

# **The Distribution of Aerosol and Trace Gases in the Lower Troposphere over South Africa**

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A thesis submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg,  
in fulfilment of the requirements for the degree of Doctor of Philosophy.

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# Declaration

I declare that this thesis is my own, unaided work, except where otherwise acknowledged. It is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

Signed this 20th day of September 2016

A handwritten signature in blue ink, appearing to read 'R. Burger', with a stylized flourish extending from the end.

Roelof Petrus Burger.

# Abstract

Numerous studies on the sources, transport and fates of criteria air pollutants and greenhouse gases have been done in southern Africa. However, debate on the priority pollutants and areas of concern continue despite a growing national air quality monitoring network. This study attempts a novel approach to characterise sources and ambient air quality over major industrial and urban areas using a single suite of instrumentation to provide information to improve management of air quality. Over 200 hours of data were collected from an airborne platform. Another 5 ground-based campaigns characterised sources and areas out of reach of the aircraft.

The central aim of this study is to prioritise sources and areas of concern with regards to air quality management, using a mobile platform. This complements other modelling and spatial assessments and provides in situ validation for many contemporary debates. The specific aims were to characterise major anthropogenic sources; estimate the state of air quality; investigate the vertical distribution of pollutants; and prioritise sources and areas of concern for effective air quality management in South Africa.

The research has delivered many original contributions to the body of knowledge of air quality over South Africa. These findings can be divided into spatial and temporal relationships between sources and receptors, characterising source contributions and understanding the contribution of atmospheric emissions. High resolution measurements show that spatial scales of prominent atmospheric plumes are much smaller than current remote sensing estimates. In situ measurements further confirm that coal-fired power stations and petrochemical facilities have well defined plumes with high concentrations of criteria pollutants, most notably  $SO_2$  and  $NO_x$ . Residential solid fuel burning in low-income communities have a disproportionately large impact on the exposure to particulate matter (evening plumes exceeding  $800 \mu\text{g}/\text{m}^3$  of  $PM_{2.5}$  measured at 5 min intervals). Relatively high levels of  $NO_x$  (peak values exceeding 500 ppb  $NO$  and 300 ppb  $NO_2$  measured at 5 min intervals) close to busy highways, on the same order of magnitude as in-plume concentrations of large industrial facilities, highlights the importance of mobile sources.

In situ measurements confirm high levels of criteria air pollutants over the Vaal priority area, the Highveld priority area and to a lesser extent the Bojanala priority area, especially levels  $SO_2$  and  $NO_x$ . These areas with a large number of atmospheric emissions do however seem smaller than those estimated using satellite remote sensing. Relatively high levels of  $NO_x$ ,  $SO_2$  and  $PM$  were measured over Durban, which is not currently being managed as a priority area. This

underscores the difficulty of accurately assessing environments with diverse, clustered sources and complex meteorology through modelling studies and satellite based remote sensing.

The current conceptual model of absolute stable layers is biased because of limited data availability where a limited number of levels are reported. At least 60 levels should be reported in soundings to study absolutely stable layers. The inclusion of the standard reporting levels, (850 hPa, 700 hPa, 500 hPa and 300 hPa), further biases the detection of atmospheric stable layers. The number of observed persistent levels change in number and character when these are omitted from the analysis. Numerous vertical profiles further show that the thermodynamic model of stability as the main driver of stratification is oversimplified, especially close to source regions where different pollutants are observed to peak at different levels unrelated to absolutely stable layers. This suggests that the original buoyancy which is governed by the release temperature, exit velocity and height are important drivers for the stratification of pollutants.

The overall conclusion is made that a small team with a set of regular instrumentation can prioritise pollutants and areas of concern on a national scale. This method could be valuable for countries with limited resources and infrastructures and could be used in combination with modelling and satellite based remote sensing to assess priorities. The ability to obtain in situ data of a large number of variables over vast areas in a short time may offsets the caveats associated with mobile measurements and a limited sample volume.

# Preface

The impact of air pollution on human health, the environment and climate is well known. In the past few decades, numerous international studies have increased our understanding, surface observation networks have been installed, and satellites have been launched to observe air quality from space. In southern Africa, major international projects includes the 1992 Southern African Fire-Atmosphere Research Initiative (SAFARI-92), the Transport and Atmospheric Chemistry near the Equator-Atlantic (TRACE-A), the 2000 Southern African Fire-Atmosphere Research Initiative (SAFARI2000) and the Aerosol Research and Re-circulation Experiment (ARREX) between 1999 and 2003. Most of these projects focused on biomass burning emissions and very little attention was paid to industrial and residential sources. Some projects did focus on specific regions, like Brown Haze I in 1998 and Brown Haze II in 2003. This study was conceptualised to characterise anthropogenic pollution sources and air quality on a national scale. The aim of the study is to examine the sources, horizontal and vertical distribution and transport of aerosol and trace gases over the industrial and urbanised areas of South Africa. Specifically the objectives are to:

- (i) characterise the major anthropogenic sources of air pollution over South Africa;
- (ii) characterise the state of air quality over the major industrial and urbanised areas of South Africa using in situ measurements;
- (iii) investigate the vertical distribution of aerosol and trace gases over South Africa; and to

- (iv) prioritise areas and sources of concern for effective air quality management in South Africa.

The thesis is divided into 6 chapters. Chapter 1 provides background information on atmospheric trace gases and aerosol, their sources and fate. Chapter 2 describes data collection procedures and analysis methodologies. Major anthropogenic sources of air pollution over South Africa are characterised in Chapter 3. A summary of all airborne data collected over the major industrial and urban areas are presented in Chapter 4. The current conceptual model of elevated absolutely stable layers and its impact on the vertical distribution of aerosol and trace gases are evaluated in Chapter 5. A summary of key findings and recommendations for future research are presented in Chapter 6.

Sections of this thesis have been presented at conferences, or are currently under consideration for publication. The study design (Chapter 2) was presented at the *National Association for Clean Air* annual conference in 2007. Initial results were presented as a report to the then Department of Environmental Affairs and Tourism (DEAT). Chapter 3 was presented at the *16th International Union of Air Pollution Prevention and Environmental Protection Associations World Clean Air Congress* in 2013. Chapter 4 was presented at the *26th South African Society for Atmospheric Sciences* annual conference in 2010. Chapter 5 was presented at the *29th South African Society for Atmospheric Sciences* annual conference in 2013. Chapter 6 and the full conclusions of the study was presented at the combined *13th Quadrennial International Commission on Atmospheric Chemistry and Global Pollution (ICACGP) Symposium and 13th International Global Atmospheric Chemistry (IGAC) Science Conference on Atmospheric Chemistry* in 2014 where it was awarded the best presentation by a young scientist, and the International Association for Impact Assessments (IAIA) in South Africa, 2015 and the Global Emissions Initiative conference in Beijing, 2015.

This work forms part of projects funded by the then Department of Environmental Affairs (DEA), Eskom, SASOL and the city of Cape Town. The aircraft and some of the instrumentation belongs to the South African Weather Service (SAWS). Many students and staff were

involved in the field campaigns. Their help in instrument calibration, installation, data collection and stimulating discussions made this work possible. Orsemond Aviation, SkyCare and Harry McGarry kept the aircraft flying. Steve Edwards (SAWS technician) provided technical assistance to calibrate, install and operate the aircraft equipment. People that acted as flight scientists and assisted in data collection include Luanne Stephens, Stephen Broccardo, Shaazia Bhailall, Candice McKechnie, Xolile Ncipha and Michael Weston.

A special word of thanks to my family for their continued support. Thank you to Stephen Broccardo for many insightful discussions and sharing the burden. Prof. Stuart Piketh was the principle investigator on the study and was responsible for facilitating every aspect of the research. His friendship, as well as his scientific, financial and moral support are deeply appreciated.

# Contents

|                                                                    |            |
|--------------------------------------------------------------------|------------|
| <b>Declaration</b>                                                 | <b>i</b>   |
| <b>Abstract</b>                                                    | <b>ii</b>  |
| <b>Preface</b>                                                     | <b>iv</b>  |
| <b>Contents</b>                                                    | <b>vii</b> |
| <b>List of Figures</b>                                             | <b>ix</b>  |
| <b>List of Tables</b>                                              | <b>xi</b>  |
| <b>List of Abbreviations</b>                                       | <b>xii</b> |
| <b>List of Compounds</b>                                           | <b>xiv</b> |
| <b>List of Symbols</b>                                             | <b>xvi</b> |
| <b>1 Overview</b>                                                  | <b>1</b>   |
| Introduction . . . . .                                             | 1          |
| Literature review . . . . .                                        | 3          |
| Research Goals . . . . .                                           | 32         |
| Research Design . . . . .                                          | 33         |
| <b>2 Data and Methodology</b>                                      | <b>35</b>  |
| Introduction . . . . .                                             | 35         |
| Suite of instruments . . . . .                                     | 37         |
| Airborne campaigns . . . . .                                       | 47         |
| Ground-based campaigns . . . . .                                   | 60         |
| Sampling errors and uncertainties . . . . .                        | 63         |
| <b>3 Major Sources of Air Pollution in South Africa</b>            | <b>67</b>  |
| The distribution of major pollution sources . . . . .              | 67         |
| Plumes over South Africa . . . . .                                 | 70         |
| Emissions from major industrial sources . . . . .                  | 71         |
| Emissions from road traffic . . . . .                              | 86         |
| Domestic solid fuel burning emissions . . . . .                    | 89         |
| Source character . . . . .                                         | 93         |
| Limitations of in situ plume characterisation . . . . .            | 95         |
| <b>4 The Spatial Distribution of Air Pollution in South Africa</b> | <b>96</b>  |
| Sulphur dioxide overview . . . . .                                 | 97         |

|                                                                        |            |
|------------------------------------------------------------------------|------------|
| Nitrogen oxides overview . . . . .                                     | 101        |
| Ozone overview . . . . .                                               | 107        |
| Carbon oxides overview . . . . .                                       | 107        |
| Particulate matter overview . . . . .                                  | 112        |
| Volatile organics overview . . . . .                                   | 115        |
| Overview . . . . .                                                     | 118        |
| <b>5 The Vertical Stratification of Air Pollution in South Africa</b>  | <b>119</b> |
| A critical evaluation of the current conceptual model . . . . .        | 120        |
| Mixing in the unstable boundary layer . . . . .                        | 125        |
| The impact of elevated stable layers on tracer transport . . . . .     | 129        |
| Vertical distribution of aerosol and trace gases . . . . .             | 134        |
| <b>6 Summary and Conclusions</b>                                       | <b>135</b> |
| Original contributions to the current body of knowledge . . . . .      | 135        |
| Major Sources of Air Pollution in South Africa . . . . .               | 137        |
| The Spatial Distribution of Air Pollution in South Africa . . . . .    | 138        |
| The Vertical Stratification of Air Pollutant in South Africa . . . . . | 139        |
| Conclusions and significance . . . . .                                 | 140        |
| <b>References</b>                                                      | <b>141</b> |

# List of Figures

|      |                                                                                   |     |
|------|-----------------------------------------------------------------------------------|-----|
| 1.1  | The atmospheric sulphur balance. . . . .                                          | 9   |
| 1.2  | A simplified atmospheric cycle of $NO_x$ in the troposphere. . . . .              | 10  |
| 1.3  | The atmospheric $O_3$ production cycle. . . . .                                   | 13  |
| 1.4  | Comparison of coal properties from the top users. . . . .                         | 16  |
| 1.5  | Total column global NOx climatology. . . . .                                      | 18  |
| 1.6  | Global ambient pollution impacts on mortality. . . . .                            | 19  |
| 1.7  | Sources contributing most to global ambient pollution impacts on mortality. . .   | 20  |
| 1.8  | Spatio-Temporal scales and trace gas lifetimes in the troposphere. . . . .        | 22  |
| 1.9  | The diurnal evolution of the planetary boundary layer. . . . .                    | 23  |
| 1.10 | Major synoptic circulation types affecting southern Africa. . . . .               | 26  |
| 1.11 | Transport and re-circulation statistics for southern Africa. . . . .              | 28  |
| 1.12 | Absolutely stable layers over South Africa. . . . .                               | 29  |
| 2.1  | A composite map of the study area. . . . .                                        | 36  |
| 2.2  | An example of auxiliary variables for identifying sources. . . . .                | 45  |
| 2.3  | The two Aerocommander A690 used in the airborne sample campaigns. . . . .         | 48  |
| 2.4  | Flight tracks of research flights conducted over South Africa. . . . .            | 49  |
| 2.5  | A close-up of the inlet nozzle on the Aerocommander ZS-JRA. . . . .               | 52  |
| 2.6  | A conceptual diagram of the sampling system used for the airborne campaign. .     | 52  |
| 2.7  | An example of a mapping flight conducted over the South African Highveld. . .     | 58  |
| 2.8  | An example of a source flight conducted over the Highveld area of South Africa.   | 59  |
| 2.9  | An example of profile flights conducted at the edges of the Highveld. . . . .     | 60  |
| 2.10 | Photograph of the mobile monitoring station. . . . .                              | 61  |
| 2.11 | Location of Kwadela. . . . .                                                      | 63  |
| 3.1  | The major air pollution sources in South Africa. . . . .                          | 68  |
| 3.2  | Source contribution to total national emissions. . . . .                          | 69  |
| 3.3  | In-plume concentrations around power plants in South Africa. . . . .              | 73  |
| 3.4  | in situ measurement of a petrochemical plant plume. . . . .                       | 76  |
| 3.5  | in situ measurement of a steel plant plume. . . . .                               | 78  |
| 3.6  | in situ measurement of a paper plant plume. . . . .                               | 79  |
| 3.7  | in situ measurement in metallurgical smelter plume. . . . .                       | 82  |
| 3.8  | in situ measurement in cement industry plume. . . . .                             | 85  |
| 3.9  | The diurnal distribution of aerosol and trace gases next to the major highways. . | 88  |
| 3.10 | The diurnal distribution of aerosol and trace gases in an low-income settlement.  | 90  |
| 3.11 | Characterising anthropogenic sources through correlation scatter diagrams. . . .  | 94  |
| 4.1  | The spatial distribution of sulphur dioxide ( $SO_2$ ). . . . .                   | 98  |
| 4.2  | The spatial distribution of nitrogen monoxide ( $NO$ ). . . . .                   | 102 |
| 4.3  | The spatial distribution of nitrogen dioxide ( $NO_2$ ). . . . .                  | 104 |
| 4.4  | The spatial distribution of $NO_x$ . . . . .                                      | 105 |
| 4.5  | The spatial distribution of ozone ( $O_3$ ). . . . .                              | 108 |
| 4.6  | The spatial distribution of carbon monoxide ( $CO$ ). . . . .                     | 109 |
| 4.7  | The spatial distribution of carbon dioxide ( $CO_2$ ). . . . .                    | 111 |
| 4.8  | The spatial distribution of $PM_{2.5}$ . . . . .                                  | 113 |

|      |                                                                                        |     |
|------|----------------------------------------------------------------------------------------|-----|
| 4.9  | The spatial distribution of benzene, toluene, ethyl-benzene and xylene ( <i>BTEX</i> ) | 116 |
| 4.10 | Typical concentrations of pollutants in the lower troposphere. . . . .                 | 117 |
| 5.1  | Number of sounding observation levels versus stable layers. . . . .                    | 122 |
| 5.2  | The prevalence of stable layers over Durban including standard levels. . . . .         | 123 |
| 5.3  | The prevalence of stable layers over Durban excluding standard levels. . . . .         | 124 |
| 5.4  | An example of a vertical profile in a well mixed boundary layer. . . . .               | 126 |
| 5.5  | An example of a vertical profile in a well mixed boundary layer. . . . .               | 127 |
| 5.6  | An example of strong stratification in the boundary layer. . . . .                     | 128 |
| 5.7  | An example of a well defined layer at the top of the the boundary layer. . . . .       | 130 |
| 5.8  | An example of an elevated ASL without strong stratification. . . . .                   | 132 |
| 5.9  | An example of stratification in association with an absolutely stable layer. . . .     | 133 |

# List of Tables

|      |                                                                                      |    |
|------|--------------------------------------------------------------------------------------|----|
| 1.1  | Estimated global fluxes of atmospheric sulphur gases. . . . .                        | 9  |
| 1.2  | Typical elemental compositions of fuels. . . . .                                     | 15 |
| 1.3  | A classification of environmental regulatory instruments . . . . .                   | 30 |
| 2.1  | Summary of instrumentation deployed. . . . .                                         | 38 |
| 2.2  | The PCASP boundaries for the 15 size channels. . . . .                               | 42 |
| 2.3  | Logistical details of airborne campaigns as part of this study. . . . .              | 47 |
| 2.4  | Core variables measured over South Africa between 2003 and 2006. . . . .             | 50 |
| 2.5  | Summary of subjective instrument lag estimates for the different projects. . . . .   | 51 |
| 2.6  | Selected attributes for Kwadela for the 2011 census small area layers (SAL). . . . . | 62 |
| 3.1  | In-plume concentrations over South Africa. . . . .                                   | 70 |
| 3.2  | In-plume concentrations around coal-fired power stations in South Africa. . . . .    | 74 |
| 3.3  | In-plume concentrations around major petrochemical plants in South Africa. . . . .   | 75 |
| 3.4  | In-plume measurements from the steel industry. . . . .                               | 80 |
| 3.5  | In-plume measurements from the paper and kraft industry. . . . .                     | 81 |
| 3.6  | In-plume measurements from the metallurgical smelter industry. . . . .               | 83 |
| 3.7  | In-plume measurements from the cement industry. . . . .                              | 84 |
| 3.8  | Details of vehicles in South Africa for 2009. . . . .                                | 87 |
| 3.9  | Plume concentrations measured next to major highways . . . . .                       | 87 |
| 3.10 | Winter plume concentrations in an isolated low-income settlement. . . . .            | 91 |
| 3.11 | Summer plume concentrations in an isolated low-income settlement. . . . .            | 92 |

# List of Abbreviations

|        |                                                                      |
|--------|----------------------------------------------------------------------|
| AAQS   | Ambient Air Quality Standards. 17, 19                                |
| ABL    | Atmospheric Boundary layer. 22–25, 125, 126, 130, 133, 135, 140, 145 |
| ARREX  | The Aerosol Recirculation and Rainfall Experiment. 34                |
| ASL    | Atmospheric stable layer. 126–130, 133, 135, 137, 138, 140, 145      |
| CAPIA  | Cross border air pollution assesment project. 34                     |
| CCN    | Cloud condensation nuclei. 6                                         |
| CRG    | Climatology Research Group. 39                                       |
| DEM    | Digital elevation model. 59                                          |
| GC     | Gas Chromatograph. 43                                                |
| GMT    | Generic Mapping Tools. 49                                            |
| GOME-2 | The second Global Ozone Monitoring Experiment. 75                    |
| GRASS  | Geographic Resources Analysis System. 49                             |
| ITCZ   | Intertropical Convergence Zone. 25                                   |
| KZN    | Kwazulu-Natal. 81                                                    |
| LDV    | Light delivery vehicles. 90                                          |
| MODIS  | The Moderate Resolution Imaging Spectrometer. 71                     |
| NACA   | The National Advisory Committee for Aeronautics in the USA. 51, 93   |
| NCAR   | National Center for Atmospheric Research. 57                         |
| NEMA   | National Environmental Management Act. 31                            |
| NEMAQA | National Environmental Management Air Quality Act. 31                |
| NetCDF | Network common data format. 50                                       |
| OMI    | Ozone Monitoring Instrument. 75                                      |
| OPC    | Optical particle counter. 43–45                                      |

|            |                                                                                                       |
|------------|-------------------------------------------------------------------------------------------------------|
| PCASP      | Passive Cavity Spectrometer Probe. 39, 43–45, 50, 61                                                  |
| PID        | Photon ionised detector. 43                                                                           |
| ppbv       | Mixing ratio units of parts per by billion volume. 43                                                 |
| ppmv       | Mixing ratio units of parts per million by volume. 43                                                 |
| RAF        | Research Aviation Facility. 57                                                                        |
| RSFB       | Residential solid fuel burning. 19, 21, 31, 34, 37, 64, 65, 68, 73, 74, 90, 92, 93, 99, 102, 104, 105 |
| SA'ARI-94  | Southern African Atmospheric Research Initiative during 1994. 34                                      |
| SAFARI-92  | Southern African Fire/Atmospheric Research Initiative during 1992. 26, 34                             |
| SAFARI2000 | The Southern African Regional Science Initiative. 26, 34                                              |
| SANAS      | South African National Accreditation System. 39                                                       |
| SCIAMACHY  | SCanning Imaging Absorption spectroMeter for Atmospheric CHartography. 75                             |
| SRTM       | The Shuttle Radar Topography Mission. 59                                                              |
| TEI        | Thermo Environmental Instruments. 41, 42                                                              |
| USA        | United States of America. 4, 21                                                                       |
| UV         | Ultraviolet. 42                                                                                       |
| WCB        | Lines of equal entropy ahead of cold fronts called warm conveyor belts. 125, 137                      |
| WHO        | World Health Organization. 19                                                                         |

