Real-time Measurements of PM$_{2.5}$ and PM$_{1}$ Chemical Composition: Experience and Results from the UK Supersites and EMEP Intensive Measurement Periods

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Background

- **EMEP Monitoring Strategy 2004-09:**
  - Move towards a three-tier strategy
  - Intensive Measurement Periods

- **EMEP Level-2 & Air Quality Directive:**
  - Daily or better basic aerosol composition of PM$_{2.5}$ and PM$_{10}$
  - Reliable gas / aerosol partitioning (rather than EMEP filter pack)

- **UK Approach:**
  - Tried daily denuder / filter measurements in the past
  - Spatial pattern:
    - >80 sites for monthly NH$_3$ measurements
    - 32 sites monthly measurements of NH$_3$, HNO$_3$, HCl, SO$_2$, NH$_4^+$, NO$_3^-$, Cl$^-$, SO$_4^{2-}$, base cations (no cut, about PM$_{4.6}$)
  - Temporal pattern: upgrade two sites to Level-2, with hourly measurements of inorganic aerosol composition by MARGA (PM$_{2.5}$ & PM$_{10}$)

- **Intensive Measurement Periods:**
  - June 2006 & January 2007: some hourly, mainly daily
  - Only few gas-phase measurements (NH$_3$, HNO$_3$)
Monthly Denuder / Filter-pack Measurements within the NitroEurope Level-1 Network

DENUDER 2: Carbonate coated to sample HNO₃, SO₂, HCl

DENUDER 3: Acid coated to sample NH₃

DENUDER 4: Acid coated to sample NH₃

DENUDER 1: Carbonate coated to sample HNO₃, SO₂, HCl

TEFLON INLET: 10 mm OD x 28 mm (L)

DELTA Sampler above Speulder Bos, NL
UK Network
(Monthly denuder / filter pack)
Realtime Measurements

- Wet chemistry instrument (**MARGA**) to measure chemistry composition of fine and coarse inorganic particulate (**PM$_{2.5}$** and **PM$_{10}$**)
  - Since June 2006: Scottish EMEP Supersite ‘Auchencorth’
  - Since Feb 2009: English EMEP Supersite ‘Harwell’
  - Instrument intercomparisons during short measurement campaigns
  - Measurements within Intensive Measurement Periods (Auchencorth, Harwell, Cabauw, Ispra)

- Aerosol Mass Spectrometer (**AMS**) to measure non refractory submicron particulate.
  - UK Measurement campaigns
  - European aerosol climatology during EMEP/EUCAARI IMPs

- Use of data for model validation (**EMEP4UK**)
**MARGA. Principle I**

**Compounds Measured:**
- **Gas:** NH$_3$, HCl, HNO$_3$, HONO, SO$_2$
- **PM$_{10}$-PM$_{2.5}$ particles:** Cl$^-$, NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$

**Analysis:**
- Ion chromatography

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**Denuder**

- To SJAC
- Ambient air
- Absorbing solution in controlled by level detector
- Sample solution out by syringe pump

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**Image:** Diagram of a denuder setup.
MARGA. Principle II

SJAC  Steam-Jet-Aerosol-Collector

DI water in

Super saturated steam

To air pump

Sample to the syringe

Steam generator

Air from denuder

Liquid level sensor

Additional DI

Sample to the syringe
Long-term MARGA measurements

The High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS)
Aerosol Mass Spectrometer

- Transmission near 100%: 60 – 800 nm
- Non-refractory aerosol components only (evaporate at 600°C)
  - In most conditions direct measurement of NH₄NO₃, (NH₄)₂SO₄, NH₄Cl
- Size-distributions
- Mass spectrum of bulk organic composition
  - Organic aerosol classes (primary hydrocarbon-like vs. secondary oxidised organic aerosol)
  - High resolution version: C/O/H/N ratios (OM/OC)
- New Aerodyne Aerosol Chemical Speciation Monitor (PM$_{2.5}$, but still NR)
### Comparison AMS vs. MARGA

