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$PM_{2.5}$ Measurements and Source Apportionment

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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.

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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:

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

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AIRBORNE PARTICULATE MATTER: PRAGMATIC MASS CLOSURE MODEL

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

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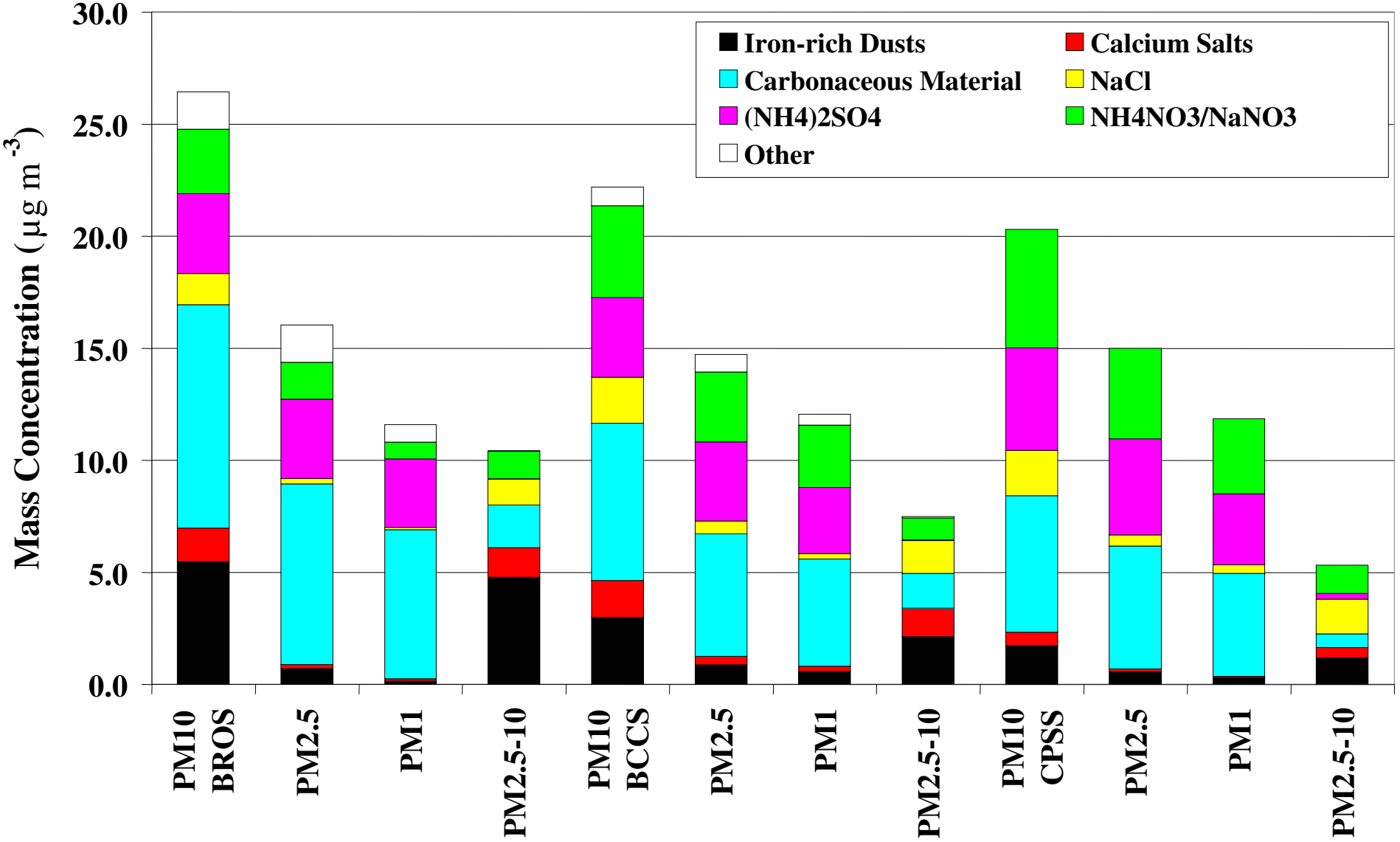

