



**High time resolution
measurements of $PM_{2.5}$ and PM_{10}
using X-ray fluorescence**

David Green

Cambridge Particle Meeting 23rd June 2017

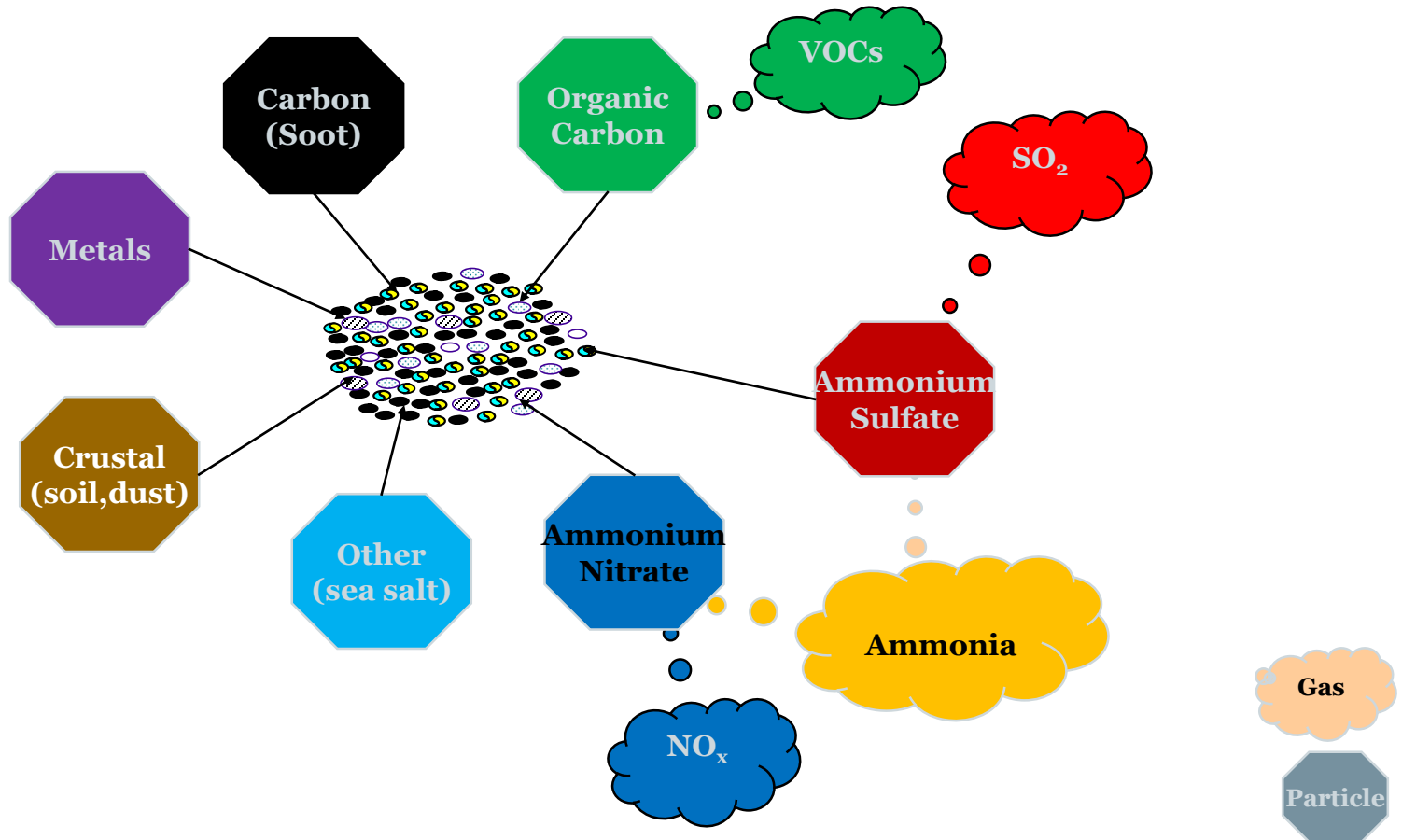
Contents

- 1. Why is this method useful?**
- 2. How does it work?**
- 3. Did it compare well to reference method and laboratory generated aerosols?**
- 4. How can we use the measurements to identify sources of PM?**

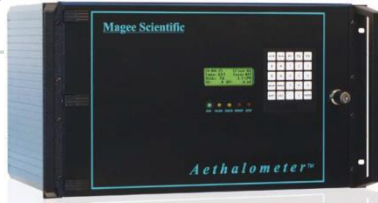
Chemical Composition

**Primary Particles
(directly emitted)**

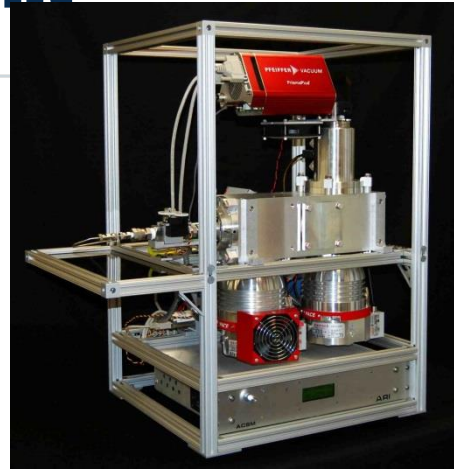
**Secondary Particles
(from precursor gases)**



PM Composition Measurement



Aethalometer



Aerosol Mass Spectrometry

Carbon (Soot)

Organic Carbon

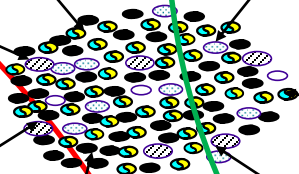
Metals

Crustal (soil, dust)

Other (sea salt)

