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 teachers of primary children.

A PowerPoint presentation explaining atmospheric pollutants is available for primary children.

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 (we will see what these names mean shortly) using a pump and they 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 and this is the essence of chromatography.

In primary school we can look at experiments to separate out mixtures: e.g. magnetic and non-magnetic objects; separate by size, for example by sieving; or separate by shape or by colour using our eyes. Children could carry out chromatography experiments using colouring pens or coloured sweets and some kitchen towel (see Appendix 1). 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 a detector. This separation technique 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 particles) 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.

Benzene (C_6H_6)

Benzene is an example of a hydrocarbon. It is produced from unburned fuel or a product of incomplete combustion. It causes cancer and other illnesses. A European study found that people breathe in 220 µg of benzene every day due to general atmospheric pollution. A smoker smoking 20 cigarettes per day takes in between 1800 and 7900 µg per day (in addition).

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).

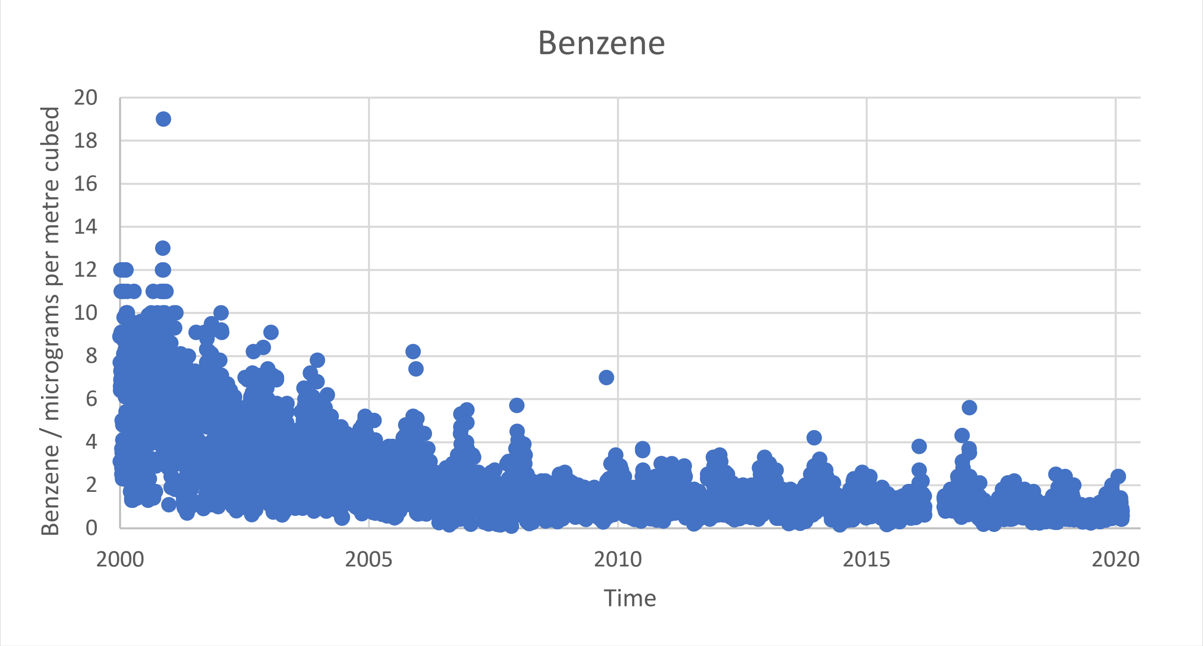


***Figure 1**. Daily average benzene level (micrograms per cubic metre, µg m^{-3}) as measured at the Marylebone Road in London from 2000 to 2020.*

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:

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

In Figure 2 we see a comparison between January 2000 and January 2020.

