

Trace Components, Tropospheric Interactions and Their Influence on Air Quality Composition over Southern Africa

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Abstract Southern Africa is now a significant source of atmospheric pollution, having transformed from a rural to a developing region. The sub-continent is a source of atmospheric pollutants, including particulates, liquid and gaseous species produced from both natural and anthropogenic sources. Prominent hotspots for nitrogen oxide (NO_x), particulate matter (PM) and biomass burning (BB) emissions can be seen on global maps and satellite retrievals. The seasonality of chemical transport mainly results from the seasonal swing of the Hadley circulation, the intertropical convergence zone (ITCZ) and subtropical westerlies along the transport pathways. The anticyclone induces strong subsidence motion, preventing vertical mixing of pollutants, hence capping high concentrations over land as they are transported across. This is manifested through temperature changes, cloud microphysical dynamics, atmospheric stability, the biosphere-atmosphere interactions as well as the oxidation processes. Once emitted chemical species show differences –either in the nearby or lower- and upper atmospheric levels in their dispersion, concentration, reaction rate, lifetime and/or oxidation capacity. Aerosols affect gas-phase chemistry via their light extinction potential and affect the photolysis rates of trace gases. Changes may occur through loss of gas-phase reactions, gas-to-particle partitioning or aerosol chemical modification. As part of efforts to understand chemical trace components and their atmospheric influence, this study highlights on the status of such species, their interactions and influence on air quality (AQ) composition over southern Africa. We propose an overview of gas- and particulate concentrations over several African localities, especially where daily WHO AQ threshold limits could be exceeded. The paper also aims to draw attention to African scientists and policy makers concerning pollution monitoring network in order to define national standards, to better control pollutant emissions and perhaps address impacts on AQ issues, pertaining to the growing African population and development.

Keywords: trace components, atmospheric composition, interactions, oxidation, photolysis, troposphere

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1. Introduction

Atmospheric trace components play critical roles in the global climate system through their interaction and modification of the climate system. These components (both particulates and gases) occur from natural and human-induced activities and form an integral part of the earth-atmosphere system [1]. They are essential to the atmospheric composition and influence atmospheric behaviour in many ways: climate modifications [2,3,4] changes in radiative forcing and oxidation capacity [5], changes in ambient air quality (AQ), and they have major impacts on human health, vegetation and ecosystems. They can also affect the abundance of the hydroxyl radical (OH) –a major oxidising agent in the troposphere. While some are directly emitted from their sources (primary species), some are generated in the atmosphere from

interactions and transformations of primary/precursors and other phase changes (secondary species).

The atmosphere is an important source of a number of trace gas and particulates (e.g. carbon monoxide (CO), sulphur oxides (SO_x), particulate matter (PM), nitrates (NO₃⁻) black carbon (BC), sea salt, lead particles etc.

Particulates exhibit large spatial and temporal variations, not only in terms of size distribution, but also in chemical composition, formation, emission and dispersal mechanisms including their removal processes from the atmosphere [6]. Many are mixtures of different chemical compounds; some of which are water-soluble inorganic and organic salts, mineral salts and other various types from the earth crust [7]. Fluctuations in meteorological parameters such as precipitation and wind speed are the main drivers and have a direct effect on species concentration (dispersal, distribution and removal from the atmosphere). Their levels in the atmosphere vary with

time and location over the globe. For example, increase in greenhouse gas (GHG) precursors such as nitrogen oxides, NO_x (where $\text{NO}_x = \text{NO} + \text{NO}_2$) concentrations causing a steady increase in the earth's global mean temperature is unequivocal [8]. Increase in GHGs can perturb the planetary energy balance by trapping more radiation, melting Arctic ice, increasing water cycle and altering storms [9].

Species concentrations have increased considerably from pre-industrial period, especially due to increases in anthropogenic emissions [10] with a large variety emitted from urban sources [11]. Projected amounts of anthropogenic emissions are thought to have risen above their environmental levels especially since the 21st century. For example, industrial emissions of ozone (O_3) precursors such as NO_x cause the chemical production of tropospheric O_3 to increase significantly, driving the large increases in O_3 columns in the northern-middle-to-high latitudes, while increased biomass burning (BB) causes significant increases in atmospheric species throughout the Southern Hemisphere [10]. In the Southern Hemisphere (SH) and equatorial regions, tropospheric composition is particularly sensitive to BB emissions [12] since emissions from combustion of fossil fuels are much lower than in the northern mid-latitudes [13]. Emissions can have a direct impact on the local, regional and global atmosphere, providing large quantities of gas- and particle phase species. Both BB and climate change are important in the long-term evolution of tropospheric O_3 and OH, and in turn can affect the regional climate and AQ. Although Africa is the least studied and most sensitive with regard to climate change and air pollution [14], the continent is a significant source of atmospheric pollutants from various sources. There are several other sources contributing to overall pollution, in addition to the three main pollution categories -BB, aeolian dust and anthropogenic as highlighted by reference [15], including oceans [sea salt], vegetation [volatile organic compounds (VOCs)], automobiles etc. Some of these are potentially high pollutant concentration sources while others are seasonal and/or fluctuate throughout the year.

Because of her geographical position, across the southern and northern subtropics, frequent occurrence of lightning and wildfires, its vast savannahs, tropical forests and seasonal migration of the inter-tropical convergence zone (ITCZ) –all this render the African continent considerable interest and importance for the global atmospheric chemistry [16]. Southern Africa is one of the sub-continental places that experience increasing aerosol loading, with most of the pollution being anthropogenic. Although pollutant concentration increases substantially during summer, the picture changes during the dry season due to the large amounts of BB emissions over land. For example, higher aerosol optical thickness ($\text{AOD} = 1.5$ and above) at 550 nm is frequently observed during the dry season [17]. Particle size is the critical parameter for cloud formation (aerosols act as cloud condensation/ice nuclei respectively), and influence cloud microphysical properties, in addition to their chemical composition that plays vital roles in atmospheric chemistry. Also, suppression of low clouds can be observed to significantly change the solar radiation flux.

The purpose of this paper is to highlight on the state of atmospheric chemical composition, interactions and influence of trace components on the AQ over southern Africa. The study aims to review concepts underpinning atmospheric chemistry, focusing on key areas upon which knowledge is rather limited. An understanding of key precursors that control chemical species and reactions is critical, especially for a region like southern Africa that experience increasing pollution. While the paper focuses on atmospheric chemistry, we also highlight on pollutant concentration levels, trends and AQ legislation measures. The rest of the paper is arranged as follows; section 2 gives an outlook on southern African climate and pollution; section 3 discusses atmospheric trace components and their evolution, section 4 deals with AQ and health impacts, section 5 discusses chemical distribution in the atmosphere, whereas section 6 discuss photochemistry and gas reactions; section 7 discusses VOC emissions. Lastly, a general discussion and summary are presented in sections 8 and 9 respectively.