<table>
<thead>
<tr>
<th></th>
<th>AMS</th>
<th>MARGA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gases</strong></td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>(NH₃, HNO₃, HCl, SO₂, HNO₂)</td>
<td></td>
</tr>
<tr>
<td><strong>Transmission</strong></td>
<td>~PM₁</td>
<td>PM₂.₅ &amp; PM₁₀/TSP</td>
</tr>
<tr>
<td><strong>Sizing</strong></td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td><strong>Aerosol fraction</strong></td>
<td>Non-refractory only: NH₄⁺, NO₃⁻, SO₄²⁻, Cl⁻, OM</td>
<td>Water-soluble NH₄⁺, NO₃⁻, SO₄²⁻, Cl⁻, (Na⁺, K⁺, Ca²⁺, Mg²⁺)</td>
</tr>
</tbody>
</table>
Size-distributions
Auchencorth Moss EMEP Supersite

- Open moorland at 255 m asl 3.2°E, 55.8°N in Scotland.
- Background site, some large towns to the north-east, intensive farming to the south and south-east.
- Long term monitoring of SO$_2$, NH$_3$, CO$_2$, wet deposition
- MARGA operation since June 2006

Average wind speed: 4.75 m/s
Comparison with gravimetric measurements

![Graph of concentration over time with various markers and legends.]

Auchencorth Moss 2008
PM$_{2.5}$ and coarse monthly composition measured at Auchencorth Moss

2007 Annual average contributions

PM$_{2.5}$: 3.3µg m$^{-3}$
- NH$_4^+$: 29%
- NO$_3^-$: 16%
- SO$_4^{2-}$: 20%
- Crustal: 6%
- Sea Salt: 28%

PM$_{10}$-PM$_{2.5}$: 1.3µg m$^{-3}$
- NH$_4^+$: 7%
- NO$_3^-$: 17%
- SO$_4^{2-}$: 10%
- Crustal: 58%
Wind sector studies on Auchencorth Moss

- **u (m s⁻¹) av**
- **u (m s⁻¹) med**
- **Frequency**

- **HNO₃**
- **SO₄²⁻·PM₁₀**
- **SO₄²⁻·PM₂.₅**
- **NH₄⁺·PM₁₀**
- **NH₄⁺·PM₂.₅**

- **SO₂**
- **NH₃ Average**
- **NH₃ Median**
- **Na·PM₁₀**
- **Cl·PM₁₀**
- **NO₃⁻·PM₁₀**
- **NO₃⁻·PM₂.₅**
TSP in urban environment. London-BT tower

October 2006

October 2007

REPARTEE-CityFlux
Fine / coarse nitrate

• Chemical models do not normally predict PM$_{2.5}$ and PM$_{10}$, but e.g. ammonium nitrate and other nitrate (NaNO$_3$, Ca(NO$_3$)$_2$)
• Nitrate in PM$_{2.5}$ = NH$_4$NO$_3$ + tail of other nitrate
• Combination of MARGA & AMS:
  – AMS measures NR NO$_3^-$ (NH$_4$NO$_3$ only)
  – Coarse nitrate by difference (MARGA – AMS)

• Add Harwell nitrate plot
• Add size distribution plot of chemical components to illustrate problem of PM2.5
Coarse vs. Fine Mode NO$_3^-$

- Harwell (June 2006): 49% fine : 51% coarse
- Harwell (Jan 2007): 61% fine : 39% coarse
- BT Tower (Oct 2006): 34% non-refractory : 66% refractory
Comparison of MARGA with Filter Sampler (Harwell)

June 2006

Chloride

\[ y = 1.000 \times + 0.239 \]
\[ R^2 = 0.972 \]

Nitrate

\[ y = 0.900 \times + 1.796 \]
\[ R^2 = 0.518 \]

Sulphate

\[ y = 1.385 \times - 0.842 \]
\[ R^2 = 0.821 \]

January 2007

Chloride

\[ y = 1.179 \times - 0.783 \]
\[ R^2 = 0.943 \]

Nitrate

\[ y = 0.925 \times - 0.127 \]
\[ R^2 = 0.953 \]

Sulphate

\[ y = 0.894 \times + 0.0933 \]
\[ R^2 = 0.747 \]
Comparison filter sample (PM$_{10}$) vs. MARGA (TSP) (BT Tower)
AMS Size Distribution at CEH EMEP (Bush)
UK Non-Refractory Submicron Aerosol Composition Measured by Aerosol Mass Spectrometry