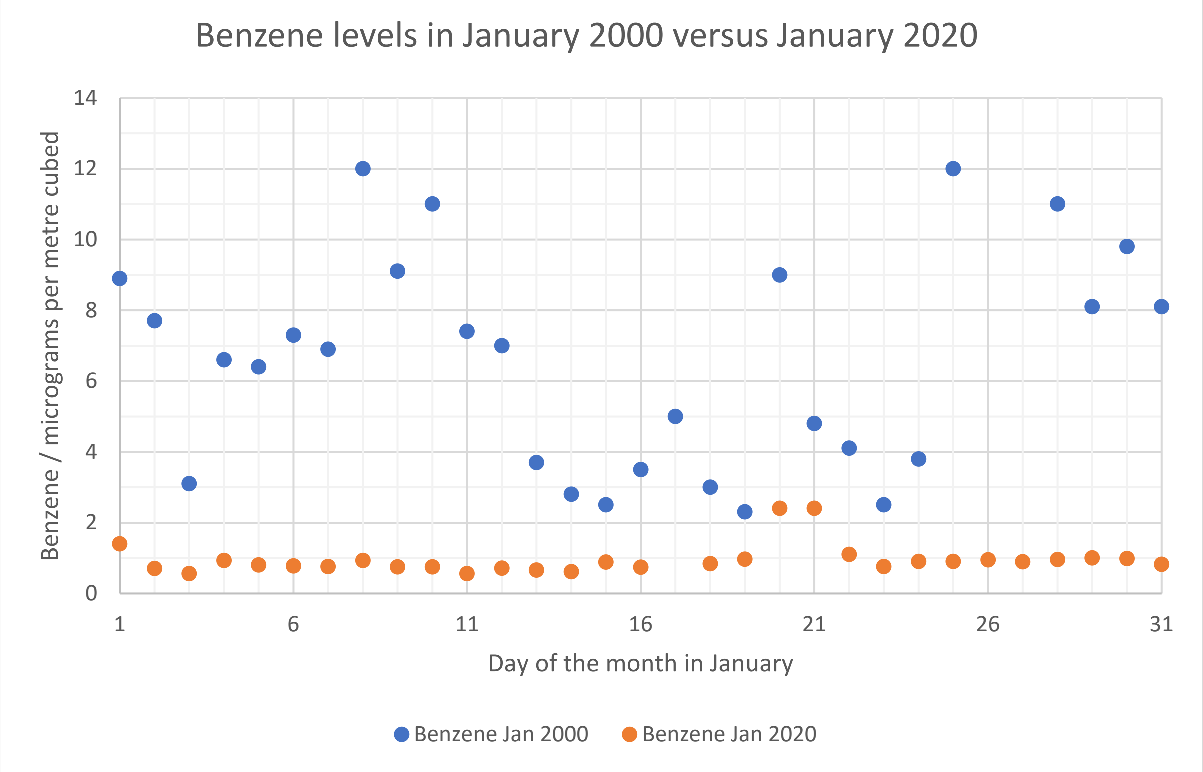


Figure 2. *Daily average benzene level (micrograms per cubic metre, µg m^{-3}) as measured at the Marylebone Road in January in 2000 and 2020.*

January 2020 has much lower levels of benzene and 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) has reduced benzene levels. 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? Perhaps petrol/diesel has changed.
- Maybe fuel in 2000 contained a lot more benzene than 2020.

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?

