

Background Information on Atmospheric Pollutants & Air Quality:

what data is there and how are the measurements made?

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Note:

This document is intended for Post 16 students and their teachers.

Measuring air pollutants

Why should we measure air pollutants? Some chemicals that are in the air have limits imposed by governments. Above these levels the chemicals may be harmful to health to people, other animals or plants. These atmospheric chemicals need to be monitored accurately. It is no use in just measuring in one place in the UK on one day per year. Different areas, towns, cities, countryside may have different concentrations of pollutants and different times of night and day at different times of the year. An industry or natural process may only produce during the evening in the summer. The wind conditions (strength and direction) may move that pollutant to different places each year (or may not move it at all).

How can we measure pollutants in the air around us? Where can we measure pollutants? Running an air quality network (<https://uk-air.defra.gov.uk/>) is expensive and so there are a limited number of sites around the U.K. that The U.K. Department for Environment, Food and Rural Affairs (Defra) can site science instruments to make these measurements. First, we will think about what pollutants are measured, second, how they are measured and third, look at some examples of where they have been measured.

Pollutants

Most of the pollutants measured by the U.K. Air Quality Network are called primary pollutants. This means that they are produced directly by a source, which could be from transport, e.g. vehicles of various types, construction, heating, burning of waste, cleaning agents and of course natural sources such as from animals, plants etc. The network focuses on primary pollutants that are produced from human activity and we will look at each of these in turn.

Hydrocarbons

Hydrocarbons (chemicals that just contain hydrogen and carbon atoms bonded together) are major components of fuel that is burned in combustion engines that propel vehicles. Some unburned fuel will be released, and this is measured by the network. Higher levels of hydrocarbon will be found near busy roads and near other sources such as petrol stations, oil refineries, etc.

How are they measured?

First, all the hydrocarbons present in the air are sucked into an instrument, a GC-FID or GC-MS (see later on) using a pump and flow into a tube containing a solid adsorbent material, to which the hydrocarbons stick. When enough time has passed (often minutes to an hour), the flow of air to the adsorbent is shut off and air is directed to a new collecting tube. The solid used as an adsorbent must be sticky enough for the hydrocarbons to stick to it, but not too sticky that they are permanently stuck or react on the surface and are lost. Once collected, the solid material is heated to drive off the hydrocarbons sticking to its surface. We then need to separate out the hydrocarbons. This is the essence of chromatography.

In the systems used to measure hydrocarbons, they are separated out by boiling point, the heavier ones will boil at higher temperatures than the lighter ones. As the solid is heated, different hydrocarbons boil off and are carried by a stream of pure air (it is important not to

contaminate the sample) to the detector. This separation part is called gas chromatography (GC) and the two detectors used are a flame ionisation detector (FID) or a mass spectrometer (MS). In an FID, the hydrocarbon gas is burned and in doing so creates some ions (charged species) that can be detected. By running a sample of known concentration through the system the FID can be calibrated and so when an unknown amount of hydrocarbon passes through, its concentration can be determined. A mass spectrometer effectively weighs the sample and so its concentration can be determined.

An example of where hydrocarbons have been measured

Benzene (C₆H₆)

Benzene is a hydrocarbon. It is produced from unburned fuel or a product of incomplete combustion. Measurements of benzene from the Marylebone Road in London from around 2000 to the present day illustrate some interesting points about air quality.