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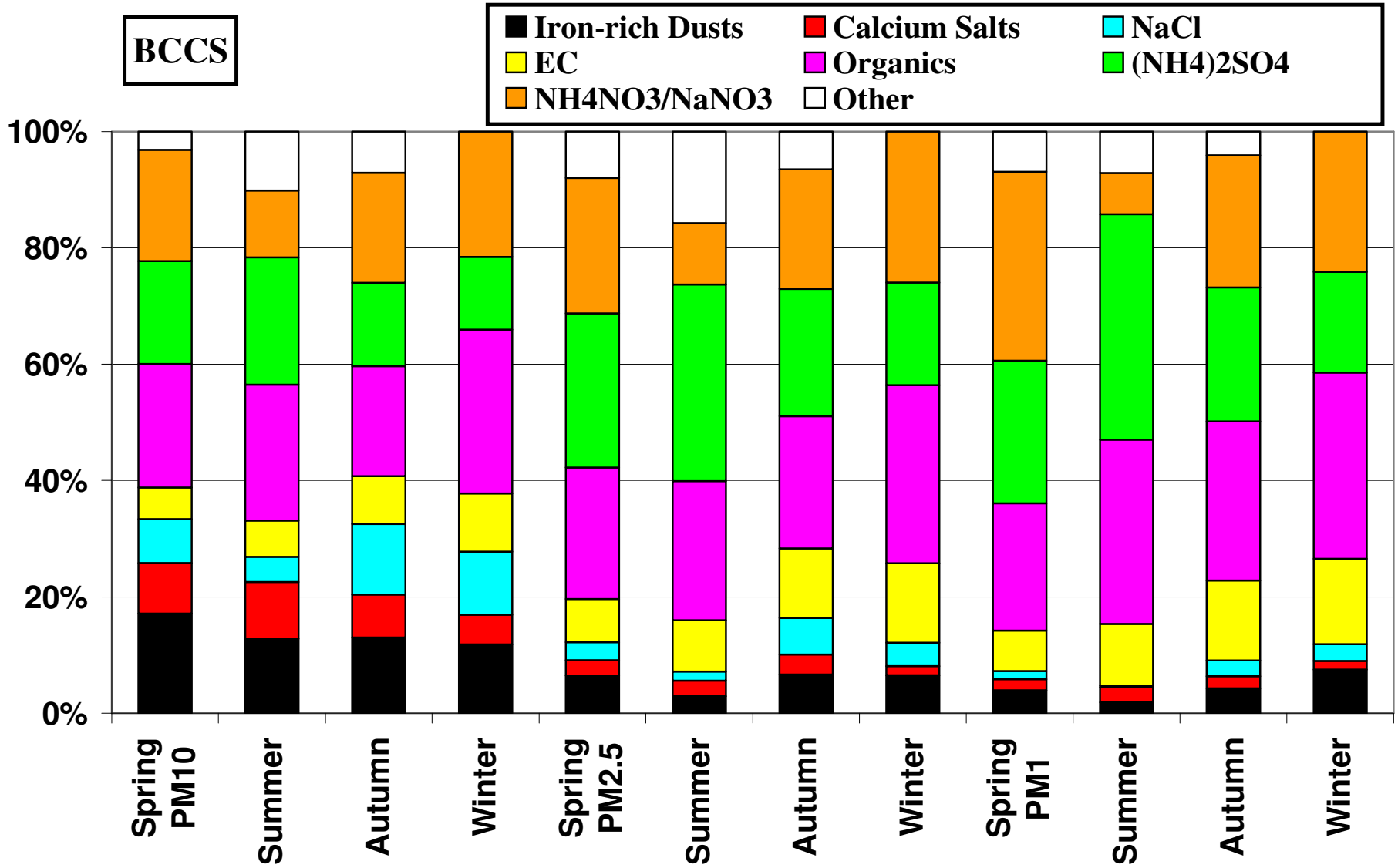

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Some Conclusions from Three Site Study

- "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.

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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})

	Urban Background	Rural
$PM_{2.5}$	11.63	10.48
Chloride	0.47	0.34
Nitrate	2.23	1.99
Sulphate	1.57	1.52
EC	1.45	1.07
OC-primary *	1.46	1.20
OC-secondary *	1.34	1.31

* According to method of Castro et al. (1999)

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Days with Concentrations of $PM_{10} > 50\ \mu g\ m^{-3}$

- As in earlier work, the component showing the greatest enhancement in concentration on high pollution days is nitrate in both PM_{10} and $PM_{2.5}$

