

**UNDERSTANDING ON THE ESTIMATION OF FOSSIL
FUEL DERIVED CO₂ OVER INDIAN REGION USING
RADIOCARBON MEASUREMENTS**

RAJVEER SHARMA



**CENTRE FOR ATMOSPHERIC SCIENCES
INDIAN INSTITUTE OF TECHNOLOGY DELHI
APRIL 2025**

© Indian Institute of Technology Delhi (IITD), New Delhi, 2025

**UNDERSTANDING ON THE ESTIMATION OF FOSSIL
FUEL DERIVED CO₂ OVER INDIAN REGION USING
RADIOCARBON MEASUREMENTS**

by

Rajveer Sharma
Centre for Atmospheric Sciences

Submitted
in fulfillment of the requirements of the degree of Doctor of Philosophy
to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI
APRIL 2025

Certificate

This is to certify that the thesis entitled “**Understanding on the estimation of Fossil Fuel derived CO₂ over Indian region using radiocarbon measurements**” being submitted by Mr. **Rajveer Sharma** for the award of the degree of **Doctor of Philosophy**, is a record of the original bonafide research work carried out by him. He has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis. The results presented in this thesis have not been submitted in part or full to any University or Institution for award of any degree/diploma.


Prof. Ravi Kumar Kunchala

Associate Professor
Centre for Atmospheric Sciences,
Indian Institute of Technology Delhi,
Hauz Khas, New Delhi-110016, India


Dr. Sundeep Chopra

Scientist H
Inter University Accelerator Centre
Aruna Asaf Ali Marg
New Delhi – 110067, India

Acknowledgments

To complete my PhD journey, I would like to express my sincere gratitude towards my supervisors, Prof. Ravi Kumar Kunchala and Dr. Sundeep Chopra, for their valuable guidance, patience, enthusiasm, constant encouragement, and immense knowledge. Prof. Ravi provided insightful suggestions and supported the development of independent thinking and research capabilities. His pleasant and polite nature made all my interactions with him fruitful for my PhD journey. Dr. Chopra provided fruitful suggestions and a research atmosphere to complete this thesis's objectives in a planned manner. He has provided me with a great environment to learn and grow at IUAC. I thank all my SRC members, Prof Manju Mohan, Prof Sagnik Dey and Prof Vamsi, for providing critical comments to improve my thesis work. I want to thank the HOC, CRC chairperson, and all the faculties at the Centre for Atmospheric Sciences (CAS), IIT Delhi, for providing the necessary help during my PhD tenure.

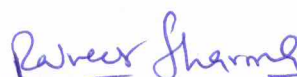
I thank the Director, IUAC for providing permission to pursue PhD. I thank my seniors, Mr. Sunil Ojha and Dr. Pankaj Kumar at IUAC for their constant support and suggestions. I also thank Mr. Satinath Gargari and other Pelletron group members for solving a lot of ion source and accelerator-related problems during this thesis work. I am also thankful to my other group members Deeksha Khandelwal, Leema Saikia, Dr. Meenakshi, Dr. Mahadev for their help in different ways during this work. I also want to sincerely thank all my colleagues, collaborators, relatives and friends who have sent plant samples from various locations across India for this thesis work. I am also thankful to all my friends from the Centre for Atmospheric Science (CAS) for making my coursework days enjoyable and providing help whenever required.

I want to express my gratitude and love to my family members (Mother, Father,

Brother, Sisters, Wife and Daughter) for their constant encouragement through this journey. My parents and Uncle (Tauji) always taught me to dream big and achieve my goals through hard work, dedication and discipline. A special thanks to my wife, Dr. Dipika Sharma, for her constant support, encouragement and patience during this journey. It was not possible to complete this work without her support. I am also thankful to my daughter, Diveera Sharma for her beautiful smile which was my stress buster during this journey.

Finally, I thank the almighty God for the passion, strength, perseverance, and resources to complete this study.

