



The past, present and future of Metals and PAH monitoring in the UK

Dr Richard J. C. Brown
National Physical Laboratory

RSC Monitoring Ambient Air 2011
12th December 2011

Summary

- Fourth Daughter Directive requirements
- UK delivery of metals and PAH measurement
- Historical trends in concentrations
- Current performance
- Future directions and current research



The Fourth Daughter Directive












- Directive 2004/107/EC, published in 2005
- Covers PAHs, metals in PM₁₀ & Hg vapour
- Target (not limit) values and assessment thresholds for Ni (20 ng/m³), As (6 ng/m³), Cd (5 ng/m³) & B[a]P (1 ng/m³)
- Measurement of deposition of these species, Hg & of other PAHs also required
- Other measurements (Hg in PM₁₀ and RGM) recommended
- Pb (limit value: 500 ng/m³) is covered by 2008/50/EC
- Expecting 2013 revision to coalesce 2004/107/EC & 2008/50/EC



Directive Requirements

Species Phase	Metals	Mercury	Polycyclic Aromatic Hydrocarbons
PM ₁₀ phase	Ni, As, Cd (Pb: 2008/50/EC)	<i>Hg – recommended at background sites (BS)</i>	B[a]P + 6 other PAHs at selected sites
Gaseous phase	<i>N/A</i>	TGM – BS <i>RGM – recommended at BS</i>	
Deposition	Total Ni, As, Cd – BS	Total Hg – BS	Total B[a]P + 6 other PAHs – BS

UK's Delivery: multi-day filter-based networks

Species Phase	Metals	Mercury	Polycyclic Aromatic Hydrocarbons
PM ₁₀ phase	 National Physical Laboratory  Centre for Ecology & Hydrology <small>NATURAL ENVIRONMENT RESEARCH COUNCIL</small>	 National Physical Laboratory  Centre for Ecology & Hydrology <small>NATURAL ENVIRONMENT RESEARCH COUNCIL</small>	 National Physical Laboratory
Gaseous phase	N/A	 National Physical Laboratory  Centre for Ecology & Hydrology <small>NATURAL ENVIRONMENT RESEARCH COUNCIL</small>	 National Physical Laboratory
Deposition	 Centre for Ecology & Hydrology <small>NATURAL ENVIRONMENT RESEARCH COUNCIL</small>	 Centre for Ecology & Hydrology <small>NATURAL ENVIRONMENT RESEARCH COUNCIL</small>	 National Physical Laboratory

25 'urban and industrial' sites
14 metals measured in PM₁₀
13 co-located TGM sites



Urban
Metals

31 sites
39 PAHs measured in PM₁₀
2 co-located PAH vapour sites



PAHs

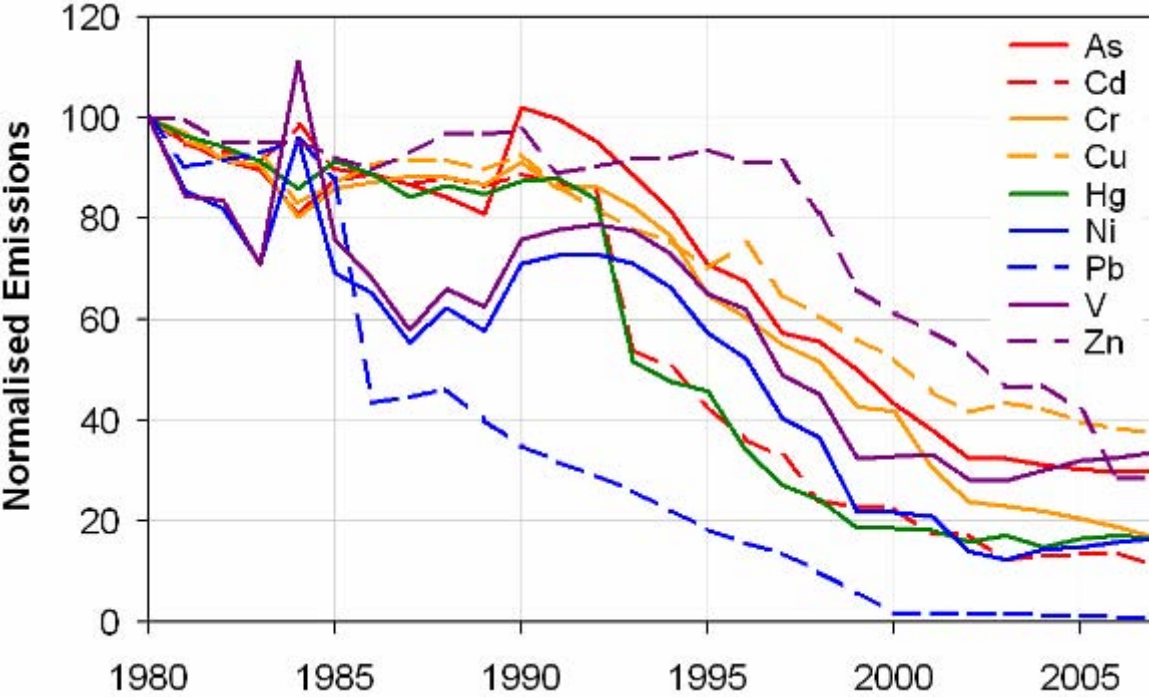
Weekly/monthly
sampling, 6 L/h
TD-AFS,
EN15852



Weekly sampling, 1 m³/h
Acid digestion, ICP-MS, EN14902



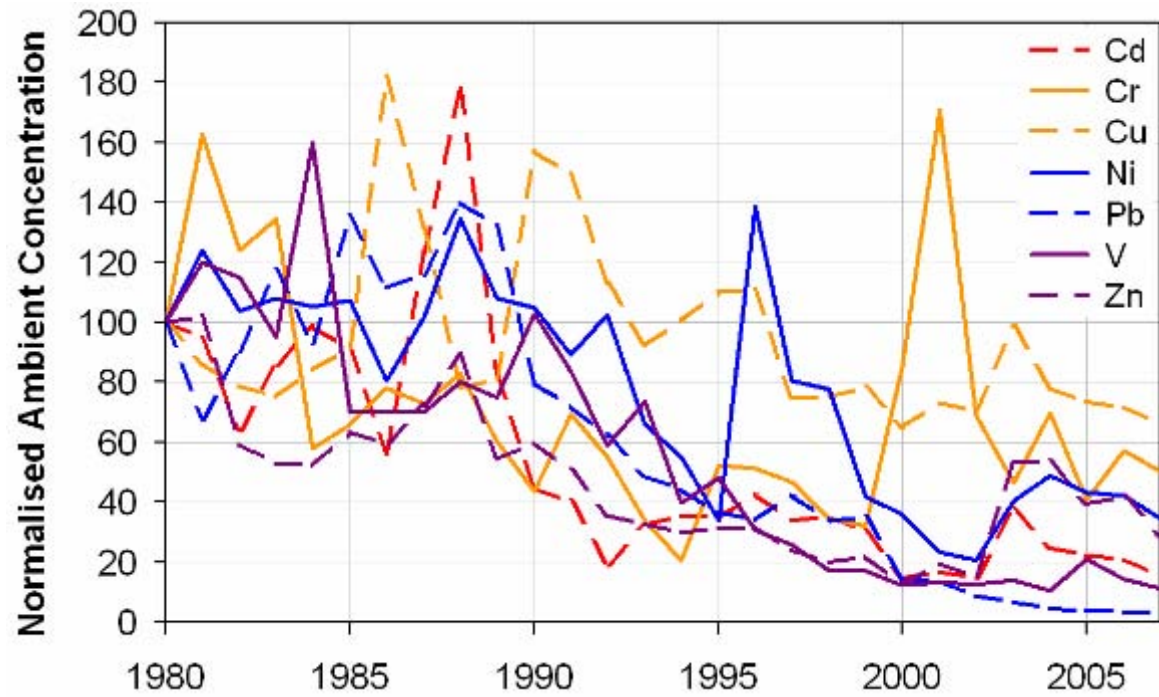
Daily sampling, 30 m³/h
Solvent extraction, GC-MS, EN15549



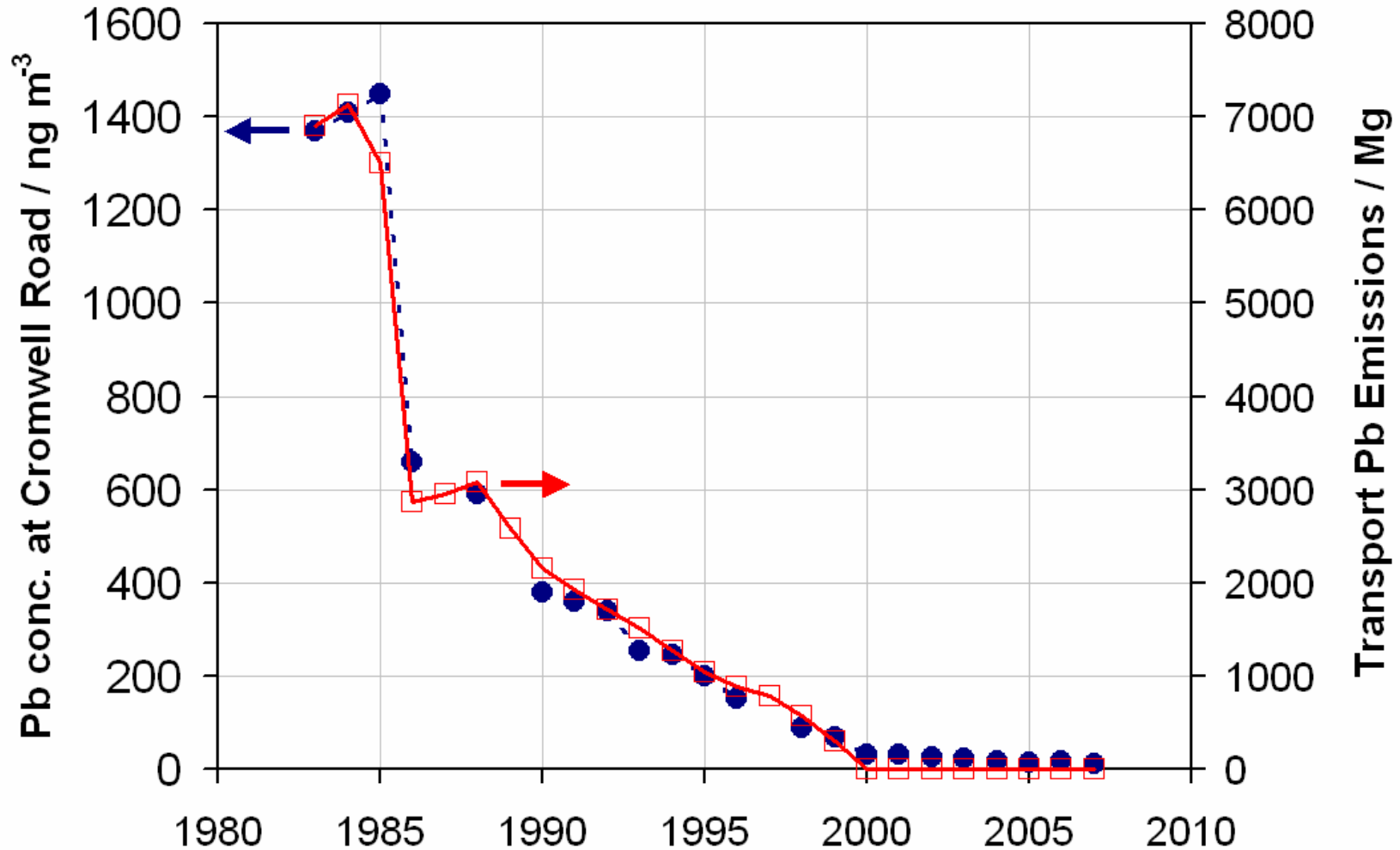
Emissions & concentrations – Metals

- Emissions have decreased over time
- Ambient concentrations have followed

- Emissions estimated by stable algorithms
- Real measurements of concentration subject to changes in monitoring & meteorological parameters etc