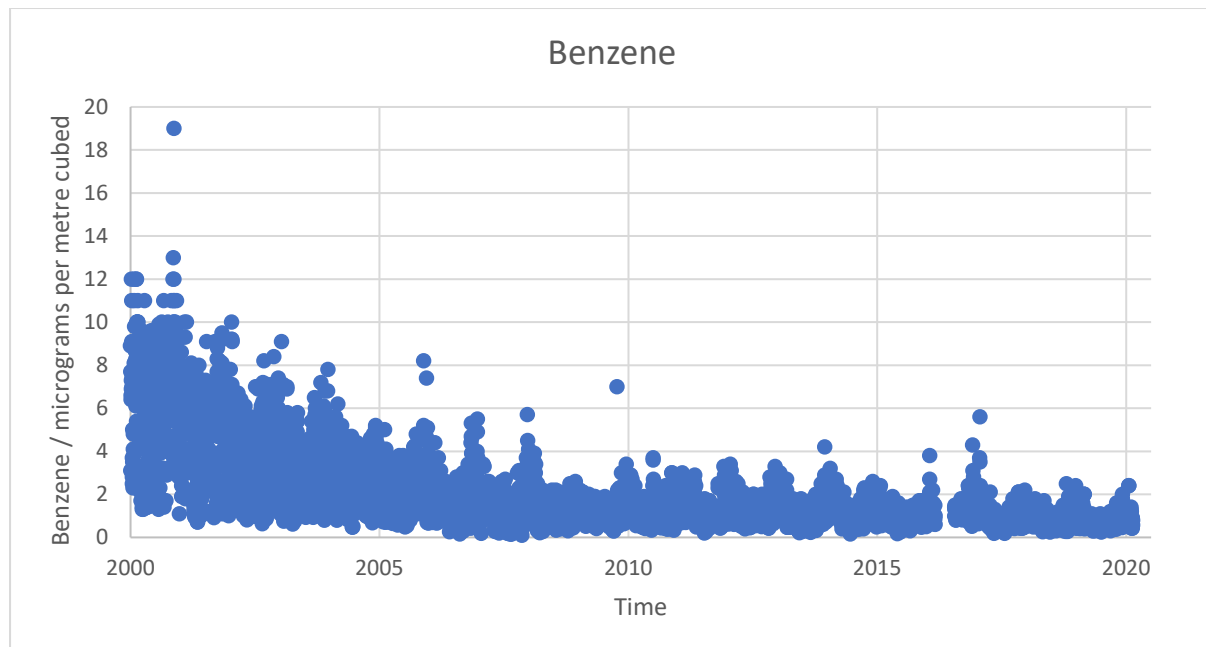


Figure 1. Daily average benzene level (micrograms per cubic metre, $\mu\text{g m}^{-3}$) as measured at the Marylebone Road in London from 2000 to 2020.

Figure 1 shows the clear decline in the level of benzene since 2000, where the decline was sharp from 2000 to about 2010 but has been much slower since then.

We might ask why benzene has gone down? Some possible reasons:

- Less cars?
- Cleaner cars? (more electric cars?)
- Cleaner fuel? (less benzene in unleaded petrol?)

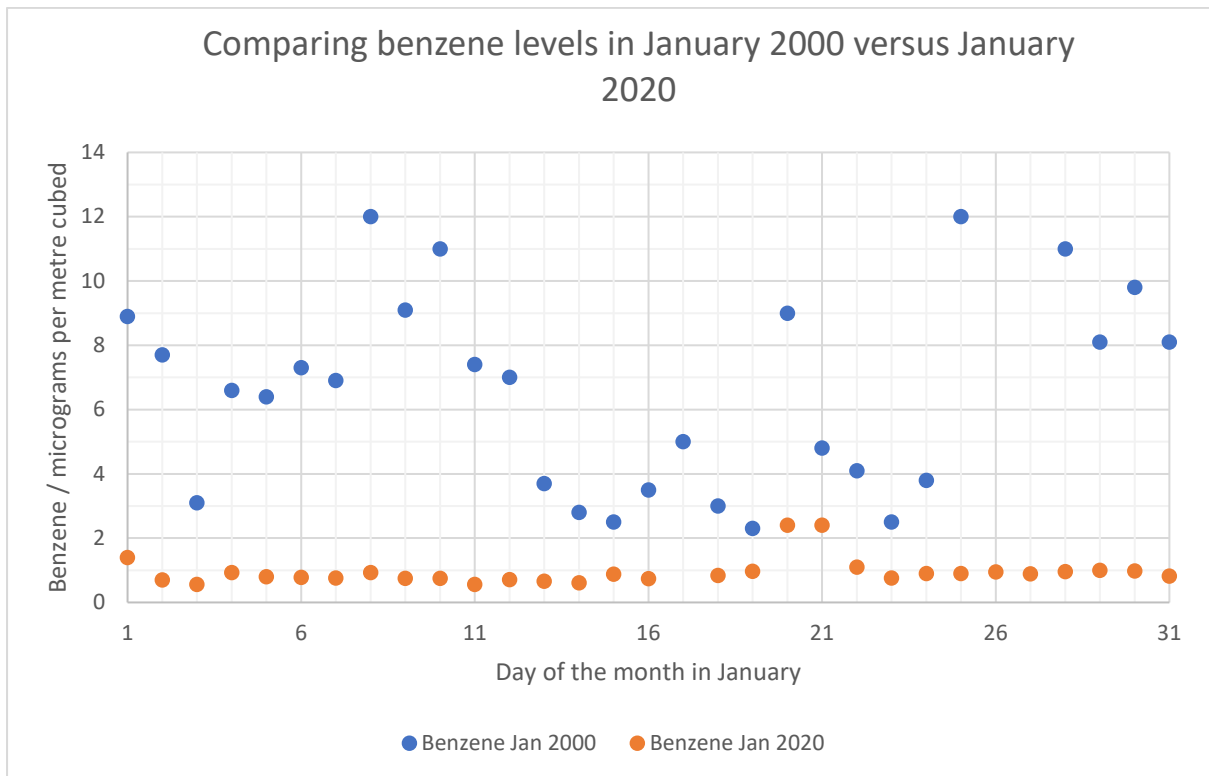


Figure 2. Daily average benzene level (micrograms per cubic metre, $\mu\text{g m}^{-3}$) as measured at the Marylebone Road in January in 2000 and 2020.