# List of Compounds

|                                   |                                                                                                                                                  |
|-----------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|
| <i>As</i>                         | Arsenic. 6                                                                                                                                       |
| <i>BTEX</i>                       | Benzene, Toluene, Ethyl-benzene and Xylene. xii, xv, 5, 7, 40, 43, 120, 121, 144, 310, 312                                                       |
| <i>CCl<sub>4</sub></i>            | Carbon tetrachloride. 22                                                                                                                         |
| <i>CH<sub>4</sub></i>             | Methane. 6, 7, 12, 15, 22, 73                                                                                                                    |
| <i>CO</i>                         | Carbon monoxide. xi, 5–7, 11, 12, 34, 39–41, 55, 68, 73, 74, 76, 78, 79, 81, 83, 85, 86, 88, 95, 96, 99, 104, 113, 114, 116, 117, 123, 144       |
| <i>CO<sub>2</sub></i>             | Carbon Dioxide. xi, 5–8, 11, 12, 22, 39–41, 50, 55, 73, 74, 76, 78, 79, 81, 83, 85, 86, 88, 95, 96, 99, 113, 115, 116, 143, 144                  |
| <i>C<sub>6</sub>H<sub>6</sub></i> | Benzene. 6, 7, 73                                                                                                                                |
| <i>Cd</i>                         | Cadmium. 6                                                                                                                                       |
| <i>Cr</i>                         | Chromium. 6                                                                                                                                      |
| <i>Cu</i>                         | Copper. 6                                                                                                                                        |
| <i>HCHO</i>                       | Methanal, also known as formaldehyde. 5, 6                                                                                                       |
| <i>HCl</i>                        | Hydrogen chloride. 6                                                                                                                             |
| <i>HNO<sub>3</sub></i>            | Nitric acid. 8, 10, 11                                                                                                                           |
| <i>HO<sub>2</sub></i>             | Hydroperoxyl or perhydroxyl radical. 5, 12                                                                                                       |
| <i>H<sub>2</sub>O</i>             | Water. 7, 11                                                                                                                                     |
| <i>H<sub>2</sub>O<sub>2</sub></i> | Hydrogen peroxide. 5                                                                                                                             |
| <i>H<sub>2</sub>S</i>             | Hydrogen sulphide. 5–8, 40, 55, 78, 79, 81, 83, 85, 86, 88                                                                                       |
| <i>Hg</i>                         | Mercury. 6, 7, 20                                                                                                                                |
| <i>Mn</i>                         | Manganese. 6                                                                                                                                     |
| <i>NH<sub>3</sub></i>             | Ammonia. 6, 8, 10                                                                                                                                |
| <i>NO</i>                         | Nitrogen monoxide or nitric oxide. xi, 8, 13, 22, 39, 42, 43, 74, 76, 78, 79, 83, 85, 86, 88, 90, 95, 96, 106, 107, 110, 111, 133, 142, 143, 308 |
| <i>NO<sub>2</sub></i>             | Nitrogen dioxide. xi, 3, 7, 8, 10, 13, 14, 18, 39, 42, 43, 74, 76, 78, 79, 83, 85, 86, 88, 90, 95, 96, 106, 108, 110, 111, 117, 142, 143, 308    |
| <i>NO<sub>x</sub></i>             | Oxides of nitrogen. 5–7, 10–14, 17–19, 40, 42, 43, 55, 73, 74, 76, 79, 81, 85, 97, 99, 106, 111, 133, 135, 137, 142, 144                         |
| <i>NO<sub>y</sub></i>             | Reactive odd nitrogen. 5, 43                                                                                                                     |
| <i>NO<sub>3</sub><sup>+</sup></i> | Aerosol nitrate. 10                                                                                                                              |
| <i>N<sub>2</sub></i>              | Nitrogen. 41                                                                                                                                     |
| <i>N<sub>2</sub>O</i>             | Nitrous oxide. 7, 8, 22, 73                                                                                                                      |
| <i>N<sub>2</sub>O<sub>5</sub></i> | <i>N<sub>2</sub>O<sub>5</sub></i> . 11                                                                                                           |

|                         |                                                                                                                                         |
|-------------------------|-----------------------------------------------------------------------------------------------------------------------------------------|
| <i>Ni</i>               | Nickel. 6                                                                                                                               |
| <i>OH</i>               | Hydroxyl radical. 5, 8, 10, 13, 14, 22                                                                                                  |
| <i>O<sub>2</sub></i>    | Oxygen. 5, 8, 10, 42                                                                                                                    |
| <i>O<sub>3</sub></i>    | Ozone. xi, 3–7, 10, 12–14, 18–20, 34, 35, 39, 40, 42, 55, 76, 110–112, 123, 133, 144                                                    |
| <i>PAN</i>              | Peroxy-acetyl-nitrate. 11, 43                                                                                                           |
| <i>PCBs</i>             | Polychlorinated biphenyls. 6                                                                                                            |
| <i>PGM</i>              | Platinum group metals. 16                                                                                                               |
| <i>PM</i>               | Particulate matter. 3, 5–7, 19, 33, 35, 39, 40, 43, 45, 50, 65, 73, 76, 78, 79, 81, 83, 85, 86, 88, 93, 97, 99, 133, 137, 142, 144      |
| <i>PM<sub>10</sub></i>  | Particulate matter smaller with an aerodynamic diameter smaller than 10 $\mu m$ . 6, 40, 93, 95, 96                                     |
| <i>PM<sub>2.5</sub></i> | Particulate matter smaller with an aerodynamic diameter smaller than 2.5 $\mu m$ . 6, 7, 19, 20, 40, 93, 95, 96, 142                    |
| <i>PM<sub>3</sub></i>   | Particulate matter smaller with an aerodynamic diameter smaller than 3 $\mu m$ . 74–76, 82, 117, 119                                    |
| <i>Pb</i>               | Lead. 6, 7, 20, 21, 73                                                                                                                  |
| <i>SO<sub>2</sub></i>   | Sulphur dioxide. xi, 3, 5–8, 17, 34, 35, 39–42, 55, 73, 74, 76, 78, 79, 81, 83, 85, 86, 88, 95–97, 101–105, 111, 117, 119, 135, 142–144 |
| <i>SO<sub>x</sub></i>   | Oxides of sulphur. 18, 99                                                                                                               |
| <i>SVOCs</i>            | Semi-volatile organic compounds. 6                                                                                                      |
| <i>Se</i>               | Selenium. 6                                                                                                                             |
| <i>TOCs</i>             | Total organic compounds. 73                                                                                                             |
| <i>TSP</i>              | Total suspended particles. 6                                                                                                            |
| <i>V</i>                | Vanadium. 6                                                                                                                             |
| <i>VOC</i>              | Volatile organic compounds. 3, 6, 13, 14, 19, 32, 81, 90                                                                                |
| <i>Zn</i>               | Zinc. 6                                                                                                                                 |

# List of Symbols

|           |                                                        |
|-----------|--------------------------------------------------------|
| $C_p$     | Specific heat at constant pressure for dry air. 57, 58 |
| $C_v$     | Specific heat at constant volume for dry air. 57, 58   |
| $M$       | Mach number. 57, 58                                    |
| $R$       | Gas constant for dry air. 57–59                        |
| $RH$      | Relative humidity. 58                                  |
| $T$       | Ambient air temperature. 56–59                         |
| $T_{TAT}$ | Total air temperature. 56–58                           |
| $T_m$     | Measured temperature. 56–58                            |
| $T_r$     | Recovery temperature. 56–58                            |
| $\Gamma$  | Environmental lapse rate. 59                           |
| $g$       | Gravitational acceleration. 59                         |
| $p$       | Static pressure. 56, 57, 59                            |
| $p_d$     | Differential pressure. 55, 57                          |
| $p_{sm}$  | Measured static pressure. 55, 56                       |
| $r$       | Recovery factor. 57, 58                                |
| $v$       | Velocity / true air speed. 56–58, 60                   |

# Chapter 1

## Overview

The context for the study is set out in this chapter. This includes a detailed literature review on the state of knowledge of the sources, fates and meteorological influences on aerosol and trace gases. The detailed research objectives and design are only outlined at the end of the chapter. However, the study is briefly framed in the following section to help guide the reader as to the overall aim of the thesis.

## Introduction

The impact of man on the environment is one of the key issues faced by scientists and politicians in the new millennium (King, 2004). Accelerated growth in global population and accompanied use of resources (Crutzen, 2002a; Steffen et al., 2015) since 1750 has made humans a dominant force in global change (Castree, 2015; Crutzen, 2002b; Steffen et al., 2007, 2011). While political solutions to climate change are debated, growing scientific consensus dictates that recent warming can be attributed to fossil fuel burning (Doran and Zimmerman, 2009). Anthropogenic emissions do not only impact on climate, but pose a threat to health and biodiversity. Air pollution and climate change issues are intrinsically linked (Ramanathan and Feng, 2009), but in practice each are dealt with exclusively. Political mitigation efforts and scientific investigations typically aims either at climate change or air quality. Studies show, however, that these two interrelated issues are best resolved when treated as one (Bollen et al., 2009; West

et al., 2013). This is apparent, considering the same physical sources typically contribute both as agents of climate change and air pollution. However, complex interaction and trade offs between mitigation actions further emphasise the need to deal with air quality on a regional scale, focusing on both air pollution and climate change. The need to prioritise and manage a variety of different pollutants on a national scale lies central to this thesis.

South Africa faces the unique challenge of having a well-developed, industrialised, coal-dependent economy coupled with a poor, vulnerable working class. This results in having one of the highest per capita emissions of agents of climate change as well as millions of people exposed to poor air quality. International pressure calls for renewable alternative energy sources, however, currently coal-fired power plants produce electricity at a lower price. Links between the affordability of electricity and residential solid fuel burning are not well understood. A careful strategy that prioritise air pollution problem sources and areas is therefore crucial for sustained development in South Africa.

This thesis reports on a series of campaigns between 2003 and 2013 that collected in situ data from a diverse suite of instrument. The primary aim is to provide a comprehensive set of air quality data that will enable evidence-based setting air quality management priorities on a national scale. Measurements of air pollutants and greenhouse gases were done around major industrial and urban areas of South Africa. Ground based data sets of selected trace gases and aerosols are available, however, this project is the first to use an extensive suite of instruments to study all major areas with a large number of atmospheric emissions in South Africa. This enables a nationwide estimate of background and in-plume concentrations of major trace gasses and aerosol. The aims and objectives are outlined in detail on page 32, after the current body of knowledge is presented.

The first chapter of the thesis gives a background literature review on atmospheric trace gases and aerosols, their distribution and transport over South Africa, and laws and regulations pertaining to management of air quality. Chapter 2 deals with data and methods of analysis. Chapter 3 presents measurement results around major pollutant sources and typical background values in South Africa. Chapter 4 discusses the horizontal distribution of trace constituents in the atmosphere and their implications to remote sensing and modelling. The vertical distribution is discussed in chapter 5 and the conclusions in chapter 6.

## Literature review

Evidence exist for biological effects due to acute short term exposure and lower concentrations of particulate matter (*PM*),  $O_3$ ,  $NO_2$ ,  $SO_2$  and various other hazardous volatile organic compounds (*VOC*). Epidemiological and panel/cohort studies have linked hospital admissions, mortality, asthma and cancer to air pollution (Brunekreef and Holgate, 2002; Filleul et al., 2005).

Air pollution has significant health and environmental impacts in South Africa. Globally, household air pollution from solid fuels is estimated to be the third highest risk factor to the global burden of disease and the seventh for southern Africa (Lim et al., 2012; Newby et al., 2015; Silva et al., 2013). Ambient *PM* is the 9th highest global risk factor, and only 25th for South Africa. Diseases of the respiratory system accounts for 11.2 % of deaths for males and 11.6 % for females in South Africa (StatsSA, 2002), the 5th leading for male and fourth leading for female broad group of causes of death. Poverty and associated poor living conditions of the majority of South Africans (StatsSA, 2000) aggravates exposure to poor air quality (Muller et al., 2003). An estimated 17 % of South African households live in shacks; 42 % of households have no access to electricity. For cooking, 23 % of households use wood, 22 % paraffin and 3 % use coal (Christopher, 2014). Recent studies suggest that air pollution effects on life expectancy depends on factors such as education and antioxidant vitamin status (Abbey et al.,

1999; Brunekreef, 1999; Pope et al., 2002), implying a larger impact in disadvantaged population groups. A crude estimate of the total health cost due to fuel combustion related emissions is R4.7 billion per year (Scorgie et al., 2004). In 2000, outdoor air pollution is estimated to attribute 0.9 % of all deaths and 0.4 % of all years of life lost in South Africa (Norman et al., 2007). Links between air pollution and asthma (White et al., 2009) and an increase in the prevalence of pollution related symptoms (Zar et al., 2007) have been reported. Modelling studies suggest a significant threat of  $O_3$  to agricultural production in southern Africa (van Tienhoven et al., 2005, 2006). Air pollution, in particular  $O_3$ , has also been identified as a contributory cause to biodiversity loss in southern Africa (Tarr, 2003).

Apart from these health and environmental effects, there is clear and rapidly growing evidence that air pollution has a profound impact on the thermodynamic and radiative energy budgets of the Earth (Andreae et al., 2005; Andreae and Rosenfeld, 2008; Solomon et al., 2007). Increases in greenhouse gases have a positive radiative forcing component while total aerosol loads have a direct negative forcing (Junge, 1975). Indirectly, aerosol influence the radiative forcing negatively by changing cloud properties (Charlson et al., 1992; Twomey, 1977). The total net anthropogenic radiative forcing is estimated between  $0.6 \text{ W/m}^2$  to  $2.4 \text{ W/m}^2$  with the direct and indirect aerosol impacts being the largest uncertainties (Solomon et al., 2007).

Changes to the precipitation processes in clouds lead to other cloud-mediated climatic effects (Andreae and Rosenfeld, 2008; Bruintjes, 1999; Mather et al., 1997; Rosenfeld et al., 2008; Ross et al., 2003; Terblanche et al., 2000, 2005). Recently surprising correlations between daily summertime rainfall and day of the week have been found over the southeast USA (Bell et al., 2008). This corresponds to weekly cycles in pollution concentrations (Murphy et al., 2008) and therefore underline the profound link between air pollution and precipitation. No weekly precipitation cycles were found over Korea (Choi et al., 2008) or Europe, however, significant weekly cycles in surface temperature exist over Europe (Laux and Kunstmann, 2008).

Changes to climate impact on health by increasing the risk of infectious disease, expansion of mosquito-infested areas and activity, contamination of water and foods with bacteria and other

direct effects (Kurane et al., 2008). Furthermore, air pollutants are transported across national borders (Garrett and Hobbs, 1995) and across oceans (Stohl et al., 2002). This necessitate an integrated approach to managing local, regional and global air pollution issues.

It is clear that the affects of air pollution are far reaching and some of the most serious of our generation. This research is primarily concerned with the source of emissions and the fate of these pollutants in the atmosphere. in situ aircraft measurements over South Africa was used to characterise the main urban and industrial areas. Vertical distributions of aerosol and trace gases are investigated. The overall aim is to prioritise air quality management strategies on a national scale. The current study focuses on  $PM$ ,  $SO_2$ , hydrogen sulphide ( $H_2S$ ),  $CO_2$ ,  $CO$ , nitrogen oxides ( $NO_x$ ),  $O_3$  and  $BTEX$ .

A review of relevant literature is presented in the following sections. The first section gives an overview of the indicated atmospheric pollutants. The second section deals with their sources in southern Africa. The third section offers an overview of the current conceptual model on transport of pollutants over southern Africa. The fourth section provides an overview of principles and practices in managing air pollution while the last section explores the use of airborne measurements in pollution studies.

## **Atmospheric trace gases and aerosol**

Tropospheric chemistry involves oxidants like oxygen ( $O_2$ ),  $O_3$ , hydroxyl ( $OH$ ), hydrogen peroxide ( $H_2O_2$ ), formaldehyde ( $HCHO$ ) and hydroperoxyl ( $HO_2$ ), gases that can be oxidised, like hydrocarbons, reactive odd nitrogen ( $NO_y$ ) and sulphur compounds, oxidation products like carbonyls and organic nitrates and the interaction of these with aerosol and clouds (Roscoe and Clemitshaw, 1997). The atmosphere is mostly an oxidising environment, owing to the abundance of  $O_2$ . However, the main oxidising agents are  $O_3$  and more importantly  $OH$  (Crutzen and Lelieveld, 2001; Pielke and Helas, 1996). The  $OH$  radical is believed to be an important player in the main removal process for almost all trace gases, despite its very low

background concentrations (averaged volume mixing ratios below  $10^{-13}$ ) (Levy, 1971; Seinfeld and Pandis, 2006). Generally, after being oxidised gases are removed through precipitation, deposited as aerosol, taken up by soil and vegetation or dissolved into the oceans. The time scales of these events determine the atmospheric residence times, the abundance and global distribution of trace gases.

The origin and fate of aerosols are intertwined with atmospheric chemistry. Nucleation mode aerosols precipitate from gases. Species like  $SO_2$  oxidise onto aeolian particles changing their hygroscopic nature and therefore their cloud condensation nuclei (CCN) potential (Piketh et al., 1999a). Aerosols link the chemistry of the continents with that of the oceans and other ecosystems (Likens et al., 1981). Phyto-plankton blooms off the east coast of South Africa have been linked with major transport routes of fine iron aerosols (Piketh et al., 2000). An estimated 52 % of phosphates and 30 % of nitrates in the Okavango Delta ecosystem originates from atmospheric aerosol deposits (Piketh et al., 2000). The chemistry and size of aerosols impacts on their suitability as CCN and therefore directly and indirectly control climate.

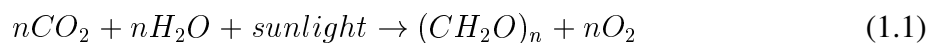
### ***Anthropogenic and biomass burning impacts on the atmospheric cycles***

All four grand nutrient cycles are strongly perturbed by human activity, namely the Carbon, Sulphur, Nitrogen and Phosphorus cycles. Although the scope of these impacts are known, the delicate balance, feed-backs and inter-dependency of the grand cycles remains one of the biggest uncertainties (Ayres, 1997). Pollutants associated with combustion and industrial process emissions include:  $PM$ ,  $NO_x$ ,  $CO$ ,  $CO_2$ ,  $VOC$ , semi-volatile organic compounds ( $VOCs$ ), methane ( $CH_4$ ), ammonia ( $NH_3$ ), hydrogen chloride ( $HCl$ ),  $H_2S$ ,  $O_3$ , other photochemical oxidants and various trace elements. Organic compounds released include  $HCHO$ , benzene ( $C_6H_6$ ), poly-aromatic hydrocarbons, polychlorinated biphenyls ( $PCBs$ ) and dioxins and furans. Trace elements may include arsenic ( $As$ ), cadmium ( $Cd$ ), chromium ( $Cr$ ), copper ( $Cu$ ), mercury ( $Hg$ ), nickel ( $Ni$ ), lead ( $Pb$ ), selenium ( $Se$ ), zinc ( $Zn$ ), manganese ( $Mn$ ), vanadium ( $V$ ).  $PM$  is defined as either total suspended particles ( $TSP$ ), particulate matter with an

aerodynamic diameter smaller than  $10\ \mu m$  ( $PM_{10}$ ) or particulate matter with an aerodynamic diameter smaller than  $2.5\ \mu m$  ( $PM_{2.5}$ ).

The species that are most important for health impacts include  $SO_2$ ,  $NO_2$ ,  $PM_{2.5}$  and  $O_3$  (Brunekreef and Holgate, 2002). Other pollutants of concern include agents of climate change such as  $CO_2$ ,  $CH_4$ , nitrous oxide ( $N_2O$ ) and halocarbons, and hazardous pollutants typically associated with carcinogenic effects after long-term exposure (for example benzene) as well as  $Hg$  and  $Pb$ . The age-standardised death rate of cancer seems to be reasonably unchanged for South Africa (Anderson and Phillips, 2006), this suggests that exposure to carcinogenic air pollutants (such as benzene), might not be that significant on a national scale.  $CO$  only poses health risks at high concentrations, but because it is fairly stable in the atmosphere it serves as a tracer for anthropogenic emission (for example automotive emissions).  $CO$  plays an important role in tropospheric chemistry. Atmospheric gases that contribute primarily to the greenhouse effect in clear skies are water vapour ( $\sim 60\%$ ),  $CO_2$  ( $\sim 25\%$ ),  $O_3$  ( $\sim 8\%$ ) and the remainder from trace gases including  $CH_4$  and  $N_2O$  (Karl and Trenberth, 2003). The current study will focus on  $PM$ ,  $SO_2$ ,  $H_2S$ ,  $CO_2$ ,  $CO$ ,  $NO_x$ ,  $O_3$  and  $BTEX$ .

Fuel burning emissions are the largest anthropogenic contributor to perturbing natural atmospheric chemistry processes. Almost all fuels are hydrocarbons, either fossil or contemporary, derived from solar radiation through the photosynthesis reaction (de Nevers, 2000):



where  $(CH_2O)_n$  is the generic formula for hydrocarbons. When fuels are burned, equation 1.1 is essentially reversed, producing  $CO_2$  and water ( $H_2O$ ). A simplified overview of anthropogenic modification to the sulphur, nitrogen carbon and atmospheric cycles will be presented from a range of different sources (Akimoto, 2003; Ayres, 1997; Crutzen and Andreae, 1990;

Crutzen and Lelieveld, 2001; Gruber and Galloway, 2008; Pham et al., 1996; Seinfeld and Pandis, 2006; Vitousek et al., 1997; Warneck, 1988). Modifications to the phosphorus cycle falls outside the scope of this document.

The oxidising nature of the atmosphere results in sulphur emitted into the atmosphere being converted into sulphate before being deposited (dry or wet) on the surface (Figure 1.1). Gaseous  $SO_2$  converts to particulate sulphate through many reaction mechanisms. Heterogeneous processes occur predominantly during wet conditions when  $SO_2$  and its oxidants dissolve into liquid drops and subsequently oxidise in the liquid phase. These dissolved sulphates may either be removed from the atmosphere as wet deposition or stay in the atmosphere as particulate sulphate after the liquid drops evaporate (Claes et al., 1998; Warneck, 1988). In the absence of significant atmospheric moisture, the dominant oxidising reaction mechanisms is through  $OH$ . The rate of this reaction chain is critically dependent on  $OH$  concentration.

Sulphur in the pedosphere include fossil fuels (coal, oil and natural gas), metallic sulphates and non-metallic sulphates (Komarnisky et al., 2003).  $SO_2$  emissions are associated with coal combustion, fossil fuel refining and ore smelting (see Figure 1.1). Power generation and industrial fuel burning accounts for the major sources of atmospheric sulphur in South Africa. Other atmospheric emission sources of sulphur include  $H_2S$ , which gets oxidised to  $SO_2$  mainly by  $OH$  with a tropospheric lifetime of approximately 12 hours (Jaeschke et al., 1978). Anthropogenic sources contribute more than 60% of global sulphur emissions (Table 1.1). Volcanic eruptions are a major source of global  $SO_2$  and some  $H_2S$  ( $SO_2$  to  $H_2S$  ratio approximately 10:1) (Von Glasow et al., 2008). Biomass burning and domestic fuel use are the only significant non-industrial regional sources of  $SO_2$ .

$N_2O$ ,  $NO$ ,  $NO_2$ , nitric acid ( $HNO_3$ ) and  $NH_3$  are important nitrogen-containing trace species in the atmosphere (Figure 1.2).  $N_2O$  is an important greenhouse gas despite its relatively low concentrations, due to its long lifetime and a warming potential about 300 times that of  $CO_2$  (Seinfeld and Pandis, 2006). Its predominant sources include biological processes in soils and water (both natural and anthropogenic), biomass burning and industrial sources. The major

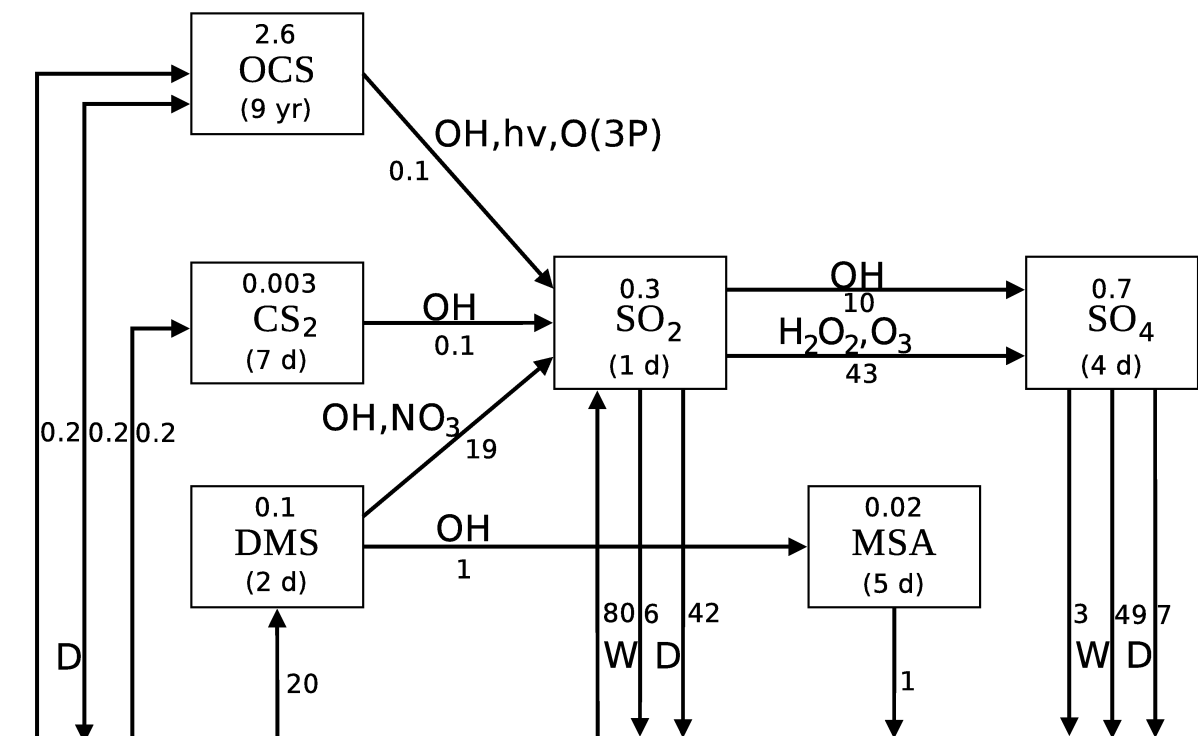


Figure 1.1: The main reservoir contents (TgS) and fluxes (TgS /a) in the atmospheric sulphur balance. Numbers in brackets refer to residence times. The main oxidants are indicated. Wet (W) and dry (D) deposition fluxes are indicated. Data from several sources, including Chin et al. (1996); Feichter et al. (1996); Kjellstrom (1998); Rodhe (1999).