Ammonium Nitrate

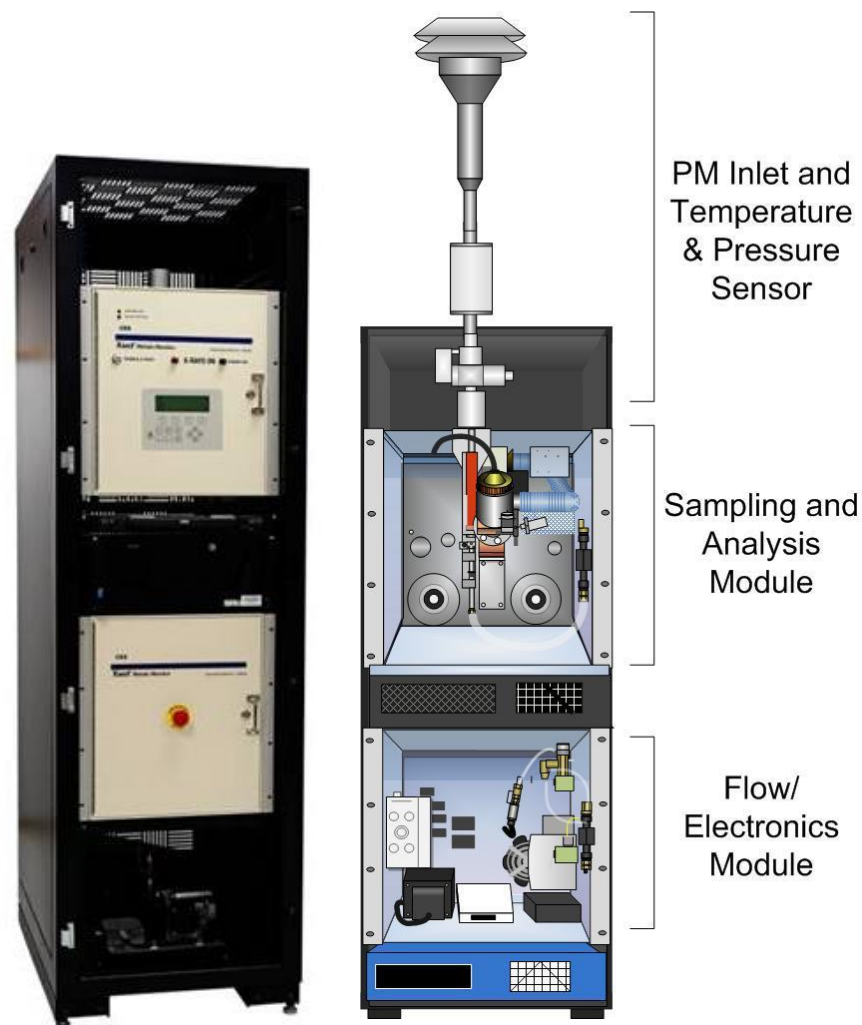
Ammonium Sulfate



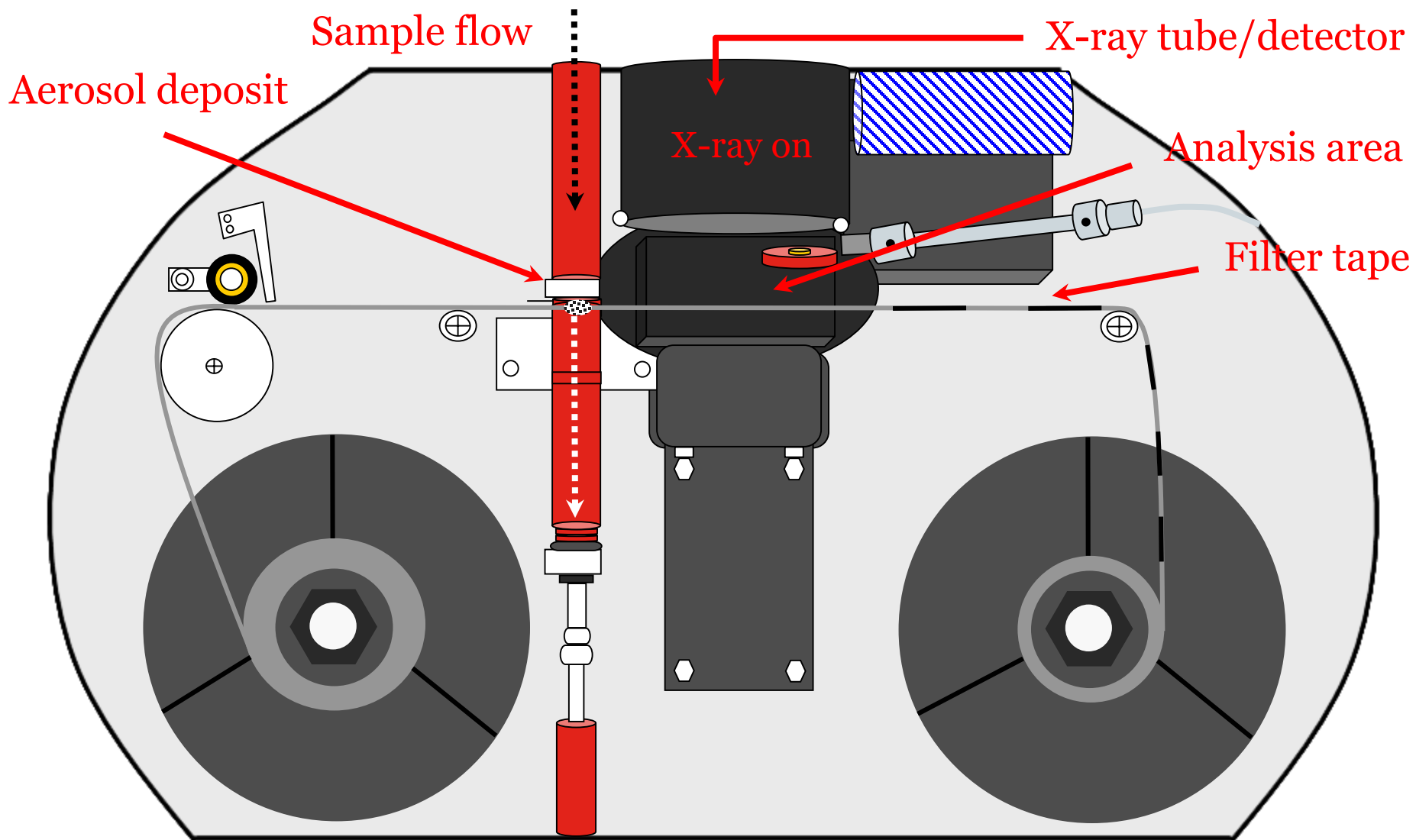
X-Ray Fluorescence

XACT 625

- Cooper Environmental Services
- Measures a suite of elements in near real time using X-Ray Fluorescence
- Sampled through a PM size-selective inlet onto filter tape
- Sampling time between 15 min and 4 hrs
- Sampling and analysis is performed continuously and simultaneously
- Some automatic quality assurance and control
- Remote polling and operation
- Measures 23 elements, we chose:
 - Regulatory (Ni, As, Cd, Pb)
 - Abrasion (Ba, Cu, Sb, Zn)
 - Mineral (Ca, Fe, Mn, Mo, Si, Ti)
 - Traffic (Ce, Pt, Se, V)
 - Marine (Cl, K)
 - Industrial (Cr)
 - Fireworks (Sr)
 - Secondary Aerosol (S)



XACT Sampling and Analysis Module



Mobile Atmospheric Research Platform (MARPL)

- X Ray fluorescence (XACT 625) - 23 metals at hourly resolution
- Aerosol Mass Spec (ACSM) - Organics, nitrate, sulphate, ammonium, chloride
- Black Carbon (Aethalometer)
- SMPS and APS (Particle Size)
- NO_x (NO + NO₂) (Blue Light Converter)
- Met data: wind, humidity, temperature (10m mast)
- Location – Marylebone Road, Pontardawe, Port Talbot, Sheffield



Field Evaluation

ICP-MS - Partisol Filter Sampler



- Acid digested and analysed with ICP/MS (HF or HNO₃/H₂O₂)
- As, Ba, Ca, Cd, Ce, Cu, Fe, K, Mn, Mo, Ni, Pb, Pt, Sb, Sr, Ti, Zn
- PM₁₀ and PM_{2.5}

