CHAPTER-2

LITERATURE REVIEW

CHAPTER 2

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2.1: History of discovery of Ozone (O_3)

The discovery of Ozone (O_3) first started during 1775, using direct sensation methods signifying a strong odor associated with lightning and electrical machinery. This method was considered as the earliest methods for O_3 discovery [1]. During that period people supposed that the sensation was due to an unusual action of electricity on olfactory organs and not because of some material substance [2]. However in 1839, Christian Schonbein noticed a similar odor during his electrolysis experiment and proposed that it was due to the presence of a material substance as electricity does not have an odor itself. This substance was named as "ozone", from Greek word Ozien, "to smell' [3]. In 1865, after the discovery of ozone, Soret formulated the molecular formula of ozone to be "O_3" by a study of volumetric relationships [4] and confirmed by diffusion studies in 1867 [5].The UV spectrum and role of O_3 as a filter of UV radiation in the atmosphere was first identified by the works of Hartley [6]. During 1870 to 1910, tropospheric O_3 measurements were mainly done by the Schonbein method [7-9]. An UV absorption analyzer was used for measuring ground level O_3 during 1982 and 1984 [9-10]. However during 1990s finally an O_3 analyzer was installed based on the principle of UV absorption which allowed continuous acquisition of tropospheric O_3 data [10]. Thermal decomposition of O_3 was first studied by Warburg in 1902 [11]. The distribution of O_3 as a function of altitude in the atmosphere was first modeled by Chapman in 1930 [12]. During 1950s to 1970s significant research advances in O_3 monitoring were made due to extreme pressure of the population to solve the problems related to photochemical smog. The significance of catalytic loss of ozone by the reaction of nitrogen oxides was first formulated by Crutzen in 1970 [13]. Research on O_3 monitoring was led by the growing scientific interest on the structure of the atmosphere and military interest on stratosphere. The last 2-3 decades has shown a rise in O_3 concentrations which had led to the doubling of background O_3 concentration [14]. Thereby studies on O_3 started on a large scale to know its effects on both human biota and ecosystem. Various effects of O_3 were also noticed which included its effect on human health, crops and animals. It was found that

ozone causes "catarrh" (inflammation of mucous membranes) and causes death in case of animals [15]. Thus by the end of the 19th century successive progression on O_3 study was formulated. Ozone was obtained as a pure liquid and its structure was also obtained [16].

2.2: Trends on ozone

Ambient O_3 trends globally were evaluated by Intergovernmental Panel on Climate Change [17] and by [18]. During earlier times, before 1970 the only measurements made were of some rural locations in Antarctica [19] and during 1950 in Mauna Loa, Hawaii [20]. Tropospheric O_3 trends has shown a varied trend from 1990 to 2010; for e.g western part of Europe showed an increasing O_3 trend during 1990 however it showed a decreased pattern since 2000 [18]. Clifton et al; Simon et al and Bloomer et al. observed O_3 seasonal cycle shifts in continental USA [21-23]. Naja et al. using a time travel approach, which included measurement of O_3 concentrations associated with residence time of corresponding air parcel over Europe, determined the background O_3 concentration at two high elevation locations in Europe [24]. Considerable works by Lefohn and co-workers on background ozone were also done [25]. Their work was based upon making measurements during the month of February, at background sites when the production of photochemical O_3 is low. This method used by them was used to delineate the background concentration of O_3. Fiore et al. used a 3-dimensional global tropospheric model with chemistry (GEOS-CHEM) to investigate background O_3 in North America by using two different approaches [26]. Similar studies were also reported in Europe using GEOS-CHEM model for studying background contribution to O_3 [27]. Vingarzan, by collecting data at background sites reviewed background O_3 levels and through this study the annual median and maximum concentrations of O_3 were reported [28]. McKendry also reported the background O_3 concentrations for British Columbia based on the review provided by Vingarzan in 2004. He found that maximum occurrence of background concentration of O_3 was during spring time with a range of 20-35 ppb [29]. Similar studies were also done by Jaffe et al. who reported background ozone concentrations ranging from 32-44 ppb for six coastal California sites [30] and by Altshuller and Lefohn who reported background ozone concentration in the US to be 35± 10 ppb [25]. Lindskog and Kindboom reported a little significant change for ozone concentrations measured at remote locations in northern Scandinavia [31]. However

