### ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AQA</td>
<td>Air Quality Act</td>
</tr>
<tr>
<td>As</td>
<td>Arsenic</td>
</tr>
<tr>
<td>BC</td>
<td>Black carbon</td>
</tr>
<tr>
<td>BTX</td>
<td>Benzene, toluene and xylene</td>
</tr>
<tr>
<td>CAAA70</td>
<td>Clean Air Act Amendments of 1970 (United States)</td>
</tr>
<tr>
<td>CCN</td>
<td>Cloud condensation nucleus</td>
</tr>
<tr>
<td>Cd</td>
<td>Cadmium</td>
</tr>
<tr>
<td>(CH₃)₂S</td>
<td>Dimethylsulphide</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>Ethane</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>Propane</td>
</tr>
<tr>
<td>C₆H₅CH₃</td>
<td>Toluene</td>
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<tr>
<td>C₆H₄(CH₃)₂</td>
<td>Xylene</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>Benzene</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>Chloride ion</td>
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<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>COS</td>
<td>Carbonyl sulphide</td>
</tr>
<tr>
<td>DEAT</td>
<td>Department of Environmental Affairs and Tourism</td>
</tr>
<tr>
<td>DMS</td>
<td>Dimethylsulphide</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gas</td>
</tr>
<tr>
<td>HCHO</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
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<tr>
<td>Hg⁰</td>
<td>Elemental mercury</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>Ionic mercury</td>
</tr>
<tr>
<td>HNO₂</td>
<td>Nitrous acid</td>
</tr>
<tr>
<td>HNO₃</td>
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<td>HO₂</td>
<td>Hydroperoxy radical</td>
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<td>Water vapour</td>
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<tr>
<td>H₂O₂</td>
<td>Hydrogen peroxide</td>
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<tr>
<td>H₂S</td>
<td>Hydrogen sulphide</td>
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<tr>
<td>H₂SO₃</td>
<td>Sulphurous acid</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Sulphuric acid</td>
</tr>
<tr>
<td>M</td>
<td>Inert molecule</td>
</tr>
<tr>
<td>MeHg</td>
<td>Methyl mercury</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Term</td>
</tr>
<tr>
<td>--------------</td>
<td>------</td>
</tr>
<tr>
<td>NMHC</td>
<td>Non-methane hydrocarbon</td>
</tr>
<tr>
<td>NO</td>
<td>Nitric oxide</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Nitrogen dioxide</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Nitrous oxide</td>
</tr>
<tr>
<td>NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Nitrogen oxides</td>
</tr>
<tr>
<td>NO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Particulate nitrate</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Molecular oxygen</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Ozone</td>
</tr>
<tr>
<td>OH</td>
<td>Hydroxyl radical</td>
</tr>
<tr>
<td>PA</td>
<td>Peroxyacetyl radical</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>PAN</td>
<td>Peroxyacetylnitrate</td>
</tr>
<tr>
<td>Pb</td>
<td>Lead</td>
</tr>
<tr>
<td>pH</td>
<td>Measure of the acidity/alkalinity of a solution</td>
</tr>
<tr>
<td>PM&lt;sub&gt;2.5&lt;/sub&gt;</td>
<td>Particulate matter with a diameter &lt; 2.5 µm</td>
</tr>
<tr>
<td>PM&lt;sub&gt;10&lt;/sub&gt;</td>
<td>Particulate matter with a diameter &lt; 10 µm</td>
</tr>
<tr>
<td>ppb</td>
<td>Parts per billion</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>R&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Organic radical</td>
</tr>
<tr>
<td>RH</td>
<td>Reactive hydrocarbon</td>
</tr>
<tr>
<td>RO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Peroxy radical</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Sulphur dioxide</td>
</tr>
<tr>
<td>SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Sulphur trioxide</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>Sulphate ion</td>
</tr>
<tr>
<td>SOA</td>
<td>Secondary organic aerosol</td>
</tr>
<tr>
<td>STE</td>
<td>Stratospheric-tropospheric exchange</td>
</tr>
<tr>
<td>TSP</td>
<td>Total suspended particulates</td>
</tr>
<tr>
<td>US EPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organisation</td>
</tr>
</tbody>
</table>
GLOSSARY

Absorption
A process in which atoms, ions, or molecules enter into the bulk mass of a substance.

Acid deposition
The deposition of acid gases (dry deposition) and liquids (wet deposition) to the surface.

Adsorption
A process in which atoms, ions, or molecules adhere to the surface of a substance.

Advection
Horizontal transport of air.

Aerosols
Liquid or solid particles suspended in the atmosphere.

Air quality standard
The prescribed level of a pollutant in the ambient air that should not be exceeded during a specific time period to protect public health. The level is established by legislation.

Air quality guideline
The recommended level of a pollutant in the ambient air that should not be exceeded during a specific time to protect public health. The level is not enforced by legislation.

Alkalinity
A measure of the capacity of water to neutralise acids. Also known as the buffering capacity.

Ambient concentration
Considered to be the concentration of a pollutant in the environment excluding indoor air.

Anaerobic process
Refers to processes occurring in oxygen-deficient environments.
**Anthropogenic sources**
Pollution sources that are related to human activities.

**Asthma**
A chronic condition of the lung characterised by wheezing and difficulty in breathing.

**Averaging time**
The period of time over which observations are averaged.

**Biogenic emissions**
Emission of a range of pollutants from soils and vegetation.

**Biomass burning**
The combustion of organic matter from either natural or human-induced fires.

**Boundary layer**
The lowest layer of the atmosphere, adjacent to the ground and having properties affected by the nature of that surface.

**Bronchitis**
An inflammation of the mucous membranes of the bronchi or tubes leading to the lung. It causes a persistent cough that produces large amounts of phlegm.

**Carcinogen**
A cancer-causing agent or substance.

**Cardiovascular disease**
A disease affecting the heart and circulatory system.

**Catalytic converter**
An air pollution abatement device fitted to a motor vehicle exhaust. It removes pollutants either by oxidizing them into carbon dioxide and water or reducing them to nitrogen.

**Chronic obstructive pulmonary disease**
A general term for diseases in which there is narrowing of the bronchi connected to the lungs.
Coalescence
A process whereby two particles of equal or unequal size join to form a larger particle.

Combustion
Burning, or rapid oxidation, accompanied by release of energy in the form of heat, light and waste products.

Criteria pollutants
A group of air pollutants which are deemed to have human health and/or environmental effects and as such are regulated by the setting of air quality standards. In the United States, these include carbon monoxide (CO), nitrogen oxides (NOx), ozone (O$_3$), particulate matter, sulfur dioxide (SO2), and lead.

Denitrification
The process in which soil bacteria convert nitrate (and/or nitrite) to nitrogen-containing gases such as N$_2$O and N$_2$.

Dimethylsulphide
An organic compound containing sulphur that is produced in the ocean by certain phytoplankton species.

Dissolution
The process of going into solution.

Dry deposition
The process (excluding precipitation) by which atmospheric gases and particles are transferred to the surface as a result of random turbulent air motions.

Emission
Pollution discharged into the atmosphere from a range of stationary and mobile sources. These include smokestacks, vents and surface areas of commercial or industrial facilities; residential sources; motor vehicles and other transport related sources.

Emphysema
A lung disease in which the air sacs are enlarged and damaged, causing breathing problems.
**Evaporate**
To change from a liquid to a gas or vapour.

**Fossil fuel**
Materials such as coal, oil or natural gas that were formed in the ground millions of years ago from plant and animal remains and that are used to provide energy by combustion.

**Greenhouse Gas**
Any gas that absorbs infra-red radiation in the atmosphere. Greenhouse gases include water vapour, carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O), halogenated fluorocarbons (HCFCs), ozone (O$_3$), perfluorinated carbons (PFCs), and hydrofluorocarbons (HFCs).

**Guideline**
See air quality guideline

**Haemoglobin**
A protein found in the red blood cells that is responsible for carrying oxygen from the lungs to the tissues.

**Heterogeneous nucleation**
The conversion of vapour phase materials to a particulate form, whereby gaseous molecules nucleate onto an existing surface.

**Homogeneous nucleation**
The conversion of vapour phase materials to a particulate form, whereby gaseous molecules aggregate without the aid of an existing surface.

**Hydrate**
To add water.

**Hydrocarbons**
Organic compounds that contain only hydrogen and carbon atoms in various combinations.

**Incineration**
The controlled burning of wastes at high temperatures.
Incomplete combustion
Partial oxidation of the combustible constituents of a fuel, such that more carbon monoxide is released than carbon dioxide.

Inert
Not reactive under normal circumstances.

Kraft process
A process used in the pulp and paper industry to extract lignin from wood fibre by means of caustic sodium hydroxide and sodium sulphide.

Non-methane hydrocarbons
Organic compounds that contain only hydrogen and carbon atoms in various combinations and that exclude methane.

Natural sources
Pollution sources that are related to natural processes as opposed to those which are due to human activities.

