentile and 90th percentile are denoted by the solid line, box and whisker respectively.
ATOFMS reconstructed mass vs AMS/MAAP

- BC: $R^2 = 0.91$, slope = 1.23
- OA: $R^2 = 0.93$, slope = 0.95
- NH₄: $R^2 = 0.84$, slope = 0.73
- NO₃: $R^2 = 0.86$, slope = 1.05
- SO₄: $R^2 = 0.92$, slope = 0.90
ATOFMS reconstructed composition vs AMS/MAAP

Date

Mass fraction

ATOFMS-derived bulk mass fractions
AMS/MAAP bulk mass fractions
OA
NH$_4$
NO$_3$
SO$_4$
BC

15/1/2010
16/1/2010
17/1/2010
18/1/2010
19/1/2010
21/1/2010
22/1/2010
23/1/2010
24/1/2010
25/1/2010
26/1/2010
27/1/2010
28/1/2010
29/1/2010
30/1/2010
1/2/2010
2/2/2010
3/2/2010
4/2/2010
5/2/2010
6/2/2010
7/2/2010
8/2/2010
9/2/2010
10/2/2010
11/2/2010

OA
NH$_4$
NO$_3$
SO$_4$
BC

southern ontario centre for atmospheric aerosol research
ATOFMS reconstructed mass vs AMS (size resolved)