New measurements of PM composition during pollution episodes

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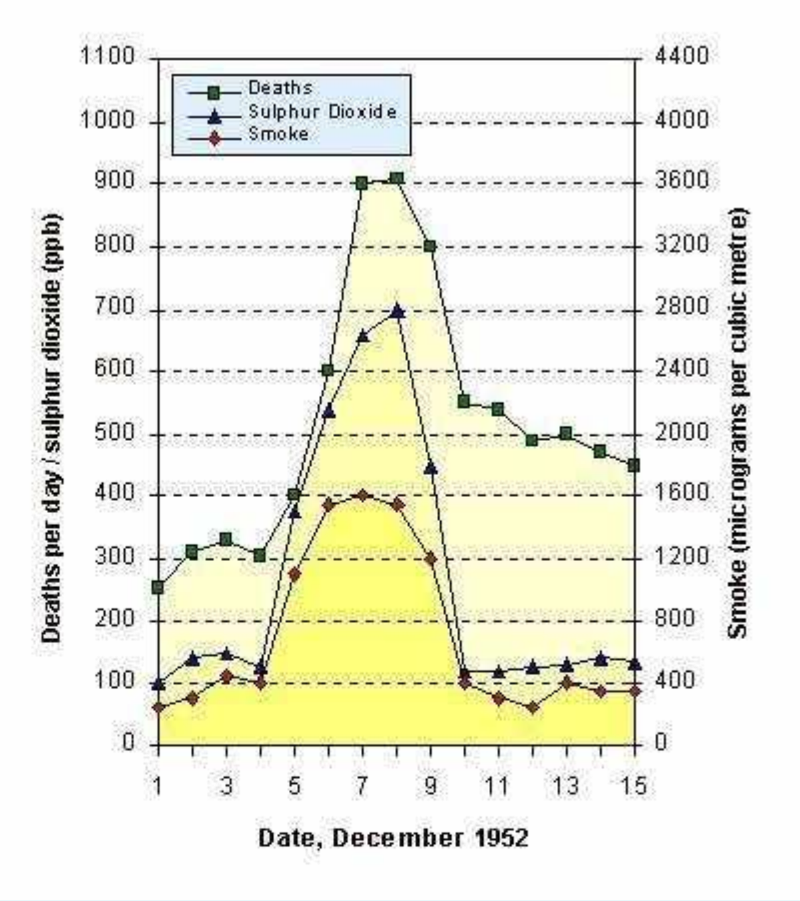
Contents

- Background
  - What are pollution episodes and why are they important?
- Current measurement methods
- New measurement methods
- How we can use these new measurements
  - Look at some preliminary results

What is an episode?

- Air pollution is episodic
- Most of the time air pollution is low
- Occasionally, emissions and meteorology conspire to increase concentrations
- Can occur at one or more site type depending on what is causing the episode



Why are episodes important?

Health

- During episodes health effects at the population level become increasingly numerous and severe
- Multi-city studies conducted in Europe (29 cities) reported short-term mortality effects for PM_{10} of 0.62% per 10 µg m^{-3} (24-hour mean) (Katsouyanni et al., 2001)

Regulation

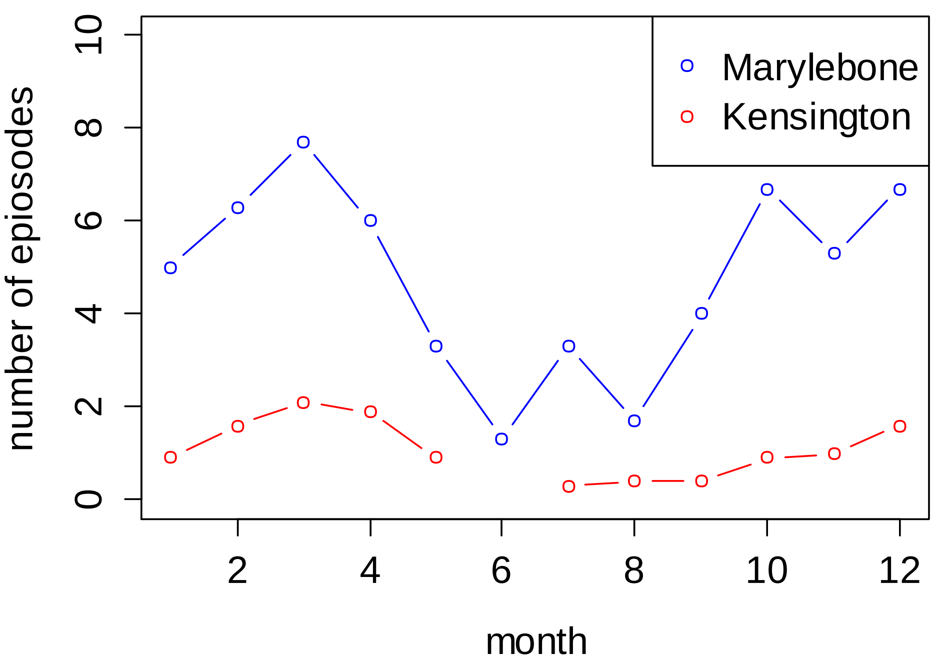
- EU Air Quality Directive limit value for protection of human health. 50 µg m^{-3}, not to be exceeded more than 35 times a calendar year

Understanding atmospheric processes

- Increased concentration 'amplifies' the concentrations above other interfering processes and emissions

Different types of episode

- How do we identify different types of episode
  - They occur at different times of the year
  - Different in magnitude and frequency at different sites?



Average number of episodes per month 2004-2011

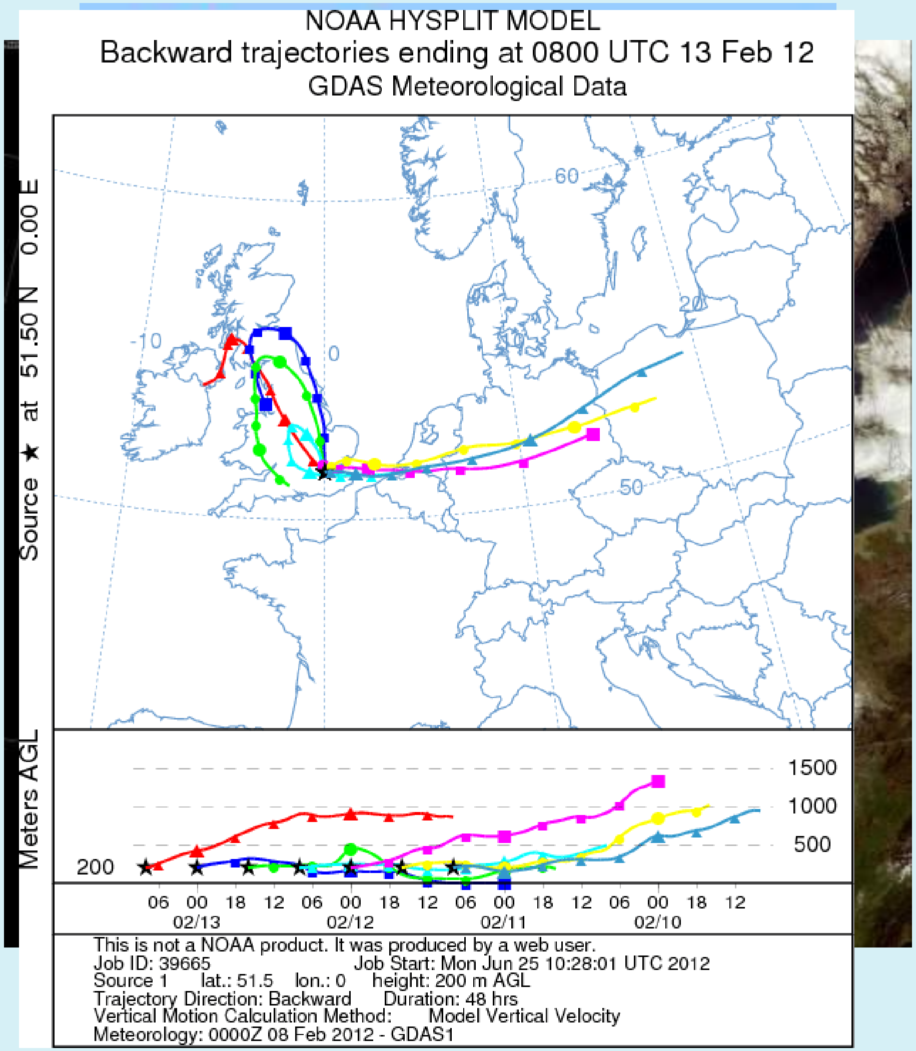
Different types of episode

Local pollution

- Urban sources (vehicles, biomass, cooking, etc)
- Poor dispersion
- Temperature inversions
- More prevalent close to source
- Chemical composition - elemental and organic carbon, wind blown dust

Long range transport

- Secondary aerosols, fires, Saharan dust
- Regionally uniform in concentration
- Additive effect close to other sources
- Chemical composition
  - Secondary aerosols (NH_4NO_3, $(NH_4)_2SO_4$, organic carbon)
  - Fires (elemental and organic carbon)
  - Saharan dust (SiO_2)



NOAA HYSPLIT MODEL
Backward trajectories ending at 0800 UTC 13 Feb 12
GDAS Meteorological Data

This is not a NOAA product. It was produced by a web user.
Job ID: 39665 Job Start: Mon Jun 25 10:28:01 UTC 2012
Source 1 lat.: 51.5 lon.: 0 height: 200 m AGL
Trajectory Direction: Backward Duration: 48 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 08 Feb 2012 - GDAS1

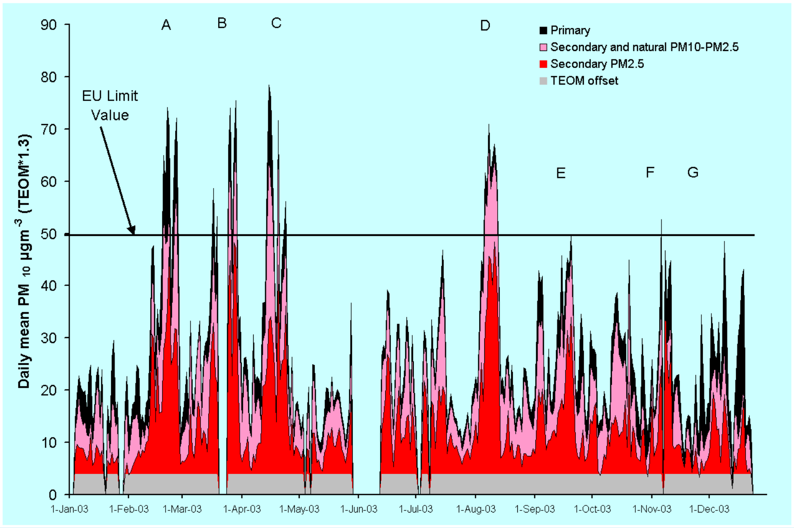
How have we understood episodes up to now?

