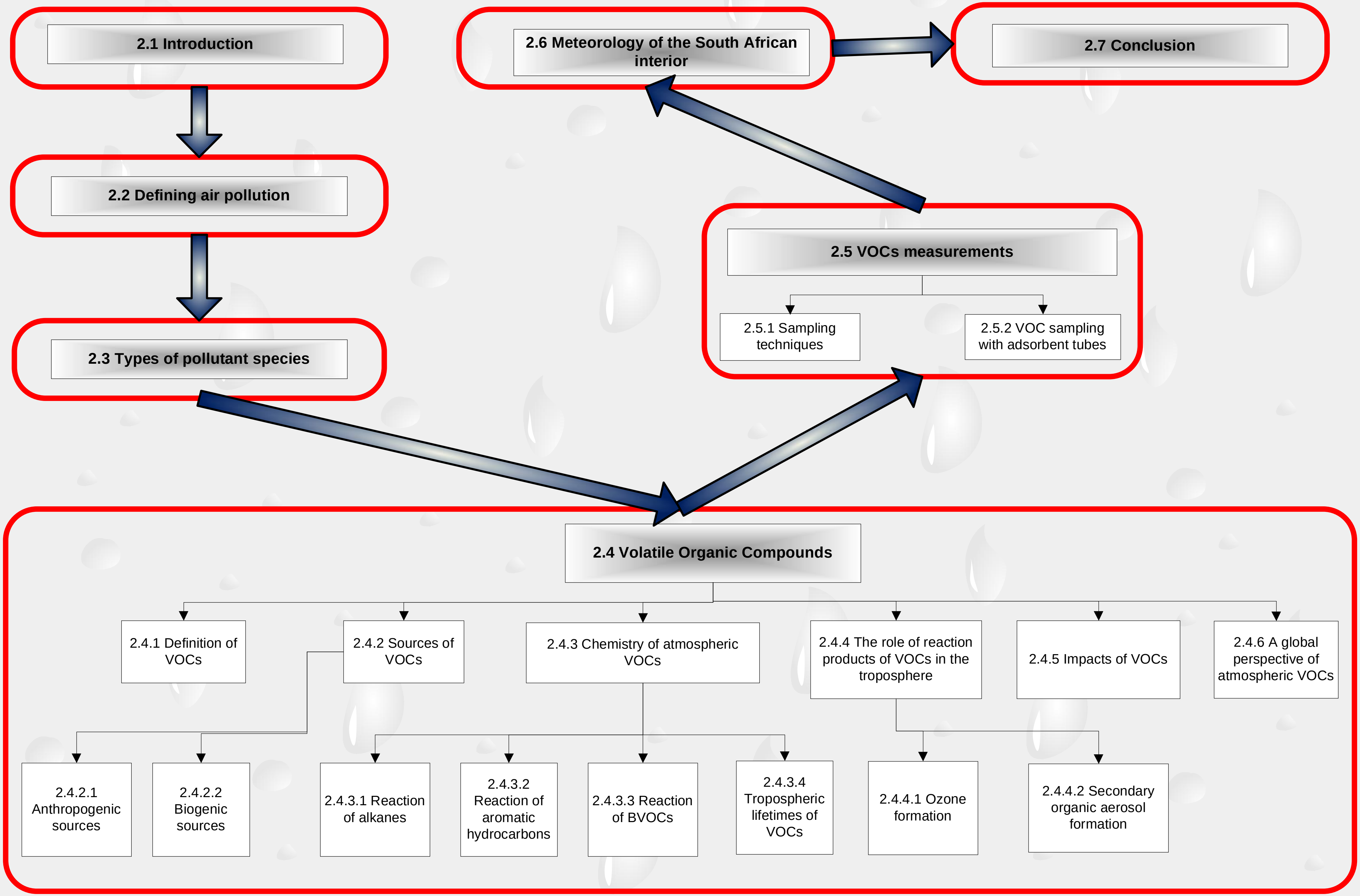
Graphical layout of Chapter 2



2.1 Introduction

2.2 Defining air pollution

2.3 Types of pollutant species

2.4 Volatile Organic Compounds

- 2.4.1 Definition of VOCs
- 2.4.2 Sources of VOCs
  - 2.4.2.1 Anthropogenic sources
  - 2.4.2.2 Biogenic sources
- 2.4.3 Chemistry of atmospheric VOCs
  - 2.4.3.1 Reaction of alkanes
  - 2.4.3.2 Reaction of aromatic hydrocarbons
  - 2.4.3.3 Reaction of BVOCs
  - 2.4.3.4 Tropospheric lifetimes of VOCs
- 2.4.4 The role of reaction products of VOCs in the troposphere
  - 2.4.4.1 Ozone formation
  - 2.4.4.2 Secondary organic aerosol formation
- 2.4.5 Impacts of VOCs
- 2.4.6 A global perspective of atmospheric VOCs

2.5 VOCs measurements

- 2.5.1 Sampling techniques
- 2.5.2 VOC sampling with adsorbent tubes

2.6 Meteorology of the South African interior

2.7 Conclusion

Chapter 2

Literature survey

2.1 Introduction

The thin layer of gases that make up the earth's atmosphere covers a surface area of 5×10^{8} km^{2} and has a mass of approximately 5.2×10^{15} metric tons (Godish, 2004). These gaseous layers can be divided into lower and upper regions. **Figure 2.1** illustrates the difference between the layers, which is characterised by significant vertical temperature and pressure gradients. These layers are termed the troposphere, stratosphere, mesosphere and thermosphere, as indicated in **Figure 2.1**.

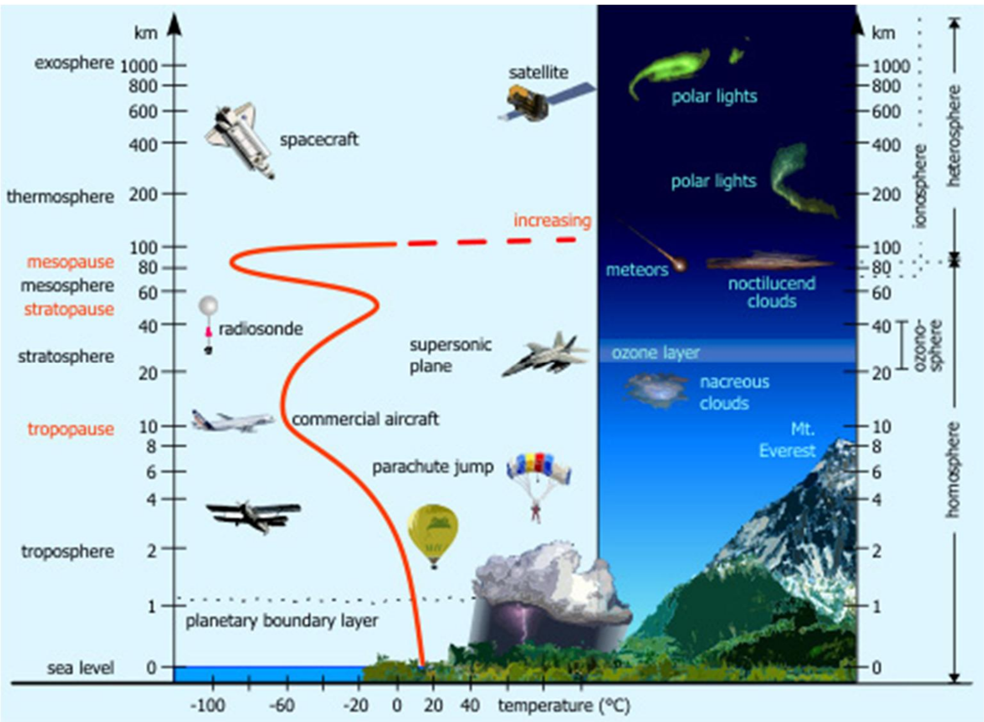


Figure 2.1: Vertical structure of the earth's atmosphere (http://www.kowoma.de/en/gps/additional/atmosphere.htm)

The earth's atmosphere has undergone several changes throughout history. The troposphere extends from the surface of the earth to the tropopause. The depth of this layer varies from approximately 8 to 16km and it depends on the latitude and seasonal changes. The troposphere is the highest over the equator, while it is the lowest over the poles. Approximately 75 to 80% of the total mass of the atmosphere is contained in this layer. Human activities and most of the weather experienced on earth occur within this layer (Harrison, 1999).

On a mole percent basis, dry air in the troposphere consists of 78.08% nitrogen (N_2), 20.95% oxygen (O_2) and several noble gases (< 1%), of which the concentrations remain constant over time (Seinfeld & Pandis, 2006; Fellenberg, 2000). These relatively inert gaseous species have long lifetimes in the atmosphere and are relatively well mixed throughout the entire homosphere (below approximately 90km altitude). Other minor gaseous species, such as water (H_2O) vapour, carbon dioxide (CO_2), and ozone (O_3) also play an important role despite their lower concentrations (Brasseur *et al.*, 1999).

2.2 Defining air pollution

In 1973, Williamson elaborated on the difference between an atmospheric ‘pollutant’ and a ‘contaminant’. He defined a contaminant as “anything added to the environment that causes a deviation from the geochemical mean composition”. A pollutant was considered to be a contaminant responsible for causing some adverse effect on the environment. Separation of these two terms revealed the limited understanding with regard to short-term and long-term adverse effects at that time. These definitions are also complicated by chemical reactions that can transform contaminants into pollutants.

An example of differentiating between these two terms is CO_2, which was considered to be a contaminant since it does not have significant immediate adverse effects to living organisms. Ice core data (EPICA, 2004) going back hundreds of thousands of years (**Figure 2.2**), as well as atmospheric measurements at Mauna Loa, Hawaii and at the South Pole (Keeling *et al.*, 2005), indicate that the annual mixing ratio of CO_2 is steadily increasing in the atmosphere and even accelerating (**Figure 2.3**). The increase of ambient CO_2 in the atmosphere is mainly associated with anthropogenic activities, in particular fossil fuel burning (e.g. combustion of coal, oil, natural gas) and changes in land use (e.g. conversion of forests to agricultural lands) (Houghton, 2003). These increases in atmospheric CO_2 concentrations are related to climate change and they are expected to lead to further increases in the average temperature of the earth. Therefore, CO_2 should be considered a pollutant and not a contaminant, according to Williamson (1973).