Nucleation
Nucleated particles are those that form from the gaseous phase.

Odour threshold
The lowest concentration of a substance in the air that can be detected by smell.

Organic compounds
Substances that contain carbon.

Oxidation
The process of adding oxygen to a substance.

Photochemical smog
A smog comprising ozone and other reactive chemical compounds formed by the reaction of nitrogen oxides and hydrocarbons in the presence of sunlight.

Photodissociation
The process in which molecules are broken down into their smallest components by radiant energy.
Photolysis
The process by which a chemical species undergoes a chemical change as the result of the absorption of light.

Precursor
A compound that precedes the formation of another pollutant. For example, volatile organic compounds (VOCs) are precursors to ozone.

Primary standard
An air quality standard designed to protect human health.

Priority pollutant
A pollutant that has been identified under the Air Quality Act as requiring intervention to reduce ambient air quality levels.

Radical
An atom containing at least one unpaired electron.

Residence time
The length of time that compounds may stay in a reservoir (e.g. atmosphere).

Saturation vapour pressure
The vapour pressure of water when air is saturated with water. i.e it holds the maximum amount of water vapour at a given temperature and pressure.

Secondary standard
An air quality standard designed to protect human welfare (e.g. property) and the environment (plants and animals).

Sink
A reservoir (e.g. ocean) that takes up pollutants from another part of its cycle.

Standard
See air quality standard

Turbulence
Flow characterised by irregular eddies or gusts.
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   3.2 Sulphur Trioxide
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1. **Introduction**

1.1 **Expression of Gaseous Compounds**

Gases may be expressed in two different ways:

- volume per volume measure where the units are parts per million (ppm), i.e. part/whole x $10^6$ or parts per billion (ppb), i.e. part/whole x $10^8$

- weight per unit volume i.e. $\mu g/m^3$

Sometimes the units are expressed as ppmv to indicate volume per volume.

It is possible to convert between the two systems using the formulae given by Stern (1977:33) and assuming standard atmospheric pressure and temperature

\[
\frac{\mu g/m^3}{24450} = \frac{ppm \times \text{molecular weight}}{40.90} \times 10^6
\]

\[
ppm = \frac{\mu gm^3 \times 2.445 \times 10^2}{\text{molecular weight}}
\]

1.2 **Averaging Time**

Concentrations of air pollutants in the ambient atmosphere may be expressed as instantaneous or time-averaged values. It is essential to specify the averaging time when giving a concentration as values vary dramatically depending on the time over which they have been averaged (Fig. 1).
The relationship among various averaging times and concentration is given in Table 1. The 24-hr average concentrations are assumed equivalent to 1.0. It is noted that the longer the averaging time, the lower the concentration.

Table 1: Generalised Relationships among Commonly Used Averaging Times (Stern, 1977)

<table>
<thead>
<tr>
<th>Averaging Time</th>
<th>Relative Maximum Average Concentration in the Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 month</td>
<td>0.5</td>
</tr>
<tr>
<td>24 hr</td>
<td>1.0</td>
</tr>
<tr>
<td>8 hr</td>
<td>1.2</td>
</tr>
<tr>
<td>2 hr</td>
<td>1.8</td>
</tr>
<tr>
<td>1 hr</td>
<td>2.2</td>
</tr>
<tr>
<td>30 min</td>
<td>2.4</td>
</tr>
<tr>
<td>15 min</td>
<td>2.7</td>
</tr>
<tr>
<td>Single measurement</td>
<td>3.3</td>
</tr>
</tbody>
</table>

2. Gaseous Compounds of Carbon

The two most important compounds are carbon monoxide (CO) and carbon dioxide (CO₂). CO₂ is not generally regarded as an air pollutant, although it is very important on a global scale in climate change as it is a greenhouse gas (GHG).
2.1 Carbon Monoxide (CO)

CO is both a natural and anthropogenic trace gas. Concentrations tend to be very high in urban areas, although there is evidence that the increasing trend in Northern Hemisphere cities has halted due to the widespread air pollution controls, chiefly on motor vehicles.

**Key Characteristics**

CO is a colourless, odourless and tasteless gas. It is slightly less dense than air. It is not usually regarded as a GHG, as its radiative properties are insignificant compared with those of other GHGs such as CO$_2$ and CH$_4$. However, it has an indirect effect, as increased CO emissions reduce the oxidising capacity of the atmosphere and may increase CH$_4$ concentrations. Further, its oxidation to CO$_2$ clearly increases CO$_2$ levels (Jacobson, 2002).

**Sources**

- Natural sources include:
  - Emissions from the ocean through decomposition of organic materials (e.g. algae)
  - Decomposition of organic material in the soil
  - Oxidation of volatile organic compounds
  - Oxidation of methane

- Anthropogenic sources include:
  - Product of incomplete combustion of fossil fuels (coal, oil), predominantly in motor vehicles (see Box 1).
  - Biomass burning
  - Industrial processes such as iron and steel production
  - Biofuel use
  - Incineration of solid wastes
  - Tobacco smoke

**Box 1: Combustion of Fuel**

The process of burning fuel in a motor vehicle is given as follows:

\[
\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO or CO}_2
\]

Either CO or CO$_2$ can be produced depending on the amount of O$_2$ in the air, the temperature of the flame and the residence time of the gas in the combustion chamber. At higher temperatures and longer residence times in the cylinder, more CO$_2$ is produced.

CO has a short residence time of about one month, and a small atmospheric reservoir, which implies that there is little likelihood of CO accumulating on a global basis, but it is a serious local problem in urban areas where concentrations may approach 100 ppm.
Sinks
- Kinetic reactions
e.g. $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$
  This reaction accounts for about 90% of CO removal
- Uptake by microorganisms or bacteria in soils
- Dissolution in ocean water

Chemical Reactions
CO contributes to photochemical smog (see Box 2) and accelerates the oxidation process.

<p>| Box 2: Role of Carbon Monoxide in Photochemical Smog |</p>
<table>
<thead>
<tr>
<th>(Jacobson, 2002: 95)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO(g)} + \cdot \text{OH(g)} \rightarrow \text{CO}_2(g) + \cdot \text{H(g)}$</td>
</tr>
<tr>
<td>$\text{Carbon monoxide} \quad \text{Hydroxyl} \quad \text{Carbon dioxide} \quad \text{Hydrogen}$</td>
</tr>
<tr>
<td>$\text{atomic} \quad \text{radical} \quad \text{atomic} \quad \text{radical}$</td>
</tr>
<tr>
<td>(4.11)</td>
</tr>
<tr>
<td>$\cdot \text{H(g)} + \text{O}_2(g) \rightarrow \text{HO}_2(g)$</td>
</tr>
<tr>
<td>$\text{Atomic hydrogen} \quad \text{Molecular oxygen} \quad \text{Hydroperoxy radical}$</td>
</tr>
<tr>
<td>(4.12)</td>
</tr>
<tr>
<td>$\cdot \text{NO(g)} + \text{HO}_2(g) \rightarrow \cdot \text{NO}_2(g) + \text{OH(g)}$</td>
</tr>
<tr>
<td>$\text{Nitric oxide} \quad \text{Hydroperoxy radical} \quad \text{Nitrogen dioxide} \quad \text{Hydroxyl radical}$</td>
</tr>
<tr>
<td>(4.13)</td>
</tr>
<tr>
<td>$\cdot \text{NO}_2(g) + \text{hv} \rightarrow \cdot \text{NO}(g) + \text{O}(g)$</td>
</tr>
<tr>
<td>$\lambda &lt; 420 \text{ nm}$</td>
</tr>
<tr>
<td>$\text{Nitrogen dioxide} \quad \text{Nitric oxide} \quad \text{Atomic oxygen}$</td>
</tr>
<tr>
<td>(4.14)</td>
</tr>
<tr>
<td>$\cdot \text{O}(g) + \text{O}_2(g) \rightarrow \text{O}_3(g)$</td>
</tr>
<tr>
<td>$\text{Ground-state atomic oxygen} \quad \text{Molecular oxygen} \quad \text{Ozone}$</td>
</tr>
<tr>
<td>(4.15)</td>
</tr>
</tbody>
</table>

Effects
The main effect of CO is to reduce the ability of the circulatory system to transport $\text{O}_2$. CO has an affinity for haemoglobin in the blood that is 210 times greater than that of $\text{O}_2$, hence the oxygen carrying capacity of blood is impaired. The physiological effects of exposure to CO are given in Figure 2. The duration of exposure to CO is shown along the horizontal axis and the percent of blood haemoglobin that is prevented from absorbing oxygen is shown on the vertical axis.
Standards

CO is one of the 6 criteria pollutants identified by the 1970 United States Clean Air Act Amendments (CAAA70) and is now regulated in many countries. It will be a priority pollutant under the Air Quality Act (AQA) in South Africa.

