How clean is our air?

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What are the health implications of air pollution? Let's tour the atmosphere, from the free troposphere, through cities and into the lungs

Exam links

This article links to the following topics in the **AQA, Edexcel, OCR, WJEC, CCEA, SQA** and **IB Diploma** exam specifications:

- atmospheric chemistry
- particulate matter, nitrogen oxides (NO_x) and volatile organic compounds (VOCs)
- oxidation reactions
- free radical species and reactions
- gas laws

You have probably encountered 'bad air' such as smog, odour and pollution. If only we could always breathe fresh, clean air from the countryside on a warm spring day. Urban areas bring together people, factories and machines, so they are one of the easiest places for air pollution to develop and spread.

Have you ever asked yourself if the air where you live is clean enough? What can be done to fight urban air pollution?

Deadly fog

In the past, London was famous for its fog. In December 1952 a thick blanket of noxious smog covered the city for 5 days. This was the worst air-pollution event in the history of the United Kingdom — recent analysis has shown an above-average mortality rate of around 12 000 fatalities during the 'Great Smog of London'.

After this episode and many others all over the world, urban air quality started to be given serious consideration. Major international organisations, like the **World Health Organization (WHO)**, have set limits on the concentrations of harmful substances such as particulate matter (PM), ozone (O_3), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) in the air. Their research has found that air pollution kills over 7 million people every year. To put that number into perspective, air pollution has more than twice the mortality rate of HIV/AIDS, diabetes and traffic accidents combined.

As public awareness has increased, new solutions have been developed, such as the three-way catalyst used on road vehicles (see CHEMISTRY REVIEW, Vol. 20, No. 3, pp. 27–31) and wet scrubbers used at power plants (see CHEMISTRY REVIEW, Vol. 9, No. 4, pp. 2–6). Despite these efforts, the WHO says that 92% of people in the world live where air pollution is above the safe exposure threshold.

There is particular concern in Asia due to a combination of urbanisation and industrialisation that has created the 'Asian Brown Cloud' of air pollution that can be seen from space. One consequence is thick smog and lack of visibility.

To fight air pollution, first we need to understand the chemistry behind the phenomenon. Urban air quality is the result of three factors:

- meteorology
- emissions of primary pollution
- formation of secondary pollution within the atmosphere

Pollution and tropospheric chemistry

In general, air pollutants can be divided into two categories, *primary* and *secondary*, depending on whether they are emitted directly by a source or if they form in the atmosphere. In a city, the most important sources are **anthropogenic** (transportation, heating, power generation, industry) and, to a lesser extent, **biogenic** (plants, animals, oceans).

Glossary

Anthropogenic Originating from human activity.

Biogenic Generated by naturally occurring processes.