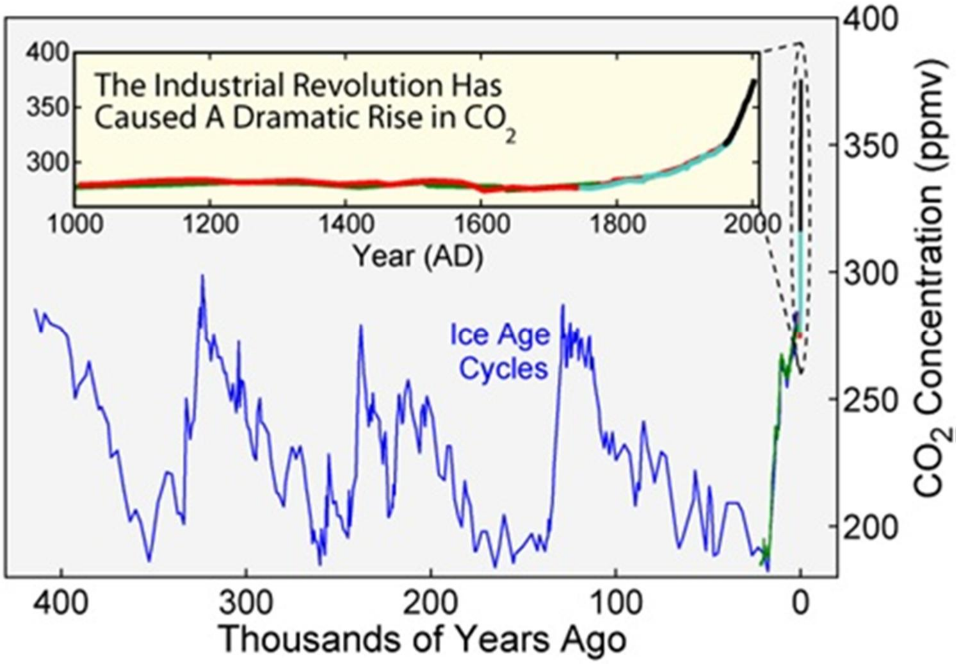


Figure 2.2: The variations in concentration of CO_2 in the atmosphere during the last 400 thousand years as measured from ice cores (Global Warming Art, 2006; EPICA, 2004)

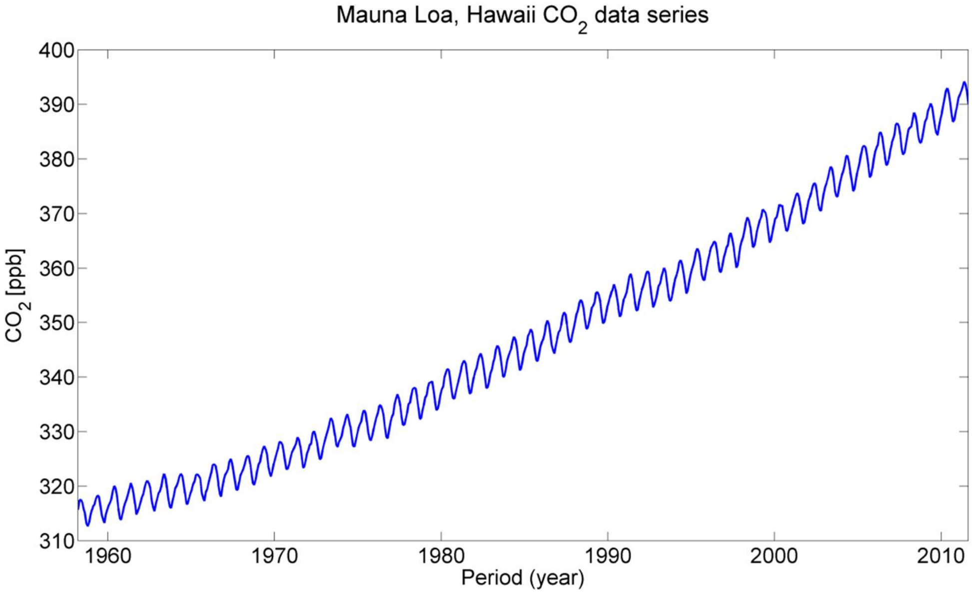


Figure 2.3: History of changes in the atmospheric concentration of CO_2 measured at Mauna Loa, Hawaii since 1958 (ftp://ftp.cmdl.noaa.gov/ccg/co2/trends/co2_mm_mlo.txt)

The United States Environmental Protection Agency (US-EPA) defines air pollution as the presence of contaminants or pollutant substances in the air that interfere with human health or welfare, or produce other harmful environmental effects (EPA, 2008). The National Environmental Management: Air Quality Act (No. 39 of 2004), which replaced the Air Pollution Prevention Act (No. 45 of 1965) in 2005 in South Africa, defines air pollution as any change in the composition of the air caused by smoke, soot, dust (including fly ash), any ashes, solid particles, gaseous species, fumes, particulates and odorous substances (Government Gazette, 2004). These are broadly similar definitions of air pollution from different air quality legislations.

Air pollutants cause many environmental problems, e.g. increases of tropospheric oxidants, changes in the self-cleaning ability of the atmosphere, the alteration of biogeochemical cycles, acid rain, radiative impacts, the depletion of stratospheric O_3, as well as other related environmental impacts that all cause global environmental changes. The general health and welfare of humans are also affected by atmospheric pollutants. Exposure to pollutants such as atmospheric particulate matter (PM) and O_3 has been associated with increases in respiratory and cardiovascular diseases (WHO, 2002; Suwa *et al.*, 2002; Brunekreef & Holgate, 2002). Scientific and public awareness of the impacts of air pollution with regard to climate change and the influence on the environment have increased in the last number of decades.

2.3 Types of pollutant species

There are many different pollutant species present in the atmosphere, which have different sources, chemical compositions and transformations, as well as different impacts on the environment and its inhabitants. These pollutants are categorised into two main groups, i.e. gaseous species and aerosols (PM). The physical and chemical properties of these species determine their impact on human health, the environment and climate (Kampa & Castanas, 2008).

Gaseous species consist of inorganic and organic compounds. Nitrogen oxides (NO_x), nitrous oxide (N_2O), O_3, carbon monoxide (CO), CO_2 and sulphur dioxide (SO_2) are considered to be the most important inorganic gaseous pollutant compounds present in the atmosphere. The main atmospheric organic pollutant compounds include methane (CH_4) and non-methane hydrocarbons, which include semi-volatile and volatile organic compounds (VOCs). CO_2, CO, O_3, CH_4, N_2O and halogenated carbons are regarded as greenhouse gases that contribute to climatic changes (Martins, 2008).

NO_x is a term used for the total concentration of nitrogen oxide (NO) and nitrogen dioxide (NO_2). Natural sources of these species include lighting, biomass burning, biological fixation by bacteria, volcanoes, biological processes in soil, as well as the oxidation of ammonium (NH_4^+) and the reduction of nitrate (NO_3^-) in the biosphere (Bell *et al.*, 2004; Vingarzan, 2004). Anthropogenic sources are mainly motor vehicles, coal-fired power plants and the combustion of fossil fuels in industries (Parrish *et al.*, 2002; Bell *et al.*, 2004; EPA, 2004). South Africa is well known for the NO_2 hotspot over the Mpumalanga Highveld that is related to coal-fired power plants and other industrial activities in that region (Lourens *et al.*, 2011).

CO is a colourless, odourless, tasteless gas that is produced by the incomplete combustion of carbonaceous fuel. The sources of CO include fossil fuel combustion, biomass burning, gasoline-powered engines, residential heating, and certain industrial processes. Biomass burning is considered to be both natural and anthropogenic, depending on how a specific biomass burning event was initiated. According to Terblance *et al.* (1996), ambient CO originating from domestic coal burning in South Africa exceeds the local and USA health standards. Laakso *et al.* (2008) have also oberved elevated CO levels at the end of winter and beginning of spring in southern Africa, which was attributed to extensive biomass burning events.

SO_2 results mainly from the combustion of sulphur-containing fossil fuels (principally coal and heavy oils) and the smelting of sulphur-containing ores. It is also submitted naturally from volcanoes and oceans. The latter contribute only ~2% of the total SO_2 emissions (Kampa & Castanas, 2008). SO_2 and NO_x lead to the occurrence of acid rain by formation of nitric and sulphuric acids, respectively, in atmospheric moisture. These acids can have detrimental effects on the environment, such as corrosion, damage to crops and forests, changes in soil makeup, and the acidity of lakes and rivers (Josipovic *et al.*, 2011, with reference therein).

CH_4 and VOCs are the main organic gaseous species in the atmosphere. The major anthropogenic sources of CH_4 include livestock, landfills, fossil fuel production and consumption (natural gas venting, leakages and coal mining), and biomass burning. The major natural sources include wetlands and termites. CH_4 is also considered the second most important greenhouse gas. VOCs are emitted into the atmosphere from both biogenic and anthropogenic sources. Since the measurement of VOCs was the main focus of this investigation, a detailed discussion on VOCs will be presented in **Section 2.4**.

O_3 is a secondary pollutant that is formed by means of photochemical oxidation in the atmosphere from precursor species, which include NO_x, VOCs and CO. In the lower atmospheric layers, O_3 plays an important role in air pollution chemistry. O_3 determines the 'oxidising capacity' of the atmosphere and, therefore, the atmospheric lifetime of biogenic and anthropogenic gaseous pollutants (Brasseur *et al.*, 1999). Atmospheric O_3 formation is discussed in detail in **Section 2.4.4**.

Aerosols are a complex multi-phase mixture of fine solid or liquid particles suspended in air (Kampa & Castanas, 2008). Aerosols are emitted from primary sources into the atmosphere or are formed as secondary pollutants. The main primary aerosols present in the atmosphere emitted from natural sources are clouds, smoke, windborne dust, sea spray and volcanoes. Primary aerosols can also be emitted from anthropogenic activities. A number of studies have indicated that the emissions from natural sources exceed emissions from anthropogenic sources on a global scale by a factor of 4 to 5 (Hobbs, 2000). It is, however, estimated that, in 2040, the emissions from anthropogenic sources will equal the level of the natural emissions. This is due to the increase in the combustion of fossil fuels, especially in fast-developing countries such as China and India (IPCC, 2007).

The formation of secondary aerosols can be ascribed to various physical (e.g. nucleation, condensation and evaporation) and chemical processes (e.g. gas-to-particle chemistry) (Kim *et al.*, 2011) and will be discussed in **Section 2.4.4.2**. Several studies have been carried out to understand the impact of the gas-phase chemical mechanism on the formation of secondary aerosols. In particular, secondary aerosols dominate atmospheric PM in Europe at many monitoring sites (Putaud *et al.*, 2010). Laakso *et al.* (2008) and Vakkari *et al.* (2011) conducted studies in South Africa where they found that the frequency and rate of new particle formation in South Africa is among the highest measured in the world. In **Figure 2.4,** the atmospheric cycle of aerosols from emission sources into the atmosphere, until their removal, is shown.

