Chemistry and Aerosols

Bernhard Vogel
But there is more…
Aerosols have an impact on human health and on climate (and weather).

by:

modifying the atmospheric radiation,
modifying cloud formation,
and mixtures of both.

AND:

They are changing the chemical composition of the atmosphere.
What is the level of scientific understanding?

- Natural and anthropogenic aerosols and global climate
  Low

- Natural and anthropogenic aerosols and regional climate
  Low

- Aerosols and weather forecast
  Unknown
What great-grandfather already knew

John Aitken:

Cloud condensation nuclei: "Without dust ... there would be neither fog nor rain" (Trans. Roy. Soc. Edinb. 30, (1880))

Sulphur when burned has been shown to be an intensely active fog-producer. Calculation shows that there are

Nature 1880
**Aerosol**: Suspension of small particles (liquid, solid, mixtures) in gases.

**Primary Aerosol**: Particles emitted directly into the atmosphere

**Secondary Aerosol**: Formed by conversion from the gas phase

Particles differ by:

- Size
- Surface
- Volume or Mass
- Chemical Composition
Interactions

$T(z)$

- $\text{VOC}$
- $\text{SO}_2$
- $\text{HNO}_3$
- $\text{NH}_3$
- $\text{HONO}$
- $\text{N}_2\text{O}_5$
Size Range
Pictures

Quelle: M. Koyro, AIDA team
Primary particle formation results from mechanical disruption of the earth’s surface.

sand/dust aerosols
Sea-spray aerosols

Combustion particle formation
Incomplete combustion of fuel (soot, carbon etc)

Secondary particle formation from gas-to-particle conversion

Homogeneous nucleation
Condensation of gaseous compounds on existing particles
Particle Composition:

Primary aerosol:
soil dust: iron, calcium, silica
sea-spray: sodium, chloride, calcium, sulphate, potassium, etc.

Secondary aerosol:
sulphates, nitrates, ammonium, organics, halogens, ...

Combustion aerosol:
sulphates, nitrates, elemental carbon, organic carbon, soot

Organic (acids):
formed by oxidation of biogenic and anthropogenic VOC
Global Emissions (primary)

Overview of emissions of primary aerosol in Tg per year, by IPCC (2001) \( d \) = diameter

<table>
<thead>
<tr>
<th>Hemisphere</th>
<th>North.</th>
<th>South.</th>
<th>Global</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbonaceous aerosols</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic Matter (0-2 ( \mu m ))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass burning</td>
<td>28</td>
<td>26</td>
<td>54</td>
<td>45</td>
<td>80</td>
</tr>
<tr>
<td>Fossil fuel</td>
<td>28</td>
<td>0.4</td>
<td>28</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Biogenic (&gt;1 ( \mu m ))</td>
<td>-</td>
<td>-</td>
<td>56</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>Black Carbon (0-2 ( \mu m ))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Biomass burning</td>
<td>2.9</td>
<td>2.7</td>
<td>5.7</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>Fossil fuel</td>
<td>6.5</td>
<td>0.1</td>
<td>6.6</td>
<td>6</td>
<td>8</td>
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<tr>
<td>Aircraft</td>
<td>0.005</td>
<td>0.0004</td>
<td>0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Industrial Dust, etc. (&gt;1 ( \mu m ))</strong></td>
<td>100</td>
<td>40</td>
<td>130</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sea Salt</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d&lt; 1 ( \mu m )</td>
<td>23</td>
<td>31</td>
<td>54</td>
<td>18</td>
<td>100</td>
</tr>
<tr>
<td>d=1-16 ( \mu m )</td>
<td>1,420</td>
<td>1,870</td>
<td>3,290</td>
<td>1,000</td>
<td>6,000</td>
</tr>
<tr>
<td>Total</td>
<td>1,440</td>
<td>1,900</td>
<td>3,340</td>
<td>1,000</td>
<td>6,000</td>
</tr>
<tr>
<td><strong>Mineral (Soil) Dust</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d&lt; 1 ( \mu m )</td>
<td>90</td>
<td>17</td>
<td>110</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>d=1-2 ( \mu m )</td>
<td>240</td>
<td>50</td>
<td>290</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>d=2-20 ( \mu m )</td>
<td>1,470</td>
<td>282</td>
<td>1,750</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>1,800</td>
<td>349</td>
<td>2,150</td>
<td>1,000</td>
<td>3,000</td>
</tr>
</tbody>
</table>
## Sources of Secondary Aerosols

Estimates for secondary aerosol sources (in Tg = $10^{12}$ g substance/yr)

