Carbonaceous Species in Atmospheric Aerosols: Sources and Temporal Variability

A THESIS

submitted for the Award of Ph. D. degree of

MOHANLAL SUKHADIA UNIVERSITY

in the

Faculty of Science

By

Kirpa Ram

Under the Supervision of

PROFESSOR M. M. Sarin
SENIOR PROFESSOR

Physical Research Laboratory,
Ahmedabad-380 009, India.

MOHANLAL SUKHADIA UNIVERSITY
UDAIPUR

2010

D E C L A R A T I O N

I Mr. **Kirpa Ram**, S/o: Mr. **Ram Raj**, resident of **A-1, PRL residences, Navrangpura, Ahmedabad – 380 009**, hereby declare that the research work incorporated in the present thesis entitled "**Carbonaceous Species in Atmospheric Aerosols: Sources and Temporal Variability**" is my own work and is original. This work (in part or in full) has not been submitted to any University for the award of a Degree or a Diploma. I have properly acknowledged the material collected from secondary sources wherever required. I solely own the responsibility for the originality of the entire content.

Date: (Kirpa Ram)

C E R T I F I C A T E

I feel great pleasure in certifying the thesis entitled "**Carbonaceous Species in Atmospheric Aerosols: Sources and Temporal Variability**" by Kirpa Ram under my guidance. He has completed the following requirements as per Ph.D. regulations of the University

(a) Course work as per the university rules.

(b) Residential requirements of the university

(c) Regularly submitted six monthly progress report

(d) Presented his work in the departmental committee

(e) Published/accepted minimum of one research paper in a referred research journal.

I am satisfied with the analysis of data, interpretation of results and conclusions drawn.

I recommend the submission of thesis.

Date: 2010 Name and Designation of supervisor

Countersigned by
Head of the Department

To my Grand parents

&

Sister Anjani

Acknowledgements

After spending the most valuable five years of my life and remembering those sweet and eventful years at the Physical Research Laboratory (PRL), Ahmedabad, India; I realize that there are many without whom this thesis would not have been a reality. To me, this thesis is by far the most challenging and significant scientific accomplishment in my career. With deep sense of gratitude and respect, I wish to express my sincere thanks and appreciation to my thesis supervisor, Prof. M.M. Sarin – a person who believes in the perfection, for introducing me to the field of Atmospheric Chemistry. His enthusiasm, integral view of handling a research project, timely planning and his mission for providing "high quality research with great perfection", has taught me very important lesson of life. His constant and enormous support, inspiration and encouragement throughout my Ph. D. period have helped to bring out the best from me in the form a thesis. He is an immense source of inspiration and I am extremely grateful to him for providing me this opportunity. I am greatly indebt to him in making me what I am today.

I thank Prof. J. N. Goswami, the Director, and Prof. Utpal Sarkar, the Dean, Physical Research Laboratory, for providing me all the necessary facilities to carry out my thesis work.

I would like to thank Prof. S. Krishnaswami who inspired me to do good work and keeping me awake all the time. It was a great opportunity and privilege for me to work in the foundation made by him. The scientific discussions with him were simply outstanding and amazing which helped me to bring out the best from me. I am extremely benefited by his class, ways of expression and talking, and am highly indebt to him for the encouragement provided to me during my research tenure at PRL, both professional and personal.

The course work taught by Profs. J. N. Goswami, M.M. Sarin, R. Ramesh, A. K. Singhvi, S.K. Bhattacharya, S.A. Haider, Drs. S.K Singh, J.S. Ray and D. Benargee during the first year at PRL was extraordinary and knowledgeable. This course work has provided an overview of the use of various tools and techniques which I use to read in text books in my early education. I wish to thank all of them for the excellent and outstanding course taught to me at PRL in the various fields' of fundamental research.

The suggestions from the core scientific committee of PRL, constituting Profs. S. Rindani, R. Ramesh, S.A. Haider, Drs. S. Ramachandran, D.A. Angom Singh and D. Benargee were always helpful. I specially thank Prof. Shyam Lal, Dr. S. Ramachandran and Dr. B. Bapat for the scientific discussion at various stages of my research work. I thank Dr. P. Sharma for the help provided in the early time of my stay at PRL.