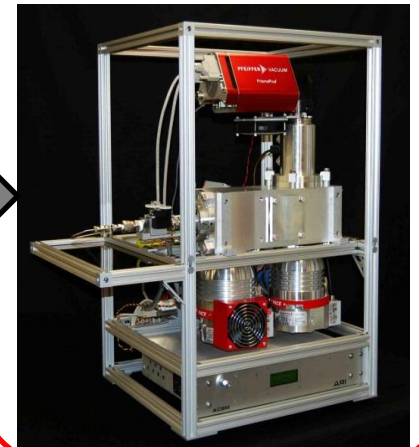
XRF - XACT 625



IC - URG 9000

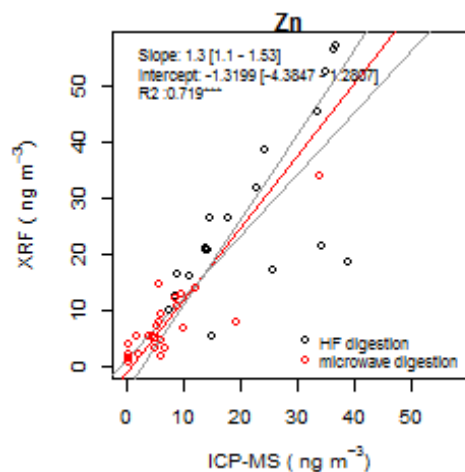
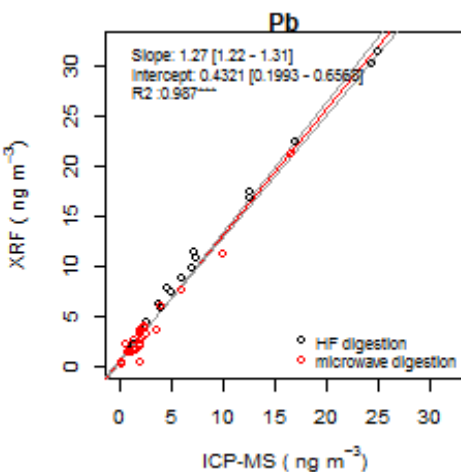
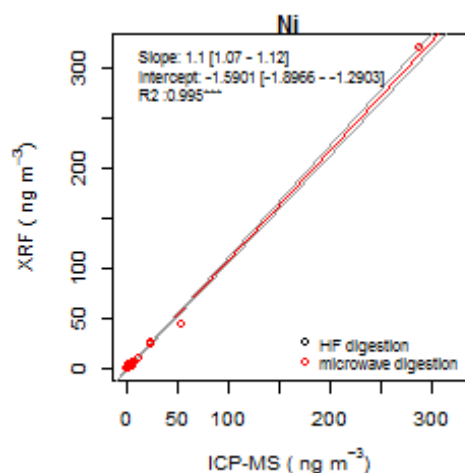
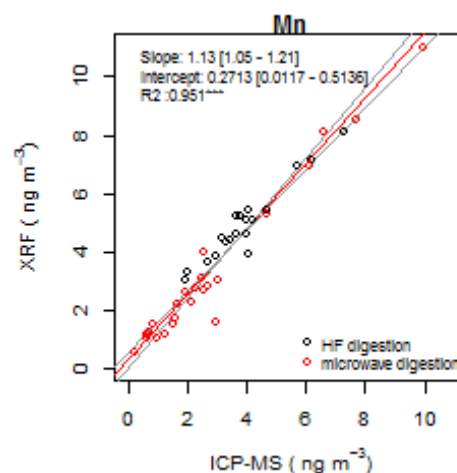
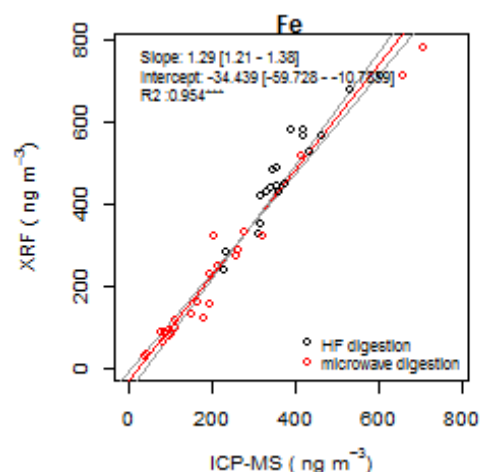
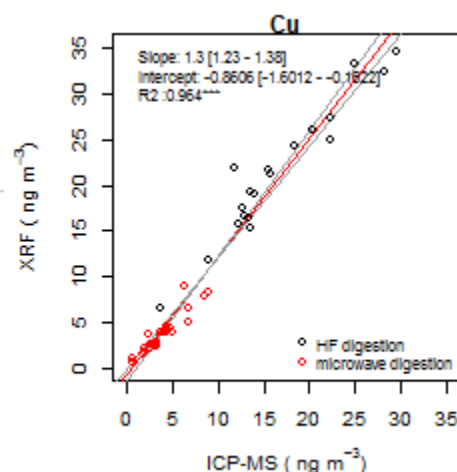


Mass Spec - ACSM



Field Evaluation Results

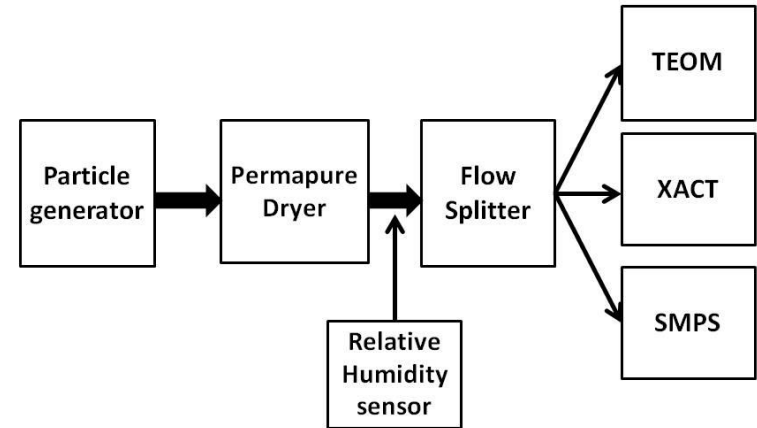
- Elements shown are common to both field trials
- All agree very well with high R^2 , except Zn, which has a slightly lower R^2
- XACT higher for all elements (slope > 1)
- All elements have a significant offset but not consistently above/below 0



Method	Element	Slope	Intercept	R^2
Partisol	Cu	1.3 (1.23,1.38)	-0.86 (-1.6,-0.16)	0.96***
	Fe	1.29 (1.21,1.38)	-34.44 (-59.73,-10.78)	0.95***
	Mn	1.13 (1.05,1.21)	0.27 (0.01,0.51)	0.95***
	Ni	1.1 (1.07,1.12)	-1.59 (-1.9,-1.29)	0.99***
	Pb	1.27 (1.22,1.31)	0.43 (0.2,0.66)	0.99***
	Zn	1.3 (1.1,1.53)	-1.32 (-4.38,1.28)	0.72***

Laboratory Evaluation

- XRF calibration
 - Thin film standards
 - Various limitations:
 - higher in concentration than most ambient samples,
 - single element standard will not be representative of the particle mix found in the environment
 - the collection properties on a filter may also differ
- Laboratory generated aerosols of $(\text{NH}_4)_2\text{SO}_4$, KCl and zinc acetate over a range of concentrations