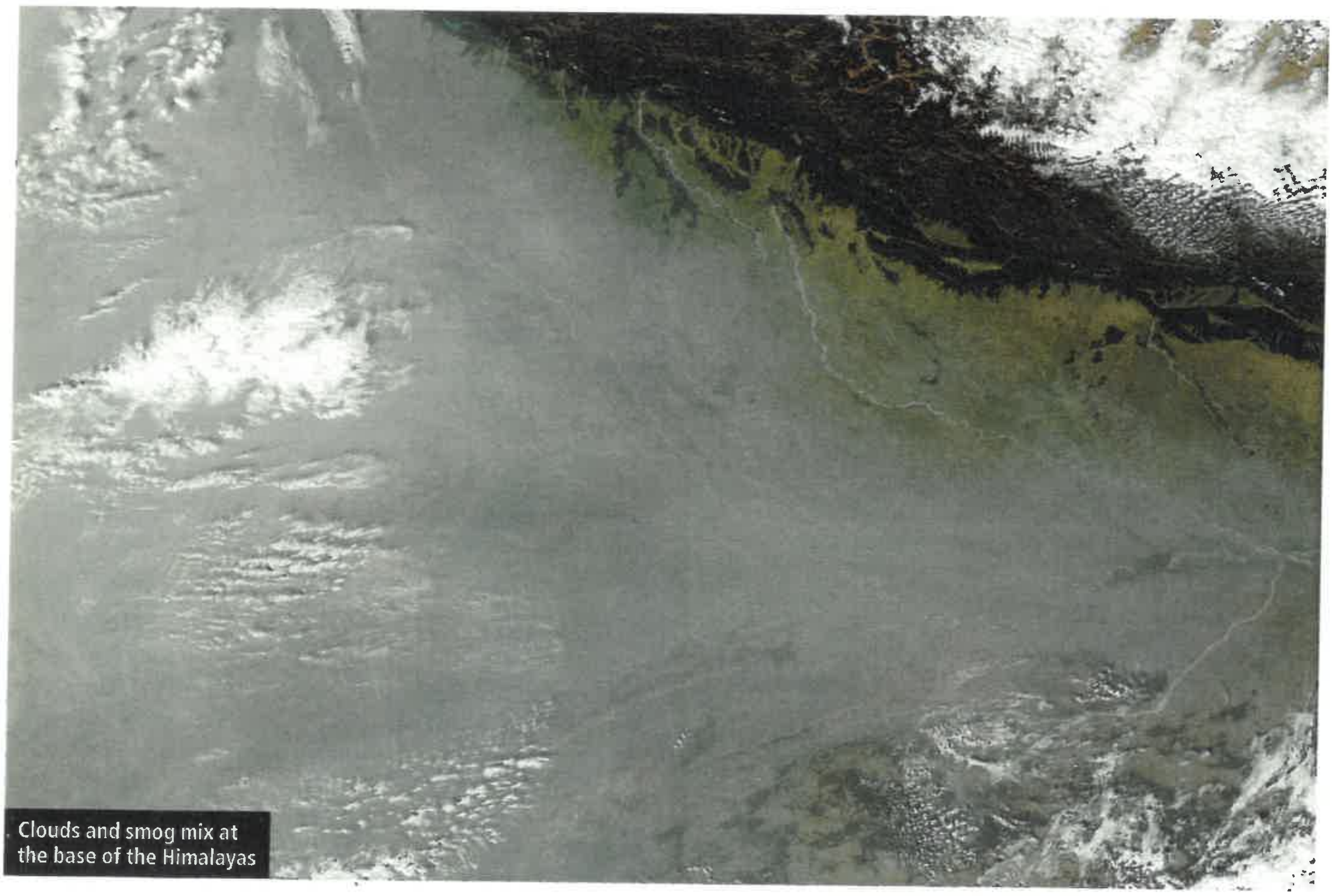
Oxidative stress When our defences cannot cope with the overwhelming amount of noxious oxidative species in our body. It is an imbalance between the introduced oxidants and the ability of the body to generate antioxidants to neutralise them.

Thermal breakdown Chemical decomposition, caused by heat.

World Health Organization (WHO) The United Nations special agency for health.

Residents of cities are exposed to primary pollutants like particulate matter, NO_x and volatile organic compounds (VOCs) on a daily basis. Secondary pollutants form over time as primary emissions react in the atmosphere — they are formed in the air over entire regions. Ozone is a good example of a secondary pollutant, as it is generated from photochemical reactions involving NO_x and VOCs.

Photosynthesis draws CO_2 out of the atmosphere and produces free molecular oxygen (see CHEMISTRY REVIEW, Vol. 24, No. 1, pp. 12–15). Oxygen comprises about one fifth of the atmosphere — it is an oxidising environment. Despite this abundance, there are almost no direct reactions between O_2 and reduced species. The reactions are allowed by thermodynamics, but inhibited by very low kinetic reaction rates. Instead, oxidation occurs by photochemical chain reactions (Box 1).



Clouds and smog mix at the base of the Himalayas

Tiananmen Square in Beijing, China, as seen on 1 December 2015, and a day later

Effects of air pollutants

NO_x is an abbreviation for reactive nitrogen oxides including NO, NO_2 and organic nitrates (see Chemistry Review, Vol. 14, No. 1, pp. 5–7). NO_x is formed from the **thermal breakdown** of air, for example in lightning, a combustion cylinder or an iron foundry. NO_x damages body tissues, leading to cardiopulmonary disease and cancer. It can be seen as a brown-orange layer when flying into a city with air pollution and has an aggressive odour that irritates the eyes and nose.

