CHAPTER-1

INTRODUCTION

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1.1: Ambient Ozone (O_3)

Ozone (O_3) is defined as a secondary pollutant in the ambient atmosphere which is harmful to the ecosystem. O_3 is formed by series of chain reactions between its precursors, NOx and VOC in the presence of sunlight and other Meterological conditions. Ozone load in the troposphere is generally increasing due to increase of the concentration of its precursors (NOx and VOC) [1]. Ozone in the lower atmosphere is one of the important green house gases contributing highly to variations in climate change and global warming. [2-3]. O_3 variability is governed by various processes like photochemical behaviour, local and regional transport etc. [1]. NOx, one of the main precursor of O_3 formation are also released in the lower troposphere by various sources like lightning, vehicular emissions, industrial effluents etc. [4-7]. Schematic diagram of O_3 formation in the Troposphere is well depicted in figure 1.1.

In nature, O_3 is highly reactive which has three key properties: (i) it is a strong oxidant; (ii) it is a strong absorber of ultraviolet (UV) radiation; and (iii) it is a participant in many important chemical reactions in the atmosphere [8]. Ozone formation in the ambient atmosphere mainly depends on absolute concentrations of NOx and VOCs, ratio of NOx to VOCs and the intensity of solar radiation [9]. The main factors contributed to formation of ozone is low wind speed, altitude, solar zenith angle, advection processes, temperature, abundant solar radiation, low relative humidity, rainfall. Other factors like cloud cover; wind direction and low wind speeds also contribute to the formation of ground level ozone. The levels of ozone are higher during the hottest part of the day. Ozone continues to increase for all day and decreases after sunset. During night time ozone reverts to other forms as it is highly reactive and dissipates quickly.

Ozone in lower troposphere is formed by the reactions between nitrogen oxides (NOx), carbon monoxide (CO) and volatile organic compounds (VOCs) react in the presence of sunlight. The reactions begin with oxidation of CO with hydroxyl radical which led to the formation of a radical intermediate. This then rapidly reacts with oxygen to give a peroxy radical $HO_2^{\bullet}$ [10]

- Reactions involved are:-

$$^{\bullet}OH + CO \rightarrow {}^{\bullet}HOCO \quad (1.1)$$
$$^{\bullet}HOCO + O_2 \rightarrow HO_2^{\bullet} + CO_2 \quad (1.2)$$

- Peroxy radicals then go on to react with NO to give NO_2 which is photolysed to give atomic oxygen and through reaction with oxygen a molecule of ozone:

$$HO_2^{\bullet} + NO \rightarrow {}^{\bullet}OH + NO_2 \quad (1.3)$$
$$NO_2 + h\nu \rightarrow NO + O\ (^3P) \quad (1.4)$$
$$O\ (^3P) + O_2 \rightarrow O_3 \quad (1.5)$$

- The balance of this sequence of chemical reactions is:

$$CO + 2O_2 + h\nu \rightarrow CO_2 + O_3 \quad (1.6)$$

1.1.1: Sink of Ozone

Ozone concentration in the ambient atmosphere is due to various photochemical reactions and physical processes like impacts of Meterological parameters on O_3, its geographical location, downward transport of O_3 from stratosphere etc. [11-16]. The net budget of O_3 production from photochemical reaction in the troposphere was about 5000 Tg yr^{-1} [17-18] while the net budget of O_3 source from stratospheric-Tropospheric exchange was about 550±140 Tg yr^{-1} [19-20]. Ozone production through chemical reactions occurs mostly in upper tropospheric zone where the concentrations of the precursors are high and O_3 removal processes is slow [21-23].Dry deposition to vegetation, ecosystem fluxes, meteorological conditions etc contributes to net removal of ground level O_3 and is estimated upto 1000±200 Tg yr^{-1} [17]. Destruction of O_3 chemically is highest in the lower troposphere where concentration of water vapour is more and also in polluted environments where chemical titration of O_3 takes place i.e. direction removal of O_3 by reaction with NO [24]. Destruction of O_3 occurs mainly in mid-troposphere where the concentration of O_3 precursors is low and near marine boundary layers [24]. Although the production and destruction processes of O_3 is much more diverse in nature but a very little change is observed since decades [21]. The main sinks of O_3 in troposphere are solar radiation, ambient temperature, stomatal and non stomatal uptake, presence of water vapour, chemical titration of O_3 by NO [24]. The sink of ozone in lower troposphere is shown in figure 1.2.