Table 1.1: Estimated global fluxes (best estimate and range of est) of atmospheric sulphur gases. From Crutzen and Lelieveld (2001). The total sulphur in the atmosphere, excluding sea-salt, is ~0.5 TgS to ~0.6 TgS

| Sources              | Amount (TgS /a) | Range (TgS /a) |
|----------------------|-----------------|----------------|
| <i>Natural</i>       |                 |                |
| Volcanic             | 8               | 3-20           |
| Terrestrial          | 1               | 0.1-5          |
| Oceanic              | 20              | 12-40          |
| Total (~33%)         | 35              | 15.1-65        |
| <i>Anthropogenic</i> |                 |                |
| Fossil fuel use      | 75              | 70-85          |
| Biomass burning      | 2.5             | 1-4            |
| Total (~67%)         | 77.5            | 71-89          |

source of anthropogenic emissions of nitrogen oxides are the combustion of fossil fuels from stationary and mobile sources. Nitrogen in fuel and atmospheric nitrogen react with  $O_2$  during high temperature ( $>1300^\circ\text{C}$ ) combustion processes to form  $NO$  and smaller quantities of  $NO_2$ . These include mainly fossil-fuel combustion, biomass burning and lightning. Other important sources of  $NO_x$  include soil release,  $NH_3$  oxidation and aircraft.  $NO_x$  plays a very important role in tropospheric chemistry, especially  $O_3$ , aerosol nitrate ( $NO_3^-$ ) and  $OH$ . It has a highly seasonal tropospheric lifetime of between 10 to 50 hours (Kunhikrishnan et al., 2004).

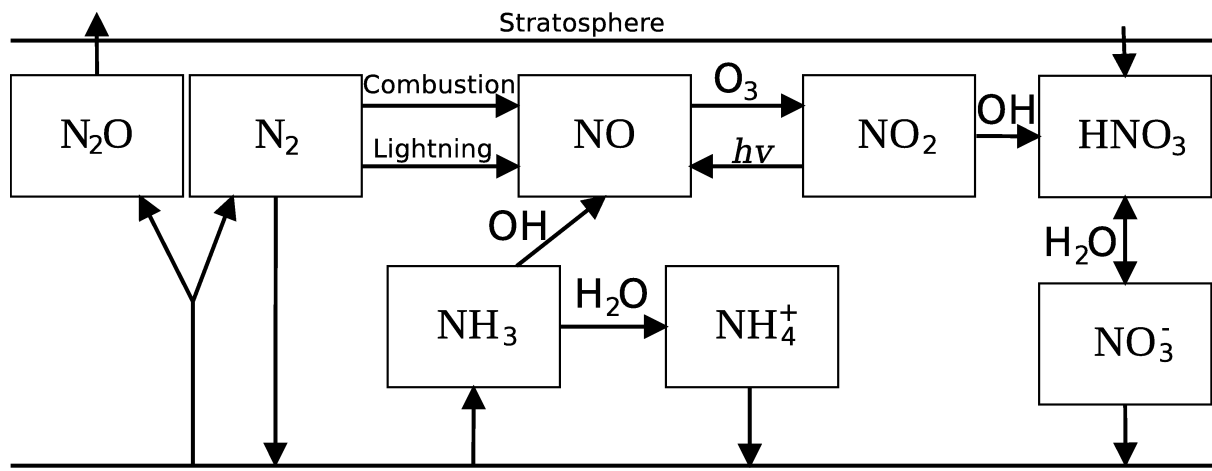
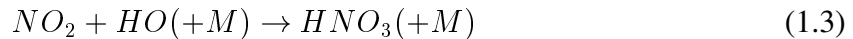


Figure 1.2: A simplified atmospheric cycle of  $NO_x$  in the troposphere (Seinfeld and Pandis, 2006).

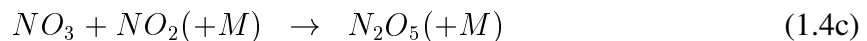
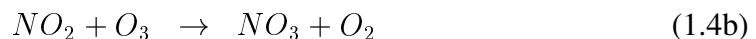
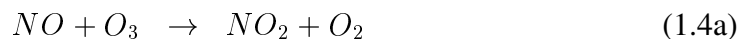
The typical  $NO_x$  chemistry is shown in equation set 1.2.  $M$  represents any other molecule (usually  $N_2$  or  $O_2$ ), which must carry away some of the released energy.



The main chemical sink of  $NO_x$  occur through the reaction of  $NO_2$  with  $OH$ , leading to the highly soluble and photo-chemically relatively long-lived  $HNO_3$  (Seinfeld and Pandis, 2006).

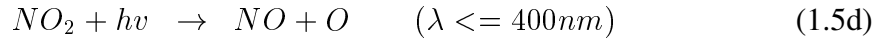
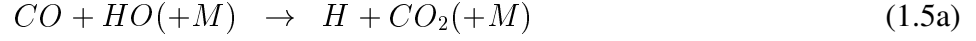


During night-time  $NO_x$  can be removed by gas-phase reactions producing  $N_2O_5$ , which then reacts with the  $H_2O$  radical on aerosol particles to produce  $HNO_3$  (reaction sequence 1.4).

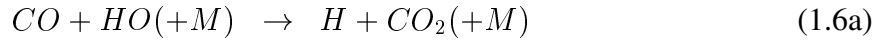


In a polluted atmosphere, oxidation reactions involving the more reactive hydrocarbons can sequester some of the  $NO_x$  by producing peroxy-acetyl-nitrate ( $PAN$ ).  $PAN$  is not readily removed through wet processes and can therefore be transported over long distances where thermal dissociation can result in a significant source of  $NO_x$ .

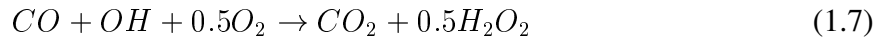
All carbon emitted into the atmosphere ends up as  $CO_2$ .  $CO_2$  plays a major role in the earth's climate and as a carbon source in photosynthesis, but does not significantly influence the chemistry of the atmosphere directly since it is very stable.  $CO$  oxidises to  $CO_2$  through reaction chain 1.5 (Seinfeld and Pandis, 2006).



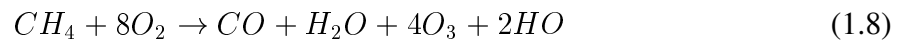
in  $NO_x$ -poor environments (less than 10 *pptv*) reaction 1.5c is limited and  $HO_2$  reacts with  $O_3$  instead (reaction chain 1.6) (Seinfeld and Pandis, 2006).



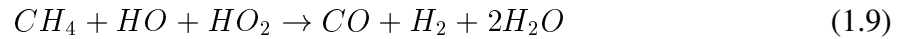
Therefore the net oxidation of  $CO$  to  $CO_2$  in a  $NO_x$ -rich atmosphere,  $CO + 2O_2 \rightarrow CO_2 + O_3$ , is an  $O_3$  source while the net oxidation in a  $NO_x$ -poor atmosphere,  $CO + 2O_3 \rightarrow CO_2 + O_2$ , is an  $O_3$  sink.  $HO_2$  in reaction 1.6c can react with other  $HO_2$  radicals to produce the following net result:



In similar, although more complex reaction sequence,  $CH_4$  and other hydrocarbons are oxidised. In a  $NO_x$ -rich atmosphere the net result is (Seinfeld and Pandis, 2006):



and in a  $NO_x$ -poor atmosphere:



$O_3$  is typically formed through the catalytic role of  $NO_x$  (Figure 1.3). The  $OH$  radicals which are integral to this reaction are mainly formed by ultraviolet radiation on  $O_3$  through reactions 1.10a and 1.10b (Seinfeld and Pandis, 2006).

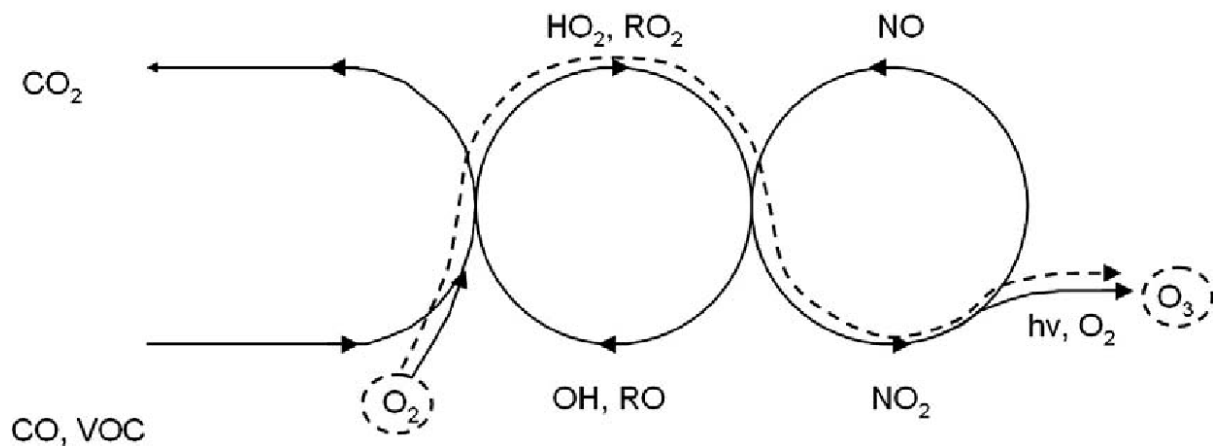
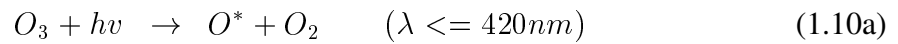
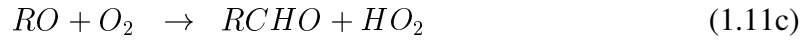


Figure 1.3: A simplified  $O_3$  production cycle in the troposphere (Von Glasow et al., 2008).

In a  $VOC$ -poor atmosphere reaction sequence 1.2 leads to an equilibrium between  $NO$ ,  $NO_2$  and  $O_3$ . This equilibrium depends on the available solar radiation and to a lesser extent on the amount of  $NO_x$ . The role of  $VOC$  is to convert  $NO$  to  $NO_2$  without destroying  $O_3$ .  $NO$  reduction will then limit reaction 1.2c. One mechanism by which  $VOC$  achieves this is through reaction sequence 1.11 (Seinfeld and Pandis, 2006).



resulting in the net reaction:



$NO_2$  reduces the available  $OH$  radicals, complicating this process (see equation 1.3). The availability of  $NO_x$  and  $VOC$  therefore regulates the amount of  $O_3$  formed (Seinfeld and Pandis, 2006).

The atmosphere is a highly interacting, non-linear system. The chemical reactions discussed all take place simultaneously. Factors such as compound concentration, available solar energy and meteorological conditions influence the relative reaction rates and preferred pathway.

## Air pollution in South Africa

The primary sources of fuel for South Africa's total energy supply (amounting to 4782 PJ in 2000) includes: coal (70.9 %), oil (17.8 %), wood and biomass (8.7 %), natural gas (1.2 %), hydro (0.7 %) and nuclear (0.7 %) (Scorgie et al., 2004). Coal-fired power stations produce approximately 90 % of South Africa's electricity, using relatively poor quality coal (Table 1.2 and Figure 1.4). In 2009, South Africa was the sixth largest producer and the fifth largest exporter (67 Mt) (Eberhard, 2011; IEA, 2010). Eskom uses 70 % of local coal, Sasol 20 %, the metallurgical sector 3 %, other industries 5% and the remaining 2 % can be attributed to

Table 1.2: Typical elemental compositions of fuels. Typical values from de Nevers (2000) and South African values from Steyn and Minnitt (2010).

| Material            | Ultimate analysis, weight %, dry basis, typical values |      |      |     |      |      | Heating value (MJ /kg) |           |
|---------------------|--------------------------------------------------------|------|------|-----|------|------|------------------------|-----------|
|                     | C                                                      | H    | O    | N   | S    | Ash  | Dry basis              | Wet basis |
| Wood                | 52.3                                                   | 6.3  | 40.5 | 0.1 | <0.1 | 0.8  | 21.05                  |           |
| Lignite             | 55                                                     | 4.4  | 13   | 1.0 | 1.7  | 24.9 | 22.63                  | 14.82     |
| Sub-bituminous coal | 72.5                                                   | 6.1  | 17.2 | 0.7 | 0.4  | 3.1  | 30.25                  | 20.33     |
| Bituminous coal     | 75.8                                                   | 5.0  | 7.4  | 1.5 | 1.6  | 8.7  | 31.63                  | 27.83     |
| Anthracite coal     | 82.1                                                   | 2.3  | 2.0  | 0.8 | 0.6  | 12.2 | 30.84                  |           |
| South African coal  | 70.8                                                   | 4.49 | 23.1 | 1.2 | 1.4  | 15   | 27                     | 25        |
| Oil                 | 87                                                     | 14   | 1    | 1   | 6    |      | 38.5 (MJ /l)           |           |

domestic use (Eberhard, 2011). The bulk of the economically extracted coal (the Ecca Group of the Vryheid formation) lies on the South African Highveld (Hancox and Götz, 2014). That is the primary reason for the high density of coal-fired power stations and other industries in this region. The Highveld is where domestic coal burning dominates other solid fuels. The Ecca/Beaufort Group in the Waterberg is the current focus for new coal extraction. Medupi, one of Eskom's new coal-fired power stations is set to produce a total of 4764 MW (Pretorius et al., 2015). Considering the remaining reserves, coal is likely to be the predominant energy source for the South African economy for the foreseeable future (Hancox and Götz, 2014).

Natural gas (essentially  $CH_4$ ) is a very clean fuel, the only problem being storage.  $CH_4$  is a common product of anaerobic bacterial decomposition of organic matter (de Nevers, 2000), generated in landfills and sewerage treatment plants. All South Africa's natural gas production (Mossel Bay) is converted to liquid fuel, contributing to about 8 % of the national liquid fuel requirements (Burger, 2008). The majority of South Africa's liquid fuel is imported in the form of crude oil, while approximately 30 % is produced from coal or natural gas by Sasol (Burger, 2008).

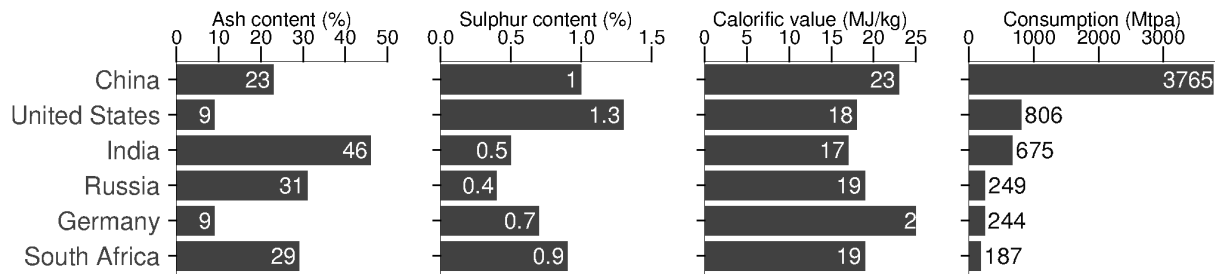


Figure 1.4: Comparison of coal properties from the top users (Pretorius et al., 2015).

South Africa's mineral wealth includes precious metals (gold and silver), platinum group metals (*PGM*), coal, non-ferrous minerals (most importantly refined copper, nickel, cobalt, titanium, zirconium followed by zink, lead and arsenic concentrates), ferrous minerals (iron, manganese and chrome) and industrial minerals (including aggregate, sand, limestone, lime, phosphate-rock and sulphur). It holds the largest global reserves of manganese, chromium, *PGM*, gold, alumino-silicates and vanadium (Burger, 2008).

Major anthropogenic pollution sources in South Africa include: petrochemical plants, power stations, smelters (iron/steel/chromium/manganese, vanadium and ferro/alloy), other metallurgical products, Sasol oil from coal plants, brick works, steelworks, foundries, fertiliser plants, pulp and paper mills, chemical works, motor vehicles, smouldering discard coal dumps, domestic fuel combustion, biomass burning, aircraft emissions and shipping operations. The bulk of these industries are found on the Highveld. Gauteng Province, for example, occupies 1.4 % of total land area of South Africa, houses 23.9 % of the population and is responsible for over 40 % of manufacturing output (StatsSA, 2014).

The emission density for sulphur for the southern African region south of 18 °S is estimated to be 3 kgS /ha and ranges from zero to as much as 200 kgS /ha over the South African Highveld (Sivertsen et al., 1995; Zunckel et al., 2000). Wet deposition rates range from 6 kgS /ha in the source region to less than 1 kgS /ha at background sites. Over the relatively dry South African Highveld the ratio of dry deposition to wet deposition rates is approximately 60 : 40 (Zunckel et al., 1996; Zunckel, 1998; Zunckel et al., 1999; Zunckel, 1999). Highveld emissions of sulphur account for nearly 40 % of all Africa's emissions south of the equator (Zunckel et al.,

2000). The oxidation rate of  $SO_2$  over the Highveld is between 6.6 % per hour during winter and 10.9 % per hour during summer (Igbafe, 2007). Monthly and annual average ambient  $SO_2$  concentrations are relatively low over the Highveld (Lourens et al., 2011; Josipovic et al., 2009, 2010; Worobiec et al., 2011). Ambient monthly concentrations range from below 2 ppbv at rural sites, to almost 15 ppbv over the Highveld (Josipovic et al., 2009). Even shorter term averages compare favourably with South African and European Ambient Air Quality Standards (AAQS) (Venter et al., 2012). Regional modelling studies suggest that higher ambient concentrations of  $SO_2$  at shorter term averages, such as 10-minute and hourly periods, might be of concern. This is increasingly the case as planned industrial development continues (Scorgie and Thomas, 2006; Thomas, 2008).

The South African Highveld is a globally prominent  $NO_x$  source (Figure 1.5). The high density of coal-fired power stations and other industries, as well as the densely populated metropolis of Gauteng causes a pronounced area of enhanced  $NO_x$  clearly visible using satellite-based instruments (Heue et al., 2008; Lourens et al., 2012; Richter et al., 2005). Surprisingly, ambient  $NO_x$  levels at the surface do not regularly exceed national ambient standards (Josipovic et al., 2009). The total nitrogen deposition on the South African Highveld is between 6.7 kg/ha/a to 13.1 kg/ha/a (Collett et al., 2010; Ferguson, 2009). This does not pose a significant threat to the environment. Furthermore, wet deposition studies over South Africa have not found significant acidity (Mphepya et al., 2004; Vet et al., 2014). Natural rainfall has a slight acidity due to biomass combustion which is a major contributor to acidification (Galpin and Turner, 1999). Industrial sulphur oxides ( $SO_x$ ) and  $NO_x$  emissions are superimposed on this natural source of acidity. While this is not currently a problem, a slight positive trend in  $NO_x$  has been observed over the Highveld (Balashov et al., 2014; Thompson et al., 2014), and a positive trend in vertical  $NO_2$  column (Richter et al., 2005). Continued development and additional coal-fired power stations will likely increase surface  $NO_x$  levels in the future.

Closely associated with the large  $NO_x$  industrial emissions is tropospheric  $O_3$ . A strong seasonal cycle in  $O_3$  has been observed in southern Africa (Diab et al., 1996; Lourens et al., 2011; Thompson et al., 1996). The southern hemisphere spring  $O_3$  maximum coincides with the end

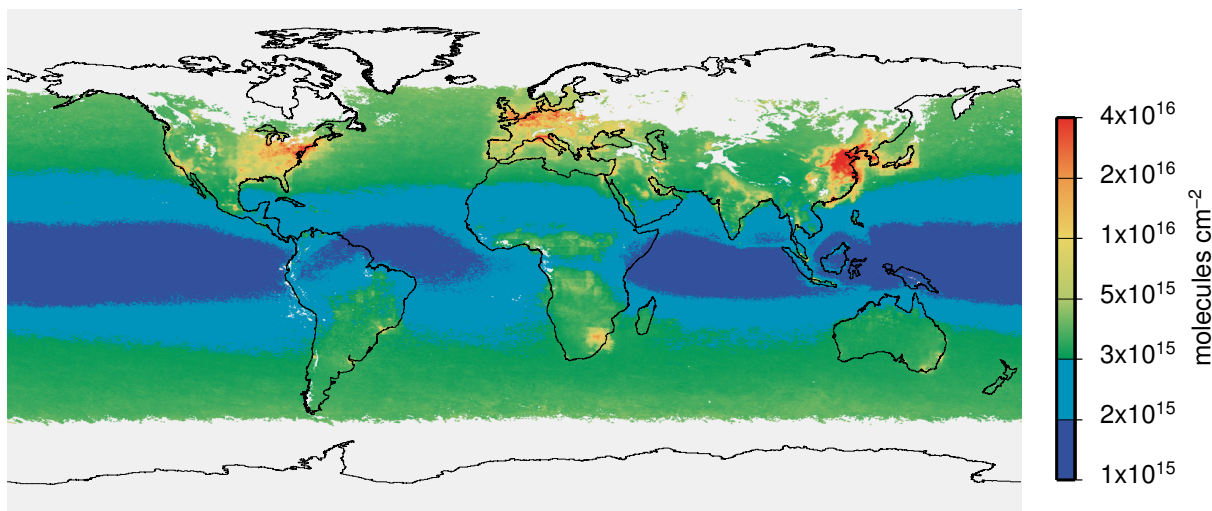


Figure 1.5: Total column global NO<sub>x</sub> climatology derived from SCIAMACHY between 2003 and 2007 (adapted from Richter et al. (2005); Heue et al. (2008); Lourens et al. (2012)).

of dry season biomass burning peak in southern Africa between August and November. The impact of the seasonal biomass burning is more pronounced in the northern parts of South Africa (Diab et al., 1996). This enhancement is mostly in the middle and upper troposphere with source regions from as far as central Africa (Diab et al., 2003). Surface  $O_3$  values sometime exceed 80 ppbv (Stevens, 1987; Venter et al., 2012) but frequently exceed 40 ppbv over large parts of central and northern South Africa (Zunckel et al., 2004, 2006). Higher values are typically experienced downwind of the industrialized Highveld (Josipovic et al., 2009) and towards the northern parts of the Highveld (Zunckel et al., 2006). Although anthropogenic *VOC* play an important role in photochemical pollution, biogenic emissions are typically the dominant source of *VOC* (Otter et al., 2003; Pike and Young, 2009). This is apparent in the maximum monthly  $O_3$  levels that coincide with the peak biomass burning season.  $O_3$ , along with  $PM_{2.5}$  are the main pollutants associated with mortality (Figure 1.6) (Lelieveld et al., 2015).