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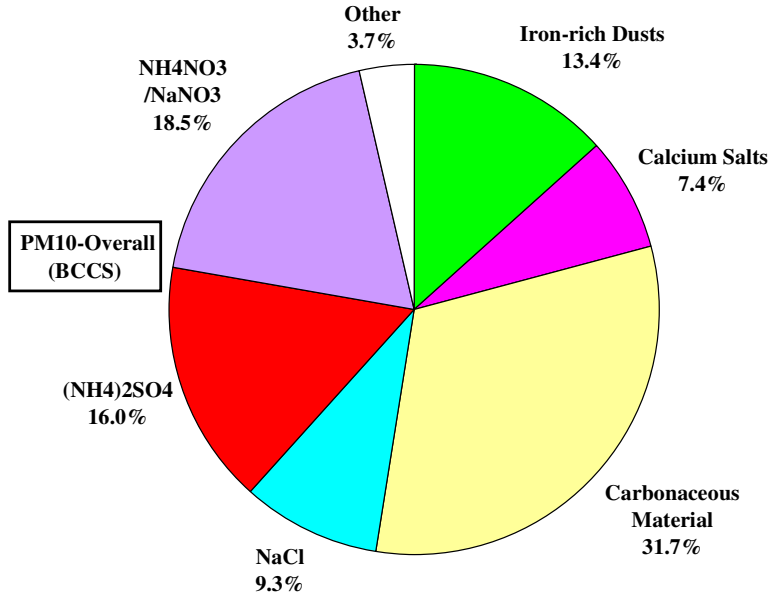
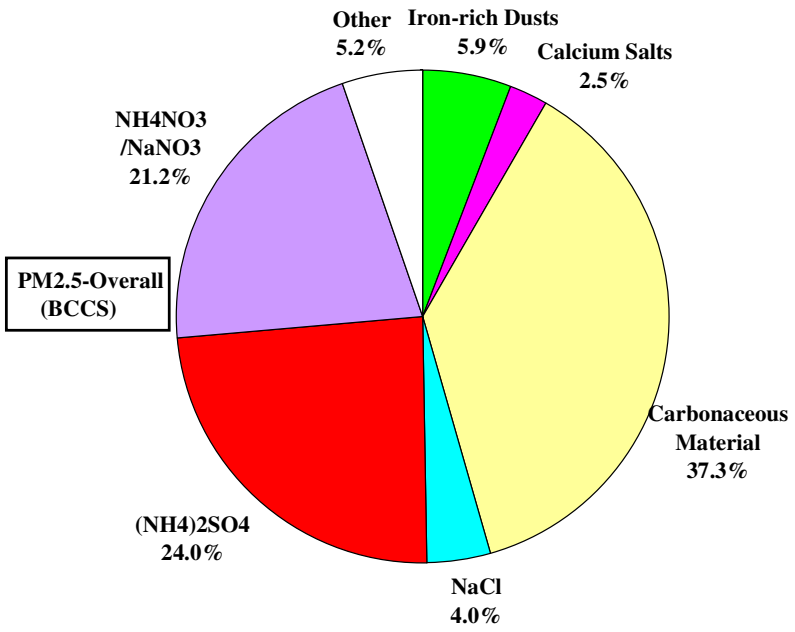
(a)





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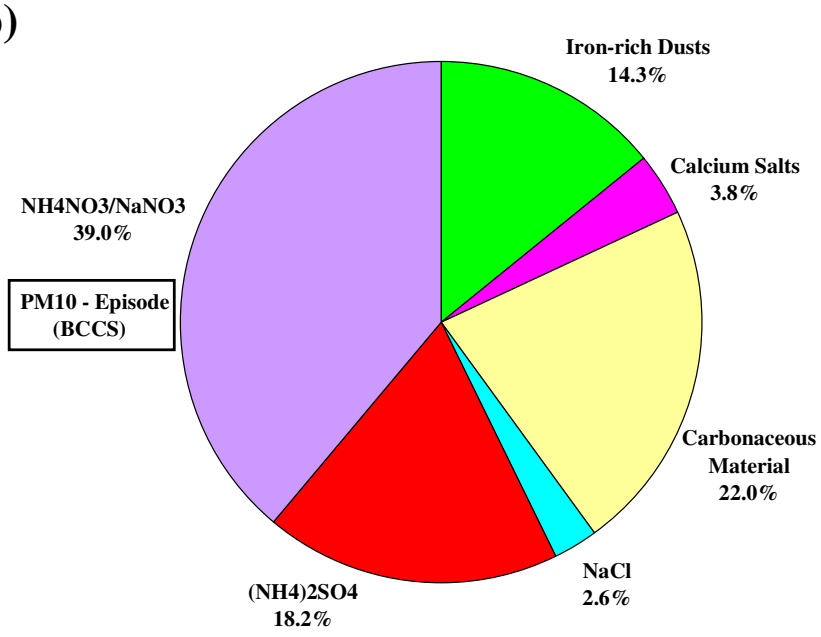