Schematic diagram of O_3 formation in the Troposphere

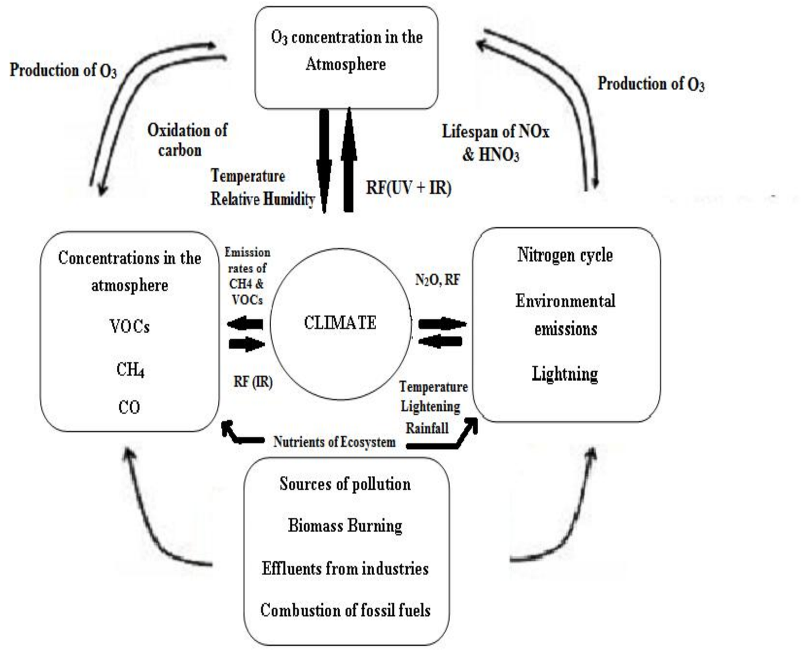

Figure 1.1. Schematic representation of the interactions of O_3 in the Earth system (Source: EPA, 2009).

Schematic diagram showing sink of O_3 in lower Troposphere

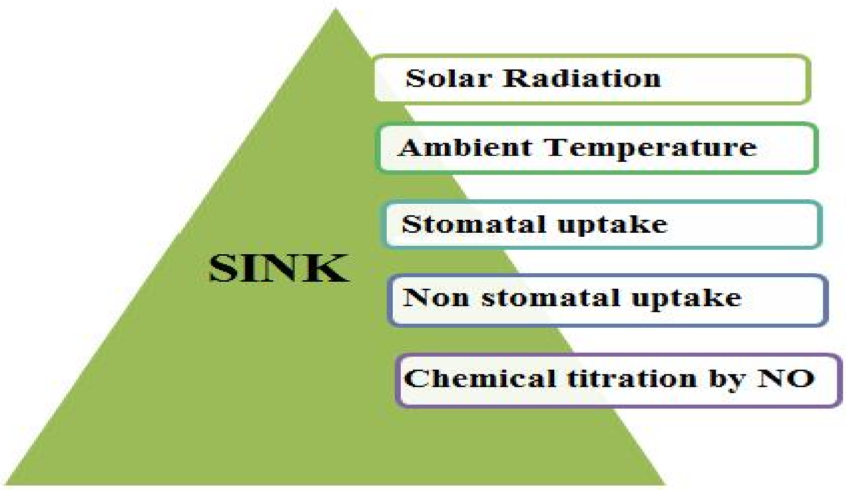

Figure 1. 2. Schematic representation for sink of ozone in lower troposphere
(Source: Monks et al., 2015)

1.2: Ozone and its precursors

Volatile organic compounds (VOCs), carbon monoxide (CO) and nitrogen oxides (NOx) are important precursors for the formation of ground-level ozone. Incomplete combustion of fossil fuel and biomass burning are main sources of VOCs, CO and NOx, while oxidation of methane (CH_4) and volatile organic compounds (VOCs) can significantly contribute to the atmospheric budget of CO [26]. Other anthropogenic sources of NOx include electric utilities, industrial, commercial, and residential sources that burn fuels [25]. Natural sources like bacterial and volcanic activity, lightning etc also contributes to NOx emissions [27].

Oxides of Nitrogen (NOx)

NOx formation in the lower atmosphere is centrally associated with local, regional and global change in the earth processes. Nitrogen oxide(NO_2 +NO) are basically emitted as NO from anthropogenic emission sources but within almost regularly gets converted to NO_2 which in the presence of ultraviolet radiation forms O_3 [28]. Concentration of O_3 production depends on NO_2 and NO reactions which are cycled catalytically and so O_3 production is greater than that of NOx concentrations [28]. The main emission sources of NOx are lightning, biomass burning, fossil fuel combustions, microbial activities in soil and stratospheric intrusions.

Total non-methane hydrocarbon (TNMHC)

Total non-methane hydrocarbons are defined as the organic species having high vapour pressure in ambient atmosphere. These are the main components in both polluted and non-polluted environments in lower troposphere. TNMHC are omnipresent and are important precursor of tropospheric O_3. Total non-methane hydrocarbons are characterized as secondary pollutants which controls the oxidizing capacity of the lower atmosphere [29]. Large amount of TNMHC are emitted from vegetation, biomass burning, manmade sources like vehicular emissions, power plant emissions, landfills, hazardous waste, usage of solvents, transportation [30-33, 6-7].

Carbon monoxide (CO)

Carbon monoxide plays an important role in the troposphere due to its influence on production and destruction of O_3 [34]. CO has a relatively long lifespan in the ambient atmosphere and its reaction with OH radicals provides the sink of CO in the troposphere [35-37]. CO is also used as an inert tracer for air masses affecting anthropogenic emissions [38]. The main sources of CO are vehicular emissions, emissions from natural hydrocarbons etc [38-39].