2. Southern African Climate and Pollution Outlook

Southern Africa generally has a spatially varying arid climate in the west through semi-arid, temperate and sub-humid in the central, to semi-arid in the far east [18]. The climate becomes largely humid towards the tropical rainforest of the Congo Basin. It is influenced to a large extent, by the prevailing air masses over the local atmosphere, which strongly influence the regional weather patterns [19,20] and the adjacent oceans on both sides. Common amongst these mechanisms include the ITCZ, the Congo Air Boundary (CAB), El Niño Southern Oscillation (ENSO) and the monsoon systems. Over the interior of the landmass, the climate is subject to a strong seasonal variability. For example, atmospheric circulation pattern over the highveld is dominated by anticyclonic circulation during winter and frequent easterly disturbances during summer [21]. These systems modulate pollutant levels and reduce vertical mixing so that pollution resides above for several days before exiting the land [19,20,22,23,24]. Precipitation is characterized by strong seasonal variation –most of it received during the wet season, typically between October and March. The long-term precipitation changes from both northern and southern hemispheres are linked to the monsoon circulations and controlled by precessional variations in summer insolation [25]. Cloud cover is often limited due to dominant pressure system created by the high altitude and the subtropical subsidence [26].

2.1. Regional Contribution to Chemical Components

The sub-continent bears an influx of aerosol and trace gas pollution from local- and to some extent, remote sources due to pollution transport. Pollutants are generated from BB, domestic fires, fossil fuels, dust particulates, VOCs and other anthropogenic emissions. Biomass burning aerosols (BBAs) comprise predominantly of

organic particles in combination with other products such as black- and organic carbon (OC), the percentage of which depends on the burning efficiency of the fires. Widespread burning activities occur mainly over Angola, Zambia, Democratic Republic of Congo and some parts of Tanzania and Mozambique, mostly during the dry season. Although vast amounts of anthropogenic aerosols are more abundant in the industrialized regions of the Northern Hemisphere [27], a significant amount is also generated in the SH, particularly southern Africa. Various authors in literature (e.g. [19,20,22,26,28,29,30,31]) have discussed the evidence of aerosol and trace gas emission over southern Africa.

2.2, Transport Patterns

The sub-continent has a unique set of meteorological and chemical characteristics influencing pollution transport and climate forcing [23]. The anticyclonic nature of atmospheric circulation results in the formation of stable layers so that aerosol and trace gas recirculation occurs in a significant local, regional or sub-continental scale [32]. Atmospheric stability and many natural and anthropogenic sources lead to accumulation of aerosols over land, with potential climate forcing consequences [29]. A significant amount of air recirculates over land [19,31] before exiting the landmass. Synoptic-scale high-pressure systems are located persistently over southern Africa, South America and/or adjacent oceans. These are associated with descending air and relatively low wind speeds, limiting the dispersion of pollutants. Under such conditions, plumes tend to recirculate above and hence resulting in large amounts of airborne particles trapped for longer periods [22,33].

Transboundary transport involves transport of substances over thousands of kilometres crossing regional, continental or geographical boundaries. An example is the fire emissions observed through the large plumes of high concentrations associated with the so-called “river of smoke” outflow [34] into the marine environment. However, because the atmosphere is a shared resource, concerns also arise from effects of transboundary pollution capable of affecting systems at a large scale. One typical example is the Mpumalanga highveld (in South Africa) –a major air pollution source area of high-elevation emissions, which can be transported to neighbouring countries. The South Atlantic and the cold Benguela Current induce surface inversion and strengthens over land. For example, owing to the temperature contrasts between the ocean and land, sea breeze can develop during the day and trap pollutants over Cape Town [35]. Also, large-scale circulation results in industrial aerosols and trace gas emissions from the highveld recirculation after several days [19,20,24].

Reference [23] postulated five basic trajectories through which pollution transport occurs over southern Africa: direct easterly or westerly transport, easterly or westerly advection out of an initially anticyclonic circulation, and anticyclonic recirculation (Figure 1). However, much of the pollution is transported westwards. On the southern periphery, wave perturbations from the trajectories occur at 18°S into the Atlantic Ocean, the bulk of pollution transported into the Indian Ocean occurs at 35°E [19,23]. Reference [19] also described two major pathways

through which pollution is transported from the main land into the South Atlantic and Indian Oceans namely, the “Angolan- and Natal plumes.” The general climatological conditions are such that the anticyclonic activities dominate and become favourable in specific locations where pollution accumulates and/or become transported away.

Persistent low-level easterlies/southeasterlies facilitate the westward transport of pollutants into the oceans.

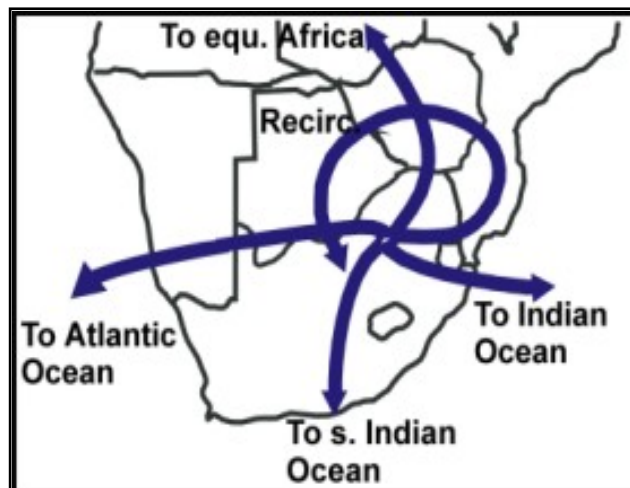


Figure 1. Air transport pathways over southern Africa [http://www.sei-international.org.rapid/atmtrans.htm]

3. Trace Components and Evolution

The troposphere behaves as a chemical reservoir to different species released into the atmosphere –both primary and secondary species. Different species have varying lifetimes, depending on their interactions, chemical composition and state conditions; some have longer lifetimes (few days to weeks), while others only last for a short period (seconds to hours) because they are quickly removed or destroyed from the atmosphere. Although there is still some uncertainty in the formation of secondary organic components [36,37] from oxidation of VOCs, Reference [38] estimate that about 10^4 – 10^5 different types of organic compounds have been measured in the atmosphere, mostly biogenic in origin. On the other hand, some studies conclude that there is an even distribution between the northern and southern hemispheres in the ratio of 51% and 49% respectively, with 90% in the SH in the region between 0 and 25°S [39]. Biogenic VOCs (BVOCs) are probably the largest global source of gaseous emissions oxidized by the OH radical and O_3 , giving rise to thousands of other compounds. These are extremely reactive species that can exert a controlling influence over the oxidative chemistry near their emission sources [40]. They are an important source of secondary organic aerosols (SOAs). However, the uncertainty is compounded by the fact that VOCs undergo various atmospheric degradation processes to produce a wide range of other species that may or may not contribute to the formation and evolution of secondary components from oxidation [36].

Formation processes evolve rapidly after primary emissions so that the chemical and physical properties

change rapidly [41], but the factors controlling species evolution are different [36]. Both BVOCs and anthropogenic VOCs can participate in reaction cycles with other trace components (e.g. NO_x) and give rise to a huge complexity of secondary components. The relative importance of the competing reactions (either by oxidation or photolysis) depends on the structure of the compounds as well as ambient conditions [42]. On the other hand, natural emissions of O_3 precursors can be affected by climate change. For example, NO_x emission from lightning (a significant source of NO_x in the tropics) generally increases in a warmer climate [13].