another report by Naja et al [32] suggested that background ozone concentrations have increased by 5 to 10 ppb over the 30 year period from 1970 to 1999, corresponding to an annual rate of increase of approximately 0.15 to 0.3 ppb. The International Panel on Climate Change, and reported by Vingarzan the rate of change of O_3 may be different in the future but projections prepared for future years suggested that levels of background concentrations will continue to increase through 2040, 2060 and 2080, but then decreasing slightly to 2100 [28].

Tropospheric Ozone mainly originates from transport from the stratosphere [33] and also by chemical production through series of reactions from its precursors under the influence of sunlight [34]. In 1950s Ozone was identified as main pollutant for photochemical smog [35]. This led to the understanding of the fundamental mechanism of O_3 formation in the troposphere. Form this other key studies were followed over next 20 years and this helped to built up the skeleton of tropospheric chemistry [34]. Ozone shows a non-linear complex relationship with its precursor's i.e NOx and VOCs and this led to the identification of two regimes NOx sensitive regimes and VOC sensitive regimes. In NOx sensitive regimes O_3 production is normally limited by the availability of NOx. The decreasing NOx emissions lead to lower O_3 production. Under such conditions, OH radicals mainly react with VOCs and CO. This condition is mainly exhibited in rural sites whereas in VOC sensitive regimes O_3 concentration depends on the availability of VOCs. A decrease in NOx leads to higher oxidation of VOCs by OH radicals, and consequently an increase in O_3 production.

2.3: Ozone trends in the Northern Hemisphere

Increased concentration of tropospheric O_3 was observed in the Northern hemisphere since the beginning of industrial revolution [36]. Varied tropospheric O_3 trends were observed at different sites of northern hemisphere midlatitudes [37-40]. NMHCs, NOx, CO, and CH_4 emissions from coal oil and natural gas were considered to be the main sources of tropospheric O_3 precursors in the Northern hemisphere [41]. Several earlier studies have shown changes in tropospheric ozone over a broad geographic coverage [40]. Ozone is transported over distances of intercontinental and hemispheric scales as the lifetime of O_3 in free troposphere ranges from few days to several months [42]. O_3

and its precursors transport may have impacts on O_3 concentrations found downwind of industrialized regions of the Northern Hemisphere, where most of the O_3 precursors (VOCs and NOx) are emitted [43]. Increased concentrations of anthropogenic tropospheric O_3 in northern midlatitudes were due to increased emission of methane in the lower

atmosphere [41]. Higher O_3 concentrations at the background sites in Northern hemisphere are found to be during spring season showing peak values during the month of May [28]. The observed O_3 trends in the Northern hemisphere were analyzed by using various chemical transport models like GEOS-CHEM and NASA GISS [44-45]. An important factor in rising O_3 concentration is the intercontinental transport. According to recent studies the tropospheric O_3 trends in North America was affected by trans-pacific transport of Asian pollution [46-49]. Li et al. reported anthropogenic emissions from North America [50] which led to an additional 20% of violations of the European council O_3 standard in summer 1997 over Europe. Studies using the GEOS-CHEM global transport model indicated that emissions from North American contribute 11% to the tropospheric O_3 annual average total burden over Europe while European sources contribute only 9% [27]. Atmospheric transport processes are widely investigated by using trajectory models.

2.4: Trends in Europe

By the end of the 19th century the concentrations in the boundary layer has been doubled due to which various control strategies were formulated to decrease O_3 precursor emissions to control concentrations of O_3 since late 1980s. This resulted in decrease in O_3 concentrations in several European sites during 1990s. This reduction in European emissions led to a decrease in O_3 peaks in summer [51] and an increase in mean O_3 during winter due to less O_3 titration [31]. Intercontinental transport also contributed to increasing trend of O_3 concentration. Europe was affected by the trans-Atlantic transport of North American pollution [52-54]. Increased tropospheric O_3 trends are observed at midlatitudes sites of Europe from pre-industrial times to 1980s due to increased concentrations from manmade emissions of O_3 precursors specifically NOx [55]. However, since late 1980s the European O_3 emissions decreased [56]. Ordonez et al., 2007 suggested that during 1990s positive O_3 trends in lower atmosphere over Europe were due to increased stratospheric O_3 concentrations [57]. Increased O_3 trends were