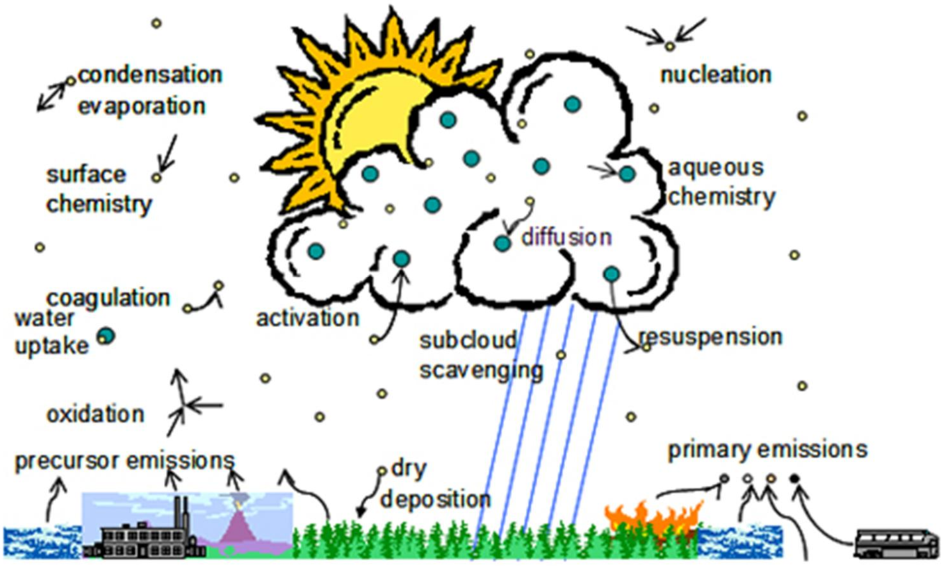


Figure 2.4: Schematic diagram illustrating the global atmospheric aerosol cycles and processes involved including chemistry, dry/wet depositions, sedimentation, scavenging, nucleation, condensation, coagulation and water uptake (Ghan, 2011)

2.4 Volatile Organic Compounds

2.4.1 Definition of VOCs

VOCs are the collective name for a large group of organic compounds with 15 or less carbon atoms that have a vapour pressure greater than 10Pa at 25°C and a boiling point of up to 260°C at atmospheric pressure. According to the US-EPA, VOCs include all the gas phase organic species that participate in atmospheric photochemical reactions in the presence of sunlight (EPA, 2008; Klouda *et al.*, 1996), with the exception of CH_4, CO, CO_2, carbonic acid, metallic carbides or carbonates, and ammonium carbonate.

2.4.2 Sources of VOCs

In **Figure 2.5,** the various processes involved in the cycle of atmospheric VOCs are presented, which include sources, sinks and atmospheric pathways of VOCs. In addition to emissions from anthropogenic activities (**Section 2.4.2.1**), vegetation releases vast amounts of BVOCs (**Section 2.4.2.2**). VOCs are also formed *in situ* in the atmosphere as products of the atmospheric transformations of other VOC species, which lead to the formation of oxygenated derivatives (**Section 2.4.3**). VOCs play an important role in atmospheric photochemistry.

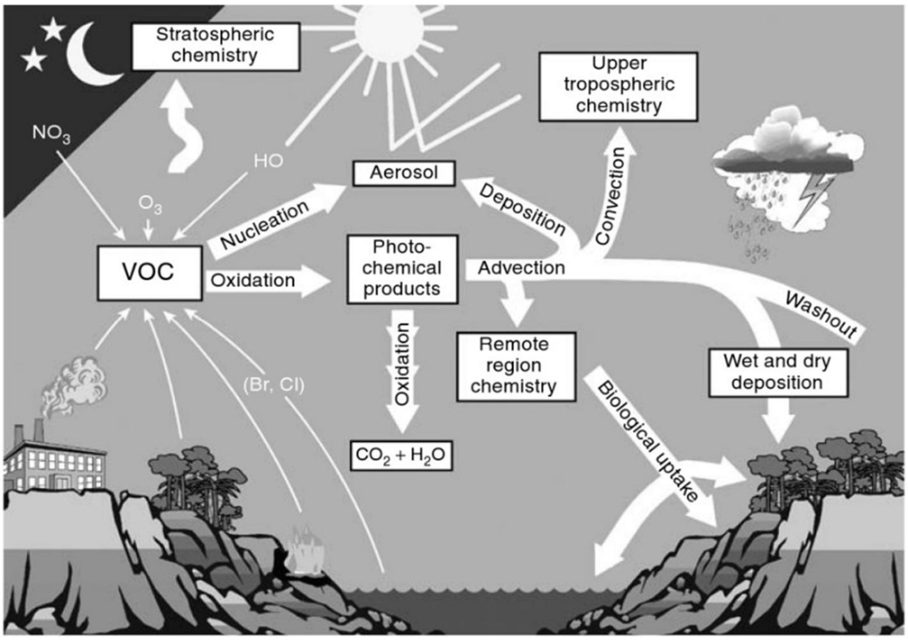


Figure 2.5: Schematic diagram of various processes involved in the cycle of atmospheric VOCs (Koppmann, 2007)

2.4.2.1 Anthropogenic sources

Anthropogenic VOCs usually consist of non-methane hydrocarbons, oxygenated organic compounds and halogenated species. As mentioned in **Section 2.4.2** these species are either directly emitted into the atmosphere or formed during photochemical processes. According to Pankow *et al.* (2003), the concentrations of certain VOCs are mainly driven by the rapidly growing human population and high rates of resource consumption. Anthropogenic emissions of VOCs are estimated to contribute 5 to 10% of the total global VOC emissions (Zunckel *et al.*, 2007; Godish, 1991). In the subsequent sections, the major anthropogenic sources of VOCs are discussed.

Fossil fuels and industrial processes

Globally, the VOC emissions from the production, storage, delivery and use of fossil fuel products are estimated to be 78Tg/year, predominately due to road transport and oil production. The regions with the highest emissions of VOCs associated with vehicle transport are the United States, Europe, Latin America and South East Asia; whereas the highest emissions from oil production are in regions with the largest oil drilling activities, i.e. the Middle East and Latin America (Koppmann, 2007). According to Godish (1991), light-duty motor vehicles account for 75% of mobile sources in the USA. The major anthropogenic VOC emission sources in South Africa are vehicles and solvent use (Van der Walt, 2008). Van der Westhuizen *et al.* (2004) calculated that 97 million litres of petrol were lost in South Africa due to evaporation in 2000, which exceeded the allowed fuel loss level set by the EPA by between 10 and 50 times. This can probably be attributed to the non-existing emission legislation for VOC emissions from vehicles in South Africa. Benzene is the only VOC for which a legislative standard exists. Industries producing paint, chemical production processes, waste management and disposal and solvent usage are all possible sources of VOC emissions (Burger, 2006, with reference therein).

Domestic coal and wood burning, and biomass combustion

The incomplete combustion of coal is a primary source of energy in South Africa. The overwhelming use of paraffin, coal and wood originates from cooking and space heating in informal settlements in the interior of South Africa, especially during the winter (**Section 3.2**). These emissions from household combustion are released less than two meters above ground within residential areas, thereby leading to people being exposed to high concentrations of pollutants (Mage *et al.*, 1996). Apart from naturally occurring biomass combustion, anthropogenically initiated biomass combustion events are also common occurrences in Southern Africa.

2.4.2.2 Biogenic sources

BVOCs are emitted from plant surfaces, wetlands, biomass burning initiated naturally (e.g. lightning), oceans, animals, microbes, and fungi (e.g. moulds) (IAQM, 2012). During photosynthesis, plants take up CO_2 and a fraction of this carbon leaks out from the plants in reduced forms such as isoprene and terpenes into the atmosphere (Fuentes *et al.*, 2000; Guenther, 2002; Kesselmeier *et al.*, 2002). The types of BVOC species emitted and the levels thereof depend on several factors, including meteorology (ambient temperature, moisture and solar radiation), the condition of the vegetation, vegetative cover and the emission characteristics of individual plant species and types (Guenther *et al.*, 1995; Kesselmeier & Staudt, 1999; Otter *et al.*, 2003). Temperature and moisture determine the rate of volatilisation, while growth rate and solar radiation determine the rate of biosynthesis.

Zunckel *et al.* (2007) estimated that approximately 80Tg C/year of BVOCs are released in South Africa from vegetation.

2.4.3 Chemistry of atmospheric VOCs

Once released in the atmosphere, VOCs are involved in various chemical reactions and are removed from the atmosphere through different reaction mechanisms and at different rates. The chemical reactions of VOCs are mostly initiated by $^{\bullet}OH$ during day time and $NO_3^{\bullet}$ during night time (Geyer *et al.*, 2001). Atmospheric VOCs also react with O_3, especially in polluted areas. At coastal and marine areas, VOCs can also react with $Cl^{\bullet}$ during the day (Bottenheim *et al.*, 1990; Jobson *et al.*, 1994; Hellén *et al.*, 2012). Atmospheric VOCs predominantly react with $^{\bullet}OH$. Over the past two decades, there have been various investigations (Atkinson *et al.*, 1989, 1994, 1997a, 1999) on the rate coefficients for the reactions of $^{\bullet}OH$ with VOCs.

In general, the alkyl radicals react in the troposphere, as presented in the schematic diagram in **Figure 2.6**. The reaction mechanism of VOCs begins with the abstraction of an H-atom from the various C-H bonds after reacting with $^{\bullet}OH$, resulting in the formation of an alkyl or substituted alkyl radical ($R^{\bullet}$), e.g. hydroxyalkyl and nitrooxyalkyl (containing an $-ONO_2$ group) radicals, or oxoalkyl (containing carbonyl, C = O, group) radicals. $R^{\bullet}$ reacts with O_2 to form $RO_2^{\bullet}$. The key intermediates in the reaction mechanism are organic peroxy ($RO_2^{\bullet}$) and alkoxy ($RO^{\bullet}$) radicals. After the alkyl peroxy radical is formed, it can react with NO, NO_2, HO_2 or other $RO_2^{\bullet}$. The HO_2 pathway acts as a sink for the radicals, because it forms relatively stable products, while the NO pathway often leads to the formation of NO_2, which can lead to the formation of O_3. The reaction with NO_2 and HO_2 terminates the reaction sequence by forming peroxy nitrates ($ROONO_2$) and peroxides (ROOH), respectively.