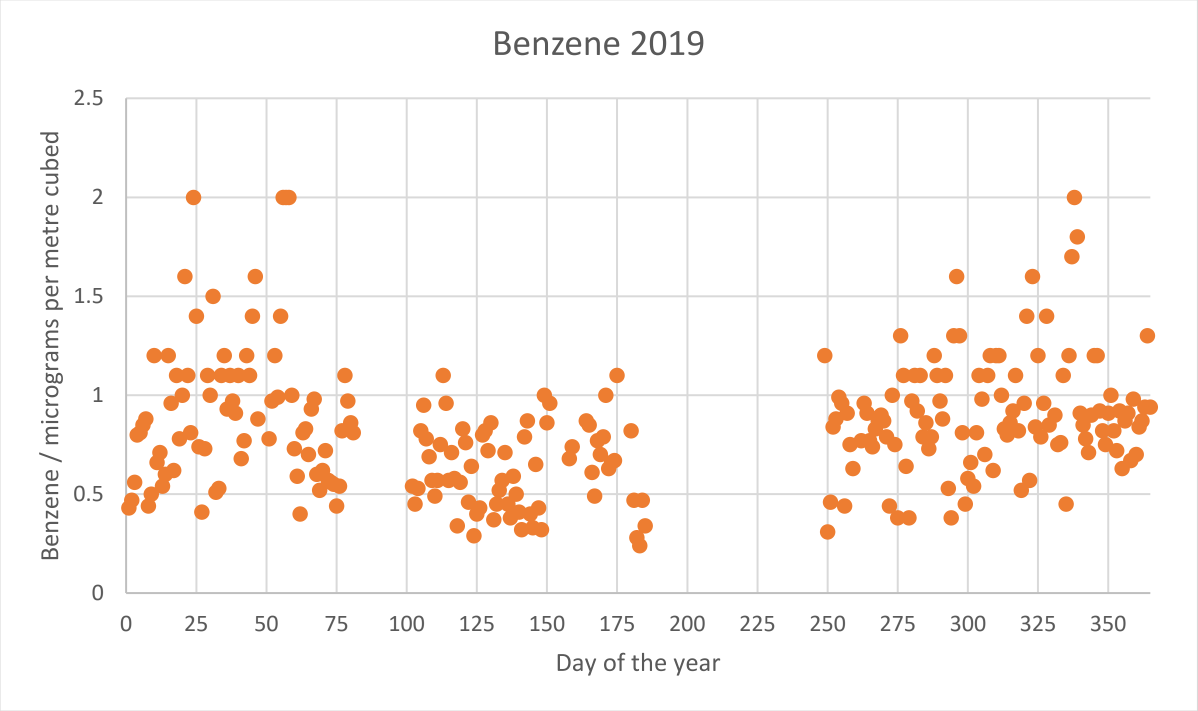


Figure 3. *Daily average benzene level micrograms per cubic metre, (µg m^{-3}) as measured at the Marylebone Road in London during 2019.*

Nitrogen oxides (nitric oxide, NO and nitrogen dioxide, NO_2)

Nitric oxide is produced inside a combustion engine. Air (mainly nitrogen and oxygen) 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 to produce nitric oxide (NO). This further combines with oxygen to create nitrogen dioxide (NO_2). This is because there is a lot of heat and pressure which allows nitrogen and oxygen to react, though in normal air conditions they do not react. Nitrogen dioxide and nitric oxide are referred to together as ‘oxides of nitrogen’ (NOx).

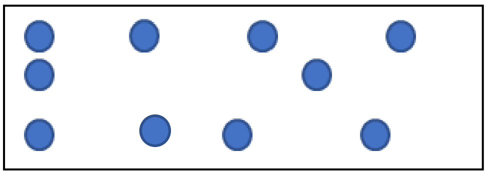
Nitric oxide is not considered to be hazardous to health at typical ambient concentrations. Nitrogen dioxide is a poisonous gas that at high concentrations causes inflammation of the airways in animals including humans. Nitrogen dioxide gas is also acidic. When it dissolves in water it causes corrosive damage to materials and animals.

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 (O_3) and measuring the light the reaction produces.

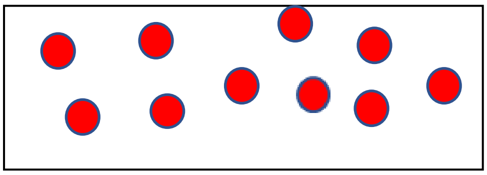
How can we represent this?

(a) Reaction at start, only first chemical (blue) is present. There are no red counters.



Blue counter	10
Red Counter	0

(b) Now add a lot of ozone. When it collides with nitrogen oxide (NO, coloured blue) it changes it (so now coloured red) so the detector can see it and count it.



Blue counter	0
Red Counter	10

For the enthusiast

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

$O + N_2 \rightarrow NO + N$ (1)

$N + O_2 \rightarrow NO + O$ (2)

Once NO is produced it can react with species in the atmosphere such as ozone (O_3, see later) and be converted to NO_2. NO_2 is a brown coloured gas and is rapidly broken down in sunlight and so NO and NO_2 are interchanging rapidly in the daytime. They are known collectively as NOx. These two species alter atmospheric chemistry dramatically, turning a low NOx 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).