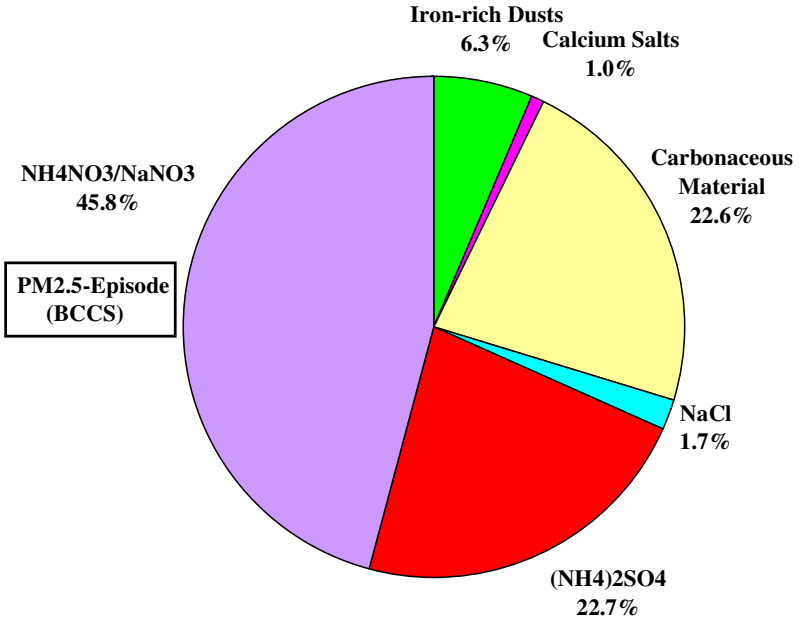

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Organic and Elemental Carbon

- 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.

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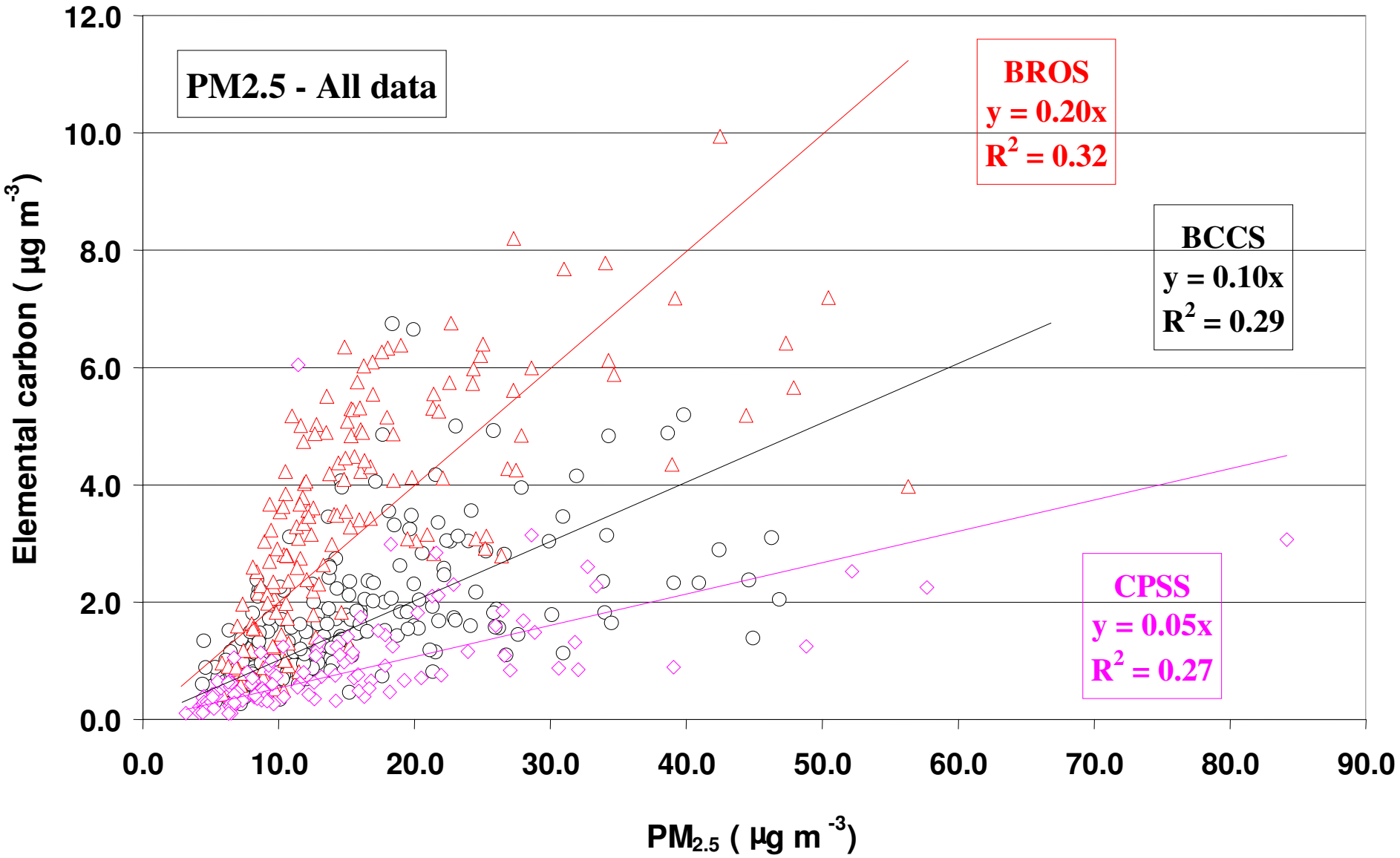

