PM$_{2.5}$ Measurements and Source Apportionment

Roy M. Harrison
University of Birmingham
United Kingdom
Overview

• A study of PM$_{2.5}$ concentrations and composition at three sites.

• The carbonaceous component.

• 3D data from London

• Chemical mass balance study using organic molecular markers.
Results of Three Site Study of Airborne Particulate Matter

Sites:  
BROS  Bristol Road, Birmingham (urban roadside)  
BCCS  Central Birmingham (urban background)  
CPSS  Rural (20 km west of Birmingham)

Sampling:
- $\text{PM}_{10}$ collected as fine ($\text{PM}_{2.5}$) and coarse ($\text{PM}_{2.5-10}$) fractions using a dichotomous Partisol sampler – two samplers run with PTFE and quartz filter substrates respectively.

- $\text{PM}_{1}$ collected by Partisol sampler, PTFE and quartz substrates on alternate days.

- Sites were operated sequentially.

- “Pragmatic mass closure” model (Harrison et al., 2003) applied to data.
Mass closure is achieved in terms of the following components:

- Sulphate - converted to ammonium sulphate mass
- Nitrate - converted to ammonium nitrate (fine fraction) or sodium nitrate (coarse fraction) mass
- Chloride - converted to sodium chloride mass
- Elemental carbon
- Organic carbon - converted to organic matter mass
  - split into primary and secondary on the basis of OC/EC ratio
- Iron – scaled to provide mass of traffic-related coarse dust
- Calcium – converted to mass of gypsum, representing soil and construction/demolition dust
- Bound water – estimated from sulphate and nitrate mass
Mass Concentration \((\mu g \, m^{-3})\)

- **PM10**
  - BROS
  - PM2.5
  - PM1
  - PM2.5-10
  - BCCS
  - PM2.5
  - PM2.5-10
  - CPSS
  - PM2.5
  - PM1
  - PM2.5-10

Components:
- **Iron-rich Dusts**
- **Calcium Salts**
- **Carbonaceous Material**
- **NaCl**
- \((NH_4)_2SO_4\)
- \(NH_4NO_3/NaNO_3\)
- **Other**
Some Conclusions from Three Site Study

• “Pragmatic mass closure model” accounts well for the full mass of particles in all three fractions.

• Expected gradient in PM$_{10}$ of mean roadside > urban background > rural concentrations is seen, but not for PM$_{2.5}$.

• Strong gradient in elemental carbon and iron-rich dusts between the sites.

• Data for all seasons from the central urban background site (BCCS) show notably higher sulphate in summer and lower nitrate in summer.
Simultaneous PM$_{2.5}$ Measurements, 2007-2008

- Five days per month at urban background and rural sites for 12 months

- Annual mean concentrations (µg m$^{-3}$)

<table>
<thead>
<tr>
<th></th>
<th>Urban Background</th>
<th>Rural</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>11.63</td>
<td>10.48</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.47</td>
<td>0.34</td>
</tr>
<tr>
<td>Nitrate</td>
<td>2.23</td>
<td>1.99</td>
</tr>
<tr>
<td>Sulphate</td>
<td>1.57</td>
<td>1.52</td>
</tr>
<tr>
<td>EC</td>
<td>1.45</td>
<td>1.07</td>
</tr>
<tr>
<td>OC-primary</td>
<td>1.46</td>
<td>1.20</td>
</tr>
<tr>
<td>OC-secondary</td>
<td>1.34</td>
<td>1.31</td>
</tr>
</tbody>
</table>

* According to method of Castro et al. (1999)
Days with Concentrations of PM$_{10}$ > 50 µg m$^{-3}$

- As in earlier work, the component showing the greatest enhancement in concentration on high pollution days is nitrate in both PM$_{10}$ and PM$_{2.5}$
PM10-Overall (BCCS)
- Iron-rich Dusts: 13.4%
- NaCl: 9.3%
- NH4NO3/NaNO3: 18.5%
- Calcium Salts: 7.4%
- Carbonaceous Material: 31.7%
- Other: 3.7%

PM2.5-Overall (BCCS)
- Iron-rich Dusts: 5.9%
- Calcium Salts: 2.5%
- NH4NO3/NaNO3: 21.2%
- Carbonaceous Material: 37.3%
- NaCl: 4.0%

PM10 - Episode (BCCS)
- Iron-rich Dusts: 14.3%
- NaCl: 2.6%
- Calcium Salts: 3.8%
- Carbonaceous Material: 22.0%
- NH4NO3/NaNO3: 39.0%
- (NH4)2SO4: 18.2%

PM2.5 - Episode (BCCS)
- Iron-rich Dusts: 6.3%
- Calcium Salts: 1.0%
- Carbonaceous Material: 22.6%
- NaCl: 1.7%
- (NH4)2SO4: 22.7%
Organic and Elemental Carbon

• Determined by a thermo-optical instrument.

• Organic carbon is determined by volatilisation at elevated temperature in a stream of helium.

• Elemental carbon is combusted in a helium/oxygen mixture at elevated temperatures.

• The instrument uses an optical technique to correct for organic carbon which pyrolyses to elemental carbon during the analysis.