$NO + O_3 \rightarrow NO_2 + O_2$ (3)

$NO_2 + hv \rightarrow NO + O$ (4)

NO is detected by reacting NO with ozone (O_3) to produce NO_2^* which then releases a photon of light and becomes stable NO_2. Now the NOx mixture is all NO_2. Converting this back to NO, by passing the gas mixture over a heated catalytic converter, allows the process to be repeated and the increase in light observed is due to the original amount of NO_2 present and so concentrations of NO and NO_2 can be determined with the same spectroscopic technique. See Appendix 2 to read about how spectroscopy works.

Figure 4 shows that the NOx and SO_2 observed at the kerbside site of the Marylebone Road is heavily influenced by traffic, with morning and afternoon peaks associated with rush hour traffic.

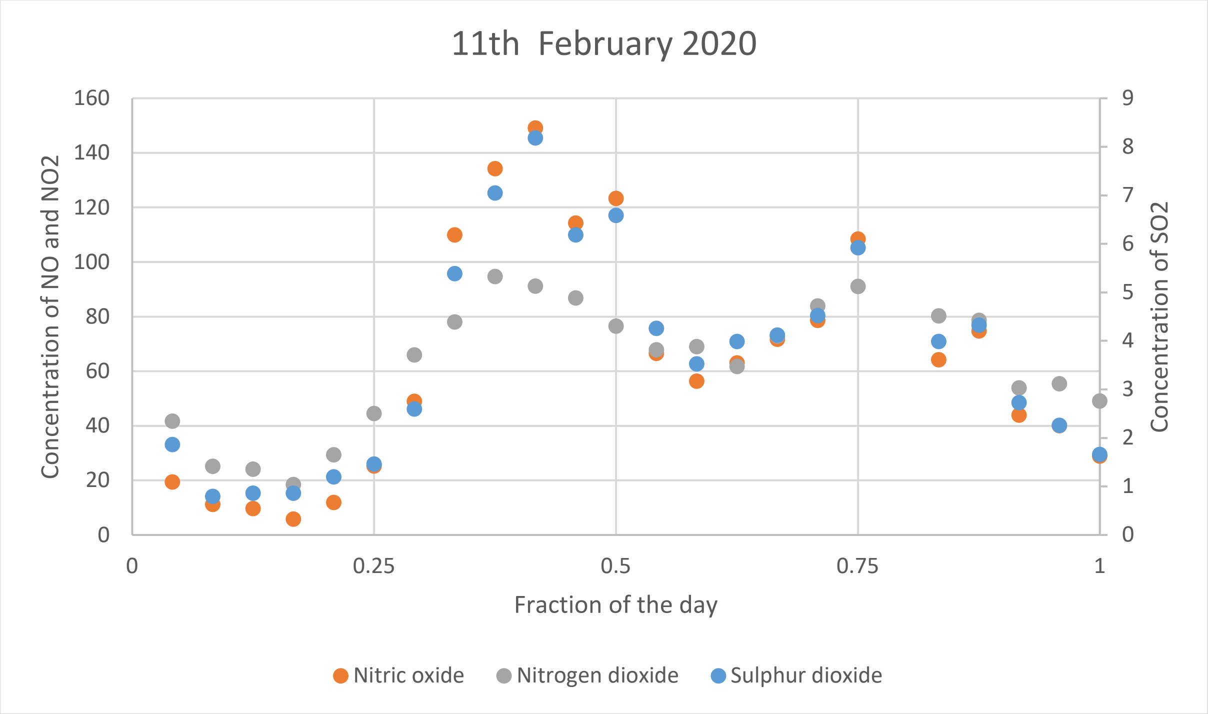


Figure 4. *NO, NO_2 and SO_2 (sulphur dioxide) concentrations measured at the Marylebone Road, London during Tuesday 11th February 2020.*

With children, teachers could consider the following questions (answers to question prompts are provided in the slide notes of the classroom presentations):

- 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. This is a poisonous gas and can replace oxygen in blood. At concentrations above 1000ppm it is considered immediately dangerous.

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.

