Chemical Characterization of Wood Smoke Particle Emissions and its Application to Source Apportionment

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Wood Smoke...

... major primary particle source in winter

- 20–50% biomass OM/OM at European Sites
  (Puxbaum et al., 2007, JGR 112, D23S05: CARBOSOL Project)

- 41% of OC / 18% of PM2.5 in Fresno (CA)
  (Gorin et al., 2006)

- 45% of primary PM2.5 in Europe
  (Schaap et al., 2005, European Emission Inventory)
Wood-Smoke in Austria

• 20 – 40% of PM10 in Winter
• Up to 60% (urban)/80% (rural) of OC
• Rural source
• Regional (Continental ?) Scale

Why is wood smoke so important?
Importance of Wood-Smoke

• Long Tradition of Wood as Source of Energy

• High Particle-Emission-Factors compared to other Heating Systems (Oil, Gas)

• High availability of Fire-Wood/Population Density
Forest Coverage

Source: UN-ECE/FAO
Forest Stock

Source: UN-ECE/FAO
Residential heating in Austria

Austrian Provinces:
2 – 30% (Vienna - Burgenland) of Households heated with Wood

Total Austria
17% of Households

Not included:
Wood fired for additional Heating in small Stoves (Spring, Autumn) and esthetic Purposes

Data for 2004, Source: Statistik Austria
Assessment of Wood Smoke

- Macrotracer Concept...
  ... using the Anhydrosugar Levoglucosan as single Tracer (conversion factor Levo → PM/OC)

- Chemical Mass Balance (CMB) Model...
  ... using a chemical Source Profile and mathematical Equation to calculate Contribution
Pros and Cons

- Macrotracer Concept
  - mostly routine Analysis
  - analytical Errors smaller
  - atmospheric Stability well known
  - only one Compound gives Source Contribution
  - no cross-checking with other Compounds
  - Source-specific Tracers necessary

- CMB Model
  - many Compounds contribute to one Source Result
  - estimation of Uncertainty possible
  - no Tracers necessary, only sufficient difference in Profiles
  - detailed Knowledge of Source Profiles
  - analytical Uncertainties for Micro-Compounds higher
  - atmospheric Stability not certain
„Macro-CMB“

... an Attempt to combine Advantages of Macrotracer and CMB Concepts:

- Reduced Number of Species (n=14)
- Only Macro-Compounds (omitting organic trace Components)
- CMB Analysis for “Crosschecking” and Estimation of Uncertainties
Macro-CMB

- Good Fit (measured/calculated) for all Macro – Compounds
- Bad Fit for Potassium (~ one Order of Magnitude)

→ Missing Source/Unsuitable Profiles

Sample:
January
Lower Austria
Source Characterization

- Started with tiled Stove Measurements (Schmidl et al., 2008)

- 2 additional Wood-smoke Projects
  - Dilution sampling System (RT, ↑ Sample)
  - Online Gas Analysis (CO, CO₂, O₂, NOₓ, CₓHᵧ)
  - Combustion Efficiency
  - 8 different Appliances (5 – 50kW)
  - > 20 Fuel Types / Wood Types
Wood-smoke Emissions

- 2 Groups:
  - Automatically fired
    - constant Conditions
    - low Emissions
    - Carbon Content low
    - K, Ca, SO\textsubscript{4}, Cl
  - Manually fired (stove)
    - highly variable
    - high Emissions
    - Carbon Content 60-80%
    - OC, EC, HULIS, Levo
Wood-smoke PM10

- Wood-smoke PM10 measurement
- Comparison of manually and automatically fired samples
- Breakdown of PM10 components:
  - Nitrate
  - Sulphate
  - Ammonium
  - Potassium
  - EC
  - OC
  - Al, Si, Ca, Ba, Cl
  - Cellulose
  - Levoglucosan
  - HULIS

130mg/Nm³
(84.5mg/MJ)

16.6mg/Nm³
(10.7mg/MJ)
Anhydrosugars

Lev/Man Correlation:
4 different Stoves
16 Wood Types

Explanation:
Differences in Structure of Hemicelluloses of Angiosperms (deciduous) and Gymnosperms (coniferous)

Schmidl et al., 2008, AE
Schmidl et al., in preparation

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Application to Source Apportionment

• Use of 2 Wood-smoke Profiles for CMB
  – Automatically fired (Boilers, Pellet Stoves)
  – Manually fired (Stoves)

• Example: Lower Austria
Measured / Calculated

Same Data – Set:

Without Boiler Profile

Including Boiler Profile
Results CMB (Lower Austria)

Boiler-Av.: 2.1 µg/m³ or 4% of PM10

Stove-Av.: 6.4 µg/m³ or 12% of PM10
Emission – CMB Comparison

Energy use for Heating and Air Condition in Lower Austria

Source: Statistik Austria

<table>
<thead>
<tr>
<th>Appliance type</th>
<th>Natural Gas (LNG) 38%</th>
<th>Oil, LPG 22%</th>
<th>District Heating 8%</th>
<th>Electric Power 6%</th>
<th>Coal Products 2%</th>
<th>Solar 1%</th>
<th>Wood 23%</th>
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<tbody>
<tr>
<td>Stove</td>
<td>(11mg/MJ)</td>
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<td>Boiler</td>
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<td>20-30%</td>
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<td>(~2µg/m³)</td>
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</tbody>
</table>

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<tr>
<th>Emission contribution (f<em>w)/Σ(f</em>w)*100</th>
<th>Ambient CMB contribution (in µg/m³)</th>
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</thead>
<tbody>
<tr>
<td>Stoves 8%</td>
<td>80% 8-80%</td>
</tr>
<tr>
<td>Boilers 15%</td>
<td>20% 20-30%</td>
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<tr>
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<td>70-80%</td>
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Conclusions

• Big Effort in Source Characterization is crucial for Quality of Apportionment Studies

• Differentiation between Wood Types seems feasible (using Levoglucosan/Mannosan Ratio)

• Use of 2 different Wood-Smoke Profiles possible and necessary

• „Macro-CMB“ Results show good Correlation with Emission Data
Acknowledgements

Working Groups „Environmental Analytical Chemistry“ and „Atmospheric Analytical Chemistry“ at Vienna University of Technology

Funding:
Contribution by Species

Source Contribution [%]

- Mineral Dust
- Salt
- Ammoniumnitrate
- Ammoniumsulfate
- Organic Material
- Plant Debris
- HULIS (sec.)
- Wood Boiler
- Wood Stove
- Traffic

Contributions by Species:
- Nitrate
- Sulphate
- Ammonium
- Potassium
- Elemental Carbon
- Organic Carbon
- Aluminium
- Silicon
- Calcium
- Barium
- Chloride
- Cellulose
- Levoglucosan
- HULIS