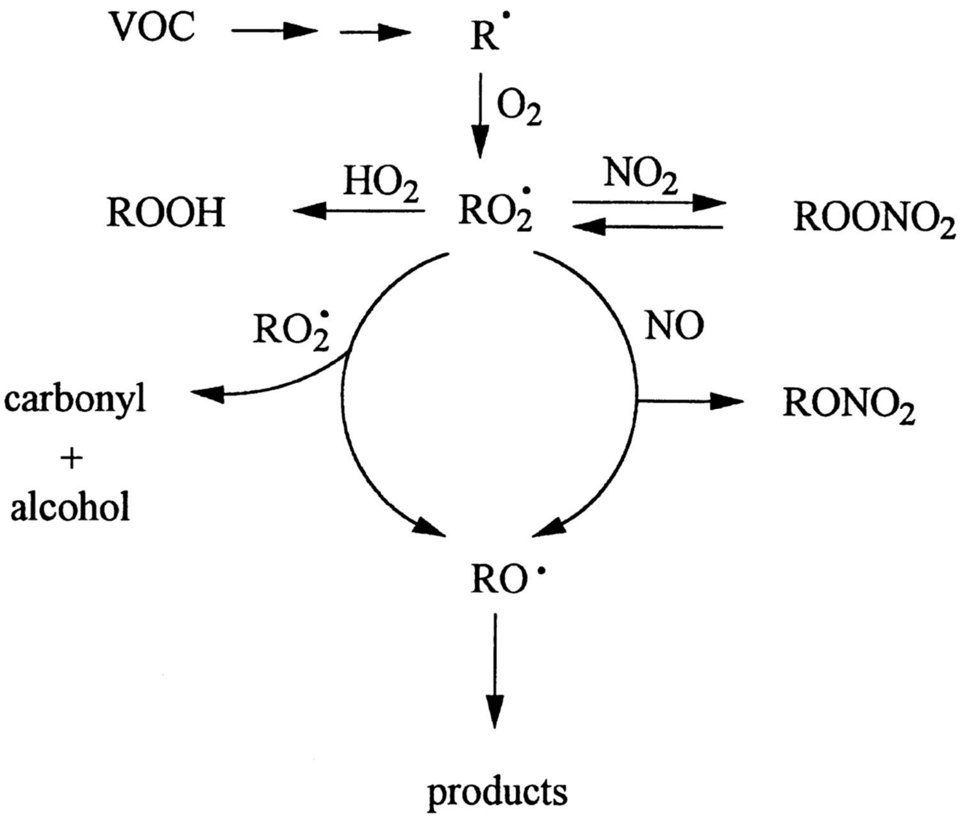


Figure 2.6: A schematic diagram of the general chemical reactions of VOCs that occur in the troposphere (Atkinson, 2000)

When the VOC-to-NO_2 ratio is sufficiently high (e.g. in a rural environment), $RO_2^{\bullet}$ can either self-react or react with HO_2, which slows down O_3 production by the removal of free radicals from the system. When the VOC-to-NO_2 ratio is sufficiently low, in polluted urban air, O_2 is abstracted from the $RO_2^{\bullet}$ to produce NO_2 and $RO^{\bullet}$. The produced NO_2 molecule promotes tropospheric O_3 formation, whereas the $RO^{\bullet}$ has several possible atmospheric reaction pathways. These include reactions with molecular O_2 forming hydrogen peroxy radicals ($HO_2^{\bullet}$), thermal decomposition and isomerisation. For longer alkanes, the addition of NO leads to the formation of an alkyl nitrate and NO_2 to form peroxynitrate (Finlayson-Pitts & Pitts, 2000).

In the subsequent sections, the specific reaction mechanisms of alkane and aromatic hydrocarbons that are usually associated with primary anthropogenic emissions are discussed. The reaction pathways of BVOCs are also described.

2.4.3.1 Reaction of alkanes

Alkanes in the atmosphere also follow the general chemical reaction pathway presented in **Figure 2.6**. A specific reaction mechanism for an atmospheric alkane (butane) is presented in **Figure 2.7**. In this diagram, the complete oxidation of butane to CO and CO_2 proceeds via the formation of the major intermediate carbonyl compounds, methyl ethyl ketone (MEK), acetaldehyde (CH_3CHO) and formaldehyde (HCHO). At each oxidation stage, the chemistry is propagated by reactions of $RO_2^{\bullet}$ and $RO^{\bullet}$ intermediates. For example, the initial oxidation of butane (C_4H_{10}) to MEK proceeds via the following catalytic cycle:

C_4H_{10} is attacked by $^{\bullet}OH$ via hydrogen abstraction, with the resulting formation of an alkyl radical ($C_4H_9^{\bullet}$) that then reacts fast with O_2 to form alkyl peroxy radical ($C_4H_9O_2^{\bullet}$):

$$C_4H_{10} + {}^{\bullet}OH + O_2 + M \rightarrow C_4H_9O_2^{\bullet} + H_2O \ (M = N_2 \text{ or } O_2) \qquad 2.1$$

In the presence of NO, oxygen is abstracted to form an alkoxy radical:

$$C_4H_9O_2^{\bullet} + NO \rightarrow C_4H_9O^{\bullet} + NO_2 \qquad 2.2$$

The produced NO_2 molecule promotes the tropospheric O_3 formation, whereas the alkoxy radical can react with molecular oxygen (O_2) that leads to the formation of a stable ketone such as MEK via the abstraction of a hydrogen atom, which is attached to the same carbon atom as the oxygen radical.

$$NO_2 + h\nu \rightarrow NO + O\,(^3P) \qquad 2.3$$

$$O\,(^3P) + O_2 + H_2O \rightarrow O_3 + H_2O \qquad 2.4$$

$$C_4H_9O^{\bullet} + O_2 \rightarrow MEK + HO_2 \qquad 2.5$$

As shown in **Figure 2.7**, the further degradation of MEK, CH_3CHO and HCHO, initiated by the reaction with $^{\bullet}OH$, leads to further NO-to-NO_2 conversion (and therefore O_3 formation). Consequently, the number of NO-to-NO_2 conversions at each oxidation step, and the lifetimes of butane and the product carbonyl compounds (which are partially determined by their $^{\bullet}OH$ reactivity), have an important influence on the rate of NO oxidation and O_3 formation.

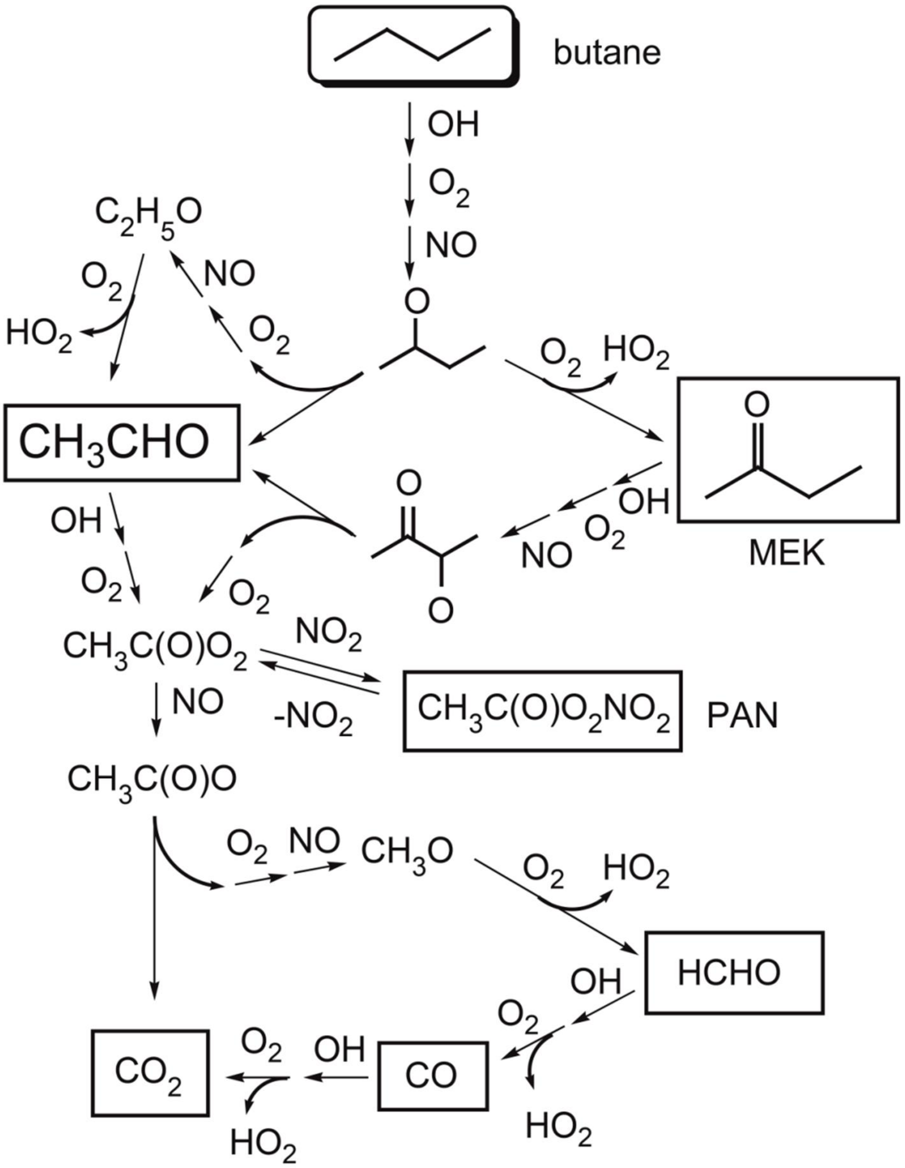


Figure 2.7: Schematic representation of the major radical propagation pathways of the $^{\bullet}$OH-initiated degradation of butane, also illustrating the sequential formation of the intermediate products MEK, CH_3CHO, HCHO and CO (Pinho *et al.*, 2005)

2.4.3.2 Reaction of aromatic hydrocarbons

Aromatic hydrocarbons can react with $^{\bullet}$OH and $NO_3^{\bullet}$ by means of two different pathways (Atkinson, 2000). The first pathway involves H-atoms abstraction from CH bonds leading to the formation of $R^{\bullet}$, while the second pathway is an oxidation reaction that involves the addition of $^{\bullet}$OH to the aromatic ring to generate an $^{\bullet}$OH aromatic adduct (Seinfeld & Pandis, 2006). Depending on the symmetry of the aromatic hydrocarbon, there can be up to six distinct points for $^{\bullet}$OH addition.

However, literature indicates that the positions on the aromatic ring favoured for $^\bullet$OH attack in relation to substituents vary in the general order *ortho*- > *para*- > *ipso*- > *meta*- ((Jenkin *et al.* 2003 with references therein). In **Figure 2.8,** a partial schematic representation of the $^\bullet$OH initiated oxidation of p-xylene obtained from the Master Chemical Mechanism (MCM) version 3 is presented. The model assumes that $RO_2^\bullet$ reacts exclusively with NO. The first generation products are shown in boxes.

