VII. How might current analysis methods be enhanced or combined to obtain more information about the nature of OC, EC, and other carbon fractions in filter samples? What can be done with existing analysis methods and samples? What might be provided by collocated measurements? What hardware and software changes would permit more of the commonly applied protocols to be applied with the same analytical instruments?

TOPIC LEADER: Hans-C Hansson, Air Pollution Laboratory, Institute of Applied Environmental Research and Department of Meteorology, Stockholm University, Sweden
Starting point

Mass of OC/EC interesting in itself

But mostly due to effects

Effect on atmospheric processes

Climate direct indirect

Health

The measure used for OC/EC should be useful in calculating the actual effect
First what is out there?
Figure 1. Dependence of particle emissions on vehicle speed for three gasoline cars and one diesel car. Dilution air particle size distributions are given as dotted lines. Exhaust flows for vehicle C5 are 0.010, 0.014, and 0.020 m$^3$/s at 50, 60, and 70 mph. For vehicle C3 they are 0.014, 0.019, and 0.026 m$^3$/s (Maricq et al., 1999).
Figure 4. Solid particles and spontaneous condensate in diluted exhaust gas at different temperatures of a thermodesorber (Mayer et al., 1998).
Several types of particles exist!

- Particles thermally stable at 300 °C
- Particles with a thermally stable core
- Particles that evaporate totally at 300 °C
- Particles are hydrophobic
Simple estimate on traffic emissions on national scale.

<table>
<thead>
<tr>
<th>Metric</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of particle per vehkm</td>
<td>3.0E+13</td>
</tr>
<tr>
<td>Number of cars in Germany</td>
<td>3.5E+07</td>
</tr>
<tr>
<td>Mean distant per year km</td>
<td>1.5E+04</td>
</tr>
<tr>
<td>Particle source strength number per sec</td>
<td>1.2E+19</td>
</tr>
<tr>
<td>Mean wind speed m/s</td>
<td>5.0</td>
</tr>
<tr>
<td>Width m</td>
<td>500000</td>
</tr>
<tr>
<td>Mixing height m</td>
<td>1500</td>
</tr>
<tr>
<td>Number of particles per cm3</td>
<td>3.2E+03</td>
</tr>
</tbody>
</table>

Measured number concentrations

<table>
<thead>
<tr>
<th>Country</th>
<th>Average</th>
<th>Night</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germany</td>
<td>5-6000</td>
<td>3000</td>
</tr>
<tr>
<td>Sweden</td>
<td>2000</td>
<td></td>
</tr>
</tbody>
</table>
After some transport:
Particle hygroskopnic growth at background site in Sweden compared with other measurements

Fraction in More Hygroscopic mode (when bimodal behaviour)

<table>
<thead>
<tr>
<th>nm</th>
<th>20</th>
<th>35</th>
<th>50</th>
<th>73</th>
<th>109</th>
<th>166</th>
<th>265</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frac</td>
<td>0.56</td>
<td>0.60</td>
<td>0.62</td>
<td>0.61</td>
<td>0.58</td>
<td>0.63</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Life cycle for main types of atmospheric particles

Weakly hygroscopic particles
- Life time: 4 - 8 days
- Transport distance: 2000 - 4000 km

Hygroscopic particles
- Life time: 2 - 4 days
- Transport distance: 1000 - 2000 km
The size distribution change and the number decrease in southerly winds.

Deposition and transformation
Summary so far:

- BC has long life time
- BC particles from motor exhaust can be dominating the number concentration far away from the sources
- BC is probably common nucleus in most particles in an aged polluted air mass and thus control the total particle size distribution. BUT have to be confirmed to reveal the importance of primary ”soot” particles in controlling particle size distributions in the atmosphere.
The global mean radiative forcing of the climate system for the year 2000, relative to 1750

- Scattering
  - Halocarbons
  - N₂O
  - CH₄
  - CO₂
  - Tropospheric ozone
  - Sulphate
  - Organic carbon
  - Biomass burning

- Absorption
  - Halocarbons
  - N₂O
  - CH₄
  - CO₂
  - Tropospheric ozone
  - Black carbon from fossil fuel burning
  - Mineral Dust
  - Aerosols
  - Aviation-induced
  - Contraction Cirrus
  - Land-use (albedo) only