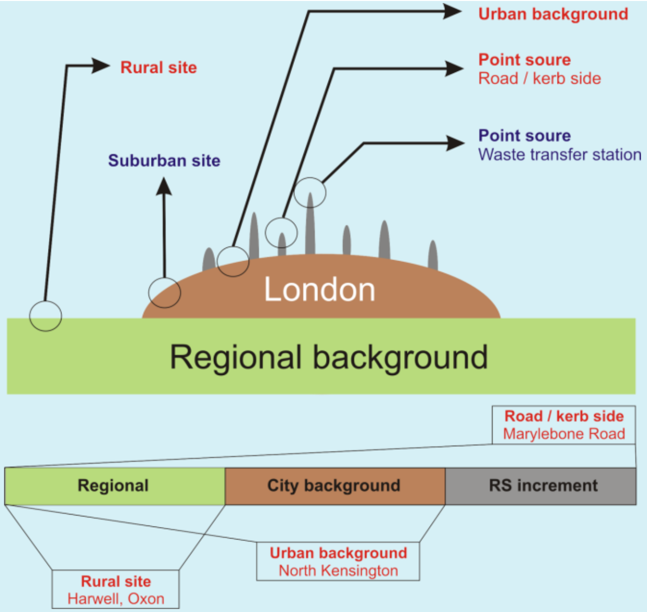
Lenschow approach
- Lenschow *et al.* 2001 (AE)

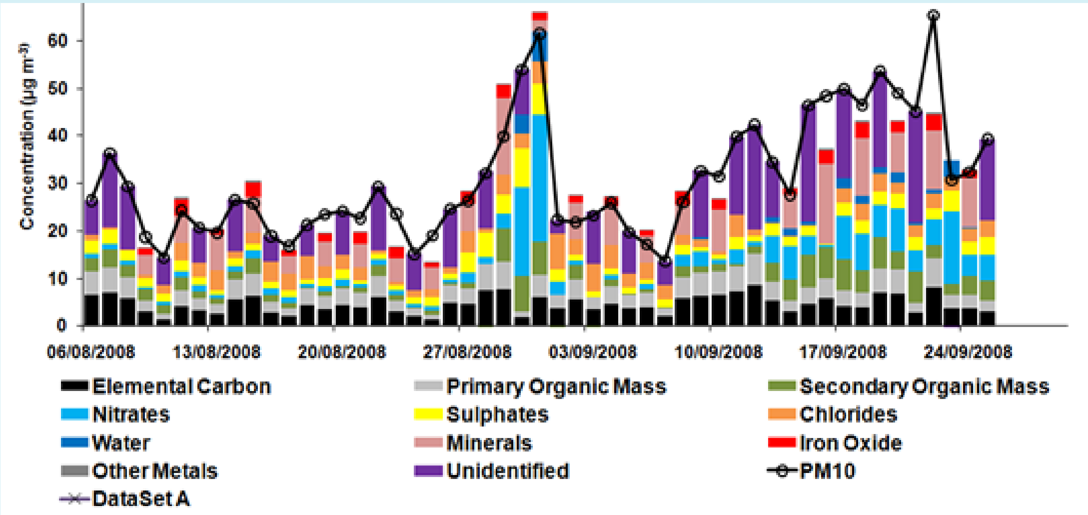
NO$_X$ tracer
- Fuller *et al.* 2002, 2004, 2006 (AE)

Chemical composition
- TfL & LB Camden

Short term academic studies
- REPARTEE, DAPPLE







Limitations in previous studies

Increments

- Relies on accurate representation of rural concentration
- If the source is on the same vector then it is impossible to distinguish
- Confounding from local emissions

NO_X tracer

- Differentiates between urban or regional sources but not between **different** urban or regional sources

Chemical composition

- Poor time resolution for sampler systems
- Expensive and labour intensive
- Analysis of sources of organic carbon are limited

Short term academic studies

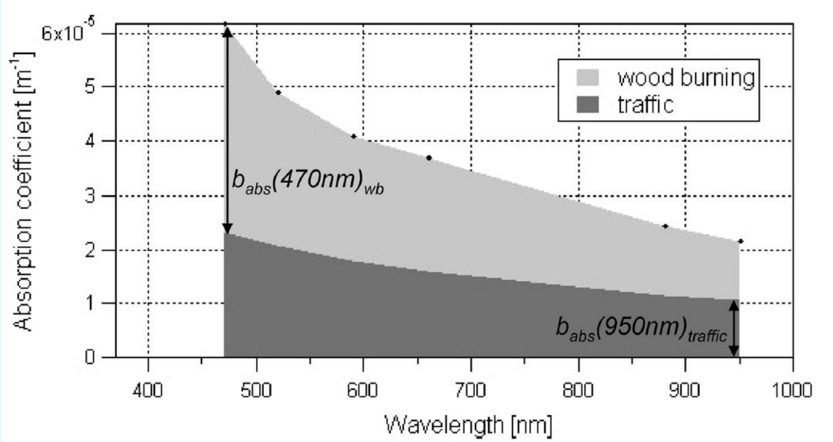
- Lack applicability to annual mean
- Hostage to weather
- Expensive and labour intensive
- Atmospheric process rather than policy driven

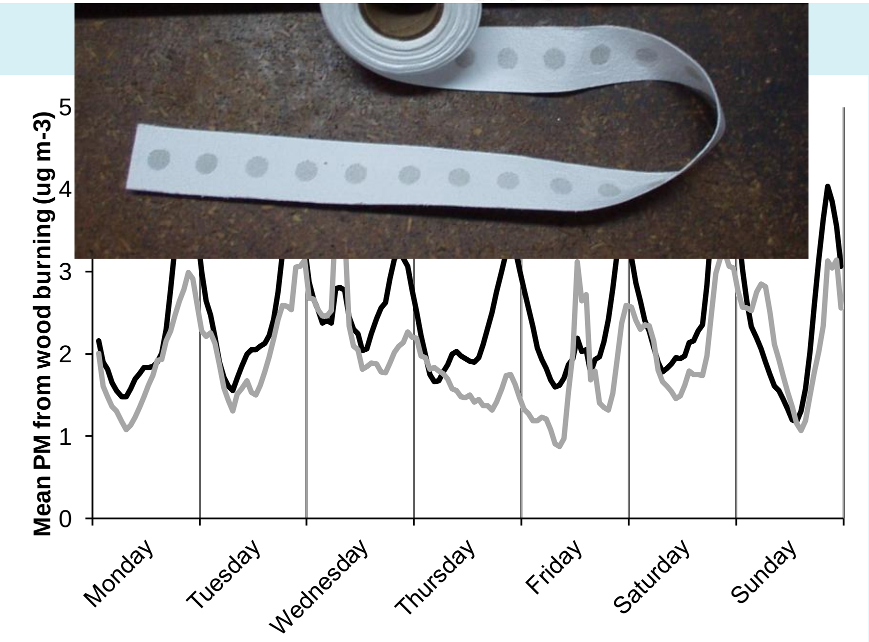
What's new?