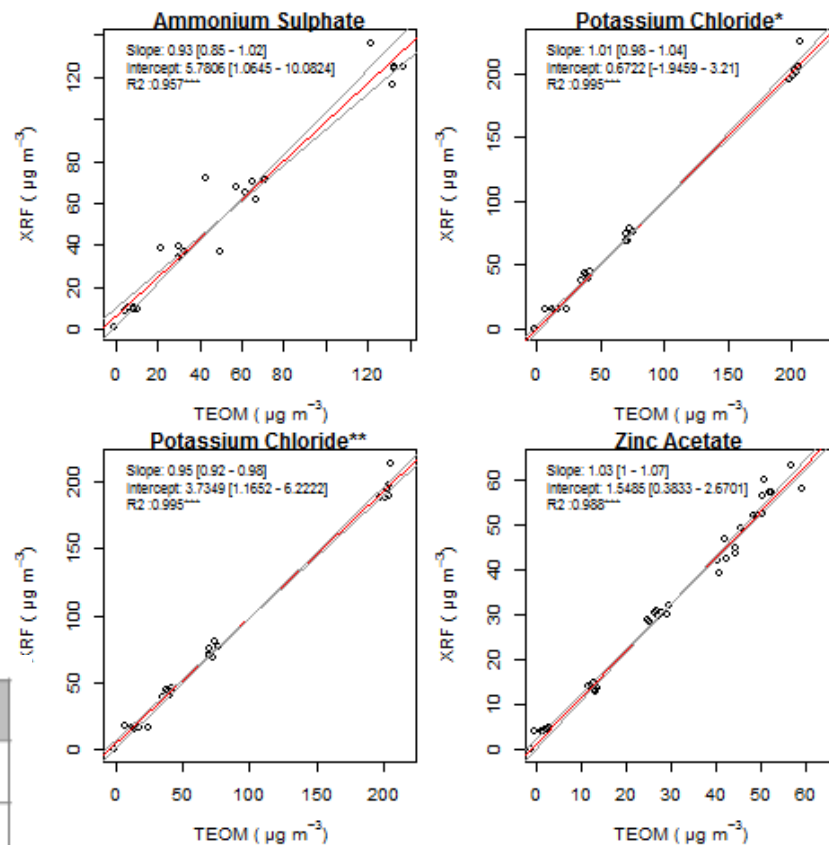
Laboratory Evaluation Results

- Measured TEOM mass and calculated mass using XACT element concentrations agree well for all solutions ($R^2 > 0.96$ for all elements)
- Slopes not significantly different from 1, except KCl calculated from K

Element	Slope	Intercept	R^2
$(\text{NH}_4)_2\text{SO}_4$	0.93 (0.85,1.02)	5.78 (1.06,10.08)	0.96***
KCl*	1.01 (0.98,1.04)	0.67 (-1.95,3.21)	1.00***
KCl**	0.95 (0.92,0.98)	3.73 (1.17,6.22)	0.99***
$\text{Zn}(\text{O}_2\text{CCH}_3)_2$	1.03 (1,1.07)	1.55 (0.38,2.67)	0.99***

* calculated using XACT Chloride results

**calculated using XACT Potassium results



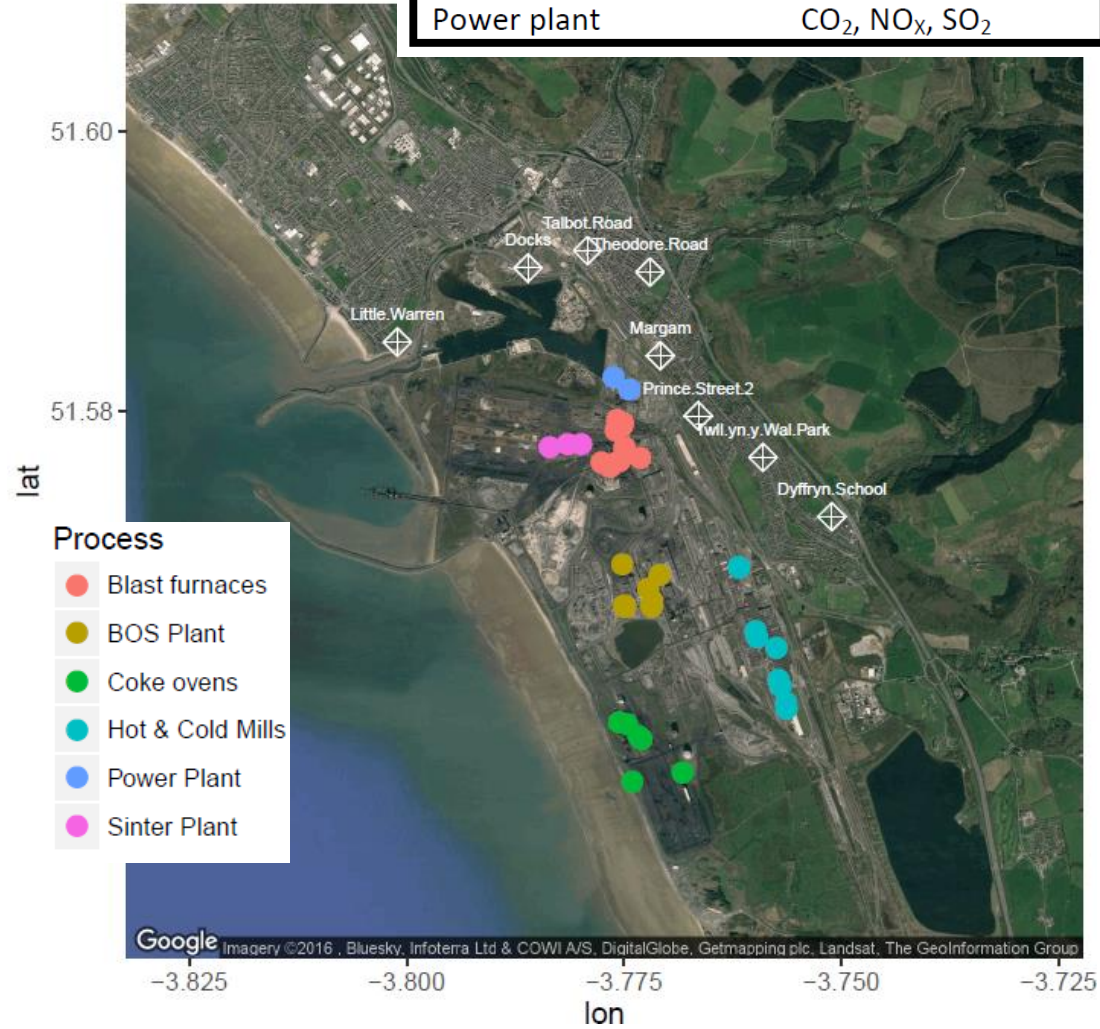
Port Talbot

- For many years, Port Talbot has suffered some of the worst AQ in the UK
- Port Talbot was declared an Air Quality Management Area in 2000
- PM_{10} in Port Talbot often exceed the daily LV (38 days daily $PM_{10} > 50 \mu g m^{-3}$ in 2015)
- The Tata Steel complex is located in Port Talbot and it has been identified as a major source of PM emissions (AQEG, 2011).
- Welsh Gov research contract – to understand the key sources contributing to peak PM_{10} concentrations