Date: 28th April 2025


Rajveer Sharma

Abstract

Atmospheric carbon dioxide (CO₂) is the most important anthropogenic greenhouse gas (GHG) responsible for recent changes in global warming and climate change. CO₂ has been rising rapidly over the globe since the industrial revolution and reached 426.8 ppm in 2024 due to an increase in anthropogenic activities and decrease in its uptake. The primary reason for this increase in CO₂ is the emission of CO₂ from the combustion of fossil fuels and anthropogenic sources. To make effective mitigation policies, precise quantification of CO₂ emissions from fossil fuels is essential. Traditionally, fossil fuel contributions are calculated based on the “bottom-up” approach in which energy statistics data and emission factors of fuels are used for the estimation of fossil fuel derived CO₂ (CO_{2ff}). This method provides reliable estimates at the national level but has significant uncertainties at regional and city scales. Another method to quantify CO_{2ff} is the “top-down” approach based on the measurements of CO₂ mole fraction in the air. However, it is challenging to identify CO_{2ff} from the CO₂ from other sources by measuring CO₂ concentration alone. An alternative method is to use radiocarbon (¹⁴C, half-life of 5730 years) measurements for this purpose. Several studies based on CO₂ observations have been reported from the Indian region, however, based on the radiocarbon-based estimations of fossil fuel derived CO₂ emissions have not been reported from the Indian subcontinent. Therefore, this thesis focuses on investigating the spatio-temporal patterns of CO₂ emissions from fossil fuel sources based on radiocarbon measurement across the Indian region.

Chapter one of the thesis describes the background on the research topic, literature review, identifying the gap areas as well as research problems followed by the objectives of the thesis. Chapter two describes atmospheric radiocarbon in detail, including its production in the atmosphere, measurement methods, associated sample preparation and data analysis. This chapter also discusses the test results of installing a silicon state barrier detector (SSBD) in the radiocarbon measurement system at Inter University Accelerator Centre (IUAC), New Delhi.

Chapter three presents a detailed analysis of the spatial distribution of fossil fuel derived CO₂ (CO_{2ff}) over India using radiocarbon ($\Delta^{14}\text{C}$) measurements using annual crop plants. For this analysis, we have collected crop plants samples from 37 locations across India. Our analysis shows that the $\Delta^{14}\text{C}$ values vary between 29.33‰ to -34.06‰ across India in 2017, where the highest value belongs to a location from Gujarat while

the lowest value belongs to a location from Chhattisgarh. The corresponding values of CO_{2ff} mole fractions are varying between 4.85 ppm and 26.59 ppm across India. Higher CO_{2ff} values are obtained for the sites from the highest coal reserve area (Chhattisgarh, Orissa and Jharkhand). The effect of sampling different plant organs on $\Delta^{14}\text{C}$ and CO_{2ff} is addressed and it is found that the sampling of grain in place of leaves (in wheat and mustard plants) can induce a difference of 2.30 ppm in CO_{2ff} values while 5.50‰ in $\Delta^{14}\text{C}$ that is larger than the measurement error in this study. Similarly, the effect of sampling different crop plants from the same season on $\Delta^{14}\text{C}$ and CO_{2ff} is also assessed. A difference of 1.76 ppm in CO_{2ff} values corresponding to the difference of 4.25‰ in $\Delta^{14}\text{C}$ values is observed for the samples collected from a location in Rajasthan which is slightly higher than the measurement error in this study.

Chapter four focuses on the spatial distribution of fossil fuel derived CO₂ across Delhi using radiocarbon measurements of Peepal tree leaves from April 2016 to March 2017 on a city scale. Our analysis results show that the $\Delta^{14}\text{C}$ values vary between -67.78 ‰ to 5.61 ‰ and corresponding CO_{2ff} values are varying from 1.63 ppm to 33.34 ppm. CO_{2ff} values from campus sites are ranging between 6.99 ppm to 16.38 ppm with an average value of 10.22 ± 3.20 ppm, while CO_{2ff} values from sites located in the parks are varying from 2.41 ppm to 33.34 ppm with an average value of 13.32 ± 9.40 ppm. Further, we observed the higher contributions of fossil fuels in the CO₂ from Northwest Delhi, Central Delhi, and some parts of east and south west Delhi.