observed in western Europe during 1990s followed by a decreasing trend since 2000 [18]. This decrease in O_3 concentration was mainly due to decrease in precursors concentrations. In rural parts of Europe peak O_3 levels show a decreasing trend due to regional pollution emission control over emissions of VOC and NOx from combustion of fossil fuels in industries and motor vehicle exhaust [56,

58-59]. Extreme O_3 concentrations were seen in Europe during summer 2003 which catastrophically affected the inhabitants of a large number of European big cities [60]. Increased concentrations of O_3 locally in regional sites of Europe were experienced due to biogenic emissions while decreasing $PM_{2.5}$ levels [61]. Further studies have shown that the polluted air can be exported to free troposphere by convection and conveyor belts from the American planetary boundary layer and subsequently transported to Europe [54]. Emissions are increasing in parts of Asia due to rapid industrialization [62]. Auvray and Bey, reported that long range transport of Asian emissions could be partly responsible for European background ozone concentrations by using a chemical transport model (CTM) [27].

2.5: Trends in India

The tropospheric column O_3 analysis over major cities Delhi, Hyderabad and Bangalore using the NASA Langley TOR data during 1979–2005 to investigate the trend was reported by Kulkarni et al [63]. The trend obtained from the model shows significant change during monsoon over Delhi and during pre-monsoon and post-monsoon over Hyderabad and Bangalore. The northern parts of India, specifically in Indo Gangetic plain region also show higher concentration of tropospheric O_3 residual (TOR) of about an average of 31.5DU (Dobson unit) in the lower troposphere [63-66]. Ground based measurements as well as model studies have shown increased level of O_3 pollution over this IGP region [67-70]. Mean annual O_3 concentrations measured at an urban site in Ahmedabad, India are reported to be a maximum of 30±3 ppbv during November and a minimum of 12±2 ppbv during August [71]. Another ground level measurement of O_3 was done at a coastal site of a Thumba, India from April 1997 to March 1998. In this study the monthly average concentrations of O_3 were found to be in the range of 13-22 ppbv which is low as compared to the urban areas [72]. Another study from western part of India (major industrial region of Gujarat) had shown an elevated level of ground level O_3 concentration of 70 to 110 ppbv during afternoon hours and a background average of

42±6 ppbv is seen in this region [73]. Another study of O_3 trend analysis was reported by Nishanth et al. over Kannur University campus in Kerala state from November 2009 to October 2010 [74]. He reported the diurnal and seasonal trends of O_3 and its precursors using backward air trajectories of CGER-METEX reanalysis data. The continental stations in both urban and rural areas show considerably low concentrations of ground level O_3 over Indian subcontinent [75-78, 71-72].

Long term study on surface O_3 was made at a high altitude region of Mt Abu, India from 1993-2000. In this study a monthly average of 46ppbv (maximum) of O_3 concentrations during winter and a monthly average of 25ppbv (minimum) during summer season was reported [32]. Another study of tropospheric O_3 from Gadanki, a tropical rural site in India was reported by Naja and Lal, 2002. In this study, a maximum of 34±15 ppbv noontime annual average of O_3 was reported during winter period. Minimum concentrations were found during summer season [78]. Anthropogenic biomass burning, vehicle emissions, industrial exhaust, long range transport, stratospheric-tropospheric exchange collectively leads to the increased ground level O_3 concentrations. Maximum tropospheric O_3 concentrations in most parts of India were during winter or premonsoon season and minimum during monsoon season. Maximum levels of O_3 concentration in Delhi-NCR of India were found to be 97.89 $\mu g/m^3$ for 3 day return period and extreme O_3 concentrations were found to be high in monsoon and premonsoon period and low in winter period [79].