*PM* is arguably South Africa's biggest air pollution problem (Hersey et al., 2015; Scorgie et al., 2003, 2004; Thomas, 2008). While industrial sources and biomass burning contribute greatly to the regional *PM* load, residential solid fuel burning contributes most to health impacts where the majority of people live. Ambient *PM* levels far exceed those prescribed by the World

Health Organization (WHO) and local AAQS even in the smallest low-income settlements (Engelbrecht et al., 2000, 2001, 2002; Hersey et al., 2015; Piketh et al., 2013, 2014; Rorich and Galpin, 1998; Worobiec et al., 2011). Coal is mostly used as a domestic fuel on the Highveld where proximity to mines make it an affordable fuel (Wagner et al., 2005). In other parts of the country, wood (Kimemia and Annegarn, 2011) and even animal dung are used for cooking and heating (Pauw et al., 2006), although much less research has focussed on these fuels (Friedl et al., 2008). *PM* plays a major role in elevated haze layers over southern Africa (Gwaze et al., 2007; Stein et al., 2003). The characteristic “brown-haze” over Cape Town has been associated with transport (Wicking-Baird et al., 1997), industrial and residential solid fuel burning sources (Walton, 2004). Global estimates point to power generation as the biggest contributor to air pollution related health impacts in South Africa (Lelieveld et al., 2015) (Figure 1.7).

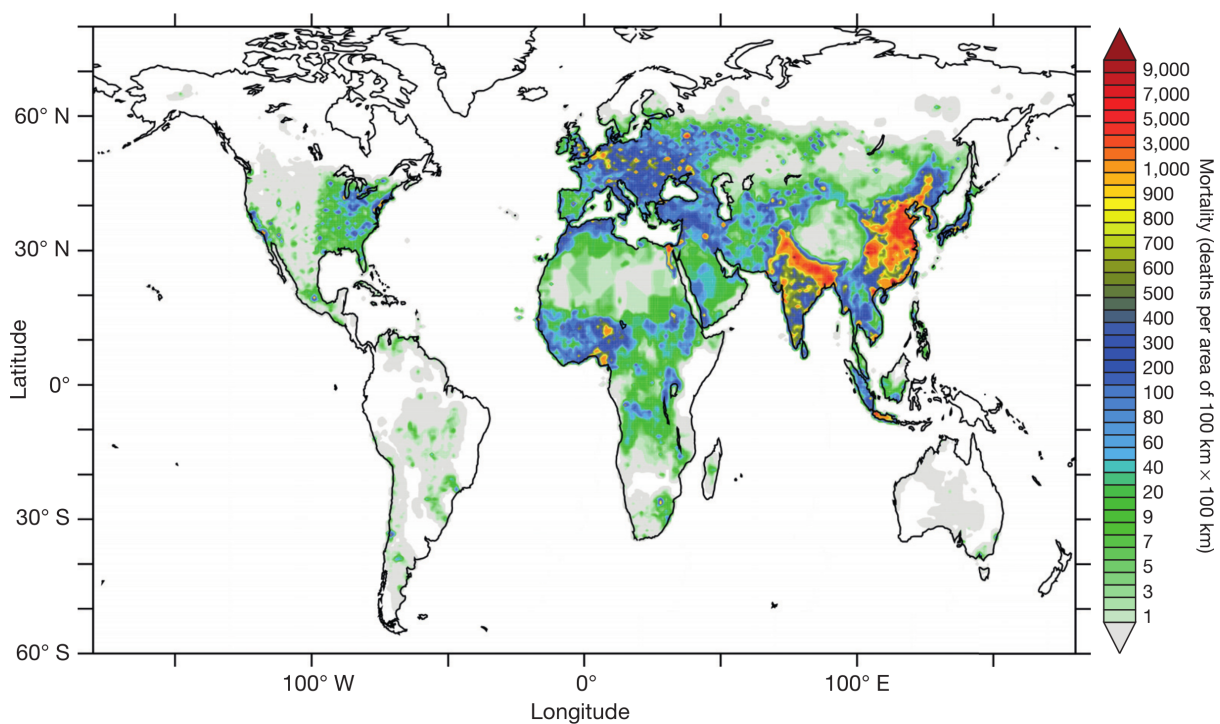


Figure 1.6: A global estimate of mortality related to ambient pollution ( $PM_{2.5}$  and  $O_3$ ) in deaths per 100 km<sup>2</sup> (Lelieveld et al., 2015).

Natural emissions to the atmosphere over South Africa include uncontrolled veld-fires (biomass burning), aeolian dust, lightning induced  $NO_x$  and biogenic releases. Biomass burning, which

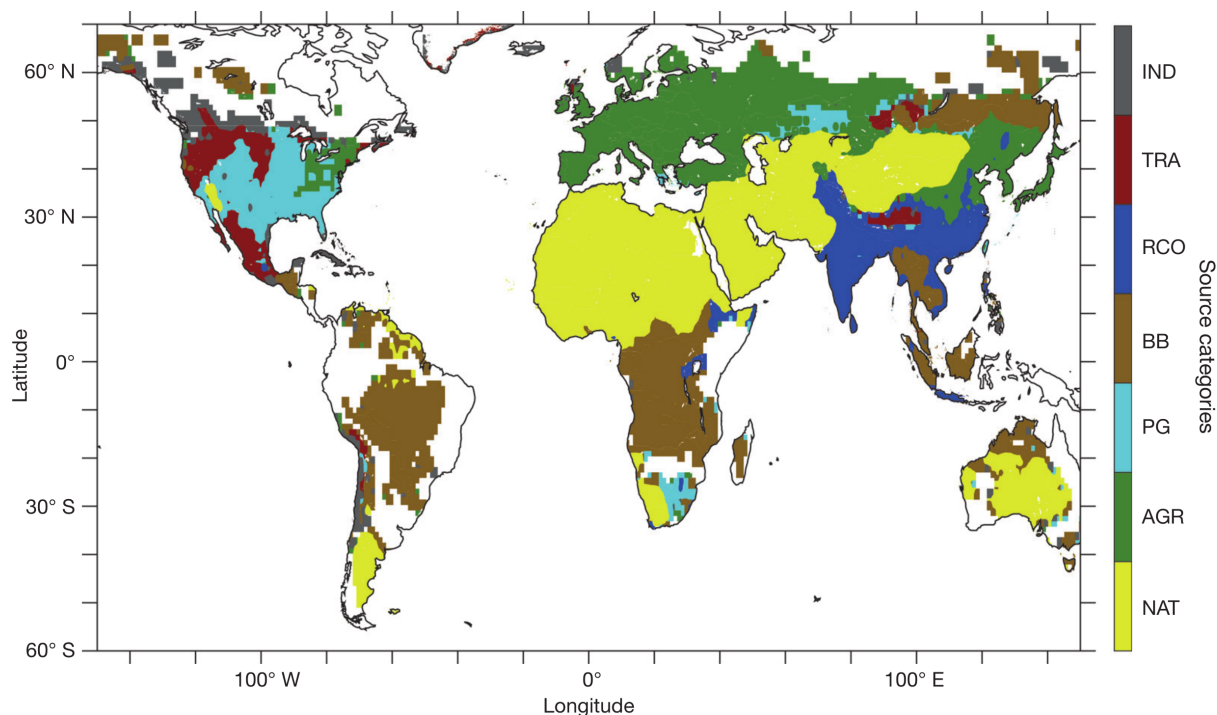


Figure 1.7: A global estimate of the sources contributing the most to ambient pollution related mortality (Lelieveld et al., 2015). Source categories include: IND, industry; TRA, land traffic; RCO, residential solid fuel burning and commercial energy; BB, biomass burning; PG, power generation; AGR, agriculture; and NAT, natural.

can be considered as both an anthropogenic and a natural source, plays an important role during the end of the dry season in the northern parts of South Africa, but is not the dominant source of aerosol (Piketh et al., 1999b,c; Piketh, 2000). The major constituents of the haze layer over South Africa are crustally-derived aeolian dust and industrially-produced sulphur aerosol with lesser contributions from biomass burning and marine aerosol (Piketh et al., 1999b,c).

### ***Other pollutants of concern in South Africa***

Trace elements that are associated with health impacts include *Pb* and *Hg*. Early estimates of *Hg* from gold mining and coal combustion listed South Africa, with an emission of 82.6 t/a, as the 2nd highest global emitter (Pacyna and Pacyna, 2002). However, even though the *Hg* content of South African coal (0.2 to 0.327 ppm) is significantly higher than the global average

(0.1+0.01 ppm) (Wagner and Hlatshwayo, 2005), a more reliable estimate ranges between 2.6 t/a to 17.6 t/a (Dabrowski et al., 2008). The impact of *Hg* on health and the environment in South Africa has not been quantified.

During 1990/91 South Africa was responsible for 4542 t/a *Pb* emissions, accounting for about 28% of the total African emissions. About 29 % of atmospheric emissions came from combustion of fossil fuels (mainly gasoline), 7 % from industrial operations and 64 % from mining and smelting operations (Nriagu et al., 1996). *Pb* blood levels in most of South African children (90 % reported by Nriagu et al. (1997) and 78 % reported by Mathee et al. (2002)) is estimated to be above the international accepted action level of 10 µg/dL. Leaded petrol was subsequently phased out in early 2006. However, atmospheric *Pb* is not the only important source of exposure. Failure to reduce *Pb* from other sources of exposure, such as paint, drinking water and consumer products (Mathee et al., 2007; Montgomery and Mathee, 2005) will probably result in slower reductions in *Pb* blood levels as compared to dramatic decreases in the USA (Goldman and Carra, 1994; Mushak, 1992).

## **Transport of pollutants**

Trace gases and aerosols are transported horizontally and vertically through different meteorological phenomena, ranging from small scale turbulence to general global circulation. The link between the scale of observed phenomena versus the tropospheric lifetime of a substance is shown in Figure 1.8. Reactive substances such as *OH* and *NO* are transported by small scale features such as turbulence, wakes and plumes in the atmospheric boundary layer (ABL). Concentrations drop off rapidly with distance from the source. Highly stable substances such as *CO*<sub>2</sub>, *N*<sub>2</sub>*O*, carbon tetrachloride (*CCl*<sub>4</sub>) and *CH*<sub>4</sub> have such long atmospheric lifetimes that they become well mixed throughout the troposphere.

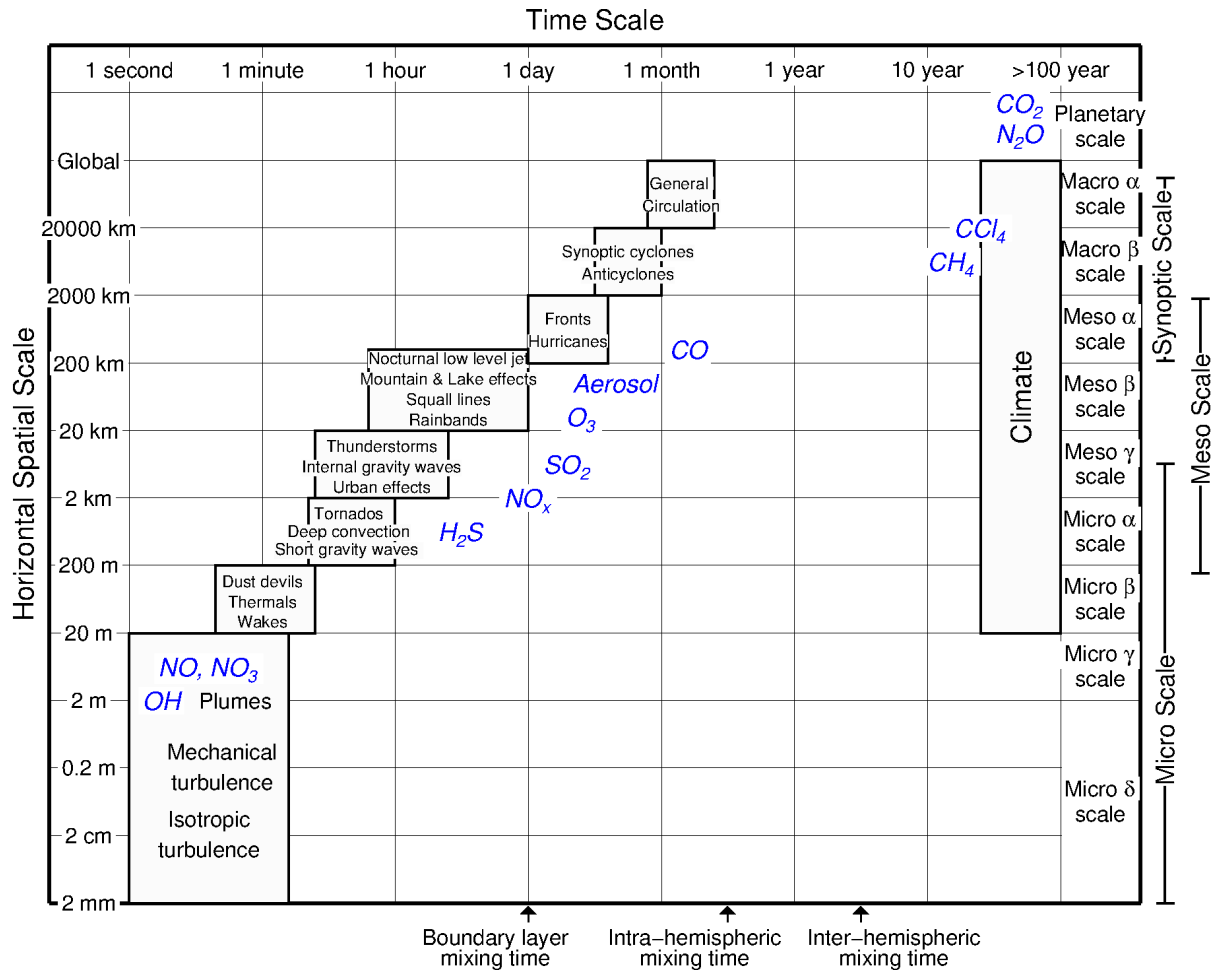


Figure 1.8: Spatial and temporal orders of magnitude for the typical scales observed in meteorology (from Stull (1988) and Seinfeld and Pandis (2006)). Tropospheric lifetimes of the trace gases considered in this study are superimposed (Thunis and Bornstein, 1996)

### Transport of pollutants in the atmospheric boundary layer

The ABL is important to us because this is where we live and breath, but because it is where most pollutants are emitted. It is usually defined as the part of the atmosphere that responds to surface forcings with time scales less than 1 hour. This definition is evident when looking at the spectral intensities of near ground wind speeds. A clear energy gap separates the turbulent scales ( $< 1$  hour) with the synoptic scales ( $> 5$  hour) (van der Hoven, 1957). Typically the ABL extends to heights between 30 m and 3 km above the surface. The free troposphere, above the 3 km, typically experiences geostrophic flow.

The top of the ABL is usually marked by a temperature inversion. Turbulent mixing from the surface creates this cap, but in turn the inversion traps turbulence below it by inhibiting vertical movement. Capping inversions therefore break the atmosphere in two parts; the ABL that responds quickly to surface influences through vigorous turbulence and the remainder of the troposphere that does not experience the strong turbulent coupling with the surface. The depth of the ABL is influenced on a local scale by surface characteristics, such as the roughness of the underlying surface, the reflectivity (albedo) of the surface, and the amount of moisture available. Factors determining wind distribution in a fair weather ABL over a homogeneous surface are: the large-scale horizontal pressure and temperature gradient (or geostrophic and thermal winds), surface friction and roughness characteristics, the earth's rotation, and thermal stratification (stability) caused by the diurnal heating and cooling cycle (Araya, 1999). A schematic of the ABL diurnal evolution in fair-weather conditions is shown in Figure 1.9.

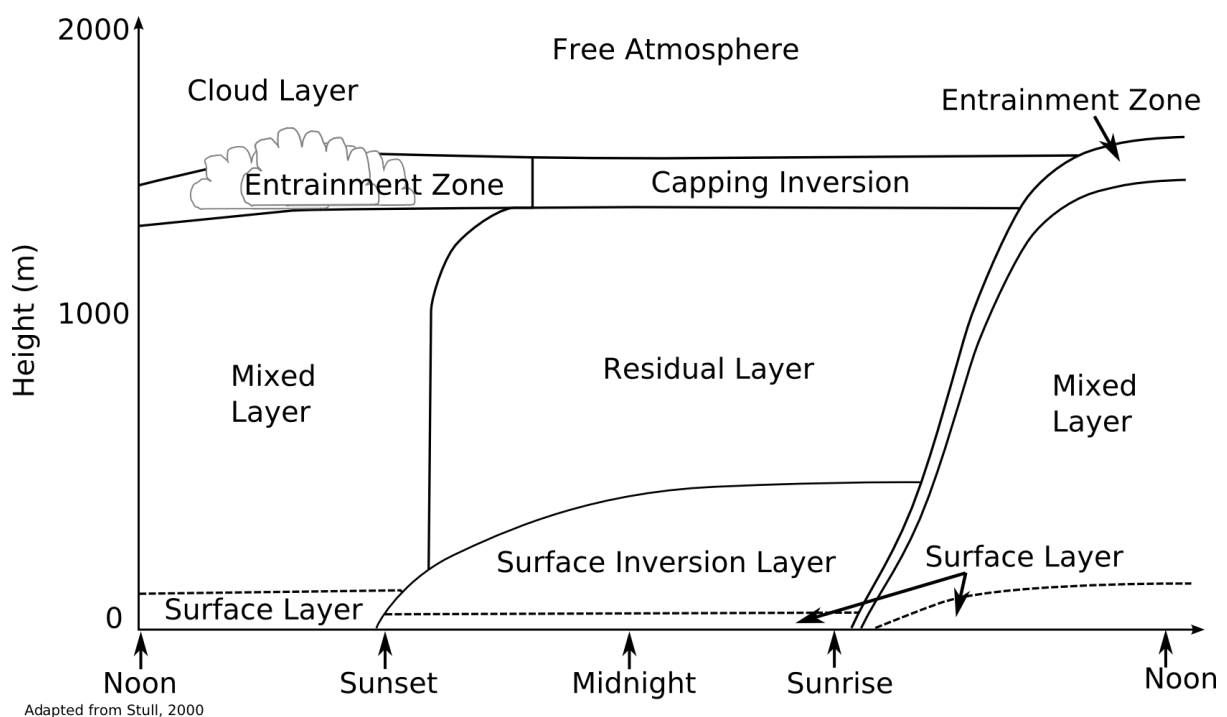


Figure 1.9: Schematic of the diurnal evolution of the planetary boundary layer structure in fair-weather conditions. Modified after Stull (2000).

The treatment of the ABL in meteorological and air quality models is critical. Meteorological models are generally not capable of simulating sub grid-scale features in relation to the ABL because too many semi-empirical parameterizations are involved (Zhang et al., 2001). Air quality models mostly use a simplified statistical approach to model the ABL (Araya, 1999; Beychok, 1994; Stull, 1988, 2000). These models are therefore extremely sensitive to errors and uncertainties in the boundary layer height profile (Berman et al., 1995; Zhang and Rao, 1999).

Numerical weather models use grid spacing or wavelength cutoffs that fall within the spectral gap. This means that larger-scale motions can be explicitly resolved and deterministically forecast. The smaller-scale motions, namely turbulence, are not modelled directly. Rather, the effects of those sub grid scales on the larger scales are approximated. These smaller-size motions need to be parameterized by sub grid-scale stochastic (statistical) approximations or models.

### **Synoptic scale transport**

Transport and dispersion of pollutants do not only influence their eventual fate, but play a very important role in its chemical processing (Kley, 1997). Local and micro scale conditions affect dispersion of an effluent in the lower part of the atmosphere in the order of minutes to hours. After a day or longer, pollutants have been thoroughly mixed over the maximum depth of the ABL. Synoptic scale circulation systems further dilute and transport pollutants.

South Africa is situated between 34° to 20° south of the Equator, largely in the sinking part of the idealised Hadley and Ferrel cells. The warm, dry subsiding air produces generally clear skies, rising surface pressure, warmer surface temperatures and semi-permanent subtropical anticyclones. On the southern side of the subtropical high pressure belt moving air is deflected by the Coriolis force. Mean westerly flow is experienced over the southern parts of South Africa. Upper level winds are strengthened by the thermal wind resulting from the strong horizontal

temperature gradient between the equator and the poles. Wind speeds of more than 50 m/s are common and are referred to as subtropical jets or jet streams (Taljaard, 1994a,b,c,d,e,f; Tyson and Preston-Whyte, 2004).

Air moving to the equator is deflected into easterly winds by the Coriolis force to the north of the subtropical high pressure belt. It converges with north-easterly trade winds in a near-equatorial zone of low pressure stretching around the globe. The several hundred km wide zone of numerous deep convective clouds visible on geo-stationary satellites any day is commonly referred to as the Intertropical Convergence Zone (ITCZ). The ITCZ migrates north and south with the seasonal progression of the sun. Over Africa it oscillates between 20° north in northern summer to about 17° south in southern midsummer. Although loosely called the ITCZ over southern Africa during southern summer, it should more appropriately be called an inter-ocean convergence zone. It is the convergence of the westward extension of the trade winds of the Indian Ocean and the re-curved air stream from the South Atlantic trades. The latter enters the Congo basin from the west and south- and eastward to the trough (Taljaard, 1994b; Tyson and Preston-Whyte, 2004).

Interactions between the tropical easterly trade winds to the north of South Africa and temperate disturbances to the south have important consequences for weather over the country. Numerous classifications of southern African weather types have been proposed (Taljaard, 1994b; Tyson and Preston-Whyte, 2004). Tyson (1986) identified the five main circulation types as continental anticyclone, ridging anticyclone, westerly trough, cut-off low and tropical disturbances in the easterlies (Figure 1.10). The continental anticyclone and the tropical easterly disturbances have a distinctly seasonal cycle. Continental anticyclones are the dominant feature (more than 60 %) during autumn and winter (March to August). Tropical easterlies dominate between November and February (30 % to 50 %). Cut-off lows have occur mostly in the transitional seasons, but even during their peak, in October, occur just over 10 % of the time. Travelling perturbations in the westerlies, called westerly waves, and trailing ridging anticyclones move over the country regularly (around once a week) throughout the year. They extend deeper to

the north over winter as the South Atlantic Anticyclone and the South Indian Anticyclone both move north and westward.

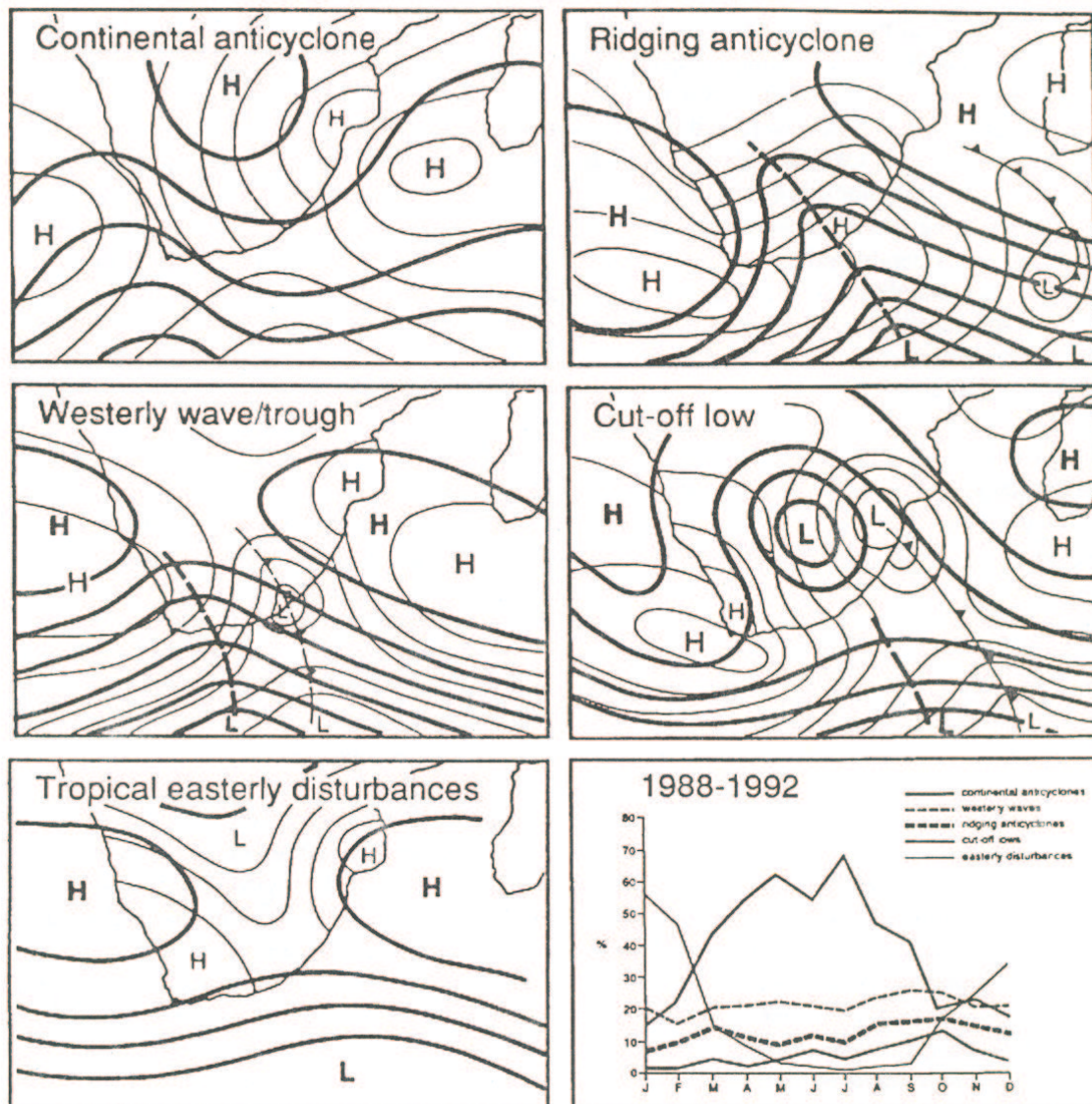


Figure 1.10: A simplified classification of the five major circulation types affecting southern Africa and their monthly frequency of occurrence between 1988 and 1992 (Tyson, 1986).