- More advanced instrumentation
- More advanced data analysis methods
- Defra black smoke network
  - Replaced old black smoke bubblers with aethalometers
- Defra PM Network
  - Replaced sampler-based measurements of anions (NO_3^-, SO_4^{2-}, Cl^-) with real time ion monitor
- NERC ClearfLo
  - Aerosol Mass Spectrometers (University of Manchester, CEH)
  - 12 month deployment at Marylebone Road
  - Short term deployment at North Kensington extended to 12 month with Defra support
- Examine the episodes at the start of 2012 using these provisional results…

Aethalometer

- Measures attenuation of light at with UV 370nm and IR 880nm wavelengths
- 5 min mean concentrations
- IR adsorption analogous to elemental carbon
- Provides continuity from black smoke measurements for epidemiology studies
- Because wood smoke has a strong absorption in UV it can be used to detect PM from wood smoke (Fuller et al. (in review), Favez et al., 2009, 2010, etc…)





NPL
National Physical Laboratory

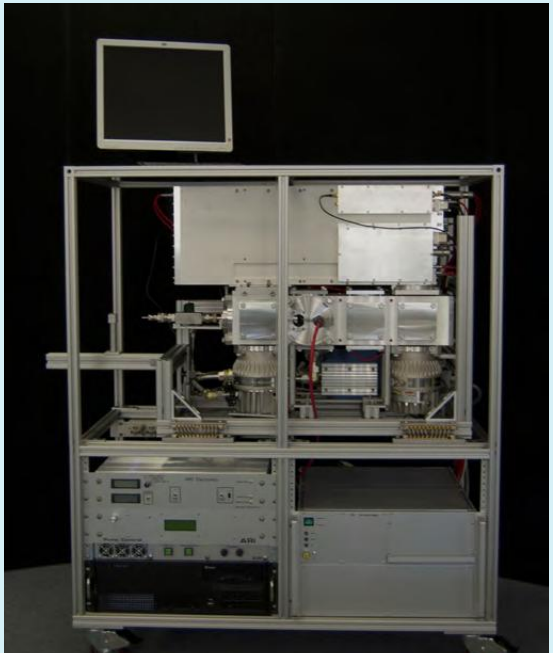
URG Ambient Ion Monitor

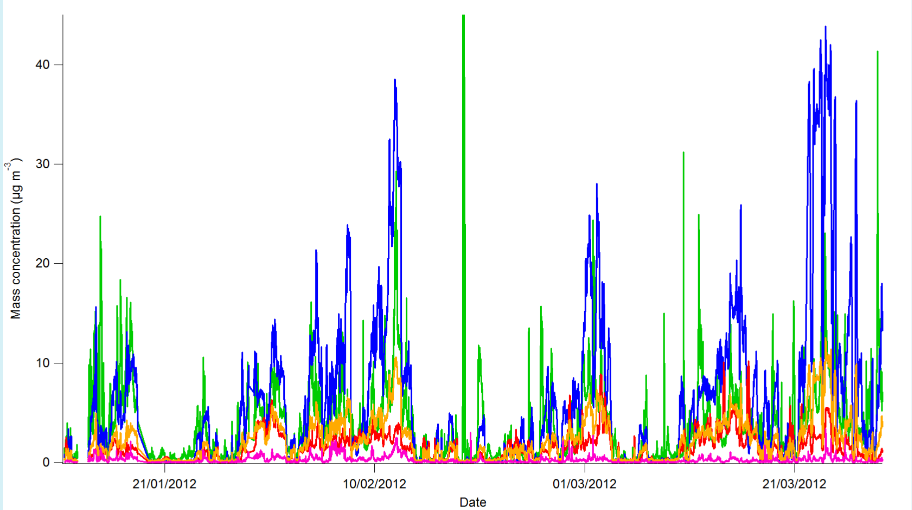
- Samples PM_{10}
- Removes interfering gases
- Extracts into aqueous solution
- Analysed using 2 ion chromatographs
- Chloride, sulphate, nitrate, sodium, ammonium, potassium, magnesium, calcium
- 1 hour mean concentrations
- Wider range of anions and cations helps to differentiate between marine and secondary aerosol
- Size fraction directly relevant to regulation

NPL National Physical Laboratory

Aerosol Mass Spectrometer

- Samples PM1
- Particles counted and sized using time of flight
- Thermal particle vaporization
- Mass / charge ratio measured using mass spectrometer
- Detection and quantification of non-refractory species such as such as sulphate, nitrate, ammonium and chloride as well as organic aerosol species
- Organics can then be grouped using positive matrix factorisation (PMF) to yield source categories
  - Biomass
  - Cooking
  - Vehicles
  - Oxidised Organic Aerosol (secondary)

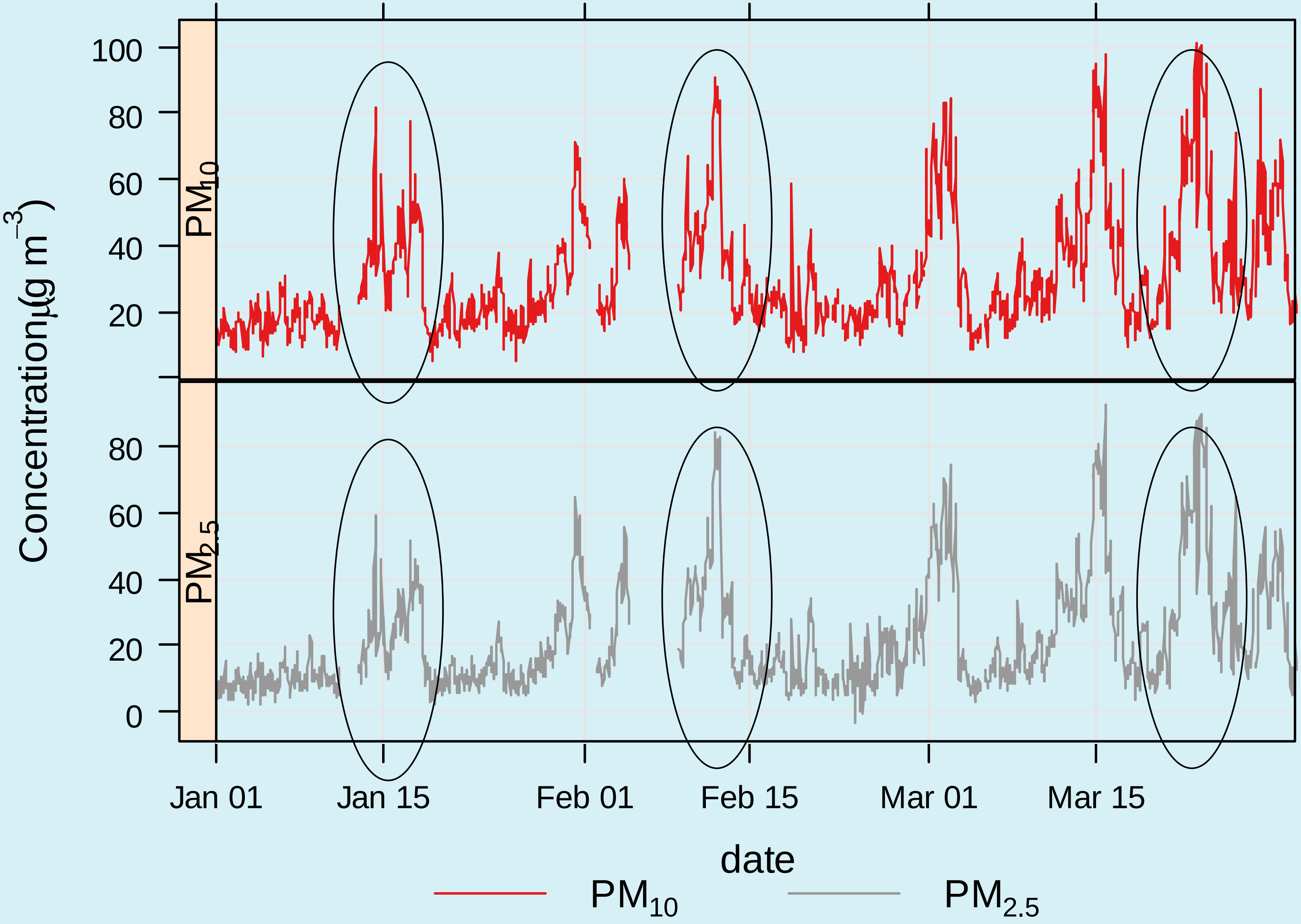




MANCHESTER
1824
The University of Manchester

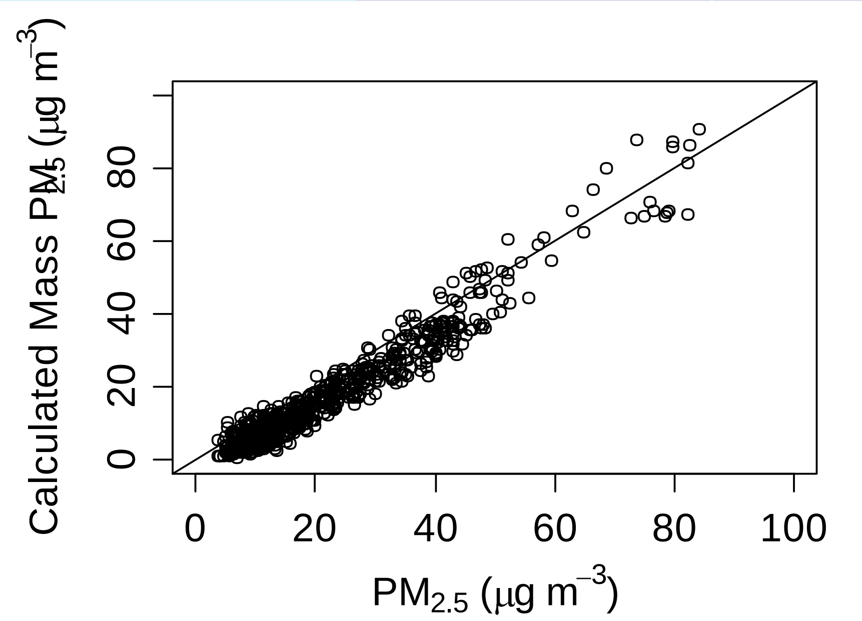
ClearfLo

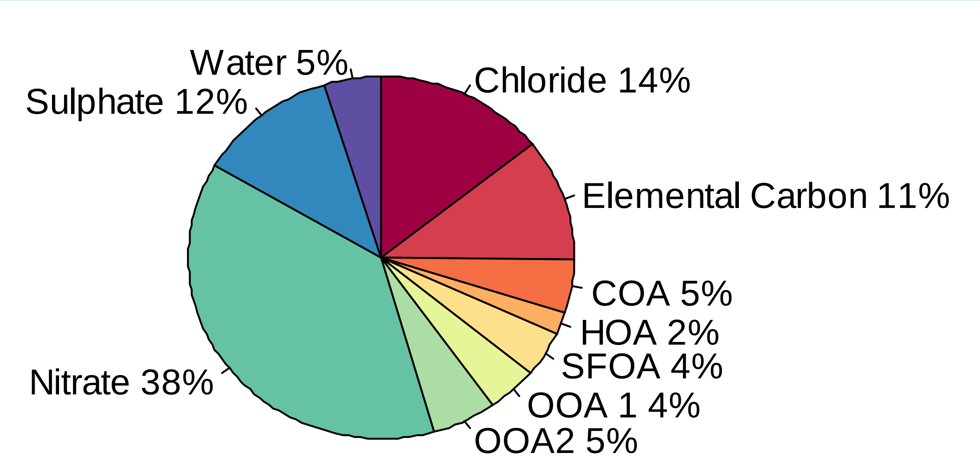
North Kensington Jan – Apr 2012



Hourly mass closure ($PM_{2.5}$)

