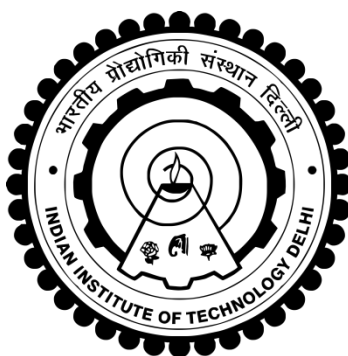


PHOTOCHEMICAL MODELLING OF GROUND LEVEL OZONE

KOMAL SHUKLA



**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
OCTOBER 2019**

© Indian Institute of Technology Delhi (IITD), New Delhi, 2019

PHOTOCHEMICAL MODELLING OF GROUND LEVEL OZONE

by

KOMAL SHUKLA

Department of Civil Engineering

Submitted

In the fulfilment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

OCTOBER 2019

Dedicated

To

The one who kept this going!

Dhara dharendra nandini vilasa bandhu bandhurasa

phuradiganta santati pramoda mana manase

Krupa kataksha dhorani nirudha durdharapadi

Kvachid digambare mano vinodametu vastuni

CERTIFICATE

This is to certify that the thesis entitled “**Photochemical modelling of ground level ozone**”, being submitted by **Ms. Komal Shukla**, to the **Indian Institute of Technology Delhi** for the award of ‘**Doctor of Philosophy**’ in Department of Civil Engineering is a record of the bonafide research work carried out by her under my supervision and guidance. She has fulfilled the requirements for the submission of this thesis, which to the best of my knowledge has reached the requisite standard.

The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any other degree or diploma.

Prof. Mukesh Khare

Department of Civil Engineering

Indian Institute of Technology Delhi

New Delhi-110016, India

ACKNOWLEDGEMENTS

I take immense pride to acknowledge the relentless support and scholarly guidance provided to me by my research supervisor, Prof. Mukesh Khare. I am extremely grateful for his valuable insights, fruitful discussions and innovative approach throughout my journey at IIT Delhi. Without his advice, experience, motivation and patience, my dream to accomplish PhD would have never come true. I specifically thank you for all the trust you had in me and the opportunities you have bestowed on me which ultimately modelled myself to what I am today. Thank you so much for everything sir! You've given me *free hand*, may it be exploring *avenues* to arrive at the solution to the problem at hand or writing a research paper, for instance, and so on; this has definitely helped me in exploiting my, hitherto unknown facets. This indeed be my real gain from my association with you, and I can say, at the end of the day, this has made me more independent and self-reliant.

I am also thankful to my SRC members, Prof. N.K. Garg, Prof. Manju Mohan and Prof. A.K. Nema for rendering me their valuable comments, encouragement and time towards my research. I would also like to thank Dr. Harsha Kota, faculty member of Environmental Engineering, for his kind support in last year. For he has patiently discussed the research problems, constantly motivated and always guided me through the best. Thank you, sir!

I would like to thank Dr. Xiaoming Cai, University of Birmingham for providing me with the opportunity to learn chemical transport models at their University. Prof. Anil Namdeo, Newcastle University, UK for providing me opportunity to be an exchange student at Newcastle University and study temperate zone pollution. A special note of gratitude to Dr. Narendra Ojha, Scientist, PRL, Ahmedabad for his technical support and giving me access to various modeling

resources and guiding me through the process. I am extremely grateful to him for fruitful discussions and for answering each one of my questions for last three years.

I would also like to express gratitude to Mr. Rajiv Sharma for his valuable support in laboratory, along with Dr. Sanjay Gupta. My sincere gratitude goes to officials working with Civil Engineering Department for their assistance.

My genuine thanks to all my PhD seniors, especially Dr. Sunil Gulia, Dr. Sumanth Chinthala, Dr. Isha Khanna and my dear colleagues Mr. Maneesh Namburath, Ms. Archana Chawla, Ms. Aparna Sharma, Mr. Shubham Sharma and Ms. Pratibha Anand. I would specially mention Mr. Shiva Kumar Gummadavlli, Mr. Sasi Kumar, Mr. Gaurav Singh Mann for listening endlessly and motivating me. Thank you for all the fun we had in institute in previous years! My close friends, Mrs. Monica Bhatt Kimothi and Mr. Furqan Saabri for keeping immense faith in me. There are many unnamed here, what goes for *whole*, also goes for *parts*. I express my thankfulness for their, at present, seemingly, implicit help!

