Supplementary information for

Partitioning of secondary organic aerosol onto nanoplastics leading to hygroscopic partially-engulfed particles

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Supporting materials and methods

Between experiments, the chamber was flushed at a flow-rate of about 8 L min\(^{-1}\). The zero-air generator was set to an outlet pressure of 30 psi. The temperature of the laboratory was monitored throughout the experiment with a NIST-traceable probe (Vaisala, HMP75) read by a commercial measurement indicator (Vaisala, M170). Before beginning an experiment, the ozone monitor had to measure no response above its detection limit. The flow rate of the CPC was 0.3 L min\(^{-1}\) while the flow rate of the ozone monitor was 1 L min\(^{-1}\). During the introduction of nanoplastics, the atomizer was supplied with ultrapure air, and the atomizer was operated in recirculating mode. The sonicator was used to prevent the settling of nanoplastics in the aqueous suspension. One of the diffusion dryers was commercial (TSI, 3062), and the other was custom-built, based on a similar design. It required 1.5 hr to reach a usable concentration of particles for each experiment for all sizes of nanoplastics.

After the introduction of nanoplastics, \(\alpha\)-pinene was injected into the chamber. The solution was 1-to-600 \(\alpha\)-pinene in hexane by volume. The syringe pump was operated at a flow rate of 0.100 mL min\(^{-1}\). The mantle used to heat the three-neck flask was controlled by a variable autotransformer. The syringe was connected to the three-neck flask with a 13” length of PEEK tubing, tapered to a point on the end and passed through a septum on the center port of the flask. The syringe pump was operated for 5 min to introduce \(\alpha\)-pinene into the chamber. Following the 5 min injection of \(\alpha\)-pinene injection, the nanoplastics and gaseous species were allowed to mix for 30 min. During this time, the CPC continued to pull from the smog chamber through the wire-mesh denuder packed with catalyst. Afterwards, the introduction of ozone began. The mixing ratios of \(\alpha\)-pinene and ozone were carefully optimized to give sufficient
coating without rapid oxidation, which led to new particle formation in preliminary experiments, since the seed particle surface area was small.

During reaction, the voltages of the DMAs were stepped to select a range of sizes based on the initial mobility diameter of the nanoplastics and the extent of reaction in the smog chamber. At each voltage, classified particles were directed to the CPC, and ten number concentration measurements were shown to be steady and averaged. Particles sampled by the second DMA were conditioned with a membrane humidifier, which was supplied by the zero-air generator, and the RH was controlled by mixing dry and humidified air. The residence volume downstream of the humidifier was an 8.2 m length of 1/4” copper tubing, with a volume of 150 cm$^3$. The sheath flow of the second DMA was also humidified using a membrane humidifier, and the sheath flow of the humidifier was controlled using a glass bubbler filled with ultrapure water and a bypass. Four of the RH probes were placed throughout the setup, one in each of the sample and sheath flows of each of the DMAs, and data was logged using a microcontroller (Arduino, UNO).

**Supporting results and discussion**

In the smog chamber experiments, the direct measurements are of the mobility diameters of particles at low and high RH, $d_{m,0.1}$ and $d_{m,0.9}$, respectively. The diameter growth factors at low and high RH, $G_{fd_{0.1}}$ and $G_{fd_{0.9}}$, respectively, are calculated as follows:

\[
G_{fd_{0.1}} = \frac{d_{m,0.1}}{d_{m,i}}
\]

\[
G_{fd_{0.9}} = \frac{d_{m,0.9}}{d_{m,i}}
\]
Here, $d_{m,i}$ is the initial mobility diameter before ozonolysis of $\alpha$-pinene begins. Note that $d_{m,i}$ includes contributions from only nanoplastics, $d_{m,0.1}$ includes contributions from nanoplastics and SOA, and $d_{m,0.9}$ includes contributions from nanoplastics, SOA, and water. Assuming the SOA coating is uniformly distributed across the initially spherical nanoplastics, the contribution of SOA and water to the particle radius at low and high RH, $\Delta r_{0.1}$ and $\Delta r_{0.9}$, respectively, is calculated as follows:

$$
\Delta r_{0.1} = \frac{d_{m,0.1}}{2} - \frac{d_{m,i}}{2}
$$

$$
\Delta r_{0.9} = \frac{d_{m,0.9}}{2} - \frac{d_{m,i}}{2}
$$

These are the apparent coating thicknesses in the absence and presence of particulate water, respectively.

The apparent volume of each constituent is calculated by assuming spherical geometry first for the initial particles then also for the coated particles at low and high RH, as follows:

$$
V_{PS} = \frac{\pi}{6} d_{m,i}^3
$$

$$
V_{0.1} = \frac{\pi}{6} d_{m,0.1}^3
$$

$$
V_{0.9} = \frac{\pi}{6} d_{m,0.9}^3
$$

Note that spherical geometry is only certain for the initial, uncoated polystyrene particles, $V_{PS}$.