Chapter five studied the temporal variations in $\Delta^{14}\text{C}$ and CO_{2ff} in the megacity Delhi from 2017 to 2022. We have collected atmospheric CO₂ over 2M NaOH solution at a frequency of one week from September 2017 to December 2022 at the rooftop of the AMS facility building at IUAC New Delhi. In this study, $\Delta^{14}\text{C}$ values range from 88.14 ‰ to 7.48 ‰, while the corresponding CO_{2ff} values vary from 40.26 ppm to a value close to zero ppm, respectively. A clear seasonal trend in CO_{2ff} values is observed, having higher values in post-monsoon (October – November) and winter (December – March) seasons and lower values in the Monsoon (July – September) season. Our study revealed that high CO_{2ff} values in Delhi during the winter and post-monsoon season are primarily due to atmospheric stagnant conditions characterized by lower PBLH supported by lower wind speeds while slightly ¹⁴C enriched air masses originating from the southern hemisphere during the southwest monsoon other than higher PBLH and high wind speed are leading to lower CO_{2ff} values in the monsoon season. We have also determined the emission ratios R_{CO} and R_{NOx} for Delhi city which

are 38.74 ± 1.88 ppb/ppm ($r^2 = 0.35$) and 2.11 ± 0.13 ppb/ppm ($r^2 = 0.51$), respectively for the period 2018 - 2022. R_{CO} values are higher than most of the other cities in the world while R_{NOx} values are similar to those of Paris. High R_{CO} values in Delhi indicate poor combustion efficiency contributions from biomass burning and reflect the high CO emissions in the South Asian cities. This chapter also presents an analysis on the effect of restrictions on CO_{2ff} values during the first and second waves of COVID-19. Our study reveals a decrease of 5.60 ppm during the 2020 lockdown, while a reduction of 4.75 ppm during the 2021 lockdown compared to a similar period in 2022 (no restrictions). Chapter six summarizes the findings of the present thesis. In addition, it provides future directions for the present research area in the Indian region.

Keywords: Carbon dioxide, Fossil Fuels, Radiocarbon, Accelerator Mass Spectrometry, Indian region

सारांश

वायुमंडलीय कार्बन डाइऑक्साइड (CO_2) को ग्लोबल वार्मिंग और जलवायु परिवर्तन के लिए जिम्मेदार सबसे महत्वपूर्ण मानवजनित ग्रीनहाउस गैस (GHG) के रूप में पहचाना गया है। औद्योगिक क्रांति के बाद से दुनिया भर में CO_2 तेजी से बढ़ रही है और मानवजनित गतिविधियों में वृद्धि के कारण 2024 में 426.8 पीपीएम तक पहुंच गई। CO_2 में इस वृद्धि का प्राथमिक कारण जीवाश्म ईंधन का दहन तथा इसके अवशोषण में कमी है। प्रभावी शमन नीतियां बनाने के लिए, जीवाश्म ईंधन से CO_2 उत्सर्जन की सटीक मात्रा का निर्धारण आवश्यक है। परंपरागत रूप से, जीवाश्म ईंधन योगदान की गणना "बॉटम-अप" विधि के आधार पर की जाती है जिसमें ऊर्जा सांख्यिकी डेटा और ईंधन के उत्सर्जन कारकों का उपयोग जीवाश्म ईंधन से प्राप्त CO_2 ($\text{CO}_{2\text{ff}}$) के अनुमान के लिए किया जाता है। यह पद्धति राष्ट्रीय स्तर पर विश्वसनीय अनुमान प्रदान करती है लेकिन क्षेत्रीय और शहर के पैमाने पर इसमें बहुत अनिश्चितताएँ हैं। $\text{CO}_{2\text{ff}}$ को मापने का एक अन्य तरीका हवा में CO_2 की मात्रा पर आधारित "टॉप-डाउन" विधि है। हालाँकि, अकेले CO_2 के मापन से अन्य स्रोतों से $\text{CO}_{2\text{ff}}$ सिग्नल को अलग करना चुनौतीपूर्ण है। इस उद्देश्य के लिए रेडियोकार्बन (^{14}C , 5730 वर्ष की अर्ध आयु) का उपयोग करना एक वैकल्पिक तरीका है। भारतीय क्षेत्र से कई CO_2 अवलोकन अध्ययन रिपोर्ट किए गए हैं, लेकिन जीवाश्म ईंधन CO_2 अनुमानों के रेडियोकार्बन-आधारित अध्ययन भारतीय उपमहाद्वीप से रिपोर्ट नहीं किए गए हैं। इसलिए, यह थीसिस पूरे भारतीय क्षेत्र में रेडियोकार्बन मापन के आधार पर जीवाश्म ईंधन स्रोतों से CO_2 उत्सर्जन के स्थानिक-कालिक पैटर्न की जांच पर केंद्रित है।