There are names, which are closest to my heart; my parents, Mrs. Aruna Shukla and Mr. Kamlesh Shukla. It's been our journey together. I would have never reached here without them. My love to both my brothers, Mr. Rahul Shukla and Mr. Rishabh Shukla for encouraging me and selflessly celebrating with me throughout. All their support has always been and will always be crucial to my personal life as well as my career endeavors.

Komal Shukla

ABSTRACT

Photochemical air pollution has become a global problem specially in developing world. During last decade, the Indian cities are constantly reported to exceed national standards of ground level ozone, including the capital city of India, Delhi. It is located in Indo-Gangetic plain that has been routinely recording high ground level ozone concentrations. As a result, adverse impacts on human health and vegetation have been observed. Ozone formation pathway is a complex and non-linear process which forms in presence of precursors such as NO_x, NMVOCs, and CO, in presence of sunlight. Entire Indo-gangetic plain, covering Delhi, have observed high ozone mixing ratios in summer and post monsoon, as analyzed from ground (Central Pollution Control Board) and satellite observations (OMI-AURA product). Major photochemical reactions involving NMVOCs emissions (due to biomass burning) and NO_x emissions (vehicular emissions) have led to increased ozone concentrations in the city.

In the present research, the photochemistry of O₃ formation, its dependency on precursors emissions, meteorology and transport have been studied. O₃ concentrations have been analysed as a function of solar radiation, temperature, relative humidity, wind speed, boundary layer, and precursors (NO_x and NMVOCs) emissions. Analysis results show that during summers, there is prevailing titration chemistry of reactive pollutants, resulting into increased ambient O₃ concentration. The site specific meteorology is one of the prime limiting factor affecting the O₃ formation, which results into higher ozone formation despite of low NO_x emissions. The study also has concluded that photochemical air pollution in general and exclusively ground level ozone in Delhi city is a trans-boundary and climate induced phenomenon. Further, photochemical pollution in Delhi city can be related to its (a) in-situ and ex-situ emissions which include controllable and non-controllable; regulated and unregulated, accountable and non-

accountable sources (b) its geographical location and meteorology; land-locked location and advection of such air within the Delhi city which at times may be severely polluted. Flexible photochemical kinetic models (regression based), using four years (2015-2018) hourly-averaged observations for forecasting O₃, *with* and *without* the impact of meteorology for the *site specific* and *city level* have been developed. Linear regression and random forest regression models, both aided with machine learning have been developed. The RMSE observed for hourly O₃ predictions in linear regression model technique is significantly larger compared to random forest based model. Linear regression prediction model has performed unsatisfactory for both, *city level*. Random forest model has satisfactory performance at city level ($R^2=0.73$, $r=0.85$). In both the regression techniques, increased uncertainty in modelling O₃ is attributed to it being secondary pollutant and non-linear dependency on NO_x, VOCs, CO, radicals (OH and HO₂) and micro-climatic meteorological parameters. Additionally, varying diurnal pattern adds to making O₃ prediction strenuous. Importance of different variables (predictors) is also computed for O₃, which lists relative solar radiation, NO₂, wind speed and NO as best predictors respectively. Analysis of importance points out toward equal role play of precursors and meteorology in O₃ formation. The research has concluded that the *site-specific* models with meteorology of lower degree polynomial transformations performs satisfactorily. The developed models can be used to forecasts the O₃ concentrations at heavily polluted sites of Delhi city.

Further, the transport of ozone and role of NO_x and individual NMVOCs have been studied using Weather Research and Forecasting model coupled with Chemistry (WRF-Chem v3.9.1) The model considers meteorology and regional emissions of NO_x, NMVOCs, and CO as its input. Emissions from anthropogenic, biogenic, and biomass burning sources are included from the EDGAR- HTAP global emission inventory, MEGAN model and NCAR FINN inventory, respectively. Model simulations have been performed over a coarse domain covering entire north

India (12 Km x 12 km resolution), and a nested domain (4 km x 4 km), both centered over the Delhi NCR. High O₃ episodes of summer (May 2016) and aerosol loaded post- monsoon (Nov 2016) seasons have been studied. WRF-Chem successfully reproduces the spatial distribution of O₃ with enhanced mixing ratios over the entire IGP, especially over the north-western part (70 ppbv), and Delhi city during summer. It is observed that improved local meteorology and dynamics in finer resolution simulations (4km x 4km) reduce the biases in O₃ simulations. Mean O₃ over Delhi city is slightly lower (55-65 ppbv) than the surrounding regions, attributed to stronger titration through anthropogenic NO_x emissions. This is consistent with higher NO₂ over Delhi (16-18 ppbv) than those over other parts of the IGP (8 ppbv or less). Model typically overestimates the seasonal average when compared with ground-based observations but is capable of replicating the diurnal mixing ratios.

