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Putting the Quality into Air Quality Measurements

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Abstract:

One of the thirteen indicators put forward to act as the Government's "quality of life" barometer, alongside health and economic prosperity, is air quality. Reliable measurements of the pollutants that determine air quality are clearly important for producing a meaningful indicator. The mechanisms in place to ensure consistent, traceable data for these analytical measurements within the United Kingdom are described.

Controlling problems with air quality used to be simple. You found out what the sources of the pollutants were; you made sure that emissions were reduced; you watched the problem go away. That, crudely, describes how the urban smogs seen in Britain in the 1940s and 1950s were eradicated, largely through the Clean Air Act of 1956 which put tight curbs on coal burning in towns and cities. Where was the need for accurate, reliable measurements?

The pollutants causing problems today have more complex origins than the sulphur dioxide and smoke from coal burning, which led directly to adverse health effects. Motor vehicles have replaced coal-burning as the dominant source of pollutants in urban areas, but the pollutants of most current concern to health - ozone and fine particles - have to be considered as arising within a much wider context of atmospheric chemistry over large geographical areas. Ozone, for example, has higher concentrations in rural areas, away from the main sources of pollutants that lead to its formation, because in towns it is destroyed by higher concentrations of nitrogen monoxide. Also, its concentrations are highest in the south of England because of its lower latitude and because of contributions from continental Europe. Although less dramatic than "pea-soupers", studies have estimated that at least 10,000 premature deaths each year in the UK are currently associated with air pollution, and the large rise in respiratory problems such as asthma is also likely to be linked to air quality.

Recent and up-coming air quality regulation, originating both from the UK Government and the European Union, is based on setting upper limits for the concentrations of an expanding number of individual pollutants, as measured in the air breathed by some substantial fraction of the population. Accurate measurements are therefore needed to apply the legislation, to gauge trends, to refine models of atmospheric chemistry which can predict future levels, and to help with studies of medical effects, which in many cases are not quantitatively established.

What pollutants?

The field of air quality is concerned with components of the atmosphere close to ground level which are linked to detrimental effects, particularly on people. These do not include any of the principal components in air - nitrogen, oxygen, argon, carbon dioxide and water vapour - and all relevant pollutants are present only in "trace" amounts, typically measured in parts per billion (ppb) by molar ratio. The range of pollutants measured depends to some extent on

established practice, and the following pollutants are those which are most commonly measured, and which also feature most prominently in regulation:

POLLUTANT	TYPICAL CONCENTRATION
ozone	0 - 100 ppb
nitrogen dioxide	0 - 150 ppb
sulphur dioxide	0 - 200 ppb
carbon monoxide	0 - 10 ppm
benzene	0 - 2 ppb
1,3-butadiene	0 - 0.5 ppb
PM ₁₀ particulates (described below)	0 - 200 µg/m ³

Other pollutants of interest include metals, such as lead, cadmium, arsenic, mercury and nickel, polycyclic aromatic hydrocarbons (PAHs), such as benzo[a]pyrene, and dioxins, which are all usually analysed after collection of particles on filters.

Traceability, from physics to chemistry

Even though the concentrations of air pollutants would be considered very low in most types of analysis, the available methods of sampling and quantifying the pollutants in the table are relatively mature - the exception being PM₁₀, which will be returned to later. For most gaseous species, air can be drawn directly into the analytical instrument, where the pollutant is measured without any need for pre-concentration or any other sample preparation.

Benzene and 1,3-butadiene are typically collected over a sampling period by absorption onto a passive solid sorbent, before being injected into a gas chromatograph, but in all these cases the measurement process is amenable to calibration by directly introducing a sample of known concentration into the sampling line.

The measurements provide an interesting range of approaches for realising traceability. In most physical measurements, say of voltage, it is generally acknowledged that accurate primary standards can be made, by reference to SI definitions, and that calibrations should be made to these standards either directly or through a short traceability chain. This is similar to the case for carbon monoxide, where mixtures at these very low concentrations can be made reliably from first principles, for example by weighing the pure components, and kept stable in gas cylinders. Calibration can then be performed using such mixtures with confidence.

At the other extreme, ozone cannot be kept as a stable, known calibration mixture for a useful length of time because of its reactivity. In common with much of analytical chemistry, ozone measurements achieve traceability through side-by-side comparisons of analysers and by an adequately defined and recognised reference method, in this case a particular design of photometer.

For moderately reactive gases such as sulphur dioxide and benzene it is possible to make stable reference mixtures, but this is more difficult than for carbon monoxide. In these cases cylinder gas mixtures are used to calibrate analysers in the field, but these are characterised and rechecked by reference to the most appropriate laboratory method, for example a dynamic absolute calibration technique, which also use gravimetry.

Automatic Monitoring Networks in the UK

The Department of the Environment, Transport and the Regions funds an extensive network of air quality monitoring sites throughout the country, which has built up over many years to the present size of about 100 sites. They are used both to supply good quality data to inform government policy, and to assess any instances of concentrations exceeding their limit values. Their locations have been carefully chosen to represent typical human exposure in a variety of roadside, urban and rural situations. They monitor some or all of the pollutants listed in the table above with automatically operated sites, generally producing hourly data which is made widely available, for example via the internet. The Department has long appreciated the need to ensure the validity of the data, and appoints Quality Assurance/Quality Control Units (currently NPL and AEA Technology) to calibrate the field instruments and process the ratified data, independent of the Management Unit responsible for operating and maintaining the sites.

