NPL
National Physical Laboratory

The L S Theobald Lecture:
Measuring airborne nanoparticles, and related topics

Richard Brown

RSC-NPL Symposium: Nanoparticle concentration – critical needs and state-of-the-art measurement

24 April 2018

Overview

- What is air quality about?
- Why measure (nano)particles in air?
- How is it done?
- What does this tell us?
- How do we know we can trust the results?

Acknowledgments

Department for Environment Food & Rural Affairs

Environment Agency

Department for Business, Energy & Industrial Strategy

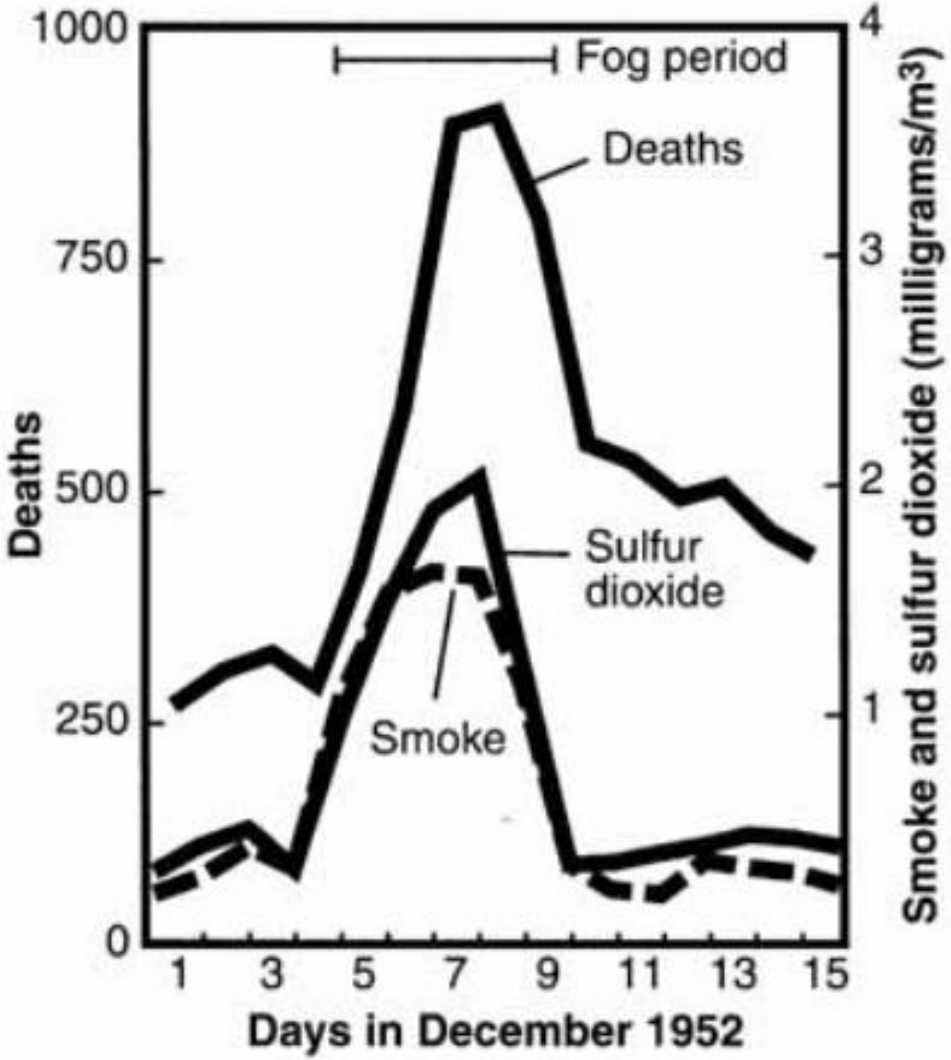
NPL National Physical Laboratory

Leslie Stuart Theobald (1898-1979)

- "…everyone was in awe of Theobald…on Fridays he made the students polish their benches."
- "…as having been kind to his demonstrators, and taking them to watch Wimbledon tennis matches, and to dinner afterwards in Kensington..."
- "Theobald was remembered…as strict and rigorous…duplicates has to agree to 1 part in 500 for volumetric analysis and 1 part in 1000 for gravimetric analysis."
- "…uncompromising in the quest for accuracy. Before one could start…**one had to calibrate the balance weights, the burette, the pipettes and calibrated flasks. These results would be checked against results obtained by previous students almost back to the dawn of time**."

Chemistry Department At Imperial College London, The: A History, 1845-2000
www.rsc.org/images/LS-Theobald_tcm18-212168.pdf

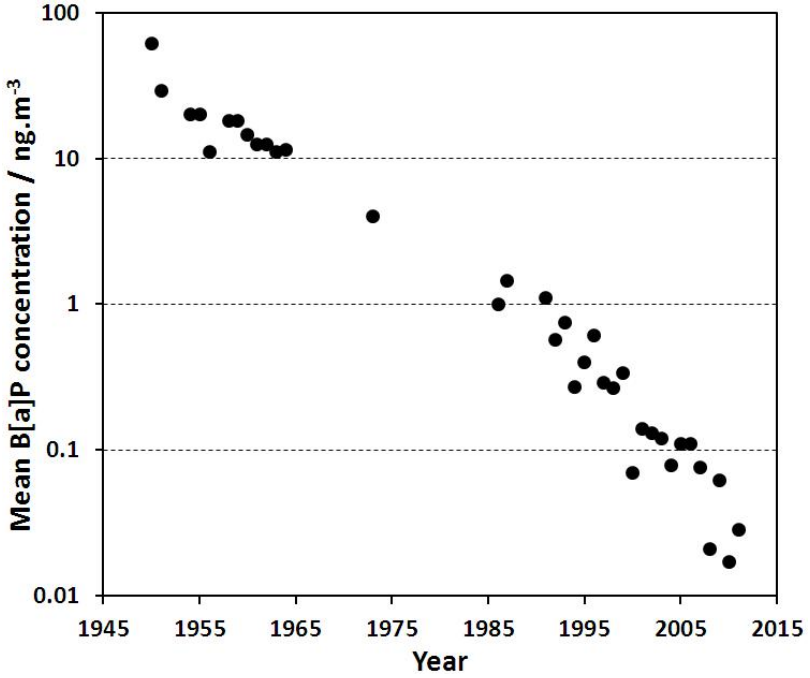
Air quality

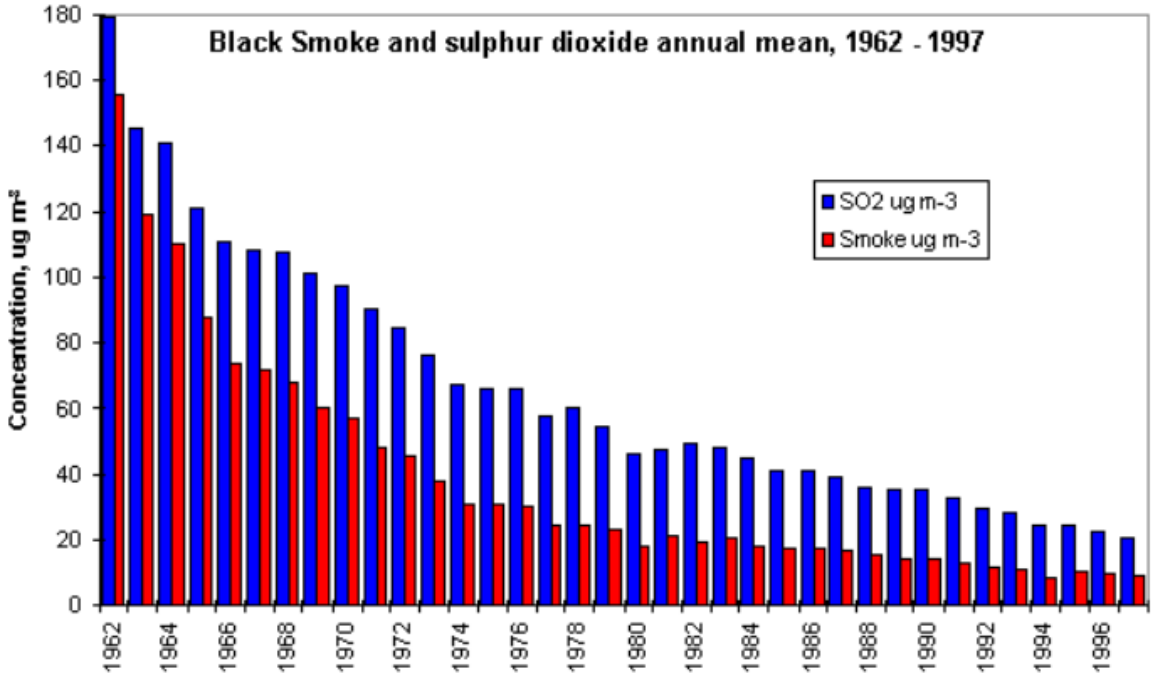


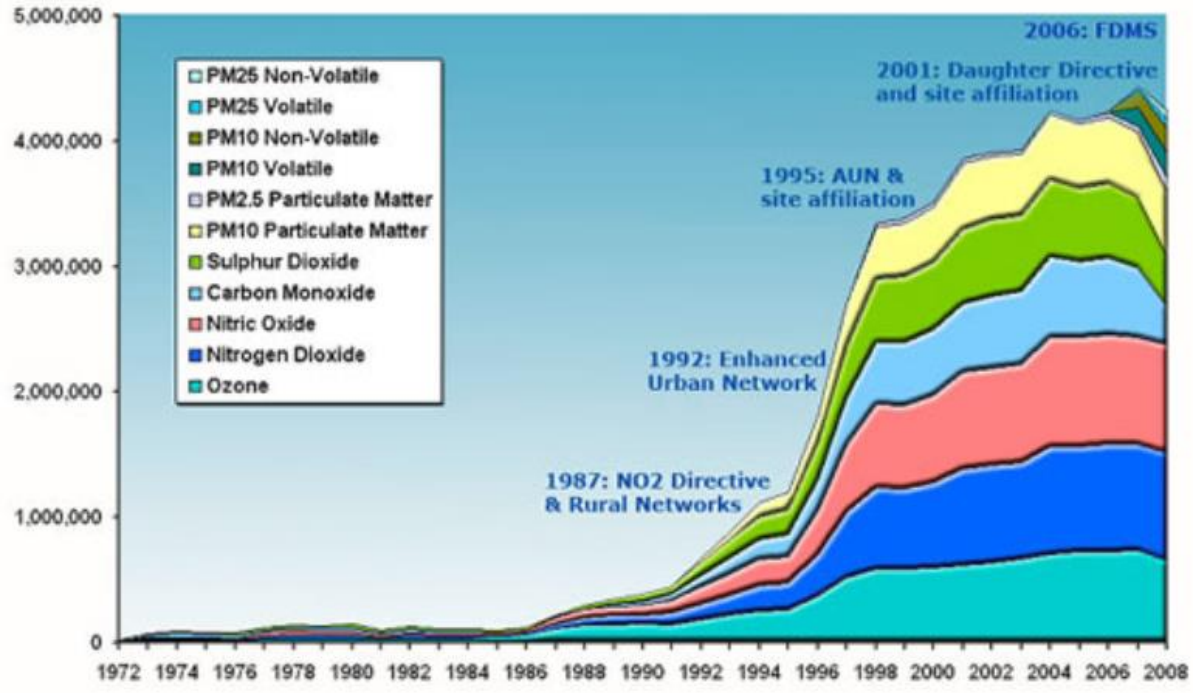
- Great Smog of London

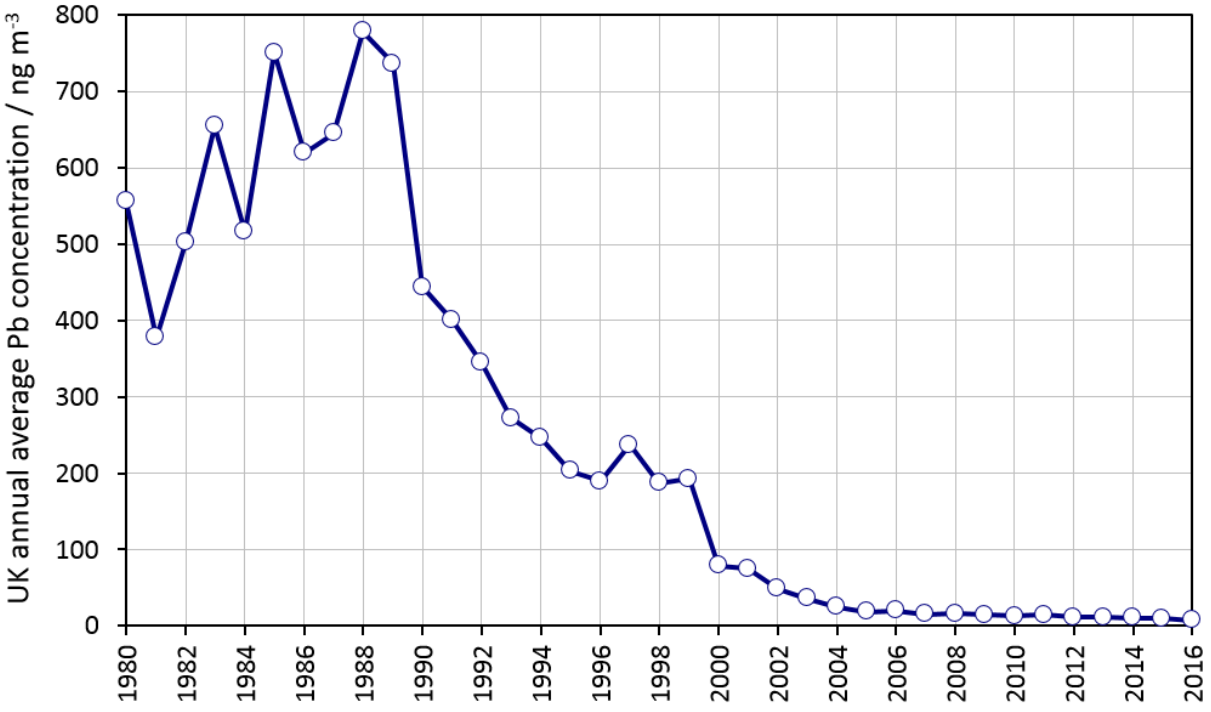
Air quality

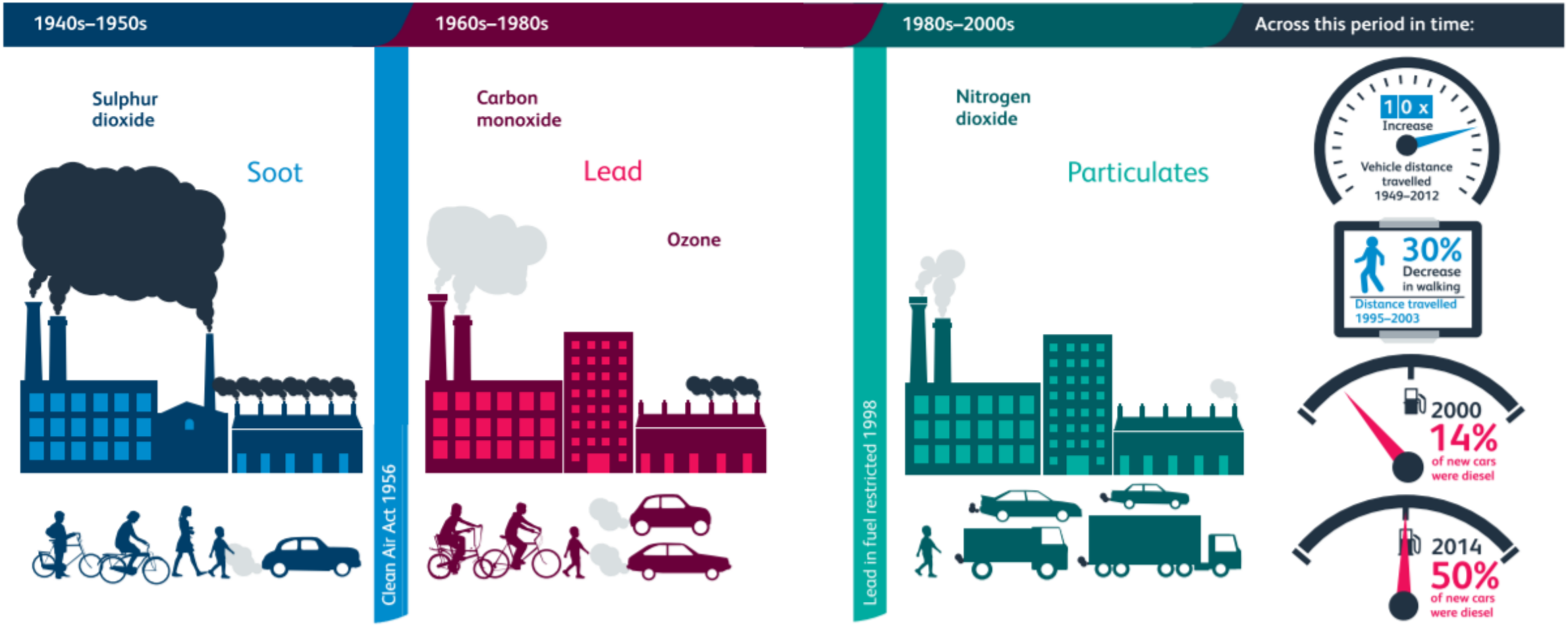
- Pollution decreased
- Other threats also decreased