The United States primary and secondary standards (Jacobson, 2002) are:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Time Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 ppm</td>
<td>8-hr average</td>
</tr>
<tr>
<td>35 ppm</td>
<td>1-hr average</td>
</tr>
</tbody>
</table>

WHO guidelines are:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Time Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 ppm</td>
<td>8-hr average</td>
</tr>
<tr>
<td>30 ppm</td>
<td>2-hr average</td>
</tr>
<tr>
<td>100 ppm</td>
<td>1-hr average</td>
</tr>
</tbody>
</table>

Current Department of Environmental Affairs and Tourism (DEAT) guidelines are:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Time Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mgm$^{-3}$</td>
<td>8-hr average</td>
</tr>
<tr>
<td>40 mgm$^{-3}$</td>
<td>1-hr average</td>
</tr>
</tbody>
</table>

The proposed standards in South Africa under the AQA are:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Time Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.7 ppm</td>
<td>8-hr average</td>
</tr>
<tr>
<td>26 ppm (30 mgm$^{-3}$)</td>
<td>1-hr average</td>
</tr>
</tbody>
</table>
3. Gaseous Compounds of Sulphur

These compounds include the sulphur oxides [mainly sulphur dioxide (SO\textsubscript{2}) and sulphur trioxide (SO\textsubscript{3})], the reduced sulphur compounds such as sulphides, mainly hydrogen sulphide (H\textsubscript{2}S), and sulphuric acid (H\textsubscript{2}SO\textsubscript{4}).

The global sulphur budget is summarized in Figure 3.

![Figure 3: Global sulphur budget (Turco, 2002:301)](image)

3.1 Sulphur Dioxide (SO\textsubscript{2})

**Key Characteristics**
SO\textsubscript{2} is a colourless, pungent (burning match odour), irritating, and reactive gas. It can be detected by taste at 0.3 ppm. Above 0.5 ppm (odour threshold) it imparts a burning acrid sensation to the nose.

**Sources**
Natural emissions (Jacobson, 2002) are from
- Volcanoes
- Geothermal sources (hot springs)
- Oxidation of biologically produced dimethylsulphide (DMS) in oceans and soils and hydrogen sulphide (H\textsubscript{2}S)

Anthropogenic emissions are as follows:
- Fossil fuel combustion in industry and power plants. Most SO\textsubscript{2} comes from coal (contains ~0.5-7% S) and to a lesser extent from oil (contains ~0.3% S). This is by far the dominant anthropogenic source. SO\textsubscript{2} can be transported long distances as a result of emission from high stacks.
• Indoor fuel combustion (domestic coal, kerosene). Chemical degradation of \( \text{SO}_2 \) in an indoor environment is slow because of the absence of the OH radical which is needed to initiate reactions.
• Combustion of fuel in motor vehicles. This tends to be a relatively minor source.
• Smelting of sulphur-containing mineral ores. Copper, lead and zinc are generally found in ore deposits as sulphides. A common method for separating out the desired metallic component is to roast the pulverized ore at sufficiently high temperatures to oxidize the sulphur and cause it to be released as \( \text{SO}_2 \).
• Sulphuric acid manufacturing, electroplating
• Phosphate fertilizer manufacturing

_Sinks_
• Chemical reactions. \( \text{SO}_2 \) is oxidised to sulphuric acid by the OH radical.
• Dry deposition. \( \text{SO}_2 \) is transported to the surface by turbulence and molecular diffusion and then removed by adsorption or absorption at the surface
• \( \text{SO}_2 \) (g) can dissolve in water droplets to form \( \text{SO}_2 \) (aq) and then fall to the surface as precipitation. This process is referred to as wet deposition.

_Chemical Reactions_
\( \text{SO}_2 \) is highly soluble in water, forming a weakly acidic sulphurous acid \( \text{H}_2\text{SO}_3 \). In clean air it oxidizes slowly to \( \text{SO}_3 \). In moist air and in presence of nitrogen oxides, hydrocarbons and particulates, \( \text{SO}_2 \) reacts much more quickly (in the order of a few days) to form \( \text{SO}_3 \).

_Effects_
\( \text{SO}_2 \) is absorbed in the mucous membranes of the nose and respiratory tract because it is soluble. A range of effects occurs depending on exposure time as shown in Figure 4.

![Graph showing health effects of SO2 as a function of concentration and exposure time](Turco, 2002:195)
**Standards**
SO\textsubscript{2} is one of the original 6 criteria pollutants for which standards were set in the United States.

The United States primary standards (designed for the protection of public health) are:

<table>
<thead>
<tr>
<th>Gibbs</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 µgm\textsuperscript{-3}</td>
<td>(30 ppb)</td>
<td>annual average</td>
</tr>
<tr>
<td>365 µgm\textsuperscript{-3}</td>
<td>(140 ppb)</td>
<td>24-hr average</td>
</tr>
</tbody>
</table>

SO\textsubscript{2} is now controlled in many countries. In South Africa, guideline values recommended by DEAT and the World Health Organisation (WHO) guideline values are:

<table>
<thead>
<tr>
<th>Gibbs</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 µgm\textsuperscript{-3}</td>
<td></td>
<td>annual average</td>
</tr>
<tr>
<td>125 µgm\textsuperscript{-3}</td>
<td></td>
<td>24-hr average</td>
</tr>
<tr>
<td>500 µgm\textsuperscript{-3}</td>
<td></td>
<td>1-hr average</td>
</tr>
</tbody>
</table>

Proposed standards under the new AQA in South Africa are:

<table>
<thead>
<tr>
<th>Gibbs</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 µgm\textsuperscript{-3}</td>
<td>(19 ppb)</td>
<td>annual average</td>
</tr>
<tr>
<td>125 µgm\textsuperscript{-3}</td>
<td>(48 ppb)</td>
<td>24-hr average</td>
</tr>
<tr>
<td>350 µgm\textsuperscript{-3}</td>
<td></td>
<td>1-hr average</td>
</tr>
<tr>
<td>500 µgm\textsuperscript{-3}</td>
<td>(191 ppb)</td>
<td>10-min average</td>
</tr>
</tbody>
</table>

### 3.2 Sulphur Trioxide (SO\textsubscript{3})

SO\textsubscript{3} is emitted together with SO\textsubscript{2} but at much lower concentrations (~1–5 % of SO\textsubscript{2} concentrations).

**Sources**

Natural emissions are:
- Volcanoes

Anthropogenic sources are:
- Fossil fuel combustion
- Sulphuric acid manufacturing, electroplating
- Phosphate fertilizer manufacturing

**Chemical Reactions**

SO\textsubscript{3}, which has formed mainly as a result of oxidation of SO\textsubscript{2}, rapidly combines with water to form sulphuric acid (H\textsubscript{2}SO\textsubscript{4}).

**Effects**

SO\textsubscript{3}, together with H\textsubscript{2}SO\textsubscript{4}, is frequently associated with haze in the atmosphere.
3.3 Sulphides

Biological processes are chiefly responsible for emitting sulphur to the atmosphere in a reduced form, as hydrogen sulphide (H$_2$S), carbonyl sulphide (COS) and dimethylsulphide [(CH$_3$)$_2$S]. Once in the atmosphere, the sulphides are oxidized rapidly to SO$_2$ and sulphates and as such have very short residence times in the atmosphere (with the exception of COS which has a lifetime of ~1 yr). Of the sulphides, the most important one is H$_2$S, as it has important anthropogenic as well as natural sources.

Hydrogen Sulphide (H$_2$S)

Key Characteristics
H$_2$S is colourless, toxic, and has a strong, offensive odour (rotten egg). It can be detected at concentrations as low as 0.5 ppb.

Sources
Natural emissions include:
- Biogenic emissions produced by the decomposition of organic matter and bacterial reduction of sulphate (SO$_4^{2-}$) in anaerobic conditions on land (water logged soils, wetlands) and in shallow marine surface waters (tidal flats, marine salt marshes, estuaries)
- Volcanoes
- Geothermal sources (hot springs)

Anthropogenic sources include:
- Kraft process in the pulp and paper industry. This process uses the sulphide process to extract cellulose from wood
- Rayon industry
- Coke ovens
- Sewage plants
- Oil refineries; the processing of ‘sour’ crude oil results in emission of H$_2$S and other volatile organic sulphides; today many refineries recover sour gases and process them to form sulphuric acid or elemental sulphur.

Effects
Apart from its strong odour which is a nuisance factor, H$_2$S blackens lead based paints.

Chemical Reactions
In air, H$_2$S is oxidized to SO$_2$ within a few hours, adding to the ambient SO$_2$ level.

3.4 Sulphuric Acid (H$_2$SO$_4$)

Key Characteristics
Sulphuric acid (H$_2$SO$_4$) is one of the most important strong acids in the atmosphere. In its gaseous state, H$_2$SO$_4$ condenses easily as it has a low saturation vapour pressure. Once it condenses it does not readily evaporate. Water vapour molecules readily hydrate the acid forming a solution of sulphuric acid and water.
**Sources**

$\text{H}_2\text{SO}_4$ is not directly emitted to the atmosphere but forms as a result of various chemical reactions in the atmosphere. For example, $\text{H}_2\text{S}$ and $\text{SO}_2$ are oxidized in the atmosphere to $\text{H}_2\text{SO}_4$.