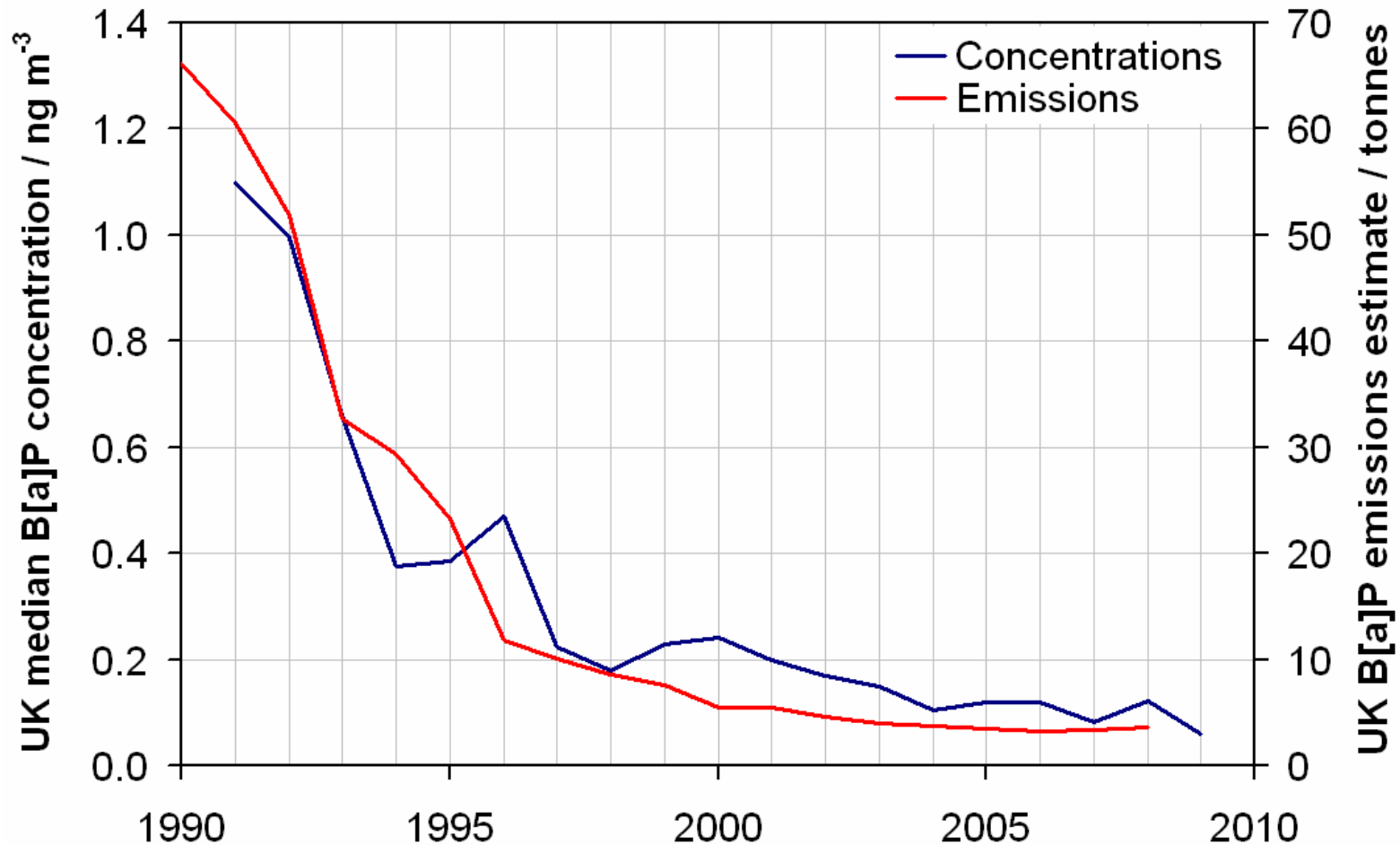


Pb at Cromwell Road, London

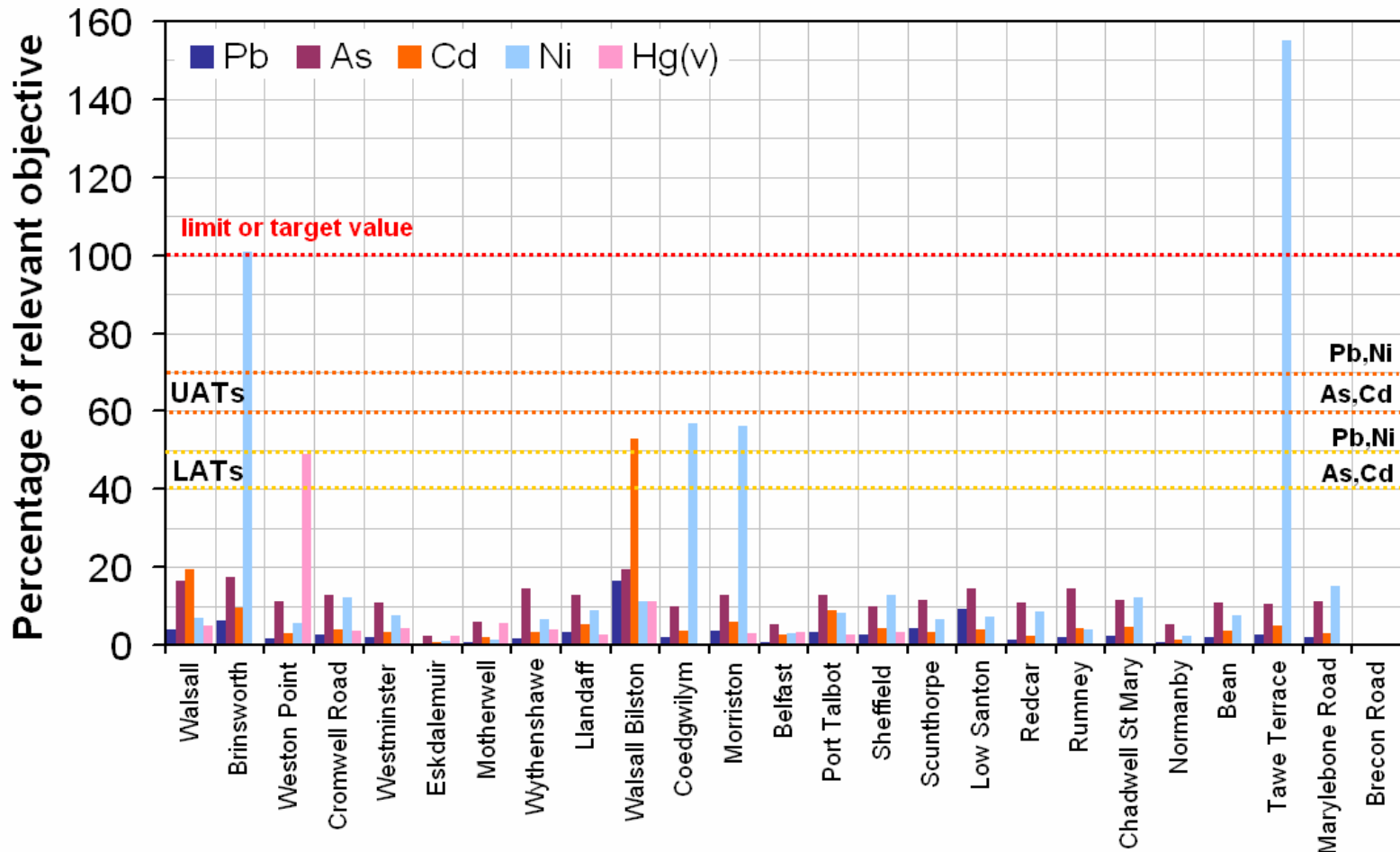


- If only all air quality relationships were this clear...

Temporal concentration and emission trends for B[a]P

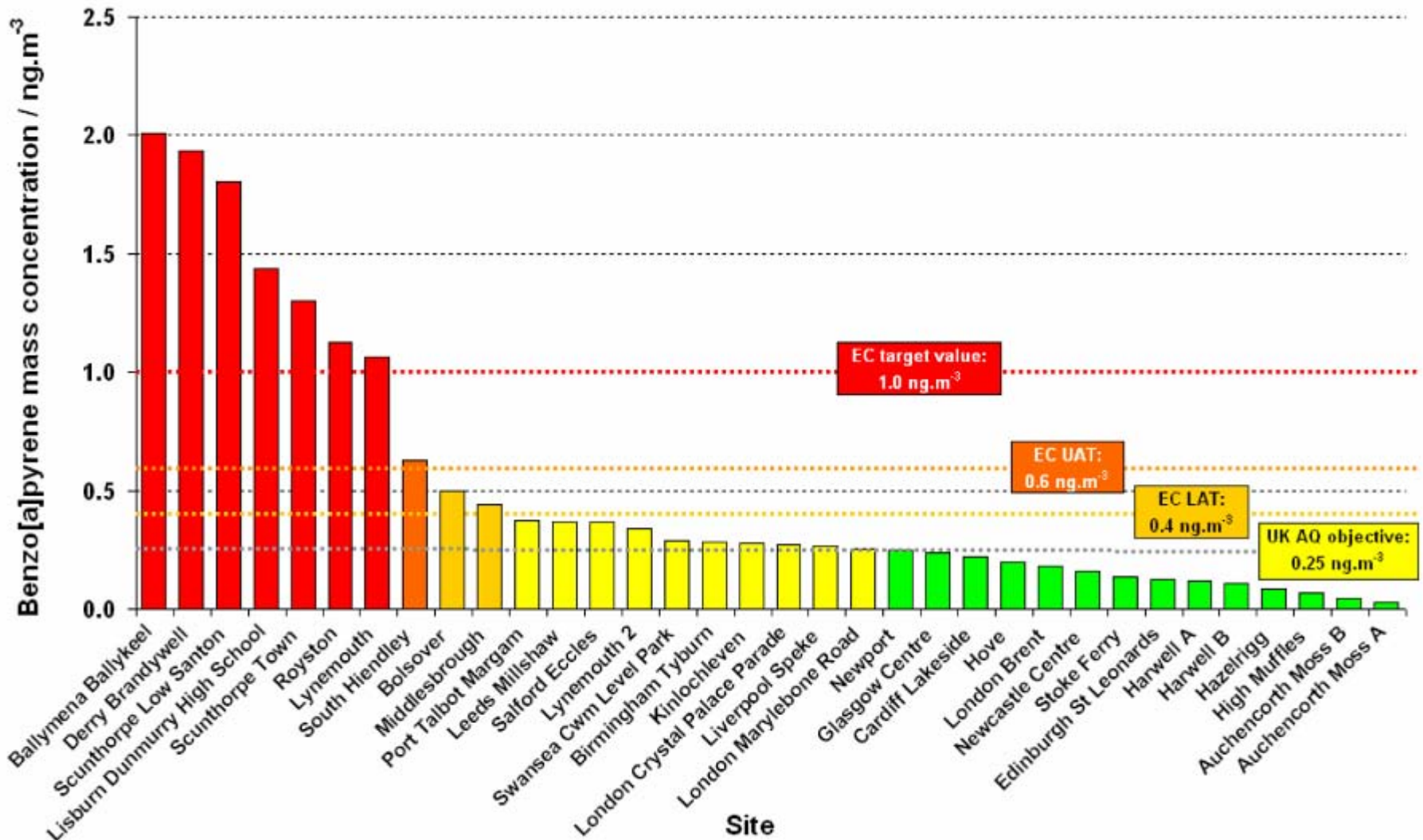


Current concentrations (Metals) – 2011



- Despite the general trend of falling concentrations there are some monitoring stations with higher concentrations
- Metals processing and refining industries

