Aerosol source apportionment from long term measurements at the CESAR tower Cabauw, NL

P. Schlag, R. Holzinger, J. S. Henzing, F. Canonaco, and A. Kiendler-Scharr

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Effects of Atmospheric Aerosols

Direct effect on climate

Indirect effect on climate

Adverse health effects
Atmospheric Aerosols: Composition

Jimenez et al., Science 2009
### Effects of Atmospheric Aerosols

<table>
<thead>
<tr>
<th>Emitted Compound</th>
<th>Resulting Atmospheric Drivers</th>
<th>Radiative Forcing by Emissions and Drivers</th>
<th>Level of Confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>CO₂</td>
<td>1.68 [1.33 to 2.03]</td>
<td>VH</td>
</tr>
<tr>
<td>CH₄</td>
<td>CO₂, H₂O, O₃, CH₄</td>
<td>0.97 [0.74 to 1.20]</td>
<td>H</td>
</tr>
<tr>
<td>Halocarbons</td>
<td>O₂, CFCs, HCFCs</td>
<td>0.18 [0.01 to 0.35]</td>
<td>H</td>
</tr>
<tr>
<td>N₂O</td>
<td>N₂O</td>
<td>0.17 [0.13 to 0.21]</td>
<td>VH</td>
</tr>
<tr>
<td>CO</td>
<td>CO₂, CH₄, O₃</td>
<td>0.23 [0.16 to 0.30]</td>
<td>M</td>
</tr>
<tr>
<td>NMVOC</td>
<td>CO₂</td>
<td>0.10 [0.05 to 0.15]</td>
<td>M</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Nitrate, CH₄, O₃</td>
<td>-0.15 [-0.34 to 0.03]</td>
<td>M</td>
</tr>
<tr>
<td>Aerosols and precursors (Mineral dust, SO₂, NH₃, Organic Carbon and Black Carbon)</td>
<td>Cloud Adjustments due to Aerosols</td>
<td>-0.27 [-0.77 to 0.23]</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.55 [-1.33 to -0.06]</td>
<td>L</td>
</tr>
<tr>
<td>Albedo Change due to Land Use</td>
<td></td>
<td>-0.15 [-0.26 to -0.05]</td>
<td>M</td>
</tr>
<tr>
<td>Changes in Solar Irradiance</td>
<td></td>
<td>0.05 [0.00 to 0.10]</td>
<td>M</td>
</tr>
</tbody>
</table>

**Total Anthropogenic RF relative to 1750**
- 2011: 2.29 [1.13 to 3.33]  
- 1980: 1.25 [0.64 to 1.85]  
- 1950: 0.57 [0.29 to 0.85]

IPCC 2013
17 ACSM (Aerosol Chemical Speciation Monitor) instruments measuring ambient aerosol at monitoring sites across Europe.

Many since summer 2012.

3-week intercomparison in Nov. 2013:

- 12 Q-ACSM
- 1 ToF-ACSM
- 1 HR-ToF-AMS

Crenn et al., 2015
Fröhlich et al., 2015
Cabauw Experimental Site for Atmospheric Research (CESAR)
Aerosol instruments used in this work

- **Aerosol Chemical Speciation Monitor (ACSM)**
  - PM$_1$ **Organics, Nitrate, Sulfate, Ammonium, Chloride**

- **Multi-Angle Absorption Photometer (MAAP)**
  - PM$_1$ **Black Carbon**

- **High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS)**
  - PM$_1$ **Organics, Nitrate, Sulfate, Ammonium, Chloride**

- **Monitor for AeRosol and GAses (MARGA)**
  - PM$_{1/2.5}$ water soluble like **Nitrate, Sulfate, Ammonium, Chloride**

- **Scanning Mobility Particle Sizer (SMPS)**
  - PM$_1$ total aerosol mass concentration
Fractional species contribution to PM$_1$ mass (a) and time series of species mass concentration (b); **Total average mass loading: 9.5 µg/m$^3$**
Instrument Comparison (2012 – 2013)

Good correlations were seen in general over the whole campaign as well as during periods with high mass loadings!

- **ACSM** slightly overestimated **nitrate** by 23% and 17% and underestimated **sulphate** by 37% and 51% comparing to MARGA and AMS, respectively. **ACSM chloride** was largely below the detection limit.