**Chemical Reactions**

$\text{SO}_2$ is oxidized by OH to produce $\text{H}_2\text{SO}_4$. The reactions are as follows:

\[
\text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{HSO}_3 + \text{M}
\]

\[
\text{HSO}_3 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2
\]

\[
\text{SO}_3 + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_2\text{SO}_4 + \text{M}
\]

Where $\text{M} = \text{any inert molecule required to stabilise the excited intermediate } \text{HSO}_3 \text{ by collision.}$

The lifetime of $\text{SO}_2$ in the presence of OH is 1-2 weeks, whereas the next two reactions occur very rapidly. The acid condenses on to existing aerosols or forms new aerosols through the process of nucleation.

**Effects**

- $\text{H}_2\text{SO}_4$ weakly absorbs visible and ultraviolet radiation and as such contributes to haze and a reduction in visibility.
- $\text{H}_2\text{SO}_4$ (aq) is soluble and can be deposited in the respiratory tract. Penetration depends on the size of the particle on which it dissolves.
- Acid deposition affects lakes, forests, agriculture and building materials (see Box 3).

**Box 3: Acid Deposition** (Jacobson, 2002)

Acid deposition includes both dry deposition (deposition of acid gases) and wet deposition (deposition of acid liquids). The latter comprises acid rain, acid fog and acid haze aerosols. Of these, acid rain has received the most attention, particularly for its damaging trans-boundary effects on forest and lakes in Europe and North America.

The pH values range between 2 and 5.6, but typically, acid rain has a pH of 4. Acid rain consists predominantly of sulphate ions ($\text{SO}_4^{2-}$) and nitrate ions ($\text{NO}_3^-$) and to a much smaller extent, chloride ions ($\text{Cl}^-$).

Sulphuric acid ($\text{H}_2\text{SO}_4$) is the main contributor to acid rain. Others are nitric acid ($\text{HNO}_3$) and hydrochloric acid ($\text{HCl}$), although the latter is a relatively minor contributor.

Acid rain is produced in two ways. The first mechanism involves gas phase sulphuric acid ($\text{H}_2\text{SO}_4 (g)$) condensing on to water droplets and the resulting aqueous phase sulphuric acid ($\text{H}_2\text{SO}_4 (aq)$) dissociating to release the sulphate ion ($\text{SO}_4^{2-}$) and two $\text{H}^+$ ions, which increase the acidity of the water. The reactions are as follows:

\[
\text{H}_2\text{SO}_4 (aq) \xrightarrow{\text{H}^+} 2\text{H}^+ + \text{SO}_4^{2-}
\]

[Note: Nitric acid ($\text{HNO}_3 (aq)$) also dissociates to yield a $\text{H}^+$ ion and the nitrate ion ($\text{NO}_3^-$)].
Box 3: Acid Deposition cont.
A second mechanism is the oxidation of SO$_2$ by hydrogen peroxide (H$_2$O$_2$) to release the same number of H$^+$ ions, as follows:

$$\text{SO}_2(\text{ag}) + \text{H}_2\text{O}_2(\text{ag}) \rightarrow 2H^+ + \text{SO}_4^{2-}$$

The effects of acid deposition on soils and water bodies depend to a large extent on the buffering capacity (degree of alkalinity) of the receiving surfaces.

The following effects are experienced:

- Acid deposition to lakes can change the pH of the lake. Since fish and microorganisms can only tolerate a particular pH range, they may die off as a result.
- Damage to leaves of trees and plants. Acid deposition on a leaf surface gives rise to a liquid film on the leaf, which then erodes the cuticle wax on the leaf and causes the leaf to dry out and can lead to injury.
- Acid deposition to the soil can cause the mobilisation of metals (e.g. aluminium and iron) in the soil. These metals are toxic to plants if absorbed by the roots. Certain nutrients (e.g. calcium, magnesium and potassium) can also be leached from the soil and cause mineral deficiencies.
- Acid deposition also impacts on agricultural crops, causing reduction in yields and loss of quality.
- Buildings made of limestone and marble (composed of calcium carbonate) are vulnerable to attack by acid deposition. Acids also damage copper, bronze and brass.

4. Gaseous Compounds of Nitrogen

These include:

- Oxides of Nitrogen
  - Nitric Oxide (NO)
  - Nitrogen Dioxide (NO$_2$)
  - Nitrous Oxide (N$_2$O)

- PeroxyacetylNitrate (PAN)

- Nitrous Acid (HNO$_2$) and Nitric Acid (HNO$_3$)

Only NO and NO$_2$ are found in fairly high quantities and are often grouped together as nitrogen oxides (NO$_x$).

4.1 Nitric Oxide (NO)

**Key Characteristics**
Nitric oxide is a colourless, odourless and tasteless gas. It is a very reactive gas.

It is important because it is a GHG and a precursor to ozone, which is a constituent of photochemical smog. It is also a precursor to nitric acid (important in acid precipitation) and particulate nitrate (NO$_3^-$), which affects global climate.
It has a residence time in the atmosphere of ~1 month.
Sources
Natural sources are:

- process of denitrification by anaerobic bacteria in soils and plants
- lightning
- photolysis and kinetic reactions (see Box 4)

Anthropogenic sources include:

- fossil fuel combustion
- biomass burning

Sinks

- kinetic reactions (see Box 4)
- dissolution in ocean water
- deposition to the surface

Box 4

Photolysis reactions involve only one molecule and occur when solar radiation strikes a molecule and breaks it into two or more products, for example:

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \cdot\text{O} \quad \lambda < 0.42 \mu\text{m} \]

where \( h\nu \) is a photon of light and \( \lambda \) is the wavelength of the radiation

Chemical Reactions
In a polluted atmosphere, NO is oxidised to NO\(_2\) as follows:

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]

If NO concentrations are high the NO is rapidly oxidised. NO is also converted to NO\(_2\) through a number of other photochemical reactions.

Effects
NO has no harmful health effects at concentrations which are typically found in an urban atmosphere. However, it is an important precursor to ozone, nitric acid and particulate nitrate. NO is also responsible for ozone reduction in the stratosphere.

4.2 Nitrogen Dioxide (NO\(_2\))

Key Characteristics
Nitrogen dioxide absorbs strongly in the yellow and blue wavelengths of the visible part of the solar spectrum and transmits the remaining green and red wavelengths. As such it appears brown. Brown layers are a common feature of many cities (e.g. Cape Town).

NO\(_2\) has a pungent, irritating odour and is highly corrosive.

Sources

- photolysis and kinetic reactions – chemical reactions are the major source (see Box 4)
fossil fuel combustion – includes industrial and domestic sources and motor vehicles
biomass burning
industrial processes using nitric acid
explosives industry
biological emissions

Sinks
- photolysis and kinetic reactions – chemical reactions are the major sink (see Box 4)
- dissolution in ocean water
- deposition to the surface

(Jacobson, 2002)

Chemical Reactions
$\text{NO}_2$ is important in the formation of $\text{O}_3$, and in an unpolluted atmosphere the following set of three reactions (involving $\text{NO}$, $\text{NO}_2$ and $\text{O}_3$) determine the concentration of $\text{O}_3$.

\[
\text{NO} + \text{O}_3 \rightarrow \text{O}_2 + \text{NO}_2 \quad (1)
\]

\[
\text{NO}_2 + h\nu \rightarrow \cdot\text{O} + \text{NO} \quad (2) \quad \lambda < 0.42 \ \mu\text{m}
\]

\[
\cdot\text{O} + \text{O}_2 \rightarrow \text{O}_3 \quad (3)
\]

Because $\text{NO}$ concentrations are much lower than $\text{O}_3$ concentrations in background air, the first reaction does not deplete $\text{O}_3$ either during the day or night. In a polluted atmosphere, when $\text{NO}$ concentrations are high, $\text{O}_3$ can be depleted at night.

During the day, $\text{NO}_2$ can be removed as follows:

\[
\text{M} + \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3
\]

This is a slow process. $\text{HNO}_3$ can photolyze back to $\text{NO}_2$ and OH but since $\text{HNO}_3$ has a long lifetime and because it is soluble it dissolves in cloud droplets or aerosol particles, $\text{HNO}_3$ is a sink for $\text{NO}_2$.

At night reaction (2) shuts down and so $\text{NO}_2$ then becomes available to participate in other reactions.