सार

विशेष रूप से विकासशील दुनिया में फोटोकैमिक वायु प्रदूषण एक वैश्विक समस्या बन गई है। पिछले एक दशक के दौरान, भारतीय शहरों को जमीनी स्तर के ओजोन के राष्ट्रीय मानकों से अधिक होने की सूचना है, जिसमें भारत की राजधानी दिल्ली भी शामिल है। यह इंडो-गंगा के मैदान में स्थित है जो नियमित रूप से उच्च जमीनी स्तर ओजोन सांद्रता की रिकॉर्डिंग कर रहा है। नतीजतन, मानव स्वास्थ्य और वनस्पति पर प्रतिकूल प्रभाव देखा गया है। ओजोन गठन मार्ग एक जटिल और गैर-रैखिक प्रक्रिया है जो धूप की उपस्थिति में नाइट्रोजन आक्साइड, गैर-मिथेनोजेनिक वीओसी और कार्बन ऑक्साइड जैसे अग्रदूतों की उपस्थिति में बनती है। दिल्ली को

आवरण करने वाले पूरे इंडो-गैंगेटिक मैदान ने गर्मियों और वर्षा ऋतु के उपरांत में उच्च ओजोन मिश्रण अनुपात का निरीक्षण किया है, जैसा कि जमीन (केंद्रीय प्रदूषण नियंत्रण बोर्ड) और उपग्रह टिप्पणियों (ओएमआई-एयूआरए उत्पाद) से विश्लेषण किया गया है। गैर-मिथेनोजेनिक वीओसी उत्सर्जन (बायोमास जलने के कारण) और नाइट्रोजन आक्साइड उत्सर्जन (वाहन उत्सर्जन) को शामिल करने वाली प्रमुख फोटोकैमिकल प्रतिक्रियाओं ने शहर में ओजोन सांद्रता को बढ़ाया है।

वर्तमान शोध में, ओजोन के गठन की फोटोकैमिस्ट्री, अग्रदूतों के उत्सर्जन, मौसम विज्ञान और परिवहन पर इसकी निर्भरता का अध्ययन किया गया है। ओजोन सांद्रता का विश्लेषण सौर विकिरण, तापमान, सापेक्षिक आर्द्रता, हवा की गति, सीमा परत और अग्रदूत (नाइट्रोजन आक्साइड और गैर-मिथेनोजेनिक वीओसी) उत्सर्जन के कार्य के रूप में किया गया है। विश्लेषण के परिणाम बताते हैं कि ग्रीष्मकाल के दौरान, प्रतिक्रियाशील प्रदूषकों के प्रचलित रसायन विज्ञान का प्रचलन है, जिसके परिणामस्वरूप परिवेश ओजोन एकाग्रता में वृद्धि हुई है। साइट विशिष्ट मौसम विज्ञान ओजोन गठन को प्रभावित करने वाले प्रमुख सीमित कारकों में से एक है, जिसके परिणामस्वरूप कम नाइट्रोजन आक्साइड उत्सर्जन के बावजूद उच्च ओजोन गठन होता है। अध्ययन ने यह भी निष्कर्ष निकाला है कि दिल्ली शहर में सामान्य और विशेष रूप

से जमीनी स्तर ओजोन में वायु रासायनिक प्रदूषण एक ट्रांस-बाउंड्री और जलवायु परिवर्तन की घटना है। इसके अलावा, दिल्ली शहर में फोटोकैमिकल प्रदूषण इसके (क) से-सीटू और एक्स-सीटू उत्सर्जन से संबंधित हो सकता है जिसमें नियंत्रणीय और गैर-नियंत्रणीय शामिल हैं; विनियमित और अनियमित, जवाबदेह और गैर जवाबदेह स्रोत (ख) इसकी भौगोलिक स्थिति और मौसम विज्ञान; भूमि बंद स्थान और दिल्ली शहर के भीतर ऐसी हवा का संवहन जो कई बार गंभीर रूप से प्रदूषित हो सकती है। लचीले फोटोकैमिक कैनेटिक मॉडल (प्रतिगमन आधारित) का उपयोग करते हुए, साइट विशिष्ट और शहर के स्तर के लिए मौसम विज्ञान के प्रभाव के बिना, ओजोन पूर्वानुमान के लिए चार साल (2015-2018) प्रति घंटा औसतन टिप्पणियों का उपयोग किया गया है।