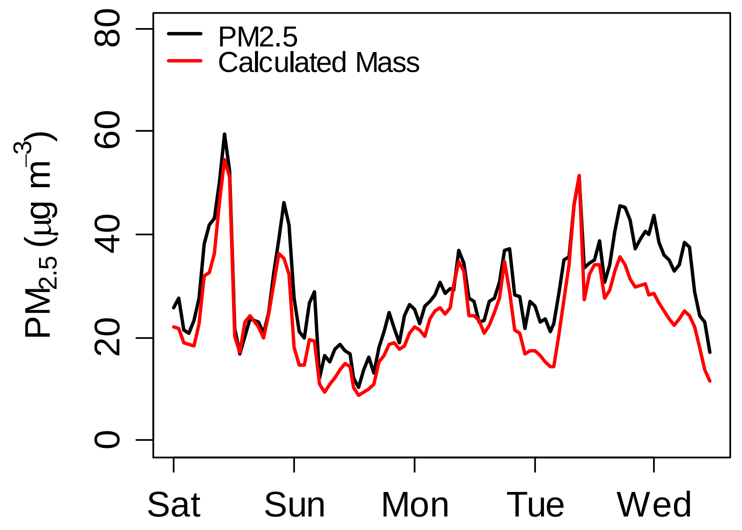
Species	Data source	Factor
Chlorides	URG	1.65
Nitrates	AMS	1.32
Sulphates	AMS	1.38
Elemental Carbon	Aethalometer	-
Organic Carbon	AMS PMF	-
Water	Frank et al. 2006	$0.24*(SO_4+NH_4)$
Metals	None	