4. Pollutants, Air Quality and Human Health

Air pollution is one of the major concerns to human health affecting both developed and developing nations. It is widely recognized that atmospheric pollutants can substantially degrade AQ, thereby presenting substantial problems to humans and the ecosystem. This is so because of the wide-ranging potential consequences in terms of visibility, weather modification, radiative forcing and changes in the tropospheric oxidation capacity [43,44]. For many decades, air pollution has been associated with the export of pollutants from urban (e.g. large cities and industrial areas) to regional and/or rural environment. The rapid development and increased urbanization have been the major environmental driving forces regarding AQ degradation due to vehicular emissions, stack release, construction dust and other gaseous emissions where humans can be exposed to high levels of pollution. Air pollution is increasingly recognised as a major environmental hazard and global health risk, leading to millions of premature death annually [45]. Depending on the duration of exposure and type of pollutants, effects can be severe or long lasting (e.g. respiratory diseases and disorders) and mortality rate [46]. For example, world

health organisation (WHO) estimate about 80% of outdoor pollution-related premature deaths due to heart disease and stroke, 14% due to chronic obstructive pulmonary disease or acute respiratory infections and 6% due to lung cancer (www.who.int/mediacentre/factsheets/fs313/en/).

Adverse health effects related to PM exposure is mainly concerned with respiratory and cardiovascular systems. Children and adult population are the most vulnerable groups due to PM exposure impacts [47]. WHO also report that outdoor air pollution is carcinogenic to humans and PM is closely associated with increased cancer risk. For example, exposure to PM_{10} through ambient outdoor pollution in both rural and urban areas was estimated at 3.7 million premature deaths worldwide in 2012.

5. Distribution of Chemical Species in the Atmosphere

Accumulation of pollution in the boundary layer enhances chemical reactions in the atmosphere. However, species' concentrations vary depending on factors such as emission flux, rate of reaction and particle size (influencing the rate of emission dispersion). After entering the atmosphere, primary pollutants undergo different transformations and can react with other species –eventually leading to secondary species, which have their greatest concentrations higher in the atmosphere. On the other hand, primary and freshly emitted species have their greatest concentrations near the earth surface and decrease with vertical height due to dilution, reactions and transformations into other chemical species. Pollutants can accumulate within the boundary layer height, above it or just below (depending on the injection factors). An example is the profiles of vertical mixing ratios of dinitrogen pentoxide (N_2O_5) gas precursors and aerosol characteristics relevant for its production or directly affected by its hydrolysis [48]. The figure below illustrates the low NO_x condition profiles, indicating how chemical concentrations vary with height and temperature.

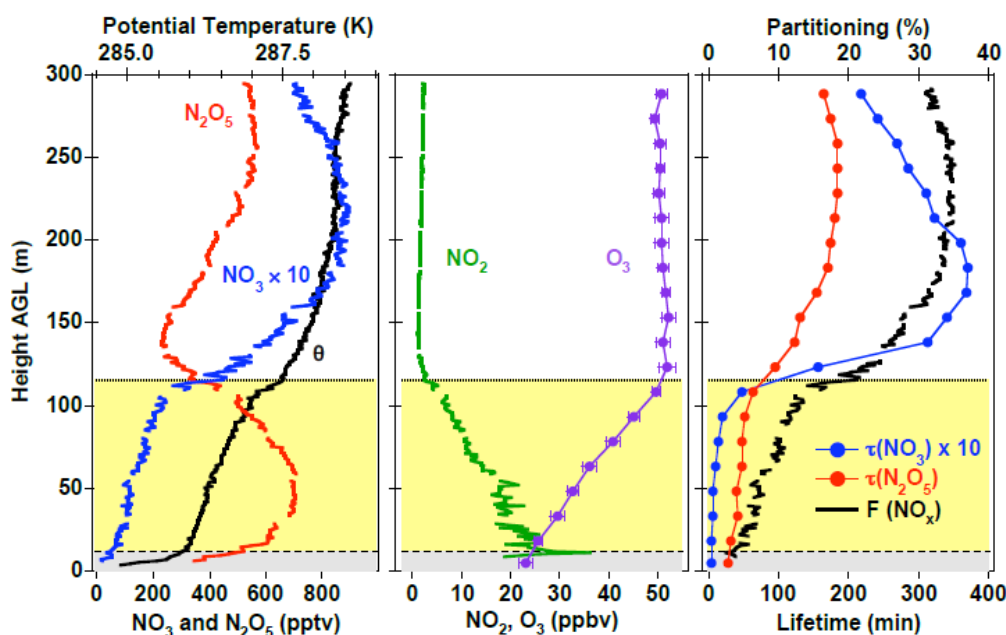


Figure 2. Simulated vertical profiles of NO_3 , N_2O_5 and potential temperature as a function of height for different parameterizations of heterogeneous hydrolysis of N_2O_5 . O_3 and NO_2 profiles are from measurement and calculations. The right-most panel shows calculated lifetime profiles [49]

There are similarities observed in the profiles: mixing ratios decrease with height, although for some species (e.g. nitrogen dioxide [NO₂]), concentrations become steeper above ground level, perhaps because of reaction with other species and conversions from nitric oxide (NO) with height. It is also evident that the NO_x cycle dominates in the middle troposphere. We shall show in the succeeding section, different chemical reactions and processes in the atmosphere. For example, during the night, species such as O₃ decline in the nocturnal boundary layer (NBL); its chemical sink in urban areas occurs through reaction with freshly emitted NO—a process that leads to nitrate (NO₃) or O₃ titration by NO. Ozone is depleted within the NBL by NO and NO₂ because of its reactivity. This pattern indicates how the NO₃ chemistry and its reservoir species (e.g. N₂O₅) strongly influence the rate of O₃ concentration [50]. Reduction in the vertical mixing layer due to reaction with freshly emitted NO_x and O₃ depletion at the surface leads to a steep vertical gradient [48]. In highly polluted regions, O₃ elevation is enhanced by its production (we show this through a sequence of reactions described later). At night and at the immediate vicinity of high NO emissions, O₃ concentrations are depressed through the process of NO_x titration. The process is balanced during daytime by the photolysis of NO₂.

