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The Vertical Distribution of Atmospheric BrO from Ground-Based Measurements

Robyn Schofield

A thesis submitted in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy in Environmental Science,
The University of Auckland, 2003

The University of Auckland

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Abstract

Ground-based UV-Visible measurements targeting BrO were made at Lauder, New Zealand (45.0°S, 169.7°E) and Arrival Heights, Antarctica (77.8°S, 166.7°E). Differential Optical Absorption Spectroscopy (DOAS) was used to determine differential slant column densities (DSCDs) from the radiance measurements. UV-Visible measurements have been made in the two complementary viewing geometries of direct-sun and zenith-sky.

A spherical curved earth single scattering radiative transfer model was developed. The effects of refraction, molecular absorption, Rayleigh and Mie scattering were included. Singularity at the tangent point was avoided and a complete intensity calculation performed. The DSCDs for both the direct-sun and zenith-sky viewing measurements were calculated with this forward model.

A general optimal estimation retrieval algorithm was developed to retrieve altitude information by combining DSCDs from the direct-sun and zenith-sky viewing geometries. A complete retrieval characterisation and error analysis was performed. The characterisation illustrated that tropospheric sensitivity was obtained from the direct-sun viewing measurements, while the zenith-sky measurements were essential for stratospheric sensitivity.

Stratospheric and tropospheric BrO columns were retrieved for the diurnal stages of 80°, 84° and 87° SZA for Lauder. The diurnal and seasonal variation of the stratospheric column was successfully retrieved from the measurements. The stratospheric columns were consistent with a stratospheric Br_y loading of 20 ppt. The tropospheric BrO column retrieved over Lauder was less than 0.9 ppt if a uniform distribution throughout the troposphere is assumed. This is consistent with, though lower than, previous estimates of BrO in the free troposphere of 0.5-2.0 ppt (*Richter et al.*, 2002).

The results of a ten week measurement campaign at Arrival Heights for the spring 2002 are presented. Stratospheric and tropospheric BrO columns were retrieved at 80°, 84° and 88° SZA. A high variability was observed for the retrieved stratospheric columns, due in part to the unusual stratospheric warming in the Antarctic spring 2002 (*Allen et al.*, 2003). A mean ubiquitous tropospheric background of 0.3 ppt was retrieved. Also a 'bromine explosion' event was observed, corresponding to a BrO mixing ratio of 7 ppt for a uniformly mixed boundary layer.

Acknowledgements

I wish to thank Karin Kreher and Brian Connor for their invaluable supervision, and making this such a great experience for me.

I would also like to thank David Shooter for his guidance and supervision.

I would like to thank all of the staff at the National Institute of Water and Atmospheric research at Lauder. Thanks for all your help. In particular: Paul Johnston and Alan Thomas developed the direct-sun viewing instrument and I owe them many thanks for their patience and helpful guidance. Greg Bodeker for much guidance, help with the radiative transfer and for ozonesonde data over Lauder. Ben Liley for many helpful discussions and for the aerosol extinction profiles over Lauder. Hamish Struthers for the UMETRAC model runs. Jill Scott for all of the computer and technical support. Andrew Matthews for making this possible.

I wish to thank Antarctica NZ and staff at Scott Base for Winfly 2002 for all their support. Sam Oltmans for the surface ozone measurements at Arrival Heights. Thanks also to the Network for the Detection of Stratospheric Change for the Antarctic aerosol and ozonesonde data.

Clive Rodgers for many great discussions and help with retrieval theory.

Udo Frieß, Andreas Richter and François Hendrick for the many useful discussions and data.

I wish to thank the Foundation for Research Science and Technology Bright Future Top Achiever Doctoral Fellowship scheme for providing my funding.

My family and friends (new and old) for their unwavering support.

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