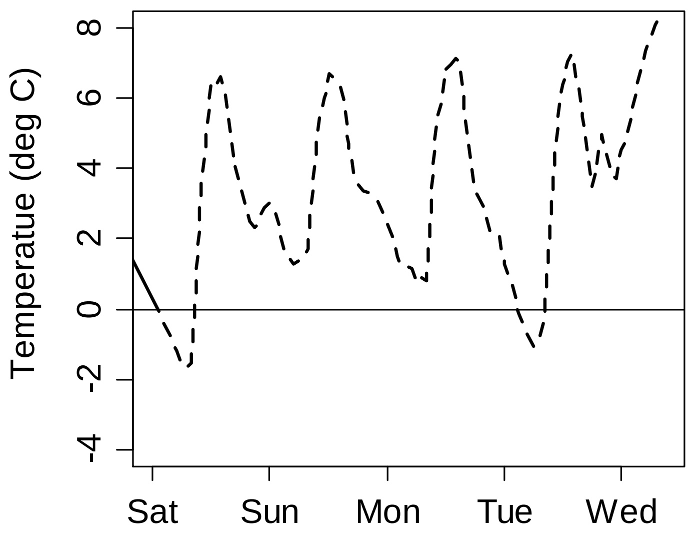


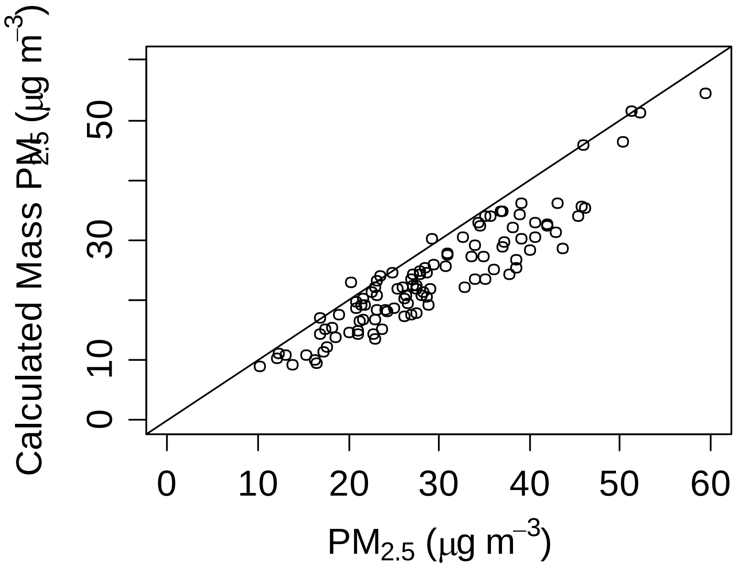


Episode 1 – 14th & 16th January

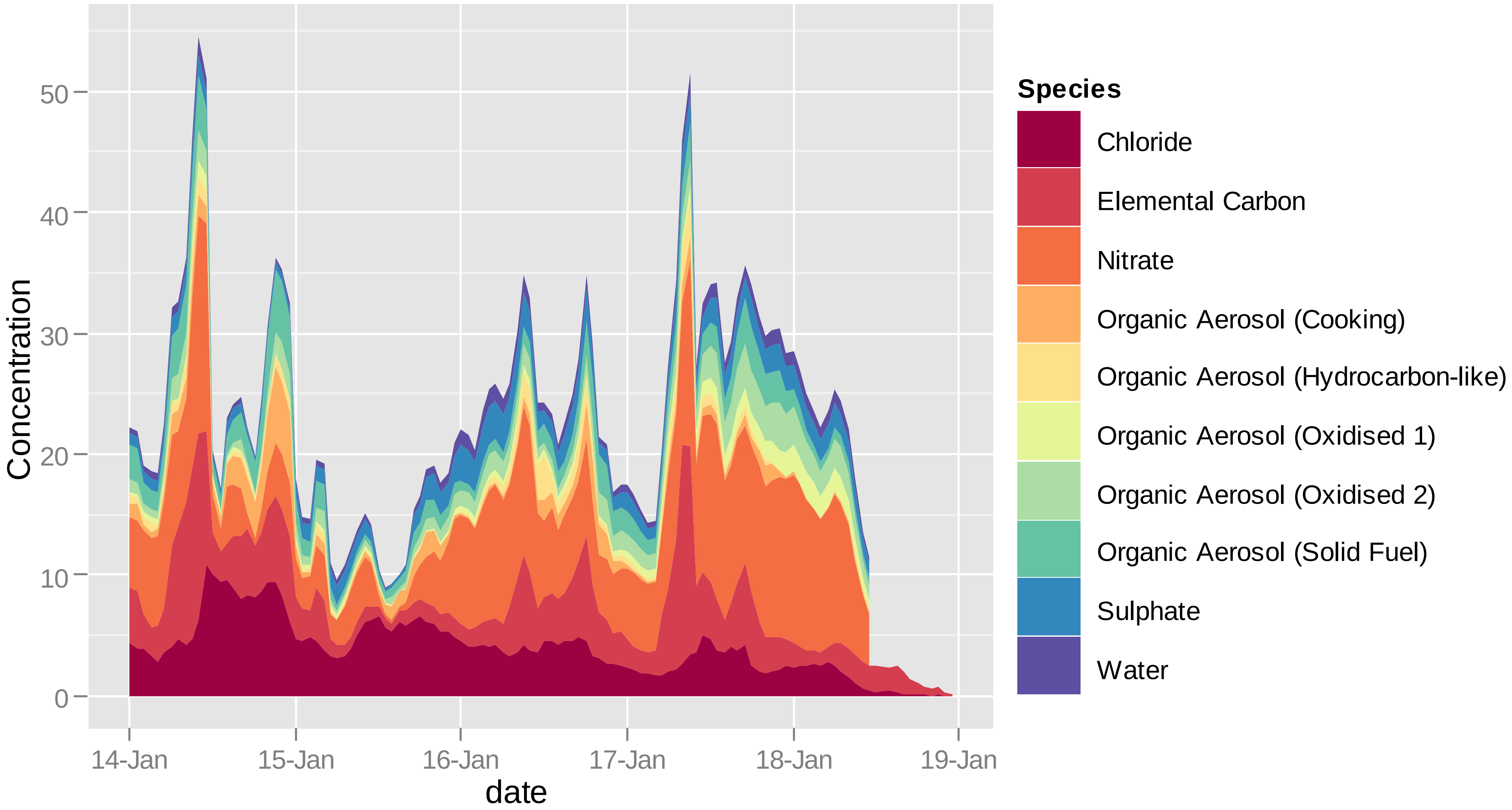
- Low temperature
- Poor dispersion



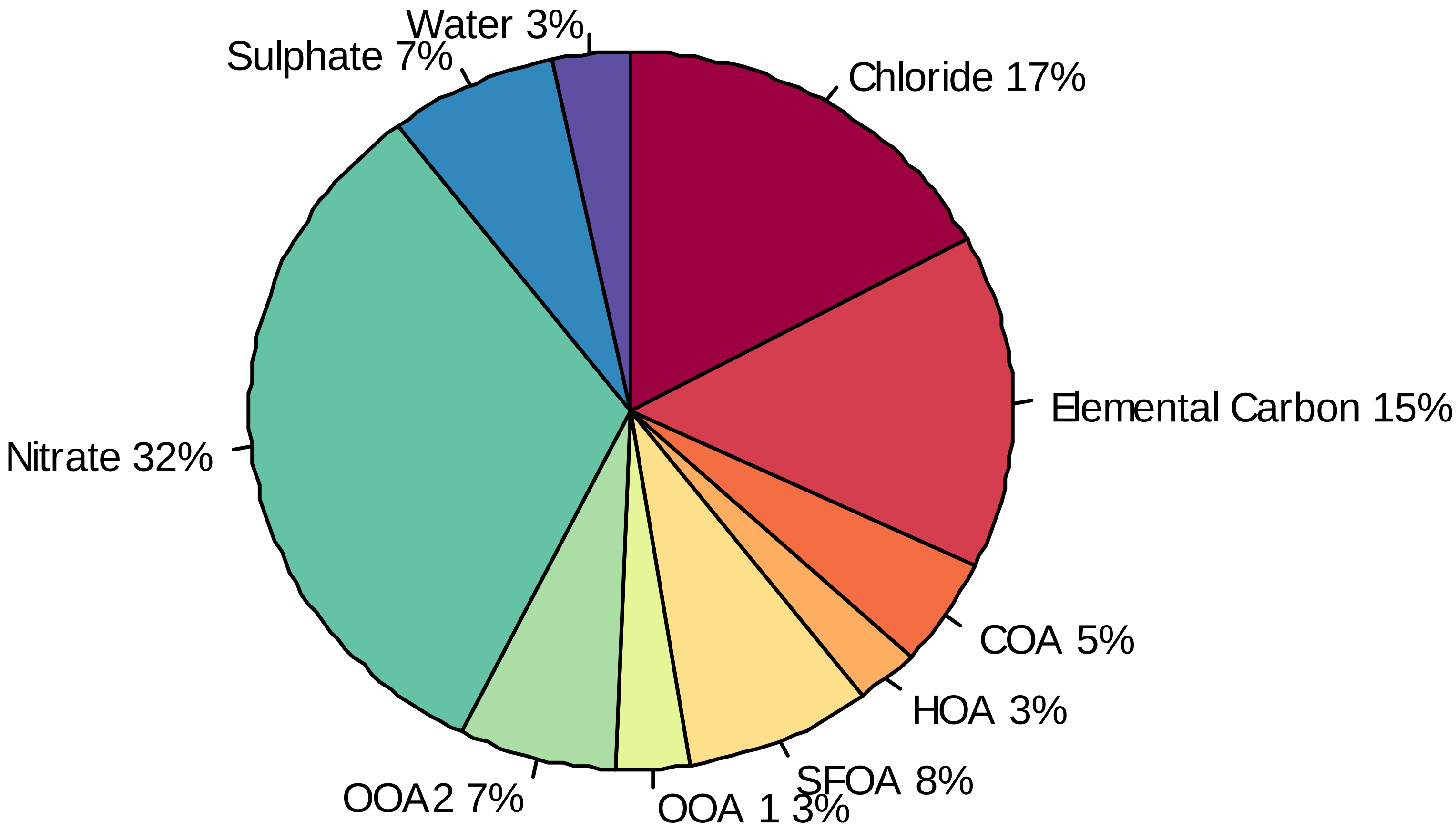




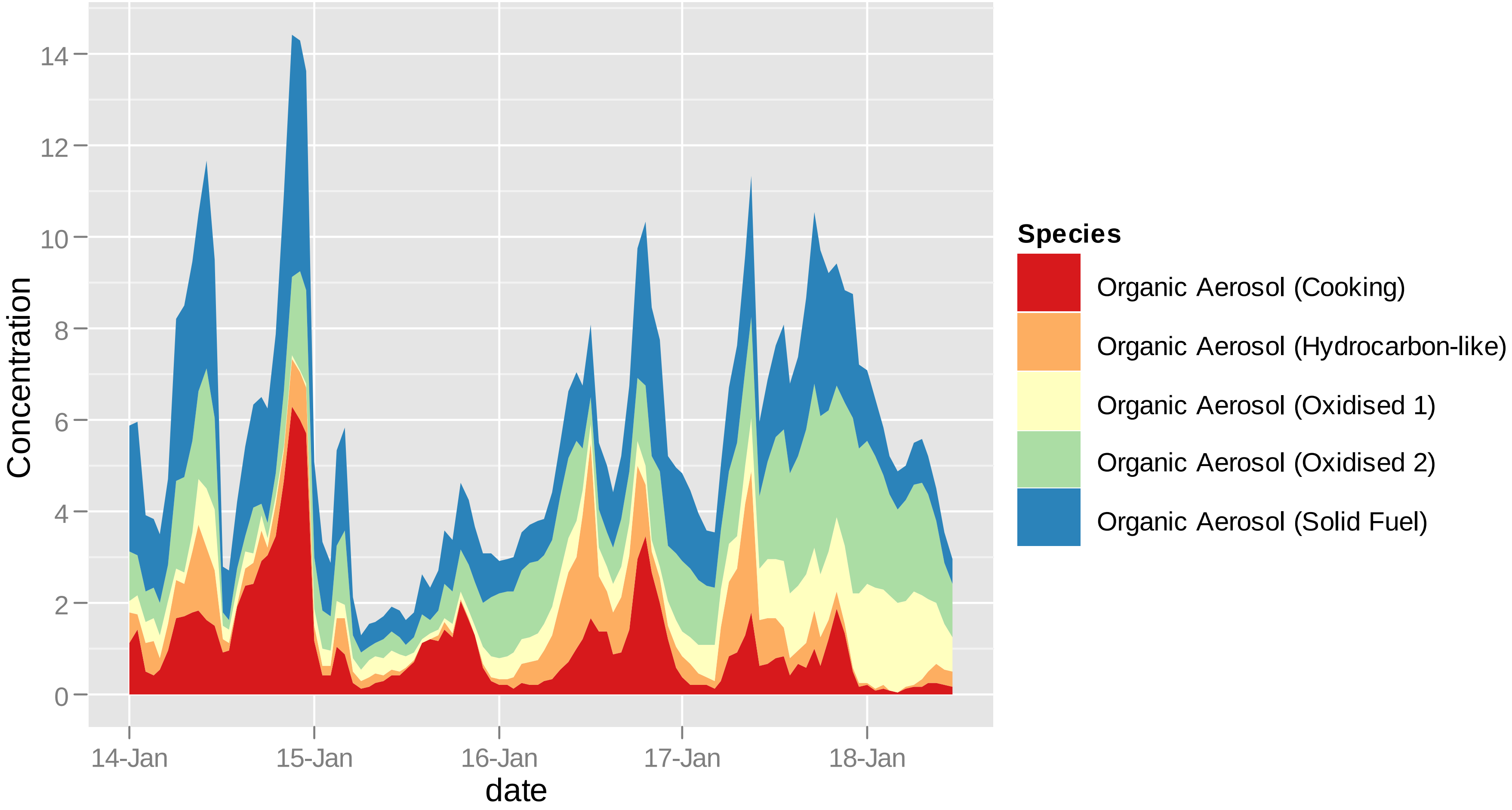
Episode 1 – 14th-18th January



Episode 1 – 14th-18th January