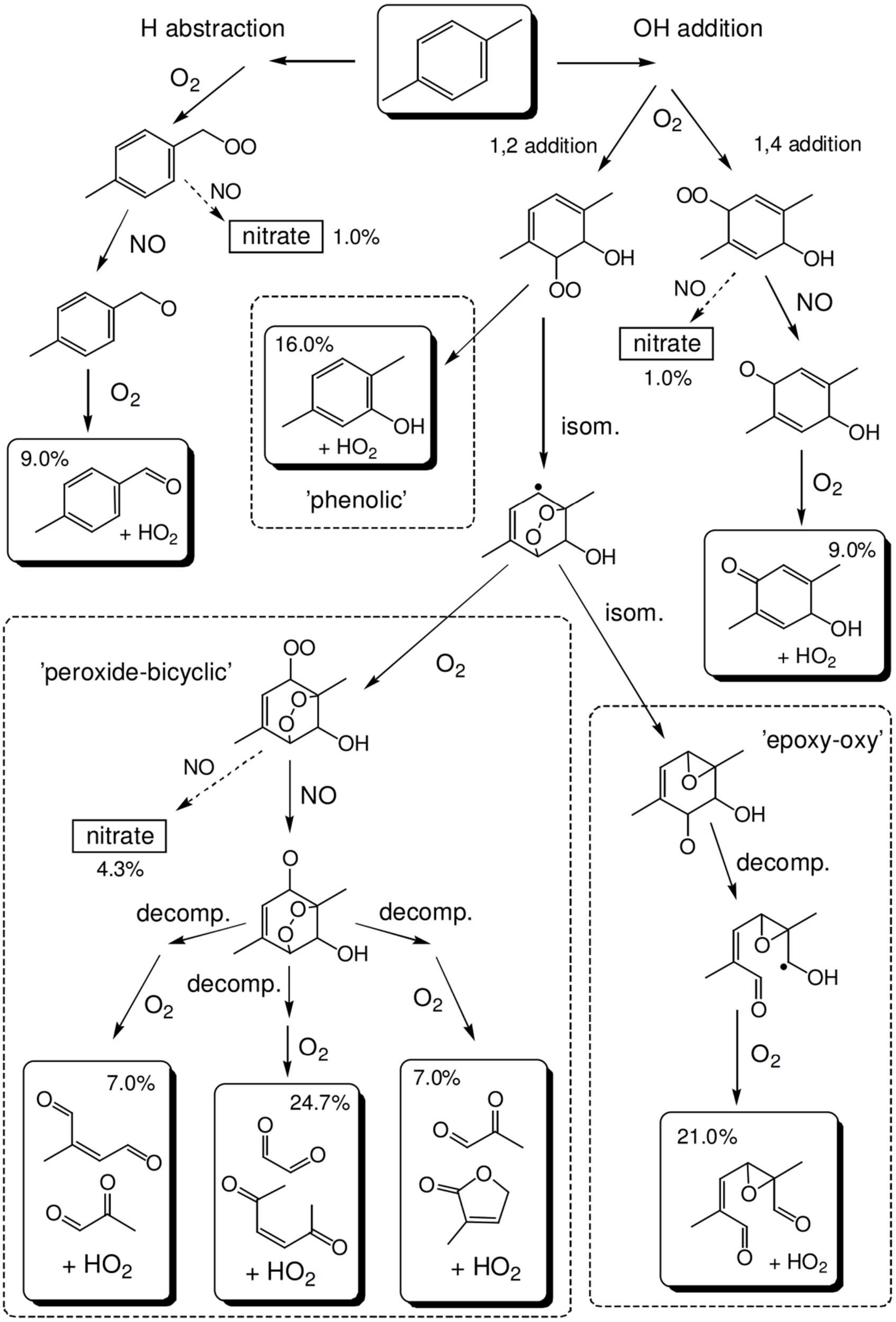


Figure 2.8: Partial schematic representation of the $^{\bullet}$OH-initiated oxidation of p-xylene to first generation products determined by the MCM v3 model (Jenkin *et al.*, 2003)

2.4.3.3 Reaction of BVOCs

Although BVOCs also react predominantly with $^{\bullet}OH$, reactions with O_3 are also important removal processes for BVOCs (Hakola *et al.*, 2003; Atkinson, 2000). Reaction rates with $NO_3^{\bullet}$ are also fast and are important during night time (Hakola *et al.*, 2003). BVOCs also follow the two reaction pathways that aromatic compounds follow (Finlayson-Pitts & Pitts, 2000). BVOCs, however, are more likely to react through the addition mechanism of $^{\bullet}OH$ (or O_3 and $NO_3^{\bullet}$), rather than the abstraction mechanism.

An example of the oxidation of BVOCs is presented in **Figure 2.9**, where isoprene reacts with $^{\bullet}OH$. These chemical reactions were determined with MCM v3. The $^{\bullet}OH$-isoprene reaction proceeds almost entirely by means of the addition of the $^{\bullet}OH$ to the C=C bonds. There are six different possible hydroxyalkyl radicals that can form from this reaction, after which the addition of O_2 may occur. The addition of the $^{\bullet}OH$ radical to the first and second carbon of isoprene dominates this reaction (Finlayson-Pitts & Pitts, 2000). The primary products formed by the $^{\bullet}OH$-isoprene reaction are methyl vinyl ketone (MVK), formaldehyde and methacrolein (MACR).

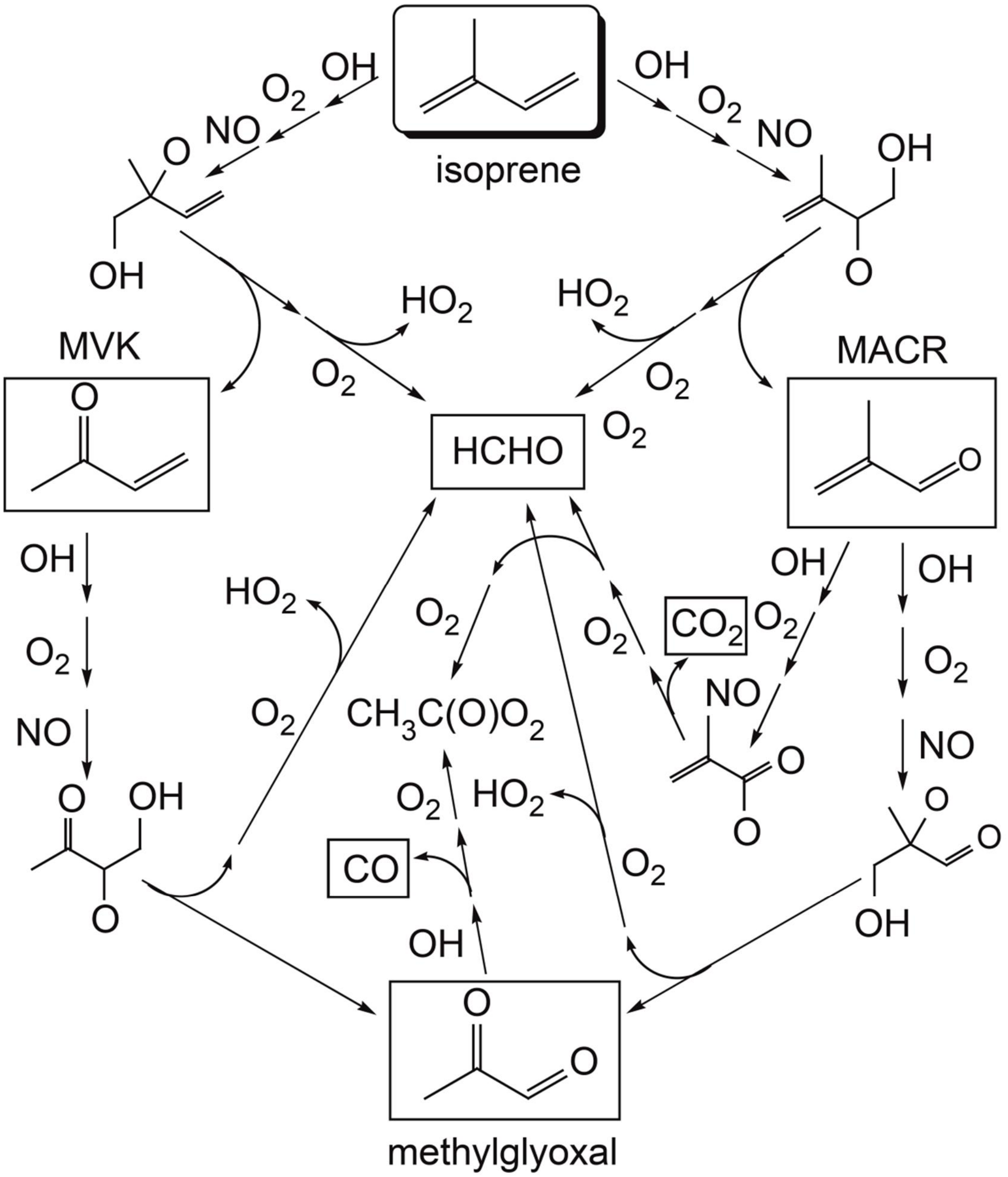


Figure 2.9: Partial schematic diagram of the radical propagation pathways of the $^{\bullet}$OH -initiated degradation of isoprene determined with MCM v3 (Pinho *et al.*, 2005)

2.4.3.4 Tropospheric lifetimes of VOCs

VOCs are removed from the atmosphere by chemical reactions or by wet and dry deposition. According to first, second and third order reaction kinetics, the lifetime, τ, of an organic compound is defined as the time for the organic compound to reach 1/e of its initial concentration (Atkinson & Arey, 2003; Finlayson-Pitts & Pitts, 2000).

The natural lifetime (ι) of an organic compound can be calculated with the equation, $\iota = 1/k_p[X]$, where k_p is the reaction rate of the compound and [X] is the initial concentration of the oxidant. **Table 2.1** lists the calculated atmospheric lifetimes according to the reaction rates with $^\bullet OH$, $NO_3^\bullet$ and O_3 of VOCs that are typically found in the atmosphere (Atkinson, 2000; Atkinson & Arey, 2003). The atmospheric lifetimes of VOCs associated with anthropogenic emission, i.e. alkanes and aromatics are usually in the order of days. The calculated lifetimes of BVOCs, which include isoprene and terpenes, are typically a few hours or less (**Table 2.1**). This is due to the higher atmospheric reactivity of most BVOC species (Atkinson & Arey, 1998; Atkinson, 2000).