My research journey at PRL started with a project carried out under the supervision of Dr. Sunil K. Singh during the course work. I am extremely benefited by this project and learnt the basics of chemistry and experiments. With great respect and gratitude, I thank Dr. S.K. Singh for providing me an excellent opportunity. I can not forget to thank Dr. Ravi Bhushan (Ravi Daa) – a friend, philosopher, and a person with great sense of humanality whom you can always trust. He can always find time to talk to you and always ready to help. I am extremely thankful to him for

the help, care and support provided to me in the Laboratory. I wish to thank Dr. R. Rengarajan and Mr. A.K. Sudheer for helping me in doing the experimental work during my early time. The scientific discussion and advices from them were very helpful. To run a good laboratory, one would always wish to have a person like Mr. J. P. Bhavsar (Bhavsar Bhai). Whatever scientific material/equipment you look for in the Laboratory, you should first ask Bhavsar Bhai. I thank Bhavsar Bhai for his help and support. My special thanks to all the members of our atmospheric research group (Ashwini, Timmy, Prashant and Srinivas). I wish to thank my closest friends (Gyana, Rahaman, Vineet, Jayati and Pal) for their help and support in the Laboratory. Thanks to Ms. Sneha Acharya for the help in computer related work. I thank Mrs. Pauline Josheph for all the help, care and support provided to me. I thank all the family members of the Chemistry group for a nice and comfortable company during trips of holidays. I specially thank Mrs. Renu Singh and Mr. Markandeya for inviting us at all the festivals and happy occasions and providing a homely environment.

I thank all the faculties, scientists and staff members of the Geosciences Division. My special thanks to Profs. A.K. Shinghavi, R. Ramesh, S. K. Bhattacharya, S.V.S. Murty, Drs. M.G. Yadava, Kuljeet Kaur, Vinay K. Rai, Navin Juyal, A.D. Shulkla, Som K. Shrama, K. Rao and R.D. Deshpande for their help and kind support during my stay at PRL. I must thank Pranav Bhai, Deepak Panda, T.A. Rajesh, T.K. Sunil Kumar, Venkat Ji, Manan and Lakhan bhai for helping in instrumental related problems.

The time spent at PRL hostel with my closed friends will be an unforgettable moment of my life. I must thank all of my seniors (Drs. Rohit Srivastava, Shreyas Managave, Ritesh K. Mishra, P. Morthekai, Sanat Das, Uma Kota, Rajesh Kushwaha, Salman Silotri, Jayant, H. Zeen Devi and A. S. Maurya), my batch-mates (Gyana, Naveen, Sumita, Alok, Bhavik, Vishal, Harnider, Manan, Sumanta, Shuchita, Lokesh, Brejesh, Sanjeev, Ram, Rohan and Arvind) and junior-mates (Rohit, Amjad, Naveen Chauhan, Rabiul, Neeraj, Ashish, Tapas, Sunil, Arun, Surichi, Moumita, Arvind Suxena, Chinmay, Iman, Patra, Suman, Ashok, Praveen, Anand, Sandeep, Srikant, Soumya, Subrata, Suratna, Vimal, Yogita, Zulfikar and Arvind Rajpurohit). It was a great pleasure for me to have seniors and friends like you all. Thank you all my dear friends for making my stay very pleasant at PRL. The discussions at tea-time were always awesome and one would not like to miss tea-time at PRL.

I was inspired by the good quality of research work done by our seniors. I thank Drs. N. Rastogi, D. Ganguly, A. Mishra, L. Sahu, R. K. Mishra, Ashutosh K. Singh, Santosh K. Rai. My special thank to Dr. N. Rastogi who taught me a lot on the experimental techniques before he left PRL. The scientific discussions with Drs. D. Ganguly, L. Sahu and A. Mishra were always fruitful and I learned a lot from them.

I take this opportunity to thank all the members of PRL work shop. I specially thank Mr. G.P. Ublae, Vishnu Patel, Bankim, Jayanti bhai for the help and fulfilling the requirement to carry out my research work at various stages. I must thank Jitu Bhai, Rakesh, Jokhakar Ji, Sivadasan Ji and all the members of electric sections for their help and support. I thank all the members of the

administration department for their help and support for admin related works. My special thanks to Deekshitullu Ji, Ghanshyam Bhai, Ranganathan Ji, Bhupendra Ji, Senthil Bhai, Pradeep, Hemal Bhai, Mrs. Nandini Rao, Usha Ji for their help and support at various levels.

I must thank all the members of the Computer center, Subedar and Dolakia Ji, Tejas, Jigar, Alok, Mishra Ji and Kailash for the help in computer related problems. The help from Mrs. Nishtha A. Kumar, Uma Ji, Thakore Bhai and all the supporting staffs of PRL library is thankfully acknowledged.