In Figure 2 we see a comparison between January 2000 and January 2020. First, January 2020 has much lower levels of benzene. Second, there is a lot more variability (change) in January 2000. Why might this be?

- Perhaps, weekday and weekend differences in the number of vehicles on the road?
- Perhaps, the congestion zone coming into force in London on 17th February 2003 (Marylebone Road was on the edge of the zone)? A congestion zone is where a charge is made to bring your vehicle into an area hoping the cost will put off people so less vehicles will use the roads.
- Were cars in 2000 more polluting than in 2020? If so, why?
- Maybe fuel in 2000 contained a lot more benzene than 2020?

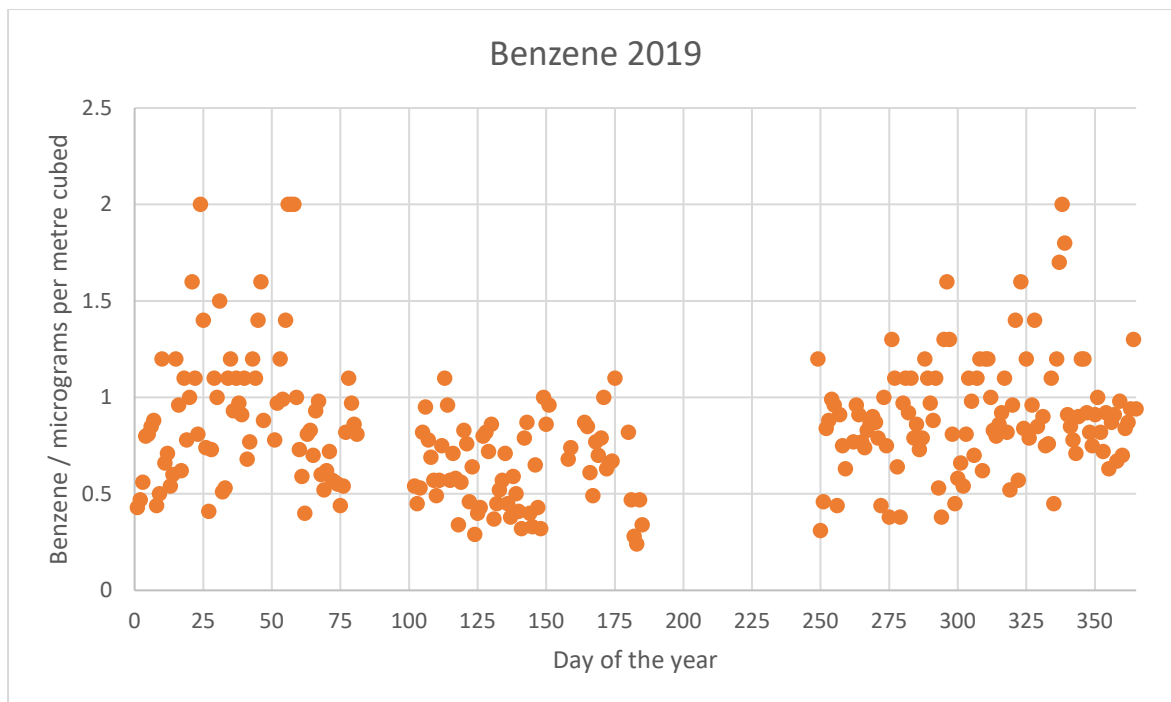


Figure 3. Daily average benzene level micrograms per cubic metre, ($\mu\text{g m}^{-3}$) as measured at the Marylebone Road in London during 2019.

In figure 3 we see that the level of benzene goes through a minimum in the summer and a maximum in the winter in 2019. (This is seen clearly in more recent years; it is less clear in 2000). Why might this be?

- Less cars in the summer? People walking and cycling more?
- Hotter in the summer, perhaps this is a reason somehow?
- More sunlight in the summer? This might remove the benzene directly or help to remove it?

Nitrogen Oxides (nitric oxide, NO and nitrogen dioxide, NO₂)

NO is produced inside a combustion engine. Air is needed in the engine so the oxygen can be used to burn the fuel (petrol/diesel). Some of the nitrogen and oxygen reacts together instead producing nitrogen oxides. This is because there is a lot of heat and pressure which allows nitrogen and oxygen to react, in normal air conditions they don't react.

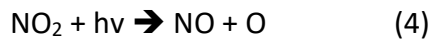
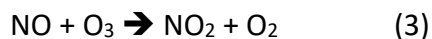
How are nitrogen oxides concentrations measured?