The synoptic systems interact temporally and spatially to form characteristic transport patterns over southern Africa (see Figure 1.11) (Garstang et al., 1996; Piketh et al., 2002; Piketh and

Watson, 2004). Southern African Fire/Atmospheric Research Initiative during 1992 (SAFARI-92) and the Southern African Regional Science Initiative (SAFARI2000) (Swap et al., 2002, 2003) identified the dominant sub-continental transport pathways of southern Africa. The *River of Smoke* gathers emissions from as far north as 10° South before being transported eastwards over the Indian Ocean, leaving the continent between Port Elizabeth and Maputu (Billmark et al., 2003; Stein et al., 2003; Swap et al., 2003). Recirculating over the northern interior, caused by persistent anticyclonic conditions, is an important feature (Tyson et al., 1996a,b; Tyson and D'Abreton, 1998). Westerly waves are the dominant transport mechanism (more than 75 % of the time) out of southern Africa (Tyson et al., 1996b; Tyson, 2000; Piketh et al., 1999a; Piketh, 2000; Piketh et al., 2002; Freiman and Piketh, 2003; Piketh and Watson, 2004). These pathways were identified using trajectory modelling studies (D'Abreton, 1996; Tyson and D'Abreton, 1998) and were later confirmed by ground based measurements (Piketh et al., 1999a; Piketh, 2000; Piketh et al., 2000, 2002). The *River of Smoke* have been shown to travel all the way to Australia under certain conditions (Wenig et al., 2003). In the process it plays an important roll in iron fertilisation of the South Indian Ocean (Piketh et al., 2000).

The South African troposphere has been found to be vertically stratified (Preston-Whyte et al., 1977; Cosijn and Tyson, 1996; Garstang et al., 1996; Freiman and Tyson, 2000) sometimes containing not well understood *clean air slots* (Hobbs, 2003). These stable discontinuities have been identified as factors governing the vertical distribution (Tyson et al., 1997; Swap and Tyson, 1999) and horizontal transport (Freiman, 2001) of aerosol and trace gases. Radiosonde climatologies were used to identify prominent absolutely stable layers at 850 hPa, 700 hPa, 500 hPa and 300 hPa.

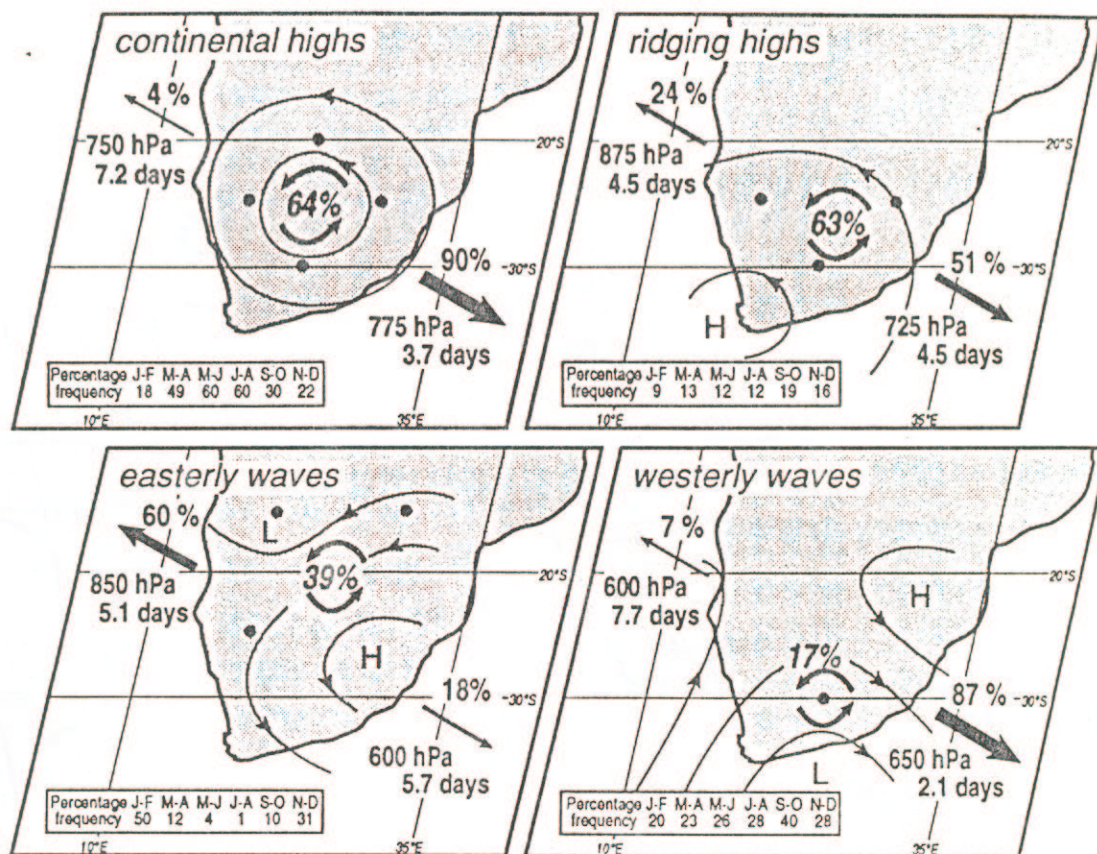


Figure 1.11: Mean percentage transport and re-circulation by circulation type between the surface and 800 hPa. Frequency of occurrence and the mean heights of transport and times to reach 10°E or 35°E are given (Tyson et al., 1996b).

### Transport on a planetary scale

General circulation and semi-permanent highs, lows and jet streams affect the long-range transport of pollutants. At these large scales, however, chemical transformation, diffusion and dispersion by micro-, macro- and synoptic scale processes have changed the character of individual sources into a well-mixed polluted air masses. Synoptic and planetary scale circulation patterns disperse an effluent uniformly in a hemisphere with limited transport across the equator (Machta, 1958; Lovelock et al., 1973). Inter-hemisphere mixing occurs over much longer time frames. It is estimated that a pollutant with a 20-day lifetime and a global emissions field similar to that of CO would result on continents even with high domestic emissions, receiving

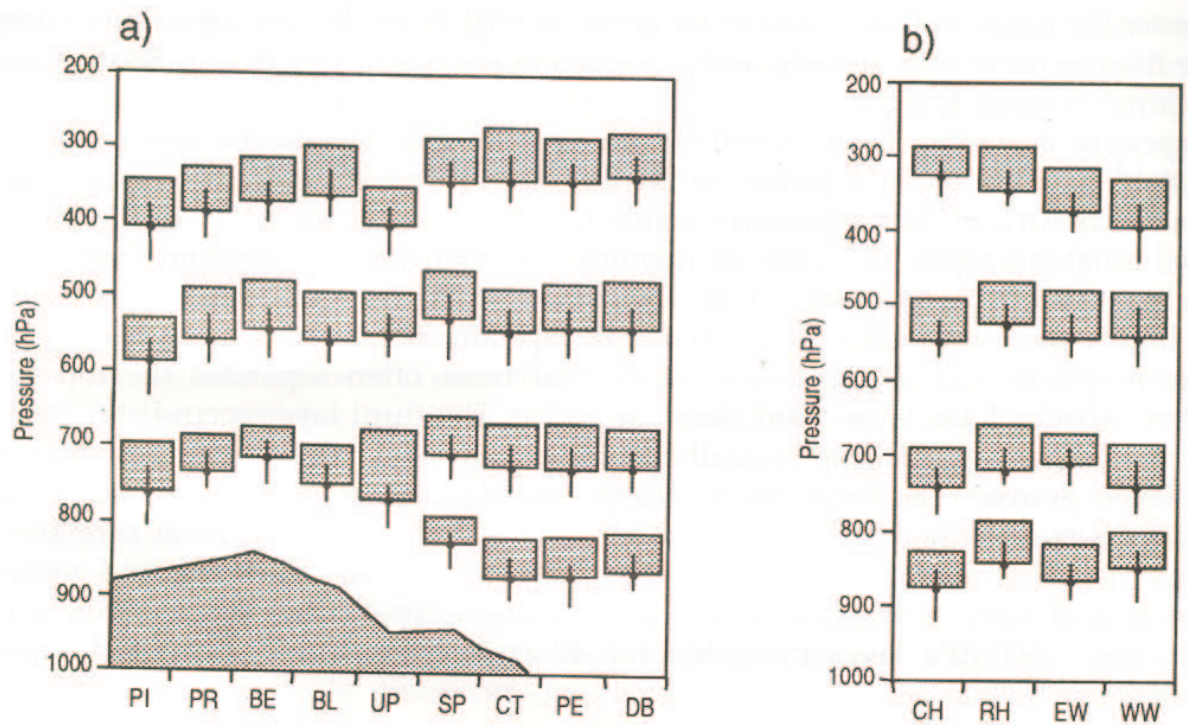


Figure 1.12: Absolutely stable layers over South Africa (Tyson et al., 1996b).

the majority of their pollutant burden from foreign continents (Stohl et al., 2002, 2003a). Intercontinental transport of air pollutants of the type seen between South Africa and Australia (Wenig et al., 2003) are therefore not that unique (Stohl et al., 2003b).

## Air quality legislation and regulations

Effective air quality management requires a blend of technological inventiveness, legal constraints, economic incentives and political willingness (Preston-Whyte, 1989). Different philosophies and strategies to achieve this have been proposed or adopted with varying success (see Table 1.3). These strategies have to balance the health and well-being of society, economic growth, opportunities for the poor and ultimately the willingness of society to bear the cost of air pollution. These costs, direct and indirect, will typically realise on time scales much

longer than that of a politician's term in office. Air quality and climate impacts are therefore particularly challenging to regulate.

Table 1.3: A classification of environmental regulatory instruments

|                            | <i>Direct Instruments</i>                                | <i>Indirect Instruments</i> |
|----------------------------|----------------------------------------------------------|-----------------------------|
| <i>Economic Incentives</i> | emission fees<br>marketable permits<br>public disclosure | environmental taxes         |
| <i>Command and Control</i> | emission standards<br>ambient standards<br>cost benefit  | technology standards        |

Environmental regulatory instruments can be classified according to two criteria (Table 1.3): (i) do they dictate how much to abate and what technology to use (command and control) or simply create financial incentives for industry to abate (economic incentives), and (ii) do they require the regulator to monitor emissions (direct instruments) or not (indirect instruments) (Blackman et al., 2000). Command and control philosophies include emission control, ambient air quality control, technology standards (de Nevers, 2000; van Tienhoven et al., 1995) and detailed analysis of cost versus benefit (Scorgie et al., 2004; Leiman et al., 2007). Economic incentives include emission fees, marketable permits, environmental taxes (Atkinson, 1991; Blackman and Harrington, 1999) and public disclosure programs (Afsah et al., 1996, 1995; Tietenberg, 1998; Foulon et al., 2002; Blackman et al., 2000). Some economic incentive strategies promise lower cost for environmental improvement (Krupnick, 1997; Alberini and Krupnick, 2000).

Environmental regulation in developing countries is far more challenging because of a number of financial, institutional, and political constraints. Four key constraints have been identified in the literature (Eskeland and Jimenez, 1992; Afsah et al., 1996; Krupnick, 1997; Eskeland, 1998; Blackman and Harrington, 1999). Public sentiment favours economic development over environmental protection and private-sector environmental advocacy is less organised than in industrialised countries. Environmental regulatory instruments, such as legislation and data collection institutions, are not well established. Technical and fiscal resources geared toward

environmental protection are limited. Finally, industry is dominated by small firms which are difficult to monitor. South Africa suffers from all these constraints. Additionally, important sources that are difficult to regulate contribute significantly to ambient air quality where a large portion of the population live. This includes residential solid fuel burning and biomass burning during the dry season. Furthermore, South Africa has one of the most heavily coal-dependent economies in the world. Electricity generation is therefore a key source to regulate and integrally link to residential solid fuel burning through the cost of electricity.

South Africa had its first fully democratic national elections in 1994. This was followed by a radical change in policy to principles of accountability, participation and transparency, laid out in the Constitution (RSA, 1996). The South African constitution lays the foundation of air quality management by including “an environment that is not harmful to health or well-being” in the Bill of Rights (RSA, 1996). Other important South African legislation related to air quality management include the National Environmental Management Act (NEMA) (RSA, 1998), and the National Environmental Management Air Quality Act (NEMAQA) (RSA, 2005). NEMA established principles for decision making on environmental matters. South Africa’s legislation provides the scope for a variety of direct and indirect regulatory instruments, but in practise, command and control philosophy dominates through emission and ambient air quality standards (RSA, 2005). South Africa’s socio-economic problems put special pressure on the environment (du Pisani and Sandham, 2006). Even though environmental legislation embodies sound democratic principles, it lacks implementation, compliance and enforcement (Rossouw and Wiseman, 2004).

South African legislation mostly attempts to regulate air quality through ambient air quality standards (RSA, 2009, 2012) for criteria pollutants and emissions limits (RSA, 2013) for certain activities (RSA, 2005). “*Criteria pollutants*” is a phrase commonly used to refer to specific pollutants in the atmosphere that pose a health risk to humans, animals or the environment. These pollutants have concentrations elevated above the natural background levels. Managing the concentrations of criteria pollutants is an attempt to manage the overall quality and safety of the air we breath. Focusing on criteria pollutants as a management strategy works well where

sources are significant, such as power generation or large smelters. Its deficiencies become apparent however, when dealing with substances released from smaller sources which pose a significant threat even at low concentrations, for example some species of *VOC*. Frameworks exist in the current legislation to use additional regulatory instruments. An example of this is the use of air quality offsets in instances where the economic cost of compliance are deemed too high.

Measurements of air pollution in the ambient environment are the basis for sound air quality management in the new South African air quality legislation. Air quality monitoring is important both for problem identification and prioritisation, and monitoring compliance. Although significant progress has been made over the past five years in developing good air quality monitoring networks, many gaps remain in large parts of the country concerning the actual measurable levels of criteria pollutants and greenhouse gases.

## Research Goals

The aim of the study is to examine the horizontal and vertical distribution and transport of aerosol and trace gases over the industrial and urbanised areas of South Africa in order to assist prioritising national strategies to manage atmospheric emissions. The use of a consistent strategy and a single suite of instrumentation enables an unbiased approach for a large scale assessment.

More specifically, the objectives are to:

- (i) characterise the major natural and anthropogenic sources of air pollution over South Africa using in situ measurements
- (ii) characterise the state of air quality over the major industrial and urbanised areas of South Africa using in situ measurements

- (iii) investigate the vertical distribution of aerosol and trace gases over South Africa
- (iv) prioritise the areas and sources of concern for effective air quality management in South Africa.

## Research Design

This study uses a novel approach of deploying a single suite of equipment on a mobile platform to monitor ambient concentrations of *PM* and trace gases. Airborne measurements of criteria pollutants were collected between the winter of 2000 and the Autumn of 2006 to investigate the state of air quality over the major industrial and urbanised areas of South Africa. These measurements were made by means of intensive field campaigns that focused on each of South Africa's urban and industrial zones, including the Highveld, Cape Town, Port Elizabeth, East London, Durban, Richards Bay, Polokwane and Rustenburg. Ground based measurements using the same instrument set were made in Johannesburg, Cape Town, Witbank and a small low-income settlement on the Highveld between 2008 and 2014 to investigate traffic and residential solid fuel burning emissions.

Aircraft measurements have formed part of studies to investigate the nature (Schroder and Strom, 1997; Terblanche et al., 2000; Haywood et al., 2003a,b), long-range transport (Jeffery et al., 1999; Prospero, 1999; Clarke et al., 2001; Kim et al., 2001; Han et al., 2006) and spatial distribution (Kim et al., 1997; Nunnermacker et al., 2004; Hatakeyama et al., 2004) of air pollution. A series of airborne projects have studied the background seasonal distribution of aerosols and trace gases over southern Africa. These included SAFARI-92 (Lindesay et al., 1996) and Southern African Atmospheric Research Initiative during 1994 (SA'ARI-94) (Helen et al., 1995). Kirkman et al. (2000) provides a synthesis of the  $O_3$ ,  $CO$  and aerosol data collected during these experiments. These projects prompted investigation of atmospheric composition and transport on a larger scale through SAFARI2000 (Swap et al., 2003). The Aerosol Recirculation and Rainfall Experiment (ARREX) studied the impact of industrial and biomass

aerosol on cloud processes (Terblanche et al., 2000; Ross et al., 2003). Regional  $O_3$  and  $SO_2$  modelling studies were conducted as part of the cross border air pollution assesment project (CAPIA) (van Tienhoven and Zunckel, 2004; Zunckel et al., 2006). This study was designed using an in situ approach targetting urban and industrial zones, using suite of instruments similar to Taubman et al. (2006).

South African legislation calls for ambient monitoring of air quality by different levels of government. More than 100 surface monitoring stations have been deployed by industry, metropolitan, provincial and national government. The quality and availability of data from these sites vary drastically making it difficult to compile a comprehensive national overview of air quality in urban and industrial areas, and hence to devise an evidence-based strategy to prioritise air quality management interventions. This project therefore aims to supplement existing observations with an assessment of all the major industrial and urban areas in South Africa.

\*\*\*\*\*

South Africa has a strong industrial sector. Many anthropogenic sources of atmospheric emissions exists around major urbanized and industrialized areas. These emissions perturb all four the grand nutriant cycles. The current conceptual model dictates that thermodynamic stability governs the observed the vertical stratification of pullutants over South Africa. This study deploys mobile laboratories to provide a novel characterization of atmospheric emission sources, areas enhanced levels of pollutants, and the vertical transport of pollutants.

## **Chapter 2**

# **Data and Methodology**

Data collection and analytical procedures are discussed in this chapter. A suite of aerosol and trace gas instrumentation was deployed on an airborne platform to sample over the major industrialised and urban areas in South Africa. Further ground-based measurements were done to study sources not well captured in the airborne campaigning, such as residential solid fuel burning and traffic.

### **Introduction**

Significant progress has been made over the past years in developing good air quality monitoring networks, however, many gaps remain in large parts of the country about the actual measurable levels of criteria pollutants and greenhouse gases. In this project an attempt has been made to measure all the major criteria pollutants over all major cities and industrial centres around the country. This section outlines the details of the equipment, ground-based and aircraft flight strategies utilised to collect multi-season ambient pollution concentrations in South Africa. It details methods used to assess national priorities.

## Study Area

Major cities and industrial centres were identified in the project to be evaluated. This facilitated a comparison of different regions using the same set of instrumentation and methodology. The areas with a large number of atmospheric emissions that were the focus of this project were Cape Town, Vereeniging, Rustenburg, Gauteng urban, Witbank, Secunda, Richards Bay, Pietermaritzburg, Durban and Port Elizabeth (Figure 2.1).

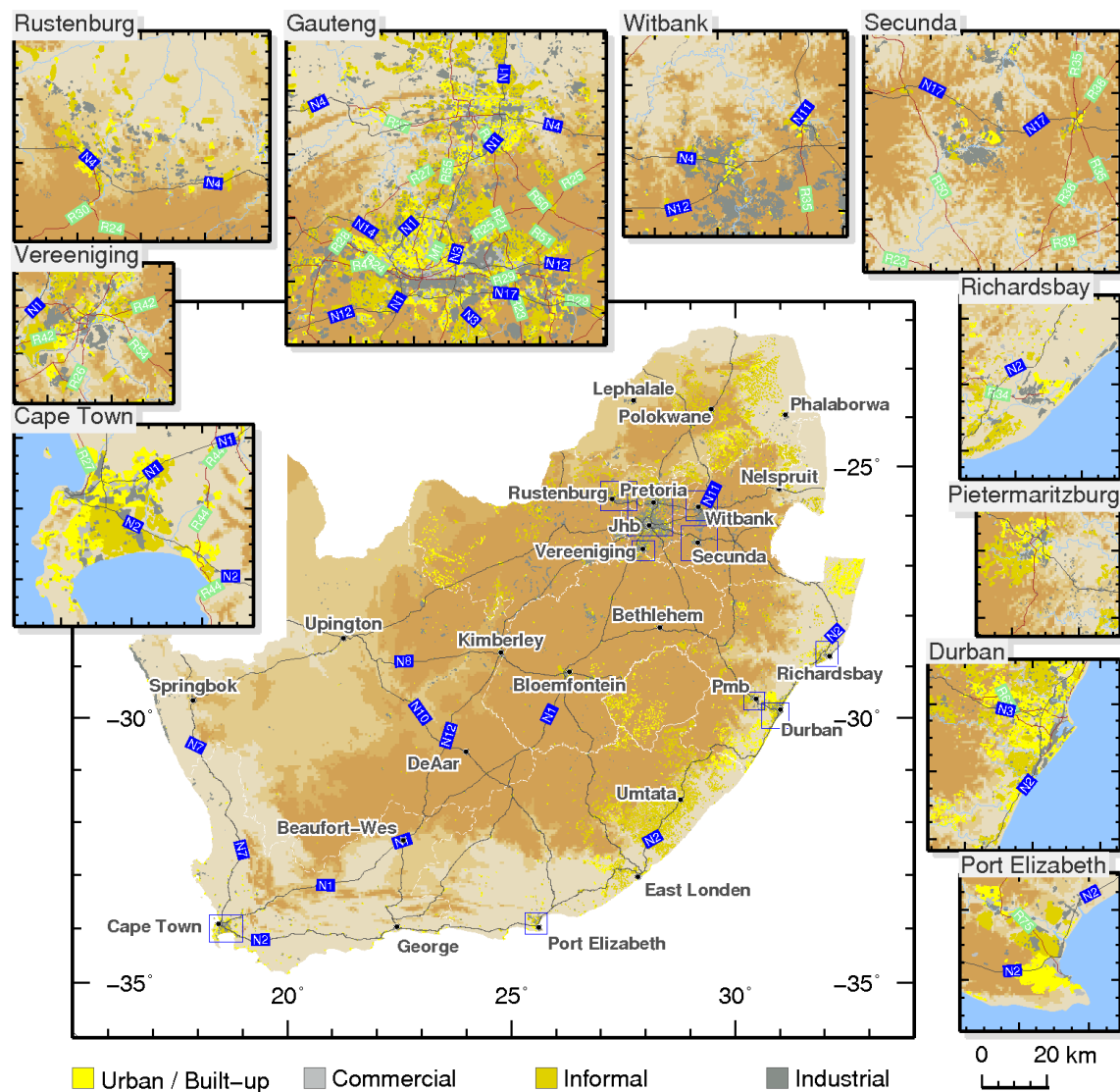


Figure 2.1: The urban and industrial areas over which observational campaigns were conducted between 2003 and 2013.