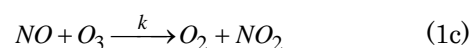
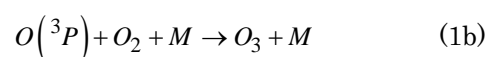
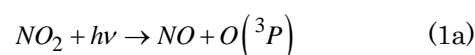
6. Photochemistry and Gas Reactions in the Atmosphere

Tropospheric gaseous processes are driven largely by daytime photochemistry when the sun's energy interacts with trace molecular absorbers (as well as being attenuated by clouds and aerosols). Photochemistry is the underlying mechanism concerned with the chemical effects of light and reactions in the atmosphere, initiated by photons absorbed by molecules. It is the main driver of the atmospheric chemistry controlling most of the chemical processes through gases (e.g. OH, O₃ and NO₃) during daytime and nighttime. The gas-phase oxidation initiated by reaction with OH, NO₃ and O₃ radicals or via photolysis is the primary process through which most species evolve in the atmosphere [51]. These reactions can alter the chemical or physical properties of most species and lead to the formation of other species or transformation of primary components. When molecules absorb light photons, they get into 'excited state' because of the excess energy. Consequently, the bonds between the atoms can be altered as the molecule wants to get rid of excess energy absorbed; it may either remain in the same or different state at the end. This leads to energy loss to the environment in the form of heat or reduced light energy, resulting in one or more chemical transformations via the formation of excited states [52]. The process is driven by two basic principles: (i) light of a particular wavelength must be absorbed by a compound for the reaction to take place, and (ii) for each photon absorbed, only one molecule will be activated per subsequent reaction [53]. All subsequent physical and chemical reactions then follow from the excited species. The absorbed light energy acts to 'break' or reorganize the bonds within the compound molecules.

Chemical reactions depend greatly on NO_x [49]—an important primary pollutant produced from anthropogenic and natural sources (e.g. fossil fuel combustion, BB, soil bacteria, lightning, oxidation of ammonia, mobile transport and other heavy machinery). Precisely, NO_x dominates the tropospheric O₃ budget, the abundance of OH and the nitrate aerosol (NO₃⁺) formation [54]. It is emitted into the troposphere during the day, mainly as NO, and later establishes a rapid equilibrium state with NO₂. At night, NO₂ is oxidized by O₃ into NO₃—a photochemically unstable specie, but one of the most chemically important atmospheric species [55]. The reaction can influence vertical profiles of O₃ and NO₂, which are precursor species of the NO₃ radical. Consequently NO₃ becomes a major oxidant during the night at the expense of the OH radical (when there is no photolysis), usually accompanied by the presence of N₂O₅ produced from the reaction between NO₂ and NO₃. NO_x can also be oxidized in the atmosphere to form nitric acid (HNO₃). Similarly, N₂O₅ can react with water molecules (H₂O) to form HNO₃—a reaction responsible for depleting NO_x from the stratosphere, especially in Polar Regions. Because of its short lifetime (~1s), the OH radical is only present during the day, whereas the NO₃ radical plays a major role in nocturnal chemistry. Reaction of NO₂ with O₃ is perhaps the largest source of NO₃ in the atmosphere.

6.1. Daytime Chemistry

Tropospheric daytime chemistry is driven by photolytic reactions. During the day, NO₂ is efficiently photolysed by solar radiation ($\lambda \leq 420 \text{ nm}$) into O₃ and NO. The resulting O₃ can react with NO to form NO₂. The NO_x photo-stationary state process can be described through the reactions [51,56]:

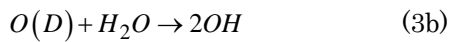
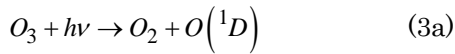


where $k = 1.4 \times 10^{12} \exp[1310/T] \text{ (cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1})$ is the rate constant at temperature T [56], M could be the sum of all abundant third molecules (e.g. nitrogen [N₂] and oxygen [O₂]) at a given pressure height. The photo-stationary state for O₃ equilibrium concentration is defined by:

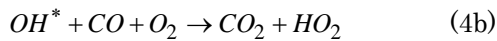
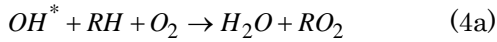
$$[\text{O}_3] = \frac{J_{\text{NO}_2} [\text{NO}_2]}{k [\text{NO}]} \quad (2)$$

where J_{NO_2} is the photolysis rate of NO₂. Reaction (2) controls the partitioning between the NO_x family. Because O₃ reacts quickly with NO, the reaction leads to O₃ destruction. Therefore, the overall reactions result in no net formation or loss of O₃, unless VOCs are present to consume NO or convert it back to NO₂ [43,57]. Because NO is consumed, it would no longer be available to react with O₃, but if more VOCs are added into the atmosphere, more NO can be oxidized to NO₂ and increase O₃. On the other hand, O can be photolysed ($\lambda = 290\text{--}320 \text{ nm}$) in the

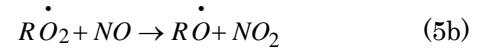
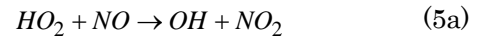
presence of water vapour, which is the main source of OH in the troposphere:



Once OH exists, it can oxidise VOCs and initiate the formation of the intermediate HO_x (HO_x = OH + HO₂) and RO_x radicals. Within the oxidation chain, O₃ is produced from the reactions of the peroxy radicals (RO₂ and HO₂) with NO. The main source of peroxy radicals is the reaction of the OH radical with VOCs or CO [58], given by:



These radicals can react with NO and convert it to NO₂ [59] that would later photolyse to produce the ground-state oxygen atoms O(³P) for the net O₃ production [60], as illustrated in Figure 3.



The influence of varying VOCs and NO_x concentrations on the O₃ production strongly depends on the ambient conditions (i.e. relative concentrations of NO_x and VOC). For example, the O₃ isopleth (Figure 4) shows that O₃ concentrations are sensitive to both VOC-limited and NO_x-limited regimes. A reduction in O₃ positively correlates with a decrease in both VOC and NO_x concentrations [61,62].

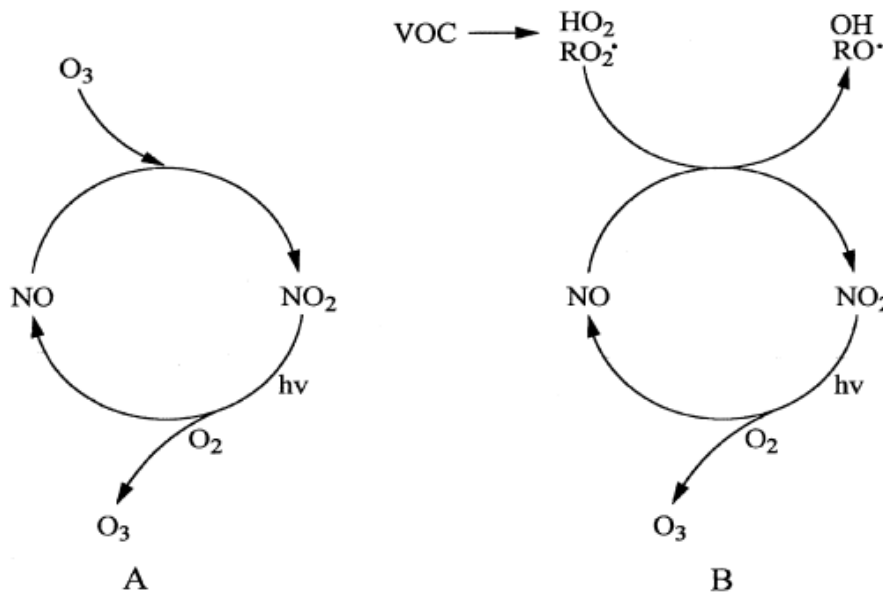


Figure 3. Schematic reactions involving NO-to-NO₂ conversion and O₃ formation, (A): NO-NO₂-O₃ systems without VOCs and (B): NO-NO₂-O₃ systems in the presence of VOCs. [60]