<table>
<thead>
<tr>
<th>ACSM vs.</th>
<th>MARGA</th>
<th>HR-ToF-AMS</th>
<th>Organics</th>
<th>Nitrate</th>
<th>Ammonium</th>
<th>Sulfate</th>
<th>Total</th>
<th>(No. of points)</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>1.00 (R²=0.73)</td>
<td>1.17 (R²=0.89)</td>
<td>Organics</td>
<td>Nitrate</td>
<td>Ammonium</td>
<td>Sulfate</td>
<td>Total</td>
<td>(No. of points)</td>
</tr>
<tr>
<td>1.23 (R²=0.96)</td>
<td>1.17 (R²=0.89)</td>
<td>0.82 (R²=0.71)</td>
<td>Nitrate</td>
<td>Ammonium</td>
<td>Sulfate</td>
<td>Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.88 (R²=0.93)</td>
<td>0.82 (R²=0.71)</td>
<td>0.49 (R²=0.76)</td>
<td>Ammonium</td>
<td>Sulfate</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>0.63 (R²=0.86)</td>
<td>0.49 (R²=0.76)</td>
<td>0.90 (R²=0.84)</td>
<td>Sulfate</td>
<td>Total</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1.05 (R²=0.93)</td>
<td>0.90 (R²=0.84)</td>
<td></td>
<td>Total</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(1943 data points)</td>
<td>(289 data points)</td>
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</table>

**ACSM + MAAP** total mass vs. **SMPS** total mass (12275 data points):

Slope: 0.84 (R² = 0.82)
### Air quality standards of the World health organization (WHO)

<table>
<thead>
<tr>
<th></th>
<th>24h-mean</th>
<th>Annual mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>25 µg/m$^3$</td>
<td>10 µg/m$^3$</td>
</tr>
</tbody>
</table>

- Keep in mind that we have PM$_1$ composition measurements
- ACSM campaign: 9.5 µg/m$^3$
Total ACSM+MAAP PM$_1$ mass: Daily means

- 12 exceedances of WHO PM$_{2.5}$ daily mean limit
ACSM/MAAP: Diurnal Variations

- **NO$_3$**: heterogeneous conversion from NO$_y$ in the night / volatilization of semi-volatile nitrates and photolysis of gaseous precursors during the day
- **SO$_4$**: Daytime maximum due to it’s photochemical formation from SO$_2$
- **NH$_4$**: Neutralization of NO$_3$ and SO$_4$ and by NH$_3$ into NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$
- **BC**: Direct emissions from traffic (morning and evening rush hours) and biomass burning events (domestic heating in the evenings/nuights)
Positive Matrix Factorization (PMF)

- Bilinear unmixing model
- Least squares algorithm
- No a priori information, except: values are non-negative
- Factors represent sources (primary OA; POA) / aging (secondary OA; SOA)

Ulbrich et al., ACP 2009
These factors were seen in most seasons investigated by AMS and ACSM
- Red bars: site specific reference mass spectra from Crippa et al., ACP 2014, used as constraints for ME-2 (a-value in brackets)
- HOA showed diurnal pattern from traffic rush hours, while BBOA was mainly emitted by domestic heating in the evening/night. Highly oxidized HULIS (attributed to humic like substances) showed no diurnal variation
No biomass burning was found in summer. High contributions of chemically formed SOA (OOA and HULIS) were found where the HULIS concentration remained largely constant during the campaign, emphasizing its role as background aerosol at Cabauw.

HULIS: Paglione et al., ACP 2014
Sources of high particulate mass

Pie charts show fractional abundances averaged over two selected high mass periods.
Wedges highlighted in red represent secondary aerosol fractions.
Summary

- Performed 1-year PM$_1$ aerosol chemical composition measurements in Cabauw:
  - 12 exceedances of WHO PM$_{2.5}$ daily mean limit
- Nitrate and organics are the most dominant species
- Nitrate (mainly as NH$_4$NO$_3$) was the main contributor in periods with high mass loadings
  → Reducing NO$_x$ and/or NH$_3$ emissions should have a large effect on reducing particulate matter
- PMF/ME-2 analysis of the organic fraction show high contributions of chemically formed SOA
  - Typical for rural sites
  - The local reduction of organic aerosol mass is more challenging, especially as the HULIS fraction showed no designated source.
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