VOCs include a wide range of hydrocarbons like plant terpenes, liquid hydrocarbon fuel and solvents. Some VOCs smell bad, some cause cancer and all act as fuel for free radical chain reactions catalysed by NO_x that form photochemical smog (see Chemistry Review, Vol. 26, No. 1, pp. 18–22).

Particulate matter (see Chemistry Review, Vol. 9, No. 5, pp. 16–17) is microscopic solid or liquid matter suspended in the air as an aerosol. As for general pollutants, there are two types of PM:

- primary: emitted directly by a source, e.g. soot from diesel motors, wind-blown dust, particles from tyres and brakes
- secondary: generated in the atmosphere as a result of reactions (for example VOC oxidation, or HCl and NH_3 reacting to form ammonium chloride)

PM is sometimes written with a subscript (e.g. PM_{10}, $PM_{2.5}$) that indicates the total mass of particulate matter per volume of air with an aerodynamic diameter smaller than the number, for example smaller than 2.5 µm. Size is important: smaller particles have a higher toxicity per unit mass than larger ones. As air goes through the channels of the nasal passage, heavy particles may not follow the airstream, sticking onto mucus, which is continually removed. However, small particles have less momentum, so they follow the airstream and manage to penetrate deep into the lungs where they can deposit, delivering foreign chemicals directly into the bloodstream.

Carbon monoxide (CO) is a toxic, transparent, odourless gas found at trace levels in the atmosphere (see Chemistry Review, Vol. 20, No. 3, pp. 16–20). Its primary sources are due to incomplete combustion, e.g. a smouldering forest fire or an engine with a rich fuel-to-air mix. CO is also a secondary pollutant produced in the atmosphere (*in situ*) by photo-oxidation of methane and higher hydrocarbons.

Box 1 Chain radical reactions

Many reactions in the atmosphere involve the hydroxyl radical •OH. Chemists are familiar with hydroxide (OH^-) from work in the aqueous phase. The radical •OH can be formed by pulling a hydrogen atom away from water. In the atmosphere it can be formed as follows:

$$O_3 + UV \rightarrow O_2 + O^* \quad (1)$$

$$O^* + H_2O \rightarrow 2^\bullet OH \quad (2)$$

Photolysis of ozone in Reaction 1 produces molecular oxygen and an oxygen atom in an excited electronic state, O*. This excited state reacts with water vapour to produce hydroxyl radicals. These radicals are able to pull hydrogen atoms from virtually any reactant in the atmosphere, producing water and opening up the reactant to attack by molecular oxygen, yielding organic acids and aldehydes.

$$^\bullet OH + RH \rightarrow H_2O + {}^\bullet R \quad (3)$$

$$^\bullet R + O_2 \rightarrow RO_2^\bullet \rightarrow \text{Oxidised hydrocarbons} \quad (4)$$

About two thirds of the time, •OH reacts with carbon monoxide:

$$CO + {}^\bullet OH \rightarrow CO_2 + {}^\bullet H \quad (5)$$

$$^\bullet H + O_2 \rightarrow HO_2^\bullet \quad (6)$$

$$HO_2^\bullet + {}^\bullet NO \rightarrow {}^\bullet OH + {}^\bullet NO_2 \quad (7)$$

$$^\bullet NO_2 + \text{Sunlight} \rightarrow {}^\bullet NO + O \quad (8)$$

$$O + O_2 \rightarrow O_3 \quad (9)$$

Overall: $CO + 2O_2 \rightarrow CO_2 + O_3$

In this sequence, the reduced molecule CO is the fuel leading to the formation of ozone air pollution. The cycle is catalysed by NO_x, which allows the formation of •OH radicals (Reaction 7) and ozone (Reactions 8 and 9).