The concentration of the gases can be measured using the way the gases react with a poisonous gas called ozone (O₃) and measuring the light the reaction produces.

NO is produced inside a combustion engine through the Zeldovich mechanism.



Once NO is produced it can react with species in the atmosphere such as ozone (O₃, see later) and be converted to NO₂. NO₂ is a brown coloured gas and is rapidly broken down in sunlight and so NO and NO₂ are interchanging rapidly in the daytime. They are known collectively as NO_x. These two species alter atmospheric chemistry dramatically, turning a low NO_x atmosphere that removes surface ozone to one that produces surface ozone. This is bad for two reasons, first ozone in the Troposphere is a potent greenhouse gas and second, ozone is a powerful oxidant that can affect plant and animal health (adversely).



NO is detected by reacting NO with ozone (O₃) to produce NO₂* which then releases a photon of light and becomes stable NO₂. Now the NO_x mixture is all NO₂. Converting this back to NO by passing the gas mixture over a heated catalytic converter allows the process to be repeated. The increase in light observed is due to the original amount of NO₂ present and so concentrations of NO and NO₂ can be determined with the same spectroscopic technique. See Appendix to read about how spectroscopy works.

An example of where nitrogen oxide concentrations have been measured

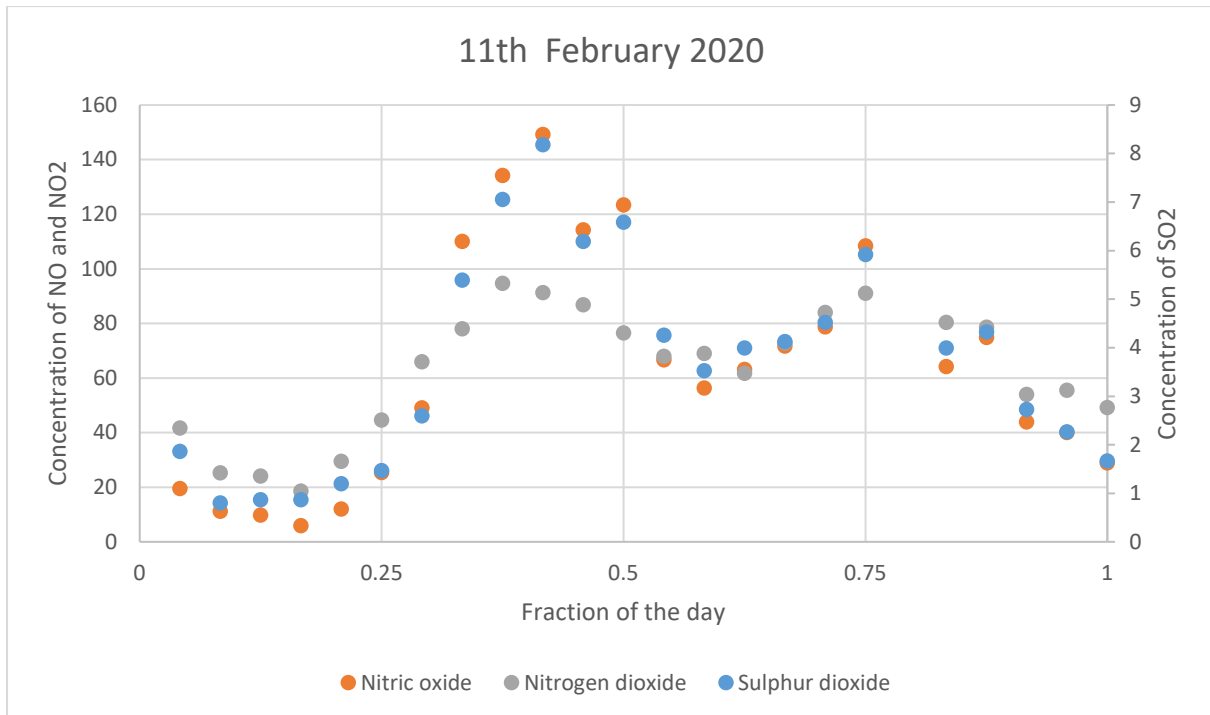


Figure 4. NO, NO₂ and SO₂ (sulfur dioxide) concentrations measured at the Marylebone Road, London during Tuesday 11th February 2020.

Figure 4 shows that the NO_x and SO₂ observed at the kerbside site of the Marylebone Road is heavily influenced by traffic, with morning and afternoon peaks associated with rush hour traffic.

Using figure 4:

- Why is the peak in the morning larger than the peak in the evening?
- Would this pattern be different on the weekend?
- Would this pattern be similar in other places in the U.K.?

