

Investigation of radicals and oxidant chemistry in north-west India using in-situ trace gas measurements and box modeling

Kalik Kumar Vishisth
MS13057

*A dissertation submitted for the partial fulfilment of
BS-MS dual degree in Science*



Indian Institute of Science Education and Research Mohali
April 2018

Certificate of Examination

This is to certify that the dissertation titled “Investigation of radicals and oxidant chemistry in north-west India using *in-situ* trace gas measurements and box modeling ” submitted by Mr. Kalik Kumar Vishisth (Reg. No. MS13057) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr.Vinayak Sinha Dr.Bärbel Sinha Dr.P.Balanarayan
(Supervisor)

Dated: April 20, 2018

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Vinayak Sinha at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Kalik Kumar Vishisth
(Candidate)

Dated: April 20, 2018

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Vinayak Sinha
(Supervisor)

Acknowledgement

I would like to express my gratitude to Dr. Vinayak Sinha, my project supervisor for his kind supervision and guidance in completing my dissertation. I would also like to thank Prof. Debi.P.Sarkar, Director, IISER Mohali and Prof. Purnananda Guptasarma, Dean R&D, IISER Mohali for providing the suitable environment which was very helpful for completing the thesis in time.

I am thankful to Dr. Bärbel Sinha and Dr. P.Balanarayan for providing their valuable inputs. I would also appreciate my lab mates Vinod Kumar, Abhishek Mishra, Haseeb Hakkim, Ashish Kumar Sharma, Abhishek Verma, Harshita Pawar, and B. Prafulla Chandra for their assistance.

Abstract

Atmospheric oxidants control the lifetime and abundance of atmospheric constituents. The most important atmospheric oxidant is the hydroxyl (OH) radical, which is also called the ‘detergent of the atmosphere’. OH oxidizes the vast majority of the trace gases present in the troposphere such as VOCs to form water-soluble products that can be washed out by rain or undergo dry deposition due to lowering of volatility. In this study I have focused on daytime oxidants that is O_3 and OH radical and the fate of different radicals such as alkyl peroxy (RO_2) and hydro peroxy (HO_2) radicals formed from the oxidant chemistry in north-west India. Due to very short lifetime ($< 1s$), experimental measurements of these radicals in ambient air are very challenging and are unavailable for Indian region till date. To investigate oxidant chemistry at a representative suburban site in north-west India, in-situ measurement of 38 VOCs and trace gases were performed at IISER Mohali. A detailed 0-D chemical box model was set up and constrained by the in-situ data for investigating the photochemical production of oxidants such as O_3 and OH radical and determining radical concentrations. Using box model I was able to calculate average daytime (06:00 - 17:00) concentrations of radicals such as OH, HO_2 , RO_2 which were 5.0×10^6 , 5.8×10^8 , 6.7×10^8 molecules cm^{-3} respectively. The peak concentrations of OH, HO_2 and RO_2 were 7.3×10^6 , 9.5×10^8 , 1.1×10^9 molecules cm^{-3} . Box model simulated ozone overestimated the measured peak ozone by circa 15 ppbv suggesting the absence of important ozone loss processes in the model. Our analysis pointed to a major role for isoprene oxidation via the high NO_x regime isoprene nitrate formation pathway resulting in production of HOx. This thesis has provided new insights pertaining to role of VOCs on oxidant chemistry in the atmospheric environment of north-west India.