2.6: Relationship among the Precursor compounds and tropospheric O_3

Ground level measurements of ambient O_3 along with its precursor NO, NO_2 and NOx were carried over a rural site of Anantapur in southern India. Highest monthly mean concentration of O_3 was found to be 56.1 ± 9.9 ppbv during April and the lowest to be 28.5 ± 7.4 during August with an annual mean of 40.7 ± 8.7 ppbv for the study period. However higher NOx values were observed to be 12.8 ± 0.8 ppbv during winter followed by the summer season with 10.9 ± 0.7 ppbv, and least values appeared in the monsoon season with 3.7 ± 0.5 ppbv. Anthropogenic pollution, vehicle exhaust, biomass burning, long range transport etc were considered to be the major sources of tropospheric O_3 pollution along with its precursors [80]. Continuous monitoring of ambient ozone (O_3), carbon monoxide (CO) and oxide of Nitrogen (NOx) have been carried out at Udaipur in India. The daily mean values of O_3, CO and NOx were found to be in the ranges of 5–51

ppbv, 145–795 ppbv and 3–25 ppbv, respectively. Highest mixing ratios of O_3 were found to be 28 ppbv during premonsoon and lowest during monsoon with 19 ppbv but highest mixing ratios of both CO and NOx were seen during winter season and least during monsoon. The long range transport related mainly with the summer and winter monsoon circulations over the Indian subcontinent were considered as the main reason for seasonal variations of O_3, CO and NOx [81]. Annual average mixing ratios of ambient O_3, NO, NO_2, CO,

CH_4 and NMHC were found to be 30 ± 6 ppb, 24 ± 6 ppb, 15 ± 4 ppb, 1.5 ± 0.4 ppm, 2.4 ± 0.4 ppm and 0.4 ± 0.1 ppm, respectively at an urban site of Delhi. Maximum concentrations were observed during summer and minimum during monsoon season. The results during the study period signify a negative correlation of tropospheric O_3 with NOx and CO. The presence of pollutants like $PM_{2.5}$ and PM_{10} in surface air influences the concentration of tropospheric O_3 in the study site [82]. Average concentrations of NO, NO_2, NOx, O_3 (ppb), and CO (ppm) were observed to be 17.2, 12.5, 29.3, 23.6, and 1.97, respectively at an urban site of New Delhi, India. High concentrations were observed during summer months and lower during monsoon [83]. Measurements of tropospheric ozone (O_3), oxides of nitrogen (NOx), methane (CH_4) and total non-methane hydrocarbons (TNMHCs) were carried out in a rural coastal area at Kannur, India. The diel variations of O_3 and its precursors were observed. Surface O_3 shows a peak in the afternoon hours and gradually declines during Night time [84]. Meticulous measurements of ambient O_3, NO_2, CO, SO_2 and particulate matter ($PM_{2.5}$) were carried out in Agra, India. Maximum hourly levels recorded for these Pollutants exceeded 116.5 ppb for O_3, 96.2 ppb for NO_2, 16 ppb for SO_2, 4.60 ppm for CO and 188 μg/m3 for $PM_{2.5}$ [85]. Ground based measurements of surface O_3 and NOx were carried out in a rural place of southern India named as Gadanki. Monthly average of O_3 mixing ratio is found to be in the range of 9 ppbv to 37 ppbv with high values during spring and low values during late summer. Low mixing ratios of NOx were found in Gadanki [86]. Annual, seasonal and diel measurements of ambient O_3 along with the effects of its precursors NOx and CO were carried out for the first time in North east India at Dibrugarh. The diel variations exhibits a increasing pattern of Surface O_3 after sunrise attaining a peak around 1500 hours LT and then decreases from evening till sunrise next day. The highest monthly maximum concentration of ambient O_3 is observed to be 42.9±10.3 ppb during March and the lowest concentration observed is 17.3±7.0 ppb during July. Maximum