Typical diurnal variations in $\text{NO}$, $\text{NO}_2$ and $\text{O}_3$ in an urban atmosphere are shown in Figure 5. $\text{NO}$ reaches a maximum in the early morning, coinciding with peak traffic hours. After sunrise, $\text{NO}$ is converted to $\text{NO}_2$, such that $\text{NO}_2$ peaks a few hours after sunrise. $\text{NO}_2$ then declines because it is photodissociated (Reaction 2) and converted to other secondary compounds such as PAN and $\text{O}_3$. $\text{O}_3$ thus peaks in the early to mid-afternoon. Both $\text{NO}_2$ and $\text{O}_3$ eventually disappear through formation of nitrated organic compounds, peroxides, aerosols and other terminal products.
Figure 5: Typical diurnal variations in ozone and precursor gases (Turco, 2002:157)

Effects
- Reduction in visibility if concentrations are high
- Damage to the lungs and the cause of increased respiratory infections. Generally, health effects are minor at typical ambient concentrations
- Leads to ozone formation in the troposphere
- Precursor to nitric acid and a component of acid deposition
- Reduces ozone in the upper stratosphere

Standards
NO\textsubscript{2} is one of the original 6 criteria pollutants identified in the United States under the CAAA70. It is regulated in many countries. In the United States, the federal standards are:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 µgm\textsuperscript{-3} (530 ppb)</td>
<td>1-hr average</td>
</tr>
</tbody>
</table>

Together with carbon monoxide and ozone, NO\textsubscript{2} levels are used to trigger smog alerts in California if the standards are exceeded.

WHO guideline values:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>40-50 µgm\textsuperscript{-3}</td>
<td>annual average</td>
</tr>
<tr>
<td>200 µgm\textsuperscript{-3}</td>
<td>1-hr average</td>
</tr>
</tbody>
</table>

In South Africa, the current guideline values recommended by DEAT are:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ppb (96 µgm\textsuperscript{-3})</td>
<td>annual average</td>
</tr>
<tr>
<td>100 ppb (191 µgm\textsuperscript{-3})</td>
<td>24-hr average</td>
</tr>
<tr>
<td>200 ppb (382 µgm\textsuperscript{-3})</td>
<td>1-hr average</td>
</tr>
<tr>
<td>500 ppb (955 µgm\textsuperscript{-3})</td>
<td>instantaneous peak</td>
</tr>
</tbody>
</table>
The proposed standards under the AQA are:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>1-hr average</th>
<th>Annual average</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 µgm⁻³</td>
<td>(21 ppb)</td>
<td>200 µgm⁻³</td>
</tr>
</tbody>
</table>

4.3 Nitrous Oxide (N₂O)

**Key Characteristics**
Nitrous oxide is a colourless, slightly sweet, non-toxic gas that is often called laughing gas. It strongly absorbs infrared radiation (at ~4.8 µm and 7.9 µm) and thus is an important greenhouse gas. It is 270 times more efficient at absorbing infrared radiation than CO₂.

**Sources**
Natural sources include:
- process of denitrification by anaerobic bacteria in soils and ocean

Anthropogenic sources include:
- combustion of fossil fuel
- emissions by bacteria in fertilizers
- emissions by bacteria in sewage
- biomass burning
- nylon manufacture

**Sinks**
Nitrous oxide is removed through transport to the stratosphere, chemical reactions (N₂O to NO by atmospheric oxidation) and by deposition to the surface. The rate of depletion is slow and so it has a long lifetime.

4.4 PAN (CH₃C(O)O-ONO₂)

PAN or peroxyacetylnitrate was first identified as a component of photochemical smog in Los Angeles in the 1950s. There are a large number of peroxyacyl nitrates that have been found in urban air, but PAN is the most common.

PAN is a product of photochemical reactions between hydrocarbons and nitrogen oxides. Hydrocarbons are oxidised by OH radicals to produce peroxy radicals (RO₂), which then react with NO to produce a variety of carbonyls. These in turn are highly reactive and break down to produce PA (peroxyacetyl) radicals which then react with NO₂ to form PAN.

PAN causes damage to agricultural crops but it is mainly known as an eye irritant.

Since PAN is entirely a product of photochemical reactions and has no known primary source, its presence is a good indicator of photochemical smog.
5. Volatile Organic Compounds (VOCs)

VOCS are a class of organic compounds that are best known for their contribution to the production of secondary pollutants (e.g. ozone). Together with NO\textsubscript{x} and sunlight, VOCs lead to the formation of ozone and other compounds of photochemical smog, such as PAN. They also play an active role in acid deposition by contributing to the generation (or inhibition) of radicals responsible for converting sulphur oxides to sulphuric acid and nitrogen oxides to nitric acid. They are also involved in the formation of peroxide that influences acid formation in clouds. Some VOCs undergo phase transformation leading to aerosols implicated in visibility degradation.

The term VOCs is commonly used to include all the many gaseous organic compounds that are emitted to the atmosphere. Sometimes the term hydrocarbons is used to refer to organic compounds that are composed only of hydrogen (H) and carbon (C) atoms.

VOCs have high vapour pressures, meaning that they tend to evaporate easily. VOCs can be classified into a number of groups, of which the following are the most important:

- Alkanes
- Alkenes
- Aromatics
- Oxygenated hydrocarbons
- Terpenes

5.1 Alkanes (C\textsubscript{n}H\textsubscript{2n+2})

These include methane, ethane, propane, pentane and hexane.

*Methane (CH\textsubscript{4})* is the most important in this group and usually comprises ~ 40-80 % of the total hydrocarbons in an urban atmosphere. Methane has a low photochemical activity and so it is often separated from the other hydrocarbons and the term non-methane hydrocarbons (NMHC) is used.

Sources

Natural sources are:

- Biological production - decomposition of organic matter by bacteria under anaerobic conditions in wetlands, flooded soils and sediments of lakes and oceans
- Volcanic activity
- Termites
- Kinetic reactions

Anthropogenic sources, which contribute a larger proportion (~60% of emissions) are:

- Combustion of fossil fuels (coal, oil and natural gas)
- Biomass burning due to deforestation, savanna burning, burning of agricultural waste
- Use of biofuels
- Domestic sewage
- Digestive tracts of ruminant animals (e.g. cattle)
- Rice paddies
**Sinks**
Methane has a residence time of ~1 year in the atmosphere. Removal of methane from the atmosphere is via:
- Precipitation
- Biological uptake
- Gas phase oxidation process initiated by the hydroxyl radical (OH)

\[ \text{CH}_4 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3 \]

**Effects**
Methane is a GHG and absorbs infrared radiation 25 x more efficiently than CO\(_2\). It is the second most important GHG (after CO\(_2\)) on a global basis. Methane has little impact on the formation of photochemical smog compared with the other VOCs. It has no harmful human health effects at typical concentrations.

**Ethane** (C\(_2\)H\(_6\)) and **propane** (C\(_3\)H\(_8\)) are usually present in fairly high concentrations in the urban atmosphere and have fairly long lifetimes against photochemical destruction. In both cases, the hydroxyl radical (OH) initiates breakdown to form ozone.

### 5.2 Alkenes (Olefins) (C\(_n\)H\(_{2n}\))

These include ethene, propene and butene. They have double carbon bonds. Alkenes react rapidly with the hydroxyl radical (OH), O\(_3\) and NO\(_3\). They are important in ozone formation.

### 5.3 Aromatic Hydrocarbons

The most important of the aromatic hydrocarbons are benzene, toluene and xylene, often referred to as the BTX group. All aromatics have a benzene ring and may have other carbon and hydrogen atoms attached to the ring.

**Toluene** (C\(_6\)H\(_5\)CH\(_3\)) is the most abundant aromatic compound found in polluted air, accounting for about 6% of NMHCs. Sources of toluene are almost entirely anthropogenic and include petrol combustion, petroleum refining, the use of industrial solvents, detergent production, paint and biomass burning. Some plants when under stress will emit toluene. Toluene reacts fairly rapidly with the hydroxyl radical (OH) and so has a lifetime of the order of hours to days.

**Xylene** [(C\(_6\)H\(_4\)(CH\(_3\))\(_2\)] is the most important organic gas in the urban atmosphere in terms of ozone production. Sources of xylene are petrol, lacquers and glues.

The simplest of the aromatic hydrocarbons is **benzene** (C\(_6\)H\(_6\)), which has a hexagonal ring consisting of double bonds, which makes it relatively stable. Sources of benzene once included a dry cleaning agent, but now it is chiefly emitted from motor vehicles as a result of combustion of fuel. It is also emitted from biomass burning. Benzene is the only aromatic that does not react rapidly with the hydroxyl radical (OH) making it a very stable compound. It has a lifetime of a few days and can be transported hundreds of kilometres.

**Effects**
The aromatic hydrocarbons have severe health effects:
• Benzene is extremely toxic and is listed fifth on the US EPA top hazardous substance list. It is a known carcinogen, causing leukaemia (cancer of the blood).
• Toluene affects the brain and can cause tiredness, confusion, memory loss, nausea and hearing loss. It also affects the kidneys.
• Xylene affects the brain and can cause headaches, lack of muscle coordination, dizziness and confusion.