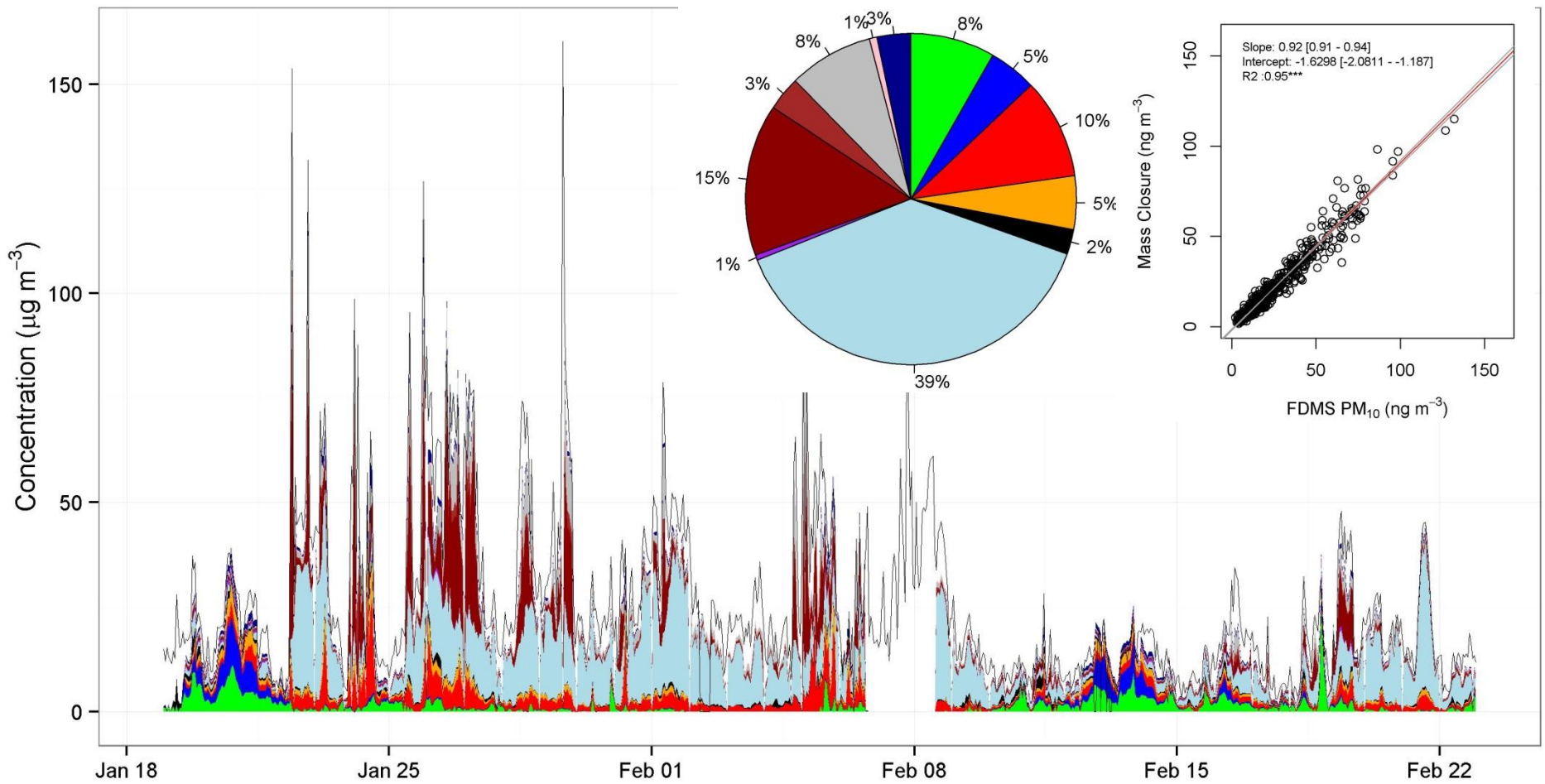


Complex mixture of sources

Process	Pollutants
Stockyards	PM _{coarse} , Ca, Fe
Coke ovens	Black Carbon, NO _x , S, SO ₂
Sinter plant	Fe, Mn, Pb, Zn
Blast furnaces	Ca, Fe, S, Si
BOS	Fe, Mn, Zn
Cold & hot mills	Ca, Fe S, Si,
Power plant	CO ₂ , NO _x , SO ₂



Mass Closure PM₁₀



■ OM
 ■ Nitrate
 ■ Sulphate
 ■ Ammonium
 ■ BC
 ■ NaCl
 ■ NH₄Cl
 ■ IronOxides
 ■ Minerals
 ■ CalciumCompounds
 ■ K
 ■ H₂O

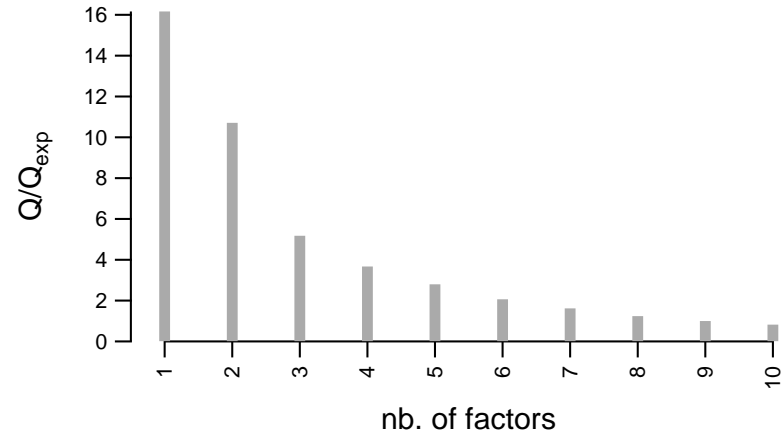
Source Identification



Receptor Modelling - PMF

- Combined data set (XACT, ACSM, Aethalometer)
- ‘Missing’ mass
 - FDMS PM₁₀ - $\sum \text{ChemicalComponents}$ included in PMF algorithms
- PMF runs were configured to yield between 1 and 10 sources.
- Number of factors based on
 - Correlation between factor time series
 - Minimum model residuals

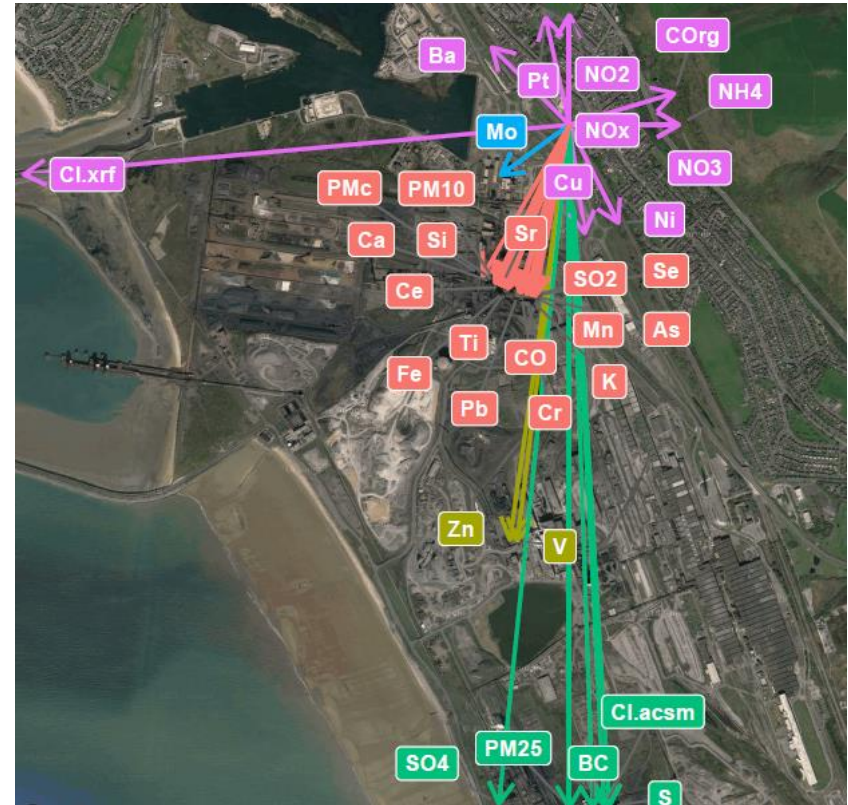
How many factors?