रैखिक प्रतिगमन और यादृच्छिक वन प्रतिगमन मॉडल, दोनों मशीन सीखने के साथ सहायता प्राप्त किए गए हैं। रैखिक प्रतिगमन मॉडल तकनीक में प्रति घंटा ओजोन भविष्यवाणियों के लिए मनाया गया RMSE यादृच्छिक वन आधारित मॉडल की तुलना में काफी बड़ा है। रैखिक प्रतिगमन भविष्यवाणी मॉडल ने शहर के स्तर, दोनों के लिए असंतोषजनक प्रदर्शन किया है। रैंडम फ़ॉरेस्ट मॉडल का शहर के स्तर पर संतोषजनक प्रदर्शन ($R^2 = 0.73$, $r = 0.85$) है। दोनों प्रतिगमन तकनीकों में, मॉडलिंग ओजोन में अनिश्चितता बढ़ गई है, इसका श्रेय, नाइट्रोजन आक्साइड, गैर-मिथेनोजेनिक वीओसी, कार्बन ऑक्साइड रेडिकल (OH और HO_2) और सूक्ष्म-जलवायु उल्कापिंड मापदंडों पर द्वितीयक प्रदूषक और गैर-रेखीय निर्भरता को दिया जाता है। इसके अतिरिक्त, अलग-अलग प्रतिदिन पैटर्न ओजोन भविष्यवाणी को ज़ोरदार बनाने के लिए जोड़ता है। ओजोन के लिए अलग-अलग चर (भविष्यवाणियों) का महत्व भी गणना की जाती है, जो सापेक्ष सौर विकिरण, नाइट्रोजन डाइऑक्साइड, हवा की गति और नाइट्रोजन मोनो डाइऑक्साइड को सर्वश्रेष्ठ भविष्यवक्ता के रूप में सूचीबद्ध करता है। ओजोन गठन में अग्रदूतों और मौसम विज्ञान की समान भूमिका निभाने की दिशा में महत्वपूर्ण बिंदुओं का विश्लेषण। अनुसंधान ने निष्कर्ष निकाला है कि कम डिग्री बहुपद परिवर्तनों के मौसम विज्ञान के साथ साइट-विशिष्ट मॉडल

संतोषजनक रूप से प्रदर्शन करते हैं। विकसित मॉडल का उपयोग दिल्ली शहर के भारी प्रदूषित स्थलों पर ओजोन सांद्रता का अनुमान लगाने के लिए किया जा सकता है।