Carbon Monoxide (CO)

Primary sources give off CO directly into the air and account for 55% of world emissions. The two major sources of CO are the incomplete combustion of fossil fuels (burning with insufficient oxygen present) and biomass (trees, bushes and grass) burning. Some CO is emitted from the oceans and vegetation. The incomplete combustion of fossil fuels produces 23% of global CO.

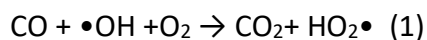
How is carbon monoxide concentration measured?

CO can be detected directly using an appropriate light sensor. Using light to make measurements is called spectroscopy. However, by reacting the CO with another compound, one of the products can be detected even more sensitively and so this is the method used.

Carbon monoxide concentration is measured with a peak performer 1 (PP1) instrument. The CO gas is reacted with a poisonous chemical called mercury oxide and in doing so makes mercury vapour. The mercury vapour can be measured by seeing how much ultraviolet light it absorbs (takes in). This is then a measure of the carbon monoxide.

CO is the main global loss process (sink) of the hydroxyl radical ($\bullet\text{OH}$), a key atmospheric oxidant. $\bullet\text{OH}$ reacts with and removes greenhouse gases, such as methane (CH_4). If CO reacts with $\bullet\text{OH}$ instead, more methane is left in the atmosphere for longer with negative effects on the Earth's climate.

When $\bullet\text{OH}$ reacts with CO it forms carbon dioxide (CO_2) and the hydroperoxyl radical ($\text{HO}_2\bullet$), (1). $\text{HO}_2\bullet$ goes through a series of reactions with NO_x (2–3) that form ozone in reaction (4).



CO is measured using a peak performer 1 (PP1) instrument. Sampled air is injected onto a gas chromatographic column at a constant temperature of 105 °C within the PP1. Once separated from other gases, CO flows over a bed of heated mercuric oxide (HgO) at 265°C, where it is oxidised to CO_2 while the solid mercury (II) oxide ($\text{HgO}_{(s)}$) is reduced to mercury (Hg) vapour. The vapour is then measured quantitatively by atomic absorption of UV light using spectroscopy. See Appendix to read about how spectroscopy works.

An example of where carbon monoxide concentration has been measured

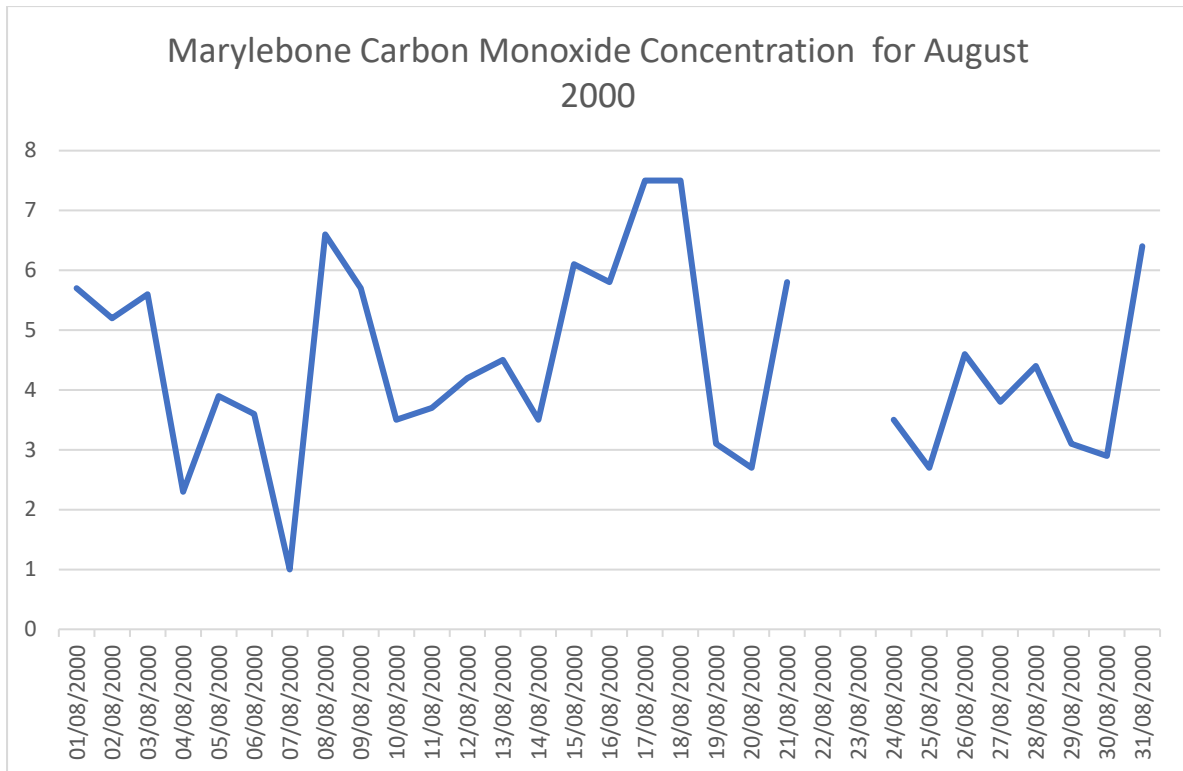


Figure 5. August 2000 carbon monoxide maximum concentrations (milligrams per cubic meter of air, mg/m³) in Marylebone, London.

