Source apportionment of the particulate organic mass during winter and summer in Zurich, Switzerland

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Discussion of Aerodyne aerosol mass spectrometer and 14C-data

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Places in Switzerland with AMS Measurements
Average composition in Zürich in summer and winter
(Aerosol mass spectrometer and aethalometer data)

Zürich (July) 23 μg/m³
- Black Carbon: 7%
- Organic mass: 13%
- Nitrate: 14%
- Sulfate: 11%
- Ammonium: 7%

Zürich (January) 49 μg/m³
- Black Carbon: 15%
- Organic mass: 32%
- Nitrate: 11%
- Sulfate: 15%
- Ammonium: 27%

14C analysis of EC in summer and winter in Zürich

14C-analyses (Szidat et al., 2004, 2006, 2007) of HiVol-Quartzfilter allow for the determination of the fossil and non-fossil carbon fractions of the EC, OC, and more fractions like water-soluble OC, ...

winter
- EC (fossil): 19%
- EC (non-fossil): 81%

summer
- EC (fossil): 7%
- EC (non-fossil): 93%
Organic aerosol mass spectra in Zurich

Positive Matrix Factorization (PMF): Bilinear unmixing

\[ X_{n \times m} = G_{n \times p} F_{p \times m} + E_{n \times m} \]

Mass peaks: \( j = 1 \ldots m \)

Samples in time: \( i = 1 \ldots n \)

number of factors/reduced dimensions

Source profiles

Source strengths

Zurich, winter

Zurich, summer
Positive Matrix Factorization of OM in Zürich summer

Lanz et al., ACP (2007)

Temporal evolutions of OOA I and OOA II

Lanz et al., ACP, 2007

\(^{14}\text{C}\) analysis indicates that most SOA is non-fossil (probably a combination from oxidation of terpenes, sesquiterpenes, isoprene, and possibly from biomass burning emissions)
If contribution of various OA components do not vary much in time Positive Matrix Factorization or similar unmixing methods do not work: Example Zürich winter

A solution could be to use chemical mass balance (CMB) methods or hybrid versions of CMB and PMF

\[ x_j = \sum_{p} g_{pj} f_{pj} + \sum_{p'} g_{pj} f_{p'j} + e_{ij} \]

unknown sources/ free factors (PMF)
known sources/ fixed factors (CMB)

- In Zurich winter we used HOA as the known source, OOA and wood burning could be additionally identified

solved by the multilinear engine, ME (Paatero, 1999)

Lanz et al., ES&T, accepted
Sensitivity analysis toward the degree of freedom of the constraint HOA factor

Campaign average

- a = 0.0
  - wood burning: 57%
  - OOA: 40%
  - HOA: 3%
- a = 0.6
  - wood burning: 55%
  - OOA: 38%
  - HOA: 7%
- a = 0.8
  - wood burning: 52%
  - OOA: 50%
  - HOA: 8%

Highest concentrations during campaign

- High PM episode (a = 0.0)
  - wood burning: 43%
  - OOA: 52%
  - HOA: 4%
- High PM episode (a = 0.6)
  - wood burning: 45%
  - OOA: 46%
  - HOA: 9%
- High PM episode (a = 0.8)
  - wood burning: 45%
  - OOA: 45%
  - HOA: 10%

Plausibility of solution including 3 factors

- Wood burning (modelled) vs CO (measured): $R^2 = 0.78$
- OOA (modelled) vs AMS-ammonium (measured): $R^2 = 0.72$
- HOA (modelled) vs NOx (measured): $R^2 = 0.70$
- Roveredo MS: $R^2 = 0.93$
- Chestnut MS: $R^2 = 0.87$
- Aged rural MS: $R^2 = 0.93$
- Fulvic acid MS: $R^2 = 0.87$

Lanz et al., ES&T, accepted

2006
Look at residuals after statistical analysis
Carbon apportionment using $^{14}$C analysis
Estimation of fossil and non-fossil SOA contribution

Use of AMS analysis:
- Wood burning 38%
- HOA 7%

Assumptions:
- Only SOA, HOA and wood burning present
- OM/OC=2 for wood burning and SOA and OM/OC=1.2 for HOA

RESULT: SOA_{nonfossil}: 69% SOA_{fossil}: 31%

Lanz et al., submitted to ES&T

PSI mobile laboratory
Estimation of wood burning contribution to OM as a function of location

Conclusion

• PMF and hybrid versions of PMF and CMB are very powerful tools for the source apportionment of organic aerosol mass spectra
• Be careful with PMF results: validate as much as possible (time traces with other indicators, comparison to reference spectra), look carefully at remaining structure in the residual.
• Question/concern: is the ionization efficiency the same for OOA1, OOA2, HOA, wood burning organics?!
• The combination of $^{14}$C analyses with AMS data is very promising. We would like to do that more often and would like to offer our cooperation in the analysis of Hi-Vol filters concerning $^{14}$C…

Measurements expensive and time-consuming:
Costs per analysis: 300 (costs to use the accelerator MS at ETH) – 800 dollars (including all the preparation, analysis, etc.) (typically 4-5 filters per campaign and station good enough: if EC and OC analyzed, one needs 10 analyses. A very limited amount we might be able to do for free..
• We are interested in a limited amount of measurement campaign data including high temperature, considerable temperature variation and supposedly high SOA amounts. Idea: Assessment of OOA1, OOA2 spectra and their partitioning.