इसके अलावा, ओजोन के परिवहन और नाइट्रोजन आक्साइड और व्यक्तिगत गैर-मिथेनोजेनिक वीओसी की भूमिका का अध्ययन वेदर रिसर्च और पूर्वानुमान मॉडल का उपयोग करके किया गया है जो रसायन विज्ञान (WRF-Chem v3.9.1) के साथ मिलकर है। मॉडल मौसम विज्ञान, नाइट्रोजन आक्साइड, गैर-मिथेनोजेनिक वीओसी, और कार्बन ऑक्साइड के इनपुट के क्षेत्रीय उत्सर्जन को अपना इनपुट मानता है।। एंथ्रोपोजेनिक, बायोजेनिक, और बायोमास जल स्रोतों से उत्सर्जन क्रमशः एडगर- एचटेप वैश्विक उत्सर्जन सूची, मेगान मॉडल और एनकार - फिन सूची से शामिल हैं। मॉडल सिमुलेशन पूरे उत्तर भारत (12 किलोमीटर x 12 किमी संकल्प), और एक नेस्टेड डोमेन (4 किमी x 4 किमी) को कवर करने वाले एक मोटे डोमेन पर प्रदर्शन किया गया है, दोनों दिल्ली एनसीआर में केंद्रित हैं। गर्मियों के उच्च ओजोन एपिसोड (मई 2016) और एरोसोल से भरा वर्षा ऋतु के उपरांत (नवंबर 2016) के मौसमों का अध्ययन किया गया है। डब्ल्यूआरएफ-केम ने पूरे आईजीपी पर विशेष रूप से उत्तर-पश्चिमी भाग (70 पीपीबीवी) और गर्मियों के दौरान दिल्ली शहर में मिश्रित मिक्सिंग अनुपात के साथ ओ 3 के स्थानिक वितरण को सफलतापूर्वक पूरा किया। यह देखा गया है कि बेहतर रिज़ॉल्यूशन सिमुलेशन (4 किमी x 4 किमी) में स्थानीय मौसम विज्ञान और गतिशीलता में सुधार हुआ है, जो ओजोन सिमुलेशन में पूर्वाग्रह को कम करते हैं। दिल्ली शहर पर औसत ओजोन आसपास के क्षेत्रों की तुलना में थोड़ा कम (55-65 ppbv) है, जिसे एंथ्रोपोजेनिक एनओएक्स उत्सर्जन के माध्यम से मजबूत अनुमापन के लिए जिम्मेदार ठहराया गया है। यह दिल्ली के उच्च नाइट्रोजन डाइऑक्साइड (16-18 ppbv) के साथ संगत है, जो आईजीपी (8 पीपीपीवी या उससे कम) के अन्य भागों की तुलना में अधिक है। मॉडल आमतौर पर जमीन-आधारित टिप्पणियों के साथ तुलना करने पर मौसमी औसत को कम कर देता है, लेकिन प्रतिदिन मिश्रण अनुपात को दोहराने में सक्षम है

Table of Contents

Certificate	i
Acknowledgments	ii
Abstract	iv
Table of Contents	vii
List of Figures	x
List of Tables	xii
Table of Abbreviations	xiii
Chapter 1 Introduction	1
1.1 General background	1
1.2 Motivation for the present problem	6
1.3 Scope of the study	7
1.4 Objectives	7
1.5 Outline of the thesis	8
Chapter 2 Ground Level Ozone	10
2.1 Ozone formation	10
2.1.1 Formation of tropospheric ozone	11
2.2 Precursors of ground level ozone	16
2.3 Photochemistry of GLO	18
2.4 Environmental Standards	22
Chapter 3 Review of Relevant Literature	24
3.1 Role of NO _x in GLO formation chemistry	24
3.2 Role of VOCs in GLO formation chemistry	28
3.3 Role of radicals in GLO formation chemistry	29
3.4 Influence of meteorology in GLO formation chemistry	31
3.5 GLO monitoring	36
3.5.1 Ground based monitoring	36
3.5.2 Satellite based monitoring	40
3.6 GLO modelling	41
3.6.1 Statistical approach based photochemical kinetic models	42

3.6.2 Chemical transport models	45
A. Global CTMs	46
B. Regional CTMs	49
C. Urban CTMs	52
3.6.3 Model sensitivities: Domain resolution sensitivity	55
3.7 Research Gap	57
Chapter 4 Data Methodology and Model Description	58
4.1 Site characteristics	58
4.1.1 Delhi city	58
4.1.2 Meteorology of the site	60
4.1.2 Terrain	64
4.2 Site selection	66
4.3 Data collection	68
4.3 Methods for analysis and model building framework	68
4.3.1 Ground level ozone variations in Delhi	71
4.3.2 Formulation of photochemical kinetic model of GLO	72
A. Training and Testing	76
B. Performance Indices	76
4.3.3 Modelling GLO using WRF-Chem	77
A. Meteorological modelling	79
B. Photochemical pollutants modelling	80
Chapter 5 Result & Discussions	85
5.1 GLO formation in India	85
5.2 Ground level ozone in Delhi	92
5.2.1 Statistical behaviour	92
5.2.2 GLO dynamics with precursors and meteorology	99
5.3 Photochemical kinetic model formulation	111
5.3.1 Importance of variables in GLO formation	115
5.3.2 Developed photochemical kinetic models	116
5.4 WRF-Chem GLO simulations	117