Weather and photochemical smog

Meteorological conditions strongly influence urban air quality. Rain and wind improve air quality by washing out pollution or blowing it away (ventilation and dilution). Bad air-pollution

Box 2 The universal gas law

The universal gas law is derived from a combination of *Boyle's law* (which states that at a constant temperature, the volume of a given mass of gas is inversely proportional to the pressure) and *Charles' law* (at constant pressure, the volume of a fixed mass of gas is directly proportional to the absolute temperature). We can express the gas laws using the following:

- P = pressure (in Pa)
- V = volume (in m^3)
- n = amount of gas (in mol)
- R = the universal molar gas constant (8.314 $J\,K^{-1}\,mol^{-1}$)
- T = temperature (in K)
- Boyle's law: at constant T, PV is a constant
- Charles' law: $V = kT$ (where k is a constant)

From these we can get the universal gas equation:

$PV = nRT$

Note that this equation is only completely obeyed by an *ideal gas*. An ideal gas is a hypothetical concept, as the molecules of an ideal gas occupy negligible space, have negligible forces between them and the collisions between these molecules and the walls of a container are completely elastic. To find out about many useful applications of the gas laws, see Chemistry Review, Vol. 19, No. 1, pp. 8–10.

events are often associated with temperature inversions at the surface (see Chemistry Review, Vol. 26, No. 4, p. 27). Warm air is less dense than cold air, as seen by rearranging the universal gas equation (Box 2). Density is the ratio of amount to volume, $\frac{n}{V} = \frac{P}{RT}$. Warm air cools when it rises, giving a normal condition of the atmosphere where temperature decreases with height. However, the surface itself can get cold, for example by loss of heat radiation into a starry sky at night. This cools the air at the surface more than the air above, which prevents vertical mixing, and so causes the cool air and any pollution to be trapped near the ground.

In summer, when there is a lot of sunlight, the main problem in many urban areas is *photochemical smog* (see Chemistry Review, Vol. 5, No. 5, pp. 22–27). The word 'smog', a combination of the words 'smoke' and 'fog', was coined in the 1940s in Los Angeles. Photochemical smog is a severe perturbation of normal tropospheric chemistry due to an excess of NO_x (the catalyst) and VOCs (the fuel). With an acceleration of photochemistry and overproduction of ozone, secondary organic aerosol (SOA), nitric acid and other products form. SOA is formed because many volatile hydrocarbons (e.g. solvents, fuels and plant terpenoids) are oxidised in the atmosphere. The tiny static electrical charges within the oxidised molecules make them

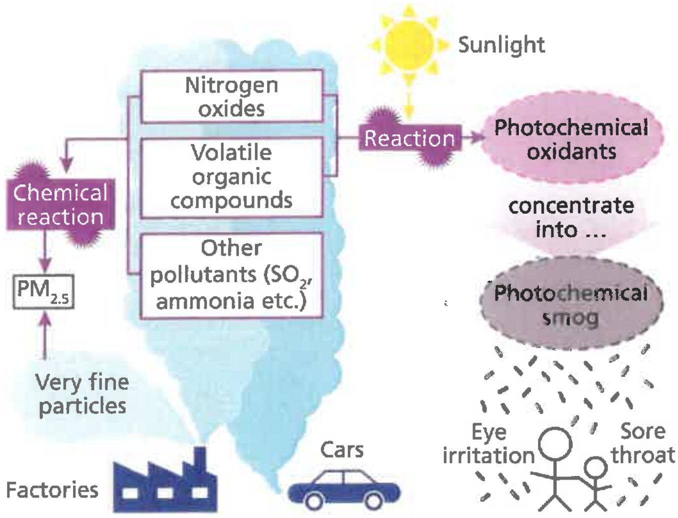


Figure 1 Formation of photochemical smog in urban areas.

sticky for each other and for water. They agglomerate into particles, such as in the left-hand photo on p. 4.

The compounds that make up photochemical smog are toxic to humans, animals and plants (Figure 1). They degrade many materials due to their strong oxidising power. For example, ozone adds into the double bonds found in polymers, causing cracks and brittle dryness in plastics and rubber. It is toxic and damages the respiratory tract, causing coughs and nose and throat irritation. On a molecular level, ozone inserts into double C=C bonds, damaging tissues and causing **oxidative stress** (see Chemistry Review, Vol. 28, No. 1, pp. 2–5).