• In practice, the split between elemental and organic carbon is “operationally defined” and inter-laboratory comparisons reveal some major differences from analyses of the same samples.
PM2.5 - All data

BCCS
\[ y = 0.10x \]
\[ R^2 = 0.29 \]

BROS
\[ y = 0.20x \]
\[ R^2 = 0.32 \]

CPSS
\[ y = 0.05x \]
\[ R^2 = 0.27 \]
Relationship of Elemental Carbon to PM$_{2.5}$ Mass

- Elemental carbon shows a strong gradient from roadside to central urban to rural sites.

- The range of PM$_{2.5}$ concentrations between sites is much smaller.

- Elemental carbon derives mainly from diesel engine emissions and correlates strongly with NO$_x$ ($R^2 = 0.75$).

- Organic carbon shows a small gradient between sites and appears to be a largely regional component.
Relationship of Elemental Carbon to PM$_{2.5}$ Mass (cont’d)

- If elemental carbon is plotted versus total carbon, the ratio is highest at the roadside site, and the upper bound of the data corresponds to EC/TC = 0.70 which is close to the value typical of diesel traffic (0.78).

- The ratio of inter-site differences

  \[
  \frac{\text{EC}_{(\text{BROS-BCCS})}}{\text{TC}_{(\text{BROS-BCCS})}} = 0.71 \quad \text{(i.e. roadside increment)}
  \]

  \[
  \frac{\text{EC}_{(\text{BCCS-CPSS})}}{\text{TC}_{(\text{BCCS-CPSS})}} = 0.80 \quad \text{(urban increment)}
  \]

  This indicates that diesel traffic probably accounts for not only the roadside increment, but also the general urban increment in EC and OC above rural levels.

- This leaves a great deal of rural organic carbon unaccounted for.
Relationship of Organic Carbon to Elemental Carbon

- It is assumed that there is a characteristic urban signature of combustion-derived carbon which represents the minimum OC/EC ratio when OC is plotted versus EC. Similar minimum ratios have been observed across Europe and are thought to represent primary OC.

- The OC above the minimum ratio is considered to be secondary.

- Secondary OC = OC (measured) – EC x primary OC/EC ratio.
PM2.5 - BCCS

$y = 0.65x$

**Organic carbon (µg m$^{-3}$)**

**Elemental carbon (µg m$^{-3}$)**
PM2.5 - BCCS

Concentration (µg m\(^{-3}\))

Ratio - SecOC/PrimOC

Month

TC - NO3 - SecOC/PrimOC

Concentration (µg m\(^{-3}\))

Ratio - SecOC/PrimOC

Month

Jan  Feb  Mar  Apr  May  Jun  Jul  Aug  Sep  Oct  Nov  Dec
PM2.5 - BCCS

Concentration (µg m⁻³)

Month

SecOC
NO3
SO4
Seasonal Pattern in OC at the Urban Centre Site

- The only pronounced seasonality in the ratio secondary/primary OC in this study is due to a major spring peak.

- This peak correlates with a peak of nitrate often observed at this time of year, and a much lesser maximum in sulphate.

- This result is attributed to frequent advection of continental European air at this time of year, together with the effect of climate factors on the particle/vapour partitioning of semi-volatile nitrates and organic carbon.

- This behaviour is consistent with observations of diurnal variation in secondary organic aerosol particle types in Athens measured by Aerosol-Time-of-Flight Mass Spectrometer.
Map of London Sampling Sites
Meteorological instruments
And fast response pollution sensors

Height of most pollution instruments

BT Tower site – vertical profile measurements
Chemical Mass Balance Study using Molecular Markers

- PM$_{2.5}$ samples were collected and analysed for
  - $n$-alkanes from C$_{24}$ – C$_{36}$
  - 9 specific hopanes
  - 13 PAH
  - 14 carboxylic acids
  - levoglucosan
  - cholesterol
  - inorganic marker elements (Si, Al)
CMB Model Results

- Model used to apportion sources of organic carbon to:
  - diesel engine exhaust
  - gasoline engines
  - smoking gasoline engines
  - vegetative detritus
  - dust and soil
  - wood smoke
  - coal combustion
  - natural gas combustion
Main Conclusions from CMB Model

• Road traffic contribution to primary OC is dominant.

• Split between diesel, gasoline and gasoline smoker emissions requires further study.

• Vegetative detritus is significant at the rural site.

• Small contributions from coal and natural gas combustion, very small from meat cooking.

• “Other” OC correlates highly with secondary OC estimated by the method of Castro et al. (1999).

• Wood smoke contribution is small, but studies at other sites using a multi-wavelength aethalometer shown substantial concentrations.
A Few Conclusions

- As expected, major PM$_{2.5}$ components are sulphates, nitrates and carbonaceous material.

- Nitrate is especially important in episodes of high PM$_{10}$.

- There is a gradient from roadside to urban background to rural sites, most particularly in the EC/OC content.

- Secondary OC is important and shows similarities in seasonal behaviour to nitrate.

- Road traffic is normally the main contributor to primary carbonaceous particles, but the gasoline/diesel split is hard to determine from the CMB model.

- Non-exhaust particles from traffic may be significant.
ACKNOWLEDGEMENTS

• To those who did the work:
  Dr Jianxin Yin
  Dr Manuel Dall’Osto

• Those who advised on the CMB modelling:
  Professor Jamie Schauer and Dr Andy Rutter,
  University of Wisconsin-Madison

• Those who paid for the work:
  Department for Environment, Food and Rural Affairs
  Natural Environment Research Council
  BOC Foundation