The volumes of SOA and water are calculated from the following differences:

$$
V_{SOA} = V_{0.1} - V_{PS}
$$

$$
V_{water} = V_{0.9} - V_{0.1}
$$
Since the measurements of mobility diameter at low and high RH alternate, it is necessary to interpolate the timeseries at one condition to the reaction times of the other. The interpolation is done linearly. The apparent volume growth factors at low and high RH, \( G_{fv,0.1} \) and \( G_{fv,0.9} \), respectively, are the following:

\[
G_{fv,0.1} = \frac{V_{0.1}}{V_{PS}}
\]

\[
G_{fv,0.9} = \frac{V_{0.9}}{V_{PS}}
\]

The magnitude of \( G_{fv,0.1} \) reflects the contribution of SOA, and the magnitude of \( G_{fv,0.9} \) reflects the contribution of SOA and water. The hygroscopic volume growth factor, \( H_{Gfv} \), reflects the contribution of water taken up by the SOA, calculated as the following:

\[
H_{Gfv} = \frac{V_{0.9}}{V_{0.1}} = \frac{V_{PS} + V_{SOA} + V_{water}}{V_{PS} + V_{SOA}}
\]

The apparent mass of each constituent is calculated from its volume, calculated as above, and its density, as follows:

\[
m_{PS} = V_{PS} \rho_{PS}
\]

\[
m_{SOA} = V_{SOA} \rho_{SOA}
\]

\[
m_{water} = V_{water} \rho_{water}
\]

Here, \( \rho_{PS} \) is the density of polystyrene (1.05 g cm\(^{-3}\)), \( \rho_{SOA} \) is the density of SOA (1.28 g cm\(^{-3}\)), and \( \rho_{water} \) is the density of water at the laboratory temperature (1.00 g cm\(^{-3}\)). The density of \( \alpha \)-pinene SOA has been reported, based on parallel mass and diameter measurements. The apparent particle mass at low and high RH are then the following summations:

\[
m_{0.1} = m_{PS} + m_{SOA}
\]

\[
m_{0.9} = m_{PS} + m_{SOA} + m_{water}
\]
The apparent mass growth factors at low and high RH, \( \text{Gfm}_{0.1} \) and \( \text{Gfm}_{0.9} \), respectively, are the following:

\[
\text{Gfm}_{0.1} = \frac{m_{0.1}}{m_{\text{PS}}}
\]

\[
\text{Gfm}_{0.9} = \frac{m_{0.9}}{m_{\text{PS}}}
\]

As above in terms of volume, the magnitude of \( \text{Gfm}_{0.1} \) reflects the contribution of SOA, and the magnitude of \( \text{Gfm}_{0.9} \) reflects the contribution of SOA and water. The hygroscopic mass growth factor is the following:

\[
\text{HGfm} = \frac{m_{0.9}}{m_{0.1}} = \frac{m_{\text{PS}} + m_{\text{SOA}} + m_{\text{water}}}{m_{\text{PS}} + m_{\text{SOA}}}
\]

The mass fraction contributed by SOA alone at low RH, \( f_{0.1} \), and SOA and water together at high RH, \( f_{0.9} \), are calculated as follows:

\[
f_{0.1} = \frac{m_{\text{SOA}}}{m_{\text{PS}} + m_{\text{SOA}}}
\]

\[
f_{0.9} = \frac{m_{\text{SOA}} + m_{\text{water}}}{m_{\text{PS}} + m_{\text{SOA}} + m_{\text{water}}}
\]
Fig. S1. Schematic of the experimental setup for the smog chamber experiments.
Fig. S2. Representative size spectrum from an experiment with initially 250 nm nanoplastics. Each size spectrum, or measurement distribution function, was monodisperse, so data inversion was not required to determine the peak diameter. The total number concentration in the size spectrum does not account for the transfer function, diffusion losses, and dilution between classification and counting, so it is lower than the number concentration measured during injection using only the condensation particle counter.
**Fig. S3.** Mobility diameters of initially 100 and 250 nm nanoplastics as a function of temperature during volatility differential mobility analysis.
Fig. S4. Mobility diameter of initially 100 nm nanoplastics as a function of temperature during volatility differential mobility analysis. The slight decrease in mobility diameter occurs above the glass transition temperature of polystyrene at 107 °C.
Fig. S5. Volume (top) and mass (bottom) growth factors as functions of reaction time in the smog chamber for a representative experiment with initially 250 nm nanoplastics.
Fig. S6. Mass fraction of coating as a function of reaction time in the smog chamber for a representative experiment with initially 250 nm nanoplastics. For dry particles, the coating includes only SOA; for humidified particles, the coating includes both SOA and water.
Fig. S7. Hygroscopic volume growth factor as a function of reaction time in the smog chamber for a representative experiment with initially 250 nm nanoplastics.
Fig. S8. Hygroscopic volume growth factors as a function of the volume growth factor of the dry particles, a measure of the SOA coating volume, for three experiments with initially 200 nm (top) and 100 nm (bottom) nanoplastics. It was during Expt 3 for 200 nm nanoplastics that the DMAs were interchanged, and the same trend occurs. Note the change in the scale along the x-axis. Although the 100 nm nanoplastics require much less SOA coating, in absolute volume, this is a greater multiple of the nanoplastic volume.
Fig. S9. Apparent volume of water as a function of the apparent volume of SOA during each individual experiment.
Table S1. Nominal, reported, and measured diameters of the nanoplastics. The measured diameters are either smaller or larger than the reported diameters, so there is not a systematic increase, which might be expected if surfactants were internally mixed with the nanoplastics.

<table>
<thead>
<tr>
<th>Nominal diameter (nm)</th>
<th>Reported diameter in aqueous suspension (nm)</th>
<th>Measured mobility diameter in aerosol (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>100 ± 1</td>
<td>107 ± 1</td>
</tr>
<tr>
<td>200</td>
<td>198 ± 2</td>
<td>216 ± 1</td>
</tr>
<tr>
<td>250</td>
<td>244 ± 3</td>
<td>242 ± 1</td>
</tr>
</tbody>
</table>