5.4.1 Photochemical pollutant modelling	117
5.4.2. Observational datasets for validation	118
5.4.3 Result and analysis	118
A. Analysis of meteorological parameters	118
B. GLO simulations in Delhi megacity	122
5.4.4 Impact of resolution and seasonality	122
5.4.5 Peak hour GLO formation: summer and post-monsoon	130
5.4.6 Photochemical pollutants interaction in urban atmosphere: NMVOCs and NO _x	133
Chapter 6 Conclusions	139
6.1 Summary	139
6.2 GLO distribution in India	139
6.3 GLO distribution using ground observations in Delhi	140
6.4 Photochemical kinetic model (PKM) for Delhi	141
6.5 Chemical transport modelling (CTM) using WRF-CHEM	141
6.6 Contribution to the present research	143
6.7 Future scope of research	144
REFERENCES	145
Appendix I Statistical formulae used for analysing observations	187
Appendix II Emissions used in WRF-Chem	188
Curriculum Vitae	190

LIST OF FIGURES

Figure 1.1 Increase radiative forcing of GLO	2
Figure 1.2 Modelled global changes in GLO	3
Figure 2.1 Stratospheric and tropospheric O ₃ in the atmosphere	11
Figure 2.2 Formation of O ₃ in troposphere	13
Figure 2.3 Mechanism for the tropospheric O ₃ formation	15
Figure 2.4 Vehicle category-wise distribution of NO _x , VOC, and CO emissions	17
Figure 2.5 Typical modified process of GLO formation	22
Figure 3.1 GLO formation through hydrocarbon oxidation	30
Figure 3.2 Sectoral and precursors share in GLO formation in India (2010-2011)	33
Figure 3.3 Annual crop loss (Mt) due to GLO in northern India	34
Figure 3.4 Maximum observed GLO in various cities (2017)	34
Figure 3.5 Typical continuous automatic GLO monitor	37
Figure 3.6 Global O ₃ measured by OMI on 28th February 2017	40
Figure 4.1 Delhi — City map	59
Figure 4.2 Delhi's average meteorology in last ten years	62
Figure 4.3 Biomass and stubble burning in Punjab (red dots represents fires) in November 2015	64
Figure 4.4 Elevation height in meters in (a) north India covering IGP (b) and Delhi region	65
Figure 4.5 (a) Temperature and wind speed with direction in northern India (b) Delhi region	65
Figure 4.6 Sites showing hotspot sites (a)Punjabi bagh (b)Anand vihar (c)Mandir Marg (d)RK Puram	67
Figure 4.7 Research methodology framework	69
Figure 4.8 Methodology for modelling GLO using PKM and WRF-Chem	70
Figure 4.9 Model development framework for GLO	73
Figure 4.10 WRF-CHEM model	78
Figure 4.11 WRF-CHEM module and integration	79
Figure 5.1 Spatio-temporal variation in tropospheric columnar O ₃	87
Figure 5.2 Annual, summer and MDA8 GLO distribution across different Indian cities (2018)	89
Figure 5.3 : Annual probability density function of GLO	96

Figure 5.4 Seasonal probability density functions of GLO	97
Figure 5.5 Seasonal statistical distribution of GLO	98
Figure 5.6 Hotspot sites showing monitoring stations at a)RK puram b)Mandir marg c)Punjabi bagh d)Anand vihar	100
Figure 5.7 Diurnal various of GLO in different seasons at various hotspots	101
Figure 5.8 Monthly GLO variation across sites (2015-2017)	103
Figure 5.9 GLO variation with mixing height in various seasons	104
Figure 5.10 GLO variation with precursors and meteorology at RK Puram	107
Figure 5.11 GLO variation with precursors and meteorology at Mandir marg	108
Figure 5.12 GLO variation with precursors and meteorology at Punjabi bagh	109
Figure 5.13 GLO variation with precursors and meteorology at Anand vihar	110
Figure 5.14 Hourly GLO predictions using PKM (linear regression and random forest regression) build including meteorology	112
Figure 5.15 Validation of GLO prediction doing using PKMs	114
Figure 5.16 Importance of various variables (Predictors) against GLO	115
Figure 5.17 Nested domains (a)Res ₂ : 12 kmx12 km over IGP (b)Res ₁ : 4 km x4 km gridded over Delhi and nearby regions	117
Figure 5.18 WRF-Chem modelled versus observed meteorology in summer	119
Figure 5.19 Modelled diurnal meteorology (Relative Humidity and Temperature)	121
Figure 5.20 Planetary boundary layer behavior in GLO generation in different seasons	123
Figure 5.21 GLO simulation using WRF-chem at Res ₂ (12 km x 12 km gridded) in summer	125
Figure 5.22 GLO simulation using WRF-Chem at Res ₂ (12 km x 12 km gridded) in post-monsoon	126
Figure 5.23 GLO simulation using WRF-Chem at Res ₁ (4 km x 4 km gridded) in summer	127
Figure 5.24 GLO simulation using WRF-Chem at Res ₁ (4 km x 4 km gridded) in post-monsoon	128
Figure 5.25 WRF-Chem modelled GLO versus ground observations in summer	129
Figure 5.26 WRF-chem modelled GLO versus ground observations in post-monsoon	130
Figure 5.27 Peak hours modelled GLO at Res ₂ and Res ₁ in summer	131
Figure 5.28 Peak hours modelled GLO at Res ₂ and Res ₁ in post-monsoon	131
Figure 5.29 Modelled NO emissions in summer and post-monsoon	133
Figure 5.30 Modelled NO ₂ emissions in summer and post-monsoon	134