For the enthusiast

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

When •OH reacts with CO it forms carbon dioxide (CO_2) and the hydroperoxyl radical ($HO_2\bullet$), (1). $HO_2\bullet$ goes through a series of reactions with NO_x (2–3) that form ozone in reaction (4).

$CO + \bullet OH + O_2 \rightarrow CO_2 + HO_2\bullet$ (1)

$HO_2\bullet + NO \rightarrow NO_2 + \bullet OH$ (2)

$NO_2 + \text{light} \rightarrow NO + O$ (3)

$O + O_2 \rightarrow O_3$ (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 ($HgO_{(s)}$) is reduced to mercury (Hg) vapour. The vapour is then measured quantitatively by atomic absorption of UV light using spectroscopy. See Appendix 2 to read about how spectroscopy works.

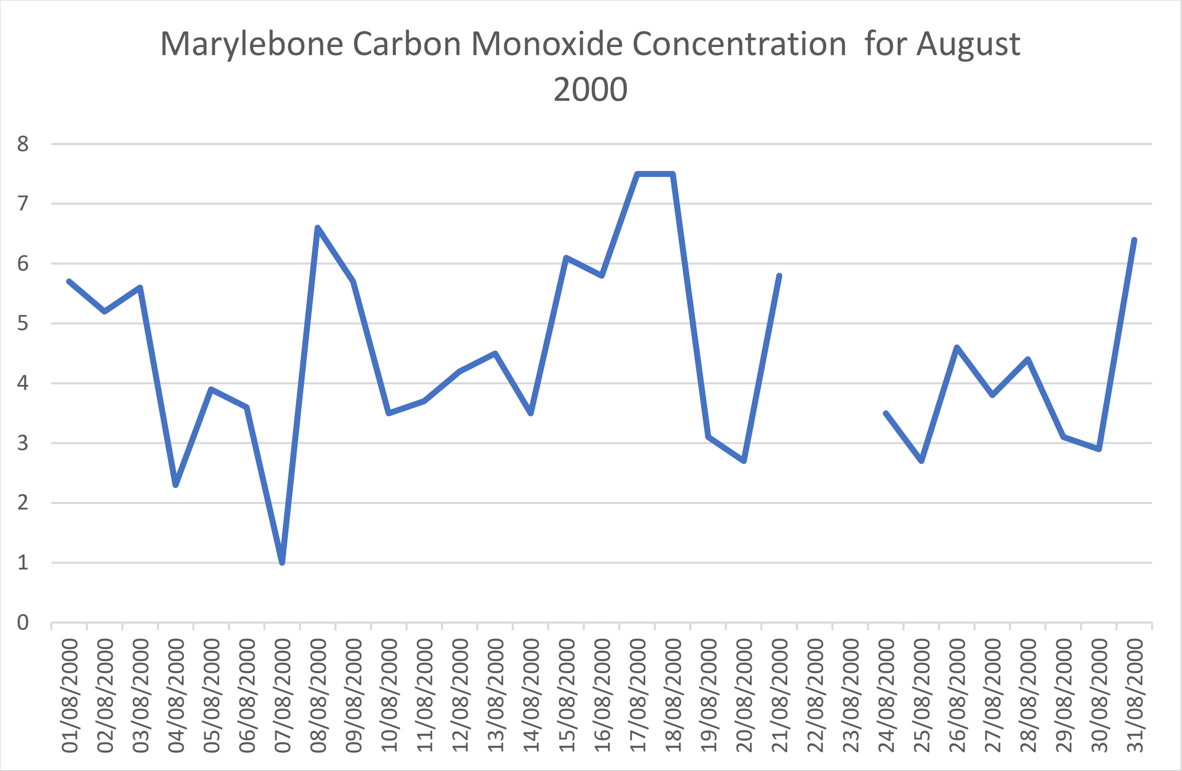


Figure 5. *August 2000 carbon monoxide maximum concentrations (milligrams per cubic meter of air, mg/m3) in Marylebone, London.*

With children, teachers could consider the following questions (answers to question prompts are provided in the slide notes of the classroom presentations):

- 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 (O_3)

Ozone is a poisonous form of oxygen. We breath oxygen as O_2. O_3 is present in the atmosphere in tiny amounts, but it is important and is involved in the breakdown of other atmospheric pollutants.