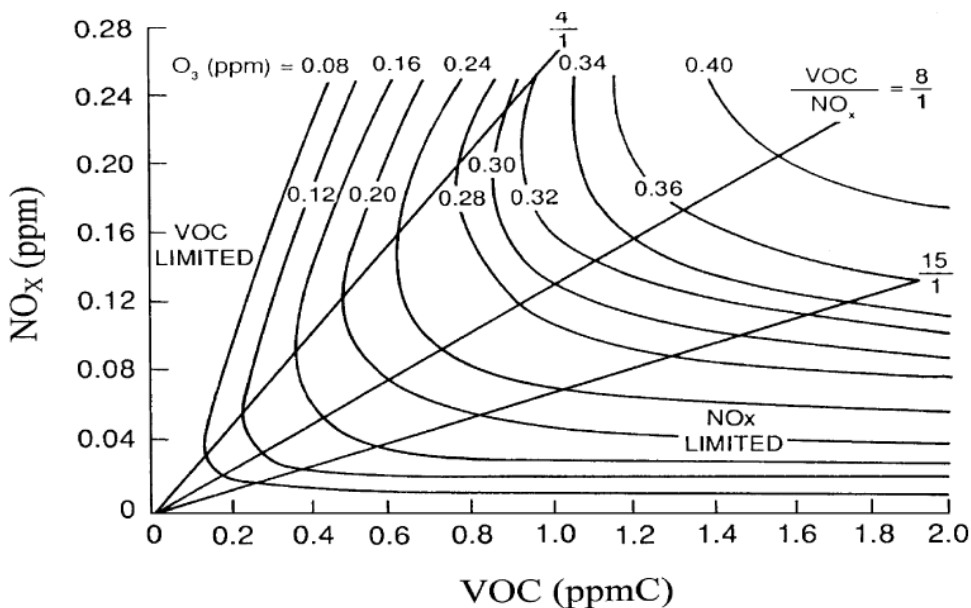
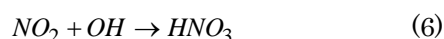


Figure 4. Daily maximum O₃ concentrations [in ppmv] (curved lines) generated from various NO_x and VOC mixtures. O₃ shows an equal sensitivity to the VOC/NO_x ratio at a proportion of 8 to 1 (diagonal line through the origin) [61]

The isopleth is a useful regulatory control for O₃. For example, in highly polluted areas, the VOC:NO_x ratio is lower than 8:1, indicating that limiting VOC emissions is the most effective method for controlling O₃ [63]. Some studies (e.g. [64,65]) also indicate that the ratio of NO_x in the lower troposphere is determinant in the O₃ production or consumption. However, this conclusion does not always stand out because O₃ mixing ratios depend on other factors (e.g. meteorology, gas-to-particle partitioning), in addition to the chemical processes. Consequently high NO₂ leads to depletion of O₃. Thus, the reaction between NO₂ and OH is favoured leading to production of HNO₃ (the most active removal pathway for NO_x in the atmosphere during the day). The reaction is given by:



The nitric acid produced is a direct gas-phase precursor of ammonium nitrate aerosols (NH₄NO₃), removed mostly through wet or dry deposition rather than photolysing back to its products. Reaction (6) also provides an important OH loss mechanism under polluted conditions. The reaction terminates the cyclic chain reactions shown in Figure 3 and removes both NO_x and HO_x from the system [11].

6.1.1. Radical Chemistry

Radical chemistry describes a branch of atoms, molecules or ions with unpaired number of electrons in their shell(s), usually existing independently. Due to the unpaired electrons, species (often referred to as 'free' radicals) can be highly reactive towards other substances and/or between themselves. Free radicals play a central role in the chemical processes that transform trace components in the atmosphere [40]. They can either be positively or negatively charged, depending on the electron-to-proton ratio. Although most of their reactions are very spontaneous, most radicals are stable at low concentrations in the atmosphere at ground state. The most notable examples include OH, NO₃⁺ and O₃ radicals respectively.

6.1.2 Hydrogen Radicals (HO_x)

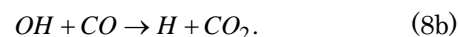
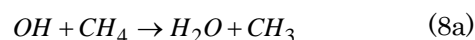
Hydrogen oxide radicals are very pivotal to the tropospheric photochemistry due to their pervasive effect [66,67]. They owe their origin from water vapour molecules in the atmosphere. For example, OH is the most primary self-cleansing agent in the lower atmosphere [40,68] produced by the photolysis of O₃, followed by the reaction of excited oxygen atoms with water molecules (see Figure 5). It is a powerful and neutral oxidant, largely defining the oxidative power of the tropospheric chemistry, and affects both aerosols and O₃ in different ways despite being very short-lived specie.

OH can also act as a source sink to most greenhouse (e.g. CFCs and HCFCs) and pollutant gases (e.g. CO and NMHCs) [70]. Its atmospheric abundance is controlled by the presence and abundance of species such as NO_x, CO, O₃, methane (CH₄) and other high-order hydrocarbons, including UV solar radiation. OH can react with CO, NO₂ and dihydrogen sulphide (H₂S) to form carbon dioxide (CO₂), HNO₃ and sulphur dioxide (SO₂) respectively. Reaction can also occur between OH and SO₂ to form

sulphuric acid (H₂SO₄). Increase in atmospheric NO_x concentration levels increases the rate of hydrocarbon oxidation, hence forming more OH through photolysis as O₃ absorbs solar radiation. However, the upper atmospheric photochemistry has always been thought to be slow because of the low water concentration thought to preclude significant HO_x chemistry [67]. Although OH is an atmospheric oxidising agent [71], it is unreactive towards O₂, but can react with almost all other species in the atmosphere. The most abundant oxidising species of O₂ and O₃ have larger bond energies than OH and are generally uncreative. Therefore, the OH radical can be described as the driving force behind the oxidation of primary organic particles into secondary pollutant species. The main source of the OH radical in the atmosphere is the reaction between water (H₂O) and the excited oxygen O(¹D) atoms as given by equation (3b) above, while its loss can occur from the reaction with the HO₂ radical (i.e. radical-radical reaction), to produce water vapour and oxygen gas. The excited oxygen atom is generated from the photolysis of the ozone molecules (see Equation (3a)) in the atmosphere. The OH lifetime in air is given by:

$$\tau_{\text{OH}} = \frac{1}{\sum_i k_i n_i} \quad (7)$$

where; n_i is the number density of species i reacting with OH, k_i is the rate constant. Since OH is controlled by the abundance of other trace species, reactions with OH lead to the removal mechanism for hydrocarbons and CO through:



Reaction (8b) also suggests that its atmospheric lifetime is relatively less important than most other molecules in the atmosphere.