- Level of Scientific Understanding
  - High
  - Medium
  - Medium
  - Low
  - Very Low
  - Very Low
  - Very Low
  - Very Low
Effect of organics on $S_c$
Cloud condensation nuclei (CCN)

\[
e' = 1 + \frac{2\sigma M_w}{kTpr} - \frac{3M_w}{4\pi \rho r^3} \left( \frac{i_{\text{DOC}} X_{\text{DOC}} m_{\text{OC}}}{M_{\text{OC}}} + \frac{i_{\text{sulf}} m_{\text{sulf}}}{M_{\text{sulf}}} \right)
\]

- \(\sigma\) = solution surface tension
- \(M_w\) = molecular weight of water
- \(k\) = Boltzmann constant
- \(T\) = temperature
- \(\rho\) = solution density
- \(i_{\text{DOC}}\) = van't Hoff factor for the dissolved OC
- \(i_{\text{sulf}}\) = van't Hoff factor for sulfate
- \(m_{\text{OC}}\) = mass of OC
- \(m_{\text{sulf}}\) = mass of sulfate
- \(M_{\text{OC}}\) = molecular weight of OC
- \(M_{\text{sulf}}\) = molecular weight of sulfate
Parameters in calculating the activation probability

- TC
- Water soluble OC
- Surface tension
- Molecular weight
- van’t Hoff factor for the solution in question
Health:

WHO review on Particulate Matter and Health, 2003

“The present information shows that fine particles (commonly measured as PM2.5) are strongly associated with mortality and other endpoints such as hospitalization for cardiopulmonary disease, so that it is recommended that air quality guidelines for PM2.5 be further developed. Revision of the PM10 WHO AQGs and continuation of PM10 measurement is indicated for public health protection. A smaller body of evidence suggests that coarse mass (particles between 2.5 and 10 µm) has some effects on health as well, so a separate guideline for coarse mass may be warranted. The value of Black Smoke should also be re-evaluated as indicator for traffic-related air pollution.”
FIGURE 4. Simulated and measured concentration profiles of different lipophilicity toxicants in the tracheal mucosa of the dog. The curves to the left show the simulated concentration profiles at the first half-time of absorption. Concentrations were normalized to that of the liquid layer at the air interface. Autoradiographs to the right show distribution of radioactivity in transverse sections of the dog tracheal mucosa for NNK, pyrene, and BaP at respectively 25, 45, and 60 min after instillation.

Gerde and Scott, 2001, Inhalation Tox, 13:903
Parameters important

- Insoluble TC
- ”Soluble” OC
- Toxic components
<table>
<thead>
<tr>
<th>Effect</th>
<th>Needed measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>Number of particles with a “non volatile” core (BC)</td>
</tr>
<tr>
<td>Direct radiation effect</td>
<td>Single scattering albedo</td>
</tr>
<tr>
<td>Indirect radiation effect</td>
<td>TC</td>
</tr>
<tr>
<td></td>
<td>Soluble fraction of OC</td>
</tr>
<tr>
<td></td>
<td>Surface tension</td>
</tr>
<tr>
<td></td>
<td>Molecular weight</td>
</tr>
<tr>
<td></td>
<td>van’t Hoff factor</td>
</tr>
<tr>
<td>Health</td>
<td>Insoluble TC</td>
</tr>
<tr>
<td></td>
<td>”Soluble” fraction of OC</td>
</tr>
<tr>
<td></td>
<td>Toxic content</td>
</tr>
</tbody>
</table>
So let’s drop BC / EC and focus on

➢ TC
➢ Soluble OC
➢ Single scattering albedo

when concerned about the atmosphere

BUT
Fig. 2. Thermograms of parallel samples collected with quartz filters in Berkeley, California on 6 May 1999 t9.75 h duration. The filters were cut from two different batches of quartz filter paper purchased from the same manufacturer: (a) front and back filters were cut from lot A; (b) front and back filters were cut from lot B; (c) front filter from lot A, back filter from lot B; (d) front filter from lot B, back filter from lot A.
**Statement:**

<table>
<thead>
<tr>
<th>Measure</th>
<th>TC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Soluble OC</td>
</tr>
<tr>
<td></td>
<td>Optical properties of TC</td>
</tr>
</tbody>
</table>

Sampling should be done on inert media or using a denuder before the sampling media.