As indicated by **Table 2.1,** the lifetime of benzene in the atmosphere (9.4 days) is much longer compared to that of the other aromatic hydrocarbons (Atkinson, 2000). These variations in lifetimes between the BTEX compounds allow researchers to determine the probable source, as well as the age of the pollution plume, based on ratios of the compounds (Holzinger *et al.*, 2001; Hoque *et al.*, 2008; Guo *et al.*, 2007; Kerbachi *et al.*, 2006; Khoder, 2007). As indicated by **Table 2.1,** the other aromatic hydrocarbons will react faster with $^\bullet OH$ than benzene, thereby increasing the ratio. Therefore, the higher the benzene/toluene ratio, the older the air mass and the more distant the source.

Table 2.1: Tropospheric lifetime of selected VOCs calculated from reactions rates with $^{\bullet}OH$, $NO_3^{\bullet}$ and O_3 (Atkinson & Arey, 2003; Atkinson, 2000)

	Lifetime for reaction with		
	$^{\bullet}OH$	**$NO_3^{\bullet}$**	**O_3**
isoprene	1.4 h	50 min	1.3 days
Monoterpenes			
camphene	2.6 h	1.7 h	18 days
2-carene	1.7 h	4 min	1.7 h
3-carene	1.6 h	7 min	11 h
limonene	50 min	3 min	2.0 h
α-pinene	2.6 h	5 min	4.6 h
β-pinene	1.8 h	27 min	1.1 days
terpinolene	37 min	0.7 min	13 min
Sesquiterpenes			
β-caryophyllene	42 min	3 min	2 min
α-humulene	28 min	2 min	2 min
iso-longifolene	2.9 h	1.6 h	> 33 days
Oxygenates			
1,8-cineole	1.0 days	1.5 year	> 110 days
2-methyl-3-buten-2-ol	2.4 h	7.7 days	1.7 days
Aromatics			
benzene*	9.4 days	> 4 year	> 4.5 year
toluene*	1.9 days	1.9 year	> 4.5 year
ethylbenzene*			
m-xylene*	5.9 h	200 days	> 4.5 year
styrene*	2.4 h	3.7 h	1.0 days
1,2,4-trimethylbenzene*	4.3 h	26 days	> 4.5 year
Alkanes			
2,2,4-trimethylpentane*	3.2 days	1.4 year	
n-octane*	1.3 days	240 days	

Note: VOCs considered to be hazardous air pollutants, according to the US-EPA, are marked with asterisks (*)

2.4.4 The role of reaction products of VOCs in the troposphere

2.4.4.1 The role in O_3 formation

As mentioned previously, VOC can react with various species in the atmosphere to form a wide variety of reaction products, e.g. O_3 and secondary aerosols. Many scientists have studied these reaction products of VOCs by using models or chamber experiments. On the MCM website, laboratory data for the degradation of 142 non-CH_4 atmospheric VOC are represented. The full degradation scheme of butane, for instance, includes 510 reactions and 186 species, of which 20 are primary, emitted

VOC for which separate schemes are given (Hellén, 2006). The reaction products formed in chamber studies are mainly carbonyls, alcohols, organic nitrates and acids with concentrations in most instances 1 000 times higher than the levels detected in the atmosphere (Hamilton *et al.*, 2004; Hamilton *et al.*, 2005; Forstner *et al.*, 1997; Yu *et al.*, 1997; Edney *et al.*, 2003).

VOCs play a significant role in the formation of tropospheric O_3, which has impacts on human health, as well as on crops and forest ecosystems (Sillman, 1999, with reference therein). O_3 is formed photochemically from the photolysis of NO_2, which then rapidly oxidises NO back to NO_2, as shown in reactions 2.6 to 2.10.

$NO_2 + h\nu \rightarrow NO + O\ (^3P)$ 2.6

$O\ (^3P) + O_2 + M \rightarrow O_3 + M\ (N_2 \text{ or } O_2)$ 2.7

$NO + O_3 \rightarrow NO_2 + O_2$ 2.8

NO_2 is also formed by means of the reaction of NO with other oxidants, e.g. hydroperoxy ($HO_2^{\bullet}$) and alkylperoxy radicals ($RO_2^{\bullet}$). These free radicals are formed in the degradation reactions of VOCs (**Section 2.4.3**), which in conjunction with sufficient NO_x can increase the formation of tropospheric O_3. These $HO_2^{\bullet}$ and $RO_2^{\bullet}$ react with NO, converting NO to NO_2, which is then photolysed to form O_3.

$HO_2^{\bullet} + NO \rightarrow {}^{\bullet}OH + NO_2$ 2.9

$RO_2^{\bullet} + NO \rightarrow RO^{\bullet} + NO_2$ 2.10

The photochemistry between O_3, NO_x and VOC is very complex and nonlinear. It is generally known that under certain conditions, O_3 formation is controlled almost entirely by NO_x concentrations, while in other instances, O_3 production depends on VOC levels (Sillman, 1999; Torres-Jardón, 2004). The VOC/NO_x ratio is very important to determine which species will dominate the formation of O_3 (Rickard *et al.*, 2002; Sillman, 1999).

The dependency of O_3 formation on initial VOC and NO_x concentrations is illustrated by means of an O_3 isopleth diagram, which is a contour plot of maximum O_3 concentrations as a function of initial VOC and NO_x concentrations. The diagram is generated by plotting the predicted O_3 maxima as obtained from a large number of simulations from a chemical mechanism with varying initial concentrations of VOC and NO_x. A generic O_3 isopleth plot is illustrated in **Figure 2.10**. A prominent feature of this plot is the diagonal line (ridge line) that extends from the lower left to the upper right corner of the graph, corresponding to the VOC/NO_x ratio at which O_3 is most effectively formed (Fujita *et al.*, 2002; Torres-Jardón, 2004). The line divides the plot into areas of low VOC/NO_x ratios (above the O_3 ridge line) and areas of high VOC/NO_x ratios (below the O_3 ridge line). The O_3 ridge line provides the maximum O_3 concentration at a specific VOC level. The region below the ridge line is considered NO_x limited, while the region above the line is NO_x saturated. The exact dependence of O_3 formation on NO_x and VOC concentrations obtained from isopleth plots varies greatly depending on assumptions and conditions used to generate the graph.

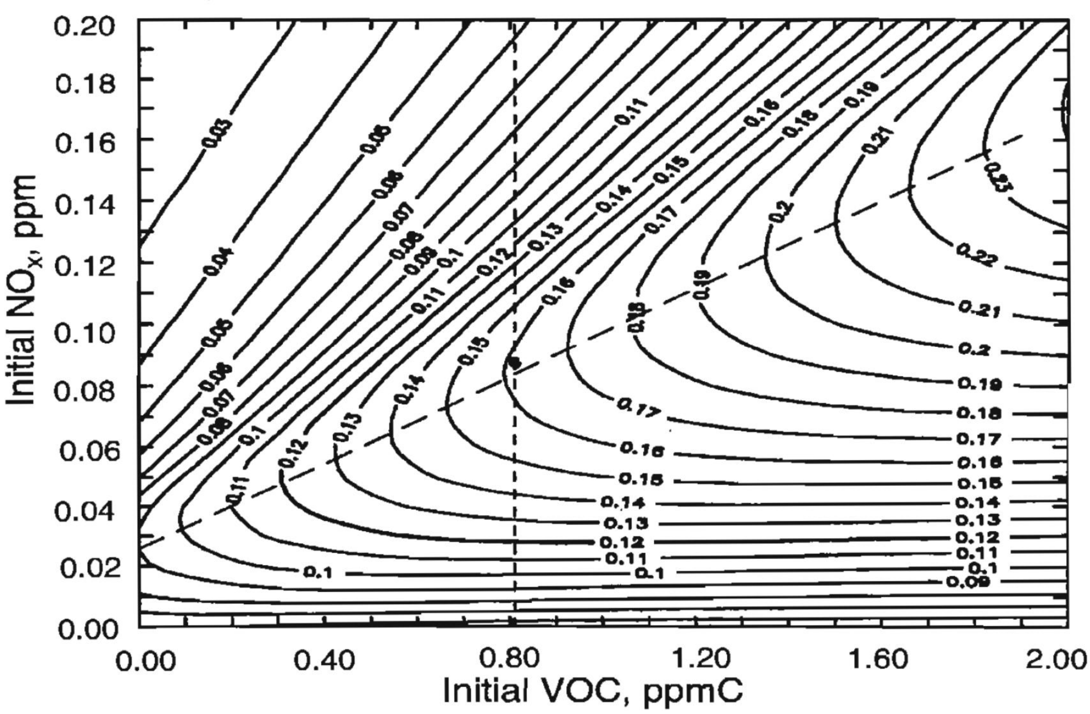


Figure 2.10: Generic O_3 isopleth providing net rate of O_3 production as a function of VOC and NO_x (Seinfeld & Pandis, 1998)

The contributions of VOCs to O_3 formation can vary for different compounds due to differences in reactivity and structure. The Photochemical Ozone Creation Potential (POCP) scale for VOCs was developed, where the POCP values are calculated with MCM and air parcel trajectory models (Derwent *et al.*, 1998; Derwent & Jenkin, 1991; Jenkin & D., 1999). The POCP values are calculated by assessing the effect of incremental changes in O_3 formation due to changes in the specific VOC concentration relative to the change in O_3 formation to a reference VOC concentration, e.g. for ethene:

$POCP_i$ = ((ozone increment with *i*th VOC)/(ozone increment with ethene))*100

Another method used to determine the contribution of specific VOCs to O_3 formation is the Maximum Incremental Reactivity (MIR). In this method, the amount (in grams) of O_3 formed per gram of VOC added to an initial VOC-NOx mixture is determined (Carter, 1994). **Table 2.2** summarises POCP values relative to ethene and MIR coefficients for selected VOCs.

The POCP values for the aromatic hydrocarbons, except for benzene, exhibit values in the range 50 to 138. The monoalkyl-substituted aromatic hydrocarbons are calculated to have comparatively low POCP values (in the range 35 to 53), whereas those for the dialkyl- and trialkyl species are significantly higher, lying in the ranges 69 to 84 and 101 to 113, respectively. The latter two sets of species have relatively high POCP values, making them among the most potent O_3 generators. Styrene is a highly reactive compound, but despite this, its POCP value is the lowest of all the aromatic hydrocarbons. The alkanes generally fall in the range 30 to 54; however, alkanes, such as methane, ethane, propane, neopentane and 2,2-dimethylbutane, exhibit significantly lower values. As can be seen from **Table 2.2,** isoprene has a POCP of 109.2, ranking it as one of the largest contributors to O_3 formation in the troposphere (Derwent *et al.*, 1998). In light of this, many researchers have highlighted the importance of constructing detailed VOC emission inventories in order to accurately estimate tropospheric O_3 concentrations.