Current concentrations (B[a]P) – 2010

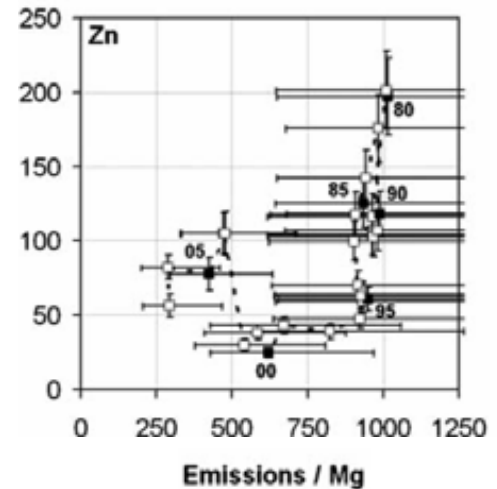
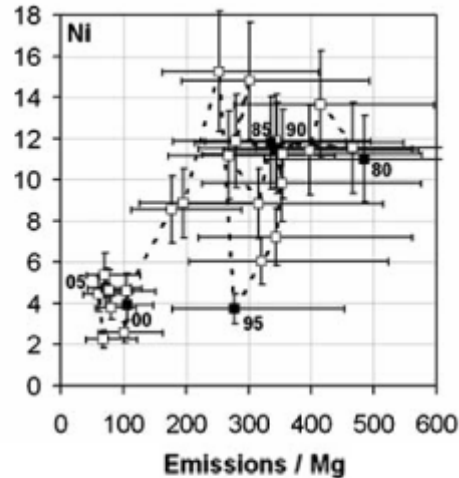
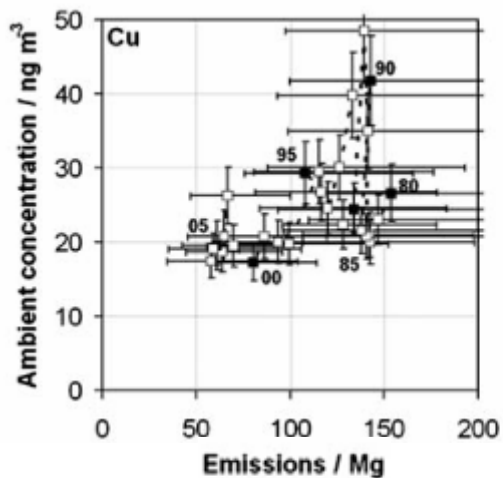
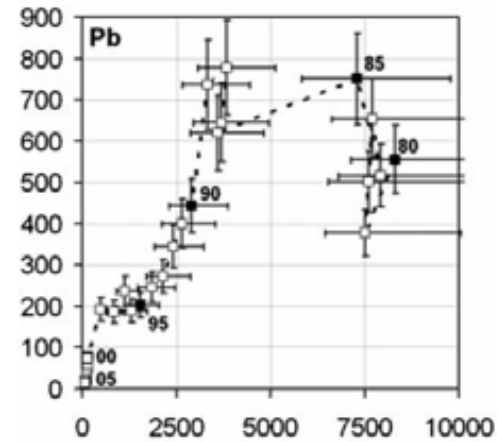
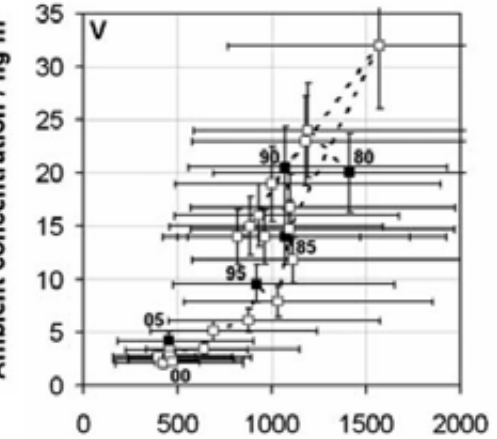
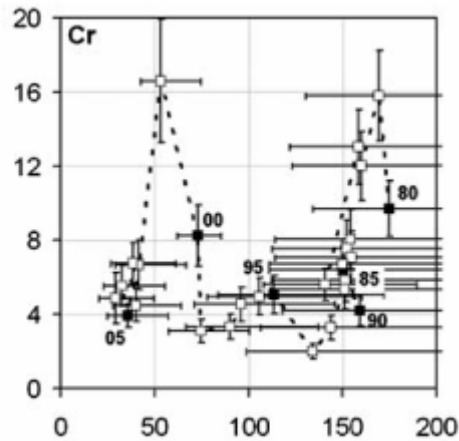
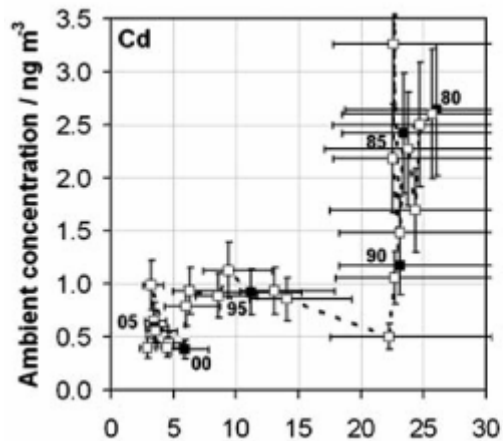


- Oil refineries, coke works and Northern Irish solid fuel use

The future...

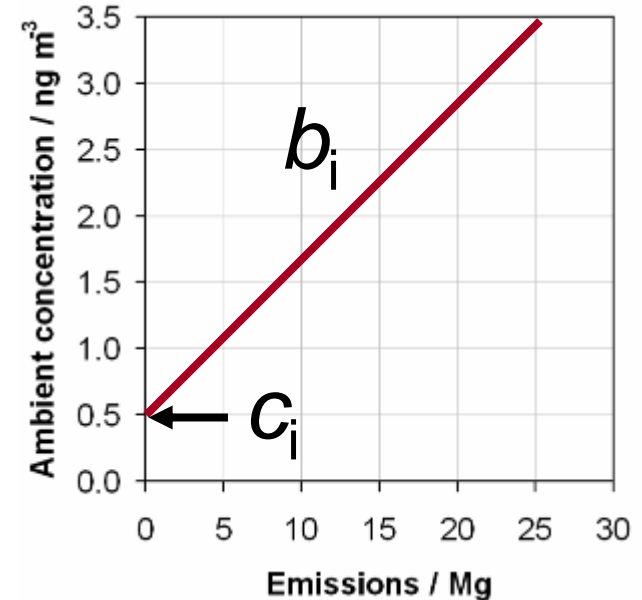
- There are still some 4th DD compliance issues to be addressed in the UK: activities already in place
- Extensive monitoring is still required to assess these concentrations (and to calibrate modelling – emissions inventories alone are not good enough)
- Revisions to Directives are forthcoming; in this context:
 - What might happen to concentrations in the future?
 - Could/should we use different analytical techniques?
 - Can we add more value to the data sets produced?
 - Should we perform extra Hg monitoring in urban areas?

Regression of ambient concentrations against emissions – Metals



Results

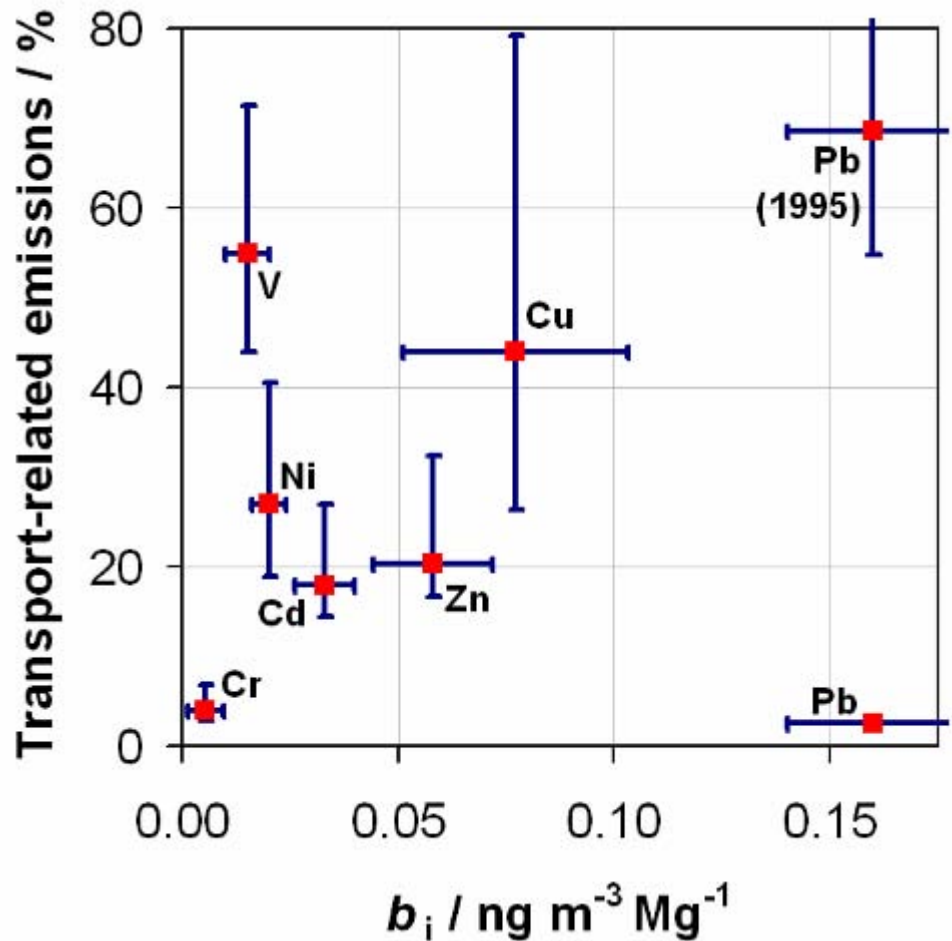
Metal	$b_i / \text{ng m}^{-3} \text{ Mg}^{-1}$	$c_i / \text{ng m}^{-3}$	c_i as percentage of 2007 ambient concentration (%)
Cd	0.033 ± 0.007	0.37 ± 0.06	78–107
Cr	0.0054 ± 0.0041	4.0 ± 0.5	72–92
Cu	0.077 ± 0.026	14 ± 3	63–97
Ni	0.020 ± 0.004	1.8 ± 0.5	34–61
Pb	0.16 ± 0.02	11 ± 3	53–93
V	0.015 ± 0.005	-4.4 ± 2.8	N/A
Zn	0.058 ± 0.014	11 ± 10	2–37



- c_i is an indication of the concentration in the absence of emissions (owing to re-suspension, natural emissions etc) – and shows how much lower concentrations may go. V is an outlier
- b_i is an indication of the sensitivity of ambient concentration to emissions
- Why does the range of b_i range between 6 and 185 $\text{Mg}/(\text{ng m}^{-3})$
- Too much to be explained by differences in the proportion of emissions in the PM_{10} fraction
- Related to balance of emissions between point and diffuse sources

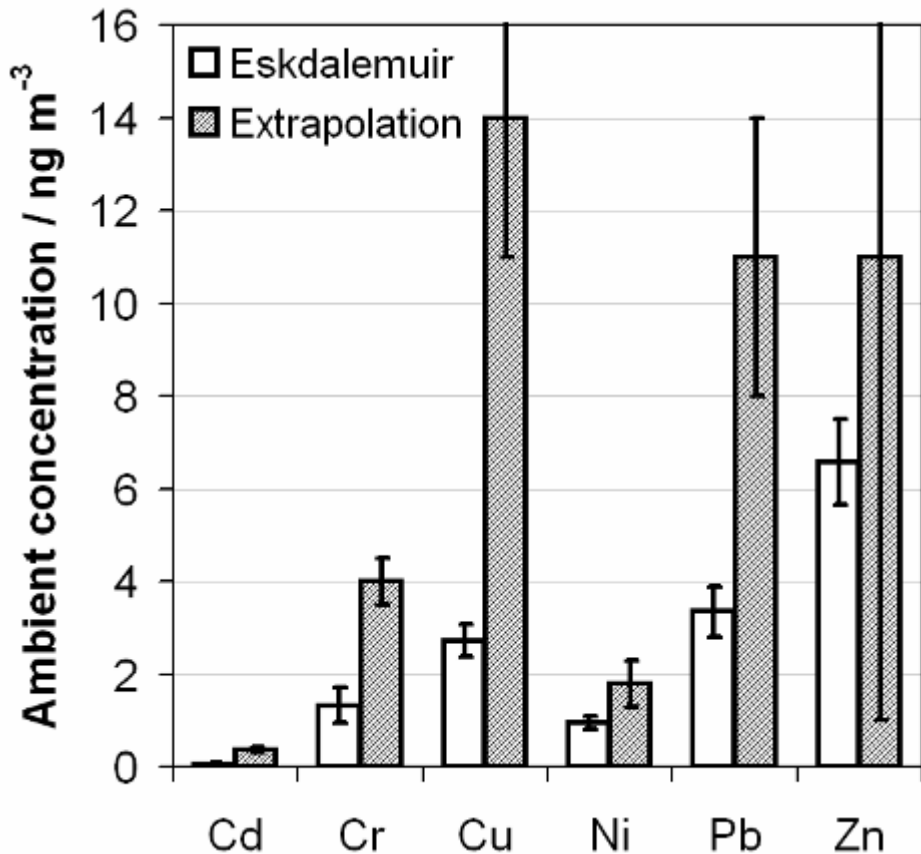
Correlation of sensitivity with diffuse sources

- Percentage of transport related emissions a surrogate for diffuse emissions
- Almost all sites close to roads / transport sources
- Therefore as % transport emissions go up so does the sensitivity
- Metals generally emitted from point source sites which impact on few sites
- V again somewhat of an outlier
- Are emissions estimates correct for V?