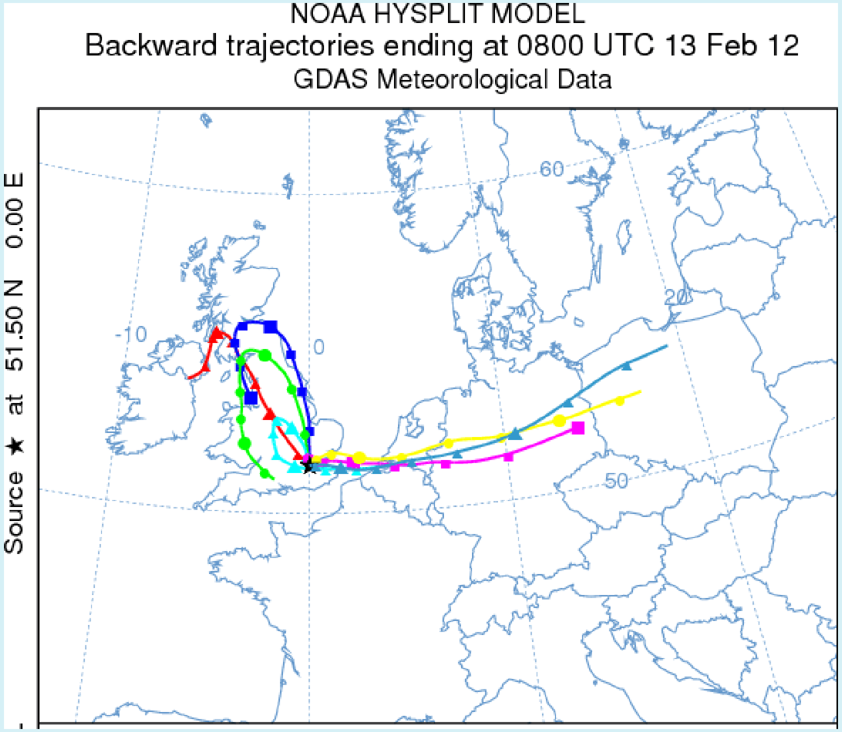
Episode 1 – Organic aerosol

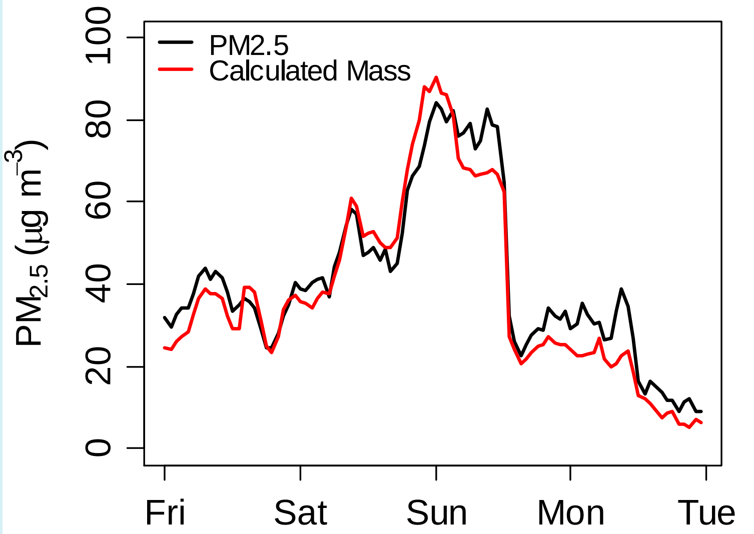


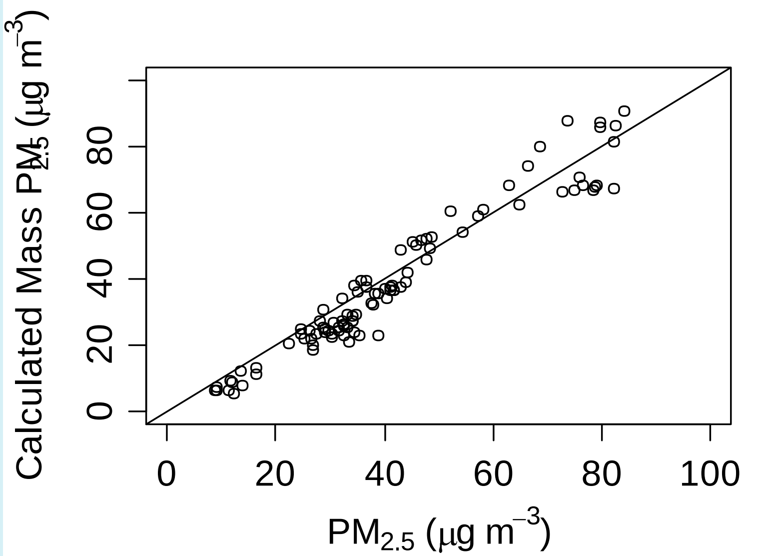
Episode 2 – 10th -14th February

Low temperature

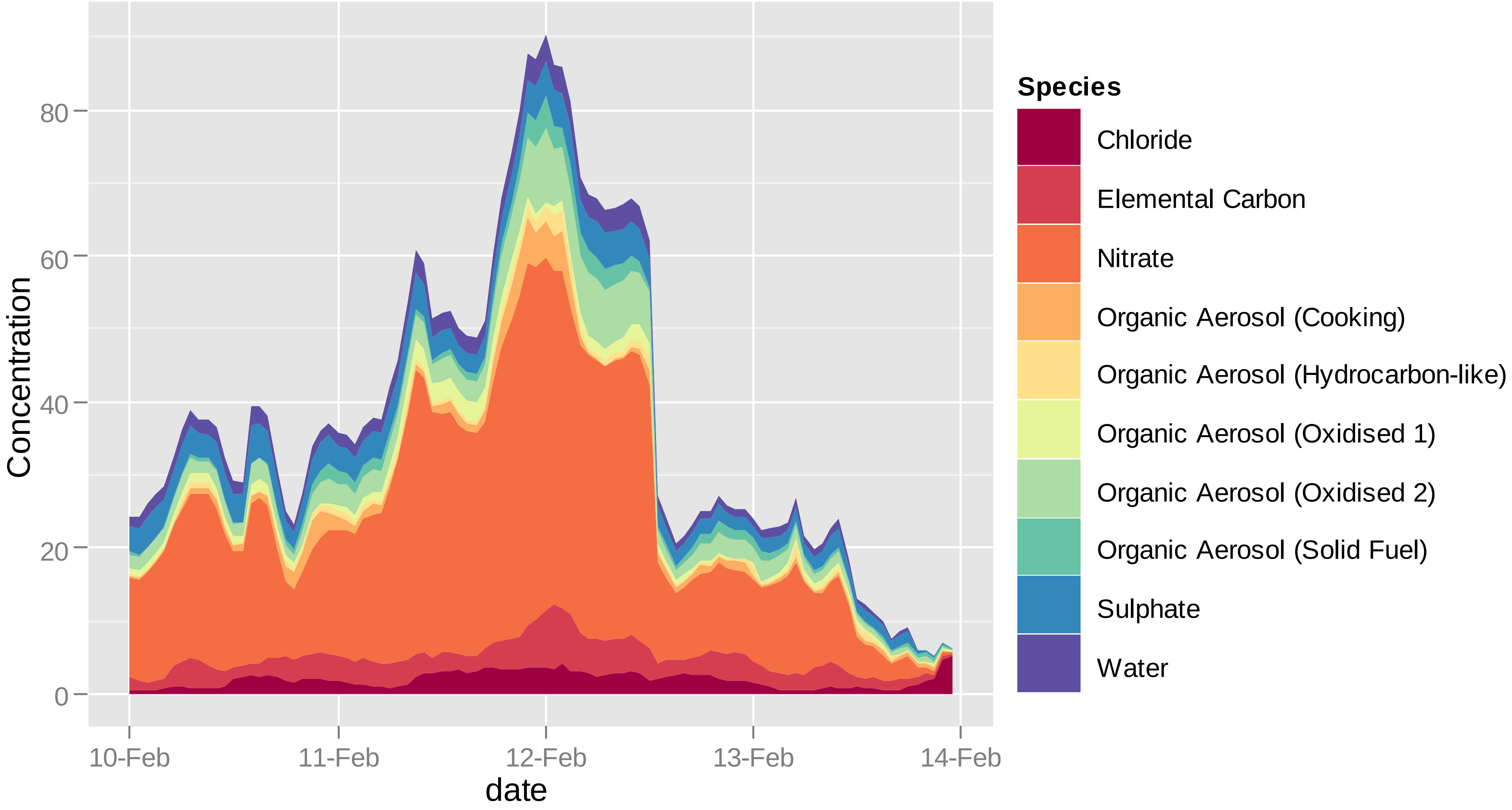
Long Range transport



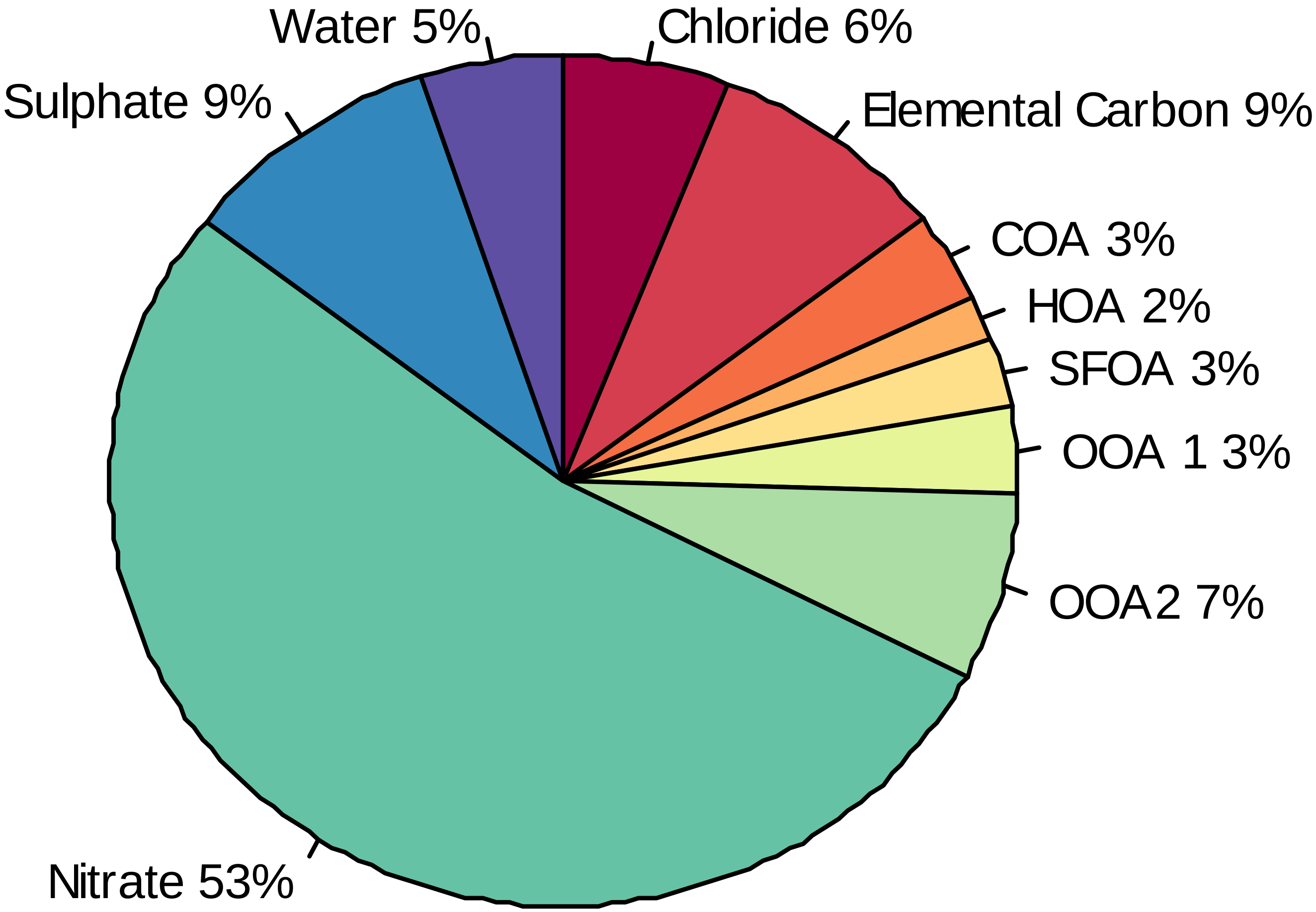




Episode 2 – 10th-14th February

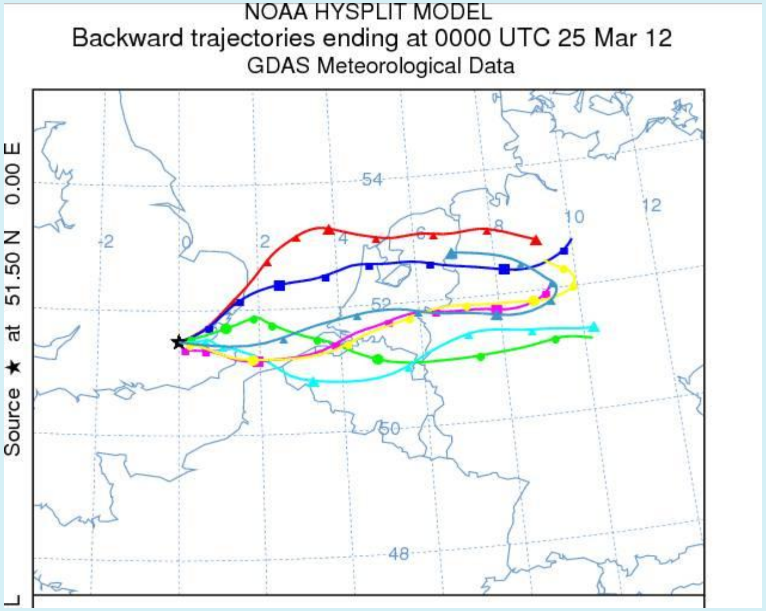