Table 2.2: POCP values and MIR coefficients for the most common atmospheric VOCs; POCP values for the aromatics relative to ethane were adapted from Jenkin *et al.* (2003); The alkane and BVOC values were adapted from Saunders *et al.* (2002); The MIR coefficients were adapted from Carter *et al.* (1994)

Aromatics	POCP	MIR coefficient
ethene (reference VOC)	100	
benzene	20.3	0.42
toluene	51	2.70
o-Xylene	84.1	6.50
m-Xylene	85.6	8.20
p-Xylene	77.5	6.60
ethylbenzene	52.5	2.70
propylbenzene	42.7	2.10
1,2,3-trimethylbenzene	108.2	8.90
1,2,4-trimethylbenzene	113	8.80
1,3,5-trimethylbenzene	106.2	10.10
styrene	14.5	2.20
Alkanes		
hexane	45.6	0.98
2-methylpentane	40	1.5
heptane	44.8	0.81
octane	40.1	0.60
nonane	40.4	0.54
decane	40.2	0.46
Biogenic VOCs		
isoprene	109.2	9.1
α-pinene	57.5	3.3
β-pinene	62.1	4.4

2.4.4.2 Secondary organic aerosol formation

The oxidation of VOCs emitted naturally from anthropogenic activities can lead to the formation of SOA. The organic fraction of atmospheric aerosols accounts for a large, often dominant, part of the total organic aerosol mass. These species can therefore contribute significantly to changes in the radiative balance (Kanakidou *et al.*, 2005). SOA includes aliphatic acids, aromatic acids, nitroaromatics, carbonyls, esters, phenols, aliphatic nitrates and amides (Grosjean, 1992). BVOCs play an important role in SOA formation in rural and remote areas (Griffin *et al.*, 1999;

Hoffman *et al.*, 1997; Bonn & Moortgat, 2003), while in urban areas, anthropogenic VOCs are more significant (Pandis *et al.*, 1992).

2.4.5 Impacts of VOCs

VOCs and other pollutants are increasingly regarded as posing unacceptable risks to public and occupational health, as well as to biological and physical environments (WHO, 2002). The US-EPA has listed certain VOCs as hazardous air pollutants (HAPs) that have to be controlled. In **Table 2.1** (**Section 2.4.3.4**), compounds listed as HAPs are marked with asterisks (*). It is evident that many aromatic VOCs, e.g. benzene, toluene, ethylbenzene and xylene, are considered to be harmful. According to Hellén (2006), there are only a few HAPs among the alkanes, alkenes, alkynes and carbonyls. Usually, HAP concentrations are much higher closer to the source and can therefore be more harmful.

Toxicological research has indicated that many VOCs have various reversible and irreversible effects on human health, ranging from acute anaesthesia to long-term effects such as the induction of carcinomas (WHO, 2002). VOCs can enter the bloodstream through three primary exposure pathways, which include respiration, (affecting the lungs and respiratory tract directly) ingestion (e.g. eating products where they accumulated in plants and vegetation) and through dermal absorption (through direct contact with VOCs) (Kampa & Castanas, 2008). Benzene is a known genotoxic carcinogen (Hellén *et al.*, 2002; WHO, 2000) and is associated with leukaemia, whereas toluene can cause problems such as foetal malformation.

Ecotoxicological research has indicated that the effects of VOCs on the environment include changes in the population of terrestrial and aquatic ecosystems, and the extinction of vulnerable species. VOCs can also cause damage to vegetation, which include adverse impacts on growth, productivity, nutritive quality, community structure and biological diversity. All of these effects can be considered to be directly due to VOCs, although the active agent may be one or more metabolites produced by the target species (IAQM, 2012). Numerous case studies have been conducted on the impacts of emissions from specific or isolated point sources on vegetation. However, these efforts become complex on a regional scale when a number of sources emit common pollutants that have adverse effects on vegetation at a given location. The identification and apportionment of the contributions of a specific source to the observed or predicted impacts are extremely important for good environmental management.

VOCs can also have significant influences on humans and the environment through the formation of secondary pollutants, e.g. O_3 and SOA. Scientific research has shown that it is possible that the reaction products of some VOCs are more harmful than the VOCs themselves (Yu & Jeffries, 1997). O_3 is highly phytotoxic and can cause damage to crops and native vegetation (Parra *et al.*, 2006). A 33-year study in Japan showed that O_3 in the lower troposphere has increased from 1970 to 2002. According to Laurila *et al.* (2004), O_3 concentrations have also increased in Finland from 1990 to 2000. From relatively recent studies in South Africa, it is evident that almost the entire interior of South Africa has elevated O_3 levels (Lourens *et al.*, 2011; Josipovic *et al.*, 2011). Serious health effects can be associated with SOA. SOA also contributes to changes in the radiative balance of the atmosphere that has an impact on climate change. **Table 2.3** (adapted from Lourens, 2008) summarises the toxicological and carcinogenic health effects of VOCs.

Table 2.3: Toxicological and carcinogenic health effects of certain VOCs

Compounds	Toxicological effects	Carcinogenic effects
Benzene	• High concentrations cause neurotoxic symptoms • Persistent exposure causes bone marrow injury • Produces acute non-lymphocytic leukaemia and attacks the central nervous system	• A known human carcinogen. (EPA, 1996) • Leukaemia
Toluene	• Causes headache, confusion and memory loss • Attacks the central nervous system at ≥100ppm (Sheretz, 1998)	• Not carcinogenic (EPA, 1996)
Ethylbenzene	• Skin and mucous membrane irritation • Extreme eye and nose irritation ≥ 5 000ppm (Sheretz, 1998)	• Possibility of carcinogenic cancer (IARC) (WHO, 2000)
Xylene	• Causes anorexia • Vomiting and giddiness (≥350ppm)	• Teratogenic to the foetus of pregnant women (Sheretz, 1998)
Styrene	• Irritation of mucous membranes and eyes. Health effects include changes in colour vision, tiredness, feeling drunk, slowed reaction time, concentration problems, and balance problems.	• The International Agency for Research on Cancer has determined that styrene is a possible carcinogen.

Table 2.3: *Continued from previous page*. Toxicological and Carcinogenic health effects of certain VOCs

1,3,5-Trimethylbenzene	• Breathing high levels of 1,3,5-trimethylbenzene causes an immediate build-up of fluid in the lungs, causing severe shortness of breath, coughing, and nose and throat irritation. Exposure to high levels causes headaches, tiredness, dizziness, light-headedness or confusion.	
1,2,4-Trimethylbenzene	• Affects the nervous system, causing headaches, tiredness, sleepiness or dizziness. Irritates the nose, throat and lungs, causing coughing, wheezing and/or shortness of breath. Other symptoms of exposure are problems with muscle control, anxiety and confusion.	

2.4.6 A global perspective of atmospheric VOCs

International studies have indicated that the annual ambient benzene concentrations are between 0.4 and 14ppbv (Moschonas & Glavasn, 1996); Tsujino & Kuwata, 1993; Derwent *et al.*, 2000; Simon *et al.*, 2001; Brocco *et al.*, 1997)), while concentrations in close proximity to the source may be several times higher. The ambient ethylbenzene concentration worldwide is estimated to be between 0.23 to 23ppb, toluene 0.53 to 53ppb and xylene 0.69 to 89.85ppb (WHO, 1993). In **Table 2.4,** VOC concentrations measured at monitoring stations worldwide are compared.

Studies conducted at a rural site in Venezuela have indicated that rural sites tend to have much higher benzene/toluene and benzene/xylene ratios, indicating that aged polluted air masses affect this rural region (Holzinger *et al.*, 2001). Studies conducted in the United Kingdom (Derwent *et al.*, 2000) have indicated that VOC concentrations compare well with ratios determined in parts of Europe, which include Athens (Moschanos & Glavas, 1996), Hamburg (Bruckmann *et al.*, 1988) and Helsinki (Hellén *et al.*, 2002). Global studies have also indicated that aromatic hydrocarbons were generally higher in the winter months than in the summer months (Brocco *et al.*, 1997; Liu *et al.*, 2000; Na & Kim, 2001; Hellén *et al.*, 2002; Hoque *et al.*, 2008; Nguyen *et al.*, 2009; Holzinger *et al.*, 2001). These findings can be attributed to faster photochemical reactions of VOCs in the summer (Atkinson, 2000; Atkinson & Arey, 2003).

In South Africa, several researchers have conducted VOC studies (Burger, 2006; Van der Walt, 2008; Lourens, 2008; Otter *et al.*, 2003; Otter *et al.*, 2002). In most cases, these studies were limited to intensive short-term campaigns, such as SAFARI 2000 (Swap *et al.*, 2003). A recent VOC study that has been published in a peer-reviewed journal in South Africa is that of Lourens *et al.* (2011). Measurements are also performed by industries to comply with legislation. These results are, however, in most instances not peer-reviewed and are also not available in the public domain.

Table 2.4: Comparison of different VOC concentrations (ppb) measured worldwide

	Helsinki (Finland)	**Baltimore**	**São Paulo**	**Seoul**	**Highveld of South Africa**	**Delhi (India)**
Reference	**Hellén *et al.*, 2002**	**Vukovich, 2000**	**Colòn *et al.*, 2001**	**Anthwal *et al.*, 2010**	**Lourens *et al.*, 2011**	**Hoque *et al.*, 2008**
benzene	0.47	2.27	2.50	0.58	0.89	26.93
toluene	1.22	7.09	15.10	5.39	1.05	43.80
ethylbenzene	0.23	1.24	3.50	0.72	0.19	3.92
(*m*,*p*)-Xylene	0.72	3.72	7.80	0.82	0.26	15.21
***o*-xylene**	0.28	1.39	2.40	0.35	0.15	7.89
styrene	0.03	0.53	1.60	0.45		
propylbenzene	0.05					
2-ethyltoluene	0.06					
3-ethyltoluene	0.14					
4-ethyltoluene	0.06		1.80			
1,3,5-trimethylbenzene	0.06	0.67	0.70			
1,2,4- trimethylbenzene	0.25	5.35	2.30	0.27		
1,2,3- trimethylbenzene	0.07	1.17				
MTBE	0.54					

2.5 VOC measurements

2.5.1 Sampling techniques

Various sampling techniques for VOCs exist, which include (Burger, 2006; van der Walt, 2008):

- sampling bags (Tedlar bags);
- evacuated stainless steel canisters that can be used as passive samplers or with pumps to overpressure;
- tubes consisting of solid absorbents such as Tenax and/or activated carbon;
- filter/foam combinations; and
- real-time sampling instruments.