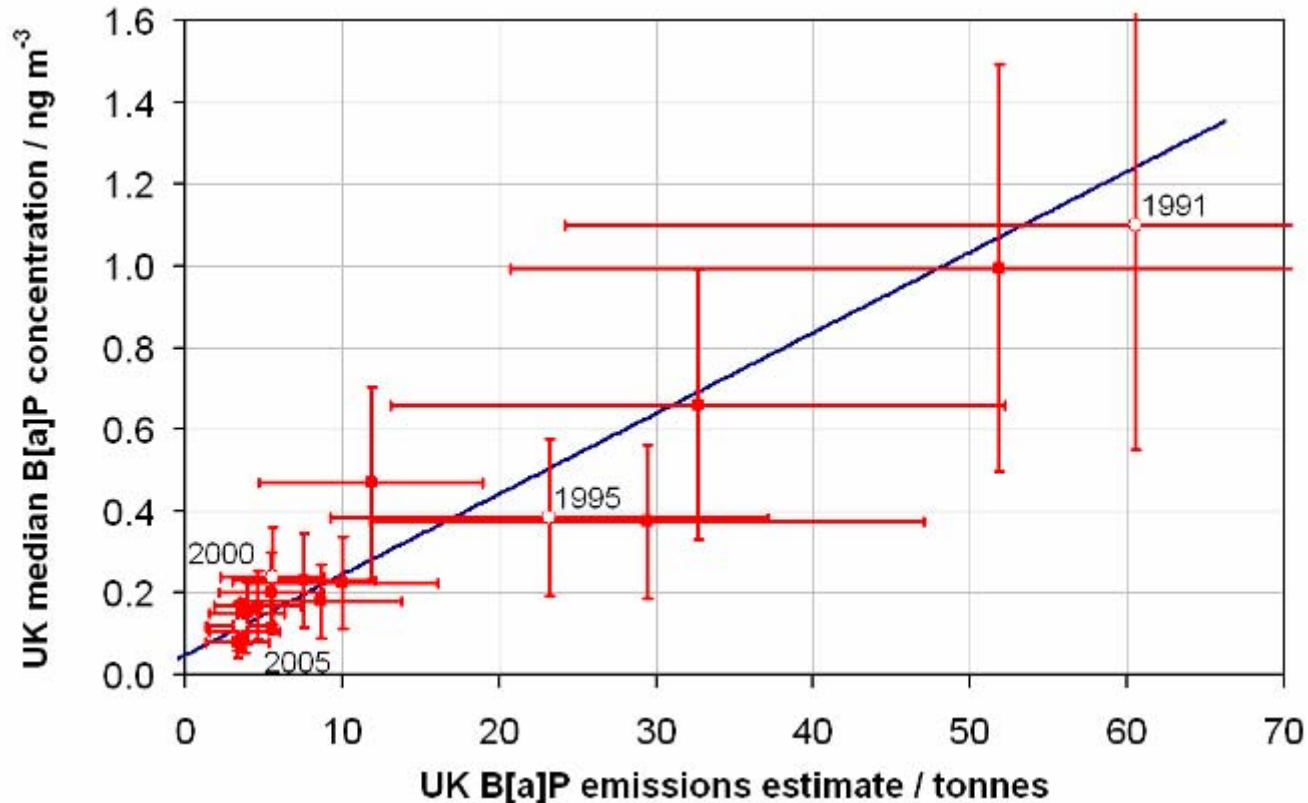


The case of no (or few) local emissions

- Extrapolated value of concentration in absence of emission benchmarked against Eskdalemuir (rural background site)
- Reasonable agreement given Eskdalemuir is only an approximation – no local re-suspension e.g. of Cu and Zn from car, road furniture wear
- Within factor of 2 for Ni and Zn and 5 for other metals



Regression analysis for B[a]P



- Extrapolation predicts intercept of 0.05 ng m⁻³
- Sensitivity 0.02 ng m⁻³ t⁻¹
- B[a]P emissions from natural sources, estimated by the NAEI as 2.88 tonnes per year

- This would represent a contribution to UK ambient air by natural sources of 0.06 ng m⁻³ – very close to the level predicted by this extrapolation.

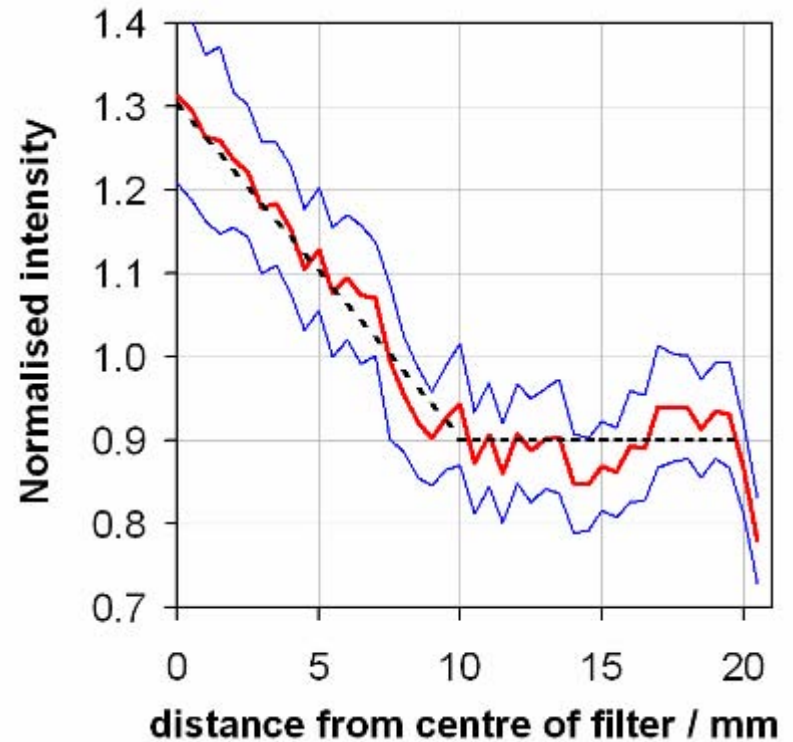
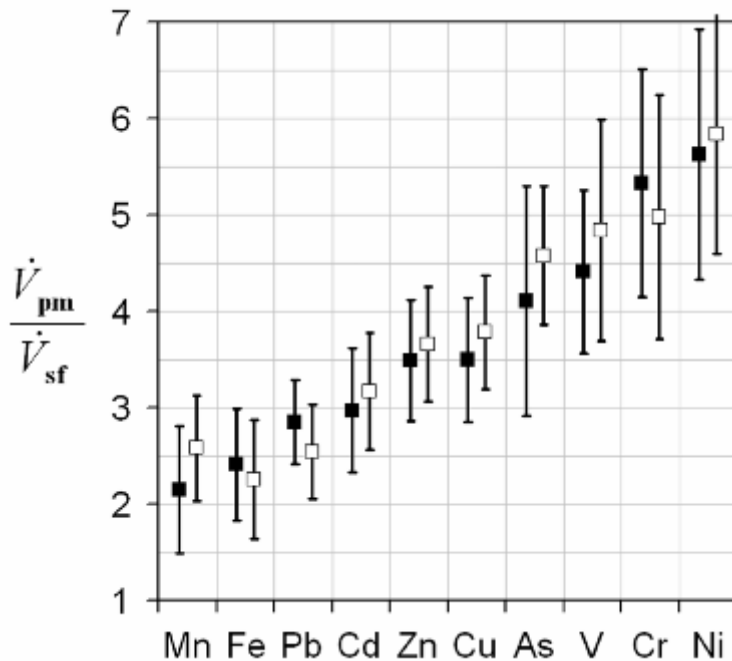
Alternative analytical methods – metals ?

- Concentrations are low and decreasing
- **Pressure on budgets is increasing**
- Should we be thinking about using different analytical techniques?
- **EN14902 for metals analysis uses GF-AAS or ICP-MS**
- Possible alternatives (if equivalence was proven):
 - LA-ICP-MS
 - ED-XRF



LA-ICP-MS

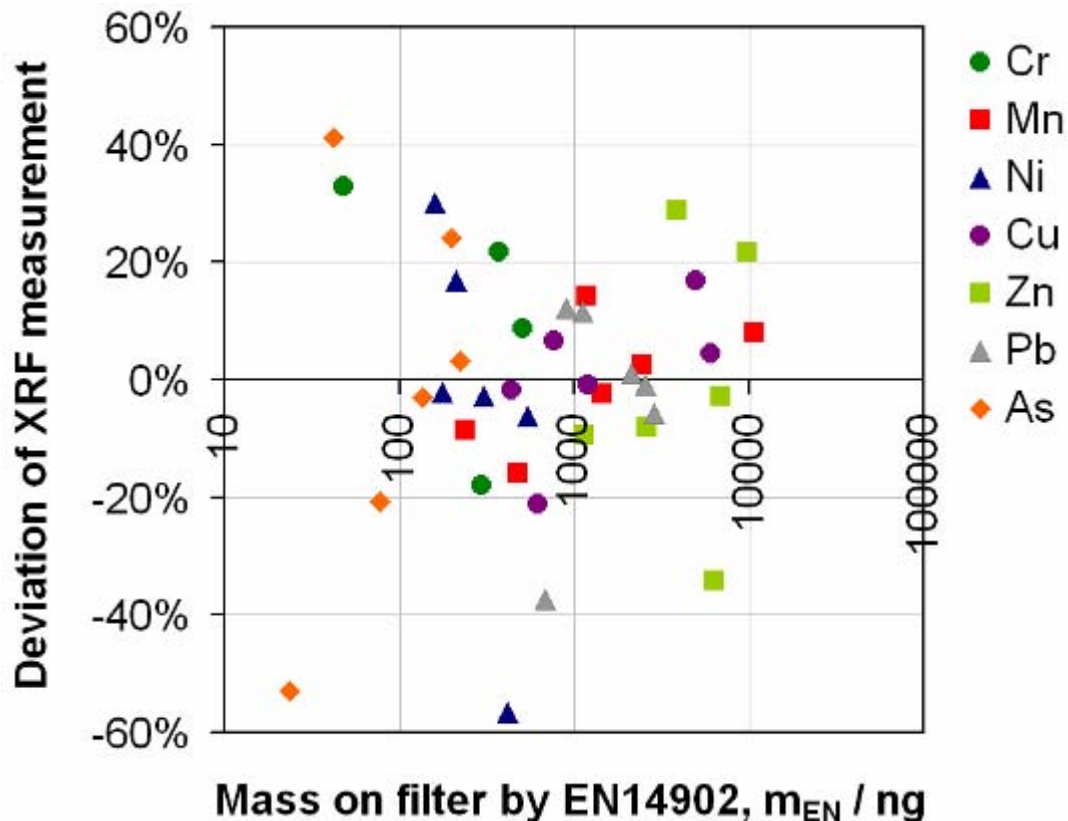
- Advantages
 - high throughput, cheaper
 - no solution pre-processing
 - spatial profiling
 - low bias wrt EN14902



- Disadvantages
 - sampling bias possible
 - detection limits not as good
 - elemental fractionation on ablation
 - calibration challenging
 - traceability to EN14902
 - worse precision than ICP-MS