	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8
Factor 1	1	0.06	0.27	0.31	0.09	-0.23	0.25	0.07
Factor 2	0.06	1	-0.02	0.09	0	-0.64	-0.04	0.24
Factor 3	0.27	-0.02	1	0.32	0.33	-0.42	0.9	-0.13
Factor 4	0.31	0.09	0.32	1	0.05	-0.41	0.2	0.19
Factor 5	0.09	0	0.33	0.05	1	-0.63	0.31	-0.31
Factor 6	-0.23	-0.64	-0.42	-0.41	-0.63	1	-0.36	-0.01
Factor 7	0.25	-0.04	0.9	0.2	0.31	-0.36	1	-0.16
Factor 8	0.07	0.24	-0.13	0.19	-0.31	-0.01	-0.16	1

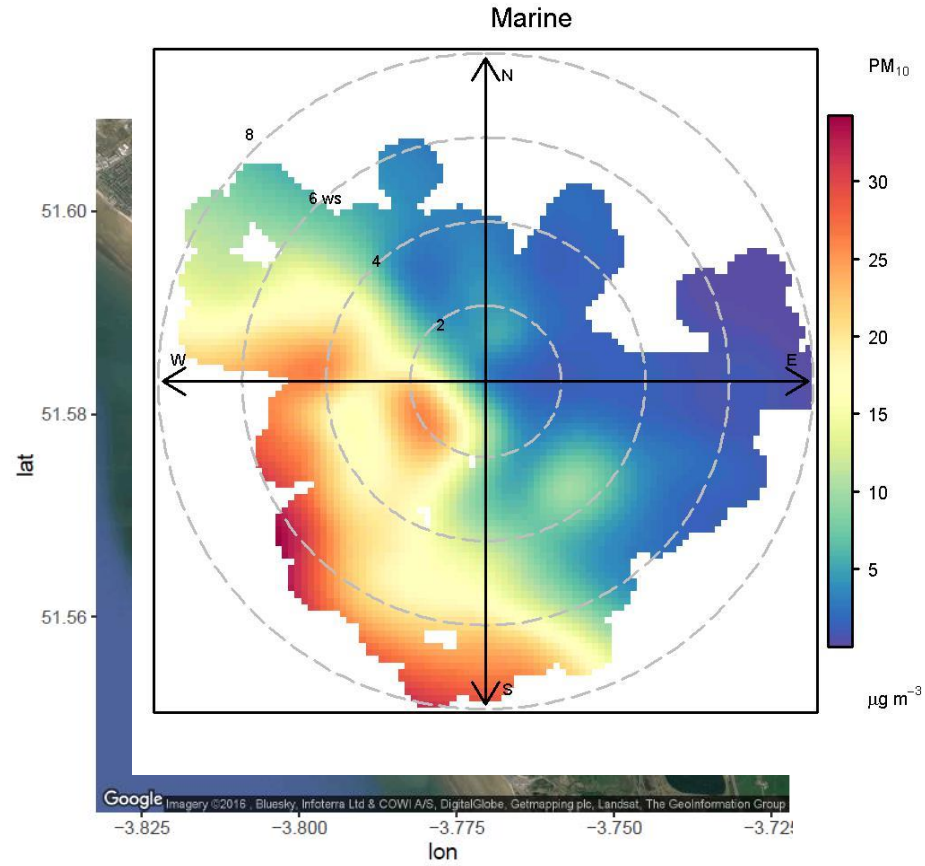
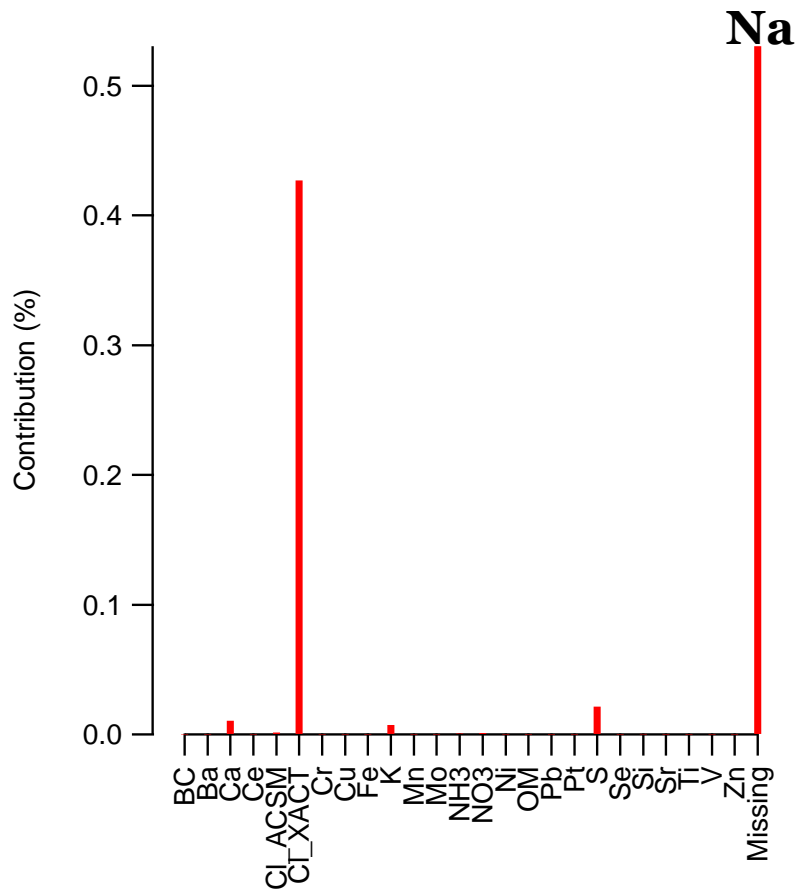
External Information

- **Source location**
- **Source activity (e.g. diurnal variations)**
- **Known factor profiles (e.g. Zn from BOS plant, S from coke production)**
- **Additional atmospheric measurements**
 - Gaseous (CO, SO₂, NO₂)
 - PM size



Processes	Distance (m)	Min angle (deg)	Max angle (deg)
Sinter Plant	1036	222	231
Blast furnace	797	191	214
BOS Plant	1912	180	190
Coke Ovens	3116	177	186
Cold-Hot Mills	2473	158	161