6.1.3. The Ozone Radical

Ozone is a tri-oxygen molecule in the atmosphere produced from the bonding of three oxygen atoms. It is found mainly in the stratosphere, forming a protective layer that absorbs harmful UV energy from the upper atmosphere. Tropospheric O₃ is formed from photochemical reactions (through oxidation) of precursor compounds (e.g. NO_x, CO and VOCs) as described in section 6.1. It is a key compound for atmospheric chemistry, and acts together with water vapour as the main OH radical precursor [72]. The reactions are initiated by the OH radical reacting with organic molecules. Major sources of O₃ precursors include motor vehicle emissions, industrial and chemical solvents, especially in urban populated regions with major industries. However, winds can also carry emissions away from the sources, causing O₃ to form in less populated/industrialized regions. Chemical compounds such as methyl chloride (CH₃Cl), methyl bromide (CH₃Br) and several other hydrocarbons from BB can also have significant impact on the ozone layer as they contribute to its depletion in the atmosphere [73]. Figure 6 summarises the main reaction processes in O₃ formation and photolysis.

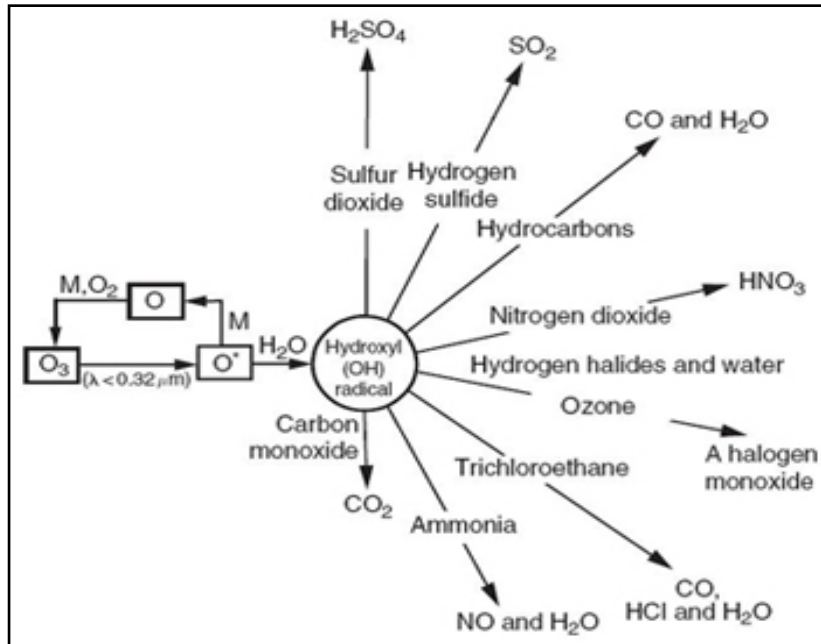


Figure 5. The OH radical cycle [69]

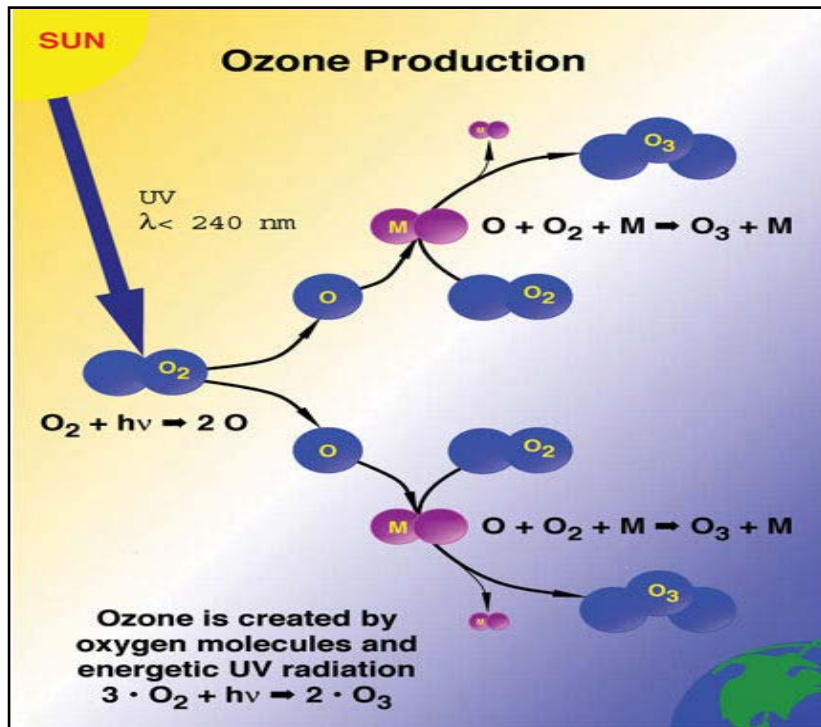
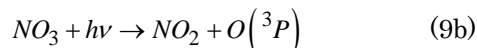
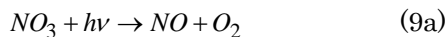


Figure 6. Schematic diagram for ozone formation and photolysis [http://www.learner.org/courses/envsci/unit/text.php]

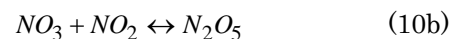
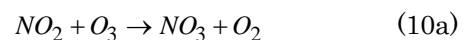
6.2. Nighttime Chemistry

Eventually, either lack of sunlight, NO or VOCs limits O₃ production. Ozone remaining at dusk can produce NO₃ –the main active nighttime chemistry driver. NO₃ is readily photolysed [40,51,74], and so cannot persist during daytime:



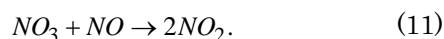
The nitrate radical can oxidise a number of nonmethane hydrocarbons (NMHCs), including sulphur-containing

compounds, and provides a route for the conversion of NO_x to nitric acid [75]. The gas-phase oxidation of NO₂ by O₃ produces N₂O₅. This is also followed by the reaction of NO₃ with NO₂, one of the most important reactions in the formation of N₂O₅:

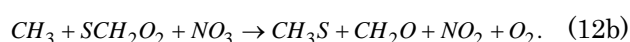


N₂O₅ is the most highly ionised form of nitrogen oxide; it is generated in the air in very small concentration, unless emitted from a process specifically designed to generate it [76]. Reaction (10b) indicates that N₂O₅ is

thermally unstable and can dissociate back to NO_3 and NO_2 respectively. The forward reaction is pressure-dependent, whereas the reverse is temperature dependant thermal decomposition [63]. NO_x are transparent to most light wavelengths; they can allow vast majority of photons to pass through and therefore have a lifetime of several days [76]. Concentrations of NO_3 and N_2O_5 depend on the changes in meteorological conditions as well as NO_x variations [77]. One of the dominant reactions at the surface at night is the reaction between NO_3 and NO :