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Relationship of Elemental Carbon to $PM_{2.5}$ Mass

- 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.

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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

  $EC_{(BROS-BCCS)} / TC_{(BROS-BCCS)} = 0.71$ (i.e. roadside increment)

  $EC_{(BCCS-CPSS)} / TC_{(BCCS-CPSS)} = 0.80$ (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.

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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.

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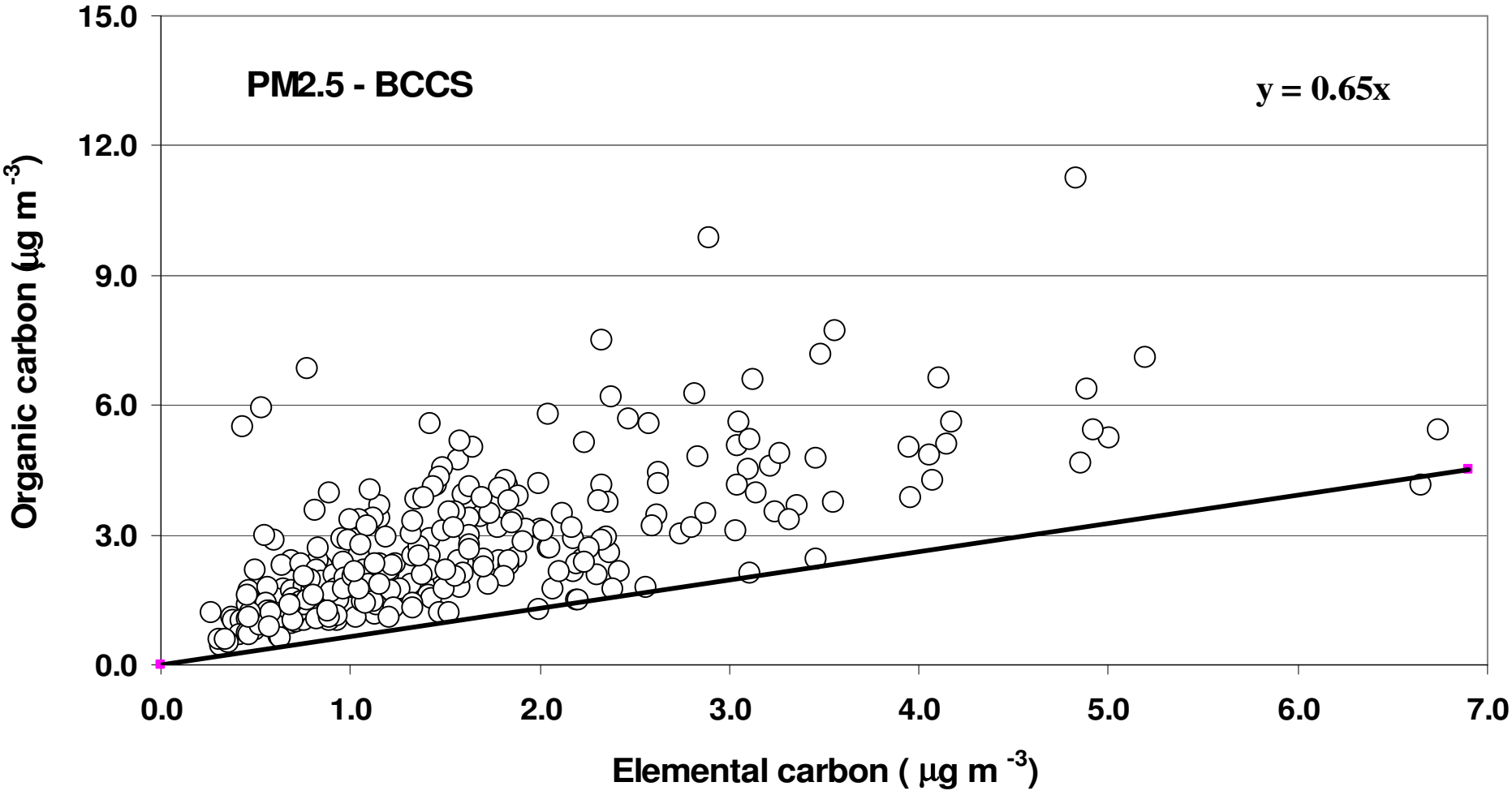