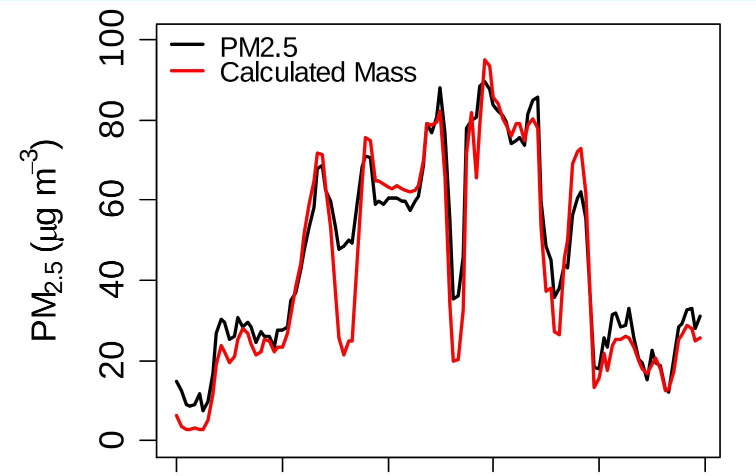
Episode 2 – 10th-14th February

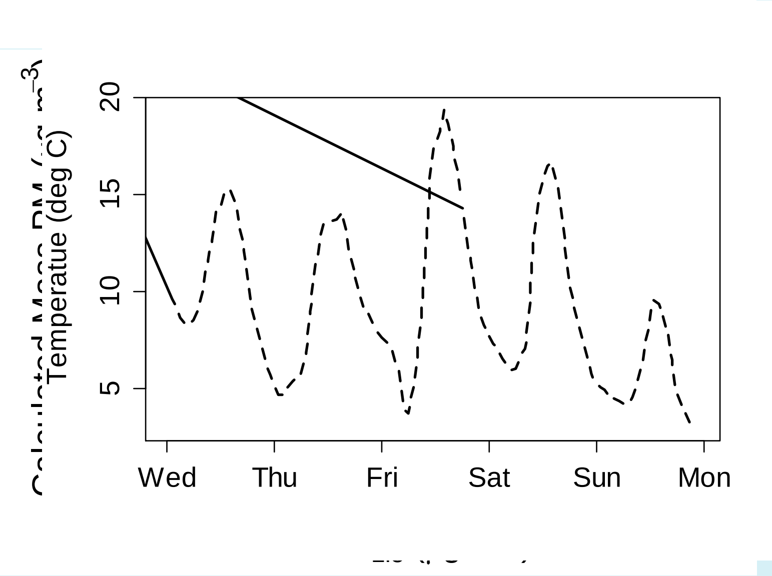


Episode 3 – 23rd March

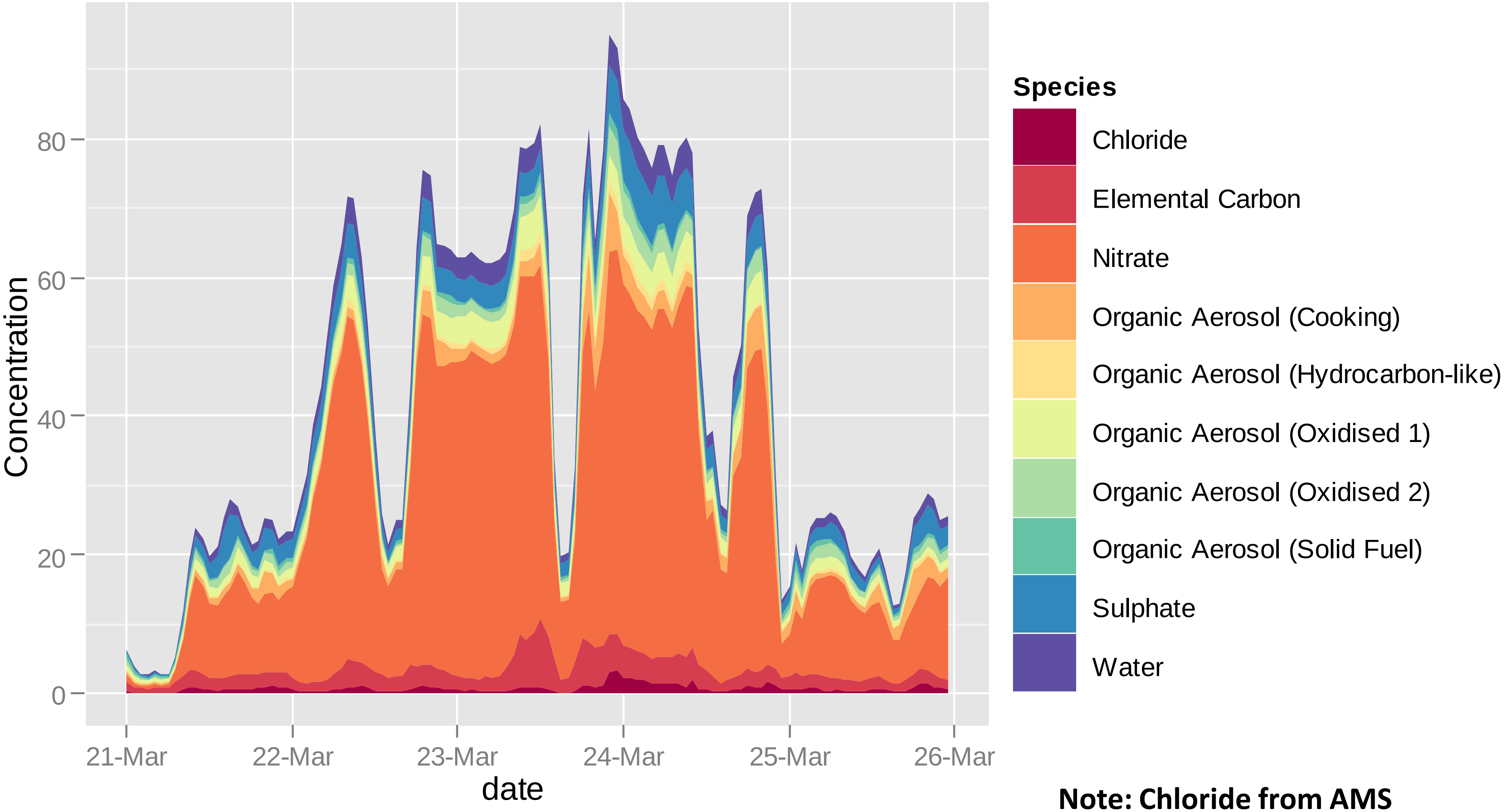
- Long range transport
- Higher % of sulphate
  - More photochemistry
- Prolonged episode


NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 25 Mar 12
GDAS Meteorological Data