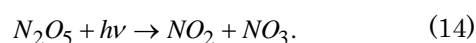
Although the above reaction leads to low NO_3 and N_2O_5 daytime concentrations, the latter concentrations can be sustained in polluted urban and agricultural conditions. But it is often assumed that for areas with large NO emissions, NO_3 chemistry is relatively less important because of its shorter lifetime [78]. Other major loss pathways for NO_3 include reactions with dimethyl sulphide (DMS or CH_3SCH_3) and hydrocarbons [75] or heterogeneous uptake. Reaction between NO_3 and DMS is mostly important in marine environments, given by:



At night (in the absence of NO), reaction (12a) leads to NO_3 removal and consequently affects the turnover of NO_3 lifetime, but not the rate of NO_x removal [75]. However, because NO_3 is water-soluble and has a high dry deposition velocity, it is easily removed from the atmosphere through wet or dry deposition. At steady state, the nitrate radical lifetime [49,75,77] is given by:

$$\tau[\text{NO}_3] = \frac{[\text{NO}_3]_{SS}}{k_1[\text{NO}_2][\text{O}_3]} \quad (13)$$

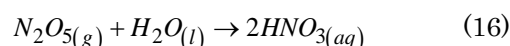
where $[\text{NO}_3]_{SS}$ is the steady state nitrate concentration, and k_1 is the first-order rate coefficient. Because N_2O_5 is only produced at night and decomposes within a short time, it becomes unimportant during daytime [63]. Daytime N_2O_5 loss by photolysis ($\lambda = 385 \text{ nm}$) occurs slowly, given by:



The NO_3 starts building up after sunset and reaches its maximum concentration around midnight; its abundance or destruction is determined by the rate at which NO_2 is oxidized by O_3 . Production ceases once all NO_2 has been consumed by O_3 . Because high O_3 mixing ratios exist during daytime within the residual layer and are constant with height, the NO_3 profile would likely resemble that of NO_2 , but production slows down at night due to decreases in O_3 concentration according to reaction (1c). Under many tropospheric conditions, NO_2 , NO_3 and N_2O_5 can reach equilibrium [16] given by:

$$[\text{N}_2\text{O}_5] = k_{eq}[\text{NO}_2][\text{NO}_3] \quad (15)$$

where k_{eq} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is a temperature-dependent equilibrium constant. The rate of N_2O_5 uptake by particles depends on aerosol composition and meteorology (e.g. relative humidity [RH] and temperature), although it is still not fully understood [79]. Its loss pathways occur through direct (hydrolysis) and indirect (any reaction that can act to limit NO_3 radical production) reactions. One of the main loss of N_2O_5 is the heterogeneous reaction with H_2O leading to nitrate aerosol production through reaction:



where the subscripts g , l and aq denote gas, liquid and aqueous phase respectively. The above reaction is thought to be a dominant pathway for N_2O_5 loss [74], whereas the HNO_3 produced contributes to the nitrate burden in the atmosphere [80]. Because HNO_3 is a longer-lived reservoir than N_2O_5 , conversion of N_2O_5 to HNO_3 slows down the reaction of NO_x and decreases its ratio. Nitric acid can be corrosive and degrade some metals and excess nitrate is harmful to ecosystems since it can lead to 'eutrophication' and deteriorate water quality [35]. From reaction (15), the mixing ratio of NO_2 can be determined [49] from the ratio of N_2O_5 to NO_3 and the ambient temperature:

$$[\text{NO}_2]_{cal} = \frac{[\text{N}_2\text{O}_5]}{k_{eq}(T) \times [\text{NO}_3]} \quad (17)$$

where $k_{eq}(T)$ is a temperature-dependent equilibrium constant for the reversible reaction of NO_2 with NO_3 to form N_2O_5 . Figure 7 highlights the main reactions between NO_x and other species, including the radicals in the atmosphere.

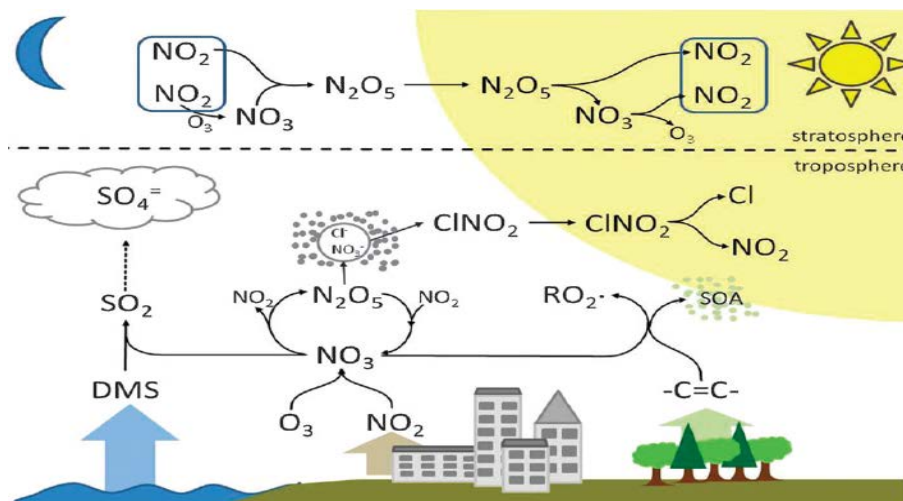


Figure 7. Schematic diagram of the nitrogen cycle and the atmospheric aerosol uptake [55]

7. Volatile Organic Compounds and Their Oxidation

Volatile organic compounds play vital role in the global carbon- and radiation budget and the oxidant composition [39]. These species are produced from anthropogenic emissions (e.g. combustion of fossil fuels [motor vehicles and industries], BB etc.) as well as natural sources (wild fires, vegetation and animals). Major anthropogenic VOC classes include alkanes, alkenes aromatic hydrocarbons, whereas BVOCs include alkenes, isoprene, monoterpenes, sesquiterpenes and other oxygenated VOCs [81]. However, relatively little is known about BVOC emissions over southern Africa, except for savannah, Kalahari- and mopane woodlands [39]. VOCs are highly reactive species [11,42,82], and once entering the atmosphere are transformed by photolysis reactions ($\lambda \geq 290$ nm) and oxidation by the OH radical during daytime, while at night transformations occur due to reactions with the NO₃ radical. Reactions with O₃ occurs in certain locations and times, whereas reactions with chloride (Cl) atoms can occur during daylight hours [42] in the marine environment [36]. Oxygenated VOCs and organic nitrates are to a large extent, similar to alkanes, alkenes and aromatics in their reactivity [81]. BVOCs influence the atmospheric O₃ chemistry in many ways and play dominant roles in the lower tropospheric chemistry and atmospheric boundary layer [83]. For example, isoprene can compete with O₃, acting as a direct sink for species such as NO_x and can contribute to the sequestration of N₂ and oxidation products [82].

The double carbon bonds (C=C) can react significantly with NO₃ and O₃ radicals, whereas those containing carbonyl (>C=O) or nitrate (ONO₂) groups absorb radiation ($\lambda \geq 290$ nm) and undergo photolysis.