When selecting the most suitable sampling method, certain factors have to be taken into consideration. The selected or preferred method depends on the nature of the analytes of interest, local environmental conditions, pollutant concentrations, specific types of data required and analytical testing equipment. Sampling methods for VOCs are described in the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (EPA, 1997). In **Table 2.5,** a list of prescribed sampling procedures, according to the US-EPA, with different sampling techniques for VOC measurements are listed.

Table 2.5: List of the sampling procedures, according to the US-EPA, with different sampling techniques for VOCs (Burger, 2006)

Sample collection device	Compendium method
Porous polymer Tenax® GC tubes for sampling non-polar VOCs	TO-1
Carbon molecular sieve for highly volatile, non-polar organics	TO-2
Single/multi-bed adsorbent tubes	TO-17
Stainless steel canisters	TO-14, TO-15
Tedlar bags	TO-14 (modified by user)
VOST tube	5040/5041

2.5.2 VOC sampling with adsorbent tubes

Adsorbent tubes are frequently used to measure ambient concentrations of VOCs and are generally used due to accurate and reliable results being obtained (Zabiegala *et al.*, 2002). According to Camela *et al.* (1995), large volumes of air can also be sampled. These tubes are made from stainless steel and typically have a 6.3mm outer diameter (O.D), 5mm inner diameter (I.D) and are 90mm long. The inside of the tube is packed with 0.1 to 2g solid adsorbent material that is either a porous polymer or activated carbon (UPA, 1997). In **Figures 2.11** and **2.12,** examples of stainless steel absorbent tubes are shown.

Figure 2.11: Stainless steel tube used for sampling air samples

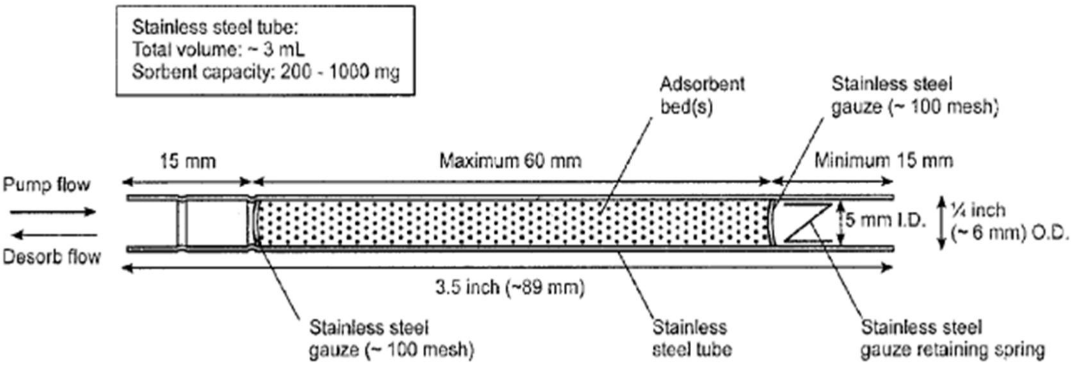


Figure 2.12: Cross section of a standard adsorbent tube (Woolfenden, 1997)

These adsorbent tubes can either be used for the passive or active sampling of VOCs. Passive sampling (diffusive sampling) involves the flow of ambient air through adsorbent tubes by means of diffusion. The rate of diffusion is governed by Fick’s Law of Diffusion and it is influenced by physical parameters, e.g. gaseous diffusion through a static layer or porous material (Brown, 1999). Air is not forced through the tube. During active sampling, air is forced through the sorbent bed with a pump. A disadvantage of this method is the possible occurrence of breakthrough. This happens when the airflow through the tube is too high causing the VOC concentration on the adsorbent material to increase up to a level where the adsorption on the packing material is exceeded. Air samples must therefore be collected over a specific time and the pump flow rate must be adjusted to prevent breakthrough.

Characteristics of different adsorbents are presented in **Table 2.6** (EPA, 1997). The efficiency of the adsorbent is determined by the capacity of adsorbent area, which indicates that with larger load ability, larger volumes can be sampled. This also decreases the possibility of artefact interference and improves the quantitative recovery of analytes. The efficiency of the adsorbent material needs to be taken into consideration in order to eliminate:

- breakthrough during sampling;
- the formation of artefacts; and
- analyte losses during thermal desorption.

Tenax TA and Carbotrap 106 porous polymeric material are the most frequently used adsorbent materials for VOC sampling. Although Tenax TA is a weaker adsorbent than Chromosorb 102/106, it contains a hydrophobic co-polymer, which enables sampling without the retention of water vapour (Lourens, 2008, with references therein).

Table 2.6: Characteristics of different adsorbents for collections of VOCs (UPA, 1997)

Sample tube sorbent	Approx. analyte volatility range	Max temp (°C)	Specific surface area (m^2/g)	Example of analytes
CarbotrapC®/ CarbopackC®	n-C_8 to n-C_{20}, Alkyl benzene and aliphatic compounds	400	12	Alkyl benzenes, PATD, PCBs
Tenax® TA	n-C_7 to n-C_{30},	350	35	Aromatics except benzene, non-polar compounds (pb>100°C), such as aliphatic hydrocarbons from n-C7 and less volatile polar compounds (pb>150°C)
Tenax GR	Bp 100°C to 450°C n-C_7 to n-C_{30},	350	35	Alkyl benzenes, PATD, PCBs and the same as for Tenax TA
Carbotrap®/ CarbopackB®	n-C_5 to n-C_{14},	400	100	A wide range of VOCs, including ketones, aldehydes and all polar compounds within the volatility range specified.
Chromosorb® 102	bp 50°C to 200°C	250	350	Suits a wide range of VOCs, including oxygenated compounds and haloforms less volatile than methylenechloride
Chromosorb® 106	bp 50°C to 200°C	250	750	Suits a wide range of VOCs including, hydrocarbons from n-C_5 to n-C_{12}. Also good for volatile oxygenated compounds.

2.6 Meteorology of the South African interior

The meteorology in a specific region has an important influence on the impact of pollutants. In South Africa, factors such as regional air movements and local climate influence the distribution of pollutants in the interior of the country, as well as the transport of these species to neighbouring countries.

Southern Africa is situated in the subtropical high-pressure belt that circles the globe between 25°S and 30°S. South African meteorology is influenced by the presence of three high-pressure cells, i.e. the South Atlantic high-pressure cell over the west coast, the South Indian high-pressure cell over the east coast and the continental high pressure cell over the interior (Liebenberg-Enslin *et al.*, 2007). The atmospheric circulation over southern Africa is dominated by anti-cyclonic circulation, especially during the winter, which traps pollutants and causes increases in pollutant concentrations contributing to poor air quality (Preston-Whyte & Tyson, 1988). In the summer months, the anti-cyclonic belt weakens and shifts southwards, allowing the tropical easterly flow to resume its influence over southern Africa. Low air pressure conditions prevail over the interior of southern Africa, with generally unstable meteorological conditions that increase the vertical motion and dispersion of pollutants in the atmosphere (Tyson *et al.*, 1996). **Figure 2.13** shows the main pollutant transport pathways over southern Africa.

Precipitation in South Africa has distinct patterns and is characterised by wet and dry seasons. During the dry seasons over the interior, almost no precipitation occurs. This distinct precipitation cycle strongly affects pollutant concentrations. During the wet seasons, the scavenging of pollutants increases, while pollution levels are usually higher during dry months.

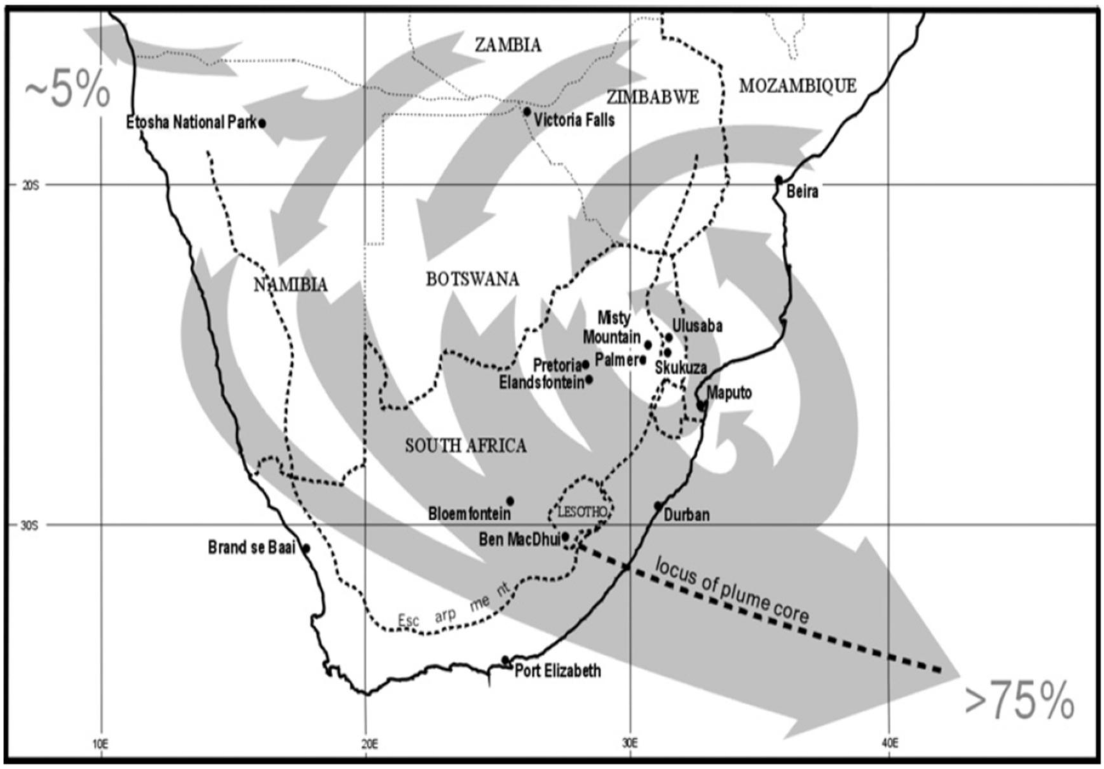


Figure 2.13: Atmospheric pollutant transport pathways over southern Africa (Reason *et al.*, 2006)

2.7 Conclusion

From the literature presented it is clear that:

1. VOCs play an important role in tropospheric chemical reactions and are major contributors to general air quality.
2. many uncertainties are associated with VOCs, especially for South Africa due to limited local measurements.

In comparison with other pollutant species, the monitoring of VOCs in South Africa is not yet well documented and there is no long-term database available. Establishing a comprehensive database and emission inventory for VOC species is important to determine the current status of VOC levels, as well as to predict future impacts with atmospheric models. The objectives of this study were therefore to obtain a comprehensive dataset for ambient VOCs at a relevant measurement station in South Africa and to determine the trends of these species.