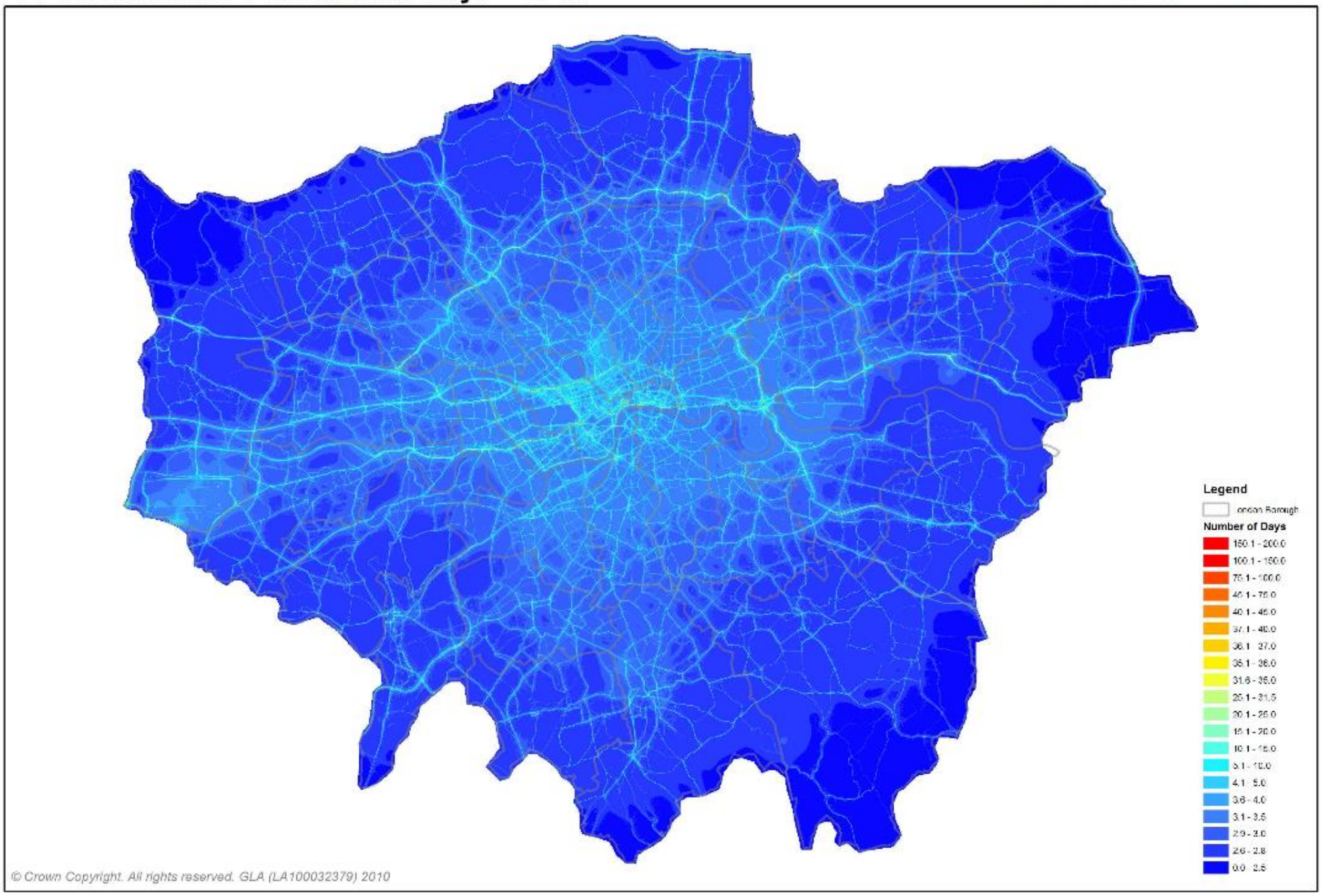






Current focus on particles and NO_2 → Greatest health effects & UK fails to meet EC limits

www.rcplondon.ac.uk/projects/outputs/every-breath-we-take-lifelong-impact-air-pollution



- In urban areas traffic emissions are clearly seen
- Industry nowadays not located in urban centres
- Industrial emissions well abated

Pollution breached EU limits at nearly 50 sites in London last year

Worst area for pollution in London revealed to be Brixton Road in Lambeth

NICHOLAS CECIL Deputy Political Editor | Friday 5 January 2018 11:37 | 6 comments

Like Click to follow The Evening Stand

Environment

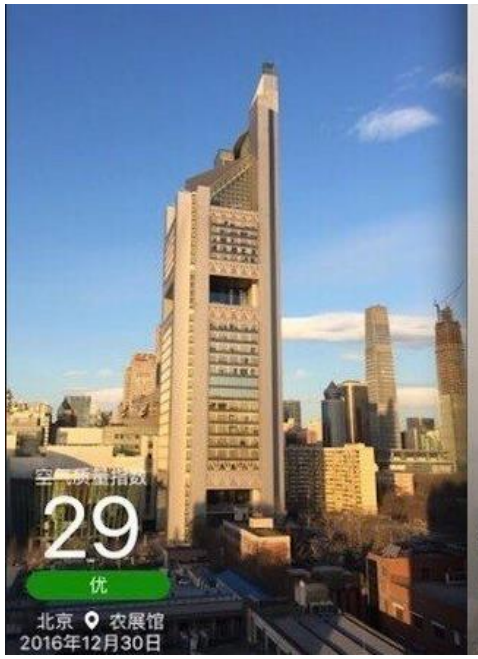
Pollution is killing millions of people a year and the world is reaching 'crisis point', experts warn

The Government must act immediately to stop millions of people dying, say researchers

Andrew Griffin | @_andrew_griffin | Thursday 19 October 2017 22:33 BST | 88 comments

959 shares

Like Click to follow The Independent Online



Tolls on polluted roads — and ALL petrol and diesel vehicles banned from 2040

WAR ON DIESELS GETTING DIRTY

Ban from 2040 on diesel and petrol car sales

UK plans follow French commitment to take polluting vehicles off the road

Anushka Asthana Political editor

Air Pollution causes cancer, confirms WHO

BY MALAVIKA SUBRAMANIAN

Air pollution causes cancer. It is now medically confirmed.

The World Health Organisation (WHO) has just classified outdoor air pollution as carcinogenic to humans.

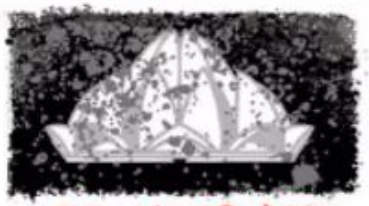
Exposure to air pollution can cause cancer in lungs, and also increase the risk of cancer in the bladder, the International Agency for Research on Cancer (IARC), the specialised cancer agency of WHO, announced this week.

Depending on the level of exposure in different parts of the world, the risk was found to be similar to that of breathing in second-hand tobacco smoke.

"The air we breathe has become polluted with a mixture of cancer-causing substances," says Dr. Kurt Straif, Head of the IARC Monographs Section that ranks carcinogens. "We now know that outdoor air pollution is not only a major risk to health in general, but also a leading environmental cause of cancer."

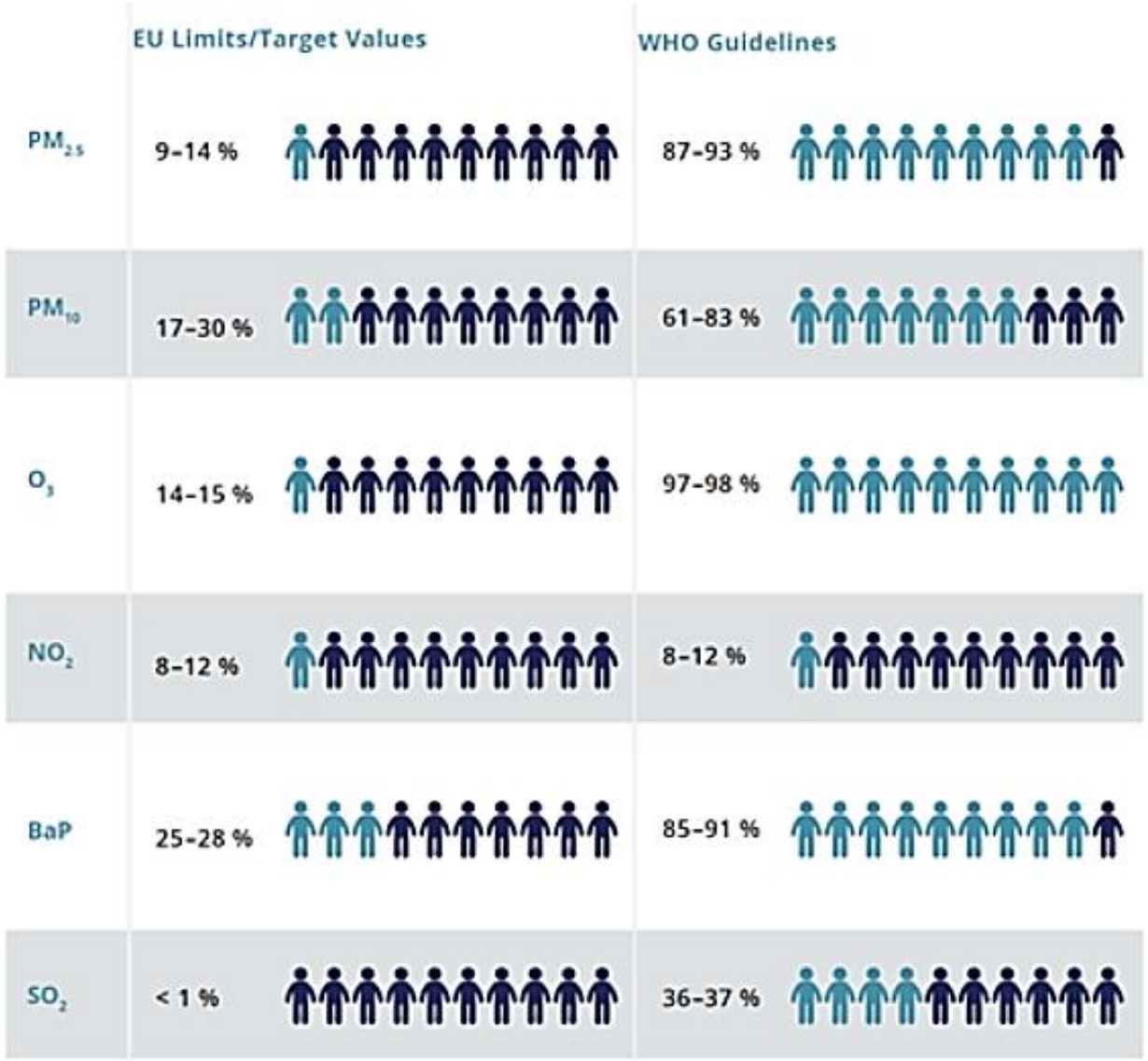
Delhi has much to worry about

- Delhi's air quality improved from an AQI of 389 on Saturday to 329 on Sunday
- Air quality remains in the "very poor" category but has come out of the "severe" category recorded on Friday — a day after Diwali
- A rise in temperature and wind speed could be the reason, say experts. Air quality may improve further in the next 24 hours



	Air Quality	AQI
Oct 22 (Sunday)	Very Poor	329
Oct 21 (Saturday)	Very Poor	389
Oct 20 (Friday)	Severe	403
Oct 19 (Thursday)	Very Poor	319
Oct 18 (Wednesday)	Very Poor	302
Oct 17 (Tuesday)	Very Poor	306

EU urban population exposed to harmful levels of air pollution (2010-2012)



- EU Limit values for many pollutant gases & also $PM_{2.5}$ and PM_{10}
- Target values for the maximum composition of certain PM components
- Metals (Pb, Ni, As, Cd), PAHs (BaP)

European Environment Agency

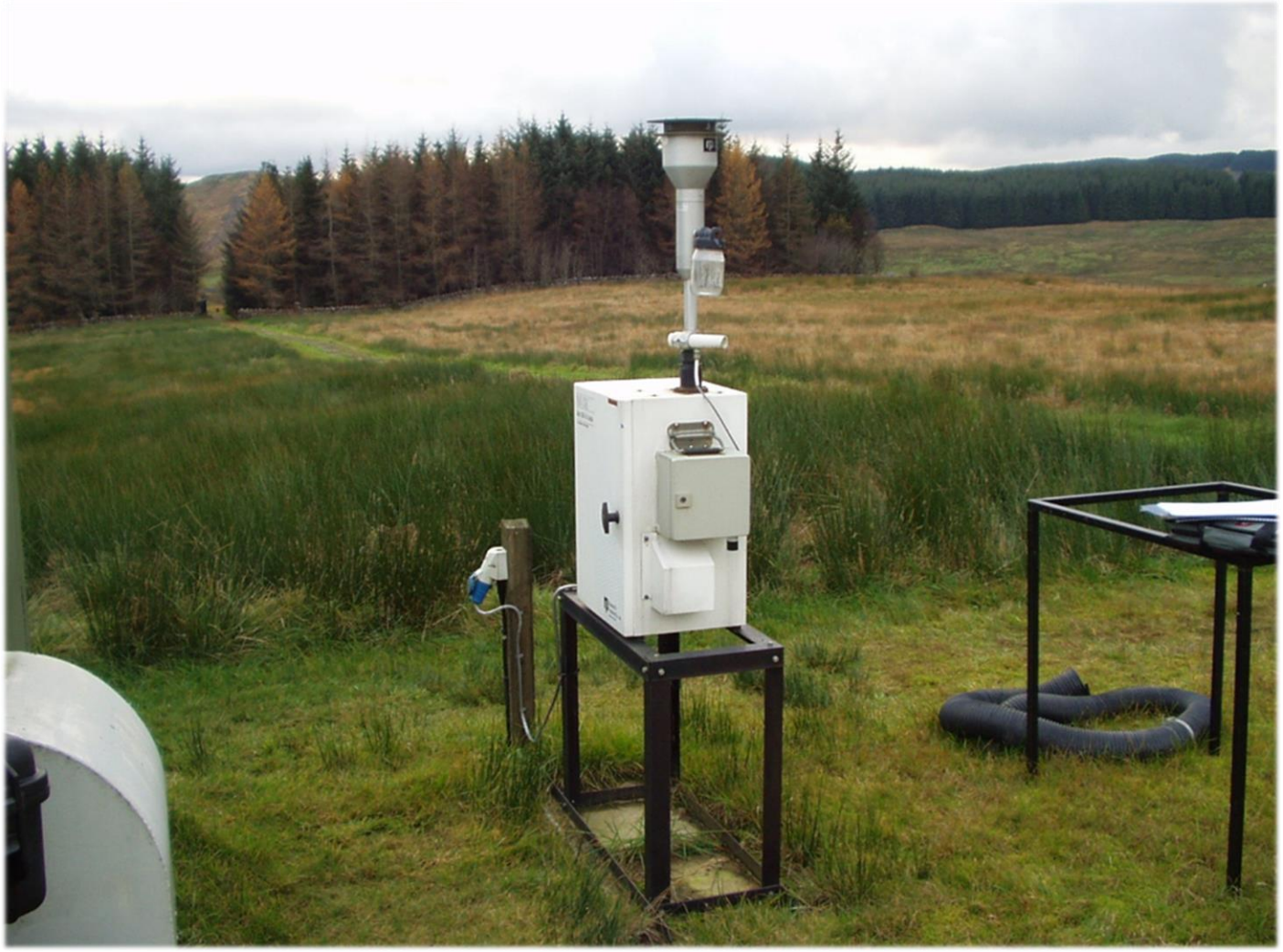
National air quality objectives and European Directive limit and target values for the protection of human health						
Pollutant	**Applies**	**Objective**	**Concentration measured as** [10]	**Date to be achieved by (and maintained thereafter)**	**European Obligations**	**Date to be achieved (by and maintained thereafter)**
Particles (PM_{10})	UK	50 µg/m^3 not to be exceeded more than 35 times a year	24 hour mean	31 December 2004	50 µg/m^3 not to be exceeded more than 35 times a year	1 January 2005
	UK	40 µg/m^3	annual mean	31 December 2004	40 µg/m^3	1 January 2005
	Indicative 2010 objectives for PM_{10} (from the 2000 strategy and Addendum) have been replaced by an exposure reduction approach for $PM_{2.5}$ (except in Scotland – see below)					
	Scotland	50 µg/m^3 not to be exceeded more than 7 times a year	24 hour mean	31 December 2010	50 µg/m^3 not to be exceeded more than 35 times a year	1 January 2005
	Scotland	18 µg/m^3	annual mean	31 December 2010	40 µg/m^3	1 January 2005
Particles ($PM_{2.5}$) Exposure Reduction	UK (except Scotland)	25 µg/m^3	annual mean	2020	Target value - 25 µg/m^3	2010
	Scotland	10 µg/m^3		31 December 2020	Limit value - 25 µg/m^3	1 January 2015
	UK urban areas	Target of 15% reduction in concentrations at urban background		Between 2010 and 2020	Target of 20% reduction in concentrations at urban background.	Between 2010 and 2020