concentration of NOx and CO is found to be 25.2±21.0 ppb and 1.0±0.4 ppm, respectively, in January [87]. A yearlong measurement of Surface O_3 along with its precursors was carried out in Salmiyah, a residential area of Kuwait. The annual average concentrations of surface O_3, NO_2 and NMHC were found to be 0.049 ppm, 0.046 ppm and 0.70 ppm respectively. Higher concentrations of ambient O_3 were observed during summer season [88]. Simultaneous measurements of tropospheric O_3, nitric oxide (NO), nitrogen dioxide (NO_2), and nitrogen oxides (NOx) were carried out in Tianjin, China. An inverse relationship was observed between O_3, NO, NO_2 and NOx. Variations in the level of oxidant, OX (O_3+NO_2) with NO_2 was also observed. The regional contribution of OX was found to be 20 ppb in Tianjin [89]. The annual average concentrations of O_3, NO, NO_2, NOx, SO_2, CO, CH_4, TNMHCs and THC were found to be 22.51 ppb, 15.58 ppb, 17.25 ppb, 23.84 ppb, 6.66 ppb, 165.13 ppb, 3.44 ppm, 0.56 ppm and 3.88 ppm, respectively in Yanbu, Saudi Arabia. The mobile emissions were considered to be the main sources of pollution in this region. The diel variations of O_3 show highest concentrations during daytime and lowest during night time. Highest concentrations of ambient O_3 were found to be in summer and lowest during winter [90]. Continuous measurements of surface ozone (O_3), nitrogen oxides (NOx = NO + NO_2) and carbon monoxide (CO) were carried out at Qinghai Lake (QHL), China, a basin in the remote Tibetan Plateau area. High concentrations of O_3 mixing ratio was found to be with average of 41±9 ppb in October 2010 and 57±10 ppb in October 2011. High concentrations of O_3 led to significant damage to the ecosystem resulting in desertification [91]. The relationships between ambient levels of ozone (O_3), nitric oxide (NO) and nitrogen dioxide (NO_2) as a function of NOx were investigated by obtaining monitoring data from the UK Automatic Urban and Rural Network observed at rural and urban sites of UK. The level of oxidant, OX was also calculated. The local oxidant source were from direct NO_2 emissions, the thermal reaction of NO with O_2 at high NOx, common-source emission of species which promote NO to NO_2 conversion and nitrous acid (HONO), emitted directly from vehicle exhaust [92].

2.7: Measurements of tropospheric O_3 along with its precursors

Tropospheric Ozone sampling is done with the help of different methods based on the objective and requirement of the study. Surface O_3 is usually measured by using O_3 analyzers. NOx, NO, NO_2, CO, and NMHC measurements were also done by using

ambient analyzers. Different types of O_3 analyzers like O_3 41 M; Environment S.A., France based on absorption of Ultraviolet (UV) radiation at 253.7 nm by ozone molecules [80]; ozone analyzer (Model O_3 42M) [93]; Ecotech analyzer named Australia (model EC 9810). This EC9810 analyzer provides accurate measurements of O_3 in the range of 0–20 ppmv with a detection limit of 0.5 ppbv [81]; Ozone analyzer based on UV radiation (Model: TECO-49C; M/s Thermo Environmental Instruments, Massachusetts, USA) [82]; UV photometric ozone analyzer (Model 49i ozone analyzer, Thermo

Scientific, USA) [83]; O_3 analyzer ($O_3$42M), based on the principle of strong absorption of UV radiation at 253.7 nm by O_3 molecules [84]; an ultraviolet O_3 analyzer (Model 49C; M/s The Thermo Environmental Instruments Inc.) [94] etc.

NO, NO_2 and NOx were measured using analyzer Model APNA-370, HORIBA, and Germany [80]; chemiluminescent analyzer (Model AC32M) [93]; Ecotech analyzer (model EC 9841), providing the mixing ratios of nitric oxide (NO) and nitrogen dioxide (NO_2) [81]; NO and NO_2 measurements were done using NOx-Analyzer (Model: CLD 88 p, M/s.ECO Physics AG. Switzerland) having a photocatalytic converter (Model: PLC 860 M/s. ECO Physics AG. Switzerland) with accuracy of ± 0.050 ppb [82]; NOx analyzer (Model 42i, Thermo Scientific, USA) (Tiwari et al., 2015); NOx analyzer (AC32M) [84]; NOX-Analyzer (Model CLD 88 p; M/s ECO Physics AG.) operating with a photocatalytic converter (Model: PLC 866; M/s ECO Physics AG.) with an accuracy of ±0.05 ppb [94] etc.