थीसिस का अध्याय एक शोध विषय की पृष्ठभूमि, साहित्य समीक्षा, अंतराल क्षेत्रों और अनुसंधान समस्याओं की पहचान के बाद थीसिस के उद्देश्यों का वर्णन करता है। द्वितीय अध्याय में रेडियोकार्बन का विस्तार से वर्णन किया गया है, जिसमें वायुमंडल में इसका बनना, मापन के तरीके, संबंधित नमूना तैयार करना और डेटा विश्लेषण शामिल है। यह अध्याय IUAC में रेडियोकार्बन मापन यन्त्र में एक सिलिकॉन स्टेट बैरियर डिटेक्टर (SSBD) स्थापित करने के परीक्षण परिणामों पर भी चर्चा करता है।

तृतीय अध्याय फसल पौधों में रेडियोकार्बन ($\Delta^{14}\text{C}$) माप का उपयोग करके भारत में जीवाश्म ईंधन से प्राप्त CO_2 ($\text{CO}_{2\text{ff}}$) के स्थानिक वितरण का विस्तृत विश्लेषण प्रस्तुत करता है। हमने पूरे भारत में 37 स्थानों से फसल पौधे एकत्र किए हैं। हमारे विश्लेषण से पता चलता है कि 2017 में पूरे भारत में $\Delta^{14}\text{C}$ मान 29.33‰ से -34.06‰ के बीच परिवर्तनीय है, जहां उच्चतम मूल्य गुजरात के एक स्थान से संबंधित है, जबकि सबसे कम मूल्य छत्तीसगढ़ के एक स्थान से संबंधित है। पूरे

भारत में CO_{2ff} मोल अंशों का संगत मान 4.85 पीपीएम और 26.59 पीपीएम के बीच परिवर्तनीय है। उच्चतम कोयला आरक्षित क्षेत्र (छत्तीसगढ़, उड़ीसा और झारखंड) के साइटों से CO_{2ff} मान प्राप्त किए जाते हैं। $\Delta^{14}\text{C}$ और CO_{2ff} पर विभिन्न पौधों के अंगों को नमूनों की तरह उपयोग करने के प्रभाव को संबोधित किया गया है और यह पाया गया है कि पत्तियों के स्थान पर अनाज का नमूना (गेहूं और सरसों के पौधों में) उपयोग करने पर CO_{2ff} मूल्यों में 2.30 पीपीएम का अंतर पैदा कर सकता है जबकि $\Delta^{14}\text{C}$ में 5.50‰ का अंतर हो सकता है। यह अंतर मापन त्रुटि से भी बड़ा है। इसी प्रकार, एक ही मौसम से विभिन्न फसल पौधों के नमूने का $\Delta^{14}\text{C}$ और CO_{2ff} पर प्रभाव का भी आकलन किया गया है। राजस्थान में एक स्थान से एकत्र किए गए नमूनों में $\Delta^{14}\text{C}$ मूल्यों में 4.25‰ तथा CO_{2ff} मूल्यों में 1.76 पीपीएम का अंतर देखा गया है, जो इस अध्ययन में मापन त्रुटि से थोड़ा अधिक है।