Breathing ozone can trigger a variety of health problems including chest pain, coughing, throat irritation, and airway inflammation. It also can reduce lung function and harm lung tissue. Ozone can worsen bronchitis, emphysema, and asthma, leading to increased medical care.

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. O_3 effectively absorbs light of a certain wavelength in the UV range. The concentration of O_3 can then be determined from how much of the UV light is absorbed in the chamber and compared to a chamber without any ozone.

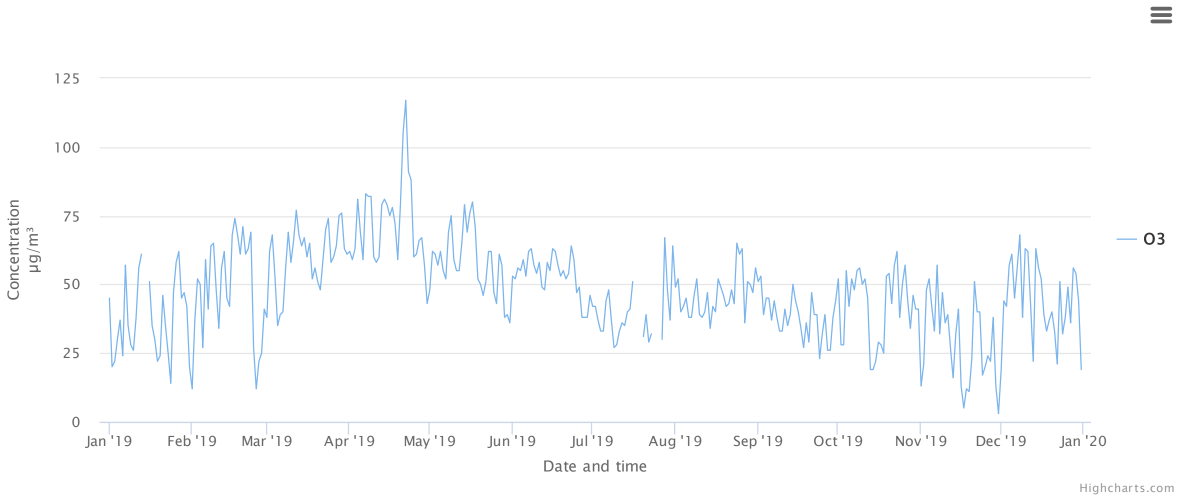


Figure 6. *Ozone concentrations from a road in Edinburgh during 2019.*

Sulfur dioxide (SO_2)

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

Sulfur dioxide gas has may sources, some from nature and some from the things we do and make. Volcanoes can produce SO_2. Much of the SO_2 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. Sulfur dioxide has many uses, including for the manufacture of sulfuric acid. It also has harmful effects: it dissolves in water making acid which corrodes some stonework, poisons lakes and rivers, and kills trees from the top down; it affects the respiratory system, particularly lung function, and can irritate the eyes and aggravates conditions such as asthma.

How is sulfur dioxide measured?

Sulfur dioxide can be measured using ultraviolet (UV) light and spectroscopy. The containing SO_2 air is drawn into a chamber using a pump and then illuminated with UV light. After absorption of UV light, the SO_2 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 SO_2 can be calculated. See Box 1 to read about how spectroscopy works.

Sometimes there are gaps in the Air Quality Data Archive (Figure 7.) What do you think happened from the end of January to the beginning of March 2020? It is possible that the detection equipment stopped working or that there were no researchers working at this time.