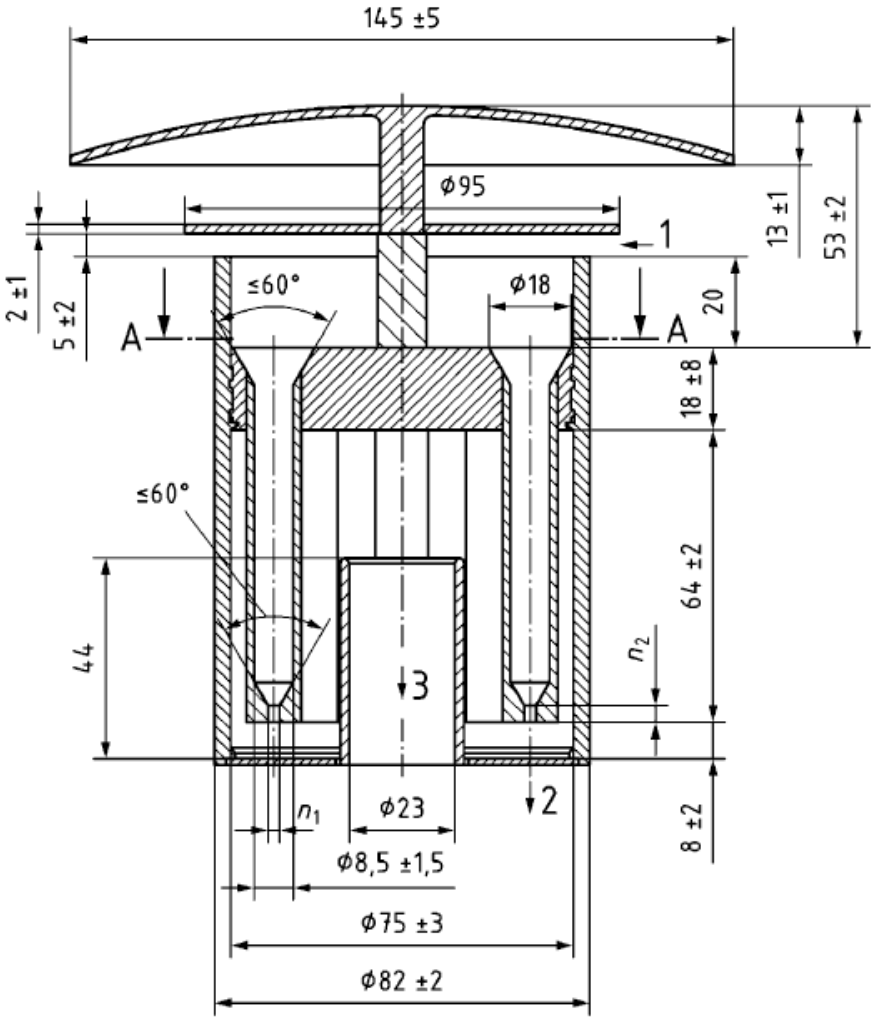
- Legislative particle metrics are all mass-based!

uk-air.defra.gov.uk/assets/documents/Air_Quality_Objectives_Update.pdf

Collecting particles

- PM_{10} and $PM_{2.5}$ sampled onto filters
- Particles that are ≤10 µm or ≤2.5 µm in diameter
- Collected PM either weighed or chemically analysed

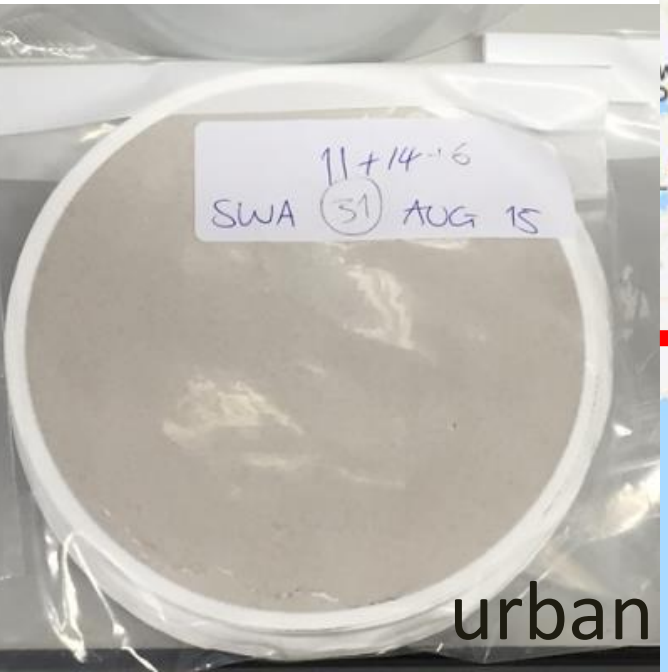




industrial

UK Polycyclic Aromatic Hydrocarbon Network

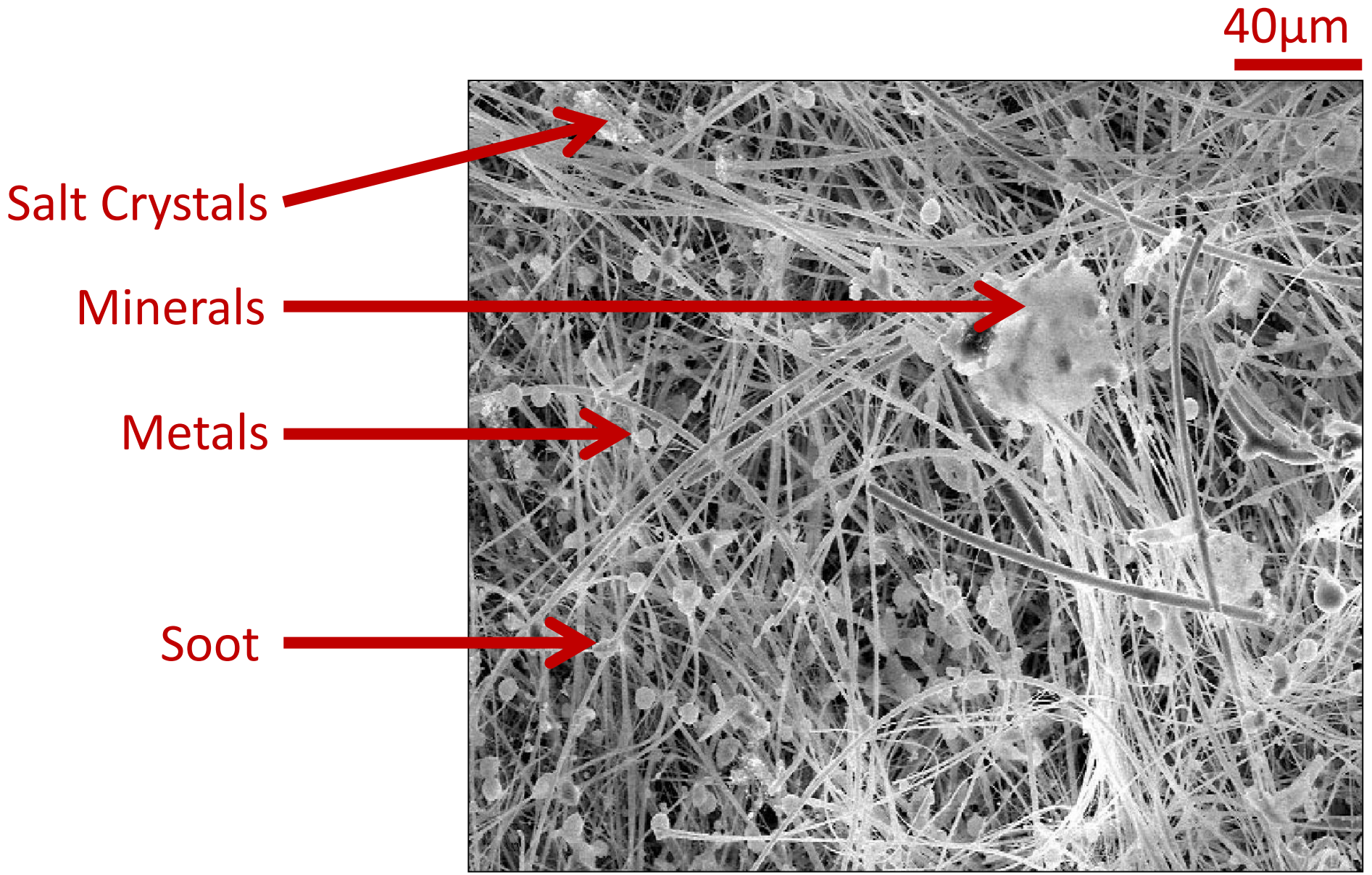
unsampled



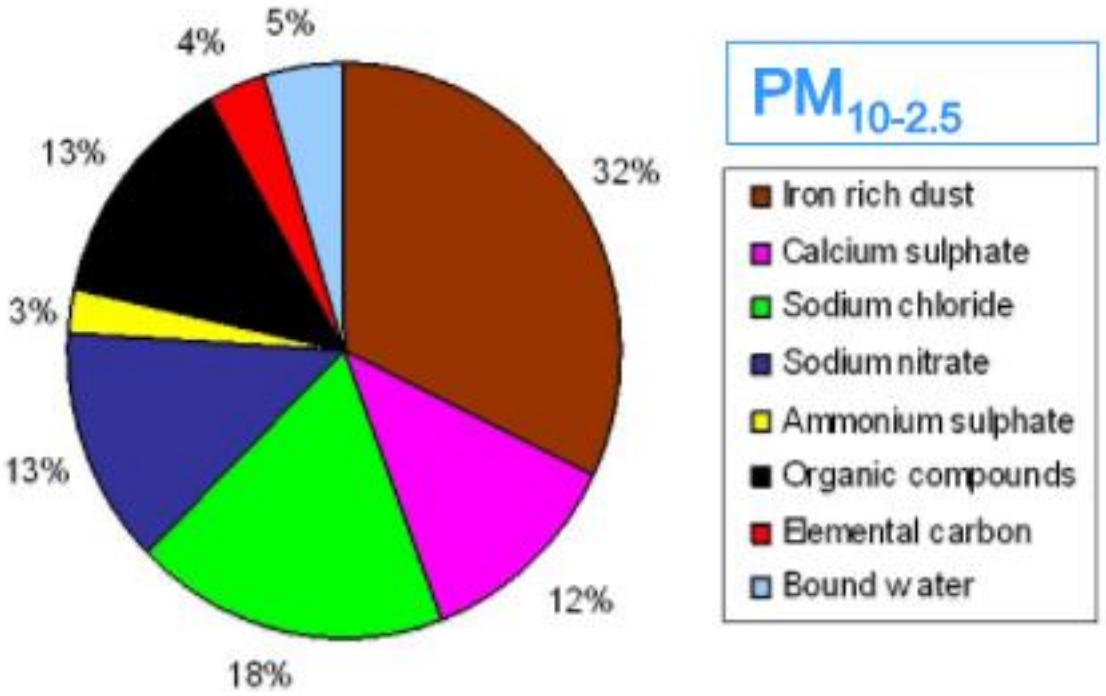
urban

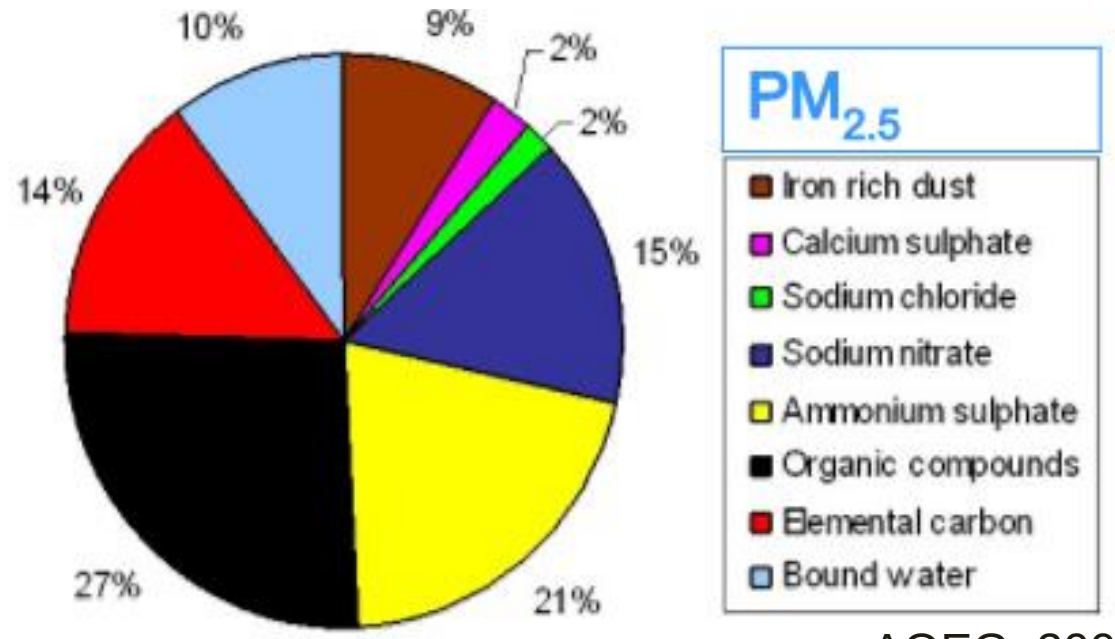
rural

Scanning Electron Microscope Image of PM_{10}



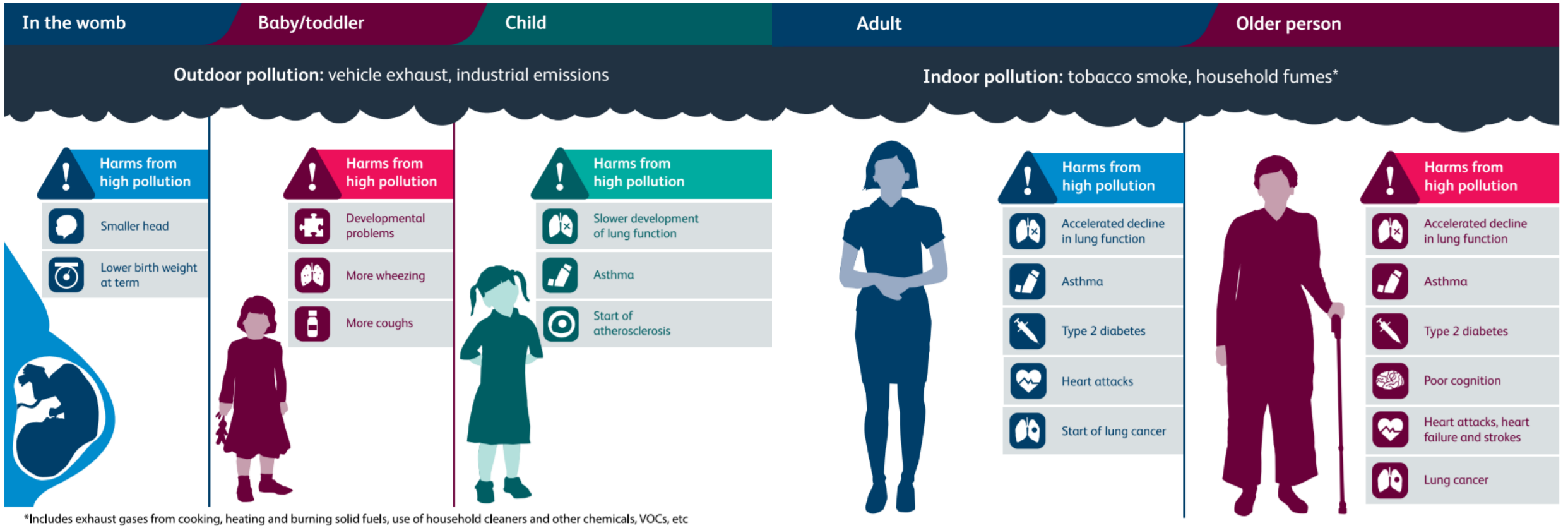
What's in Particulate Matter?