- Edinburgh 2000: 3.0 µg/m³
- Easter Bush 2002: 5.74 µg/m³
- Mace Head 2002: 1.53 µg/m³
- Edinburgh 2005: 7.42 µg/m³
- Bush Estate 2006: 8.54 µg/m³
- Mace Head 2006: 2.56 µg/m³
- Alice Holt 2005: 3.1 µg/m³
- Manchester 2002: 5.16 µg/m³
- Manchester 2001: 14.3 µg/m³
- Torch 2 2004: 7.5 µg/m³
- Manchester 2006: 9.27 µg/m³
- Torch 1 2003: 5.39 µg/m³
- London 2006: 10.43 µg/m³
- BT Tower 2006: 8.32 µg/m³

Legend:
- Green: Organics
- Blue: NO₃⁻
- Red: SO₄²⁻
- Yellow: NH₄⁺
- Pink: Cl⁻
EMEP Intensive Measurement Campaigns

<table>
<thead>
<tr>
<th></th>
<th>AMS</th>
<th>GRAEGOR</th>
<th>NH$_3$/HNO$_3$</th>
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<tbody>
<tr>
<td>June ’06</td>
<td>3</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Jan ’07</td>
<td>3</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Sep/Oct ’08</td>
<td>10</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Feb/Mar ‘09</td>
<td>10</td>
<td>4</td>
<td>5</td>
</tr>
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June 2006: Nitrate

Aerosol Mass [µg m⁻³]
Averaged diurnal cycles
\( \text{NO}_3^- \) June 2006
AMS at Montseny
Collaboration Jimenez / Querol / Nemitz
New Aerodyne PM$_{2.5}$ Aerosol Chemical Speciation Monitor (ACSM)

Size:
18”D x 22”W x 24”H
(46 cm x 56 cm x 61 cm).

Weight: 140 lbs
(64kg)

Power: 300W
universal AC power; 120/240 VAC, 50/60hz

Average total loading: 5.4 µg/m$^3$

Sulfate comparison
Application of the EMEP model over the UK - EMEP4UK

- EMEP model version 3.0
- Eulerian Chemical Transport and Deposition Model used by EMEP
- Driven by WRF 2.2 with FDDA (GFS reanalysis 1.0 °)
- EMEP4UK uses a one-way double nested domain approach
  - Outer domain covers Europe 50 km
  - British Isles 5 km
- 20 vertical layers in sigma coordinates: centre of grid point for the surface layer ~45 m, and ~16 km top.

NB: Chemical models do not normally predict PM$_{2.5}$ and PM$_{10}$, but e.g. fine nitrate ($\text{NH}_4\text{NO}_3$) and coarse nitrate ($\text{NaNO}_3$, $\text{Ca(NO}_3)_2$)
Application of EMEP4UK

Auchencorth SO$_4$$^{2-}$
June 2006 (hourly)

EMEP4UK (Auch)
MARGA (Auch)
AMS (Bush)

Application of EMEP4UK
Summary I

- Lowvol / highvol samplers (without denuder) are not suited for measurement of nitrate.

- Wet chemistry instruments (MARGA) provide chemical composition of PM$_{2.5}$ and PM$_{10}$ of inorganic aerosols with hourly resolution, 60-70% data coverage achievable.

- AMS measurements are complementary to the wet chemistry measurements adding information on NR submicron chemical composition and size distribution, organic speciation, OM/OC ratio.

- PMF can be used to distinguish the type of organic aerosols from AMS data.

- Both MARGA and AMS provide a good measure of volatiles (NH$_4$NO$_3$).
Summary II

- Hourly data provide test for models regarding emissions, transport, chemistry and thermodynamics (gas / aerosol partitioning).

- IMPs have provided first synchronised hourly measurements at European scale.

- June 2006/07 data more limited, but available through EMEP website.

- For measurement / model intercomparison need to consider what exactly the different instruments measure and how this relates to the modelled compounds. → Involve measurement providers!

- Largest AMS network achieved during EMEP/EUCAARI campaigns 2008/09, inorganic and organic European aerosol climatology.

- Data analysis May 2009.

- Not easy to implement highly time-resolved gas phase measurements ($\text{NH}_3$, $\text{HNO}_3$), database sparse.
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