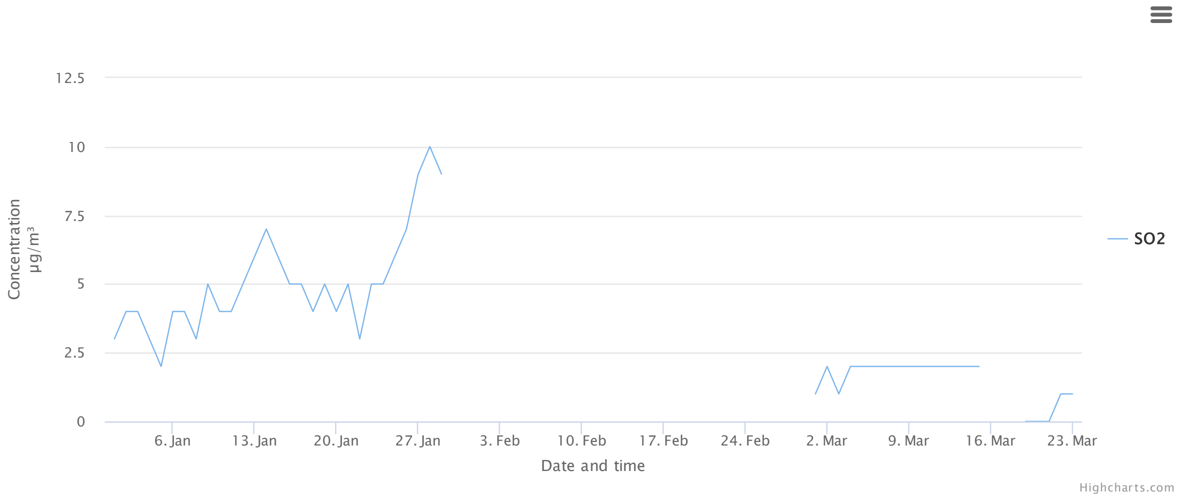


Figure 7. *Sulfur dioxide measurements for the year so far (2020) in Birmingham.*

Particulates: PM_{10} / $PM_{2.5}$

Particulates are tiny pieces of solid (dust) in the air. They come in many sizes. PM_{10} 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). Thus, PM_{10} (10 µm = 0.01 mm) could be a tenth of a human hair. Particulate matter ($PM_{2.5}$ and PM_{10}) can hang in the air for a long time and are so tiny that they can enter deep into the lungs and damage lung tissue.

How are they measured?

There are four methods, used to measure $PM_{10}/PM_{2.5}$. 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 heaver the child the bigger the effect on the spin.

For the enthusiast

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 builds 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.

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 people tidy garden debris in the spring.

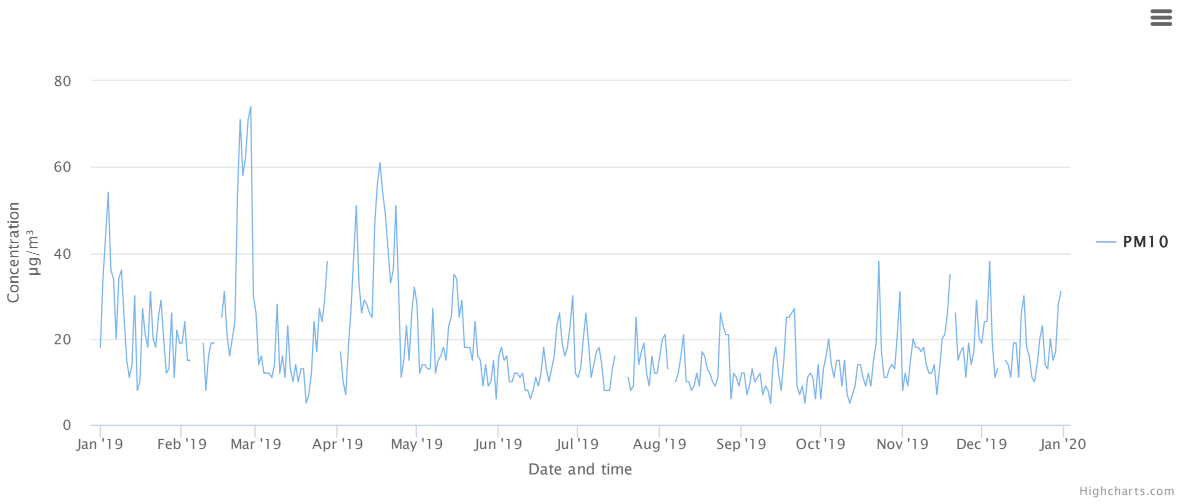


Figure 8. *The PM10 data from a busy road (Newport Road) going into Cardiff during 2019.*

Appendix 1

Separating mixtures in primary science using chromatography

Dr Alison Trew, PSTT

How many coloured compounds are in your ink?