## Suite of instruments

Horiba and Thermo environmental instruments (analysers) were used to sample ambient concentrations of  $NO$ ,  $NO_2$ ,  $SO_2$ ,  $CO_2$ ,  $CO$  and  $O_3$  continuously at 1 min average intervals and were recorded on various data acquisition systems. A summary of the equipment utilised to sample is given in Table 2.1. Calibration of each instrument was done before and after intensive campaigns.  $PM$  was sampled using a Passive Cavity Spectrometer Probe (PCASP) for the airborne and Horiba BAM 1020, MetOne E-sampler and a MetOne E-BAM for the ground-based campaigns.

Co-located at all surface sites was a fully automatic meteorological station which was equipped to measure wind speed and direction, solar radiation and temperature, humidity, atmospheric pressure and rainfall. These instruments sampled meteorological data at 1 min intervals (Table 2.1).

## Trace gas variables

Each of the instruments was set up to output an analogue signal at 1 Hz. This translates into a measurement for each of the variables every 70 to 100 m along the flight path at a median aircraft speed of 95 m/s (standard deviation of 12 m/s). Some of the instruments have a slight delay between the intake of the sample and the actual measurement. The TEI trace gas instruments have a response time of approximately 30 s for a measurement that spans from 0 to full scale range. This means that in plumes in which the concentrations rise dramatically to close to the full range of the instrument that the measurement will be underestimated.

The air pollution trace gas instruments were calibrated before and after each project. Full dynamic multiple point calibrations were conducted according to the South African National Accreditation System (SANAS) approved methodologies by the Climatology Research Group

Table 2.1: Summary of instrumentation deployed during the different monitoring campaigns.

| Parameter                  | Operating principle/Instrument model      | Range                                       | Precision                      | Response time   |
|----------------------------|-------------------------------------------|---------------------------------------------|--------------------------------|-----------------|
| <b>Trace gases</b>         |                                           |                                             |                                |                 |
| $SO_2$ concentrations      | UV Fluorescence/TEI 43C Trace             | 2-1000 ppb                                  | 1 ppb or 1 %                   | 1 min           |
| $NO_x$ concentrations      | Chemi-Luminescence/Horiba APNA-370        | 0.4-1000 ppb                                | 0.4 ppb                        | 1 min           |
| $O_3$ concentrations       | UV Photometric/Horiba APOA-370            | 1-2000 ppb                                  | 1 ppb                          | 1 min           |
| $CO$ concentrations        | Gas filter correlation/Horiba APMA-370    | 0.04-10 000 ppm                             | 0.1 ppm                        | 1 min           |
| $CO_2$ concentrations      | Licor 7000                                | 0-3000 ppm                                  | 1 %                            | 1 min           |
| $H_2S$ concentrations      | Pulsed-fluorescence/TEI 45C               | 3-10 ppm                                    | 1 ppb or 1 %                   | 80 s            |
| $BTEX$ concentrations      | Gas chromatography/Synspec GC9000         |                                             |                                |                 |
| <b>Particulate matter</b>  |                                           |                                             |                                |                 |
| $PM_{10}$ concentrations   | Horiba BAM 1020                           | 0 mg/m <sup>3</sup> to 10 mg/m <sup>3</sup> | 2.4 µg/m <sup>3</sup>          | 60 min          |
| $PM_{10}$ concentrations   | MetOne E-Sampler                          | 0 mg/m <sup>3</sup> to 1 mg/m <sup>3</sup>  | 0.003 mg/m <sup>3</sup> or 2 % | 60 min          |
| $PM_{2.5}$ concentrations  | MetOne E-BAM                              | 0 mg/m <sup>3</sup> to 65 mg/m <sup>3</sup> | 2.5 µg or 10 %                 | 5 min           |
| $PM$ size distribution     | PMS PCASP100x with DMT upgrade            | 0.1 µm to 3 µm                              | 20 % diameter                  | <1 s            |
|                            |                                           |                                             | ±16 % concentration            |                 |
| <b>Meteorology</b>         |                                           |                                             |                                |                 |
| Temperature                | Vaisala HMP60                             | −40 °C to 60 °C                             | ±0.6 °C                        | 1 min           |
| Humidity                   | Vaisala HMP60                             | 0 % to 100 %                                | ±5 %                           | 1 min           |
| Pressure                   | RM Young 61302                            | 500 hPa to 1100 hPa                         | 0.3 hPa                        | 1 min           |
| Wind speed and direction   | RM Young 05103                            | 0 m/s to 100 m/s                            | ±3 m/s or 1 %                  | 1 min           |
| Rainfall                   | RM Young 52203                            | 0.1 mm per tip                              | 2 % to 3 %                     | 1 min           |
| Solar Radiation            | LI-COR LI-200 pyranometer                 | 0 W/m to 3000 W/m                           | ±5 %                           | 1 min           |
| Aircraft Position          | Global positioning/Garmin GPS             | Global                                      | <15 meter                      | 1 s             |
| Aircraft dynamic pressure  | Transducer/Rosemount 1221F2 VL18B2A e     | 0 hPa to 68.95 hPa                          | 0.32 % FSP                     | <1 s            |
| Aircraft static pressure   | Transducer/Rosemount 1201F A1B2B          | 0 hPa to 1080 hPa                           | 0.1 % FSP                      | <1 s            |
| Aircraft temperature       | Platinum resistance/Rosemount 102 de-iced | −50 °C to 50 °C                             |                                | 3.2 s to ±0.5 s |
| Aircraft relative humidity | Capacitance/Vaisala DMP248                | 0 % to 100 %                                | <3 % RH                        | 35 s to 240 s   |

(CRG). Any discrepancies between the calibrations before and after the campaign were noted and corrected in the data.

*CO* absorbs infrared radiation at a wavelength of 4.6  $\mu\text{m}$ . The Thermo Environmental Instruments (TEI) Model 48C *CO* analyser uses this principle. The electronics convert the non-linear infrared absorption signal to a linear output. A calibration curve is used to linearize the instrument output over any range up to a concentration of 10 000 ppm. The sample is drawn through the optical bench. An infrared source emits radiation that is passed through alternating *CO* and Nitrogen ( $N_2$ ) filters. Absorption of the sample gas occurs in the optical bench once the radiation has passed through a narrow band pass interference filter and the infrared radiation exits the optical bench and falls on the infrared detector. A reference beam, which cannot be further attenuated by *CO* in the sample cell, is produced by the *CO* gas filter. A measurement beam that can be absorbed by *CO* in the cell is produced in the  $N_2$  side of the filter wheel, which is transparent to infrared radiation. Modulation of the chopped detector signal occurs through alternating filters that have an amplitude related to the concentration of *CO* in the sample cell. This system responds specifically to *CO*, as other gases absorb the reference and measure beams equally and do not cause modulation of the detector signal.

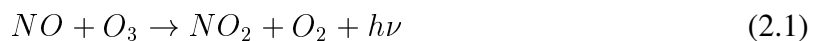
*CO*<sub>2</sub> measurements were made using a LI-7000 analyser manufactured by LI-COR. This analyser measures the pressure with a pressure transducer in the sample cell. It makes automatic pressure corrections for smaller pressure deviations (50 kPa). The LI-7000 detects infrared radiation absorption by *CO*<sub>2</sub>. It measures the difference in absorption between a known concentration (reference cell) and the unknown concentration (sample cell). On the aircraft, a soda-lime scrubber is used to provide a zero for the reference cell.

A TEI model 43C pulsed fluorescence analyser is used to measure *SO*<sub>2</sub>. Hydrocarbons are removed from the sample when the sample flows through the *kicker* and the *SO*<sub>2</sub> continues into the fluorescence chamber unaffected. Here a pulsating UV light is reflected off four selective mirrors that only reflect light at the specific wavelength to excite *SO*<sub>2</sub> molecules. The UV light emitted by the *SO*<sub>2</sub> molecules decaying to a lower energy level is proportional to the *SO*<sub>2</sub>

concentration. The photo multiplier tube (PMT) only receives the ultraviolet (UV) light emitted by the decaying  $SO_2$  particles.

A TEI model 49C UV photometric analyser was used to measure  $O_3$ . UV (254 nm) light absorption is directly related to the ozone concentration, following the Beer-Lambert Law. The air sample is split into two gas streams. One flows through an ozone scrubber and is known as the reference gas, which flows to the reference solenoid valve. The second is the sample gas and flows directly to the sample solenoid valve. The reference and sample gas streams are alternated between cells A and B every 10 seconds, where the UV light intensities of each cell are measured by detectors in the cells. The switching of gas streams between the cells allows the cells to be flushed and the light intensities are ignored during this period.

The operation of the Model 42C is based on the principle that the  $NO$  concentration is linearly proportional to the luminescence that is produced with the reaction between  $NO$  and  $O_3$ . Infrared light is emitted when electronically excited  $NO_2$  molecules decay to a lower energy state (Equation 2.1).



Before  $NO_2$  can be measured using the chemiluminescent reaction, it must be transformed into  $NO$ . This conversion occurs by a molybdenum  $NO_2$  to  $NO$  converter heated to about 325°C. Sample air flows through the particulate filter, a capillary and to the mode solenoid valve. The sample is routed through the  $NO_2$  to  $NO$  converter and to the reaction chamber in  $NO_x$  mode, or straight to the reaction chamber in  $NO$  mode. Dry air enters through the DRY AIR bulkhead and then flows through a flow sensor and through a silent discharge ozonator (ozone needed for the chemi-luminescence reaction is generated here). Electronically excited  $NO_2$  molecules are produced when the  $NO$  in the air sample reacts with the ozone.  $NO_2$  luminescence is detected by a photo multiplier tube (PMT). The concentration of  $NO$  and  $NO_x$  calculated in  $NO$  and  $NO_x$  mode are stored in memory, and the difference between the concentrations is used to

calculate the  $NO_2$  concentration. The analyser outputs  $NO$ ,  $NO_2$  and  $NO_x$  concentrations to the front panel display and to the analogue outputs.

Other reactive nitrogen oxide species, such as  $PAN$ , will be converted to  $NO$  in the abovementioned technique (Seinfeld and Pandis, 2006). It is more accurate to refer to this measurement as  $NO_y$ , however, in an urban environment  $NO$  and  $NO_2$  are typically the dominant constituent species of  $NO_y$ . In this study, these measurements will be presented as  $NO_x$ .

Volatile organic compound data were not measured in situ on the aircraft. Evacuated canisters (six per flight) were filled on each flight and then analysed for  $BTEX$  using a Gas Chromatograph (GC) with a photon ionized detector (PID) detector. The GC was calibrated using the RESTEK standard calibration gas. The position of the point samples were logged on the data system.

All gaseous concentrations are expressed in mixing ratio units of parts per million by volume (ppm) or mixing ratio units of parts per billion by volume (ppb). The  $v$  is not added as is a common convention in atmospheric science (Seinfeld and Pandis, 2006).

## **Aerosol variables**

A PCASP was used to sample  $PM$  on the airborne platform. It is from the general class of instruments called optical particle counter (OPC)s that detect single particles and size them by measuring the intensity of light that the particle scatters when passing through a laser beam. A helium-neon laser beam is focused to a small diameter at the centre of an aerodynamically focused particle laden air stream. Particles that encounter this beam scatter light in all directions and some of the light is collected by a mangin mirror over angles 35 to 135 degrees. This collected light is focused onto a photo detector and then amplified, conditioned, digitised and classified into one of fifteen size channels. The size of the particle is determined by measuring the light scattering peak intensity and using Mie scattering theory to relate this intensity to the

particle size. The size information is sent to the data system where the number of particles in each channel is accumulated over one second. The boundaries of the 15 size bins are shown in Table 2.2.

Table 2.2: The PCASP boundaries (in  $\mu\text{m}$ ) for the 15 size channels.

|     |      |      |      |     |      |     |     |     |     |     |     |     |    |     |     |
|-----|------|------|------|-----|------|-----|-----|-----|-----|-----|-----|-----|----|-----|-----|
| 0.1 | 0.12 | 0.14 | 0.17 | 0.2 | 0.25 | 0.3 | 0.4 | 0.5 | 0.7 | 0.9 | 1.2 | 1.5 | 2. | 2.5 | 3.0 |
|-----|------|------|------|-----|------|-----|-----|-----|-----|-----|-----|-----|----|-----|-----|

The PCASP was developed as an aerosol particle measurement instrument. The size that is determined by the PCASP assumes that the scattered light detected is from spherical particles of refractive index 1.58. The size distribution produced from these measurements must be viewed with great caution when measuring mixed composition aerosols. Particles will not be correctly sized due to their different refractive indices and non-spherical shapes. Volatile particles will lose their mass because of heating in the inlet and sample cavity. The probability of more than a single particle coinciding in the beam or being missed during the electronic reset time increase with concentration. Corrections were applied to account for these losses but still lead to concentration uncertainties. The PCASP is further a particle sizing instrument and not a particle surface area or volume probe. Since the surface areas and volumes are derived by integrating the size distribution, uncertainties in size measurements lead to uncertainties in surface area and volume to a factor of two and three times higher, respectively. More information about the airborne use of these instruments can be found in NCAR (2003).

The PCASP was designed for airborne use and limitations such as heating of the electronics and the lack of an adequate data acquisition system for continuous use prevented its use on the ground-base campaigns. For these purposes, a Horiba BAM 1020, a MetOne e-sampler and a MetOne e-BAM were used. The latter three are OPCs and suffer from the same bias as the PCASP.

Nucleation mode particles ( $PM$  smaller than  $1\ \mu m$ ) were measured with a TSI condensation nuclei counter. It creates a large supersaturation in a chamber and then counts nucleated particles with an OPC. This instrument was counted using a 14-bit digital counter that saturated at around 20 000 counts.

## Aerosol size distributions

The size distribution of the aerosol population was measured with the PCASP. These instruments only sampled aerosols over a limited range, for practical purposes the accumulation mode. The size distribution is presented as the natural logarithm of the derivative,  $\frac{dN}{d\ln D}$ , of the typical cumulative size distribution function described by Equations 2.2, 2.3 and 2.4. This ensures that the area below the histograms are proportional to the number concentration.

$$q_r(D_i) = \frac{N_i * D_i}{\sum n_i x_i^r} \quad (2.2)$$

$$N = \int_{D_{min}}^{D_{max}} n_N(D) dD$$

where:

$N$  = total number of particles per  $cm^3$

$D$  = equivalent spherical diameter of the particles

$D_{min}$  = size of the smallest particle

$D_{max}$  = size of the biggest particle

$n_N(D)$  = number of particles per size interval ( $\mu m^{-1} cm^{-3}$ )

$n_N(D)dD$  = number of particles per  $cm^3$  of air having diameters in the range  $D$  to  $D+dD$

(2.3)

It is important to note that the full particle size range ( $D_{min}$  to  $D_{max}$ ) was not measured. The airborne data set was limited to the accumulation mode (0.1  $\mu\text{m}$  to 3  $\mu\text{m}$ ), see Tables 2.1 and 2.2.

$$M_{k,r} = \int_{D_{min}}^{D_{max}} D^k n_N(D) dD$$

where:

$M$  = the incomplete k-th moment of a density distribution ( $n_N(D)$ )

$k$  = indicates the power of  $D$

$r$  = describes the type of quantity of the density distribution (2.4)

= 0 type of quantity is number

= 1 type of quantity is length

= 2 type of quantity is surface or projected area

= 3 type of quantity is volume or mass

## Geographical variables to stratify data set

Variables were created to assist in stratifying the airborne measurements. The distance from all major sources were calculated for each measurement point (see Figure 2.2 as an example). These, as well as other variables denoting in- and out-of-plume conditions were used to identify plume penetrations. The complex nature of the atmosphere, numerous variables, different lag times of each instrument and variations of flight patterns hindered the development of a set of algorithms that could identify and cluster plume penetrations. Subjective classification of all plumes were subsequently performed.

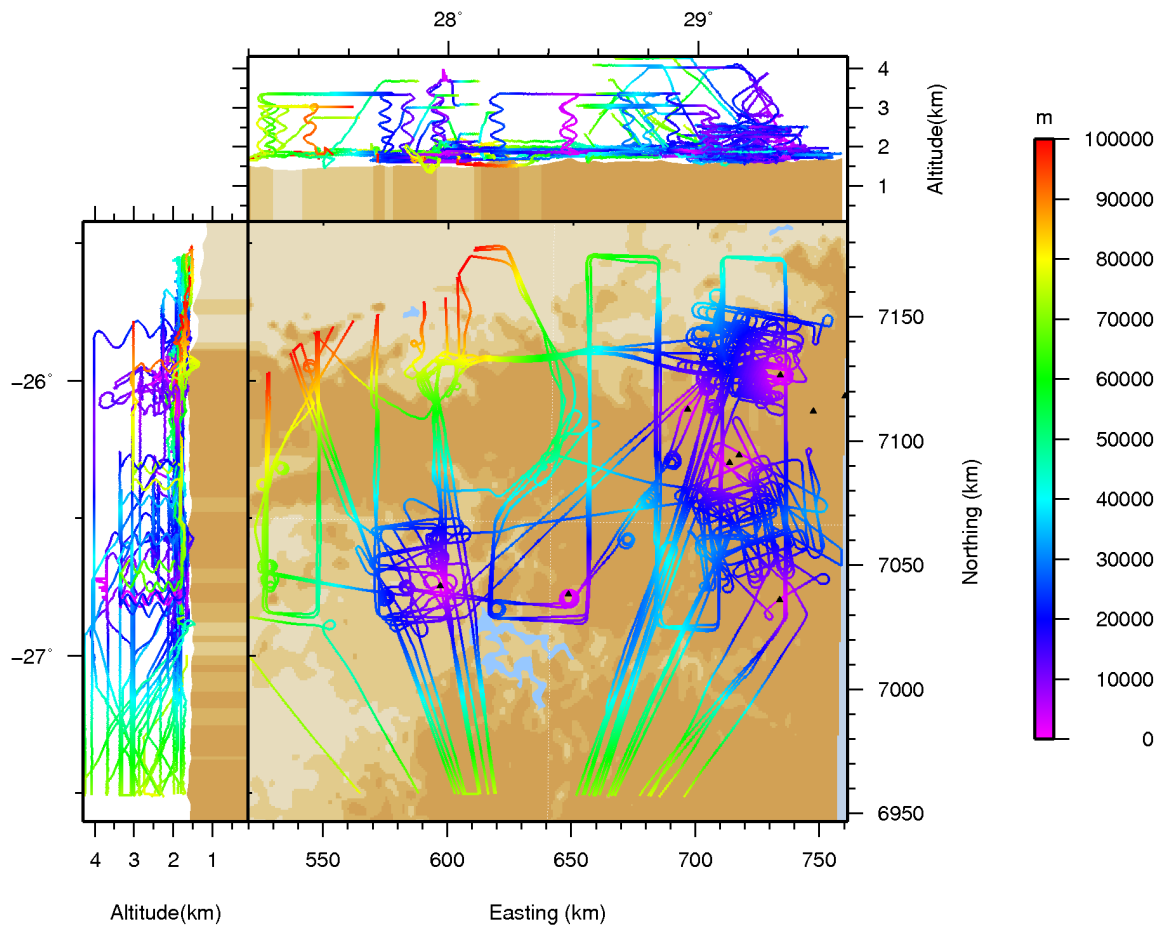


Figure 2.2: All flight tracks over the Highveld area are coloured according to their distance to the closest coal-fired power station. Power station positions are indicated with black triangles.

## Data quality assurance and measurement uncertainty

Data is filtered through a series of automatic and manual verification procedures to ensure data integrity. These procedures include:

- Fundamental instrument *sanity* checks
- Aircraft movement checks against aircraft airspeed (eliminate data for aircraft airspeed below 10 m/s)
- Buddy checks (eliminate unrealistic data caused by instrumentation spikes)
- Variable dependent corrections (pressure temperature corrections for example).

Uncertainties in measurements increase when instruments are placed on a moving platform. These further increase for the resulting plume concentrations, which were calculated as the difference of the maximum in-plume and average out-of-plume measurements. Factors that impact on the quality of identified plumes include:

- Incorrect baseline caused by proximity of other sources
- Ascending or descending through haze layers
- Proximity of sources vs. slow response of instruments
- Lack of a defined sampling methodology
- Small sources vs. aged plumes
- Sampling the same sources at different distances
- Different meteorological conditions
- Complex plume chemistry.

## **Data analysis tools**

Data were formatted and analysed using custom coded C and Python computer programs. Statistical analyses were done using the R programming language. Geographic spatial analysis was performed using Generic Mapping Tools (GMT) (Wessel and Smith, 1991, 1998) and the Geographic Resources Analysis System (GRASS GIS) (GRASS Development Team, 2015). All data visualisation was done with GMT. Raw data were kept in their original form while data analysis and visualisation modules were automated through Linux scripting. A complete trail of all quality control, derivations and visualisation are available.

## Airborne campaigns

Intensive airborne sampling campaigns between 2003 and 2006 collected close to 400 hours of data over South Africa. The campaigns that formed part of this study were projects p05 to p17 (Table 2.3). During these projects a total of 208.9 hours of data were collected from 13 projects and 172 flights.

Table 2.3: Logistical details of all field campaigns between 2003 and 2007, including area/objectives, time period, total number of flights and total number of data hours. Data from project p05 through p17 was used in this study

| Project                     | Area/Objective | Period       | Flights    | Hours         |
|-----------------------------|----------------|--------------|------------|---------------|
| p04                         | ARREX          | March 2003   | 13         | 22.83         |
| p05                         | WesternCape    | Jul-Aug 2003 | 15         | 20.71         |
| p06                         | Highveld       | Sep 2003     | 2          | 4.55          |
| p07                         | Highveld       | Nov 2004     | 1          | 3.29          |
| p08                         | KwazuluNatal   | Nov 2004     | 9          | 21.73         |
| p09                         | Highveld       | Mar 2005     | 8          | 23.32         |
| p10                         | WesternCape    | May 2005     | 8          | 22.00         |
| p11                         | Highveld       | Jul-Aug 2005 | 12         | 37.46         |
| p12                         | KwazuluNatal   | Jul-Aug 2005 | 6          | 15.10         |
| p13                         | Transport      | Jul-Aug 2005 | 4          | 12.00         |
| p14                         | Highveld       | Sep 2005     | 6          | 11.88         |
| p15                         | KwazuluNatal   | Sep 2005     | 3          | 9.00          |
| p16                         | EasternCape    | Jan-Feb 2006 | 9          | 20.78         |
| p17                         | Transport      | Mar 2006     | 3          | 7.10          |
| p18                         | Highveld       | Apr 2006     | 1          | 2.00          |
| p19                         | Highveld       | Oct 2006     | 3          | 7.82          |
| <b>Total of all flights</b> |                |              | <b>172</b> | <b>396.12</b> |

Two identical, instrumented Aero-commander A690 twin turboprop aircraft, registration ZS-JRA and ZS-JRB, were used for airborne studies in South Africa (Figure 2.3) (Adam and Hiscutt, 1995). Despite changes to the aircraft sampling inlet, data acquisition system and instrument configuration, a core set of instruments were used between 1999 and 2006 (Table 2.1). Data from these instruments were recorded on a custom built data acquisition system at 1 Hz

(Adam and Hiscutt, 1995). Flight campaigns were conducted from Bethlehem (Free State), Malmesbury (Western Cape), Langebaan (Western Cape) and Margate (Kwazulu Natal). These campaigns focused on the different areas with a large number of atmospheric emissions around the country (Figure 2.1).