Using figure 5:

- Can you work out when the minimum concentration of carbon monoxide was?
- Can you find out what dates were weekends (Saturdays and Sundays)? Do the weekend concentrations differ to weekday concentrations?
- Suggest how might this data look different to that of a winter month such as November 2000?

Ozone (O₃)

Ozone is a poisonous form of oxygen. We breath oxygen as O₂. O₃ is present in the atmosphere in tiny amounts, but it is important and is involved in the breakdown of other atmospheric pollutants.

How is ozone measured?

Ozone can be measured by absorption of ultraviolet (UV) light. The air is drawn into a chamber using a pump and illuminated with UV light. O₃ effectively absorbs light of a certain wavelength in the UV range. The concentration of O₃ can then be determined from how much of the UV light is absorbed in the chamber and compared to a chamber without any ozone.

An example of where ozone concentration has been measured

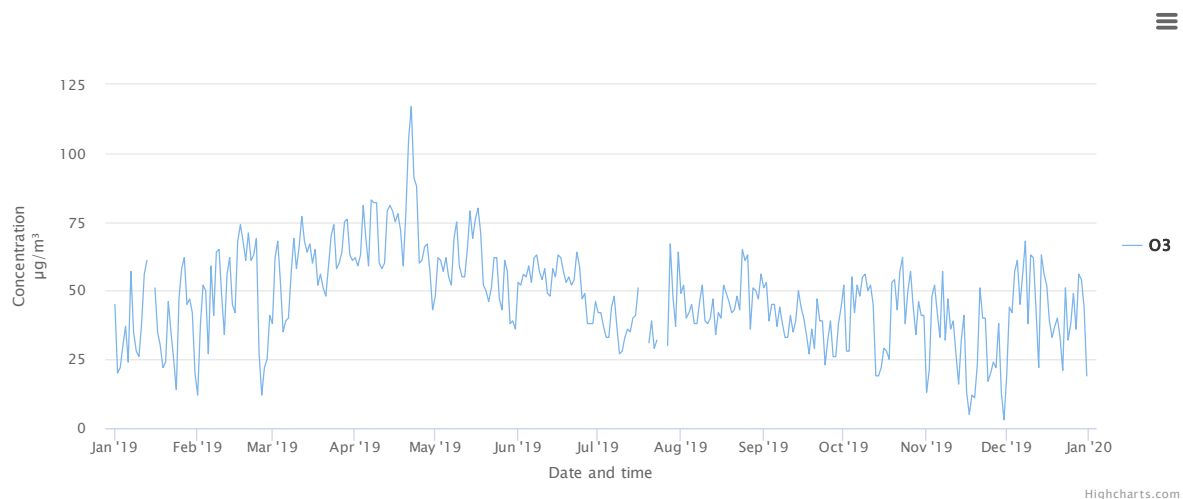


Figure 6. Ozone concentrations from a road in Edinburgh during 2019

Using figure 6, can you work out what the highest and lowest concentration of ozone was in 2019?

Sulfur dioxide (SO₂)

Note. In world science it is normal to use 'sulfur' rather than 'sulphur'.

Sulfur dioxide gas has many sources, some from nature and some from the things we do and make. Volcanoes can produce SO₂. Much of the SO₂ in the atmosphere comes from burning sulfur containing compounds such as fossil fuels. It is also produced when some metals are extracted from their ores. SO₂ has many uses including for the manufacture of sulfuric acid.

How is sulfur dioxide measured?

Sulfur dioxide can be measured using ultraviolet (UV) light and spectroscopy. The containing SO₂ air is drawn into a chamber using a pump and then illuminated with UV light. After absorption of UV light, the SO₂ molecules are excited to the upper energy levels and when they return to the ground state, light is emitted with a longer wavelength. By recording this light using a photosensor, the concentration of SO₂ can be calculated. See Box 1 to read about how spectroscopy works.