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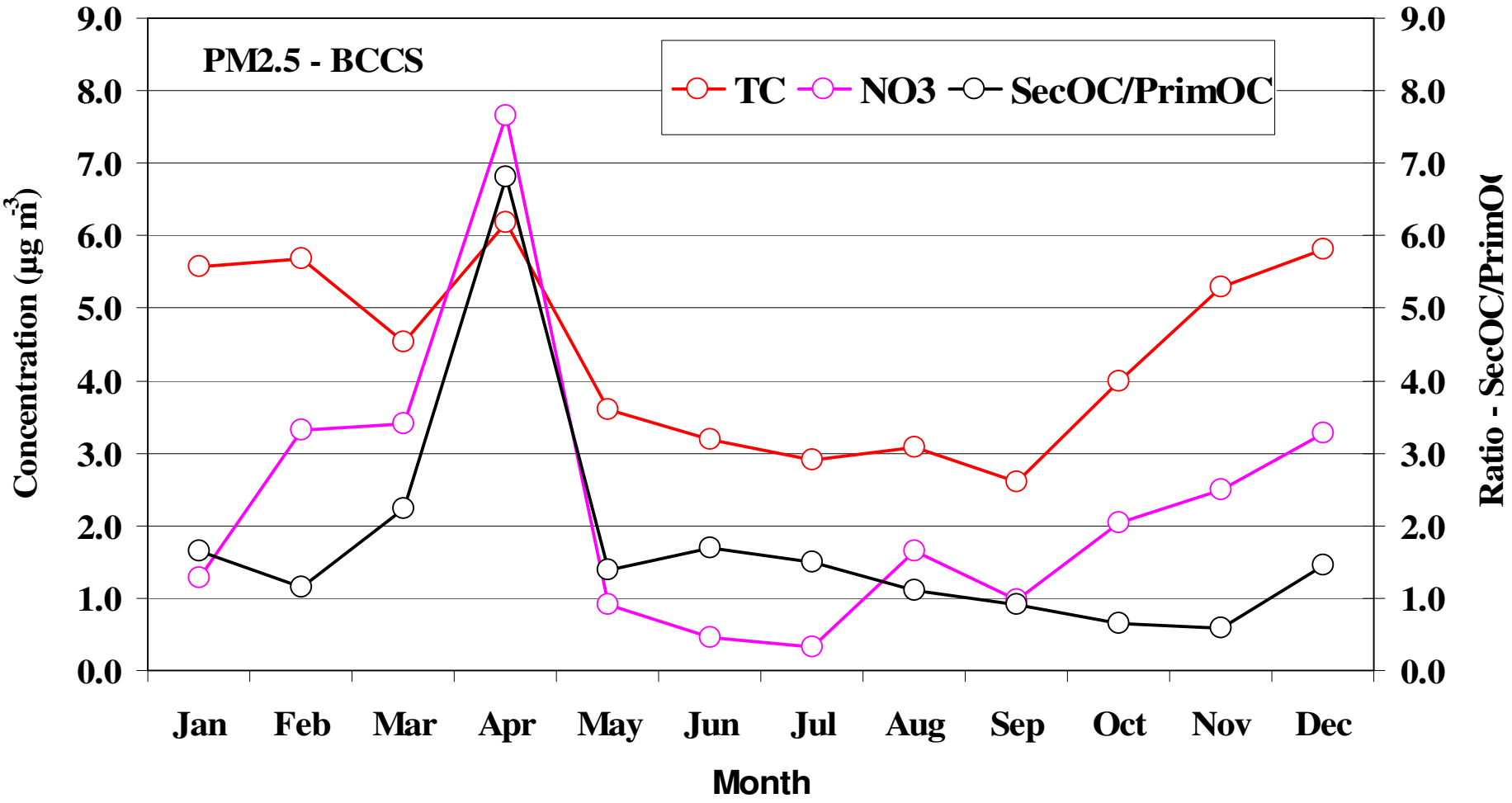