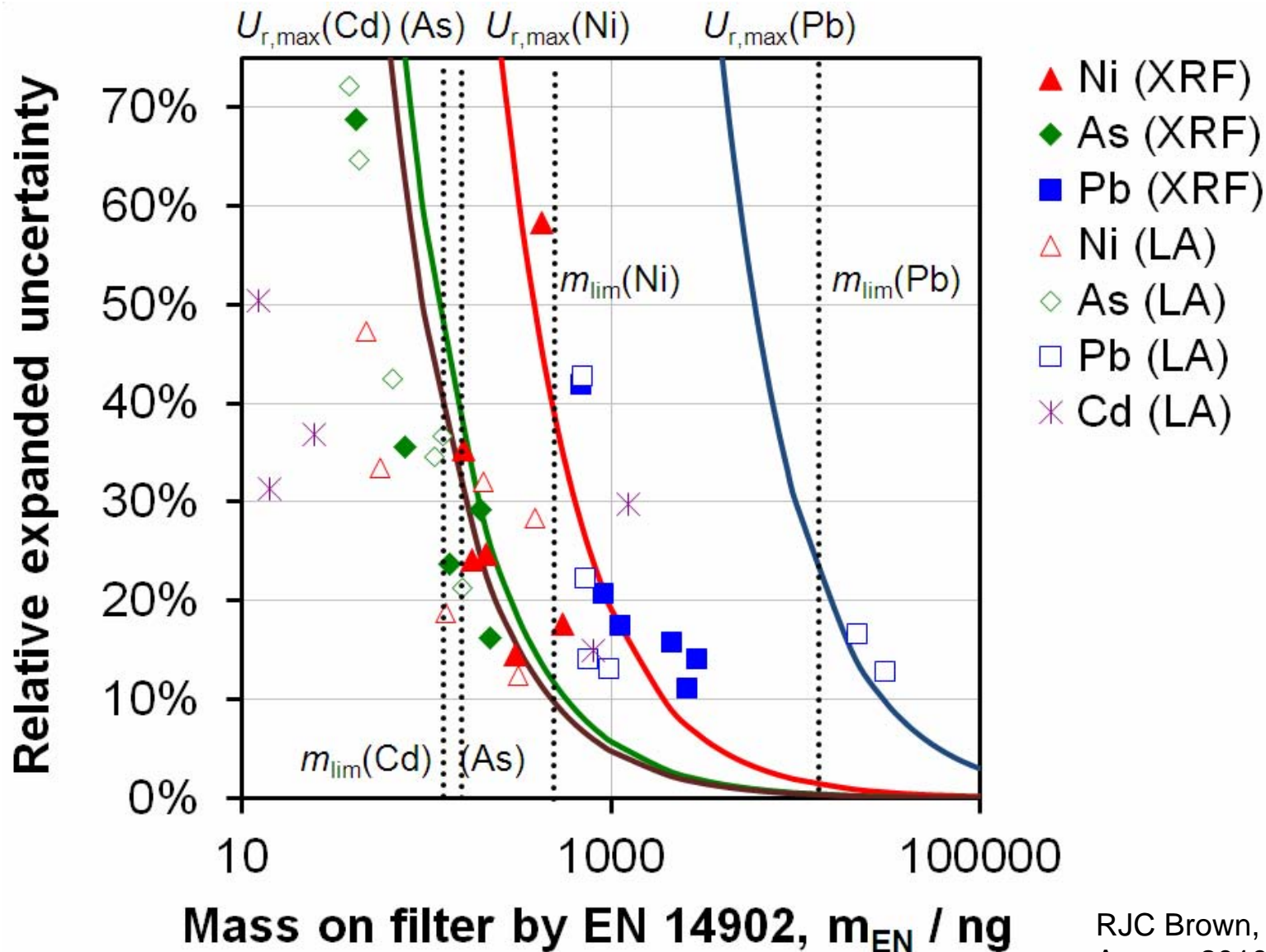
ED-XRF

Technique	Mean RAD (%)	Mean RAAD (%)
ED-XRF	-1.4	15
LA-ICP-MS	+0.4	12



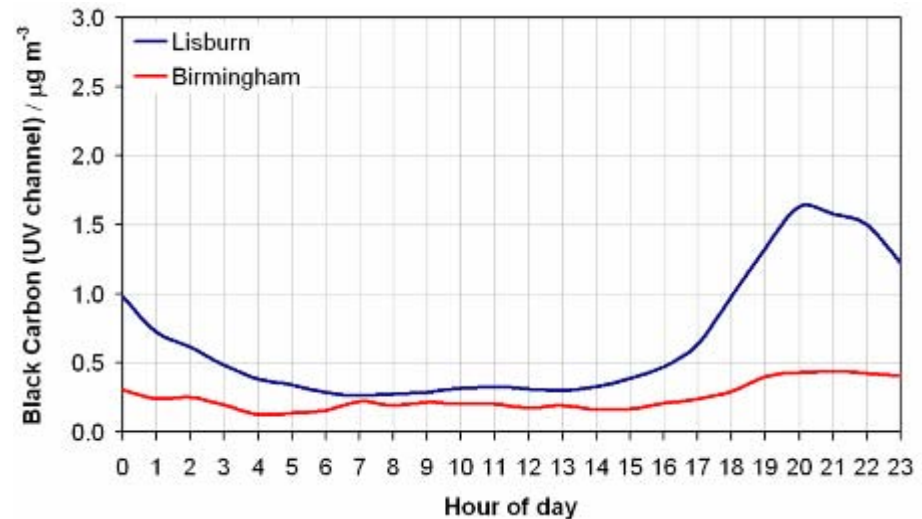
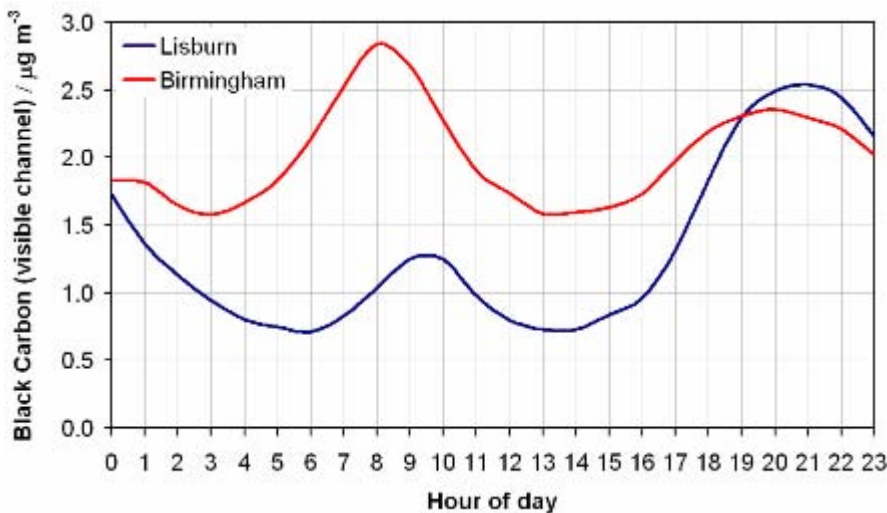
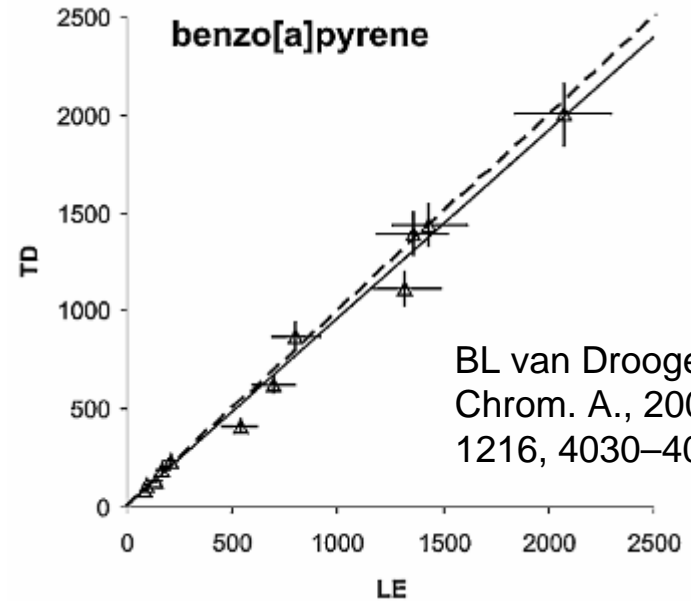
- Advantages
 - high throughput, cheaper
 - no solution pre-processing
 - non-destructive
 - low bias wrt EN14902
- Disadvantages
 - poor DLs for some elements, especially Cd
 - sampling bias possible
 - calibration challenging
 - traceability to EN14902
 - precision not as good as EN14902

Directive compliance with u/c DQOs



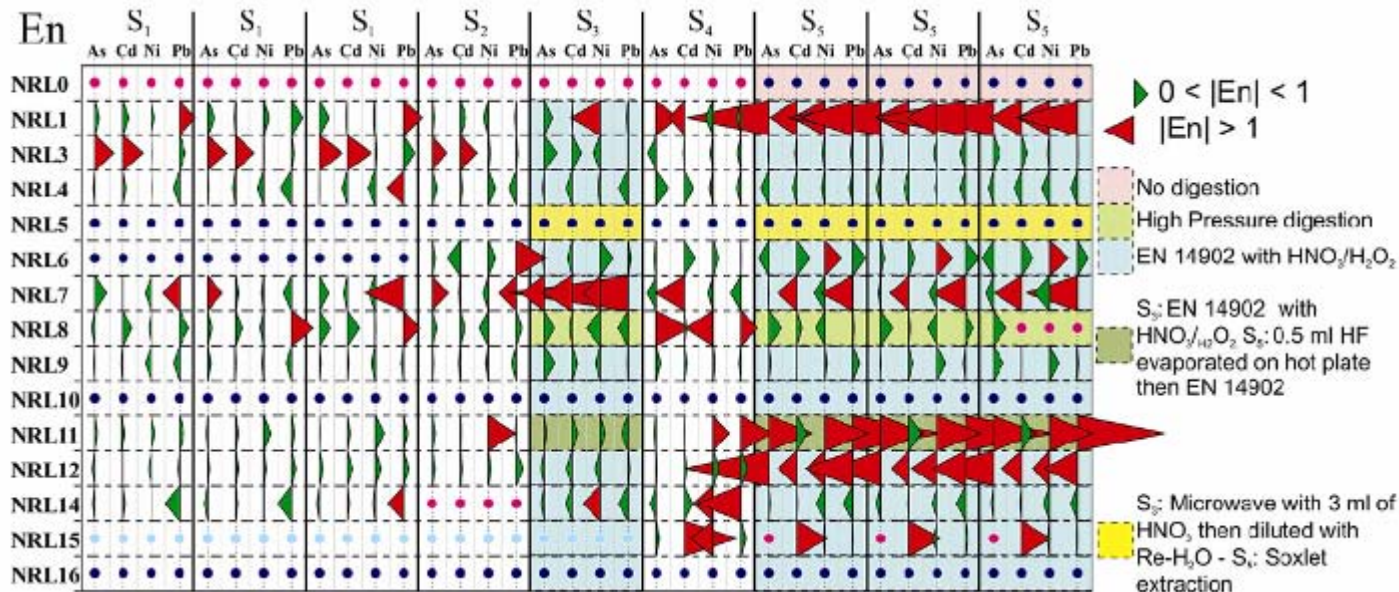
Alternative methods for PAHs?

- Successful use of thermal-desorption rather than liquid extraction methods
- Not as much scope for radically different methods
- Multi-wavelength aethalometry as a cheap assessment method



Should we be considering these techniques?

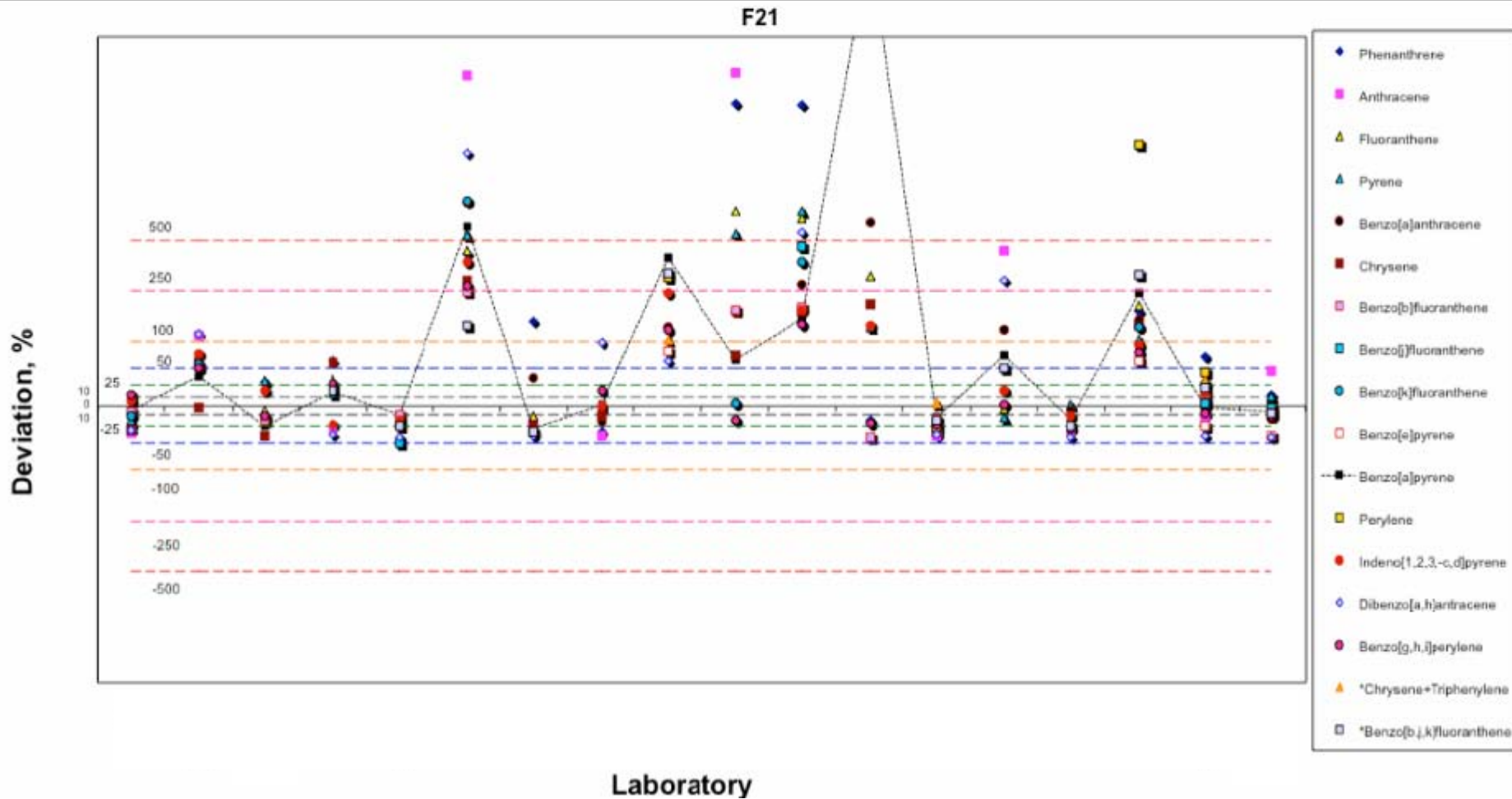
- Alternative metals analysis techniques are not independent and SI traceable calibration strategies are not available
- Measurement equations are not always fully understood
- Equivalence would need to be proven in any case
- Concentrate on getting the existing reference methods right first, and estimating uncertainties correctly!



M Gerboles, *et al*,
Atmos. Env., 2011,
45, 3488-3499

PAHs...