They also make a significant contribution to the formation of ozone and other photo-oxidants in an urban atmosphere, making the aromatics the most important class of hydrocarbons in the formation of photochemical smog.

There is also strong evidence that they lead to the formation of secondary organic aerosols (SOA).

**Standards**
The proposed South African standard under the new AQA for benzene is:

<table>
<thead>
<tr>
<th>Standard</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 (m⁻³)</td>
<td>1.6 ppb</td>
</tr>
</tbody>
</table>

### 5.4 Oxygenated Hydrocarbons

These include many different compounds, which are classified as alcohols, aldehydes, ketones and acids. Aldehydes and ketones together are called compounds. Many of the oxygenated compounds are formed as secondary pollutants, but primary sources include motor vehicles and solvent vapours from the chemical, paint and plastics industries.

Formaldehyde (HCHO) is the most abundant aldehyde. It is colourless and has a strong odour above 0.05-1.0 ppm. It is emitted by pressed wood products (plywood), resins, adhesives, carpeting and acetone from cosmetics. Health effects of formaldehyde include respiratory irritation (dissolves readily) and watering of eyes. Formaldehyde produces ozone precursors through a number of chemical reactions.

Methanol and ethanol (both alcohols) contribute to ozone production. Methanol also produces formaldehyde and ethanol produces acetaldehyde (a precursor to PAN). In countries where alcohol fuel programmes have been promoted (e.g. Brazil - ethanol), the levels of PAN have increased.

### 5.5 Terpenes

Terpenes (e.g. isoprene) are a group of naturally occurring hydrocarbons. Sources are emissions from vegetation, biomass burning (forests and grasslands), refuse burning, use of scented deodorisers and polishes, and from fabric. Since terpenes are very reactive they are readily removed from the atmosphere and contribute to ozone formation. In cities near forests terpenes can account for a fairly high percentage of ozone production.

### 6. OZONE

Ozone ($O_3$) is one of the key constituents of photochemical smog and much attention is focused on its measurement. It is also a GHG. Whilst tropospheric ozone is considered a
pollutant and the focus is on reducing concentrations, stratospheric ozone is regarded as 'good' ozone as it absorbs ultraviolet radiation and protects life on earth. The emphasis is thus on preventing depletion.

**Key Characteristics**

Ozone is a relatively colourless gas at typical mixing ratios. It appears slightly purple at high mixing ratios because it weakly absorbs green wavelengths and transmits red and blue. Its odour threshold is 0.02 ppmv.

Ozone has a short lifespan in the troposphere of ~1 week but this does range between a few days to months and thus its concentration is highly variable.

**Sources**

Ozone is a secondary pollutant that is produced in the atmosphere as a result of various photochemical reactions involving precursor gases (particularly NOx and VOCs). Sources of the precursor gases are as follows:

Natural sources include:
- Biogenic emissions. NOx is emitted from the soil, particularly after they have been wetted by spring rains. VOCs (isoprene and monoterpenes) are emitted by vegetation and CO, also a precursor of ozone, is produced by the chemical oxidation of soil organic matter, and from surface litter.
- Lightning. The very high temperatures associated with lightning produce NO from O2 and N2. This is an important source of ozone in the upper troposphere as much of the NOx produced at low altitudes by other sources has a lifetime of only a few hours.

In addition ozone can be injected into the troposphere by stratospheric-tropospheric exchange (STE). The stratosphere is very rich in ozone and large amounts of ozone are injected from the stratosphere and may even reach the surface.

Anthropogenic sources include:
- Combustion of fossil fuels used in industry and motor vehicles.
- Biomass burning. Although this can also be regarded as a natural source, the burning of agricultural wastes (e.g. sugar cane), human-induced accidents and burning for management are dominant.

**Sinks**

- Dry deposition
- Photolysis. The destruction of ozone occurs by short wave radiation as follows:

\[
O_3 + h\nu \rightarrow O_2 + \cdot O \quad (\lambda < 0.340 \mu m)
\]

The O atoms then react with water vapour

\[
O + H_2O \rightarrow 2OH
\]

The lifetime of ozone is thus limited by the level of solar radiation and the concentration of water vapour. The lifetime of ozone is greater in the middle and upper troposphere due to a
drier atmosphere than in the continental or marine boundary layer where ozone molecules survive for 2 to 5 days.

- **HO2 / OH catalysed destruction.** Ozone is destroyed in the reaction with OH and HO2 (hydroperoxy) radicals as shown in the equations below:

\[
\begin{align*}
O_3 + OH & \rightarrow O_2 + HO_2 \\
O_3 + HO_2 & \rightarrow 2O_2 + OH
\end{align*}
\]

**Chemical Reactions**

Tropospheric ozone chemistry is complex. The reactions of tropospheric ozone in background or unpolluted air are discussed first, followed by the reactions in an urban environment.

In the background troposphere, concentrations of ozone are governed by the following set of reactions, also known as the photostationary state reactions:

\[
\begin{align*}
NO + O_3 & \rightarrow NO_2 + O_2 \\
NO_2 + h\nu & \rightarrow NO + \cdot O \quad \lambda < 0.420 \, \mu m \\
\cdot O + O_2 & \rightarrow O_3
\end{align*}
\]

During the day ozone production can be enhanced by CO, CH4 and some NMHCs. For CO the set of reactions was given in Box 2.

The third equation describes a critical step in the reaction chain because a deficiency of NO will lead to a loss of ozone as HO2 will react with O3:

\[
HO_2 + O_3 \rightarrow OH + 2O_2 \tag{7}
\]

with the following net result:

\[
CO + O_3 \rightarrow CO_2 + O_2 \tag{8}
\]

CH4 and other hydrocarbons are oxidized similarly. The possible net result of the oxidation of CH4 to CO in NOx-rich air is summarised as follows:

\[
CH_4 + 8O_2 \rightarrow CO + H_2O + 4O_3 + 2OH \tag{9}
\]

which leads to a net production of O3 and OH.

In contrast, the net result in NOx deficient air may be summarised as:

\[
CH_4 + OH + HO_2 \rightarrow CO + H_2 + 2H_2O \tag{10}
\]

with a loss of OH and HO2.
The above reaction sequences emphasise that NO\textsubscript{x} plays an important role in ozone chemistry. Ozone production predominates in NO\textsubscript{x}-rich air while ozone destruction prevails in NO\textsubscript{x}-deficient air.

The photostationary state reactions, which occur in the background atmosphere, are less useful in urban areas where sunlight stimulates a reaction between the high levels of volatile organic compounds (VOCs) or hydrocarbons and NO\textsubscript{x} released during anthropogenic processes. Figure 6 summarises the formation of ozone diagrammatically.

Figure 6: Diagrammatic representation of the formation of photochemical smog

The reaction between hydrocarbons and NO\textsubscript{x} requires an initiator and the ubiquitous OH radical fulfills this role. The first reaction is therefore summarized as:

\[
\text{OH} + \text{RH} \rightarrow \text{R}^\bullet + \text{H}_2\text{O}
\]

The organic radical that is produced, subsequently reacts with oxygen (O\textsubscript{2}) and NO to produce O\textsubscript{3}. These then produce ozone and hydrocarbons.

The complete set of equations is given as follows:

\[
\begin{align*}
\text{OH} + \text{RH} & \rightarrow \text{R}^\bullet + \text{H}_2\text{O} \\
\text{R}^\bullet + \text{O}_2 & \rightarrow \text{RO}_2^\bullet \\
\text{RO}_2^\bullet + \text{NO} & \rightarrow \text{RO}^\bullet + \text{NO}_2 \\
\text{NO}_2 + h\nu & \rightarrow \text{NO} + \text{O}^\bullet \\
\text{O}^\bullet + \text{O}_2 & \rightarrow \text{O}_3
\end{align*}
\]

where reactive hydrocarbons are indicated as RH, R\textsuperscript{•} represents an organic radical and RO\textsubscript{2}\textsuperscript{•} is a peroxy radical.
The overall process can be summarized as follows:

\[ O_2 \]

\[ RH + NO + hv \rightarrow \ldots \ldots \rightarrow O_3 + NO_2 + HC \]

The products of smog formation also include a variety of photolytically stable hydrocarbon compounds which are indicated as HC. Some of these compounds are toxic air pollutants and others condense to form photochemical haze.

**Effects**

Ozone causes headaches at > 0.15 ppmv, chest pains at > 0.25 ppmv and sore throat and cough at > 0.36 ppmv. Symptoms of respiratory problems include coughing and breathing discomfort. It interferes with the growth of plants and trees and increases their susceptibility to disease. It also deteriorates organic materials such as rubber, textile dyes and fibres, some paints and coatings.

**Standards**

Ozone is one of the 6 criteria pollutants that are required to be controlled in the United States under CAAA70. It was not one of the original criteria pollutants but in 1979 ozone replaced photochemical oxidants.

