Source apportionment with a focus on organics

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Number of papers in Web of Science: «Source apportionment»

- **World-wide**
- **US**
- **China**
**Levoglucosan**: Marker for biomass burning. Levoglucosan is from the pyrolysis of cellulose

Problem: Levoglucosan /OM very variable.. Levoglucosan not stable at higher temperatures

**Hopanes**: Marker for traffic, Hopanes part of lubricating oils..

Problem: Hopanes are also prevailing in coal emissions. Hopanes found only in very small amounts and also not necessary stable

General problem: marker compounds are making up only a very limited amount of the total organic mass. There are questions on stability. Most measurements are at low time resolution

This is still useful.. Especially in combination with more advanced techniques
Initial source attribution with AMS also based on markers

McFiggans, Alfarra et al., Faraday Discussions, 2005
**m/z 57** (mostly C$_4$H$_9^+$): **Hydrocarbon-based Organic Aerosol (HOA)**

**m/z 44** (mostly CO$_2^+$): **Oxygenated Organic Aerosol (OOA)**

*Zhang, Alfarra et al., ES&T 2005*
Aerosol mass spectra

Levoglucosan

Wood burner (emissions) chestnut, very inefficient burning

Night period in Roveredo in March, more than 80% of OC non-fossil

Average in Roveredo over the whole December

Mass spectra from a Motorway site in May
\[ X_{\text{measured}} = G \cdot F + E \]

- Factor analysis but with values in G & F all positive or zero
- The minimization of errors take into account the uncertainties
- No a priori information required for PMF, constraints can be applied with ME-2

PMF: Paatero and Tapper 1994; Lanz et al., 2007, Ulbrich et al., 2009; Zhang et al. 2011 (Review)
SoFi (Source Finder) is becoming a standard statistical tool worldwide in ACSM, AMS analysis. It can be used for any PMF, ME-2 analyses of e.g. ICP-MS, GC-MS, VOC data.

Result Example traffic and cooking in Zurich

SoFi, an IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data

SoFi 6 is shared in collaboration
Organic mass in Paris in winter

Crippa et al., ACP, 2013
Measurements in Xi’an / Beijing winter 2013/2014

Xi’an

- Extreme haze*
- Visibility < 2km

Beijing

* Zhang et al., 2015

Elser et al., 2016, ACP

First Deployment of PM2.5 lens in China

<table>
<thead>
<tr>
<th></th>
<th>Xi’an</th>
<th>Beijing</th>
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<tbody>
<tr>
<td>Mean</td>
<td>Extreme haze</td>
<td>Reference</td>
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<tr>
<td></td>
<td>538.5 μg/m³</td>
<td>139.5 μg/m³</td>
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<td></td>
<td>~22xWHO</td>
<td>~6xWHO</td>
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<td>~3xWHO</td>
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<td></td>
<td>Extreme haze</td>
<td>Reference</td>
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<td></td>
<td>246.2 μg/m³</td>
<td>76.6 μg/m³</td>
</tr>
<tr>
<td></td>
<td>~10xWHO</td>
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PMF results

5 FACTORS SOLUTION (unconstrained run)

- m/z 44
- m/z 55 & 57 (oxygenated)
- m/z 55 & 57 (non-oxygenated)
- m/z 60

Unsaturated hydrocarbons

TO GET A GOOD SEPARATION OF THE PRIMARY SOURCES WE NEED TO CONSTRAIN HOA & COA

Mixing between sources?

- **HOA & BBOA:**
  High m/z 60 in HOA (also in 25 factors solution)

- **COA & OOA:**
  High m/z 44 in COA
  Diurnal COA disturbed if fixing HOA

Elser et al., ACP, 2016
Unconstrained vs. optimized solution

We can provide an idea of the uncertainty.

- Coal important in Beijing
- Wood burning important in Xi’an
- The amount of COA (cooking) and HOA (traffic) is lower for optimized ME-2 analysis compared to PMF

Elser et al., ACP, 2016
PAH

- PAH correlate very good with CCOA in Beijing but needs other sources in Xi’an

- PMF runs with Input = (OA|PAH) $\rightarrow$ PAH attributed to BBOA, CCOA and HOA

ToF-ACSM will help in China, because one measures the PAHs and in general less transmission issues

Elser et al., ACP, 2016
Source apportionment using the ToF-Aerosol mass spectrometer

- HOA: mostly traffic
- OOA: oxygenated organic aerosols, mostly secondary

Nearly everywhere, secondary organic aerosol is dominating.
- Data represents usually a few weeks per site
ACSM/AMS measurements in Europe

[Map of Europe with ACSM Stations, EMEP (summer + winter), EMEP (winter), and EMEP (summer) highlighted.]

https://www.psi.ch/acsm-stations/
ME-2 Intercomparison exercise near Paris

good results considering the rather short period

Froehlich et al., AMT, 2015
Rolling mechanism

- PMF window can be automatically shifted over the PMF input matrix
- after every shift the PMF runs are reinitialized (seed, a value, fpeak, bootstrap, etc.)
- length of window and shift are user-defined parameters
- Number of runs typically 500*352
  Use Criteria to filter good solutions. then get the average and uncertainty

See also Parworth et al. (2015) for a PMF moving window approach
SoFi can also treat other kind of data, e.g. elemental data measured by Xact625
SoFi has been used for CIMS, PTR-MS, EESI data
Conclusions Outlook

- See Off-line AMS talk later this week
- Uncertainties in the source apportionment needs to be better assessed. Only showing «the best» solution out of e.g. 10 PMF runs is not good enough
- Combination of data will get more interesting: In Canada: Combination On-line XRF, ACSM, Aethalometer: very promising
- How to combine aerosol and VOC/CIMS data
- Combination of off-line and on-line data is possible and interesting.
- Future: On-line source apportionment shall be developed using SoFi

- SoFi is a very versatile tool. Basic version for free but in collaboration (typically 2 co-author papers). Add-on : license basis by Canonacos future company: Especially for Long-term data analyses and criteria based selections of solutions and further explorations. No commercial use. Francescos company is planning to provide on-line source apportionment or also postcampaign analyses
- There will be in the future SoFi workshops. Visits at PSI can be useful to learn how to do use it in practice.
- Install PMF and SoFi on your computers for Thursday/Friday (ask for support by Jing Zheng or Liming Cao)

Huang, El Haddad, Cao, Prevot et al. (2014)