चतुर्थ अध्याय शहर के स्तर पर अप्रैल 2016 से मार्च 2017 तक पीपल के पेड़ के पत्तों में रेडियोकार्बन मान का उपयोग करके दिल्ली भर में जीवाश्म ईंधन से प्राप्त CO₂ के स्थानिक वितरण पर केंद्रित है। हमारे विश्लेषण के परिणाम बताते हैं कि $\Delta^{14}\text{C}$ का मान -67.78 ‰ से 5.61 ‰ के बीच परिवर्तनीय है और संबंधित CO_{2ff} का मान 1.63 पीपीएम से 33.34 पीपीएम तक परिवर्तनीय है। कैपस साइटों से CO_{2ff} का मान 6.99 पीपीएम से 16.38 पीपीएम के बीच है, जिसका औसत मान 10.22 ± 3.20 पीपीएम है, जबकि पार्कों में स्थित साइटों से CO_{2ff} का मान 2.41 पीपीएम से 33.34 पीपीएम तक है, जिसका औसत मान 13.32 ± 9.40 पीपीएम है। इसके अलावा, हमने उत्तर पश्चिमी दिल्ली, मध्य दिल्ली और पूर्व और दक्षिण पश्चिम दिल्ली के कुछ हिस्सों में CO₂ में जीवाश्म ईंधन के उच्च योगदान को भी पाया है।

अध्याय पांच में 2017 से 2022 तक मेगासिटी दिल्ली में $\Delta^{14}\text{C}$ और CO_{2ff} में कालिक बदलाव का वर्णन किया गया है। हमने IUAC नई दिल्ली में AMS यन्त्र भवन की छत पर सितंबर 2017 से दिसंबर 2022 तक एक सप्ताह की आवृत्ति पर 2M NaOH विलयन में वायुमंडलीय CO₂ एकत्र किया है। इस अध्ययन में, $\Delta^{14}\text{C}$ का मान 88.14 ‰ से 7.48 ‰ तक है, जबकि संबंधित CO_{2ff} का मान क्रमशः 40.26 पीपीएम से लेकर शून्य पीपीएम के करीब मान तक परिवर्तनीय है। CO_{2ff} मूल्यों में एक स्पष्ट मौसमी प्रवृत्ति देखी गई है, जिसका मान मानसून के बाद के महीनों (अक्टूबर-नवंबर) और सर्दी (दिसंबर-मार्च) के मौसम में अधिक है और मानसून (जुलाई-सितंबर) के मौसम में कम है।

हमारे अध्ययन से पता चला है कि सर्दियों और मानसून के बाद के महीनों के दौरान दिल्ली में CO_{2ff} का उच्च मान मुख्य रूप से वायुमंडलीय स्थिर स्थितियों के कारण होते हैं, जो कम हवा की

गति द्वारा समर्थित कम PBLH द्वारा उत्पन्न होती हैं, जबकि दक्षिण-पश्चिम मानसून के अलावा दक्षिणी गोलार्ध से निकलने वाली थोड़ी ^{14}C समृद्ध वायु भी इसे प्रभावित करती है। उच्च पीपीएलएच और उच्च हवा की गति के कारण मानसून के मौसम में $\text{CO}_{2\text{ff}}$ मान कम पाए गए हैं। हमने दिल्ली शहर के लिए उत्सर्जन अनुपात R_{CO} और R_{NO_x} भी निर्धारित किया है जो 2018 - 2022 की अवधि के लिए क्रमशः 38.74 ± 1.88 पीपीबी/पीपीएम ($r^2 = 0.35$) और 2.11 ± 0.13 पीपीबी/पीपीएम ($r^2 = 0.51$) हैं। R_{CO} का मान दुनिया के अधिकांश अन्य शहरों की तुलना में अधिक है जबकि R_{NO_x} मान पेरिस के मान के लगभग समान हैं। दिल्ली में उच्च R_{CO} मान बायोमास जलने और खराब दहन दक्षता के योगदान का संकेत देते हैं और दक्षिण एशियाई शहरों में उच्च सीओ उत्सर्जन को दर्शाते हैं। यह अध्याय COVID-19 की पहली और दूसरी लहर के दौरान $\text{CO}_{2\text{ff}}$ के मान पर प्रतिबंधों के प्रभाव का विश्लेषण भी प्रस्तुत करता है। हमारे अध्ययन से पता चलता है कि 2020 के लॉकडाउन के दौरान 5.60 पीपीएम की कमी हुई, जबकि 2022 की समान अवधि की तुलना में 2021 के लॉकडाउन के दौरान 4.75 पीपीएम की कमी हुई (जब कोई प्रतिबंध नहीं थे)। अध्याय छह वर्तमान थीसिस के निष्कर्षों का सारांश प्रस्तुत करता है। इसके अलावा, यह भारतीय क्षेत्र में प्रस्तुत अनुसंधान क्षेत्र के लिए भविष्य की दिशाएं प्रदान करता है।

