Chemical characterization of PM$_{10}$ at four German background monitoring stations by individual electronmicroscopic particle analysis

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Electronmicroscopic individual particle analysis (EM-IPA)

- Routinely particle sampling at monitoring stations Melpitz, Schauinsland, Waldhof and Westerland in 2012.

- Electronmicroscopic Individual particle analysis of 10 selected samples at each spot (41,000 particle analysis)

Main questions:
- refractory aerosols
- anthropogenic contribution
- carbonaceous aerosol
- artefacts at monitoring stations
Electronmicroscopic individual particle analysis

**EM-IPA**

- For significant results some 100 particles in each sample must be analyzed, what makes this kind of analysis very time-intensive.

- Method yields **size, morphology, elemental composition** \((Z > 4)\) and **mixing state** of individual particles.

- Method yields **number concentrations**, not mass concentrations as most other chemical methods.
Particle groups

Main groups

- Sea-salt
- Alumosilicates
- Ca-rich
- C – rich
- Secondary
- Metal/oxide
Classification of carbonaceous material

Identification of soot and biological particles

Classification criteria:  M-morphology   C- chemistry   B- beam stability
Average particle group number abundance
(for coarse fraction: 1 – 10 µm)

Schauinsland  Waldhof  Melpitz  Westerland

- Other
- Sea-salt
- Aged sea-salt
- Sea-salt mix
- Fe-rich
- Calcium sulfates
- Carbonates
- Silicate/carbonate
- Silicate
- Silicate/C
- C-nonvolatile
- Soot
- Secondary
- Biological
High contents of Carbonates and Carbonate/silicate mixtures in Waldhof and Schauinsland

Carbonate content in aerosol samples seems explainable from the regional soil carbonate content.
Particle group number abundance (1-10 µm)

Westerl

<table>
<thead>
<tr>
<th>SW</th>
<th>O</th>
<th>N</th>
<th>O</th>
<th>SO</th>
<th>NW</th>
<th>S</th>
<th>S</th>
<th>O</th>
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</tbody>
</table>

- other
- sea-salt
- aged sea-salt
- sea-salt mix
- Fe-rich
- calcium sulfates
- carbonates
- silicate/carbonate
- silicate
- silicate/C
- C-nonvolatile
- soot
- secondary
- biological
Subdivision of the carbonaceous fraction

PM$_{10}$-abundance of carbonates, biology, soot, volatile and nonvolatile organic particles

**Measured number abundance** of carbonaceous particles in the size-range 1 – 10 µm

<table>
<thead>
<tr>
<th></th>
<th>Schauinsland</th>
<th>Waldhof</th>
<th>Melpitz</th>
<th>Westerland</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbonates</td>
<td>12</td>
<td>11</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Soot (EC+OC)</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>volatile C</td>
<td>10</td>
<td>11</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>nonvolatile C</td>
<td>12</td>
<td>12</td>
<td>17</td>
<td>14</td>
</tr>
<tr>
<td>biological</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>5</td>
</tr>
</tbody>
</table>

**Derived mass abundance** of carbonaceous particles within PM$_{10}$-fraction

<table>
<thead>
<tr>
<th></th>
<th>Schauinsland</th>
<th>Waldhof</th>
<th>Melpitz</th>
<th>Westerland</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbonates</td>
<td>7</td>
<td>6</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>soot (EC+OC)</td>
<td>8</td>
<td>11</td>
<td>13</td>
<td>7</td>
</tr>
<tr>
<td>volatile C</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>nonvolatile C</td>
<td>6</td>
<td>7</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>biological</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>7</td>
</tr>
</tbody>
</table>

In average ~ 45% of PM$_{10}$
Anthropogenic Tracer
1. fly-ashes (Fe/Cr/Zn and silicatic) in Waldhof and Melpitz

- Increased number abundance of metal (oxides) and silicatic fly-ashes in Waldhof (Southwest) and Melpitz (East).
- Hint for contribution of Industry respectively burning of fossil fuels.
Anthropogeic Tracer

2. Lead halogenides in Westerland

- Most probable source for lead are small planes/helicopter
Local Artefacts at monitoring stations

1. Steel, Zn and brass in Westerland

Large abrasion particles clearly points to a local source (South).
Local Artefacts at monitoring stations

2. Al/Ni/Co/F- particles in Waldhof

local artefact of anodization layers
Summary and Conclusion

- Similar particle group abundances (1-10 µm) at all 4 monitoring stations
  
<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicate</td>
<td>20 – 35%</td>
</tr>
<tr>
<td>Ca-rich</td>
<td>5 – 15%</td>
</tr>
<tr>
<td>Secondary</td>
<td>25 – 30%</td>
</tr>
<tr>
<td>C-rich (nonvol.)</td>
<td>10 – 15%</td>
</tr>
<tr>
<td>Sea-salt</td>
<td>5 – 20%</td>
</tr>
<tr>
<td>Fe-rich</td>
<td>3 – 5%</td>
</tr>
</tbody>
</table>

- **Stronger compositional variability** (in dependence of air mass origin) in Westerland and Melpitz, less in Schauinsland and Waldhof.

- **Carbonaceous material** contributes to ~ 45% of PM$_{10}$
  (20% volatile, 10% soot, 8% nonvolatile, 5% carbonate, 2% biological).

- In Waldhof and Westerland local particulate artefacts (Zn, Fe, Ni) were found, which should be considered in discussion of determined metal concentrations.

- An increased abundance of fly-ashes (Fe/Si) were determined in the sub-µm fraction in Waldhof (SW) and Melpitz (O). This is a clear tracer for industrial sources respectively burning of fossil fuels.