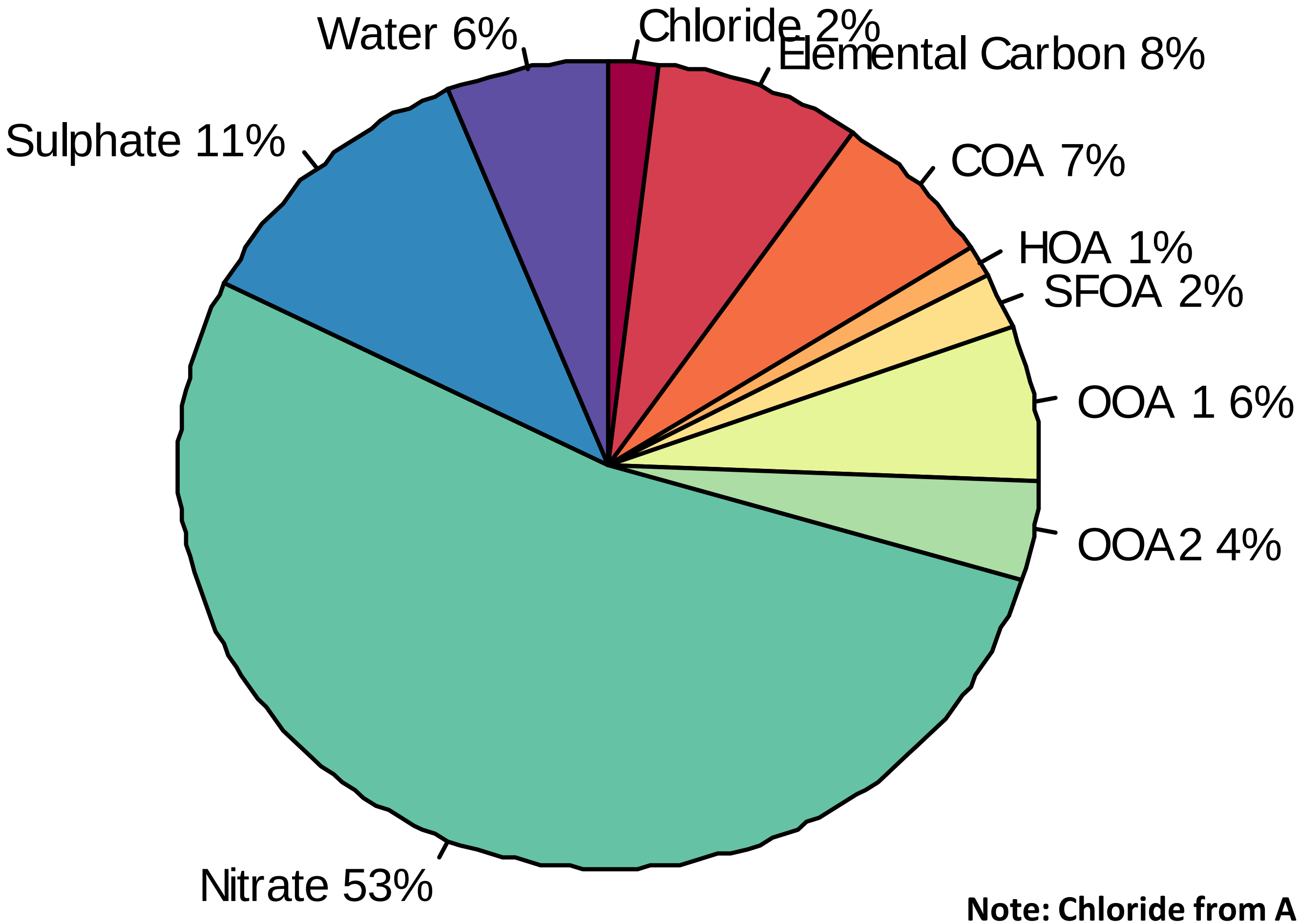


Episode 3 – 21st – 26th March



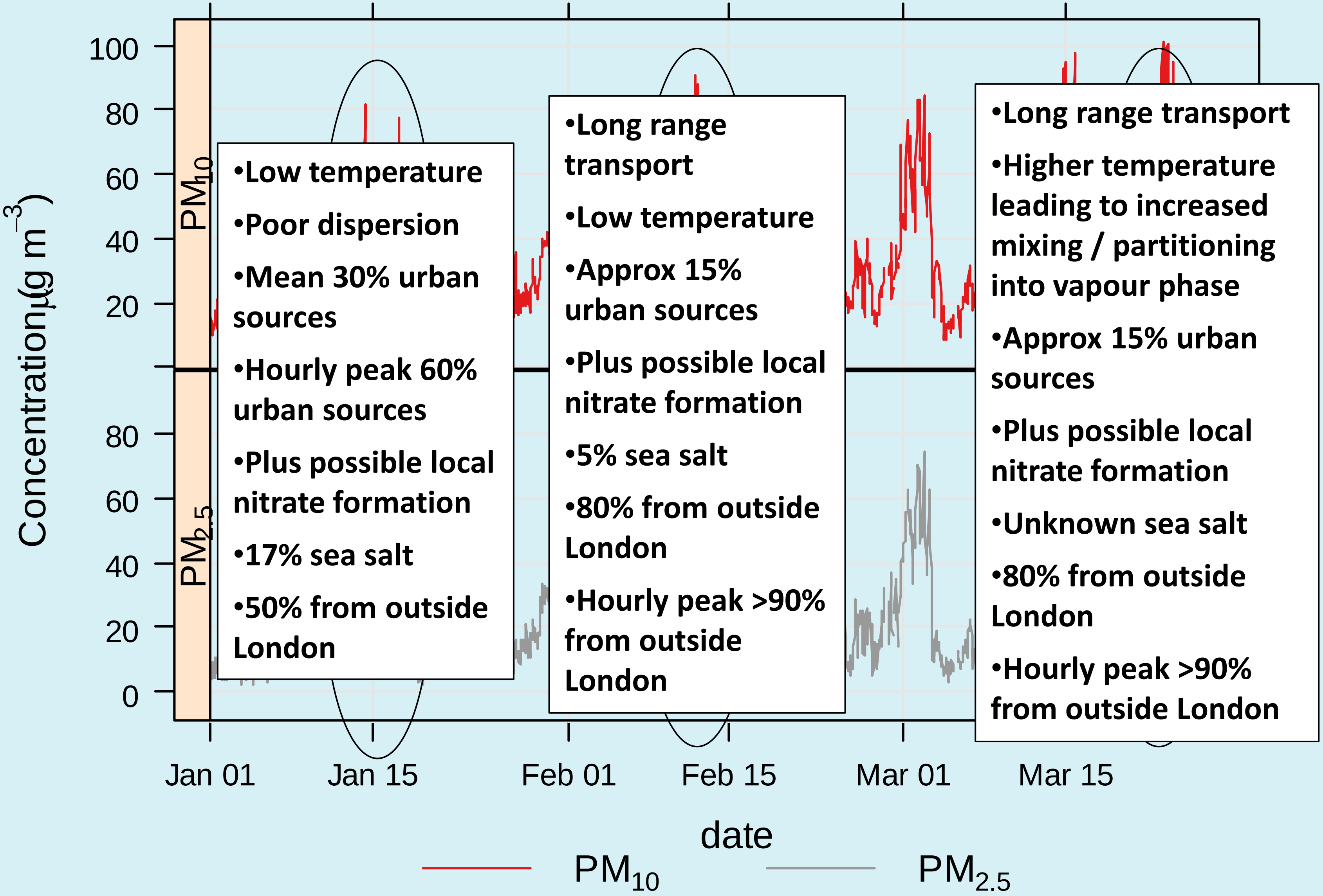
Note: Chloride from AMS

Episode 3 – 21st – 26th March



Note: Chloride from AMS

North Kensington Jan – Apr 2012



- Low temperature
- Poor dispersion
- Mean 30% urban sources
- Hourly peak 60% urban sources
- Plus possible local nitrate formation
- 17% sea salt
- 50% from outside London

- Long range transport
- Low temperature
- Approx 15% urban sources
- Plus possible local nitrate formation
- 5% sea salt
- 80% from outside London
- Hourly peak >90% from outside London

- Long range transport
- Higher temperature leading to increased mixing / partitioning into vapour phase
- Approx 15% urban sources
- Plus possible local nitrate formation
- Unknown sea salt
- 80% from outside London
- Hourly peak >90% from outside London

Model validation

- As the complexity of modelling techniques increases, so does our need for more complex measurements for model validation
- Eulerian models such as CMAQ output 30+ co-varying species at a high time resolution
- Errors in any one of these outputs could driving errors in the total PM model output
- More detailed real time measurement techniques are vital for validating complex modelling outputs
- Development / improvement of emissions inventories, - refinement through remodelling?
- An in depth knowledge of both the measurement techniques and modelling methodology is required

PM species in CMAQ4.7.1
Nitrate
Sulphate
Ammonium
Sodium
Chloride
Elemental carbon
Primary anthropogenic organic aerosol
3 products of SOA from low-yield arom (Xylene)
3 products of SOA from high-yield arom (Toluene)
3 products of SOA from benzene
SOA from "long" alkanes
anthropogenic organic oligomers
3 products of SOA from isoprene
2 products of SOA from monoterpenes
SOA from sesquiterpenes
biogenic organic oligomers
SOA produced in clouds
Primary PM2.5
soil-derived aerosol
coarse mode anthropogenic aerosol
aerosol water

Issues

- Heath warning
  - Preliminary data
  - Lots of analysis still to come
  - Jan – Mar and therefore biased towards nitrate driven episodes
- Instruments
  - Incompatibility between size fractions (AMS PM_1, aethalometer $PM_{2.5}$, URG PM_{10})
  - Complex
- Source attributions
  - Biomass / solid fuel estimates differ between aethalometer and AMS
    - Related to size fraction or data analysis methodology?
  - How much of nitrate is formed within London
    - Need equivalent rural measurement

Conclusions

- Highly time resolved measurements of chemical composition allow:
  - Quantification of the influence of different sources, both local and distant
  - Identification of new sources
  - Validation of the new modelling technique
  - Improvements to the emissions inventories
  - Provide evidence base for new abatement policy development
  - Quantify the impacts of policy once enacted
  - Provide evidence for further epidemiological studies

Acknowledgements

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    - Defra, NERC
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- University of Manchester
    - James Allan, Nicky Young