संकेतशब्द: कार्बन डाइऑक्साइड, जीवाश्म ईंधन, रेडियोकार्बन, एक्सेलेरेटर मास स्पेक्ट्रोमेट्री, भारतीय क्षेत्र

Contents

Certificate.....	i
Acknowledgements.....	ii
Abstract.....	iv
Hindi Abstract.....	vii
Contents.....	x
List of Figures.....	xiv
List of Tables.....	xvii
Chapter 1: Introduction.....	1
1. Introduction.....	2
1.1 Carbon dioxide and global carbon cycle.....	2
1.2 Estimation of fossil fuel CO ₂ (CO _{2ff}).....	6
1.3 Radiocarbon as a tracer for CO _{2ff} emissions.....	7
1.4 Literature Review.....	9
1.4.1 Radiocarbon based CO _{2ff} estimation studies reported worldwide.....	9
1.4.2 Literature and recent studies on CO _{2ff} estimation studies in India.....	14
1.4.3 CO _{2ff} estimation studies in Indian cities and urban areas.....	15
1.5 Scope of this thesis and research objectives.....	16
1.5.1 Objectives of the thesis.....	17
1.5.2 Thesis organization.....	17
Chapter 2: Radiocarbon sample preparation, measurements and data analysis techniques.....	20
2.1 Introduction.....	21
2.2 Radiocarbon measurement using AMS.....	22
2.3 Sample preparation.....	23

2.3.1 Sample pretreatment.....	23
2.3.2 Graphitization.....	24
2.3.3 Sample combustion using elemental analyzer (EA).....	25
2.3.4 Acid hydrolysis using carbonate handling system (CHS).....	28
2.3.5 Automated Graphitization Equipment (AGE).....	30
2.4 Radiocarbon measurements.....	32
2.4.1 AMS system description.....	32
2.4.2 Measurement protocol and data reduction.....	35
2.5 Test results of insertable silicon state detector (SSBD).....	41

Chapter 3: Spatial distribution of fossil fuel CO₂ (CO_{2ff}) over India using radiocarbon ($\Delta^{14}\text{C}$) measurements in crop plants.....42

3.1 Introduction.....	43
3.2 Material and Methods.....	43
3.2.1 Sampling locations and sample collection.....	43
3.2.2 Sample pretreatment, graphitization and radiocarbon measurement.....	44
3.2.3 Calculation of $\Delta^{14}\text{C}$	45
3.2.4 Calculation of CO _{2ff}	46
3.2.5 Selection of background values.....	47
3.3 Results and Discussion.....	48
3.3.1 Spatial distribution of $\Delta^{14}\text{C}$ over India.....	48
3.3.2 Spatial distribution of CO _{2ff} over India.....	51
3.3.3 Effect of sampling different plant organs on $\Delta^{14}\text{C}$ and CO _{2ff}	55
3.3.4 Effect of sampling different crop plants grown in same season.....	58
3.3.5 Annual and intra seasonal variations in $\Delta^{14}\text{C}$ and CO _{2ff} values.....	61
3.4 Summary and conclusions.....	65

Chapter 4: Spatial distribution of fossil fuel CO₂ (CO_{2ff}) across megacity Delhi using atmospheric ^{14}C measurements.....71