Continuous monitoring of pollutants were undertaken by extracting samples through a isokinetic inlet mounted on the roof of the aircraft. This resulted in a slight lag between the position of the aircraft and the actual measurements. The spatial error was further compounded by the slow response time of most of the gas analysers (Table 2.1). However, the fast responding PCASP was mounted under the aircraft wing, directly in the airflow.  $PM$  is therefore the best indicator of the location and spatial extent of plumes.

Plume events were identified using flag variables, altitude, position and high response variables from instruments such as the PCASP, sampling  $PM$ , and  $CO_2$  (Table 2.1). The different data sets were manually matched with the plume events. More than 340 plume penetrations were performed during these flights.



Figure 2.3: The two Aerocommander A690 used in the airborne sample campaigns.

Table 2.4 lists the final set of variables used in the data analysis. These were derived and quality controlled from other raw and housekeeping variables that were recorded from each flight. The following sections presents a summary of the steps to derive each of the final variables. Data

and meta-data are stored in network common data format (NetCDF), which is a self-describing data format.

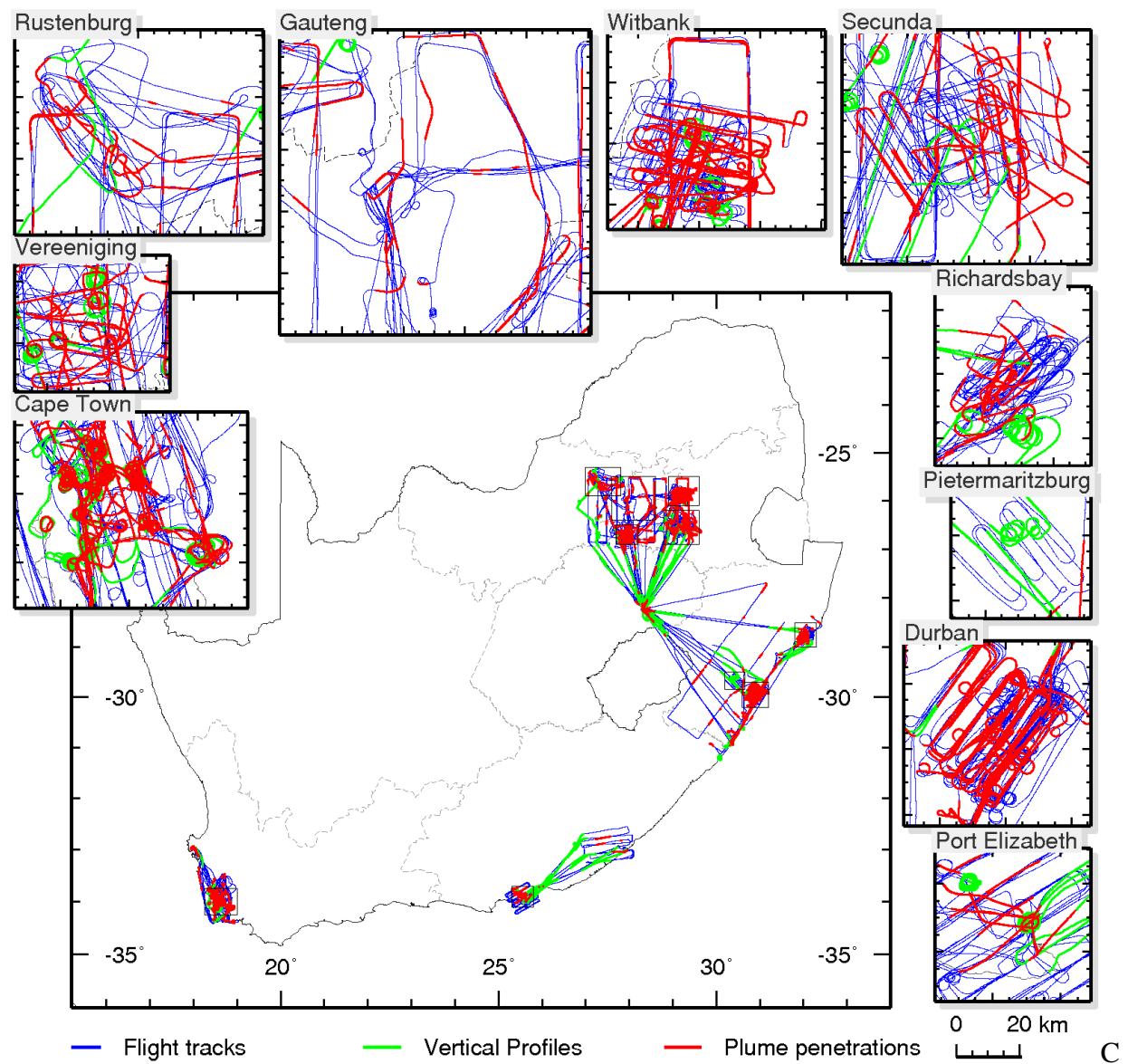


Figure 2.4: Flight tracks of research flights conducted over South Africa between 2003 and 2006 as part of this study.

Table 2.4: Core variables measured over South Africa between 2003 and 2006.

| Variable                   | Unit              | Description                         | Frequency | Availability |
|----------------------------|-------------------|-------------------------------------|-----------|--------------|
| <i>Reference variables</i> |                   |                                     |           |              |
| LONX                       | degrees east      | GPS longitude                       | 1 Hz      | 99 %         |
| LATX                       | degrees north     | GPS latitude                        | 1 Hz      | 99 %         |
| ALTX                       | m                 | Altitude above mean sea level       | 1 Hz      | 100 %        |
| SRTM                       | m                 | Ground level                        | 1 Hz      | 99 %         |
| TASX                       | m/s               | True air speed                      | 1 Hz      | 100 %        |
| ATX                        | °C                | Ambient air temperature             | 1 Hz      | 100 %        |
| PSX                        | hPa               | Static pressure                     | 1 Hz      | 100 %        |
| RHX                        | %                 | Relative humidity                   | 1 Hz      | 89 %         |
| <i>Trace gas variables</i> |                   |                                     |           |              |
| CO                         | ppm               | Carbon monoxide concentration       | 1 Hz      | 99 %         |
| CO2                        | ppm               | Carbon dioxide concentration        | 1 Hz      | 99 %         |
| H2S                        | ppb               | Hydrogen sulphide concentration     | 1 Hz      | 94 %         |
| NO                         | ppb               | Nitrogen monoxide concentration     | 1 Hz      | 98 %         |
| NO2                        | ppb               | Nitrogen dioxide concentration      | 1 Hz      | 100 %        |
| NOX                        | ppb               | Oxides of nitrogen concentration    | 1 Hz      | 100 %        |
| O3                         | ppb               | Ozone concentration                 | 1 Hz      | 99 %         |
| SO2                        | ppb               | Sulphur dioxide concentration       | 1 Hz      | 96 %         |
| TRS                        | ppb               | Total reduced sulphur concentration | 1 Hz      | 87 %         |
| <i>Aerosol variables</i>   |                   |                                     |           |              |
| CONCP                      | 1/cm <sup>3</sup> | Total PCASP aerosol concentration   | 1 Hz      | 99 %         |
| CPCAS                      | 1/cm <sup>3</sup> | PCASP binned aerosol concentration  | 1 Hz      | 99 %         |

## Sampling setup

The inlet system used on ZS-JRA consists of a stainless steel nozzle mounted approximately 30 cm from the fuselage, half a metre aft from the aircraft windscreen (Figure 2.5). The nozzle is based on a National Advisory Committee for Aeronautics (NACA) type 1 series inlet, with an inlet diameter of 15.4 mm, and a maximum radius of 48 mm. The nozzle lip has a inlet with a radius of 3 mm radius. A 5° diffuser cone brings the internal diameter to 34 mm, where the nozzle joins onto the inlet tube. The tube has two bends in it to bring it inside the aircraft cabin, where it runs parallel to the cabin roof. There are several points along the inlet manifold for connection of instrumentation (2.6). The stainless steel pipe is then connected to a flexible hose, and the exhaust is routed through the pressure bulkhead at the rear of the cabin. The

Table 2.5: Summary of subjective instrument lag estimates (in seconds) for the different projects. Each instrument lag was estimated from a range of different flights and plume penetrations. An example flight and penetration time are included for each project.

| <b>Project</b> | <b>Flight</b> | <b>Time</b> | $SO_2$ | $H_2S$ | $NO_x$ | $O_3$ | $CO$ | $CO_2$ |
|----------------|---------------|-------------|--------|--------|--------|-------|------|--------|
| p05            | f09           | 11:31:10    | 14     | -      | 14     | 8     | 18   | 4      |
| p06            | f02           | 08:27:54    | 18     | -      | 28     | 8     | 54   | 4      |
| p07            | f01           | 13:26:27    | 18     | 18     | 28     | 8     | 54   | 4      |
| p08            | f08           | 09:10:28    | 19     | 10     | 21     | 8     | 20   | 7      |
| p09            | f06           | 13:06:20    | 31     | 31     | 38     | 8     | 20   | 10     |
| p10            | f06           | 12:31:32    | 36     | 40     | 40     | 14    | 31   | 4      |
| p11            | f12           | 07:00:09    | 31     | 31     | 45     | 20    | 29   | 20     |
| p12            | f06           | 12:00:06    | 21     | 21     | 14     | 12    | 34   | 8      |
| p13            | f03           | 05:58:41    | 25     | 21     | 18     | 16    | 32   | 10     |
| p14            | f01           | 12:06:38    | 23     | 10     | 14     | 15    | 25   | 10     |
| p15            | f02           | 13:43:14    | 28     | 24     | 14     | 15    | 19   | 9      |
| p16            | f04           | 06:00:56    | 23     | 23     | 23     | -     | 36   | 9      |
| p17            | f01           | 05:41:06    | 30     | 30     | 50     | -     | 55   | -      |

inlet system exhaust is underneath the fuselage, a simple unthreaded pipe with a 45 degree rake. Typical true air speeds are between approximately 70 m/s to 130 m/s, corresponding to indicated air speeds of 130 kts to 180 kts at up to 21 000 ft altitude. The resulting lag of each analyser is presented in Table 2.5. The instrument setup and tubing was slightly different for each project. The lags are estimated for each project.

## Reference variables

Reference variables describe the position and state of the measurement platform. These variables are central to all other derived variables. Therefore bad quality or missing reference variables result in missing data for all other variables.

The aircraft latitude and longitude, LATX and LONX in table 2.4, position were measured by a Garmin GPS. Selective availability was in effect until 1 May 2000. This degraded the



Figure 2.5: A close-up of the inlet nozzle on the Aerocommander ZS-JRA.

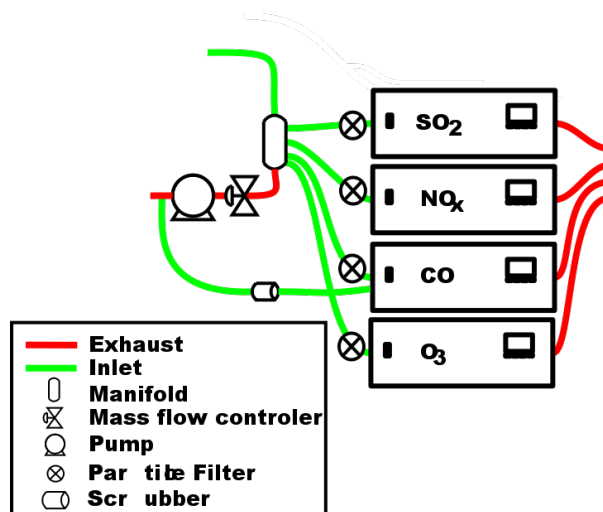


Figure 2.6: A conceptual diagram of the sampling system used for the airborne campaign.

horizontal position to about 100 m . This only affected the first campaign in August 1999. All other latitude and longitude measurements should be accurate to less than 10 m.

Static pressure ports are situated on the side of the aircraft in an area of minimum flow distortion and the pitot tube is mounted on the nose boom. The differential pressure ( $p_{sm}$ ) is obtained from a Rosemount model 1201F static pressure transducer and the differential pressure ( $p_d$ ) is measured with a Rosemount model 1221F2 transducer. The differential pressure is the difference between pitot pressure, of air brought to rest isentropically, and the static pressure. A velocity or true air speed ( $v$ ), TASX in table 2.4, dependent linear correction (Equation 2.5) is performed to derive the corrected static pressure ( $p$ ), variable PSX in Table 2.4.

$$p_s = p_{sm} + c_1 v + c_2 \quad (2.5)$$

$$c_1 = 0.021865 \quad \text{and} \quad c_2 = 5.3$$

The constants  $c_1$  and  $c_2$  were obtained by flying at different air speeds during an early morning at the same altitude as a tower with a calibrated pressure transducer. Errors in  $p_{sm}$  are a function of airspeed, angle of attack and variations in flow geometry caused by flaps, landing gear and control surfaces. The accuracy and fast response of the pressure transducers make the data interpretation relatively straightforward. Electronic noise on the output signal somewhat degrade the precision. Large angle of attack could degrade the measurements, however, steep rates as well as steep turns were avoided during sampling to limit these sources of error.

To measure the ambient air temperature from a mobile platform, four different temperatures are of concern: i) ambient air temperature ( $T$ ), the temperature of the undisturbed air through which the aircraft is about to fly; ii) total air temperature ( $T_{TAT}$ ), the maximum air temperature which will be attained if 100% kinetic energy is converted to heat; iii) recovery temperature ( $T_r$ ), the adiabatic value of local air temperature on each portion of the aircraft surface due to

incomplete recovery of the kinetic energy; iv) measured temperature ( $T_m$ ), the temperature as measured, which differs from  $T_r$  because of heat transfer effects due to imposed environments.

The relationship between these temperatures is a function of airspeed.  $T_{TAT}$  and  $T$  can be related through simple adiabatic theory. The relationship between  $T_r$  and  $T_{TAT}$  is more difficult to determine and is unique to every instrument. Typically,  $T_m$  is related to  $T_{TAT}$  and  $T$  through a recovery factor ( $r$ ) (Equation 2.6). The recovery factor for Rosemount model 102 de-iced probe has been determined by Rosemount as 0.847. The recovery factor varies according to the different environmental conditions encountered and slightly different values have been obtained by tower fly-bys. the Research Aviation Facility (RAF) at National Center for Atmospheric Research (NCAR) states a value of 0.98 for the same probe obtained through wind tunnel tests (NCAR, 2003). The Rosemount value was used for this study.

$$r = 1 - f^2 = \frac{T_r - T}{v^2/C_p} = \frac{T_r - T}{T_{TAT} - T} \quad (2.6)$$

where  $f$  is the fraction of airspeed in direct contact with the sensing element and  $C_p$  is the specific heat at constant pressure for dry air.

The Rosemount Probe derives  $T_m$  by monitoring the resistance in a platinum wire, which is a function of temperature.  $T$  can be derived from conservation of energy:

$$T = T_r - \frac{rv^2}{2C_p} \quad (2.7)$$

The circular dependence of  $T$  and  $v$  is resolved by calculating the Mach number ( $M$ ) (Equation 2.8).

$$M = \sqrt{2(C_v/R)[(p/p_d + 1)^{R/C_p} - 1]} \quad (2.8)$$

$C_v$  is the specific heat at constant volume for dry air and  $R$  is the gas constant for dry air. True air speed ( $v$  and TASX in Table 2.4) and ambient temperature ( $T$  and ATX in Table 2.4) can then be calculated using Equations 2.9 and 2.10.

$$\begin{aligned} v &= M\sqrt{\gamma RT} \\ &= \sqrt{\frac{\gamma RT_m}{[1/R^2 + r(\gamma - 1)/2]}} \end{aligned} \quad (2.9)$$

$$T = \frac{T_m}{[1 + rM^2(\gamma - 1)/2]} \quad (2.10)$$

Here  $\gamma$  is the ratio of specific heat at constant pressure to specific heat at constant volume ( $C_p/C_v$ ).

All errors are a function of airspeed, therefore uncertainties will increase with increase  $v$ . The following errors are encountered when measuring  $T_m$  on a mobile platform: thermal recovery, the relation between  $T_r$  and  $T_{TAT}$ ; thermal conduction, when the fuselage of the aircraft is at a different temperature than the sensor; thermal radiation, when relative high total temperatures are measured, heat is radiated from the sensor element and result in a reduced indication of temperature; time constant, the heat capacity of the sensor and surroundings inhibits a instantaneous response to a change in temperature; airflow direction, errors may be introduced when the air-stream approaches the inlet from other angles than directly forward.

The dewpoint transmitter incorporates the Vaisala Drycap sensor which is optimised to be used in low humidities but has an excellent tolerance against condensation. The Drycap sensor uses an operating principle based on changes in capacitance as its thin polymer film absorbs water molecules together with a combined temperature measurement with a Pt 100 resistive temperature sensor. The capacitance of the thin polymer film has a direct response proportional to relative humidity ( $RH$ ). The instrument therefore directly outputs variable RHX in Table 2.4.

The Vaisala dewpoint transmitter solves the offset error caused by drift or bad calibration by utilising a method that automatically adjusts the dry end measurement in frost points. During auto-calibration the Pt 100 element first heats and then measures the temperature of the sensor while cooling back to ambient temperature. A complete cycle of auto-calibration takes 60 - 70 seconds. When the auto-calibration is active, the output is locked to the output values prior to auto-calibration.

Ground level (variable the Shuttle Radar Topography Mission (SRTM) in Table 2.4) was obtained from SRTM (Farr and Kobrick, 2000) 3 arc second ( $\sim 90$  m) digital elevation model (DEM) based on the aircraft latitude and longitude (LATX and LONX). This variable is used to determine the above ground level altitude of the aircraft as well as deriving the pressure altitude variable (PSX).

Altitude (variable ALT<sub>X</sub> in Table 2.4) was not measured directly and had to be derived from  $p$ . The typical equation to derive altitude from static pressure is:

$$\text{ALT}_X = \left( \frac{T_{ref}}{\Gamma} \right) \left( 1 - \left( \frac{p}{p_{ref}} \right)^{\frac{R\Gamma}{g}} \right) \quad (2.11)$$

The constant  $\Gamma$  is the assumed ambient temperature lapse rate,  $g$  is the gravitational acceleration. The constants  $T_{ref}$  (reference temperature) and  $p_{ref}$  (reference pressure) depends on the specific atmospheric conditions. Typically these constants are set to  $T_{ref} = 288.15$  K and  $p_{ref} = 1013.246$  hPa for standard atmospheric conditions. However, actual temperature and pressure readings just before take-off were used for  $T_{ref}$  and  $p_{ref}$  to get more accurate derived altitude values. An approach used for this study which delivered the most accurate pressure altitude is shown in Equation 2.12.

$$\begin{aligned} \text{ALTX}_t = & \left( \text{ALTX}_0 + \sum_{i=0}^t \frac{R(T_{i+1} - T_i)}{2g} \ln\left(\frac{p_{i+1}}{p_i}\right) \right) \frac{n-t}{n} + \\ & \left( \text{ALTX}_n + \sum_{i=t+1}^{n-1} \frac{R(T_{i+1} - T_i)}{2g} \ln\left(\frac{p_{i+1}}{p_i}\right) \right) \frac{t}{n} \end{aligned} \quad (2.12)$$

This equation calculates the altitude (ALTX) for each second ( $t$ ) of the flight, provided that the data system was operating from take-off to landing. The values of  $\text{ALTX}_0$  (altitude at time 0) and  $\text{ALTX}_n$  (altitude at the end of the flight, time  $n$ ) are obtained from the SRTM variable where  $v$  is less than 55 m/s.

## Measuring strategy

In order to achieve the objectives stated above it was necessary to conduct four different types of flights in each of the identified regions. The four flights include mapping flights, source flights, profile flights, and transport flights. A brief description of each flight will be given in the following sections.

### Mapping flights

The purpose of these flights was to establish an overview of the concentrations of each of the measured variables over the region of interest. A example of a mapping flight is given in Figure 2.7. In the example a mapping flight was conducted over the South African Highveld. Flights were conducted in parallel north to south transects spaced at half degree longitudinal intervals. The resultant data are displayed as contour maps of the variable of interest. The methodology for contouring is given later in this section. Mapping flight types were done over the Highveld, Durban, Richards Bay, Port Elisabeth, Pietermaritzburg and East London.

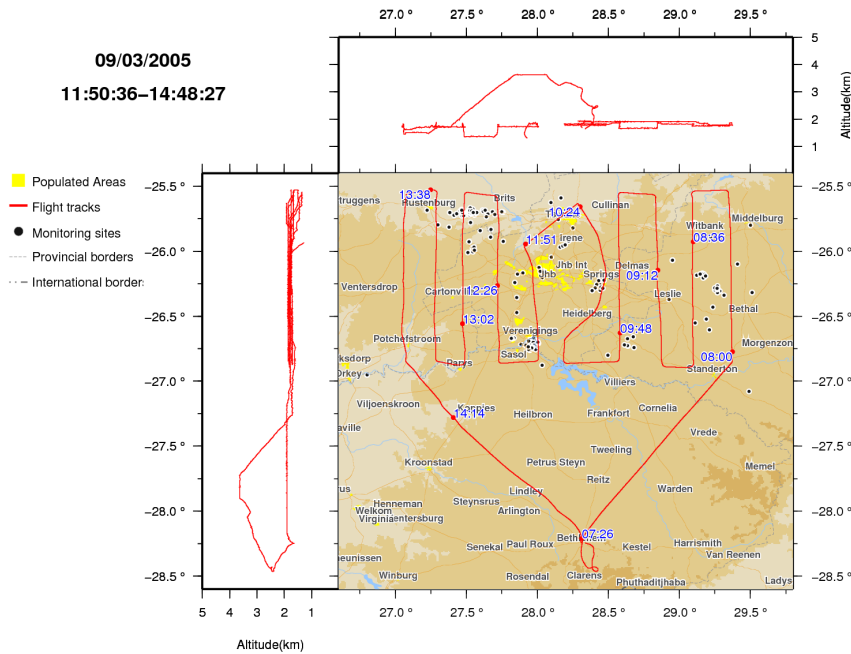


Figure 2.7: An example of a mapping flight conducted over the South African Highveld. A regular pattern with 0.5 degree longitudinal spacing were flown over the region of interest. In this example the deviation on the flight pattern was due to OR Tambo International Airport controlled airspace.

## Source flights

One of the objectives of the project was to evaluate the emissions from important air pollution sources identified by the mapping flights and from existing emissions inventories. The objectives of these flights was to characterise the emissions and to identify the plume footprint. Once the plume direction had been established from the aircraft the flight was planned to be cross plume in a downwind direction starting and ending at the stack (Figure 2.8). The source flights were conducted at one level in the atmosphere which was estimated in flight as being the core of the plume using the instantaneous PCASP data and real-time display on the aircraft. ERA-interim data was used to plot wind speed and direction at the closest available levels of the plume penetrations (Berrisford et al., 2009).