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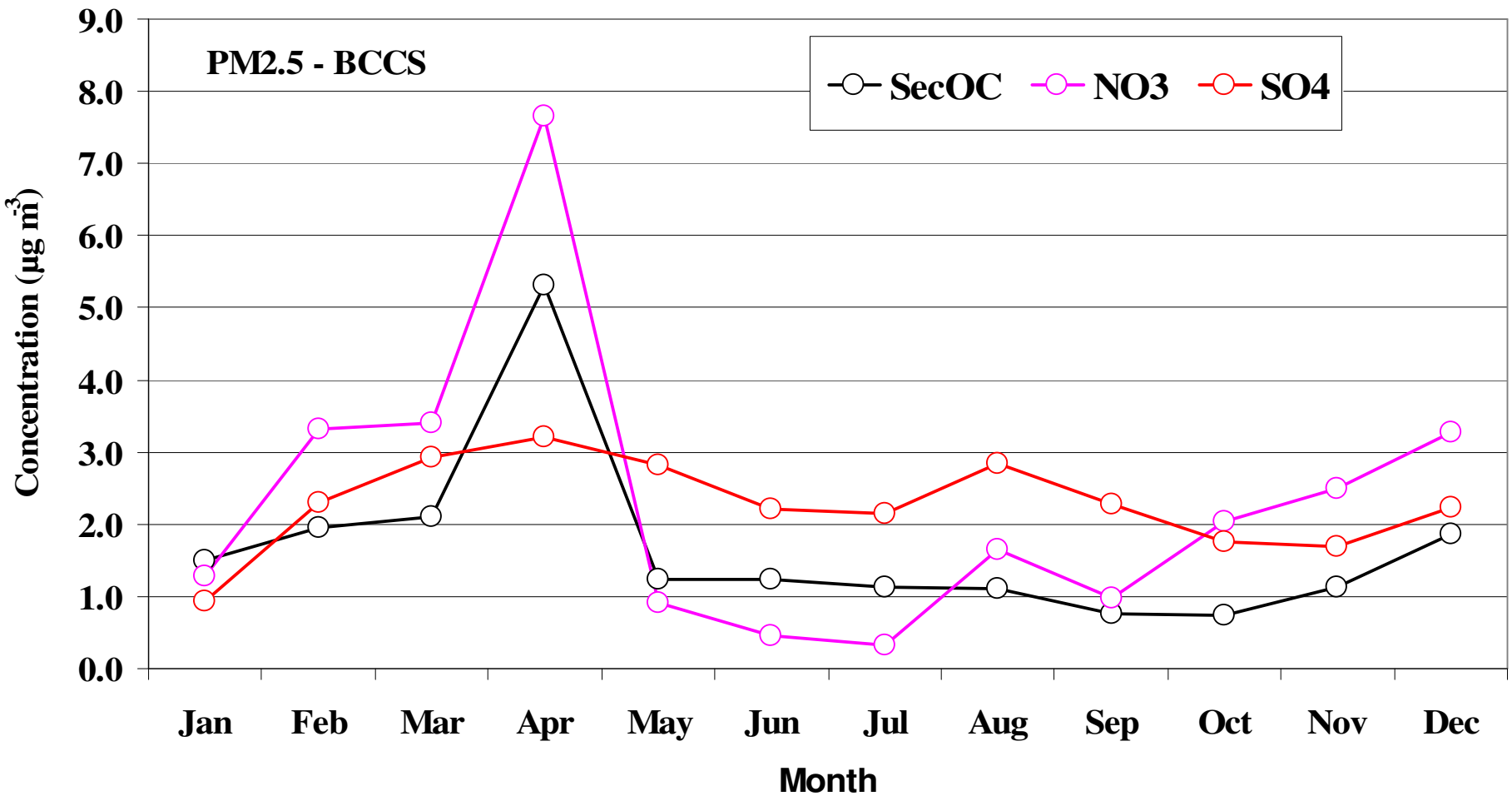

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Seasonal Pattern in OC at the Urban Centre Site

- 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.