An example of where sulfur dioxide concentration has been measured

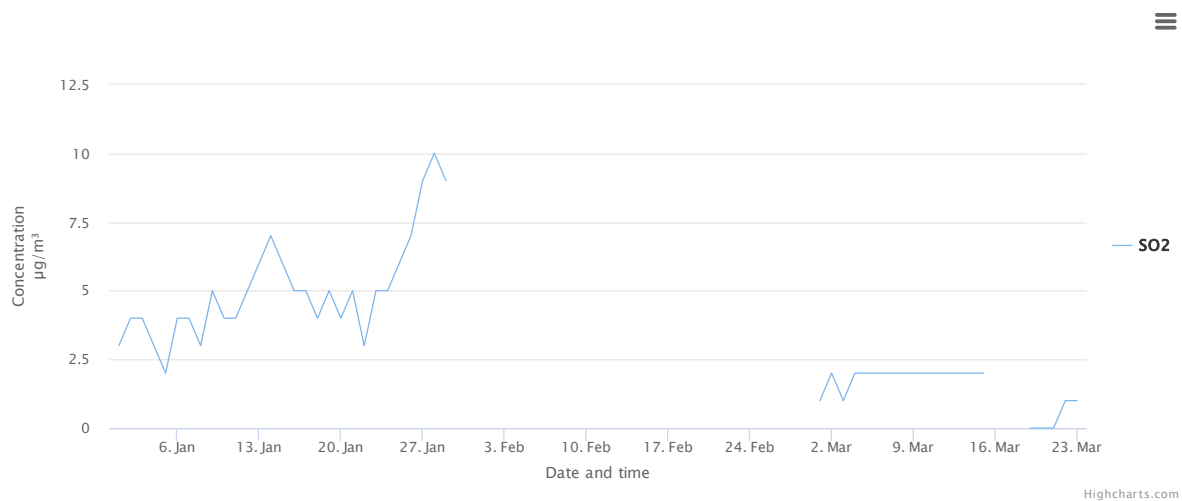


Figure 7. Sulfur dioxide measurements for the year so far (2020) in Birmingham.

Look at figure 7. What do you think happened from the end of January to the beginning of March 2020?

Particulates: PM₁₀ / PM_{2.5}

Particulates are tiny pieces of solid (dust) in the air. They come in many sizes. PM₁₀ is bigger than PM_{2.5}. The number is the size in micrometres (µm). A micrometre is a millionth of a metre. Put another way a micrometre is a thousandth of a millimetre (mm). A thick human hair is a tenth of a millimetre (0.1 mm). These particulates are tiny pieces of solid.

How are they measured?

There are four methods, used to measure PM₁₀/PM_{2.5}. In all methods the air is sucked in through a particle inlet which separates particles > 10 µm or > 2.5 µm. The mass of the remaining particles is then determined by one of four methods. These methods may use weighing, the scattering of light, using electron beams or by the effect of the mass on a spinning disc. The first method uses a very accurate mass balance. The last method is like spinning a roundabout in a playground and seeing what happens when a child jumps on board. The heavier the child the bigger the effect on the spin.

Low Volume Sampling (LVS). LVS gravimetric determination of PM values occurs by subtracting the mass of the filter without collected particles from the mass of the collected particle filter. This is then divided by the air volume that has been sucked through the filter.

Optical Light Scattering (OLS). Particle light scattering is determined by illuminating collected particles and measuring the scattered intensity at different orientations from the incident light source. The intensity of scattered light is related to mass concentration via electromagnetic theory.

Beta Attenuation. When a stream of electrons (beta rays) is directed across a thin layer of material some of it is absorbed. The amount absorbed is related to the mass. Technically the beta rays have a given energy distribution the transmitted energy is exponentially attenuated as the thickness of the sample or the number and types of atoms it encounters, increases. Immediately after collection, the mass is determined based on absorption of beta particles in the dust layer.

Tapered-Element Oscillating Microbalance (TEOM). The air sample is drawn through a filter, which sits at the end of a conical rod, which oscillates in an applied electric field. As particulates build up on the filter the frequency of vibration changes in proportion to the mass. Technically, the oscillation of the rod is maintained based on the feedback signal from an optical sensor. The vibration frequency of the rod decreases as mass accumulates on the filter, directly measuring inertial mass. The TEOM method has the advantage of being able to obtain measurements with high time resolution.