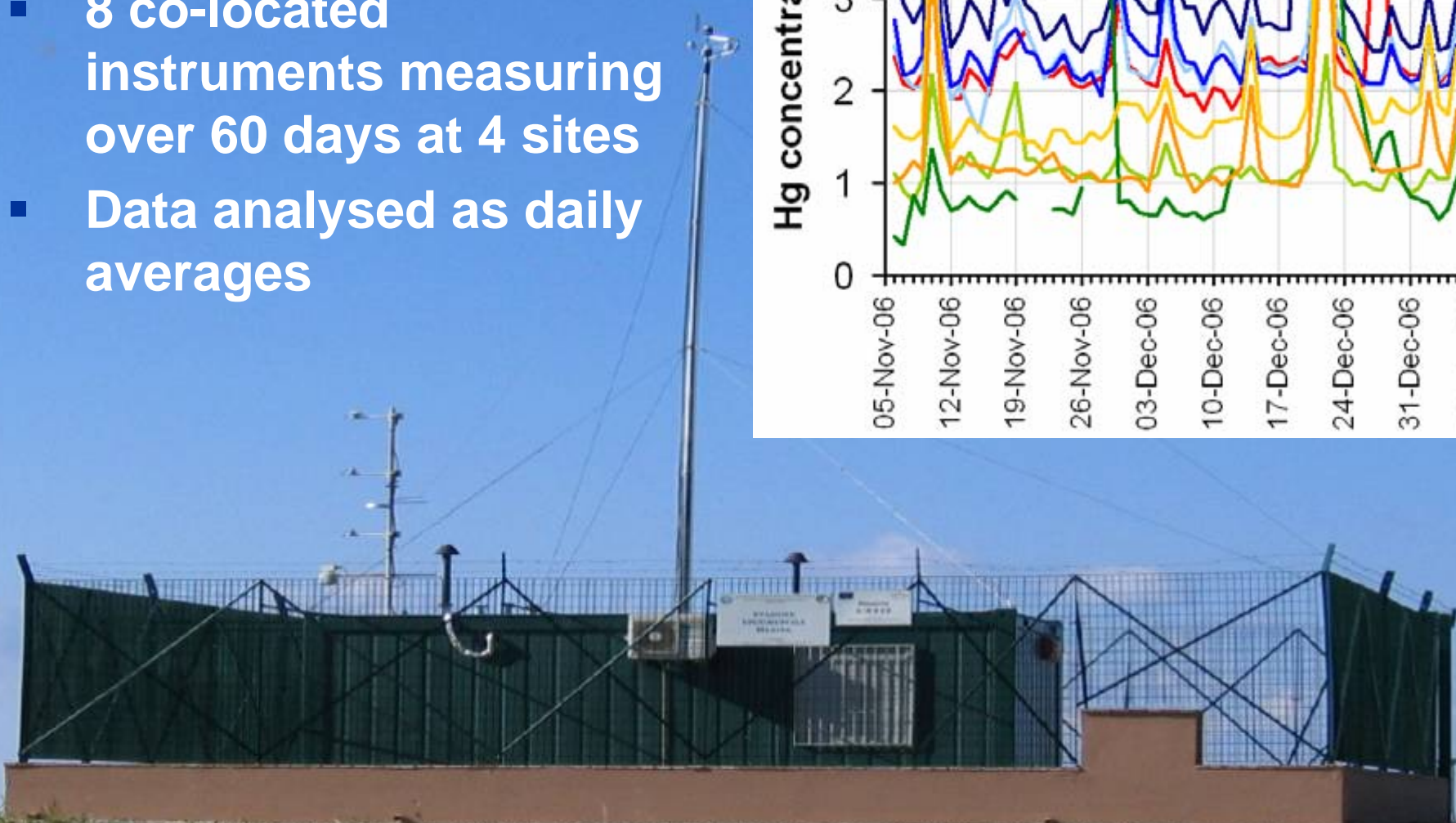
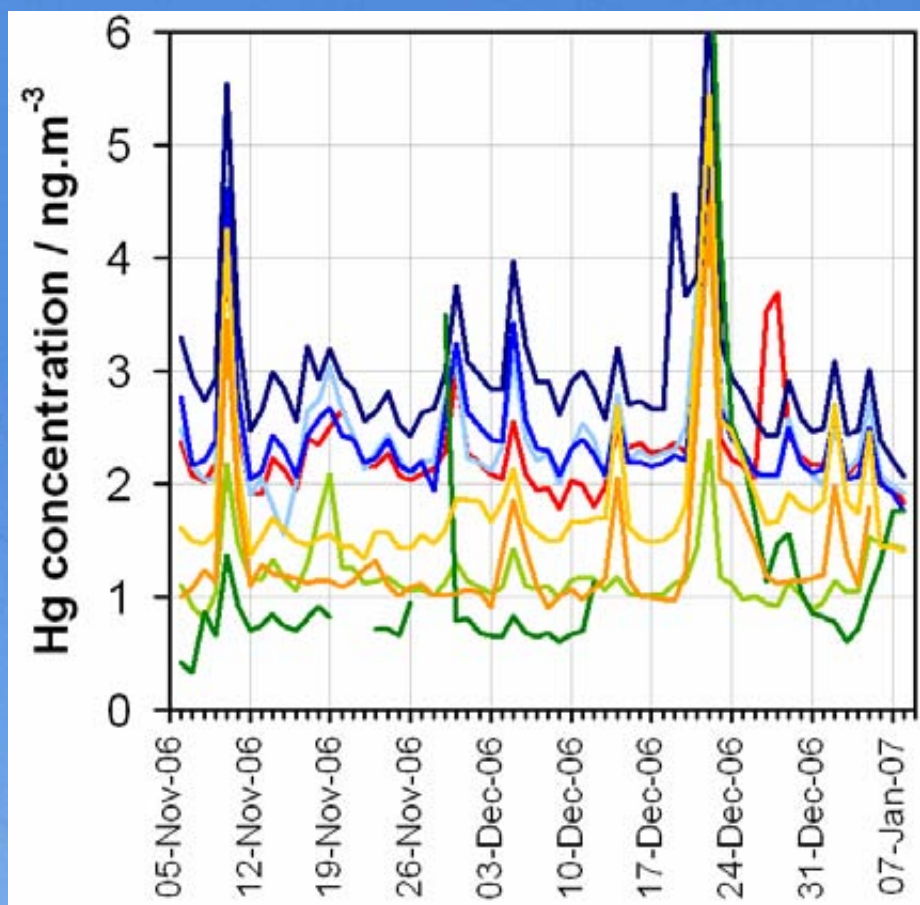
PRAGUE SUMMER 16 PAH= 1.15 ng/m³, 62 pg/m³ of BaP, Sampled Volume= 46.5 m³



Courtesy of AQUILA

CEN TC264 WG25 – Hg in ambient air

- 8 co-located instruments measuring over 60 days at 4 sites
- Data analysed as daily averages

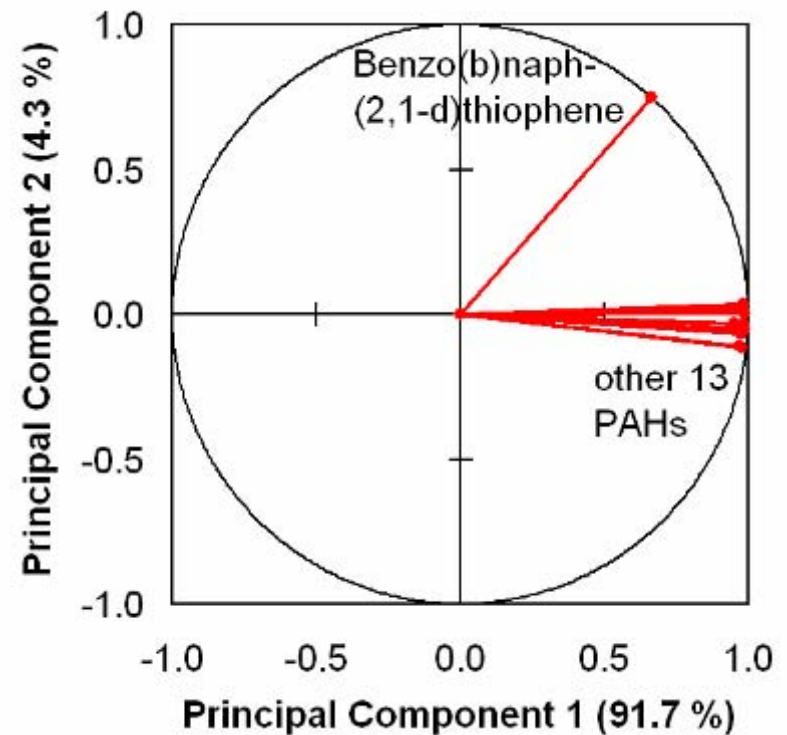
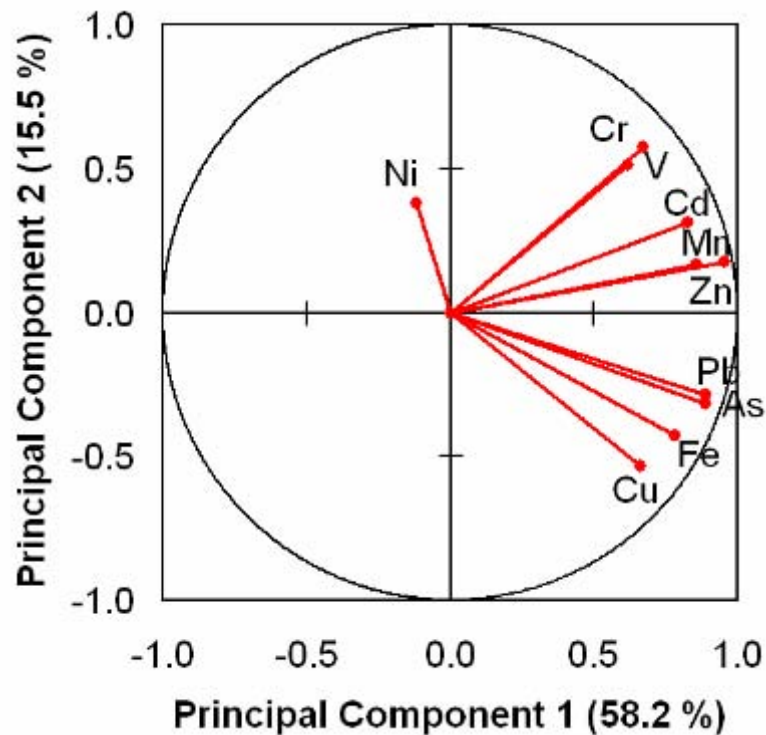


Added value from data sets

- Measurements of PAHs and metals produce multivariate data sets, i.e. multiple species for each sampling period at each location
- Provides a good opportunity to use techniques such as principal component analysis
- The outputs can be used for
 - source apportionment – helping to ensure site numbers and locations are appropriate
 - data ratification – spotting outliers and data worth of further investigation