4.1 Introduction.....	72
4.2 Material and Methods.....	72
4.2.1 Study Area.....	72

4.2.2 Sampling sites and sample collection.....	73
4.2.3 Sample pretreatment, graphitization and radiocarbon measurements.....	74
4.2.4 Calculation of $\Delta^{14}\text{C}$ and $\text{CO}_{2\text{ff}}$	76
4.2.5 Selection of background site.....	78
4.3 Results and Discussion.....	78
4.3.1 Spatial distribution of $\Delta^{14}\text{C}$ across megacity Delhi.....	78
4.3.2 Spatial distribution of $\text{CO}_{2\text{ff}}$ across megacity Delhi.....	79
4.4 Summary and Conclusions.....	82
 Chapter 5: Temporal variations of $\Delta^{14}\text{C}$ and $\text{CO}_{2\text{ff}}$ mole fractions in megacity Delhi.....	86
5.1 Introduction.....	87
5.2 Material and Methods.....	88
5.2.1 Study Area.....	88
5.2.2 Sampling site and sample collection.....	89
5.2.3 Sample graphitization.....	90
5.2.4 Radiocarbon Measurements.....	91
5.2.5 $\text{CO}_{2\text{ff}}$ calculation.....	92
5.2.6 Background selection.....	93
5.2.7 Data used in this study.....	94
5.2.8 Footprint analysis.....	95
5.2.9 R_{CO} and R_{NO_x} determination.....	96
5.3 Results.....	97
5.3.1 Annual and seasonal variations of fossil fuel CO_2	97
5.3.2 Emission Ratios (R_{CO} and R_{NO_x}).....	104
5.3.3 Effect of COVID-19 restrictions.....	108
5.4 Discussion.....	111
5.5 Summary and conclusions.....	114
 Chapter 6: Summary and future Scope/directions.....	119
6.1 Summary.....	120
6.2 Future Directions/Scope.....	123

References.....	125
Publications.....	148
Brief Biodata.....	150

List of Figures

Figure captions	Page No.
Figure 1.1 Carbon distribution in the different reservoirs of the earth system in the pre-industrialization period. Black numbers are shown in Petagram carbon Pg C) while red numbers represent the fraction (%) of the total carbon in the particular pool. Figure is adopted from Turnbull et. al., 2016a.	3
Figure 1.2 Incoming and outgoing carbon flux in the earth system reservoir since industrialization. Red numbers are showing flux due to anthropogenic activities and black numbers are showing natural flux. Figure is adopted from Turnbull et. al., 2016a.	4
Figure 1.3 Spatial distribution of $\Delta^{14}\text{C}$ (‰) across North America determined in maize leaves in 2004. Figure is adopted from Hsueh et al., 2007.	10
Figure 1.4 Observation of (A) $\Delta^{14}\text{CO}_2$ and (B) $\text{CO}_{2\text{ff}}$ in Beijing (red) and Xiamen (green) during 2014. W in the name of month stands for weekend and N stands for non-weekend. Figure is adopted from Niu et. al., 2016b.	12
Figure 2.1 Graphitization laboratory at IUAC equipped with three AGE system coupled with three elemental analyser (EA) and one carbonate handling system (CHS)	26
Figure 2.2 Closer view of AGE system with EA	27
Figure 2.3 Schematic for the combustion of samples in Elemental Analyzer (EA)	27
Figure 2.4 Carbonate handling system (CHS) at IUAC	29
Figure 2.5 Steps involved in the acid hydrolysis using carbonate handling system (CHS)	29
Figure 2.6 Steps involved in the graphitization using automated graphitization equipment (AGE)	30
Figure 2.7 (a) Electric cathode press for loading graphite into target holder (b) Target holder for graphite (c) Cathode wheel of 134 MC SNICS	32
Figure 2.8 (a) XCAMS at IUAC (b) Newly installed SSBD along with electrostatic quadrupole (EQ), magnetic steerer (MS) located between ESA and 45° bending magnet	34
Figure 2.9 Steps involved in radiocarbon measurements using XCAMS at IUAC	37
Figure 2.10 Steps for data reduction and analysis for ^{14}C measurements	38