www.epa.gov

AQEG, 2005



*Includes exhaust gases from cooking, heating and burning solid fuels, use of household cleaners and other chemicals, VOCs, etc

Costs of air pollution

The annual mortality burden in the UK from exposure to outdoor air pollution is equivalent to around 40,000 deaths. To this can be added further impacts from exposure to indoor air pollutants such as radon and second-hand smoke.

www.rcplondon.ac.uk/projects/outputs/every-breath-we-take-lifelong-impact-air-pollution

www.bbc.co.uk/news/science-environment-39129270

BBC Sign in News Sport Weather iPlayer TV Radio

NEWS

Home UK World Business Politics Tech Science Health Family & Education

Science & Environment

Reality Check: Does pollution cut short 40,000 lives a year?

6 March 2017

$PM_{2.5}$ **and** NO_2

Reality Check verdict: The 40,000 figure for the UK stems from extensive research over decades in the US. It's a statistical construct not a count of actual deaths. There is no question that air pollution, caused by many factors, is a serious health problem but it's difficult to assess its precise impact.

But the authors of this report stressed the uncertainty of their findings. In particular, COMEAP said when it used the 6% figure that it was 75% confident the actual figure was between 1% and 12%. That translates as meaning that that the number of early deaths, for which 29,000 was the central estimate, was probably between 5,000 and 60,000, but there was a one in four chance that it was even outside that range.

$PM_{2.5}$ **only**

It is not possible to count the number of people who have died early as a result of pollution because nobody has air pollution written as the cause of death on their death certificates.

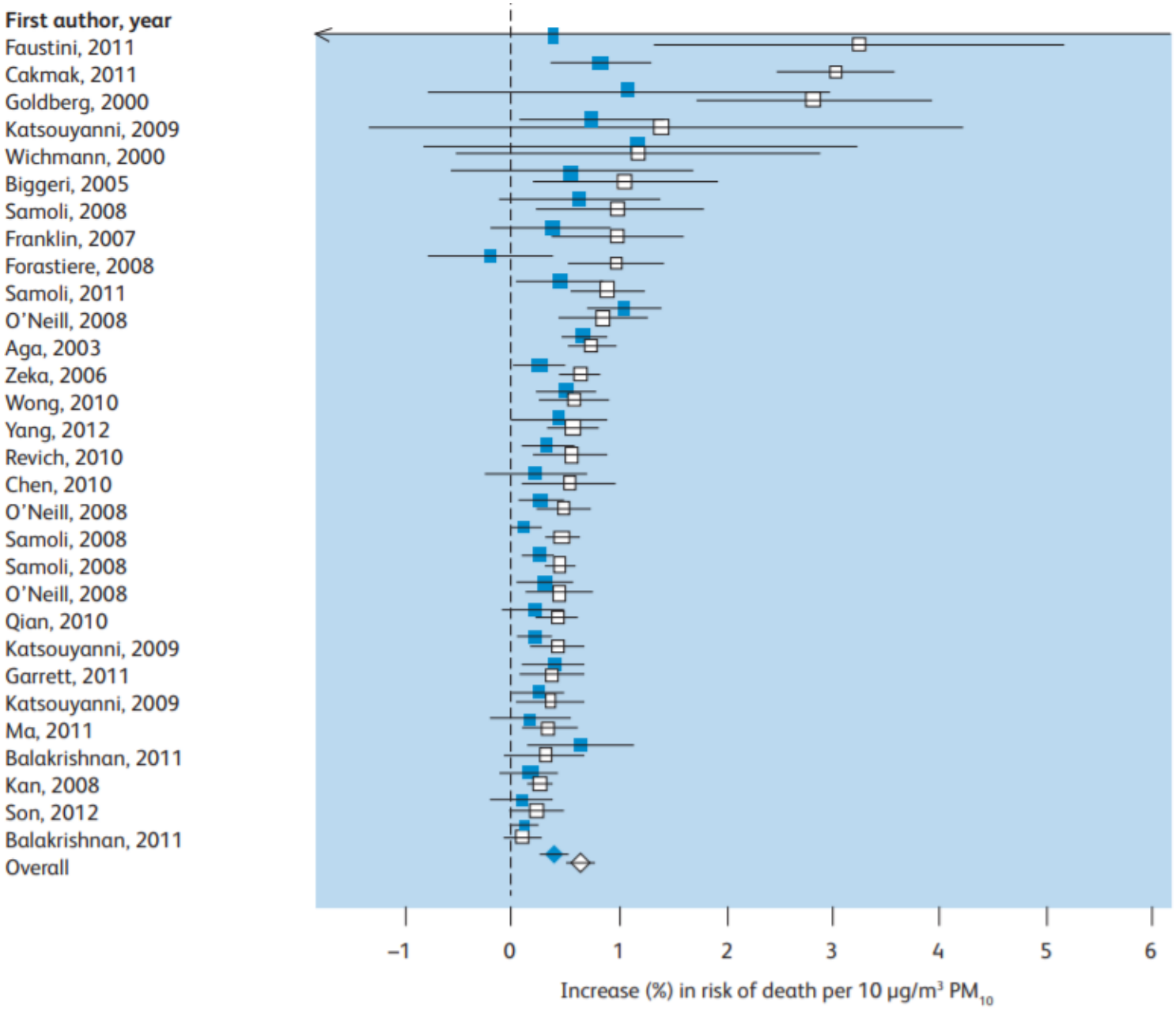
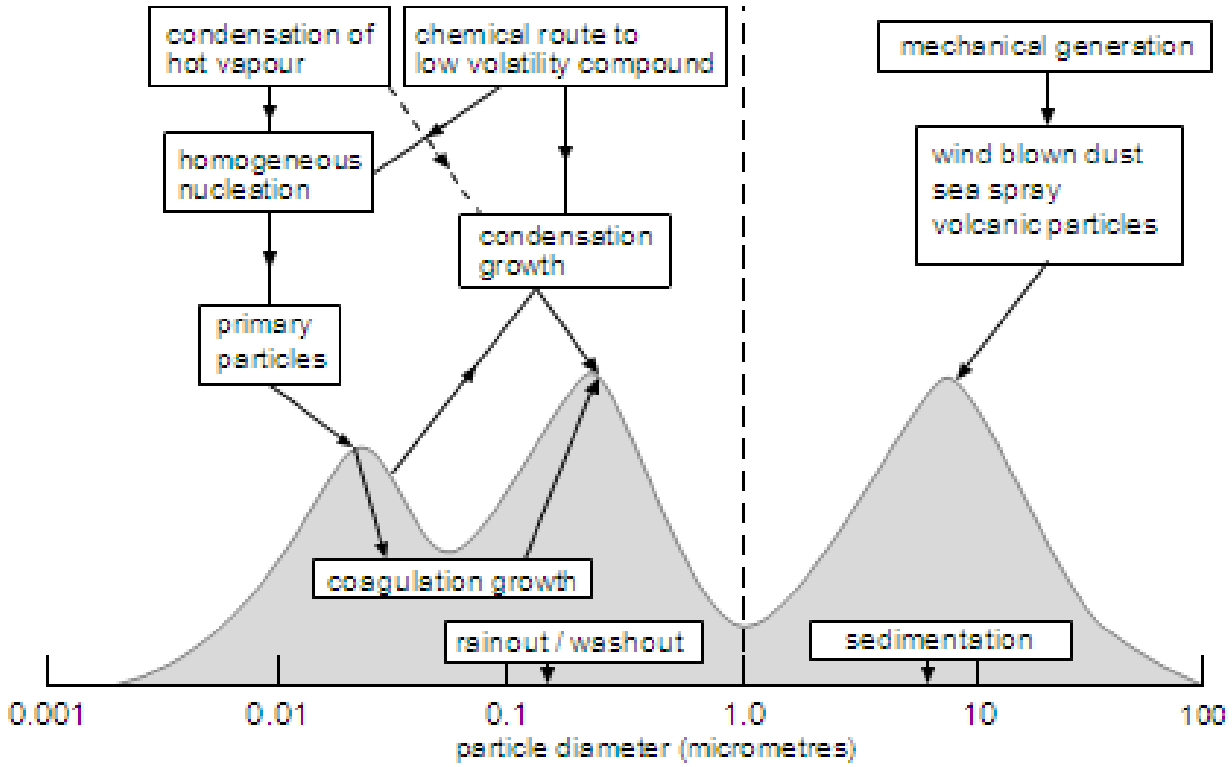


Fig 16. Meta-analysis of the association with age of increased risk of death from exposure to PM_{10}. Solid squares represent results from younger populations; open squares represent those for older populations.

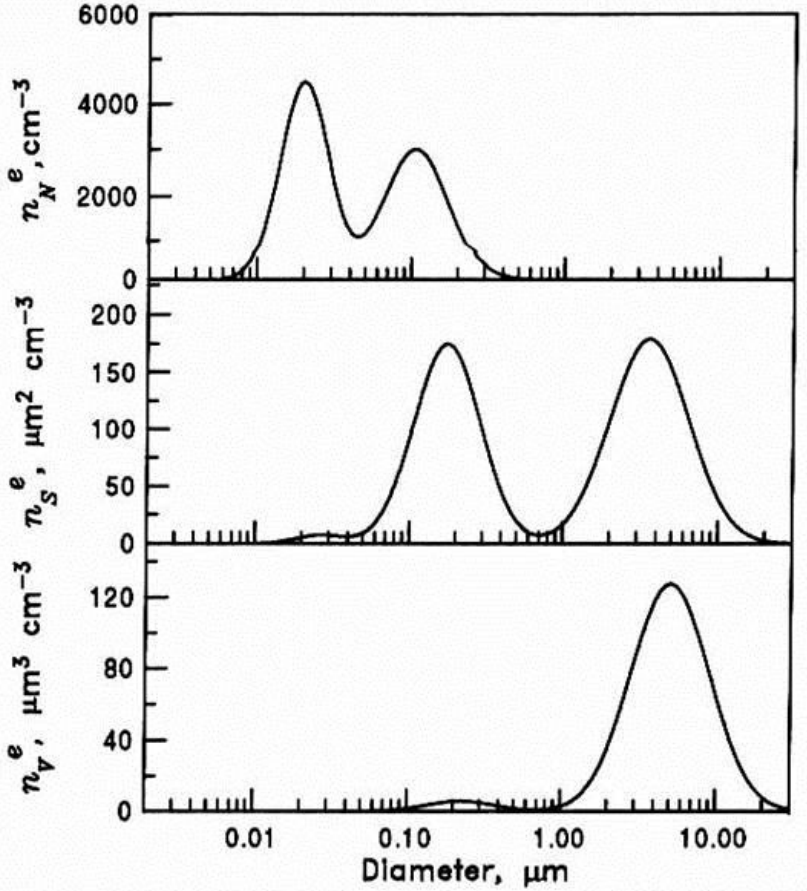
- The effects of air pollution are challenging to quantify
- Because of all the other confounding variables
- Because of the difficultly of measuring air quality accurately – in particular personal exposure
- Defining increased risk of death
- **We need better data (lower uncertainties) or better metrics**

www.rcplondon.ac.uk/projects/outputs/every-breath-we-take-lifelong-impact-air-pollution

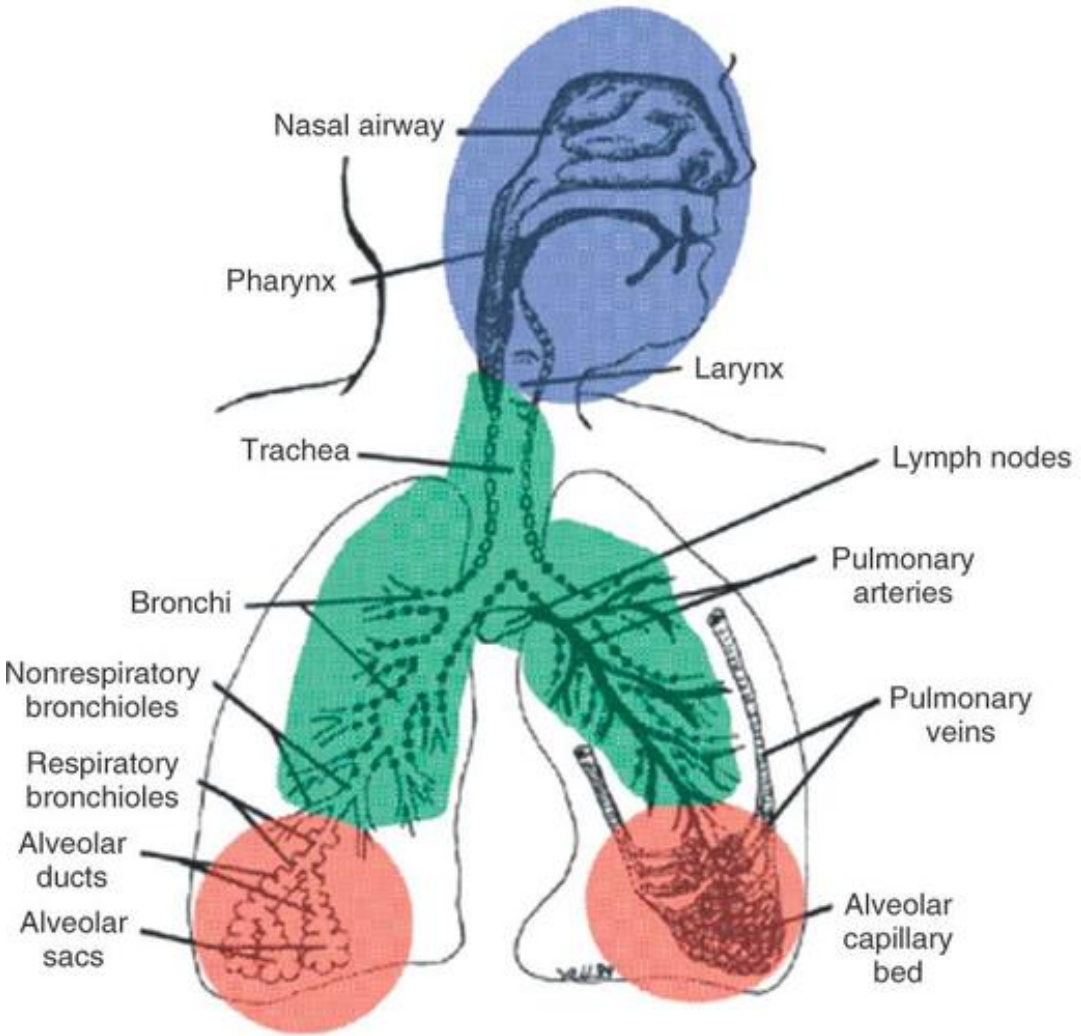
Are there better metrics we can use?