<table>
<thead>
<tr>
<th></th>
<th>North.</th>
<th>South.</th>
<th>Global</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sulfate (as NH$_4$HSO$_4$)</strong></td>
<td>145</td>
<td>55</td>
<td>200</td>
<td>107</td>
<td>374</td>
</tr>
<tr>
<td><strong>Anthropogenic</strong></td>
<td>106</td>
<td>15</td>
<td>122</td>
<td>69</td>
<td>214</td>
</tr>
<tr>
<td><strong>Biogenic</strong></td>
<td>25</td>
<td>32</td>
<td>57</td>
<td>28</td>
<td>118</td>
</tr>
<tr>
<td><strong>Volcanic</strong></td>
<td>14</td>
<td>7</td>
<td>21</td>
<td>9</td>
<td>48</td>
</tr>
<tr>
<td><strong>Nitrate (as NO$_3^-$)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Anthropogenic</strong></td>
<td>12.4</td>
<td>1.8</td>
<td>14.2</td>
<td>9.6</td>
<td>19.2</td>
</tr>
<tr>
<td><strong>Natural</strong></td>
<td>2.2</td>
<td>1.7</td>
<td>3.9</td>
<td>1.9</td>
<td>7.6</td>
</tr>
<tr>
<td><strong>Organic compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Anthropogenic</strong></td>
<td>0.15</td>
<td>0.45</td>
<td>0.6</td>
<td>0.3</td>
<td>1.8</td>
</tr>
<tr>
<td><strong>VOC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Biogenic VOC</strong></td>
<td>8.2</td>
<td>7.4</td>
<td>16</td>
<td>8</td>
<td>40</td>
</tr>
</tbody>
</table>
Size and Number

Number vs. D in μm
Number-, Area- and Volume- Density Distributions

Radius in $\mu m$
Description of Size Distributions

The size distribution function \( n_N(D_p) \): the number of particles per cm\(^3\) of air having diameters in the range \( D_p \) to \( D_p + dD_p \)

Therefore the total number of particles, \( N \), is

\[
N = \int_0^\infty n_N(D_p) dD_p
\]
in cm\(^3\)

If \( dN = n_N(D_p) dD_p \) is the number of particles between \( D_p \) to \( D_p + dD_p \)

Then

\[
n_N(D_p) = \frac{dN}{dD_p}
\]
in \( \mu m^{-1} \) cm\(^3\)

In terms of aerosol surface area:

\[
S = \pi \int_0^\infty D_p^2 n_N(D_p) dD_p
\]
in \( \mu m^{-2} \) cm\(^3\)

And Volume

\[
V = \frac{\pi}{6} \int_0^\infty D_p^3 n_N(D_p) dD_p
\]
in \( \mu m^{-3} \) cm\(^3\)

Similar arguments follow for expressing the size distribution in \( \ln D_p \) or \( \log D_p \):

\[
n^\phi_n(\ln D_p) d \ln D_p = \text{number of particles in the size range } \ln D_p \text{ to } \ln D_p + d \ln D_p \text{, where the units are now cm}^{-3}.
\]
Properties of Size Distributions:

The mean particle diameter:

\[ \bar{D}_p = \frac{1}{N} \int_0^\infty D_p n_N(D_p) \, dD_p \]

The variance:

\[ \sigma^2 = \frac{1}{N} \int_0^\infty (D_p - \bar{D}_p)^2 n_N(D_p) \, dD_p \]

The Normal Distribution is:

\[ n(u) = \frac{N}{(2\pi)^{1/2} \sigma_u} \exp\left(-\frac{(u - \bar{u})^2}{2\sigma_u^2}\right) \]

where 68% of the area below the curve is in the range:

\[ \bar{u} \pm \sigma_u \]

The Log Normal Distribution is therefore:

\[ n(\ln D_p) = \frac{N}{(2\pi)^{1/2} \ln \sigma_g} \exp\left(-\frac{(\ln D_p - \ln \bar{D}_{pg})^2}{2 \ln^2 \sigma_g^2}\right) \]

\( \sigma_g \) = geometric standard deviation
Size distribution fitted by three log-normal distributions \( \Rightarrow \) ‘modal approach’
Measured size distribution fitted by discrete sections ⇔ ‘sectional approach’

Versick, 2006
The average distance traveled by a particle between a collision is called the mean free path.

A dimensionless number describing the relative length scales is the Knudsen number, $Kn$,

$$Kn = \frac{2\lambda_{BB}}{D_p}$$

The mean free path of a pure gas is:

$$\lambda_{BB} = \frac{2\mu_B}{p \left(\frac{8M_B}{\pi RT}\right)^{1/2}}$$

**Continuum regime** ($Kn \to 0$)

**Free molecule (kinetic) regime** ($Kn \to \infty$)

**Transition regime** ($Kn \to 1$).
A particle moving in a fluid perceives a drag:

\[ F_{\text{Drag}} = 3\pi \mu D p u_\infty \]

\( u_\infty \): velocity of the fluid

\( \mu \): fluid viscosity.
Stokes Law and Non-Continuum Effects:

A slip correction factor has to be introduced:

\[ F_{\text{Drag}} = 3\pi \mu D_{p} u_{\infty} / C_{c} \]

\[ C_{c} = 1 + \frac{2\lambda}{D_{p}} \left[ 1.257 + 0.4 \exp \left( -\frac{1.1D_{p}}{2\lambda} \right) \right] \]

\( C_{c} \) is known as the Cunningham Slip correction factor

<table>
<thead>
<tr>
<th>Diameter ( \mu \text{m} )</th>
<th>( C_{c} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>216</td>
</tr>
<tr>
<td>0.005</td>
<td>108</td>
</tr>
<tr>
<td>0.01</td>
<td>22</td>
</tr>
<tr>
<td>0.05</td>
<td>4.9</td>
</tr>
<tr>
<td>0.1</td>
<td>2.85</td>
</tr>
<tr>
<td>0.5</td>
<td>1.32</td>
</tr>
<tr>
<td>1.16</td>
<td>1.016</td>
</tr>
<tr>
<td>100</td>
<td>1.0016</td>
</tr>
</tbody>
</table>
Gravitational Settling:

The equation of motion of a particle of mass $m_p$:

$$m_p \frac{dv}{dt} = m_p g + \frac{3 \pi \mu D_p}{C_C} (u - v)$$

The terminal velocity:

$$v_t = \frac{m_p C_C g}{3 \pi \mu D_p}$$
Particle diffusion coefficient

\[ D = \frac{kTC_C}{3\pi \mu D_p} \]
The Deposition Velocity

![Graph showing the relationship between particle diameter and deposition velocity. The graph plots velocity (cm s\(^{-1}\)) on the y-axis and particle diameter (μm) on the x-axis. The graph includes curves for total dry-deposition velocity, dry-deposition velocity without sedimentation, and sedimentation velocity.](image-url)
Temporal change of number density:

\[ \frac{dn(d_p)}{dt} = -\lambda(d_p)n(d_p) \]  
(Seinfeld, Pandis 1998)

\[ \lambda(d_p) = \int_{0}^{\infty} \frac{\pi}{4} \]

Collection Efficiency calculated following Slinn (1983)

\[ E(d_p, D_d) = \frac{1}{\text{Re} S} \]

Drop size

Particle size

\[ Sc = \frac{1}{\rho_a D_{diff}} \quad \rightarrow \quad D_{\text{diff}} = \frac{3\pi \mu_a d_p}{\rho_a} \quad \rightarrow \quad C_C = 1 + 2,433 \quad \exp(-0,435 \frac{d_p}{\lambda}) \]
Washout
Coagulation: Two particles collide and stick together

Coagulation:

- conserves the total mass
- reduces the total number
- changes diameter
Diffusion coagulation occurs when one mode of particles coagulate with another mode of particles.

Diffusive coagulation is described by:

$$\frac{dN_1}{dt} = -K_{12}N_1N_2$$
Brownian Coagulation

**FIGURE 12.5** Brownian coagulation coefficient $K_{12}$ for coagulation in air at 25°C of particles of diameters $D_{p1}$ and $D_{p2}$. The curves were calculated using the correlation of Fuchs in Table 12.1.

Use this figure finding the smaller of the two particles as the abscissa and then locate the line corresponding to the larger particle.
Coagulation between a small and a large particle is referred to a scavenging or collection, leading to a complete loss of the small particles whereas the volume of the large particle does not significantly change.
The growth rate of particles:

\[
\frac{dr}{dt} = \frac{M_X \beta_m D C}{r \rho}
\]

- \( r \) : is particle radius,
- \( M_X \) : molecular mass of condensable vapour \( X \),
- \( \beta_m \) : transitional correction factor for mass flux,
- \( D \) : diffusion coefficient,
- \( \rho \) : particle density,
- \( C \) : vapor concentration.

The transitional correction factor for mass flux, following *Fuchs and Sutugin* (1971):

\[
\beta_m = \frac{Kn + 1}{0.377 Kn + 1 + \frac{4}{3} \alpha^{-1} Kn^2 + \frac{4}{3} \alpha^{-1} Kn}
\]
Nucleation

Nucleation: material is transformed from one phase to another:
condensation, crystallization, sublimation, boiling or freezing.

Step 1: super saturation of the mother phase,
cooling, production of condensable material

Step 2: formation of clusters by thermal fluctuations

Step 3: growth of the clusters to critical sizes

Homogeneous nucleation: absence of foreign material

Heterogeneous nucleation: occurs on foreign substances or surfaces
Impact of Aerosol Particles on Clouds

- **Aerosol particles** act as cloud condensation nuclei (CCN) and therefore they **determine the size distribution of cloud droplets**.

Impact on:
- cloud optical properties
- coagulation of droplets
- precipitation
Effects of ice nuclei (IN) on cloud formation
Cloud albedo (Twomey) effect

4 mm clear glass balls

0.04 mm glass balls.

Stephen Salter, 2009
Photochemistry

Staehelein und Dommen (1994)
End of part 1