This is a seasonal phenomenon. During the winter, when ultraviolet (UV) light is less consistent, high levels of primary pollutants such as NO, CO and primary particulates are recorded, rather than the secondary products that are detected in the summer.

Clean technology and innovation

Scientific research and public awareness are the keys to controlling urban pollution. Universities and companies are developing new technologies that focus on air-pollution removal, industrial emissions control, pollution sensors and analysis of personal exposure to urban air pollution.

Practice exam questions

1 An air sample has a density of 1.28 $kg\,m^{-3}$ at 0°C. Assuming that the pressure remains constant, what would its density be at 20°C? (3 marks)

2 Calculate the mass of 1 mol of dry air, assuming that it has the following composition:

N_2	78.0102%	O_3	0.000009%
O_2	21.0201%	NO_2	0.000006%
Ar	0.92537%	NO	0.000003%
CO_2	0.04431%	CO	0.000002%

Relative atomic mass:

C	12.011	O	15.999
N	14.007	Ar	39.948

Give the final answer to six decimal places. (4 marks)

Online archive

Useful articles on atmospheric chemistry from past issues of Chemistry Review:

'Breath of fresh air', Vol. 7, No. 1, pp. 16–17.

'Life history of an atmospheric particle', Vol. 13, No. 4, pp. 25–28.

'Ozone', Vol. 14, No. 2, pp. 17–19.

'Chemistry in the atmosphere', Vol. 19, No. 3, pp. 16–17.

'The Cape Verde atmospheric observatory', Vol. 20, No. 1, pp. 2–5.

This Airlabs bench allows you to sit in a clean air bubble in London city centre

The Danish company Infuser has developed an 'atmospheric accelerator' that speeds up atmospheric chemistry by a factor of 1 million. It is used to replace chimneys in factories in Poland, Germany and Denmark, to trap and destroy pollution before it is emitted.

Another approach is to deliver clean air to people. Airlabs has designed a bench that is able to trap pollution and provide a bubble of clean air in a polluted city. The system has been installed at King's College London and near Oxford Street in London. There are also paving slabs containing titanium dioxide that can break down airborne pollutants (see CHEMISTRY REVIEW, Vol. 11, No. 2, pp. 22–23) and even clothes that could reduce NO_x levels (see CHEMISTRY REVIEW, Vol. 24, No. 2, pp. 8–10). Moreover, as individuals, we can all play our part to help reduce the problem of urban pollution (Box 3).

Preventing air pollution will not only help us live longer, it will also help to fight poverty and hunger, as pollution can affect crops. Since many components of air pollution are climate-active greenhouse gases, fighting air pollution has the additional benefit of helping to control climate change. As responsible citizens of our planet, we should do our best to help reduce air pollution for the benefit of all life on Earth.

Box 3 You're not alone

Many different local groups fight urban air pollution every day, in many different ways. There are also plenty of non-profit organisations, such as Greenpeace, that offer both local and international projects to get involved in. The Climate and Clean Air Coalition, along with the WHO and UN Environment, are currently promoting an initiative called Breathe Life, which aims to significantly cut deaths due to air pollution by 2030. The website **http://breathelife2030.org** is full of resources and information on simple actions that everyone can take. Your personal effort to fight air pollution is never meaningless.

Key points

- The World Health Organization (WHO) reports that 92% of people in the world live with air pollution above the safe exposure threshold.
- Urban air quality is the result of three factors: meteorology, emissions of primary pollution and formation of secondary pollution within the atmosphere.
- Primary air pollutants include particulate matter (PM), oxides of nitrogen (NO_x) and volatile organic compounds (VOCs).
- Secondary pollutants, such as ozone (O_3), form in the atmosphere.
- Photochemical chain reactions, involving radical species, bring about oxidation in the atmosphere.
- Photochemical smog is caused by an excess of NO_x and VOCs, and is toxic to both plants and animals (including humans).

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