Measurements of CO were done by using Ecotech, model EC 9830 analyzer based on the infra red (IR) photometry detection technique. The EC 9830 analyzer uses gas filter wheel correlation technique [81]; non-dispersive infrared gas filter correlation analyzer (Model: 48CTL; M/s Thermo Environmental Instruments, Massachusetts, USA) [82]. CO analyzer (Model 49i, Thermo Scientific, USA) [83]; A non–dispersive infrared (NDIR) gas filter correlation technique based on the IR absorption by EC9830 monitor [85]; A non-dispersive infrared (NDIR) gas filter correlation CO analyzer (Model 48C; M/s Thermo Environmental Instruments Inc.). This instrument was calibrated periodically using Pure Air Generator and NIST-USA certified CO gas (8.1 ppm ± 5%) with multi gas calibrator [94] etc.

Measurements of methane and non-methane analyzer were done by using HC51M analyzer from Environment SA, France. Flame Ionization Detection is used for measuring hydrocarbons present in the ambient air [84]; A flame ionization detection (FID) based hydrocarbon analyzer (Model APHA-360; M/s Horiba) [94]; A monitor fitted with sensor heads (Aeroqual Outdoor Ambient Air Quality Monitor; Auckland, New Zealand) based on Gas Sensitive Semiconductor (GSS) technology with detection range 0–25 ppm and resolution 0.1 ppm [88]; Air quality monitoring mobile station (Environment SA, France) [90]; A GC5000 analysis systems coupled with flame ionization detectors (AMA, Germany) [96] etc.

2.8: Tropospheric O_3 and its meteorological interactions

Meteorological parameters like temperature, wind speed, wind direction, relative humidity and rainfall has an immense impact on tropospheric O_3 and its precursors. A study from Anantapur in southern India reported a notable positive correlation with temperature and a negative correlation with both wind speed and relative humidity. However in case of NOx, one of the precursors of O_3 has a significant positive correlation with humidity and wind speed, and negative correlation with temperature [80]. Another study from Kannur, India also reported a direct correlation with temperature and inverse correlation with humidity. During the study period, the correlation coefficient between O_3 concentration change with relative humidity, wind speed and temperature were -0.84, -0.85 and 0.87 respectively [95]. A study from Udaipur, India recorded increase of ambient O_3 concentration with increase of wind speed while decrease concentration of CO and NOx were observed with increase in wind speed. However, increased CO and NOx levels were observed with increase in relative humidity. The study also reported the decrease of ambient O_3 and its precursors during heavy rainfall episodes [81]. A positive linear relationship of O_3 with temperature and a strong negative correlation with relative humidity was reported in a study at Kanpur, Northern India [97]. Another study of tropospheric O_3 and its precursors carried out at Agra, India revealed positive correlation of ambient O_3 with solar radiation, ambient temperature and wind speed and negative correlation with relative humidity. As mentioned in the study solar radiation controls temperature and as such the photolysis efficiency is higher and so a positive correlation is observed in between temperature and ambient O_3. But in case of higher humidity level slow down the process of

photochemical processes and as such a negative correlation is observed between humidity and surface O_3 [85]. An indirect relationship of surface O_3 and temperature was observed in a study at an urban site of Delhi, India. Production of ambient O_3 is a photochemical process which rate is promoted by high temperature. On the other hand an inverse relationship is observed between relative humidity and surface O_3 due to loss of O_3 by increased amount of water vapour in the atmosphere. Also high wind speed removes PM from the atmosphere and helps in increasing the advent of solar radiation thereby enhancing Photochemical production of tropospheric O_3 and so a positive correlation is seen between O_3 and wind speed [94,98]. Another study from Dibrugarh in North East India, exhibits a good