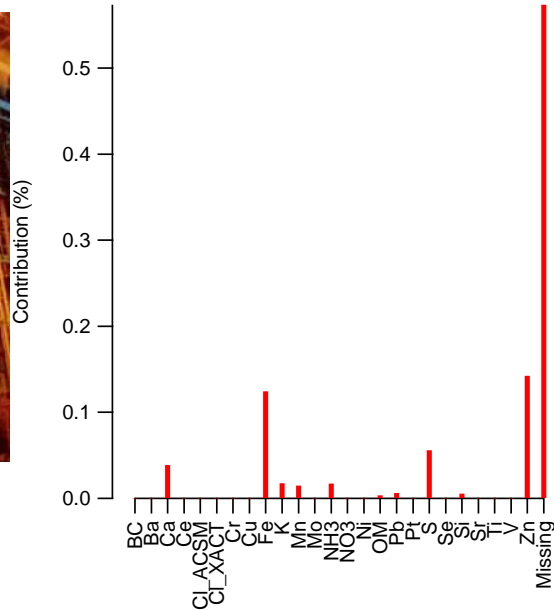
Marine



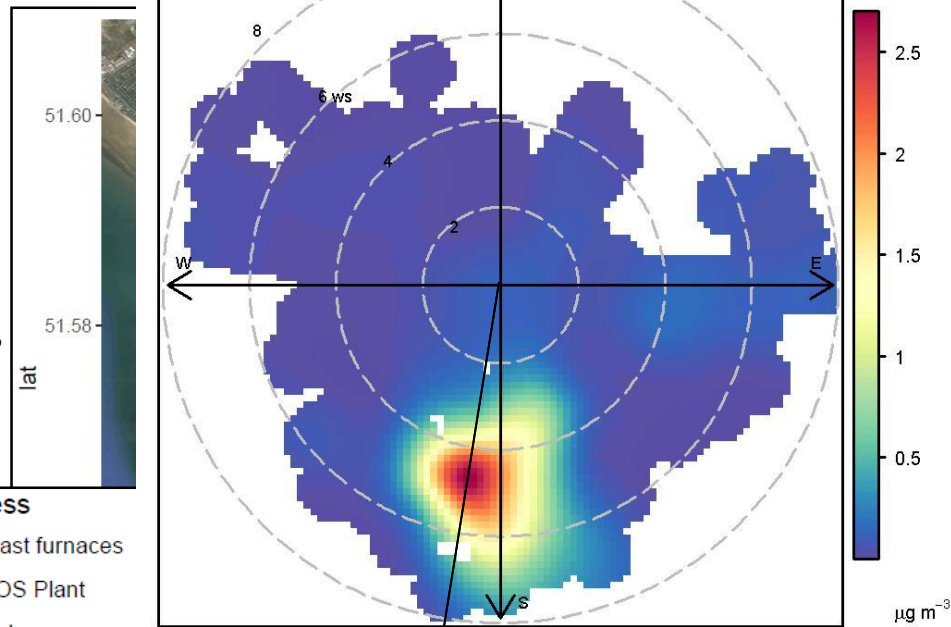
Basic Oxygen Steelmaking (BOS) Plant



25% Scrap
→ **Zn**



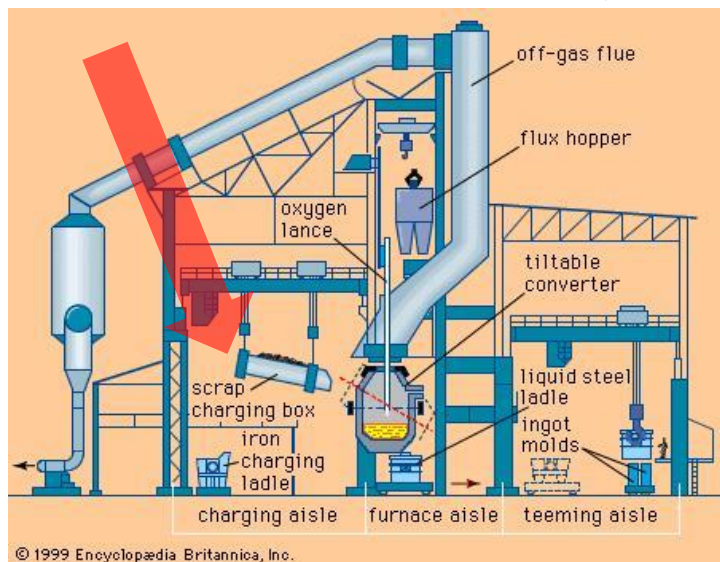
Processes	Distance (m)	Min angle (deg)	Max angle (deg)
Sinter Plant	1036	222	231
Blast furnace	797	191	214
BOS Plant	1912	180	190
Coke Ovens	3116	177	186
Cold-Hot Mills	2473	158	161



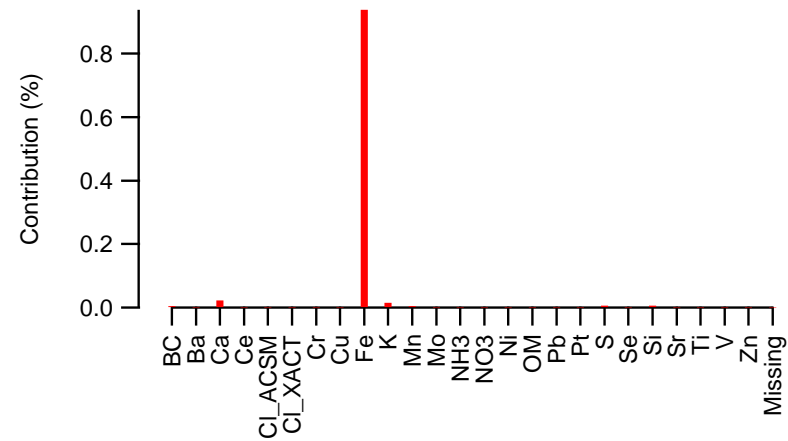
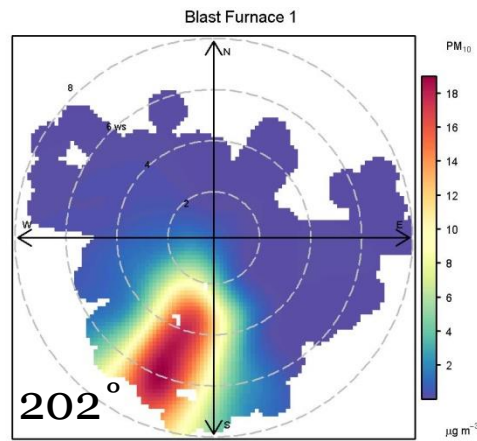
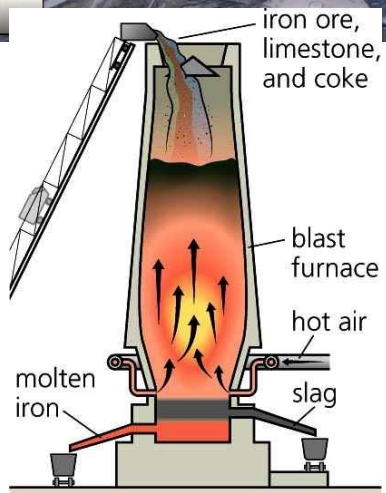
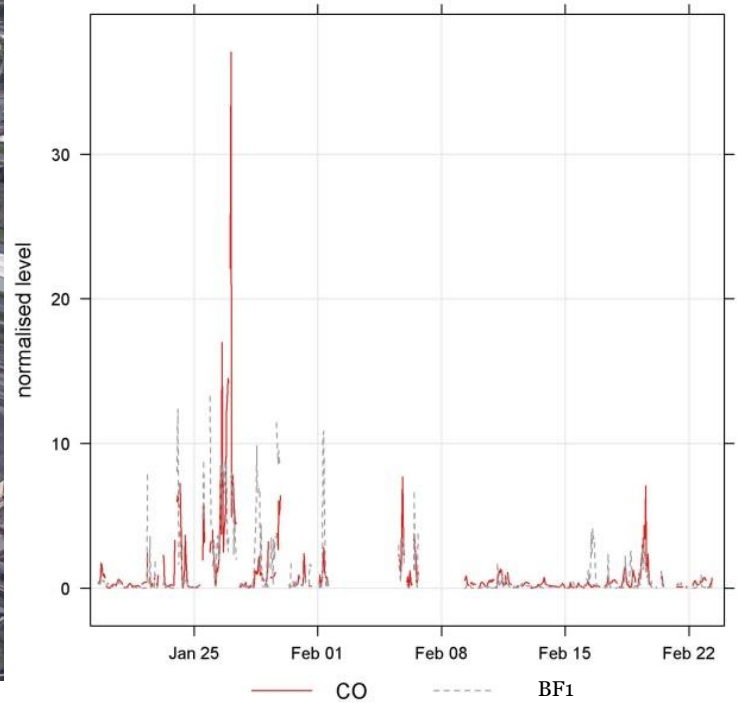
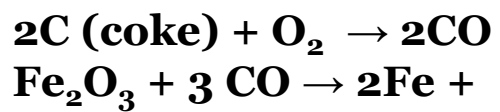
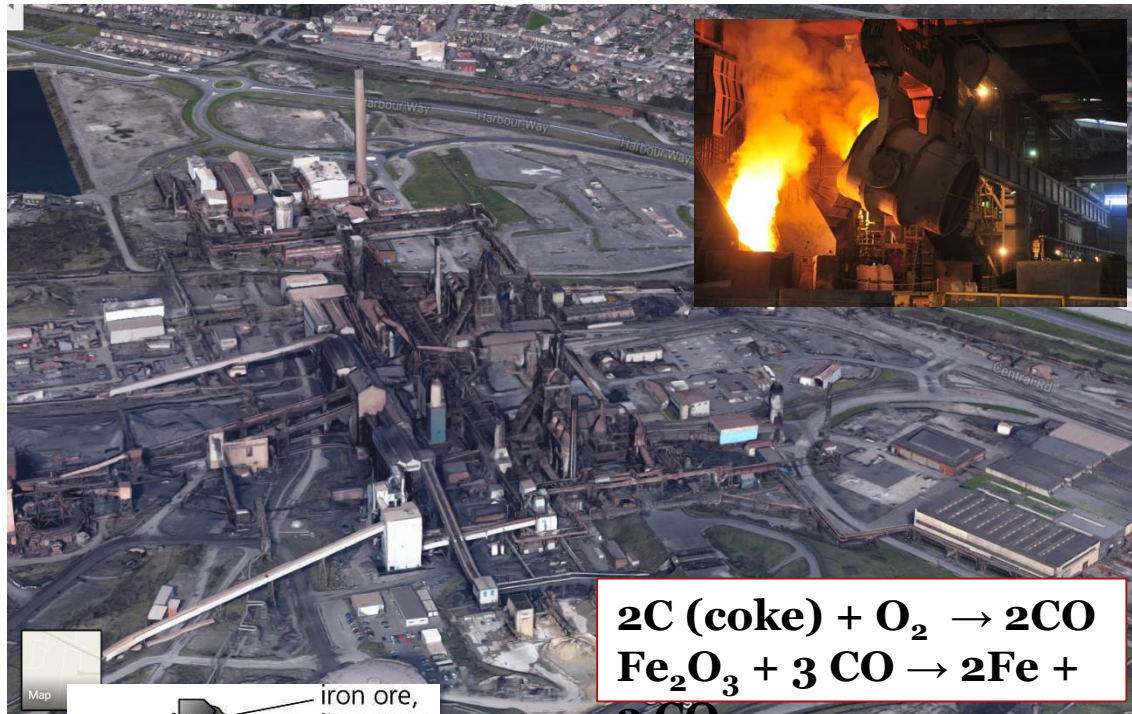
- Process**
- Blast furnaces
 - BOS Plant
 - Coke ovens
 - Hot & Cold Mills
 - Power Plant
 - Sinter Plant