I am glad to acknowledge Dr. S.N. Tripathi and his group members (Sanjay Baxala, Jai Devi, Sumit Misra, Harish Ji and Hari Shanker) and for the help provided in the collection of aerosol samples at Kanpur. The discussions with Dr. Tripathi were always fruitful. Thanks to Dr. P. Hegde for help in the aerosol sample collection at Manora Peak and providing the meteorological data of the study period.

With great respect and gratitude, I wish to thank all the faculties, scientists, staff members and the students of PRL, whose names are missing, for their love, care and support provided during my stay at PRL.

My journey at PRL was very eventful and was often falling sick at regular intervals. I wish to thank our PRL medical doctors, Dr. (Mrs.) Sheetal Patel and Dr. Sameer Dani, and staff members who kept me in good health.

I am highly indebted to my parents (Shree Ram Raj and Smt. Shanti Devi) and grand parents, who always have been a source of inspiration and motivation to me. They never let me down throughout my study period and taught me the real meaning of hard work and honesty by setting up their own examples. I dedicate this thesis to my grand parents, who left us in my early days of education. I thank to my elder sisters (Late Smt. Anjani and Smt. Laxmi) and brothers (Prashant and Shushant) for their love, care and support in my life. I would like to share this moment of achievement and happiness with my entire family, friends (Jainendra, Anil, Sunil, Navneet, Gaya, Vimlendra, Shekhar, Ashok, Shravan and Shailesh) and closed members.

I am grateful to my wife Preeti and son, Hrithivk for their moral support and patience provided to me throughout the research work. I remember the days when I have to work late night in the Laboratory but it was a great support from them without any complaint. Without their support, care and understanding it would have been impossible to complete my research work. I hope they will continue their encouragement and support in the same way in future too.

In the last, I thank all the persons who have, directly or indirectly, helped me during my Ph. D. Thesis.

Kirpa Ram

ABSTRACT

This thesis presents a comprehensive study of the chemical and optical properties of ambient aerosols (with emphasis on carbonaceous species) collected from high-altitude sites (Manora Peak and Mt Abu) and an urban location (Kanpur) in the Indo-Gangetic Plain (IGP). The mass concentrations of OC, EC and WSOC at an urban site are an order of magnitude higher than those at the high-altitude sites. The source variability, emission strength, secondary aerosol formation and boundary layer dynamics, all contribute significantly to the seasonal trend in the mass concentrations of carbonaceous species at Kanpur. Based on the chemical tracers (K^+ concentration, K^+/OC: Av= 0.06 ± 0.03 and OC/EC ratios: Av=7.8 ± 3.4), biomass burning emission (wood-fuels and agricultural waste) has been identified as a major source of carbonaceous aerosols. The WSOC/OC ratios vary within a narrow range (~0.35–0.40) at Kanpur during wintertime; whereas the elevated ratios (~0.55) during summertime suggest significant contribution from secondary organic aerosols. The highly acidic environment (SO_4^{2-} and NO_3^- aerosols) over IGP, during the wintertime, may significantly alter the morphological features of EC. In addition, the secondary aerosol formation and their hygroscopic growth (through nucleation/coagulation) can enhance the scattering properties of aerosols, a process that can be invoked for the poor visibility over northern India during the wintertime.

A novel approach is also proposed for the determination of absorption coefficient (b_{abs}) and mass absorption efficiency (σ_{abs}) of EC using simultaneous measurements of optical-attenuation (at 678 nm) in the thermo-optical EC-OC analyzer. At Manora Peak and Mt Abu, b_{abs} is 13.7 ± 7.3 and 5.8 ± 4.3 Mm^{-1} respectively; and that at urban site (Kanpur) is 42.7 ± 17.9 Mm^{-1}. The σ_{abs} varies from 4.3 to 20.9 m^2g^{-1}, unlike the constant conversion factor used in optical instruments for the determination of BC concentration. The *in-situ* measurements of optical properties along with the aerosol chemical composition (this study) are useful for the inter-comparison with other techniques/measurements.

Keywords: *Elemental and organic carbon (EC, OC), water-soluble OC (WSOC), OC/EC and WSOC/OC ratios, secondary organic aerosols, aerosol absorption coefficient (b_{abs}), mass absorption efficiency of EC (σ_{abs}), Indo-Gangetic Plain (IGP)*

CONTENTS

List of Tables

List of Figures