The double bonds within these molecules make them liable to abstraction by the O₃ or the NO₃ radical, in addition to the OH radical. However, there are cases other than those mentioned here which occur for alkenes, alkanes and aromatics [81] such as the formation of alkoxy and peroxy radicals. On a global and regional scale, emissions of BVOCs exceed those from anthropogenic compounds by a factor of ~10 worldwide, but they tend to have shorter lifetimes because of their high atmospheric reactivity [84]. In the continental boundary layer, several VOCs (particularly monoterpenes and isoprene) react rapidly with NO₃. Reactions constitute a major sink of the nitrate in rural environments where monoterpenes are usually the most important reaction species [85]. VOCs are species-specific and play important roles in O₃ formation; they can have very short lifetimes (minutes to hours) and are strongly influenced by environmental factors such as temperature, cloud cover and RH [39]. The lifetime of a VOC with respect to reaction with a compound X can be expressed [81] as:

$$\tau_X = (k_X [X])^{-1} \quad (18)$$

where k_X is a VOC rate constant for reaction with X, and for photolysis:

$$\tau_{\text{photolysis}} = (k_{\text{photolysis}})^{-1} \quad (19)$$

The overall VOC lifetime is given by:

$$\frac{1}{\tau_{\text{overall}}} = \sum \left(\frac{1}{\tau_i} \right). \quad (20)$$

VOCs can also react with NO_x in the presence of sunlight to produce O₃ – a major component of smog [35]. BVOCs are particularly important VOC sources due to their fundamental role in atmospheric chemistry in the lower troposphere. However, it is the direct and indirect effects of BVOC emissions in atmospheric chemistry and the magnitude of their contribution that make understanding their sources fundamentally important for AQ management and atmospheric chemistry at global and regional scales [39].

8. Discussion

The atmosphere over southern Africa has unique meteorological and chemical characteristics that influence pollution transport and climate forcing [28]. Common circulation systems and transport pathways play vital roles in the local meteorology and chemical evolution. For example, frequent high-pressure systems act as ‘accumulation’ mechanisms for trace gas and aerosols associated with haze layers, and the westerly wave passages are responsible for the ‘clean out’ signatures [86]. Since the late 20th Century, southern Africa has transformed from a rural to a complex society and has made great strides towards industrialization, urbanisation, and economic development [87]. The sub-continent now experiences a growing industrial infrastructure (most of which is coal powered) releasing large amounts of gas pollutants into the atmosphere. As a result, the changes – compounded with population growth brought about environmental problems virtually non-existent in the past century. Emissions exhibit a mixture of large quantities of aerosols and gases from combustion processes (BB, domestic fires [fire wood, waste burning, charcoal], fossil fuels [automobiles, industries]), construction, manufacturing, aeolian dust and vegetative emissions –especially during summer after the wet spells.

The most industrial trace gas emissions include SO_x and NO_x compounds, CO and other combustion products from the major polluting source areas such as the Mpumalanga, the Copperbelt Province and other isolated locations over land. South Africa with its major industries and power generation [15,88] as well as its major urban areas, is by far the largest industrialized country in the region [89]. Near-point source emissions have also been reported in some areas (e.g. SO₂ emissions in Selebi Phikwe before its closure: see reference [90]) exceeding health guidelines, thus affecting people downwind [87]. Emissions consist of important components in the photochemical production and destruction of other species [91] such as O₃, OH and NO₃ radicals. Although there might not be national AQ problems on record, a number of air pollution conditions exist where severe AQ problems are likely to occur, especially within locations of active BB and high anthropogenic emissions. For example, reference [35] note

that Cape Town (Africa's most populous tourist city) is usually covered with smog in winter. Both smog and O₃ are known to cause nose and throat irritation and can lead to death. Other studies have also linked the haze to unpleasant odours, health effects and visibility impairment in the city [35].

Pollutants consist of primary emitted species capable of impacting AQ and/or inducing radiative forcing in the atmosphere, and can be precursors to both photochemical and other complex compounds. The most significant formation of aerosols depends on the concentration of precursor species (e.g. NO_x, CO and SO₂) as well as meteorological conditions. However, some primary species can remain in their original conditions until being removed from the atmosphere without being transformed. They can be locally distributed at high concentrations near their emission points whereas secondary pollutants tend to be more regionally distributed. Generally, high pollution levels are concentrated over the central-southeast of southern Africa, mostly during winter. The position and geographical pattern of the concentrations are characteristic of the evolved 'river of smoke' outflow into marine environment and other global regions. However, there could be cases where episodes of aerosol transportation could occur between periods of otherwise 'clean conditions.' However, it is worth noting that BB might not be the only dominant source of aerosol concentration, implying that either anthropogenic or dust emissions could be the major primary pollutants. For example, a large part of southwest Africa is a desert, from as far as Zambia through Namibia–Botswana and South Africa, the so-called Kalahari Transect [92]. On other occasions, aerosol background levels can increase as the entire lower troposphere becomes laden with aerosols from various sources, including biogenic, dust, sea salt and industrial emissions. These particles do not only impact on the regional climate, but are also capable of affecting remote/global climate regions.

9. Summary

The release of large quantities of trace components into the troposphere exerts a significant influence and play important roles in the global atmospheric composition. These components interact with the atmosphere in various ways; they can influence atmospheric chemistry, scatter and absorb solar radiation as well as cloud modification. While some are released directly from their sources, others are generated in the atmosphere from chemical reactions and transformations of primary species. Their accumulation in the atmosphere can exceed certain levels, beyond which the atmosphere becomes polluted. Biomass burning is one of the important processes from which emissions impact directly on AQ by reducing visibility, with concurrent enhancement in aerosol concentrations and associated reduction in photochemical activity [12], and has potential consequences to human health, ecosystems and radiative forcing. AQ is sensitive to most environmental changes, including atmospheric circulation, hydrological cycle and temperature, all of which are likely to change due to the combined effects of changing stratospheric ozone and climate [45]. Southern Africa has

an abundance of industrial and other anthropogenic sources [93] and is now recognized as a major source in the southern hemisphere [17].

The rapid development and increased urbanization are the major environmental driving forces in all scales: local, regional and global where humans can be exposed to high levels of air pollution accumulating in the atmosphere or carried downwind under certain weather conditions. Also, due to shifting populations, land use change and agricultural practices, the regional aerosol composition and loading have changed in nature and quantity [94]. There is a well-documented evidence for the regional and inter-continental transport of pollution within- and outside southern Africa into other parts of the world (e.g. [19,20,23]). It should be recognised that many factors drive these trends, including changes in both natural and anthropogenic processes, climate variability and atmospheric circulations. The chemical content of atmospheric deposition is the product of numerous physical and chemical mechanisms including emission, transport, chemical reactions and removal processes [95]. For example, poor AQ is caused by emissions of NO_x, CH₄ and other VOCs that combine in the lower atmosphere to produce O₃. On the other hand, ground-level O₃ is a serious pollutant which at high levels can affect human health and vegetation. This paper examined the existence of pollution and potential influence on the AQ and atmospheric chemistry over southern Africa. The paper also accounts for the atmospheric chemical reactions, and describe characteristics of some chemical reactions. This information is important to improve our understanding of the atmospheric behaviour and its interactions with the biosphere.

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