positive correlation of r^2 = 0.8 between ambient O_3 and temperature. A positive correlation with r^2=0.5 was observed between O_3 and wind speed. On the contrary, a negative correlation with r^2=0.8 was observed between ambient O_3 and relative humidity [87]. Another study from Kannur, Southern India reported a linear relationship between tropospheric O_3 and humidity, temperature, and wind speed. The correlation coefficient between O_3 concentration change with relative humidity, wind speed and temperature were −0.84, −0.85 and 0.87 respectively during the period of observation. The correlation coefficient between O_3 and relative humidity during winter, summer, monsoon and post-monsoon were 0.82, −0.85, −0.83 and −0.86 respectively and the correlation between O_3 and temperature in these seasons were 0.88, 0.86, 0.84 and 0.90 ($p<0.01$) respectively. Thus, it clearly indicates a direct correlation with temperature and inverse correlation with relative humidity [95]. A study from Brazil also reported a positive correlation between ambient O_3, Solar radiation and temperature whereas a negative correlation was seen between O_3 and relative humidity. However the correlation observed was weak in nature [99]. A study from Istanbul, Turkey reported a strong correlation between ambient O_3 and wind speed. Positive correlation suggests transportation of O_3 to the site [100].

2.9: Night time chemistry of tropospheric O_3

Low concentrations of tropospheric O_3 were generally observed during night time. As there is no sunlight during night time therefore the concentration of OH radical is almost zero. Rather, the nitrate radical, NO_3, another oxidant is formed by the reaction between

NO_2 and O_3. This NO_3 radical formed further reacts with NO_2 to form equilibrium with N_2O_5 [101]

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \quad (2.1)$$

$$NO_3 + NO_2 \rightleftharpoons N_2O_5 \quad (2.2)$$

A study from New Delhi, India reported the night time concentration of tropospheric O_3 to be 7 to 10 ppb throughout the year except May where the average concentrations were reported to be about 25 ppb. The titration of ambient O_3 by surface emission of NO and ground level desolation of O_3 in a facile boundary layer is considered as the main reason for the decrease in concentration of tropospheric O_3. High concentrations of night time O_3 during May was may be due to thunderstorm [102]. Another study from Dibrugarh, India reported higher concentrations of seasonally averaged tropospheric O_3 on thunderstorm days as compared to clear and cloudy days during spring and summer season. An average of approximately 3 ppb concentrations of surface O_3 was observed during clear days and during thunderstorm days a concentration of approximately 18 ppb in spring and 12 ppb in summer was observed [103]. A study from Yanbu, Saudi Arabia reported decrease in concentration of tropospheric O_3 during night time. This decrease in concentration was due to the unavailability of photochemical reactions, by utilization of O_3 by deposition and O_3 reaction with NO and NO_2 which is regarded as a sink for O_3 [90]. Another study from Dibrugarh in North-east India described rapid decrease of ambient O_3 during nighttime due to lack of solar insolation. A minimum level of less than 5 ppb was observed during night time. The concentration f O_3 was continuously loss due to NOx titration, surface deposition and absence of photolysis [87].

2.10: Ozone trends during Different festivals

Festivals like Diwali, Vishu, New Year's Eve etc have long term effects on air quality and human health. A study from a semi-urban coastal region of Kannur, south India reported increased levels of tropospheric O_3 and its precursors as well as PM_{10} due to burning of fireworks during the traditional Vishu festival of Kerala. The study reported nighttime production of ambient O_3 by the photo dissociation of NO_2 from the flash of firecrackers. Concentration of O_3 increased two folds during the festival period. The diel variation of O_3, NO_2 and PM_{10} showed an increasing trend throughout the festival days [95]. Another study during New years eve in Mexico city reported increased level of

ambient O_3 to 190 on a scale with a normal cut off level of 100 [104]. A study from New Delhi, India recorded increased concentration of surface O_3, NO_2, CO, $SO4^{2-}$ and suspended particulate matter during the Diwali festival. Ozone levels during 2006 were found to be higher than 2004 and surpassed the ambient air quality standard for three hours. The main reasons for higher concentrations of O_3 as mentioned in the study were increased Vehicular traffic, emission of ozone precursor gases from fireworks, transport of ozone and atmospheric conditions during Diwali [105]. Another study dealing with the fireworks effects on air quality during the festival of Diwali over different major cities of India reported increased concentrations of pollutants like SO_2, NO_2, PM_{10} and $PM_{2.5}$ in the ambient atmosphere.