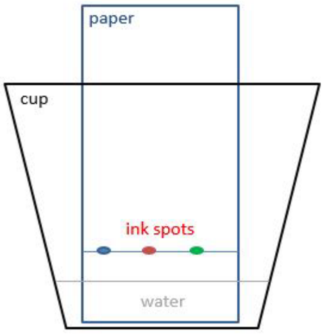
Do inks of the same colour (e.g. black) always have the same chemical composition?

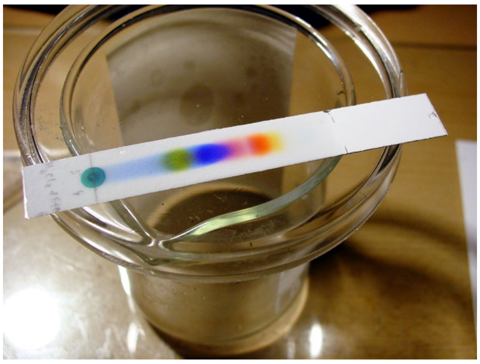
Resources

- Plastic cup, glass beaker or jam jar
- Strips of filter paper or paper towel
- Different colour water-based felt tips
- Water
- Ruler – to measure the distance the different inks and the different components within each ink have travelled.

Activity

1. Draw a pencil line about 2 cm across the bottom of the paper.
2. Make dots of ink along this line, not too close to the edge of the paper.
3. Place the bottom of the paper into the water (about 1cm depth) – do not let the ink spots touch the water.
4. Observe the inks move up the paper.





Appendix 2

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.

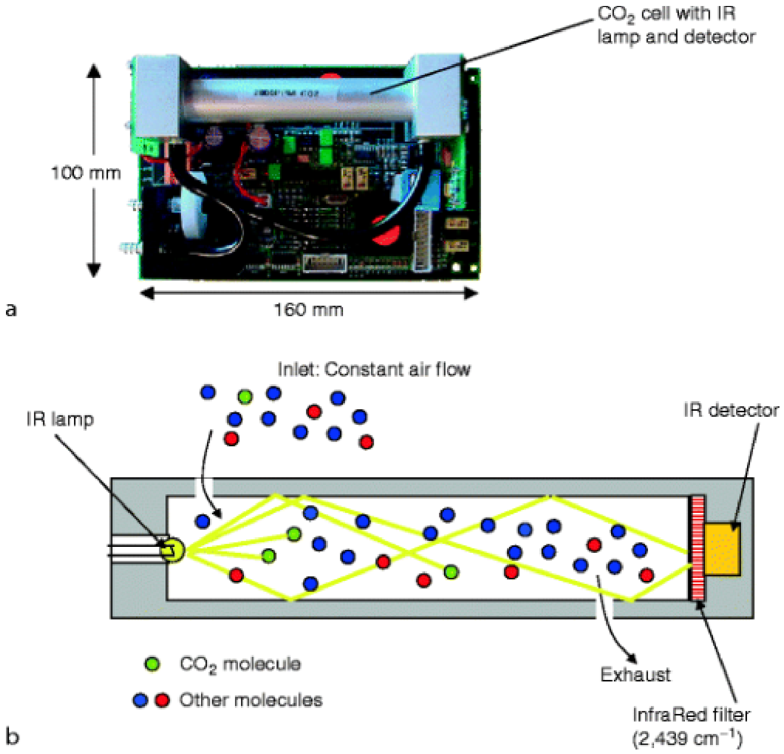


Figure 8. (**a**) The inside of a CO_2 sensor. (**b**) A diagram of the CO_2 cell within the sensor which senses light of wavelength 4.1 µm.

To detect a gas, the sensor needs to identify a characteristic of the gas that other gases do not have. In the case of CO_2, 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 CO_2 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 CO_2, allows a calculation of the concentration.

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