2010		Concentration ng m ⁻³											
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg(p)
Walsall													
46	Jan	0.02	0.34	1.19	1.5	159	2.9	0.60	13.5	0.030	1.07	24.6	0.016
Walsall Centre (Wa	Feb	1.04	0.27	0.05	12.4	325	9.4	1.54	16.4	0.001	1.43	52.2	0.015
	Mar	1.01	0.47	1.92	13.3	405	17.0	1.34	16.7	0.000	1.90	44.2	0.025
	Apr	1.00	0.46	3.74	14.4	522	15.2	1.52	13.4	0.000	1.74	59.5	0.024
	May	0.76	0.23	2.29	10.1	200	7.6	0.50	9.9	0.000	0.73	29.0	0.021
	Jun	0.60	0.20	2.34	12.2	290	6.5	0.50	10.9	0.001	1.27	31.1	0.014
	Jul	0.47	0.23	3.65	12.9	352	12.5	0.93	12.4	0.001	0.50	57.3	0.015
	Aug	0.35	0.31	2.41	15.4	253	7.3	1.62	10.1	0.001	0.68	51.2	0.020
	Sep	1.19	0.24	2.97	14.2	374	12.2	1.47	15.4	0.001	0.95	72.9	0.025
	Oct	1.52	0.74	3.50	16.3	397	12.1	2.41	19.4	0.000	1.15	63.4	0.045
	Nov	1.67	0.77	2.46	25.7	326	9.0	1.30	22.4	0.000	1.32	76.3	0.072
	Dec	0.60	0.23	0.51	4.2	504	2.9	0.21	9.6	0.000	0.80	22.9	0.015
	Annual Average	0.92	0.33	2.46	12.9	320	9.8	1.10	14.4	0.001	1.16	53.0	0.025
Aronmouth													
47	Jan	0.79	0.21	0.95	5.1	249	4.3	1.11	10.5	0.000	1.75	36.6	0.095
Bristol Aronmouth	Feb	0.63	0.20	0.81	5.4	205	4.3	1.33	10.3	0.001	1.96	24.6	0.021
	Mar	0.56	0.53	0.25	5.6	300	6.2	0.59	12.6	0.000	2.15	35.1	0.032
	Apr	0.47	0.34	4.05	7.5	467	10.6	1.64	10.2	0.000	2.46	45.7	0.049
	May	0.64	0.75	2.32	7.0	344	8.3	1.05	14.1	0.000	2.04	40.9	0.046
	Jun	0.55	0.51	1.05	5.3	305	9.4	1.10	16.1	0.001	2.43	41.2	0.027
	Jul	0.11	0.08	1.62	2.5	199	4.9	0.72	4.4	0.002	1.56	16.9	0.020
	Aug	0.32	0.15	2.55	3.6	237	5.4	0.55	6.6	0.000	0.93	27.2	0.013
	Sep	0.58	0.19	2.15	5.5	273	5.7	1.08	7.5	0.000	1.40	27.3	0.016
	Oct	0.21	0.19	1.54	5.2	240	7.4	1.03	9.6	0.000	1.20	20.2	0.017
	Nov	1.02	0.19	0.73	7.7	231	4.3	0.41	11.5	0.000	1.33	27.5	0.022
	Dec	1.06	0.24	0.67	5.3	151	4.1	1.74	10.0	0.000	3.54	22.1	0.015
	Annual Average	0.69	0.25	1.47	5.5	283	6.2	1.10	11.0	0.000	1.92	30.6	0.022
Hallen													
56	Jan	0.77	0.20	0.50	5.2	163	2.1	0.51	9.2	0.000	1.21	22.2	0.072
Bristol Hallen (Hall	Feb	0.59	0.19	0.50	4.7	133	2.4	0.57	7.7	0.001	1.14	11.3	0.012
	Mar	0.55	0.39	0.36	5.7	206	4.3	0.73	9.7	0.000	1.75	25.5	0.022
	Apr	0.42	0.30	1.97	6.1	270	6.2	0.77	9.4	0.000	1.79	17.9	0.020
	May	0.73	0.47	0.80	4.3	206	4.7	0.29	8.4	0.000	1.10	22.4	0.024
	Jun	0.41	0.24	1.22	4.9	224	5.6	0.52	9.2	0.001	1.54	22.9	0.011
	Jul	0.31	0.24	1.33	3.9	174	3.8	0.46	4.5	0.000	0.38	21.2	0.012
	Aug	0.34	0.23	1.49	4.1	132	2.5	0.25	4.2	0.000	0.40	11.0	0.012
	Sep	0.45	0.16	1.55	5.5	197	2.3	0.64	5.1	0.001	1.00	14.0	0.016
	Oct	0.72	0.19	0.64	6.4	157	3.3	0.76	6.4	0.000	0.36	14.1	0.017
	Nov	1.05	0.22	0.59	6.6	179	3.2	0.57	10.3	0.000	0.70	57.9	0.024
	Dec	1.07	0.22	0.35	6.7	159	2.3	0.67	10.0	0.000	1.33	10.4	0.024
	Annual Average	0.67	0.26	0.93	5.5	185	3.4	0.58	8.0	0.000	1.14	19.9	0.024
Brisworth													
58	Jan	1.09	0.26	15.17	53.3	354	16.3	11.44	16.7	0.007	1.65	221.4	0.021
Sheffield Brisworth	Feb	1.41	0.46	23.26	29.6	450	24.0	8.19	32.4	0.002	2.24	50.3	0.047
	Mar	1.57	0.43	43.27	28.0	770	46.8	19.24	24.1	0.002	2.50	105.3	0.051
	Apr	1.27	0.73	22.99	29.3	764	29.0	10.10	23.0	0.000	2.22	75.5	0.051
	May	0.16	0.27	39.43	23.3	533	24.4	15.14	17.3	0.002	1.35	11.7	0.049
	Jun	0.61	0.30	29.10	16.4	429	21.9	0.67	15.0	0.003	1.75	64.1	0.041
	Jul	0.50	0.21	50.40	12.4	411	46.0	16.01	16.2	0.004	0.95	129.0	0.049

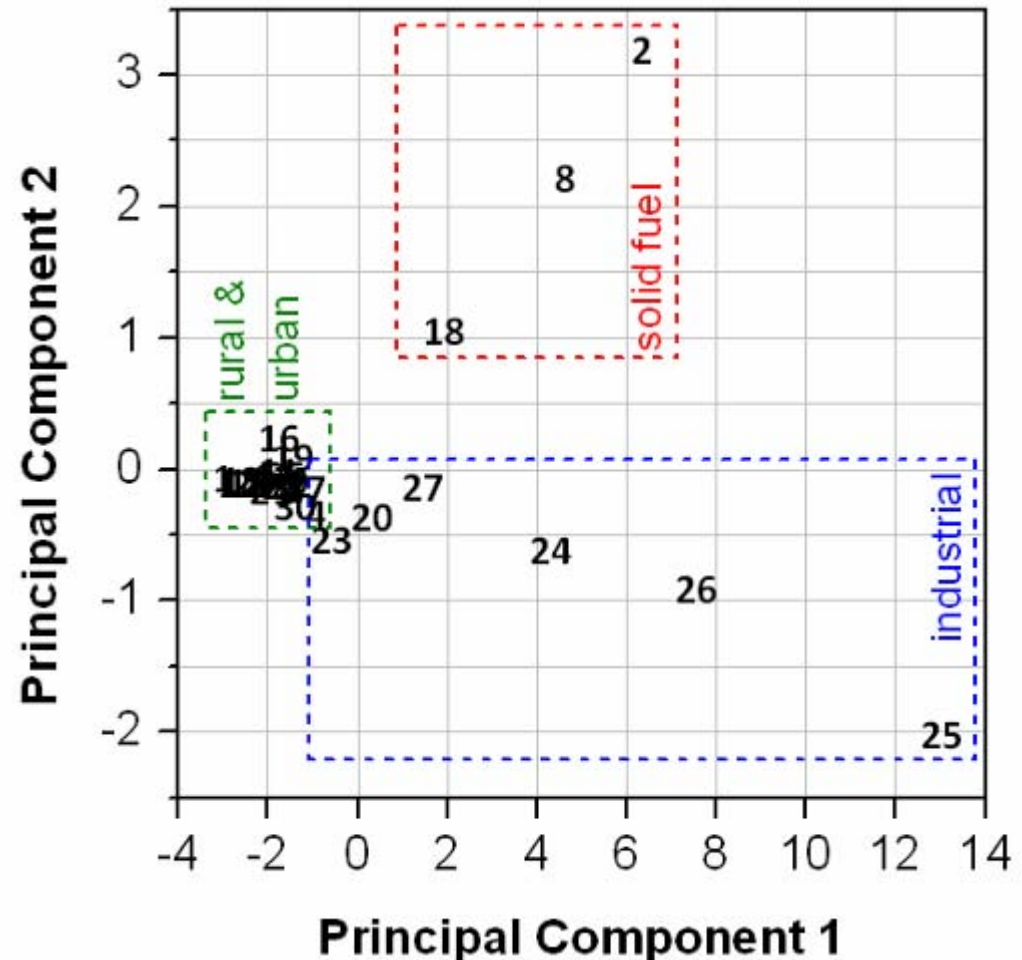
Correlations at single sites



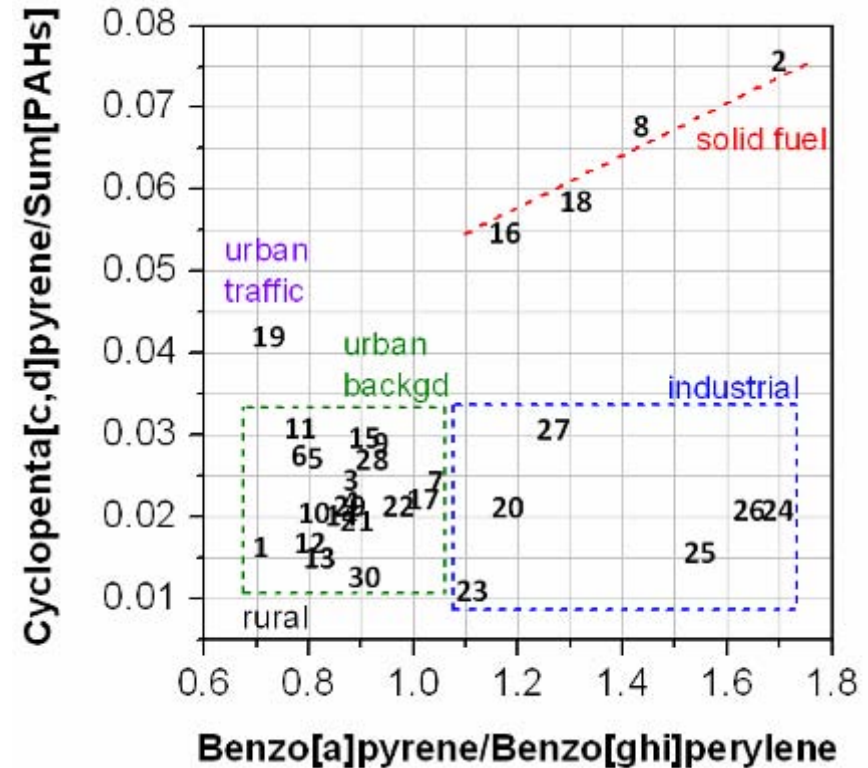
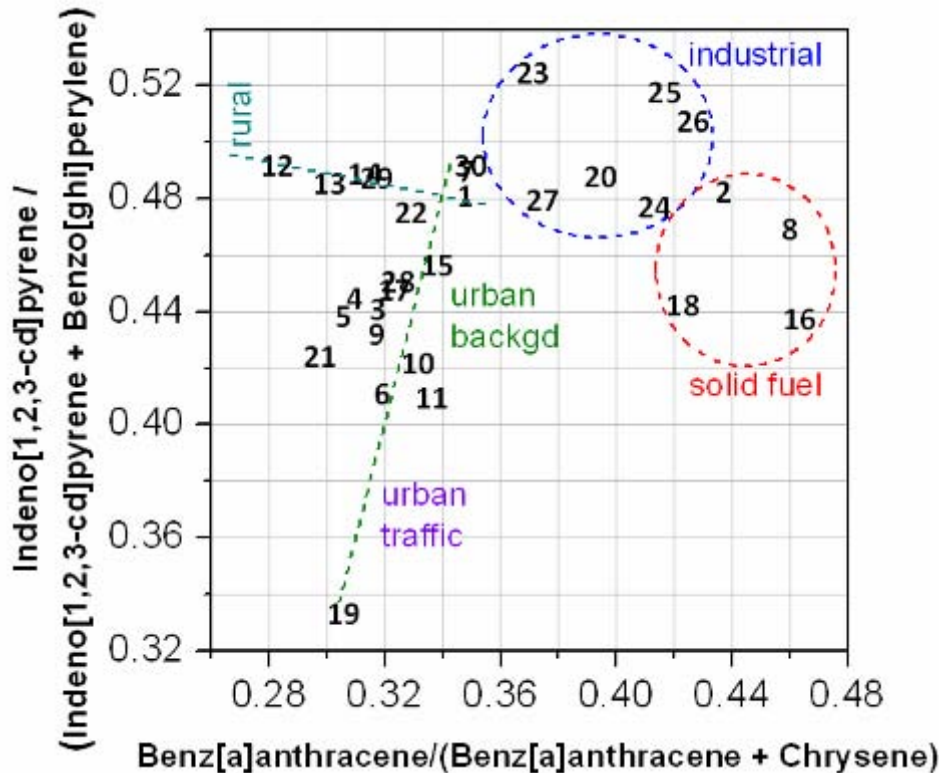
- Metals emitted from a variety of sources with different signatures
- Correlation (as here at London Cromwell Road) only partial
- PAH emitted from similar process with similar signatures
- Correlation (as here at Glasgow) very strong

Correlations across all sites

- For PAHs we can also look at the correlation pattern across all sites
- Comparison of sites in principal component space
- Delineates well between major contributing factors
- Not much detail within the urban & rural sources