These QA/QC Units visit all the sites two or four times per year to carry out calibrations and instrument checks, which are used to produce the ratified data, or to delete data if a serious fault is found. Both Units use calibration gas cylinders certified at NPL to the national standards developed under the VAM programme. All portable ozone photometers which are used as transfer standards to calibrate the field ozone analysers are in turn calibrated using the national reference photometer maintained at NPL. In this way very clear and **direct** traceability is achieved between a large number of field measurements and the national standards.

International Comparisons

One advantage of linking the UK's measurements so directly to a single reference laboratory is the ease with which international harmonisation can be assessed. As the UK's national standards laboratory, NPL participates in regular international comparisons for key measurements, organised by metrological organisations such as BIPM and EUROMET. For air quality measurements these are complemented by exercises arranged by the European Union Joint Research Centre at Ispra, and also by jointly funded European Framework projects. One of these in particular, known as HAMAQ (HARmonisation of Measurements of Air Quality) has been investigating the agreement achieved between European standards laboratories under good laboratory conditions, so that valid figures can be used to calculate the uncertainty of field measurements. The project is coordinated by NPL and is partly funded by the VAM programme.

Particulates

Airborne particulates make a good case history of a tricky measurement problem. As a visible and irritating pollutant, suspended solids and droplets have been quantified for many decades by a variety of ad-hoc methods. These have generally involved collecting the particulates on a filter, and either gauging the blackening of the filter, weighing the collected mass, or quantifying it in some other way (such as by its attenuation of beta radiation produced by a low-level radioactive source).

Standardisation has taken place along two lines: collection of the particulates, and its subsequent quantification. In the first area, larger particles are deliberately excluded, on the grounds that they do not reach human lungs when inhaled, and hence are unlikely to be the cause of health effects. The most commonly measured PM₁₀ component refers to particles less than about 10 µm in diameter, whereas PM_{2.5} corresponds to those less than 2.5 µm,

and so on. This size selection is generally achieved using inlet designs which remove larger particles by viscous drag. Different designs have different cut-off distributions and maintenance requirements, and standard reference designs have been chosen - in Europe the European Committee for Standardisation (CEN) has defined standard inlet designs for PM₁₀, although there is not yet an EU standard for PM_{2.5}.

Quantification is currently concerned predominantly with the collected mass, so that by making use of the known volume of air which passed through the collector, the unit of measurement is $\mu\text{g}/\text{m}^3$. Mass measurement is in principle a straightforward process, but in the last few years a more complex picture has emerged, in which the measured mass can vary by at least 50%, depending on the composition of the particulate matter and the temperature regime during the time between collection and weighing. This has raised the parallel issues of standardisation - which aims to ensure that different people can be confident they are measuring the same thing, and of purpose - deciding which of many variations to the measurement method is most informative with regard to health effects. Given that new studies of health effects are likely to take many years, standard methods suitable for enforcing legislation for particulates across Europe are proceeding pragmatically.

EU/CEN developments

Where harmonised methods are needed to enable European Union Directives to be properly applied across all member states, CEN is mandated to produce the necessary written standards. In the case of air quality, Working Groups within the CEN Technical Committee 264 are preparing unusually comprehensive standards which will specify reference methods and their performance, instrument performance tests, quality control procedures and other items designed to ensure that measurements made throughout the Union are valid, ie they have an uncertainty which is demonstrably within the limits set out in the Directives. NPL staff, being closely involved both in the validation of measurements and the practical operation of monitoring sites, are actively involved in many of these Working Groups.

Looking forward

Even as the immediate air quality measurement requirements are being dealt with, a number of other important issues for the future are taking shape. For example, there is a need to investigate pollutants beyond the "traditional" set, such as PAHs, to clarify their effects on health. In general this will mean measurements which are more difficult in terms of calibration and validation, but developing technologies such as combined gas chromatography and mass spectroscopy make reliable analysis more feasible. Because they have not been monitored systematically in the past, their health effects are poorly understood. Likewise, the particulate measurement issues need to be clarified and resolved.

In addition, outdoor air quality needs to be seen in the context of actual personal exposure. We spend the majority of the time indoors, breathing air which has a large set of added components from furniture and cleaning materials, for example, often at much higher concentrations than are found outdoors. These need reliable measurement techniques and scientific investigation.

Also, the small scale geographical variations in concentration need to be investigated to determine pollution "hot spots" which would otherwise be missed. This will need a combination of simpler, lower cost analysis techniques such as sampling by diffusion tubes, which can be used in large numbers for a local survey, and modelling software, which can

predict concentrations based on knowledge of the geography, local sources (including roads), meteorology and atmospheric chemistry. It goes without saying that such models are only as good as the measurements used to validate them.

Together with the growing realisation that air quality is a truly international problem needing international coordination for its solution, it is clear that mechanisms for ensuring the validity and fitness for purpose of air quality measurements will be needed for many years to come.