The US federal standards are as follows:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Unit</th>
<th>Time Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08 ppmv</td>
<td>160 µg.m(^{-3})</td>
<td>8-hr average</td>
</tr>
<tr>
<td>0.12 ppmv</td>
<td>235 µg.m(^{-3})</td>
<td>1-hr average</td>
</tr>
</tbody>
</table>

WHO guideline values:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Unit</th>
<th>Time Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 µg.m(^{-3})</td>
<td>8-hr average</td>
<td></td>
</tr>
<tr>
<td>150-200 µg.m(^{-3})</td>
<td>1-hr average</td>
<td></td>
</tr>
</tbody>
</table>

Proposed standards in South Africa are:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Unit</th>
<th>Time Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 µg.m(^{-3}) (61 ppb)</td>
<td>8-hr average</td>
<td></td>
</tr>
<tr>
<td>200 µg.m(^{-3}) (102 ppb)</td>
<td>1-hr average</td>
<td></td>
</tr>
</tbody>
</table>

**Aerosols**

Recently, aerosols have been receiving much attention and considerable advances in aerosol research have been made over the past decade or so. Aerosols have particularly important effects on global climate as they reflect solar radiation to space and hence are responsible for cooling of the earth’s surface. They also cause adverse health effects, which are cause for serious concern.

**Definition**

Aerosols are small solid particles or liquid droplets that are suspended in air. They are generally classified into two types:
- **primary particles** that enter the atmosphere either by emission e.g. pollen, sea salt and soot from combustion activities, or nucleation (see Box 5); and
- **secondary particles** that are formed in the atmosphere by chemical reactions, e.g. formation of sulphate aerosols from SO$_2$.

Aerosols include inorganic, organic and biological particles such as spores, pollens, viruses, bacteria, and plant debris.

**Key Characteristics**

- **Size**
  Aerosols usually include particles that are greater than 0.01µm in diameter and range up to ~10 µm. Naming of aerosols according to their size range differs widely amongst authors. The convention adopted here is that of Jacob (1999), which is summarized as follows:

<table>
<thead>
<tr>
<th>Size Range</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.001 µm</td>
<td>gas molecules</td>
</tr>
<tr>
<td>0.001 – 0.01 µm</td>
<td>ultrafine aerosols</td>
</tr>
<tr>
<td>0.01 – 1.0 µm</td>
<td>fine aerosols</td>
</tr>
<tr>
<td>1.0 – 10 µm</td>
<td>coarse aerosols</td>
</tr>
</tbody>
</table>

Ultrafine aerosols are formed from nucleation of gaseous molecules (see Box 5). The ultrafine aerosols may grow through collisions between particles to become fine aerosols. Growth beyond the 1 µm threshold is slow and hence aerosols tend to accumulate in the 0.01 – 1 µm size range. As a consequence, this size range is often referred to as the accumulation mode. Accumulation mode particles have increased in size through collision and coalescence (coagulation) and through condensation of gases onto the particles. The various processes are summarised in Box 6. Coarse particles are larger than 1 µm in diameter, and generally result from primary emissions such as sea spray, windblown dust and volcanoes.

- **Shape**
  Aerosols vary in shape and may be spherical, irregular, flaky or cubical in shape. In view of the different shapes it is difficult to define a size. It is customary to regard them as spheres and to define an equivalent aerodynamic radius, which is the radius of a sphere of unit specific gravity that has the same falling velocity as the particle being considered. Pollen, smoke and fly ash tend to be spherical, whereas minerals are irregular, cubical or flaky. Fibres usually consist of asbestos, wool and various synthetic materials, while flocs contain large amounts of carbon and are formed during combustion.

- **Composition**
  Aerosols have highly variable chemical compositions, as well as different electrical charges and adhesive properties. Because of their diverse origins and transformation processes in the atmosphere, there is a large variability in aerosol composition and the aerosol is continually evolving and changing properties over time and space.

- **Lifetime**
  Particle lifetimes are largely dependent on their size. Coarse particles may settle out rapidly and typically have lifetimes in the order of hours to days. Fine particles may remain in the atmosphere for months.
Sources
Aerosols have both natural and anthropogenic sources. In some cases, particularly in respect of wind blown dust from poorly managed agricultural areas, it is difficult to distinguish the source.

Natural Sources include:
- Wind blown dust consists of the minerals (mainly carbonates and silicates) and organic materials (pollen, seeds, hairs, fungi and micro-organisms) making up the soil. Most of the particles are coarse. A lack of rain, strong winds and non-vegetated surface favour the lifting of dust into the air. On a global scale, deserts are the main source of aerosols.
- Volcanic eruptions can emit vast quantities of particles over a very large size range (0.1 to 100 µm in diameter), as well as gases, which later nucleate to form particles (e.g. SO₂ oxides to gaseous sulphuric acid, which then nucleates to form new sulphuric acid-water aerosol particles).
- Biomass burning produces a variety of gases, as well as particles (ash, organic matter and soot) (see Box 7 for definitions). The particles produced by fire are usually quite small in diameter (~ 0.1 µm).
- Salt particles are important in coastal areas. They result from air bubbles that are forced to break at the sea surface by wind and waves. They are generally coarse particles.
- Pollens, spores, micro-organisms and insects make up the biological materials suspended in the atmosphere.

Anthropogenic sources include:
- Combustion of fossil fuel (coal, oil, natural gas, kerosene, diesel and petrol) in power stations, industrial boilers and motor vehicles. Particulates emitted during fossil fuel combustion include soot (black carbon and organic matter), sulphate and fly ash. Diesel engines emit up to 100 times more particulates than petrol engines.
- Agricultural burning (e.g. sugar cane burning) releases smoke or unburnt carbon aerosols
- Industrial processes (e.g. smelting, cement manufacture, waste incineration) that involve the combustion of fossil fuels together with metals produce various types of particles depending on the process.
- Metallurgical plants emit heavy metals and silicates
- Fugitive dust originates from untarred roads and construction sites

Sinks
Aerosols can be removed by:
- Dry deposition, which is the process whereby aerosols are transported by diffusion or advection to surfaces of different types and come to rest or react with the surface. This process is more efficient for solid particles (as they are heavier) than gases.
- Sedimentation, by which particles fall by their own weight and is therefore again most efficient for coarse particles
- Rainout, which is the process whereby aerosols become incorporated into raindrops and then fall to the ground.

Figure 7 summarises the sources and sinks and processes involved in aerosol formation.
Figure 7: **Sources and sinks of aerosols** (Jacob, 1999:148)

**Effects**
Aerosols are chiefly known for their impact on global climate and human health (Jacob, 1999).

- **Human Health**
The inhalation of particulate matter is linked with respiratory diseases, such as asthma and chronic constructive pulmonary diseases. The size of a particle determines the extent of its penetration and whether it can reach the lung. Particles smaller than 2.5 µm in diameter are known to cause more adverse health effects than larger particles. Some aerosols contain toxic substances and others are carcinogenic.

- **Climate**
Aerosols have a significant effect on the global radiation balance, as they scatter and absorb solar radiation and change the properties of clouds. Their net effect is to cool and as such counteract the greenhouse effect.

- **Precipitation**
They are important in the precipitation process since all cloud droplets form on aerosol particles, known as cloud condensation nuclei (CCN).

- **Visibility**
Aerosols are the major cause of a reduction in visibility due to the scattering of light.

- **Materials Damage**
The deposition of particles on clothes and buildings increases cleaning costs, damages buildings and can increase corrosion rates as they provide active surfaces on which moisture condenses.

**Standards**
The original CAAA70 in the United States identified total suspended particulates (TSP) as a criteria pollutant. This was later changed to PM$_{10}$ and PM$_{2.5}$ (defined as mass of particles with diameters < 10 µm and < 2.5 µm respectively).
Currently, the following air quality standards apply in the United States:

<table>
<thead>
<tr>
<th>PM&lt;sub&gt;10&lt;/sub&gt;</th>
<th>PM&lt;sub&gt;2.5&lt;/sub&gt;</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>50 µg.m&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>15 µg.m&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>annual average</td>
</tr>
<tr>
<td>150 µg.m&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>65 µg.m&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>24-hr average</td>
</tr>
</tbody>
</table>

WHO guideline values for PM<sub>10</sub> are:

<p>| | |</p>
<table>
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<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>70 µg.m&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>24-hr average</td>
</tr>
</tbody>
</table>

In South Africa proposed air quality standards for PM<sub>10</sub> are:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>40 µg.m&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>annual average</td>
</tr>
<tr>
<td>75 µg.m&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>24-hr average</td>
</tr>
</tbody>
</table>

The following standards are proposed under the AQA:

<p>| | |</p>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>30 µg.m&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>annual average</td>
</tr>
<tr>
<td>50 µg.m&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>24-hr average</td>
</tr>
</tbody>
</table>

Increasingly, attention is focussing on smaller size particles such as PM<sub>2.5</sub> as health concerns grow.

**Box 5: Nucleation**

Nucleated particles are those that form from the gaseous phase. Nucleation may be either homogeneous or heterogeneous.