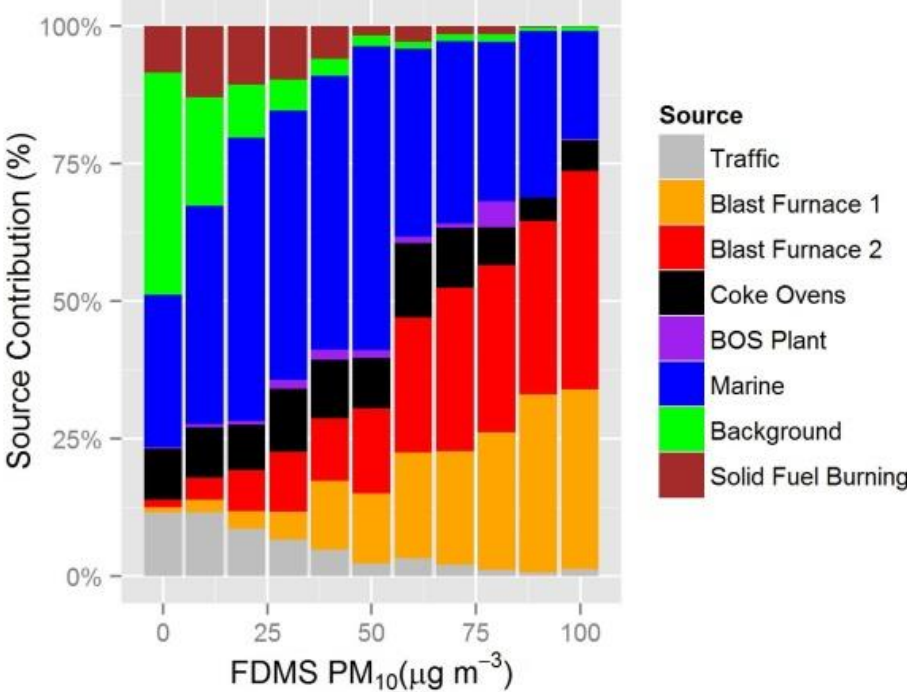
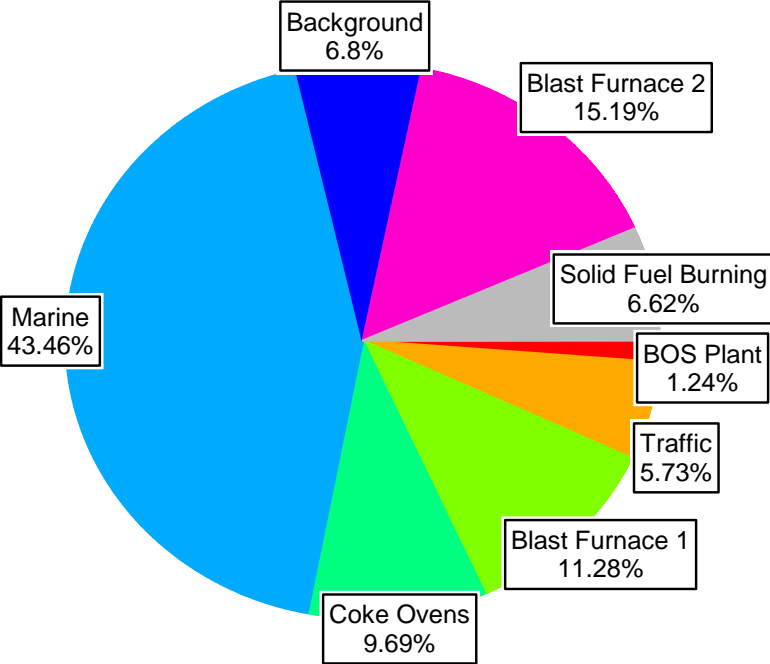
189°



Blast Furnace 1 – Main Stack?



Source Contributions



Conclusions

- Commercially available high time resolution x-ray fluorescence
- Method of quantifying range of elements important to PM mass at high time resolution not available via other methods
- Laboratory results also showed excellent agreement with nebulised aerosols
- Field deployments showed that it was robust and compared well to reference method
- Use in industrial source apportionment studies has shown its value in helping to quantify impact of range of sources

Acknowledgements

Colleagues and collaborators

- Anna Font, Max Priestman, Anja Tremper
- National Physical Laboratory

Funding organisations

- NERC, MRC, Defra, Env Agency, Welsh Gov

david.c.green@kcl.ac.uk