Figure 5.31 Clustered NMVOC distribution over Delhi in summer and post monsoon	135
Figure 5.32 WRF-chem GLO – NO _x – VOCs variation (different resolution and seasons)	138

LIST OF TABLES

Table 1.1 Trends of global GLO measurements	4
Table 2.1 Sources of major photo-oxidants and effects	16
Table 2.2 : Air Quality Index for GLO	22
Table 2.3 Revised NAAQS in India — 2009	23
Table 3.1 HCHO/NO ₂ ratio for GLO sensitivity	26
Table 3.2 GLO formation NO _x sensitivities	27
Table 3.3 Ground based ozone monitoring in last decade	38
Table 3.4 GLO monitored in 33 cities in 2010	38
Table 3.5 GLO variations studies in Indian cities	39
Table 3.6 GLO modelling methods	42
Table 3.7 Recent studies involving photochemical pollutants in Delhi	44
Table 3.8 Different global Tropospheric O ₃ modelling studies	47
Table 3.9 Application of WRF-CHEM in last 10 years	55
Table 3.10 Average model performance reported by different studies for various grid resolutions	57
Table 4.1 Average monthly meteorology description of Delhi city	63
Table 4.2 Selected sites in Delhi and their characteristics	67
Table 4.3 WRF-Chem Modelling physics and chemistry options	82
Table 5.1 : Anderson-Darling test for GLO	94
Table 5.2 : Seasonal best fit statistical distribution for GLO using AD test	99
Table 5.3 Performance of developed GLO models	113
Table 5.4 : Photochemical kinetic models for Delhi site and city level	116
Table 5.5 Statistical validation of modelled GLO with observations for summer	132
Table 5.6 Statistical validation of modelled GLO with observations for post-monsoon	132
Table 5.7 NMVOCs speciation and contribution in RADM2 mechanism in summer	136
Table 5.8 NMVOCs speciation and contribution in RADM2 mechanism in post-monsoon	137

ABBREVAIATIONS

ANN	Artificial Neural Network
AQI	Air Quality Index
BC	Boundary Condition
CAA	Clean Air Act
CNG	Compressed Natural Gas
CPCB	Centre Pollution Control Board
CSS	Constrained steady state
CTM	Chemical Transport Model
DU	Dobson Unit
EPA	Environmental protection Agency
GCM	Global Climate Model
GLO	Ground level Ozone
IGP	Indo-Gangetic Plain
IPCC	Intergovernmental Panel on Climate Change
MATCH	Multi-scale Atmospheric Transport and Chemistry Model
MDA8	Maximum Daily 8-hour Average
MLS	Microwave Limb Sounder
NAAQS	National Ambient Air Quality Standards
NCAR	National Centre for Atmospheric Research
NMVOC	Non-Methane Volatile Organic Carbon
OBM	Observation-based Model

OMI	Ozone Monitoring Instrument
OPE	Ozone Production Efficiency
PAN	Peroxyl Acetyl Nitrate
PBLH	Planetary Boundary Layer Height
PM₁₀	Particulate Matter with diameter less than 10 microns
PM_{2.5}	Particulate Matter with diameter less than 2.5 microns
ppb	Parts per billion
RH	Relative Humidity
RMSE	Root Mean Square Error
SCO	Stratospheric Column Ozone
TOC	Tropospheric Ozone Column
TOMS	Total Ozone Mapping Spectrometer
VCD	Vertical Column Densities
VOC	Volatile Organic Carbon
WHO	World Health Organization
WRF	Weather Research Forecasting