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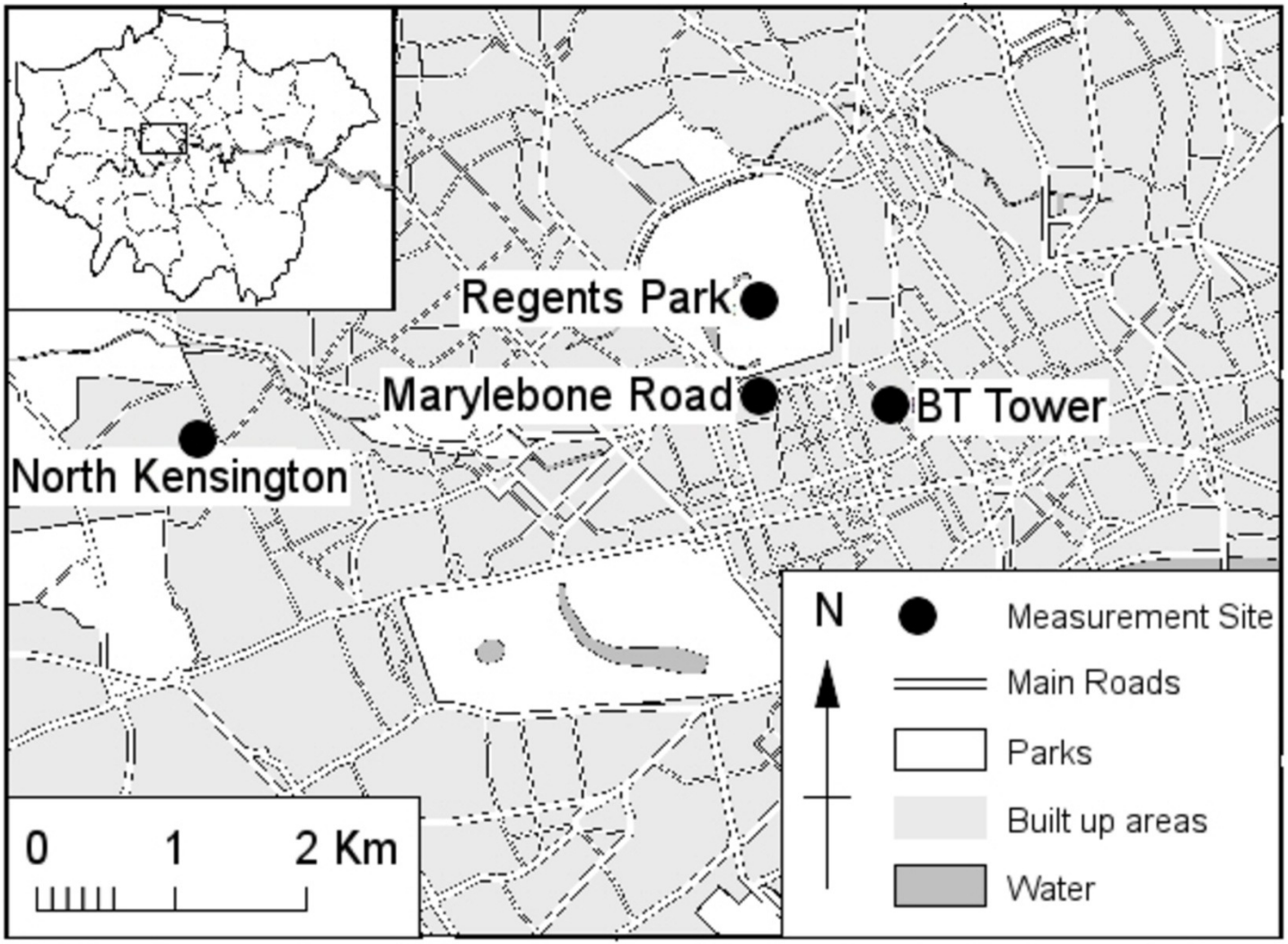
Map of London Sampling Sites



Meteorological instruments And fast response pollution sensors

Height of most pollution instruments

BT Tower site – vertical profile measurements

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Marylebone Road supersite, London

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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)

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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**

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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.**

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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.

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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