An example of where PM₁₀ particulates have been measured

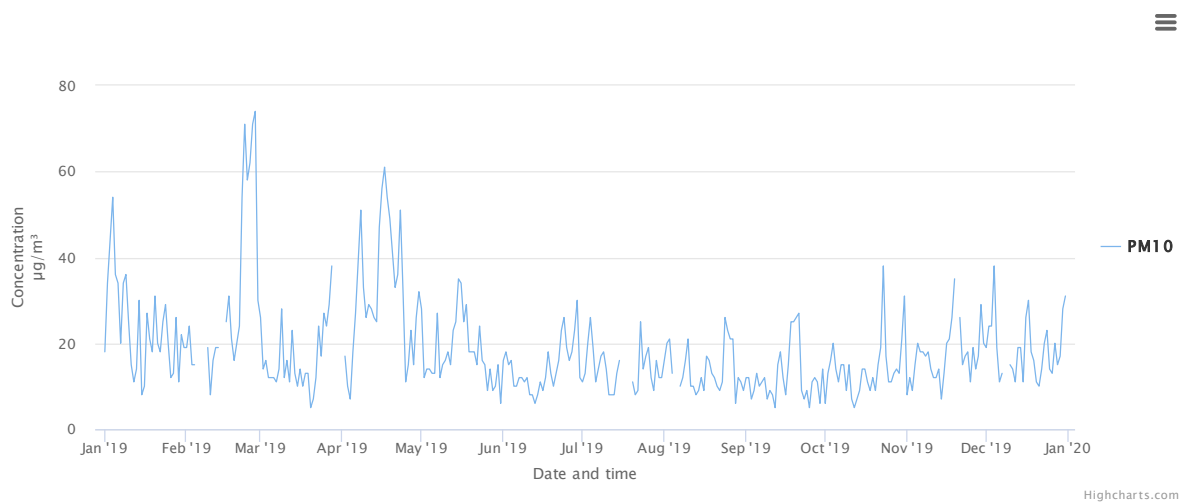


Figure 8. The PM₁₀ data from a busy road (Newport Road) going into Cardiff during 2019.

In figure 8, can you suggest why are the PM₁₀ particulates much higher in the period March to May, than in July-December? One possibility is garden bonfires as gardeners tidy debris in the spring.

Appendix

Dudley Shallcross and Tim Harrison

Using Spectroscopy methods to measure gas concentrations

Spectroscopic methods are used to measure the concentrations of several different gases. Spectroscopy uses light of different wavelengths (photons of different energies) to interact with the chemicals). This may be visible, infra-red or ultraviolet light.

Here we use an example for measuring carbon dioxide gas concentrations as an example.

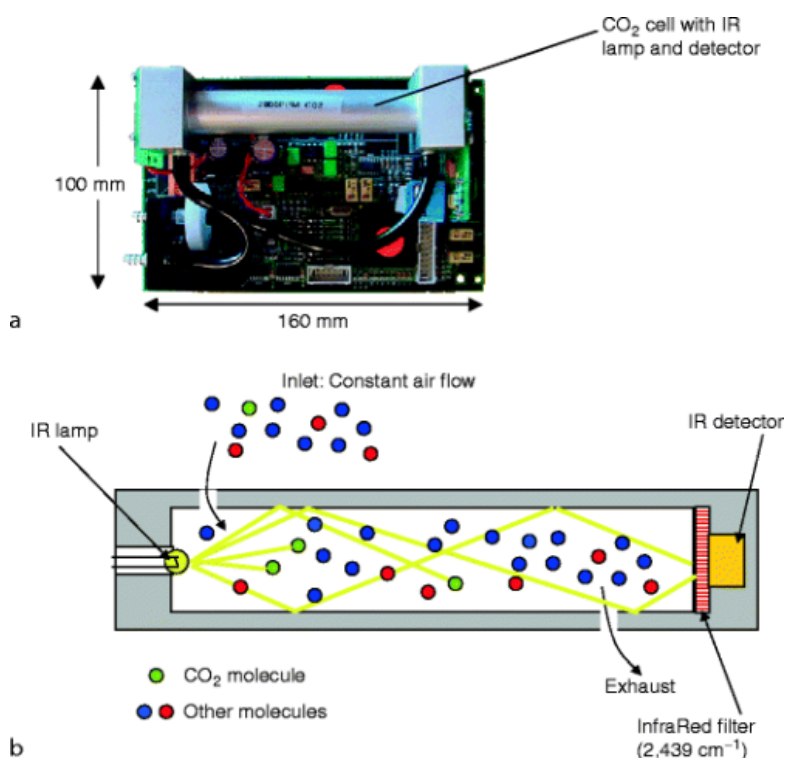


Figure 8. (a) The inside of a CO₂ sensor. (b) A diagram of the CO₂ cell within the sensor which senses light of wavelength 4.1 μm .

To detect a gas, the sensor needs to identify a characteristic of the gas that other gases do not have. In the case of CO₂, it is known that light with a wavelength of 4.1 μm causes the carbon to oxygen bonds to stretch asymmetrically (non-symmetrically). The more CO₂ molecules, the less light of wavelength 4.1 μm gets through to the detector. Measuring the decrease in the light that the detector receives, compared with light going through air containing no CO₂, allows a calculation of the concentration.

Scientists can identify characteristics of light absorption specific to materials to make other sensors.