Homogeneous nucleation occurs when gaseous molecules aggregate or cluster together without the aid of an existing surface. Thus a new particle is created. The most important homogeneous nucleation process in the atmosphere is that of the nucleation of sulphuric acid and water (both gaseous phase) to form a sulphuric acid-water particle.

Heterogeneous nucleation on the other hand occurs when gases nucleate onto an existing surface and thus a new particle is not created.
Box 6: Growth in particles through collision, coalescence and condensation

When two particles of equal or unequal sizes collide, they may coalesce and produce one large particle. The number of particles in the air thus decreases but the volume stays the same.

Particles can also grow by condensation whereby gaseous molecules condense on to a nucleated liquid surface. The condensing gas is usually water but may also be sulphuric acid gas and some organic gases such as toluene, xylene etc.

(Source: Jacobson, 2002:130)

Box 7: Inorganic particulates originating from biomass burning

Ash is the mainly inorganic material that remains after biomass burning.

(Source: Jacobson, 2002:125)

Organic matter consists of carbon and hydrogen-based compounds. Soot consists of black carbon (BC) (chains of carbon atoms) covered with a coating of organic matter (usually various VOCs such as aliphatic hydrocarbons or polycyclic aromatic hydrocarbons (PAHs)).

(Source: Jacobson, 2002:125)

High temperature fires tend to produce more BC than organic matter.
8. Trace Metals

There are many trace metals present in the atmosphere at low concentrations. All are very toxic and acute exposure to high concentrations for short periods or chronic exposure to low concentrations over a long period may have adverse human health effects due to their tendency to accumulate in tissues and organs. The following trace metals are considered here:

- Lead
- Mercury
- Cadmium
- Arsenic

8.1 Lead

Key Characteristics

Lead has a low boiling point and as such is vaporised during combustion processes and then condenses on to the surface of fine particles. It can be present in the atmosphere in a solid form (lead phosphate, lead chloride, lead bromide) or in a gaseous form as alkyl lead that has evaporated from petrol. Lead is soluble and so can be rained out. The lifetime of a lead aerosol in the atmosphere is ~7-30 days.

Sources

About 97% of the sources of lead are anthropogenic. The dominant sources are:

- Combustion of leaded fuel
- Mining of lead and smelting
- Solid waste disposal
- Lead-based paint
- Food cans soldered with lead
- Manufacture of lead-acid storage batteries
- Lead pipes in water supply systems
- Lead glazes on earthenware

(Jacobson, 2002)

Of these, the first three lead to emissions to the atmosphere. The remainder may contaminate drinking water or food.

Tetra-ethyl lead was first added to petrol as an anti-knock agent and to increase engine performance in the 1920s. Soon afterwards there was an outcry over health impacts but this was short-lived. The need to install catalytic converters on cars to reduce overall exhaust emissions is what sparked the eventual drive towards phasing out lead in fuel (catalytic converters cannot be used in conjunction with leaded fuel). Lead in petrol has been phased out in most countries. Europe began phasing out in the 1970s (France in 1988), the United States in 1975 and Japan made a complete switch to unleaded fuel in 1976. The use of leaded fuel is highest in African countries, although the move to phase out lead was given impetus after the World Summit of Sustainable Development in 2002 and the launch of the Partnership for Clean Fuels and Vehicles. The removal of lead from petrol is one of the key goals. The situation in South Africa is described in Box 8.

The use of lead in paint has been banned in the United States since 1978. In South Africa, although there are no lead standards for paint, industry has voluntarily agreed to reduce
the content. The problem is usually experienced in older buildings where paint is peeling off walls.

Natural sources are:
- Wind blown dust
- Volcanoes

**Sinks**
- Deposition to the surface
- Inhalation

**Effects**

Lead enters the body directly from the atmosphere by inhalation, as the fine particles are easily inhaled and can enter the lungs and the blood stream. Inhalation is not the only pathway by which lead can enter the body. Lead can be deposited on soil and water, from where it can enter the food chain and be ingested. The blood distributes it to all organs and tissues in the body and it tends to accumulate in bones, kidneys and liver.

Children are at greatest risk and exposure in childhood leads to behavioural problems, hyperactivity, learning disabilities and central nervous system damage. It affects brain development and lowers IQ. Lead exposure also leads to infertility and miscarriages, increased blood pressure and increased risk of cardiovascular disease.

Besides children, the poor are also at high risk as they tend to live in older houses with lead-based paint and closer to major roads where atmospheric lead concentrations are likely to be higher.

**Standards**

In the United States the following standard applies:

\[
1.5 \, \mu\text{g.m}^{-3} \quad \text{(quarterly average)}
\]

The WHO guideline value is:

\[
0.5 \, \mu\text{g.m}^{-3} \quad \text{(annual average)}
\]

The proposed South African standard is:

\[
0.5 \, \mu\text{g.m}^{-3} \quad \text{(annual average)}
\]

The proposed target is:

\[
0.25 \, \mu\text{g.m}^{-3} \quad \text{(annual average)}
\]

**Box 8: Lead in South Africa**

The phasing out of lead in petrol was delayed for various reasons. There was no strong environmental or health lobby to spearhead the move and it was necessary to increase
petroleum refining capacity to accommodate the change. Eventually the movement was
driven by the motor industry, which was having to import older generation engines
because of continued reliance on leaded fuel.

In the early 1980s the lead content of fuel was 0.836 g/l. This changed to 0.4 g/l in 1989.
Unleaded fuel was introduced in January 1996. The penetration into the market is still
small - in 1998 unleaded fuel accounted for only 10-15% of petrol sales (Murray and
McGranahan, 2003). The government intends to cease making leaded petrol by January
2006.

In most countries in the world there have been dramatic declines in ambient lead
concentrations and similar results are evident in South Africa. Reductions in blood lead
levels have also paralleled the reduction in the lead content of fuel. The Medical
Research Council has reported significant reductions in the blood lead levels of children
at Cape Town inner city schools. A mean of ~16 µg/dl was found in the 1980s and early
1990s. By 1991, this had dropped to 7 µg/dl and whereas in the early years, over 90% of
children had blood lead levels in excess of the international action limit of 10 µg/dl, by
2002 this figure stood at 21%. By comparison, in the United States, blood lead levels
around 2-3 µg/dl are common.

8.2 Mercury (Hg)

Mercury is a naturally occurring heavy transition metal and is the only metal that occurs in
a liquid state at room temperature. It can be transformed by oxidation/reduction reactions
or combined with other elements to form either organic or inorganic mercury compounds.
In the atmosphere, Hg is present as elemental (Hg⁰) and ionic (Hg¹⁺) mercury in the
gaseous phase, with the former being the most dominant. Hg⁰ has a residence time of ~1yr
in the atmosphere, whereas Hg¹⁺ is rapidly removed from the atmosphere after a few hours
or days in an aqueous form, either as a particulate or dissolved. It is deposited to the
surface and in aquatic systems can be converted to a toxic form, methyl mercury (MeHg)
and can accumulate in the food chain.

Key Characteristics
It is odourless, silver-white in colour and volatile.

Sources
Natural sources are:
• re-evaporation of mercury vapour from the earth’s surface
• windblown dust
• Volcanic activity

Anthropogenic sources are:
• Combustion of fossil fuel (coal)
• Incineration of solid wastes that contain mercury
• Cement manufacture
• Exhausts from metal smelters

Agricultural sources are:
• Food and animal wastes
• Chlorine manufacture
• Pulp and paper mills

**Effects**

Once a person is exposed to mercury or its compounds, these substances are easily transported throughout the body via the blood. Mercury is a neurotoxin, due to its ability to cross the blood-brain barrier, and is a possible human carcinogen. It causes stomach, lung and kidney damage, as well as damage to a developing foetus.

### 8.3 Cadmium (Cd)

Cadmium is a rare element in the earth’s crust. Its key characteristics are that it is silver-white in colour and is solid at room temperature but is also soft and ductile.

Natural sources of cadmium are very minor but include wind blown dust, volcanic emissions, emissions from vegetation and sea spray. Anthropogenic sources include forest fires, fossil fuel combustion, cement production and smelting of zinc, lead and copper ores.

Since atmospheric cadmium is associated with particulate matter in the respirable range (0.1-1 µm in diameter), it is inhaled and about 10-50% is deposited in the lungs. It is responsible for diseases such as bronchitis and emphysema. Once deposited in the lungs it can be absorbed into the body and stored in the liver and kidneys. Long-term exposure can result in kidney dysfunction and cadmium is also known to increase the risk of lung cancer.

### 8.4 Arsenic (As)

Arsenic is present in the atmosphere predominantly as particulate matter in the form of inorganic arsenic. Sources of arsenic are the same as cadmium. Arsenic is a strong neurotoxin and can cause skin and lung cancer. It can also lead to cardiovascular disease and anaemia, spontaneous abortion and lower mean birth rates.

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**References**