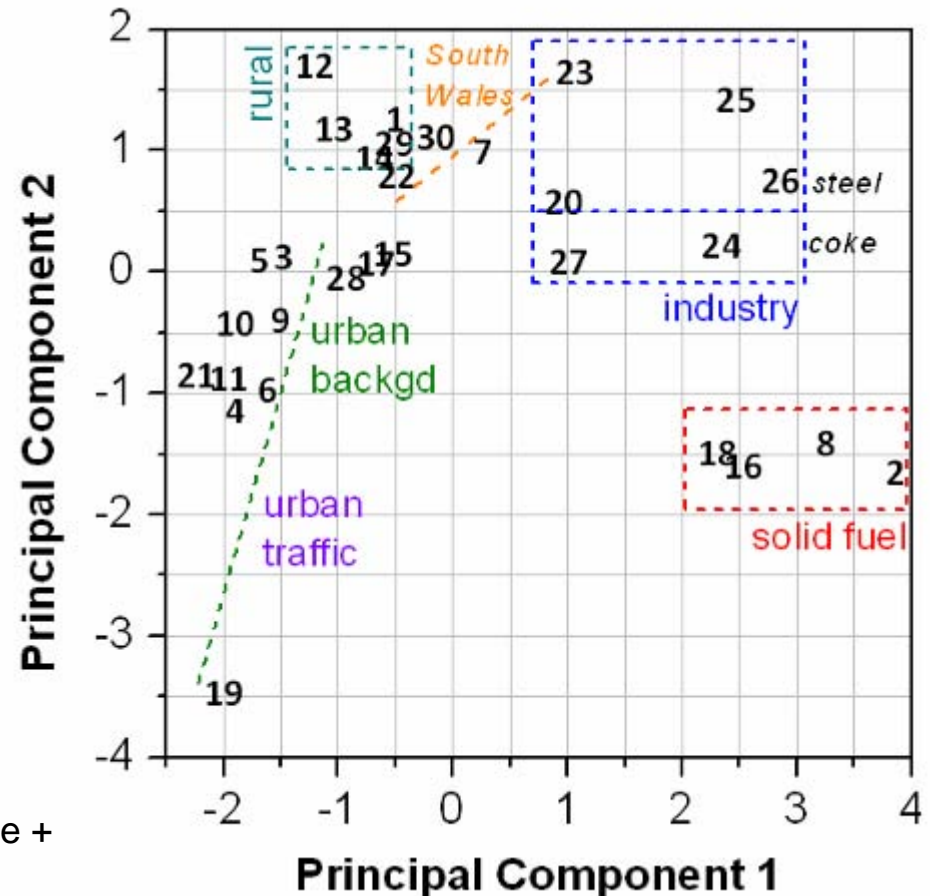
Use of diagnostic PAH ratios



- Diagnostic ratios are indicators of specific emissions processes
- Enables a greater separation of site characteristics
- Still only makes use of a few variables at once

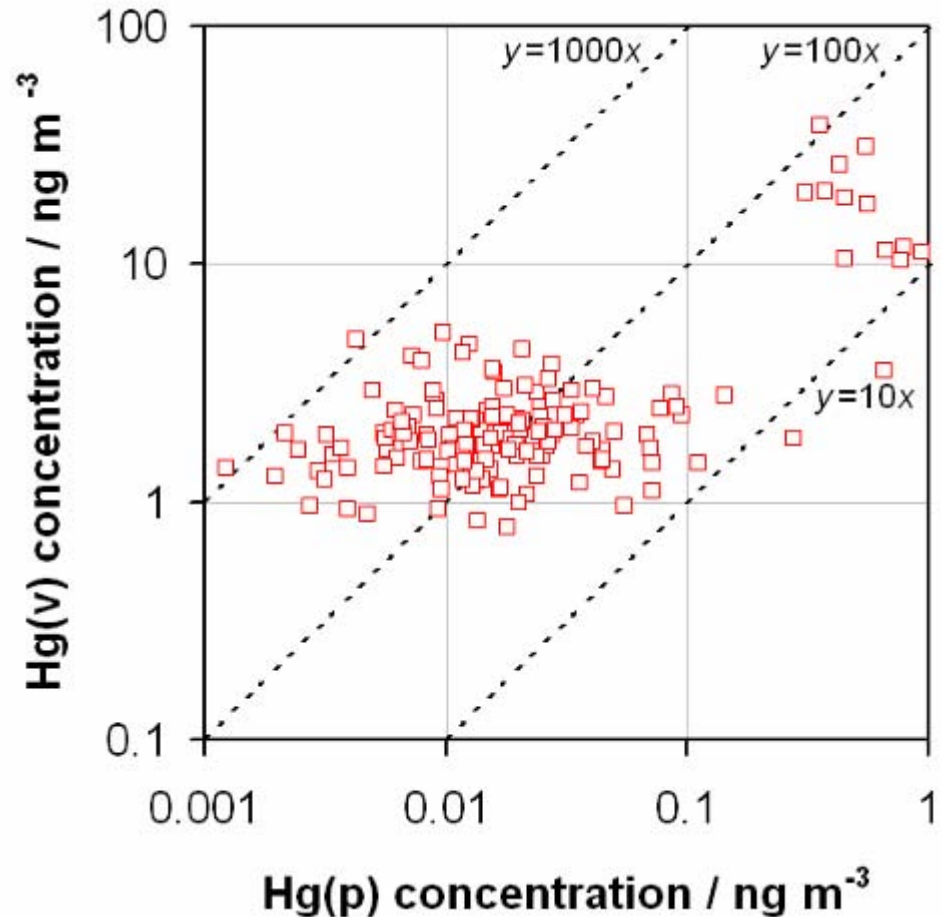
PCA of diagnostic ratios

- PCA on diagnostic ratios, rather than individual concentrations, yields the best results
 - Encompasses large quantity of variability and provides good site separation
 - Has elucidated separate 'South Wales' and 'Marylebone Road' PAH climates
- Benzo[a]anthracene / [benz[a]anthracene + chrysene]
 - Indeno[1,2,3-cd]pyrene / [indeno[1,2,3-cd]pyrene + benzo[ghi]perylene]
 - Benzo[a]pyrene / benzo[ghi]perylene
 - Coronene / sum of PAHs
 - Cyclopenta[c,d]pyrene / sum of PAHs
 - Benzo[b]naph(2,1-d)thiophene / benzo[a]pyrene



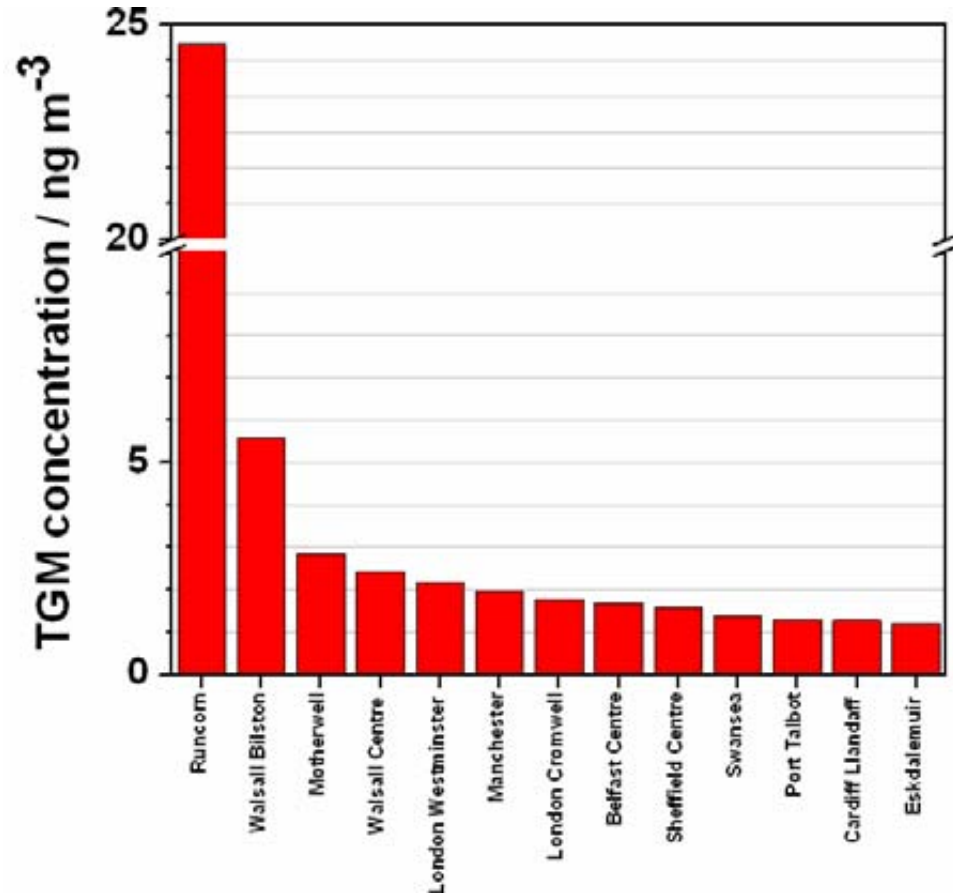
Mercury vapour

- Mercury vapour is the dominant Hg species in air
- Simplest species to measure with the most robust traceability
- Only required at background locations – because of its perceived role as long-range transport global pollutant with only ‘background’ UK concentrations
- However it is clear that some urban concentrations are significantly elevated: industrial processes, crematoria, contaminated land
- Do we need more urban monitoring?



Additional monitoring for Hg vapour

- Extra Hg measurement sites may not be same location as other air quality stations
- We might not be aware of all relevant sources – extensive initial surveys required?
- Patterns of mercury vapour relatively unknown in urban areas
- Cost-effective solutions required especially if monitoring is not at existing sites



Diffusive monitoring for Hg vapour

- Existing monitoring based on pumped adsorption tubes
- When capped at one end, may be used as diffusion tubes
- No power required
- Uses same analytical equipment as pumped monitoring
- Useful way to assess concentrations at many locations
- Permanent monitoring over longer timescales also possible



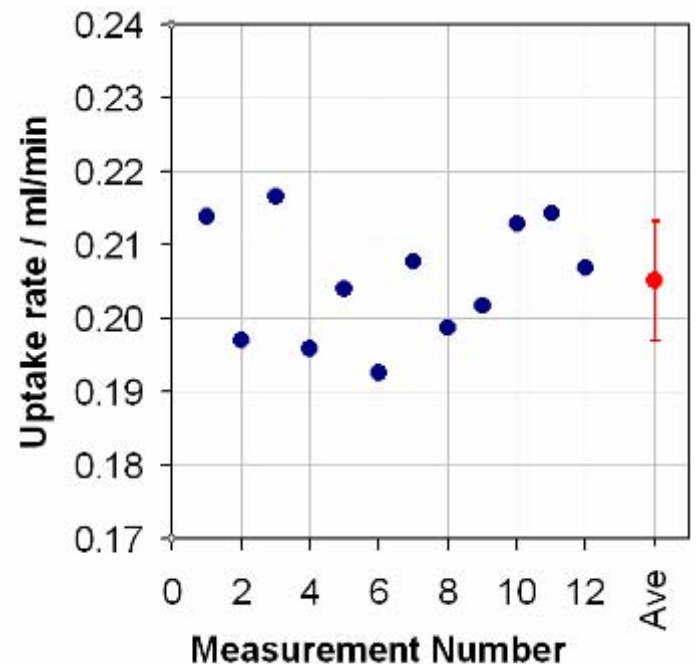
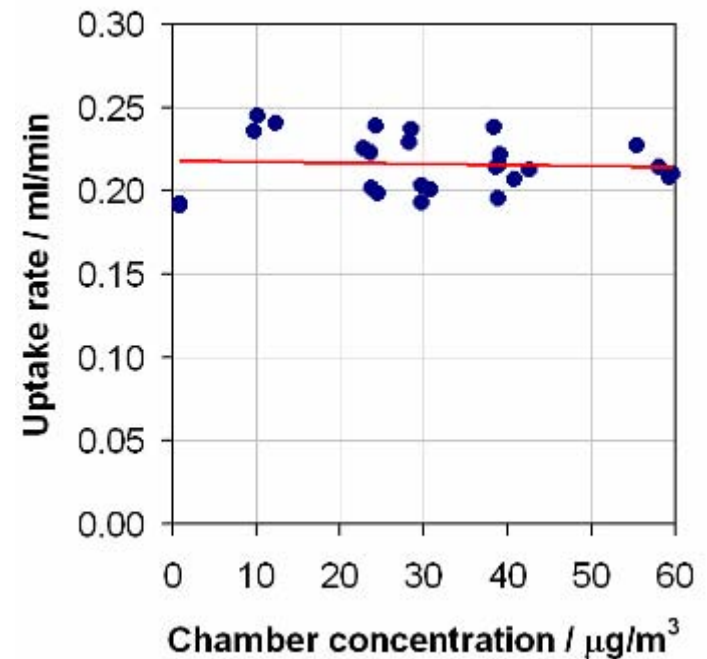
Uptake rates

- Uptake rate required prior to deployment in the field
- Since these tubes are not designed for diffusive monitoring they may have different uptake rates
- This parameter may be easily determined in a micro-exposure chamber
- Uses dynamic mercury vapour generation technology to generate atmospheres of known concentration
- Simple and quick enough to be done for individual tubes



Performance

- Very stable uptake rates over a range of concentrations
- Makes technique suitable for quick assessment of uptake rates for individual tubes
- Standard deviation of measurements on a single tube less than 5%
- More work required to assess performance in the field when exposed to wind *etc*



Summary

- Fixed measurement at multiple monitoring stations remains a key requirement to meet legislation
- Significant future effort should focus on improving existing measurements, not necessarily introducing new ones
- National networks should aim to add value to their measurements through novel data analysis techniques
- Cheaper, simpler techniques may allow more widespread monitoring for neglected pollutants such as TGM, especially in urban areas



Dr Richard Brown

e: richard.brown@npl.co.uk, t: 020 8943 6409

Metals & PAHs Network data & reports: uk-air.defra.gov.uk