Figure 3.1 (a) Spatial distribution of $\Delta^{14}\text{C}$ for the year 2017 across India. Geostatistical Analyst tools in ESRI's ArcMap software were used for mapping. An Inverse Distance Weighted (IDW) method was used as an interpolation method.	49 - 50
Figure 3.1 (b) Spatial distribution of $\text{CO}_{2\text{ff}}$ for the year 2017 across India.	52 - 53
Figure 3.2 (a) Variation in $\Delta^{14}\text{C}$ values for the study period from single location (Dholpur, Rajasthan) (b) Corresponding variations in $\text{CO}_{2\text{ff}}$ mole fractions from the same location.	62
Figure 3.3 (a) $\Delta^{14}\text{C}$ values of wheat and mustard samples on different growing stages from single season (b) Corresponding $\text{CO}_{2\text{ff}}$ values with their sampling dates.	64
Figure 4.1 Study area and sampling locations	75
Figure 4.2 Spatial distributions of $\Delta^{14}\text{C}$ and $\text{CO}_{2\text{ff}}$ across megacity Delhi. Other legends of this figure are the same as Figure 4.1.	80
Figure 5.1 Sampling location and site. Red arrow show the rooftop of AMS building at IUAC New Delhi	90
Figure 5.2 Time series of (a) $\Delta^{14}\text{C}$, (b) $\text{CO}_{2\text{ff}}$, (c) wind speed (WS), (d) PBLH in megacity Delhi from September 2017 to December 2022. Fossil fuel emissions of Delhi city from January 2020 to December 2022 are plotted in panel (e). Pink and gray shaded areas show the first and second COVID-19 waves.	98
Figure 5.3 Monthly means of (a) $\Delta^{14}\text{C}$ and (b) $\text{CO}_{2\text{ff}}$ over the period of 2017 – 2022	99
Figure 5.4 Representatives of footprints for direction (a) North West (NW) (b) South West (SW) (c) South East (SE) (d) Mixed, NW via SW, SE. Details of footprint analysis are given in method section 3.8.	101
Figure 5.4 (e) Wind rose plot in the winter season showing wind speeds (WS) and wind directions.	102
Figure 5.5 Distribution of total emissions in winter (W) + post monsoon (PM) seasons and summer (S) + monsoon (M) seasons from 2020 to 2022.	103
Figure 5.6(a) Regression plots for CO_{enh} and $\text{CO}_{2\text{ff}}$ with uncertainties in both the variables for all data (2018 – 2022) and winter season. Slope of the best-fit line (blue in colour) represent ratio R_{CO}	105
Figure 5.6(b) Same as Fig. 5.6(a) for Post Monsoon and summer season	106

Figure 5.7(a) Regression plots for NO _x and CO _{2ff} with uncertainties in both the variables for all data (2018 – 2022) and winter season. Slope of the best-fit line (blue in colour) represent ratio R _{NO_x}	107
Figure 5.7(b) Same as Figure 5.7(a) for Post Monsoon and summer season	108
Fig. 5.8 Comparison of $\Delta^{14}\text{C}$ and CO _{2ff} values of samples collected during COVID-19 (a & b) first-wave restrictions and (c & d) second-wave restrictions with the same period in 2022 when there were no restrictions.	110

List of Tables

Table captions	Page No.
Table 2.1 Measurement of standard samples using SSBD in XCAMS	41
Table 3.1 A comparison of the results from similar studies around the world	54-55
Table 3.2 $\Delta^{14}\text{C}$ values of different plant organs from 8 locations	56-57
Table 3.3 $\Delta^{14}\text{C}$ values of different plants grown in same season	60
Table 3.4 List of locations of sampling with sampling year, latitude, longitude and elevation, measured $\Delta^{14}\text{C}$ values, associated uncertainty, adjusted $\Delta^{14}\text{C}$ values to 2017, used $\text{CO}_{2\text{bg}}$ values and calculated $\text{CO}_{2\text{ff}}$ values	67-70
Table 4.1 Comparison from other similar studies	81
Table 4.2 List of locations of samples with sampling year, latitude, longitude, measured $\Delta^{14}\text{C}$ values, associated uncertainty, adjusted $\Delta^{14}\text{C}$ values to 2017, and calculated $\text{CO}_{2\text{ff}}$ values	83-85
Table 5.1 R_{CO} and R_{NOx} values in Delhi	105
Table 5.2 $\Delta^{14}\text{C}$ and $\text{CO}_{2\text{ff}}$ data of individual samples along with their corresponding uncertainties	115-118