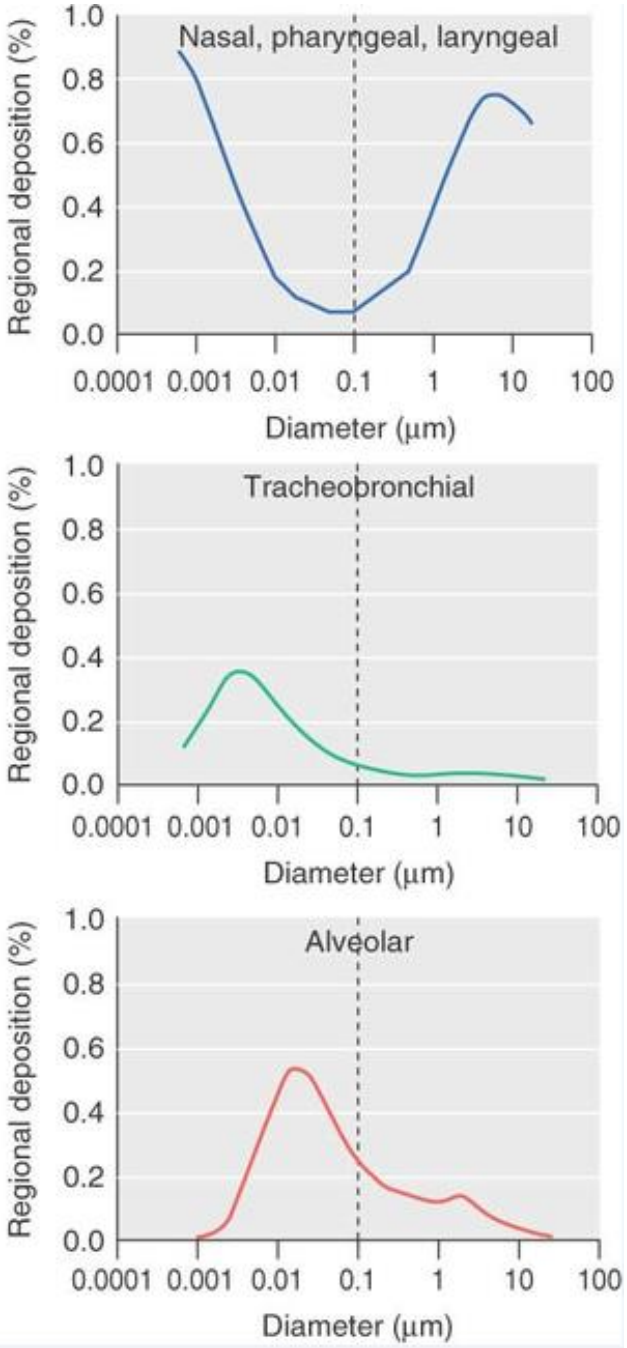


Particle Diameter / nm	Relative Mass per Particle	Relative Surface Area per Mass	Relative Number per Mass	Respiratory Penetration
10 000	8 000 000	1	1	Nasal Passage
2 500	125 000	4	64	Trachea, Bronchi
1 000	8 000	10	1 000	Alveoli
50	1	200	8 000 000	Bloodstream



An number distribution, surface distribution, and volume distribution functions plotted against log(Dp). (from Seinfeld and Pandis)



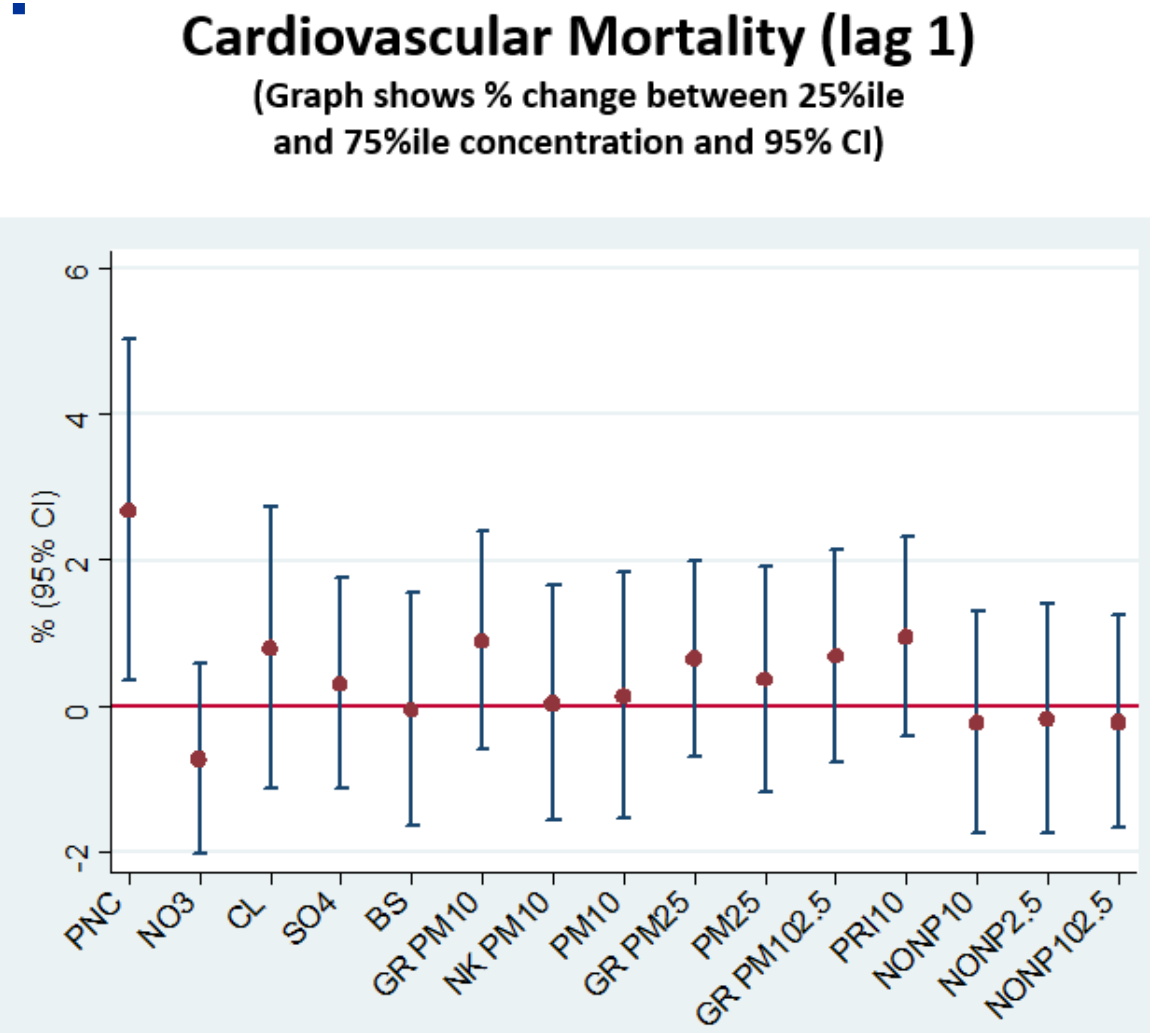


- The smaller the particle the further into the lung they can penetrate
- This is generally more dangerous since the body cannot easily remove them
- Nanoparticles can enter the bloodstream

Oberdörster G, Oberdörster E, Oberdörster J. Environ. Health Perspect. 2005, 113:823–839.

Better, more effective metrics?

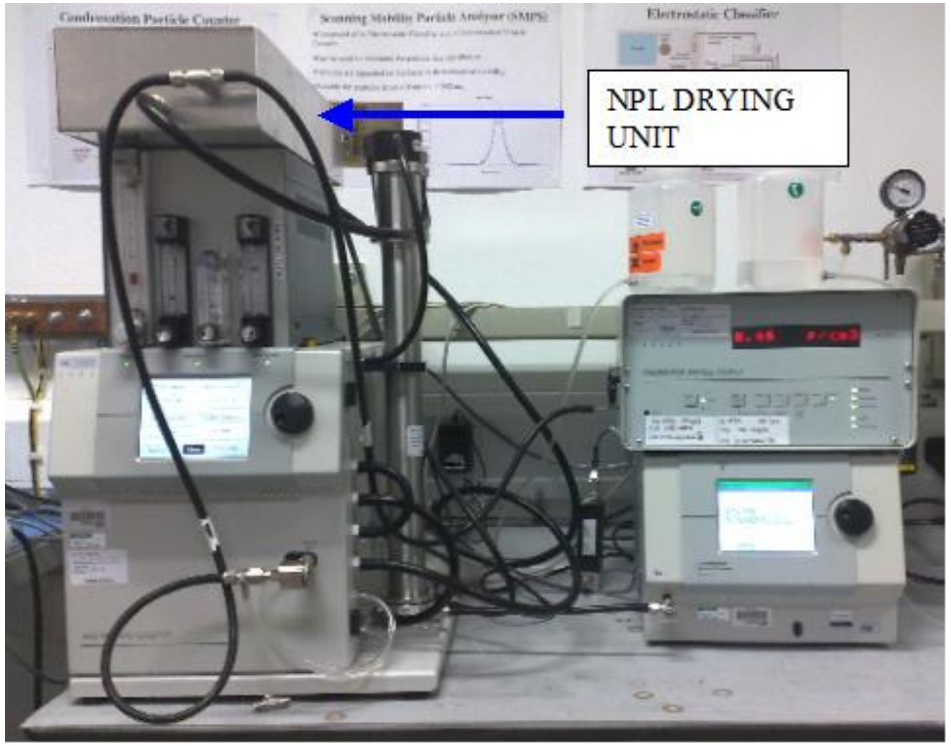
- Particle number concentration may be a **better metric for health impacts**
- **More measurements required** to know whether this is the case
- **Not as simple or as well standardised** as particle mass measurement
- Not a current requirement of air quality legislation

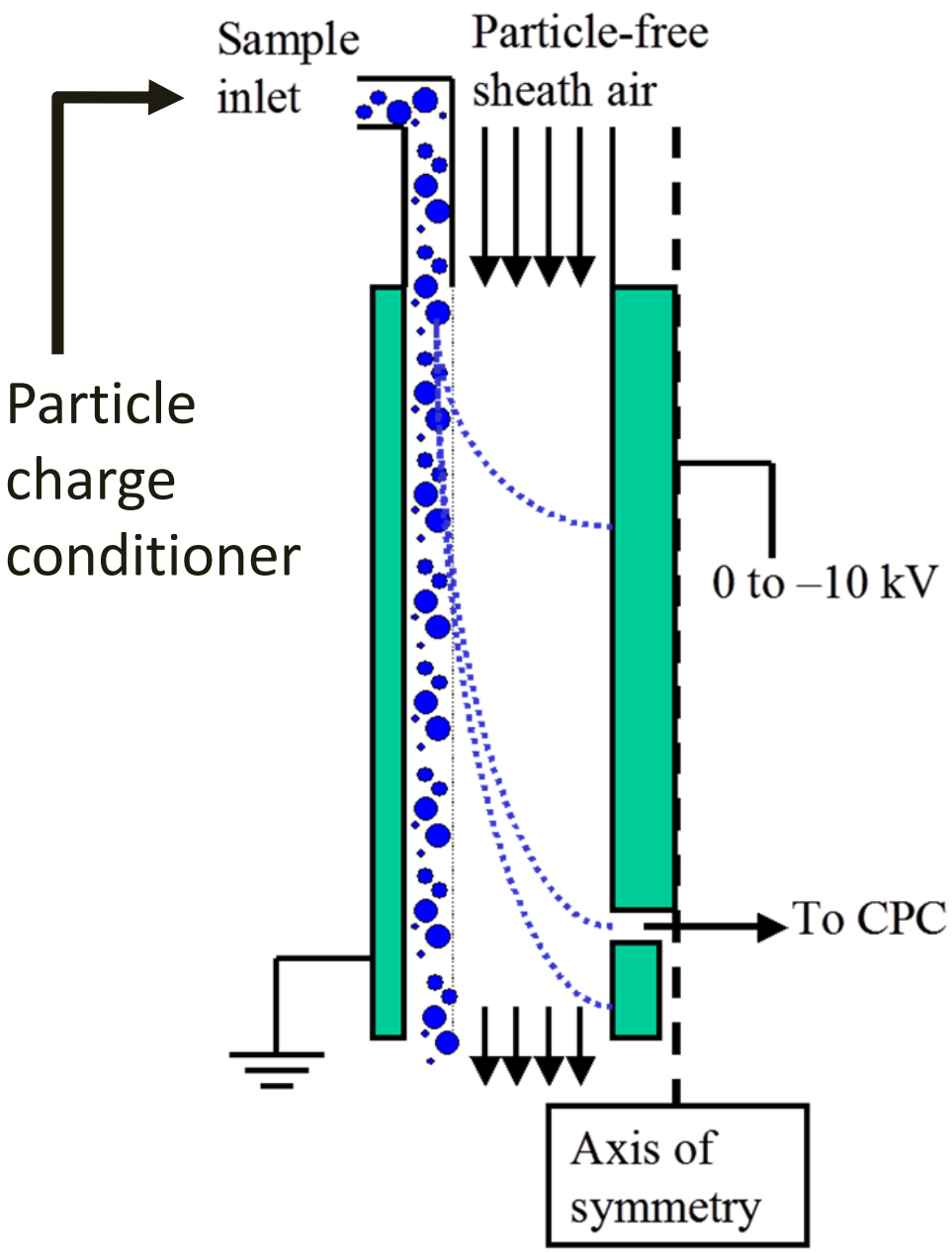


R.W. Atkinson, G.W. Fuller, H.R. Anderson, R.M. Harrison, B. Armstrong, Epidemiology, 21, 501-511 (2010)

UK Particle Number and Size measurements

- Non-regulatory research network





Differential Mobility Analyser

Condensation Particle Counter

- Traceability to aerosol electrometer, **calibrated using primary current standards**