1.3: Effects of O_3 on Environment

Ozone in the lower atmosphere is termed as 'bad' O_3 for its adverse effects on health and environment. It was termed as lung irritant soon after its discovery [40]. Health effects of increased concentration of O_3 include reduction of lung functions, increased respiratory problems, inflammation. Long term exposure will ultimately lead to chronic damage of the lungs in vertebrates [41]. Ambient O_3 is a secondary air pollutant which also has adverse effects on plants. Increased concentration of O_3 leads to loss of plant productivity by decreasing photosynthetic rate and plant growth. Although stomatal uptake is considered as an important sink of tropospheric O_3 but it has adverse effect on environment by increasing level of CO_2, thereby contributing to global warming [42]. Rising concentration of ambient O_3 has negative effect on natural ecosystem, agricultural crops and forests [43-44].

1.4: Effect of meteorology on ambient O_3

Meterological conditions like high ambient temperature, low relative humidity, higher intensity of solar radiation, high wind speed etc. contributes to O_3 formation in lower troposphere. The concentrations of O_3 against the calm conditions are seen to be low [45]. As observed by [46-47] temperature and solar radiation are important factors of O_3 formation. Tropospheric O_3 shows a strong correlation with ambient temperature even in hot climatic conditions [48-53].

High relative humidity helps removal of O_3 [54] and on the other hand, high temperature facilitates O_3 formation provided other meteorological conditions are favourable [55].

Increased water vapor may increase ozone loss by the reaction sequence:

$$O_3 + hv \rightarrow O_2 + O(^1D) \quad (1.7)$$

$$O(^1D) + H_2O \rightarrow 2 \cdot OH \quad (1.8)$$

$\cdot OH + O_3 \rightarrow HOO\cdot + O_2$ (1.9)

$HOO\cdot + O_3 \rightarrow \cdot OH + 2O_2$ (1.10)

The excited oxygen atom O (^{1}D) of Eq (1.7) may compete with reaction of N_2 or O_2, stabilizing O (^{1}D) to the ground-state atom O (^{3} P), which eventually reacts with O_2 to return ozone. But, the ·OH released from Eq (1.8) proceed with removing O_3 through Eq (1.9) and Eq (1.10) [56]. Under polluted conditions, however, this effect is more complicated, because the · OH radicals produced by Eq (1.8) would react with VOCs and CO to produce more ozone, while also competing to converting NO_2 to HNO_3.

1.5: Importance of the Study

Understanding the chemical and physical dynamics of ozone and other trace gases is becoming increasingly urgent as world population rises and economic activity increases among developing nations. Increased combustion of fossil fuels, which produces chemicals that contribute to ozone formation ("precursors”), accompanies that economic activity.

Governments need to adopt a global perspective when designing a strategy to meet regional air quality objectives for limiting ozone. The real-time and long-term measurements of Ozone from South Asia though are rather sparse. Thus, studies need to be designed to understand the characteristics of ground level atmospheric ozone, and its precursors over Indian Sub-continent.

Tropospheric ozone turns out to be an intercontinental traveler, crossing geographic and political boundaries. Furthermore, ground-level ozone is part of a complex relationship among several air pollutants and other factors such as climatic and meteorological conditions and nutrient balances.

Present study is an attempt to understand the characteristics of ground level atmospheric Ozone in a rural site of Brahmaputra Valley of Assam. Tezpur is one of the small towns situated in Brahmaputra Valley and there is rarely such recorded study on ground level atmospheric Ozone from this site. Therefore, this study in Brahmaputra Valley is taken up. A higher concentration of O_3 is harmful for agriculture and crops as the growth of plants decreases in presence of higher concentration of ozone.

1.6: Research Hypotheses

The study on tropospheric O_3 over the mid-Brahmaputra region in a rural receptor site has been undertaken by considering the following research hypotheses:

1. Remote locations have very low concentrations of O_3 and its precursors but still shows significant temporal variabilities
2. Inter relationship of O_3 and its precursors show a definite pattern.
3. Relationship of ambient O_3 with meteorology shows an important changing pattern

1.7: Research Objectives

The proposed work has been envisaged to understand all factors influencing ozone formation over mid-Brahmaputra region with the following objectives

- To characterize ambient ozone and its selected precursors over mid-Brahmaputra region.
- To investigate the relationship of ozone with its dominant precursor compounds.
- To quantify the role of atmospheric transport on local ozone concentration.

1.8: Scope of the study

Studies of tropospheric ozone is going on throughout the world, however Studies related to tropospheric ozone and its precursors in India is infrequent and mostly concentrated in major cities. Moreover very less works are done on air quality measurements in rural sites of India which are receptors of emission from the city and industrial centre's. With this background the present study was designed to understand the characteristics of ground level atmospheric ozone and its precursors at Tezpur, a rural receptor site of North east India. The present study will mainly focus on characterization of trends present in ozone and its precursor series using statistical analysis. Moreover the relationships of ozone with its precursors will also be analyzed. Meterological parameters and its effects on Ozone formation will also be analyzed to understand the Ozone trends.

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