The concentrations were found to be 2-6 times higher during the festival as large amount of firecrackers were burnt which emitted huge quantity of pollutants in the surrounding area [106]. A study carried out in Jinan and Beijing, China, during Chinese New Year, a period with intense fireworks suggested a 3–8 ppbv nighttime ozone concentration in the atmosphere. The study also reported a positive correlation of O_3 with both NO and SO_2 indicating a distinguished influence of the chemicals produced from fireworks burning in interfering with ambient ozone monitoring [107]. Another study for Delhi, India reported that burning of fireworks can lead to ambient nighttime O_3 production in the atmosphere by the colour emitting sparklers which were lit during the Diwali festival. The process involved in formation of O_3 is similar to the process induced by ultraviolet radiation in the stratosphere [108]. A study at Dumdum, India suggested an increase level of ambient O_3 concentrations before and after Diwali days. The production of O_3 was due to the bursting of crackers lit during Diwali in the absence of sunlight. During the process of burning the significant portion of the emitted light is composed of an oxidizer, a fuel, regulators and binders which have a wavelength below 240 nm which is enough to the atmospheric molecular oxygen into atomic oxygen thus leading to the formation of ambient ozone [109].

2.11: Transport of ambient O_3 and possible source regions of O_3 concentrations

Long range transport of ambient O_3 and its precursors and also the potential local and regional contributions of O_3 as well as its source directions were determined by the use of Potential source contribution function (PSCF), Concentration weighted trajectory (CWT), Conditional probability function (CPF), pollution roses and HYSPLIT air mass

trajectories. CPF and pollution roses were used to identify the possible source direction of O_3 pollution and extreme O_3 events occurring in that zone. PSCF and CWT analyses were done to indicate the possible source regions contributing to tropospheric O_3 levels in the study area. A study from two cities: Athens and Ioannina in Greece revealed the local and regional contributions of tropospheric O_3 and its source areas with the help of PSCF. CPF and pollution roses were used to specify the relationships among definite wind directions and intense O_3 events. The intense O_3 episodes in Athens were related with the impact of SSW-SW sea breeze from Saronikos Gulf because of transportation of O_3 from the city centre. Whereas in case of Ioannina, the impacts of O_3 transportation from the city centre to the sub urban monitoring site were observed to be weaker.

For Athens the possible transboundary sources of O_3 were confined over Balkan Peninsula, Greece and the Aegean Sea and PSCF hotspots were secluded over the industrialized area of Ptolemaida basin and above Thessaloniki. For Ioannina the possible regional sources of ambient O_3 were confined across northern Greece and Balkan Peninsula and PSCF hotspots were noticed over the urban area of Sofia in Bulgaria [110]. Another study from Pinnacle State Park (PSP) site in rural New York State identified the source areas directions contributing to the noticed concentrations of pollutants with the help of CPF and Source Direction Probability (SDP). No definite directionality source area was indicated by the CPF plot of O_3. In this study, the extreme pollution events emerged from the emission sources situated many hundred kilometers away from the study area which specified mid-long range transport of pollutants to the study site [111]. The influence of continental and marine origin air masses on the levels of ozone, CO, and NOy at Nainital, India were investigated by using HYSPLIT back air trajectories during spring, summer and monsoon months of the year 2011. The air masses normally circulated over continental parts of northern India during spring season before approaching the study site whereas during summer monsoon season the marine-origin air masses reach to the observation area [112]. A study at Cabaneros National Park border, Spain used back trajectories to specify the transportation of polluted air masses from remote locations. The study revealed that the source areas were mainly from the Mediterranean basin contributing to the high levels of ambient O_3 detected [113]. A study from Busan, Korea used Conditional probability function (CPF) and potential source contribution function (PSCF) analysis methods to discover the directions of local sources and to detect the potential source regions, respectively. The results of CPF and

PSCF were used to identify the major sources contributing to ozone formation at the two study areas. The CPF and PSCF results indicate the possible source areas were toward highway, express way, forest and mountains in the surrounding areas [114].

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