Calibration of a CPC with an electrometer

Ensures instruments sample ambient pressure

Selects narrow mobility distribution

Paths equal and short

Aerosol Generator

Overflow

Charge conditioner

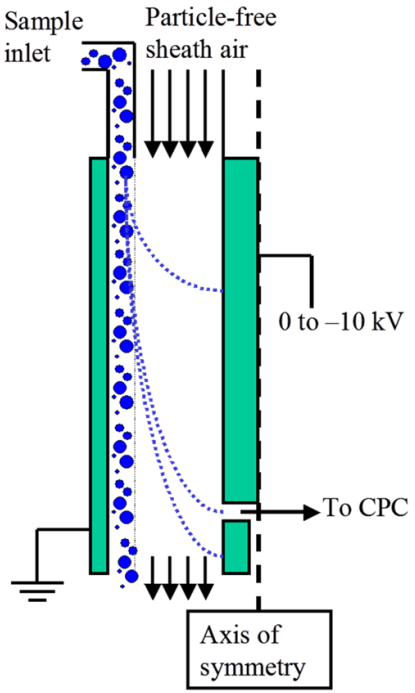
Differential Mobility Analyser

Reference Aerosol Electrometer

Test CPC

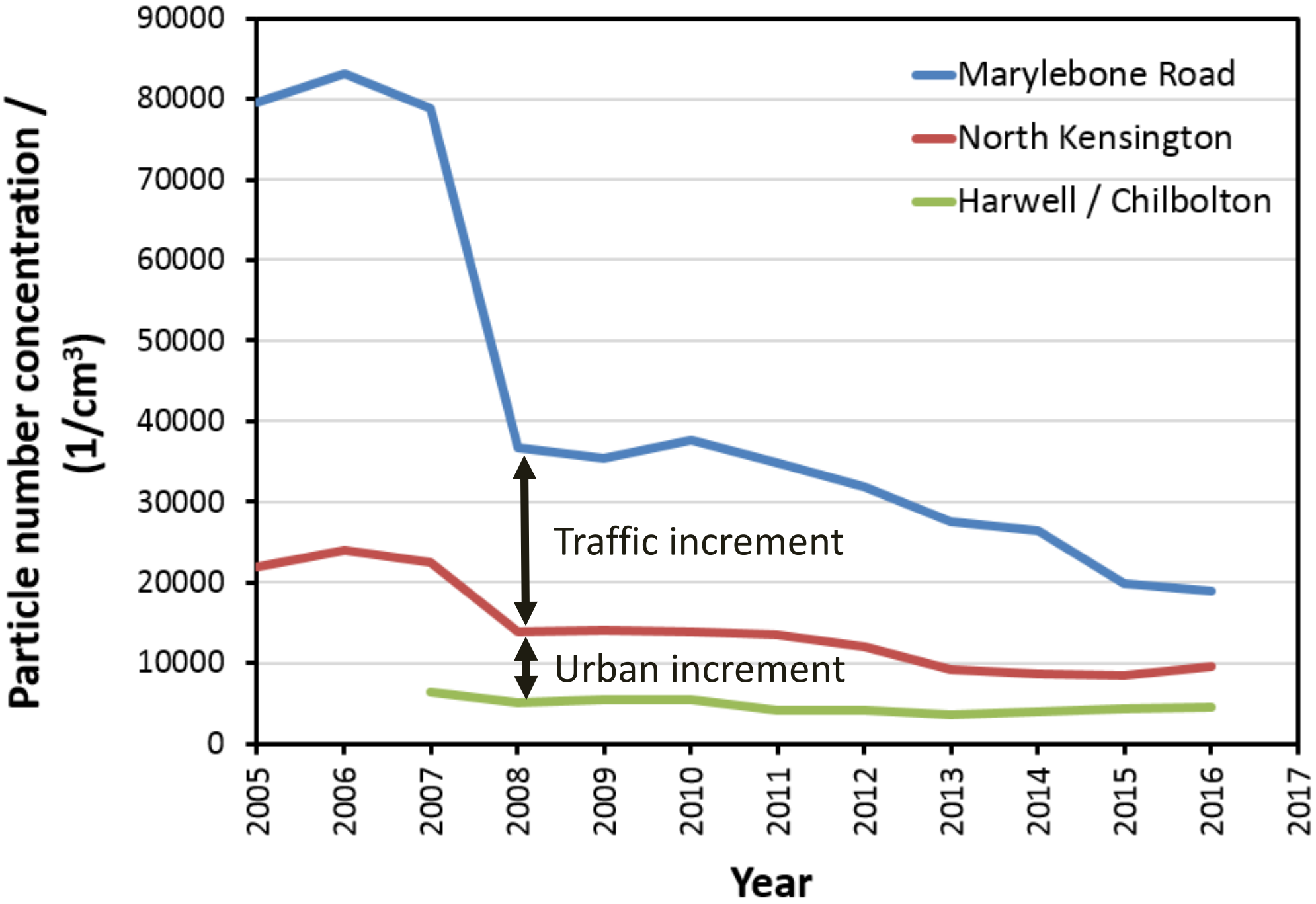
Makeup flow

Control of concentration and raw size distribution

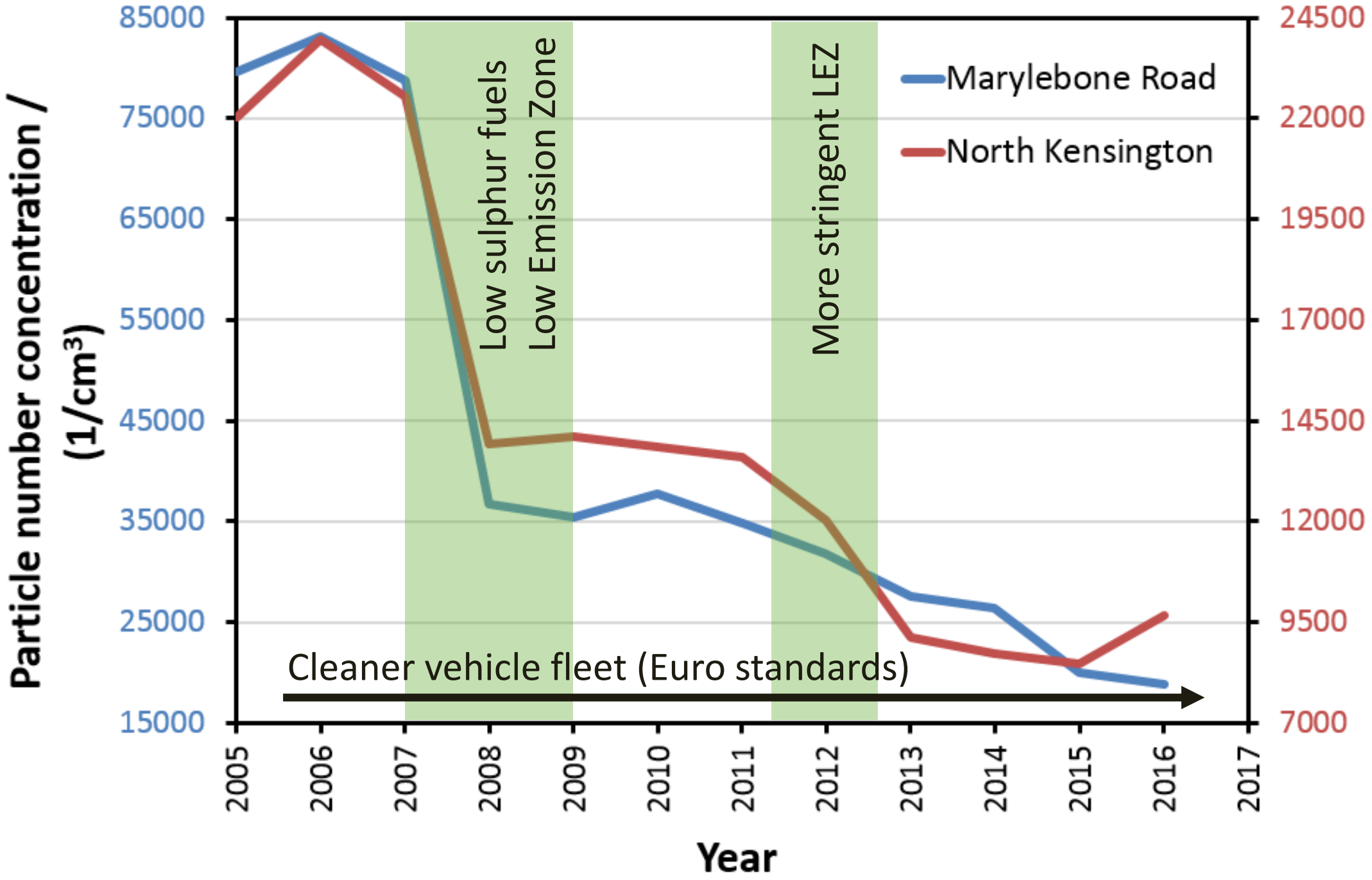


mostly singly charged particles

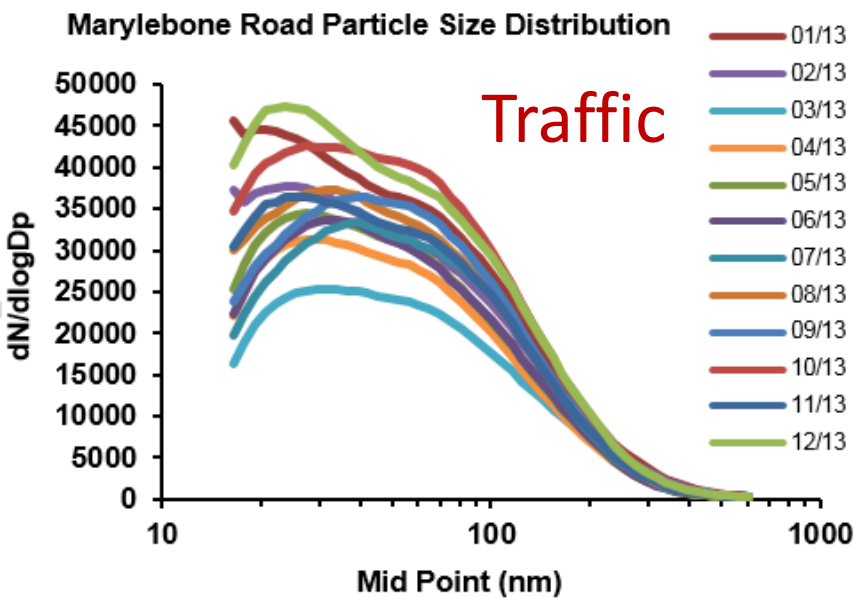
CPC results


Particle number concentration / (1/cm³)
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
Year
Marylebone Road
North Kensington
Harwell / Chilbolton
Traffic increment
Urban increment

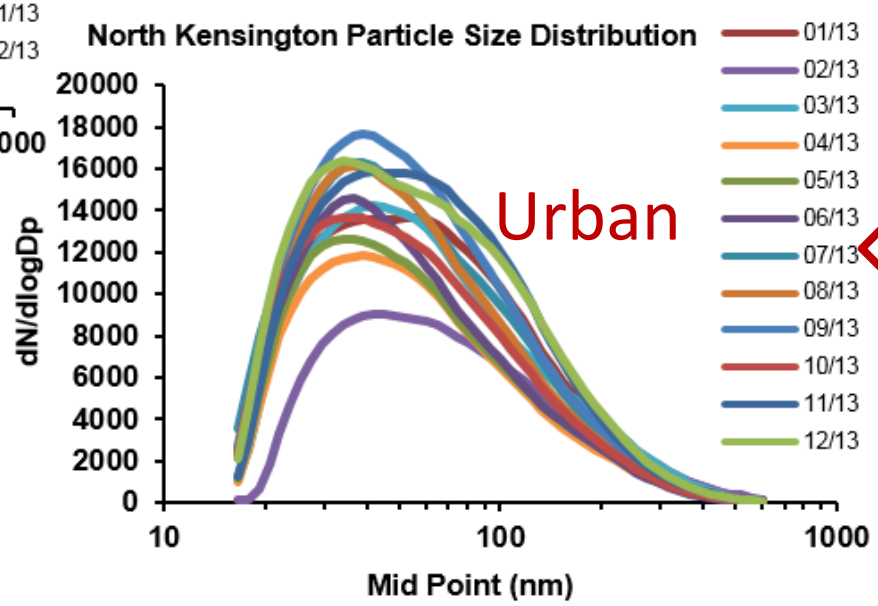
CPC results


Particle number concentration / (1/cm³)
85000
75000
65000
55000
45000
35000
25000
15000
24500
22000
19500
17000
14500
12000
9500
7000
Marylebone Road
North Kensington
Low sulphur fuels
Low Emission Zone
More stringent LEZ
Cleaner vehicle fleet (Euro standards)
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
Year

SMPS results

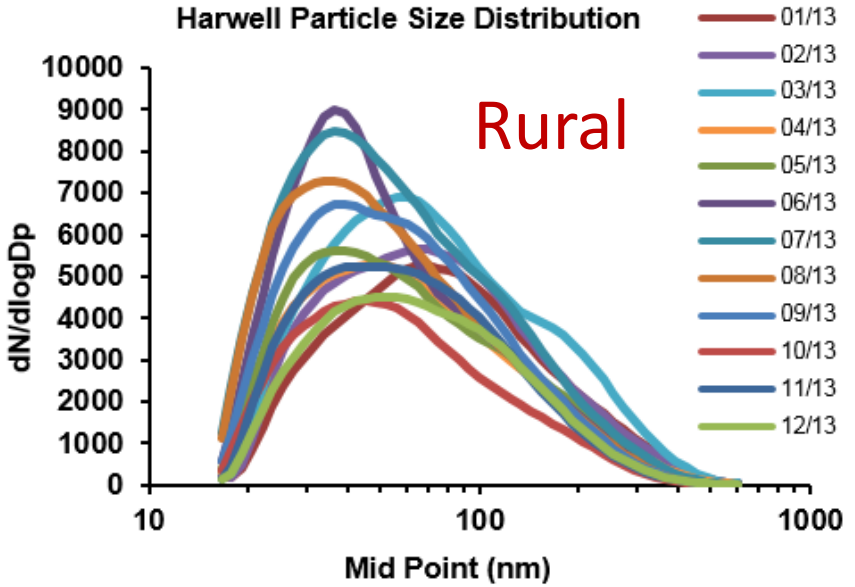


Dominated by primary emissions from vehicles



Mixed anthropogenic sources

Higher nucleation events in warmer, sunnier months



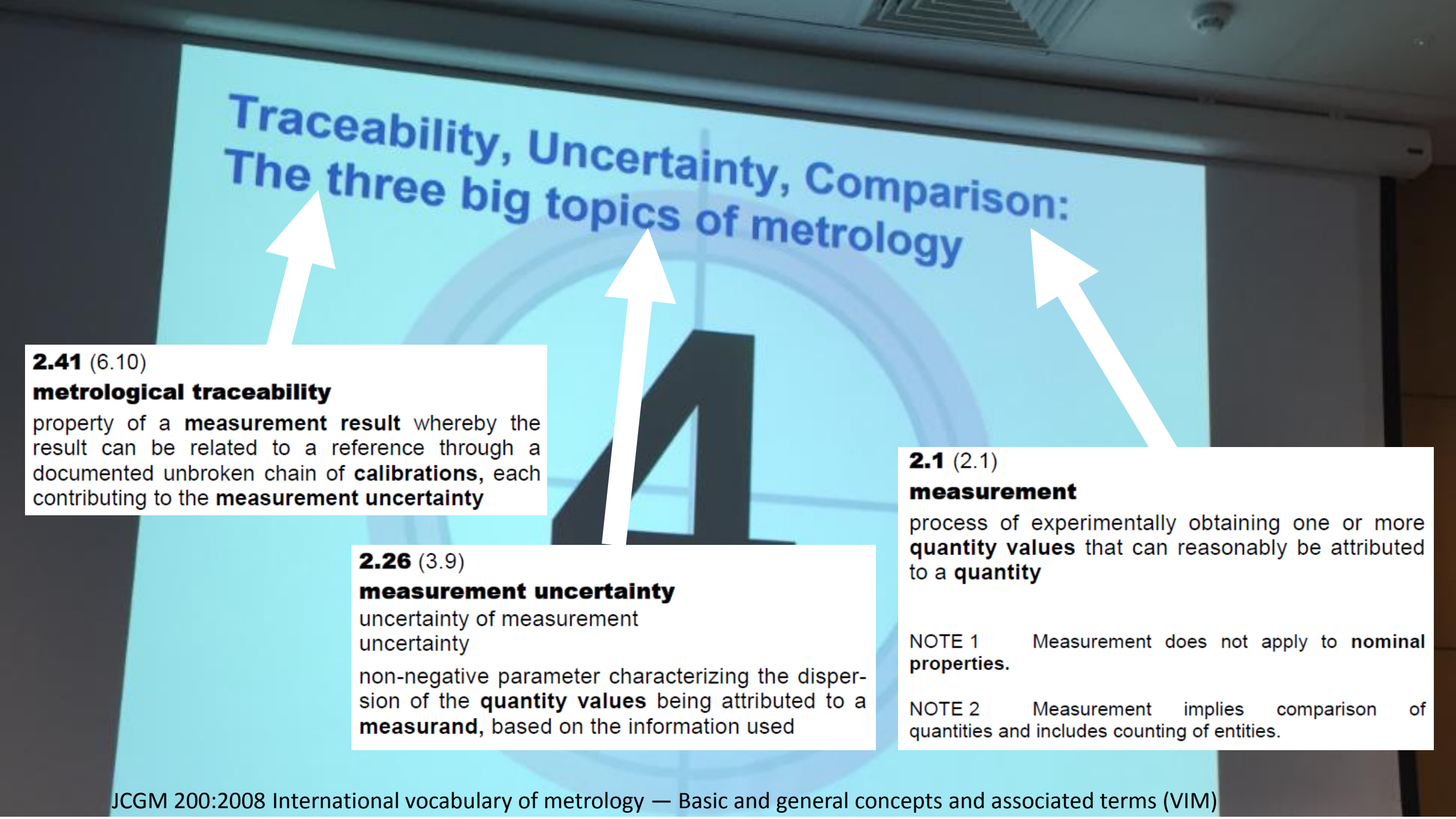
Why are these outputs useful

- This data supports **evidence-based** policy development, policy assessment, health studies and environmental research
- We are able to draw these conclusions because we have **confidence in the data** produced
- We have confidence in the data produced because we have an appropriate system of checks and controls in place to ensure the **quality of the results**
- We ensure the quality of results because we apply a rigorous **metrological approach**

→ **What is metrology?**

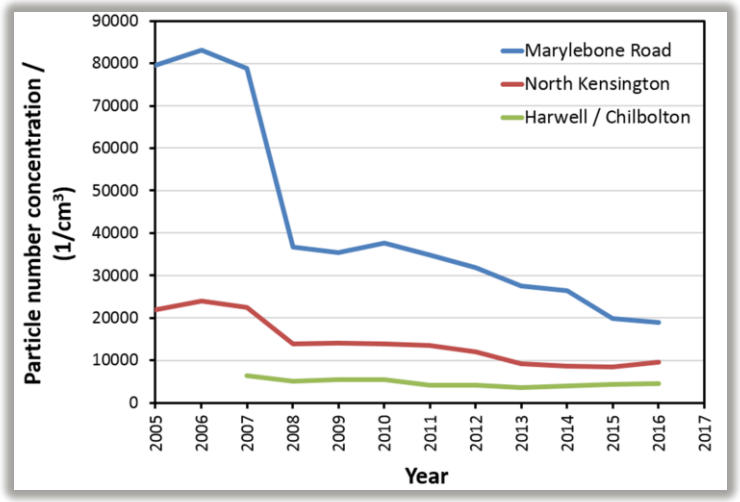
> Metrology is the science of measurement,
> embracing both experimental and theoretical determinations
> at any level of uncertainty
> in any field of science and technology.

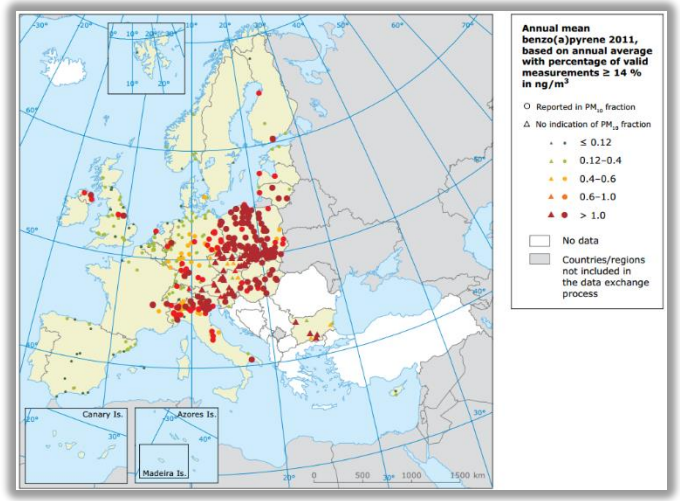
www.bipm.org/en/worldwide-metrology/



JCGM 200:2008 International vocabulary of metrology — Basic and general concepts and associated terms (VIM)

The outputs of metrology?



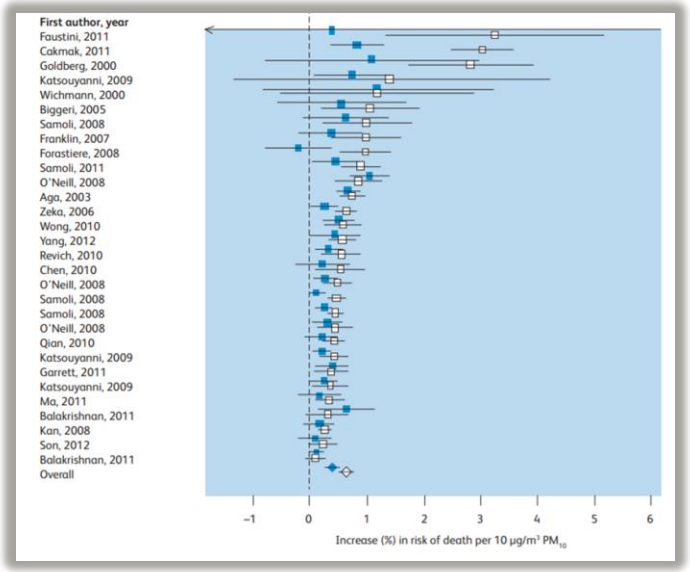


confidence in trends

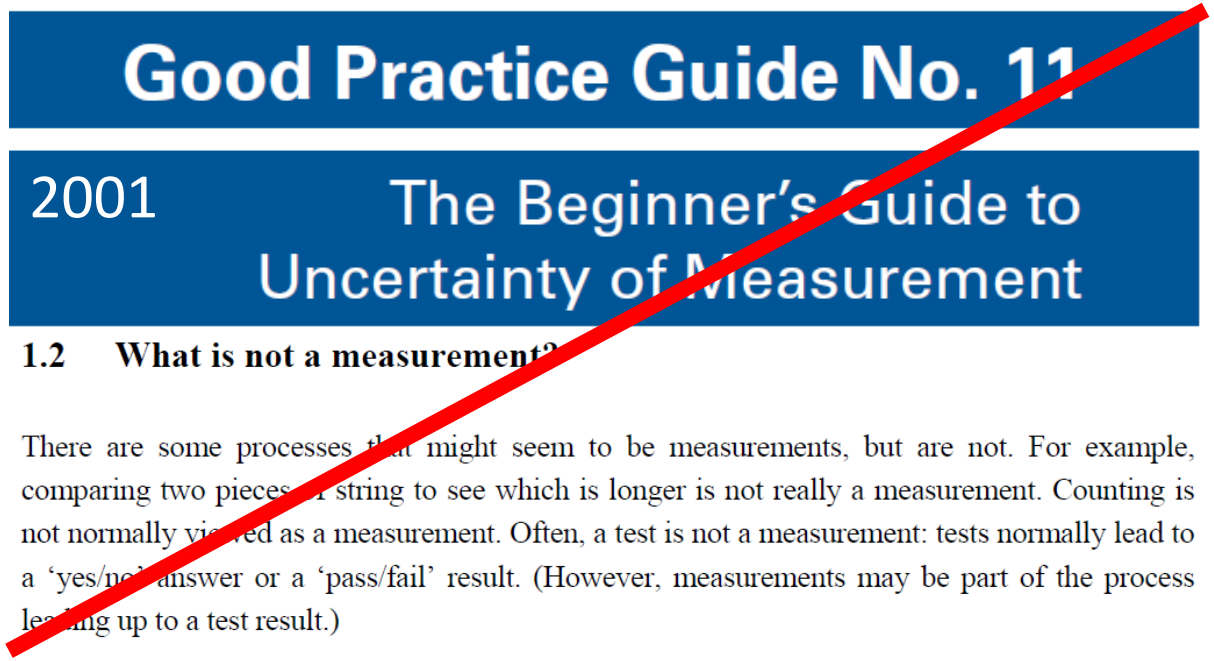
confidence in spatial data

- Metrology provides a measurement infrastructure which is ***stable*** over time, ***comparable*** between locations, and ***coherent***, allowing measurements of different properties using different methods to be combined (without scaling factors)

confidence that data can be used directly in the equations of science across disciplines



Counting (nano)particles



- Counting is a recognised measurement!
- The unit for counting quantities is one, symbol '1'
- There is only one unit for counting but an almost limitless number of quantities
- This means we need a very clear description of the measurand when expressing results
- We should also resist the temptation to mix the quantities and units

➢ In the air sampled the number concentration of particles with an aerodynamic diameter of between 10 nm and 1 µm was, $C = (1.00 \pm 0.05) \times 10^6$ 1/m^3

➢ $C = (1.00 \pm 0.05) \times 10^6$ particles$_{(10\ nm - 1\ \mu m)}$/m^3

Operationally defined measurands

3.7 ISO 17034:2006

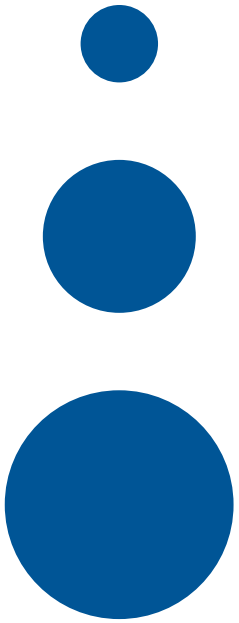
operationally defined measurand

measurand that is defined by reference to a documented and widely accepted measurement procedure to which only results obtained by the same procedure can be compared

Note 1 to entry: Examples include crude fibre in foods, impact toughness, enzyme activities and extractable lead in soils.

- It is important to be very clear about what is being measured
  - Particles of a given size range, how is the size defined, of what composition?
- And to agree on the method being used to make the measurement (if this matters)
- To some extent all measurands are method defined – just a question of whether **within-laboratory variability** or **between-laboratory variability** dominates
- CEN/TS 16976:2016: Ambient air. Determination of the particle number concentration of atmospheric aerosol

An example – Particle size distribution



Diameters:
1, 2 & 3
units

$$X_{nl} = D[1,0] = \frac{1+2+3}{3} = \underline{2.00}$$

Electron microscopy

$$X_{ns} = D[2,0] = \sqrt{\frac{1+4+9}{3}} = \underline{2.16}$$

Image analysis

$$X_{nv} = D[3,0] = \sqrt[3]{\frac{1+8+27}{3}} = \underline{2.29}$$

Electrozone sensing

$$X_{ls} = D[2,1] = \frac{1+4+9}{1+2+3} = \underline{2.33}$$

$$X_{lv} = D[3,1] = \sqrt{\frac{1+8+27}{1+2+3}} = \underline{2.45}$$

- Crucial to define the measurand & method
- This may depend on the application

$$X_{sv} = D[3,2] = \frac{1+8+27}{1+4+9} = \underline{2.57}$$

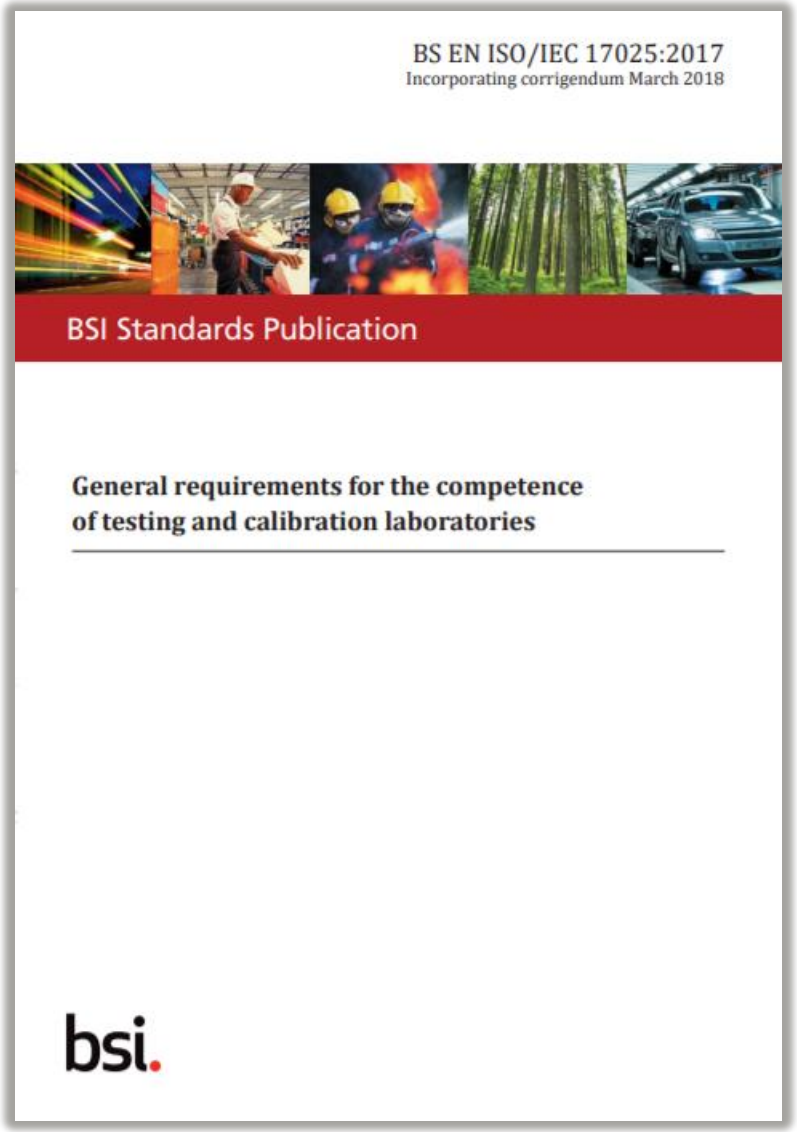
Surface area moment mean

$$X_{vm} = D[4,3] = \frac{1+16+81}{1+8+27} = \underline{2.72}$$

Laser diffraction

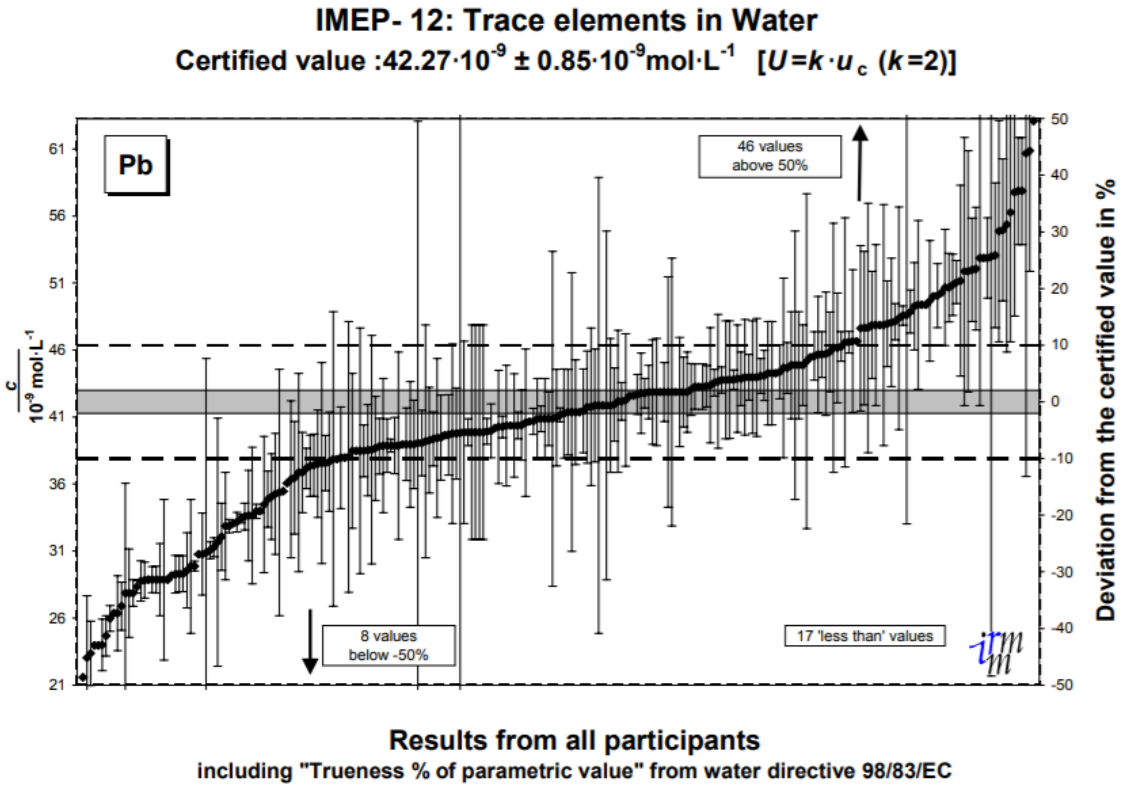
Ensuring measurement quality

1. Measurements should be fit for purpose
2. Use properly validated methods and equipment
3. Staff should be suitably qualified to perform the measurements
4. Regular independent assessment of performance
5. Well defined quality control & quality assurance procedures
6. Measurements should be stable over time and comparable across location

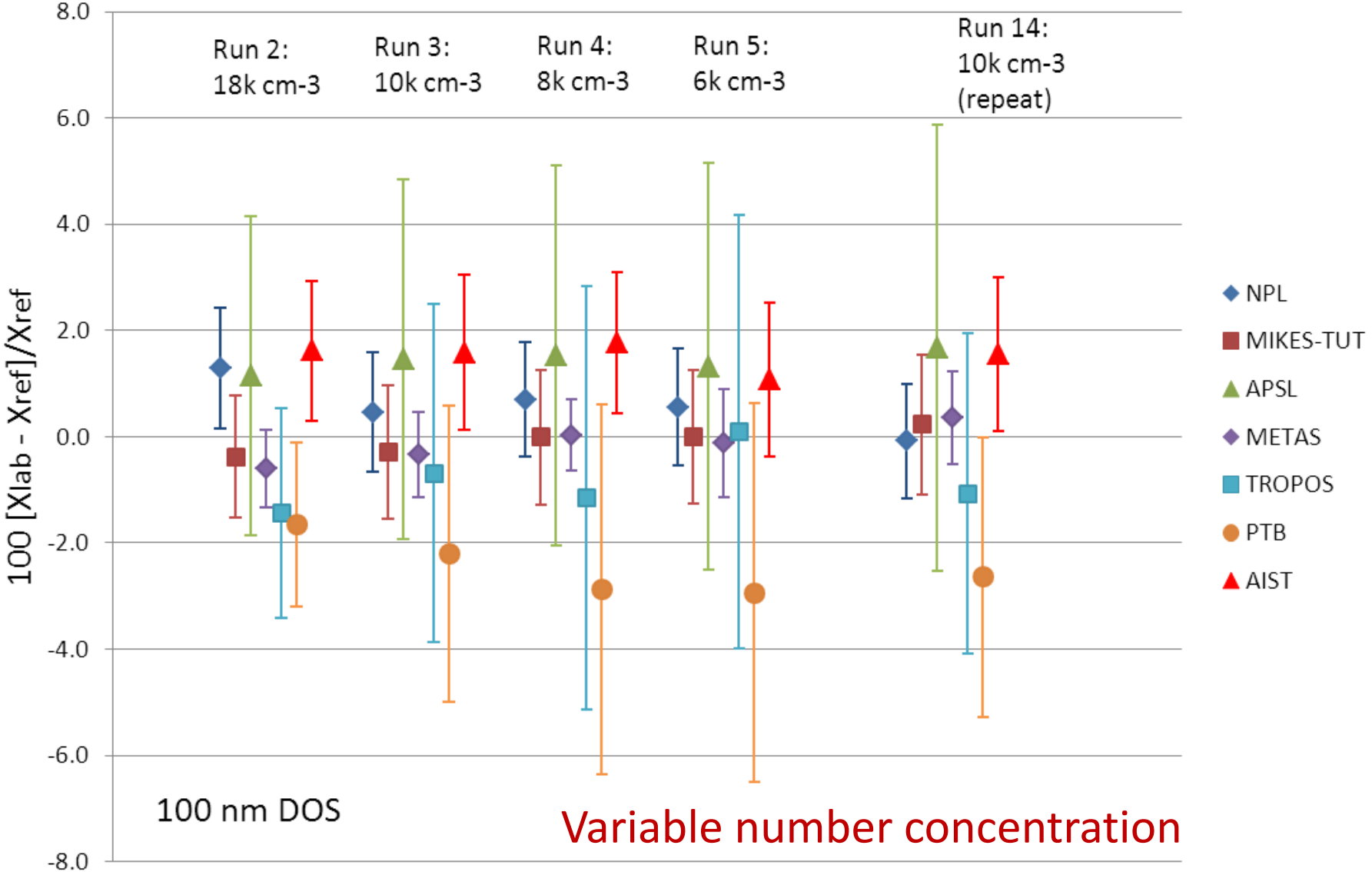


Ensuring Quality: Comparisons / Proficiency Testing

- An excellent way of demonstrating on-going competence
- Comparison of methods and measurands
- Improving performance
- Determining method precision and accuracy
- Comparing operator capabilities
- Instilling confidence in staff, management and customers
- Satisfying regulators and accreditation bodies

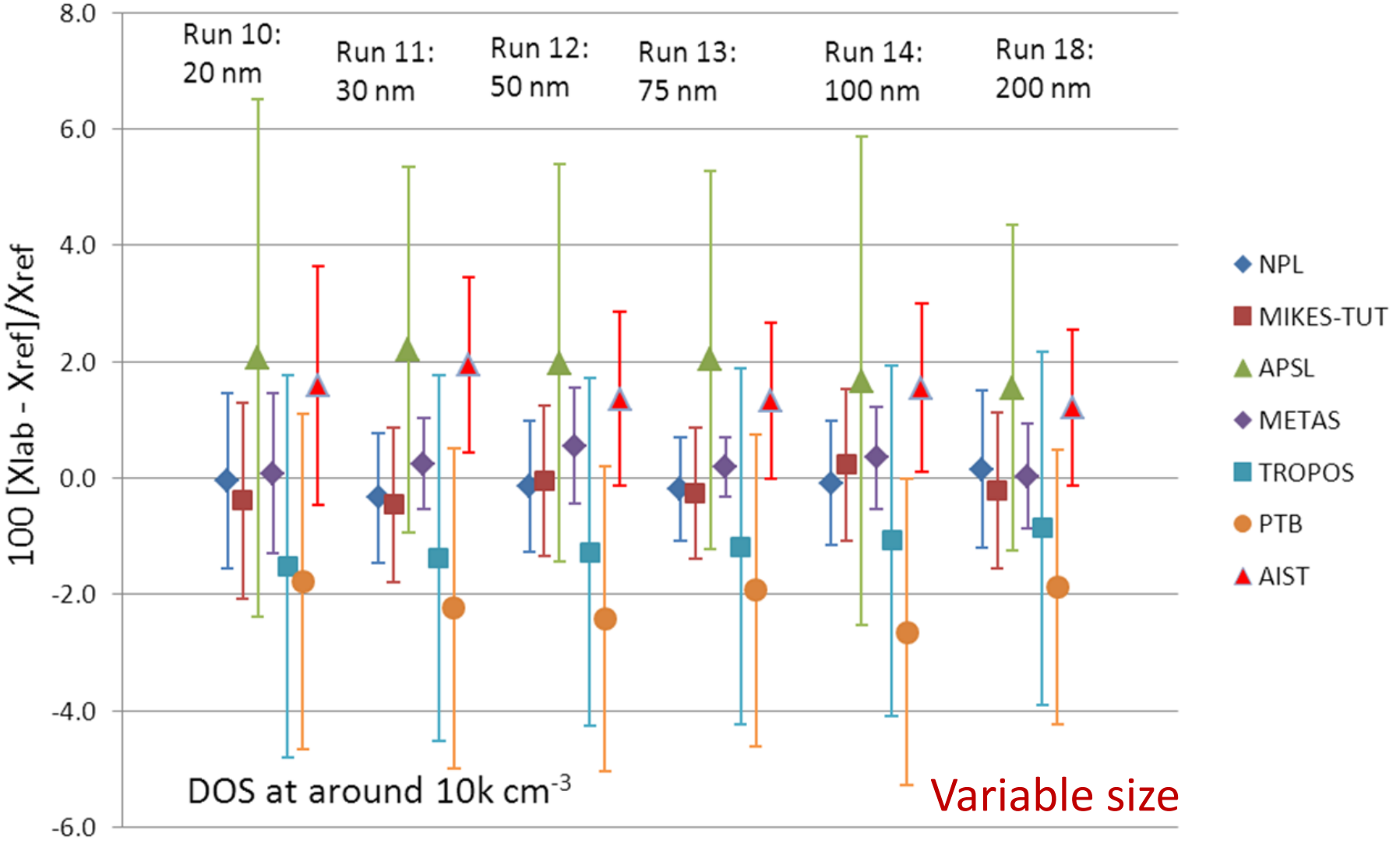


Comparisons at the National Metrology Institute level

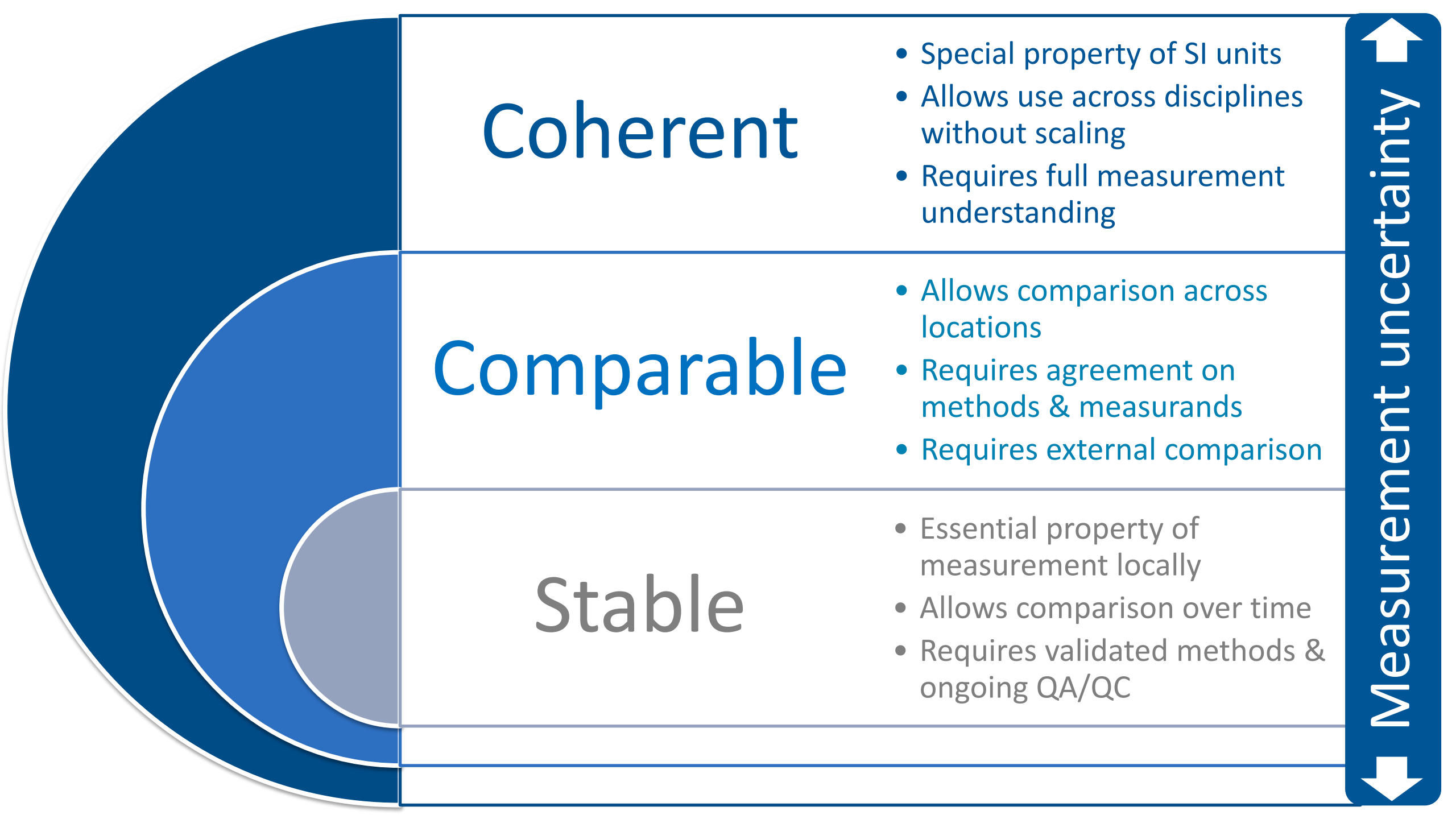


- EURAMET 1244 aerosol electrometer
- Comparison of primary standards
- Indication of how well these units can be realised
- Provides traceability for all measurements of nanoparticles in air and emissions
- **State-of-the-art is ± 2 %**

Comparisons at the National Metrology Institute level

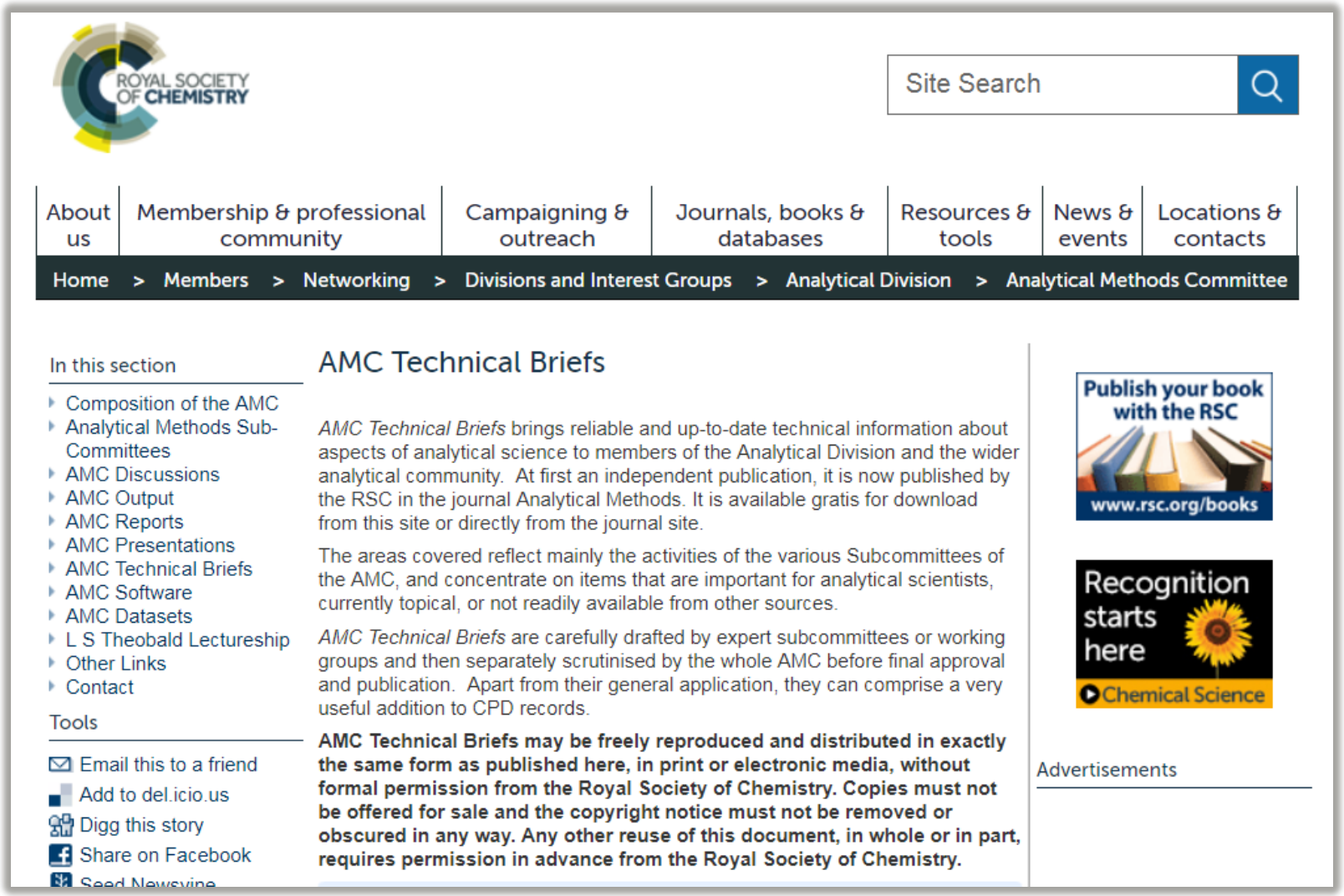


- EURAMET 1244 aerosol electrometer
- Comparison of primary standards
- Indication of how well these units can be realised
- Provides traceability for all measurements of nanoparticles in air and emissions
- **State-of-the-art is ± 2 %**


Coherent
Special property of SI units
Allows use across disciplines without scaling
Requires full measurement understanding
Comparable
Allows comparison across locations
Requires agreement on methods & measurands
Requires external comparison
Stable
Essential property of measurement locally
Allows comparison over time
Requires validated methods & ongoing QA/QC
Measurement uncertainty

RSC's Analytical Methods Committee

www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/TechnicalBriefs.asp



Search:
AMC Technical Briefs