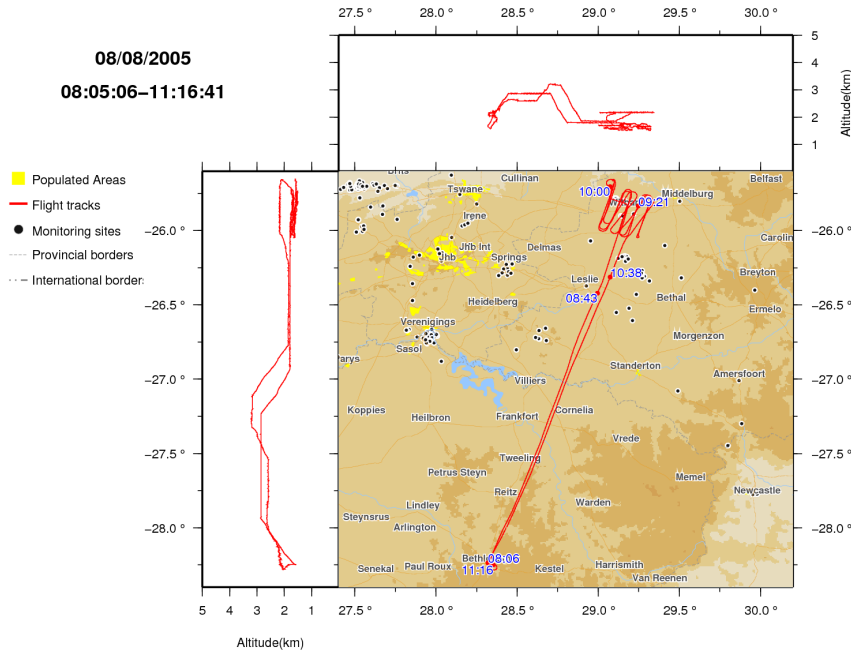


Figure 2.8: An example of a source flight conducted over the Witbank area of South Africa. The flights were conducted in the down wind direction starting and ending at the stack.

## Profile flights

Air pollution is emitted into the atmosphere at various levels. In the southern African atmosphere high concentrations of pollutants can stay in coherent plumes over extended spatial and temporal scales. The result is that pollutants are transported in high concentrations over long distances. These high concentrations of pollutants are likely to be washed down to the surface at some point in the future. Vertical profile flights were conducted in each of the identified regions to characterize the distribution of pollutants through the atmosphere. An example of a vertical profile flight is given in Figure 2.9.

Vertical profiles were flagged using an automated algorithm. It was defined as at least 1000m difference in altitude if no gradient was detected in 30 seconds. The algorithm was reset after 120 seconds of no change or a reverse in altitude. Manual inspections of all identified vertical profiles were done. Manual changes included trimming the start and end times of profiles to

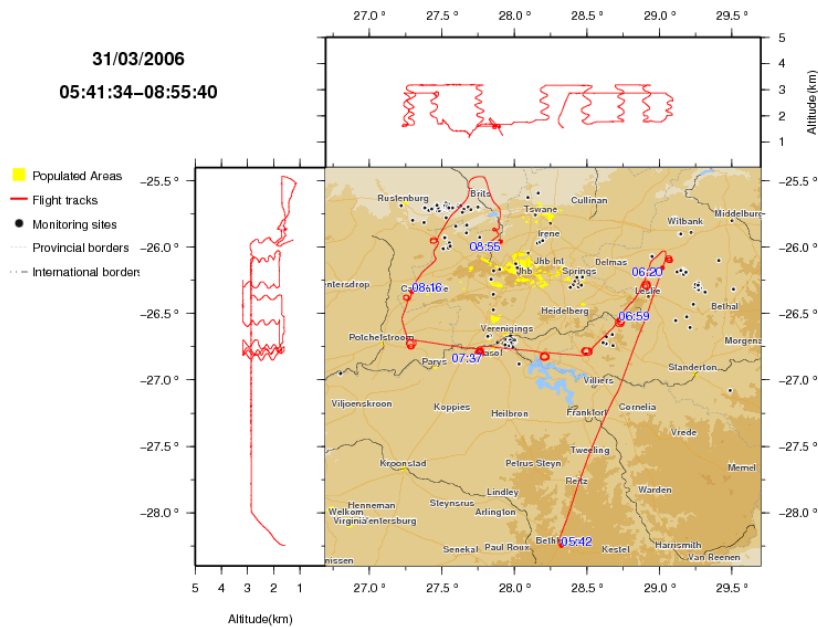


Figure 2.9: An example of profile flights conducted at the edges of the South African Highveld. The vertical extent of the flights are best viewed in the box on top of the map.

only include significant flight portion and classifying more than one profile with gaps bigger than 120 seconds but over the same area together as one profile. The location of all the vertical profiles can be seen in Figure 2.4.

## Ground-based campaigns

The suite of instruments were housed in a mobile monitoring station for the ground-based campaigns (Figure 2.10). Air was pumped into the caravan through Teflon tubing which was directed to each of the trace gas analysers and the Horiba BAM 1020 and the MetOne E-BAM. The MetOne E-sampler was deployed outside of the caravan.



Figure 2.10: The mobile monitoring station where ambient air quality measurements were made.

## **Measurements next to major highways**

Measurements next to major highways were done at three sites to characterise traffic emissions. The first was next to the M1-Empire road off ramp ( $26.1858^{\circ}\text{S}$ ,  $28.0297^{\circ}\text{E}$ ) in Johannesburg and less than 20 km from South Africa's busiest interchange where vehicle numbers exceed 15 000 per hour (Burger et al., 2009) (Figure 3.9 ). The next site was on the M1, 9 km South of the previous one ( $26.2418^{\circ}\text{S}$ ,  $28.0096^{\circ}\text{E}$ ). The third site was close the the Cape Town Convention Center next to the N1 in Cape Town ( $33.9144^{\circ}\text{S}$ ,  $18.4245^{\circ}\text{E}$ )).

## **Measurements inside a residential solid fuel burning settlement**

The Kwadela settlement is located on the South African Highveld next to the N17 between Bethal and Ermelo (Figure 2.11). The town of Davel is located just north of Kwadela. It is situated more than 50 km from large industry, surrounded by undulating terrain. Apart from

N17 and local traffic, as well as railroad traffic, residential solid fuel burning, dust and waste burning can be considered the main contributors to ambient air quality. The semi-isolated location therefore provided the opportunity to isolate typical sources in low-income settlements. Data were collected between 4 July and 13 September 2013. The cold, wintertime conditions typically represent the worst-case conditions in low-income settlements where residential solid fuel burning is used for cooking and heating purposes. Ambient *PM* concentrations are typically more than double that of the summer months where residential solid fuel burning is only used for cooking (Hersey et al., 2015).

Kwadela is situated in the Gert Sibande district of Mpumalanga. It is part of the Msukaligwa municipality. The 2011 Census estimated the total population to be 3777 people (Table 2.6). The land use around Kwadela is dominated by natural grasslands (63 % of the 19 600 km<sup>2</sup> surrounding area) and cultivated, commercial dry-land (26 % of the 19 600 km<sup>2</sup> surrounding area). This illustrates the limited woody fuel available for low-income households.

Table 2.6: Selected attributes for Kwadela for the 2011 census small area layers (SAL).

| <b>SAL</b> | <b>Households</b> | <b>Population</b> | <b>Density (1/km)</b> |
|------------|-------------------|-------------------|-----------------------|
| 8 610 070  | 114               | 462               | 11 700                |
| 8 610 121  | 120               | 546               | 5790                  |
| 8 610 129  | 123               | 567               | 12 930                |
| 8 610 173  | 189               | 651               | 7500                  |
| 8 610 178  | 201               | 654               | 5120                  |
| 8 610 240  | 237               | 897               | 7340                  |
|            | 984               | 3777              |                       |

Ambient monitoring was conducted at three different sites in Kwadela. The main ambient monitoring site was located at the Secondary School close to the centre of Kwadela (Figure 2.11). Two other ambient *PM* sites were located to the northeast and southeast.

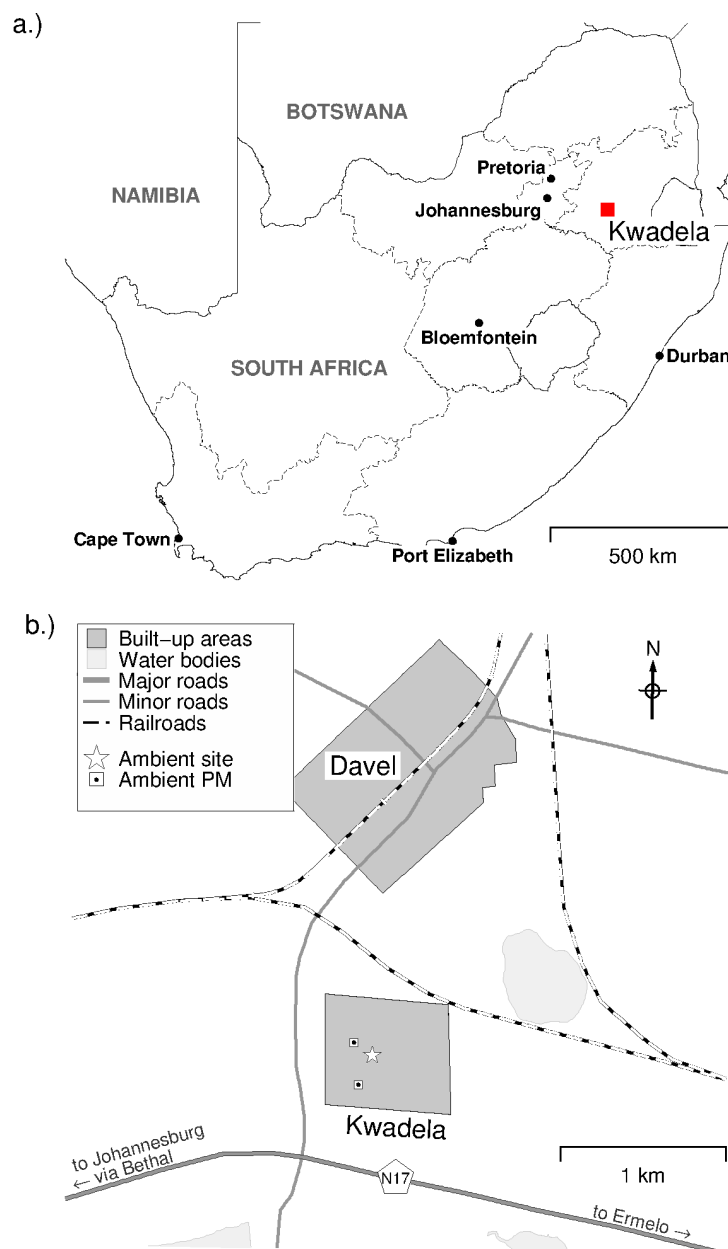


Figure 2.11: (a) Location of Kwadela in Mpumalanga. (b) Expanded view of area around Kwadela settlement including the approximate location of sampling locations.

## Sampling errors and uncertainties

The instrument suite comprised mostly of off-the-shelf regulatory equipment. A mobile platform increases sampling errors and uncertainties, although a major effort was made to limit these through the use of an external pump, a mass-flow controlled manifold and improvements

of flow through the instruments. Instrumentation does exist to make more precise measurements from aircraft. However, the infrastructure and capacity to operate such instruments on the scale of this study was out of the scope. Furthermore, a central aim of this research was to deploy a typical regulatory suite of instruments on a mobile platform to assess management priorities on a large scale both easily and affordably. The errors and uncertainties are therefore inherently part of the study design and these must always be taken into account when interpreting the data. For example, the urge to measure stack emissions directly by in-stack sampling should be resisted in favour of a more qualitative evaluation of in-plume concentrations (as presented in Chapter 3).

## **Accidental biases and mistakes**

Sampling methodology for the airborne campaign is problematic. Flight paths have to be planned well in advance. This limits the flexibility of sampling, especially in troublesome areas, such as close to airports (visible in Chapter 4). Apart from the obvious problem of sampling close to the ground, the lowest altitude are impacted by complexity of terrain and the same logistical restrictions as the flight path. The three dimensional position of the aircraft is therefore at the mercy of external factors, some of which might lead to a definite bias in measurements. For example, tall stack industries with visible plumes and well known locations are easy to plan for. The geographic location of smaller industries and much less certain. Furthermore, the vertical extent of plumes from smaller and low-level sources make them more difficult to sample.

## **Systematic sampling errors**

A range of systematic sampling errors are present in the data set. The research was conducted over a span of several years. Slight changes in the inlet, configuration of the instrument and

quality of the calibration gases can impact the baseline of measurements. The exact configuration impacts the lag of flow through the detectors. This translates into spatial uncertainty (illustrated in Table 2.5). What makes these errors more significant is that each campaign was focused on a specific area with a large number of atmospheric emissions. The relative comparison of different areas with a large number of atmospheric emissions are impacted by such (see for example Porth Elizabeth in the spatial distribution of *CO* in Figure 4.6).

One must consider that the pilot of the aircraft must manoeuvre the platform towards the point of interest. His (they were all male) skill impacts on the precision of the measurement. Since pilots varied between campaigns, this might introduce further systematic differences between geographic areas with a large number of atmospheric emissions and source types. The distance of a particular region of interest from the base of refuelling can result in under-representation. This problem was addressed by basing aircraft at different sites and allowing for refuelling at other airports.

The type of operations were restricted to daytime hours and days where visibility and weather were generally good. Most of the campaigns focused on the cold season when dispersion was limited and ambient concentrations would be at their worst. This is at least true at the level where the aircraft were sampling, as opposed to turbulent days that could have high ground-based concentrations close to tallstack sources (Held G et al., 1996). For tall and buoyant sources, weather would be less of a problem. A systematic difference could be attributed to other sources, such as traffic and residential solid fuel burning. These two were addressed in separate, ground-based campaigns.

## **Random errors and uncertainties**

Random errors and uncertainties are ever present as with any monitoring campaign. These include electronic noise (that is significantly worse on an aircraft), noise in the data acquisition system, instrument errors and errors in the sampling system. Trace gases were recorded through

an analogue to digital converter, which inherently adds random errors. These types of errors are generally significantly smaller than those mentioned previously.

\*\*\*\*\*

Aerosol and trace gas distribution over South Africa are investigated using in situ measurements. Instruments mounted on the Aerocommander's A690 used for sampling include optical aerosol counters, trace gas instruments and state measurements. The same suite of instruments was deployed on five ground-based field campaigns to characterise vehicle and domestic burning sources. Results are presented in the following chapters.

## **Chapter 3**

# **Major Sources of Air Pollution in South Africa**

Individual plumes from industrial and natural sources are ever-present over southern Africa. These typically merge into a super plume, frequently observed as a river of smoke flowing out over the east coast of South Africa when westerly waves move over the subcontinent (Swap et al., 2003). Knowing the composition and character of these plumes can help interpret remote sensing estimates, confirm desktop calculations, identify priority areas, evaluate source apportionment studies and even regulate emissions. This section characterises the major anthropogenic sources of air pollution in South Africa using in situ data.

### **The distribution of major pollution sources**

Emissions of air pollution vary in character, time and space. The location of the major emission sources in South Africa are shown in Figure 3.1. The figure was compiled using the South African national emissions database for the major industrial sources; census data for the domestic and waste burning in informal settlements; the national land cover for mining, waste, tailing and heavy industrial sources and 10 years of the Moderate Resolution Imaging Spectrometer (MODIS) fire counts for the biomass burning. The distribution of major pollution sources in South Africa plays an important role in the transport of pollutants off the continent.

The majority of these are found on the Highveld. Other important source regions include Cape Town, Rustenburg, Richards Bay, Durban and Port Elizabeth.

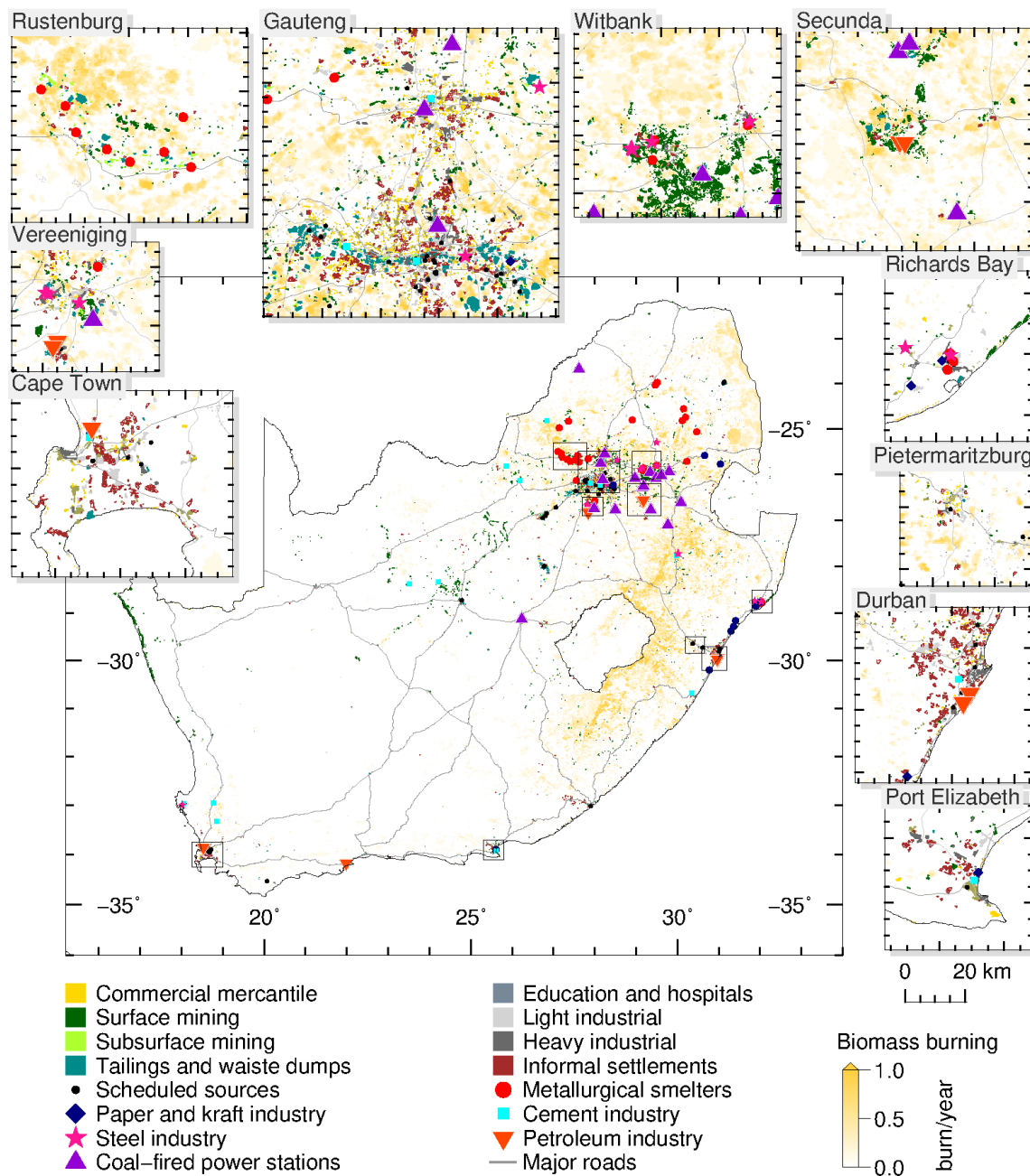


Figure 3.1: The major air pollution sources in South Africa compiled from various sources.

The contribution of these sources to the total budget have significant variability. A crude estimate of contributions derived from national fuel combustion estimates (Scorgie et al., 2004)

suggests the electricity generation sector, along with other industrial fuel combustion, is the major contributor to  $NO_x$ ,  $PM$ ,  $CO_2$  and  $SO_2$  (Figure 3.2). Vehicle emissions are important contributors to  $CO$ ,  $Pb$ , total organic compounds ( $TOCs$ ) and benzene. Residential solid fuel burning contributes to  $PM$ ,  $CO$ ,  $N_2O$ , benzene and  $CH_4$ . These estimates propose a relatively small share to biomass burning and residential solid fuel burning, with only significant contribution to  $CH_4$ .

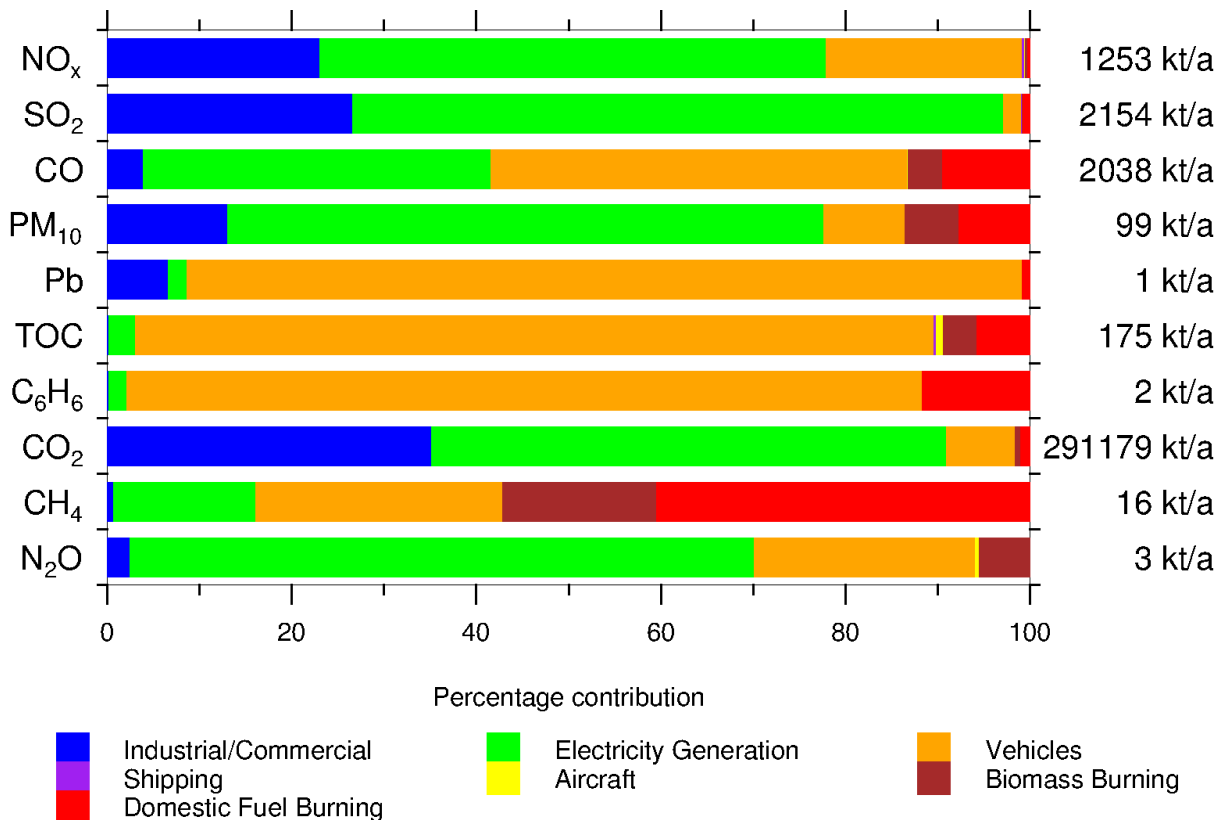


Figure 3.2: Source contributions to the total national emissions. Compiled from Scorgie et al. (2004). Only combustion related emissions were estimated using fuel consumption figures.

The significance of sources such as biomass burning and residential solid fuel burning are biased in total emission estimates these because of their significant variability in space and time. Both these have prominent seasonal cycles. Biomass burning is almost completely confined to the dry late winter, early spring months of August to October. Residential solid fuel burning has a strong diurnal cycle. These are contrasted with industrial sources that typically have relatively

constant emissions. The sources are further contrasted by their spatial distribution (Figure 3.1). Industrial sources are typically clustered around common resources and management zones, whereas biomass burning and residential solid fuel burning are spread out across larger areas.

Measurements in well-defined plumes of different source types are presented in this chapter. The in-plume measurements are shown minus up-wind (background) concentrations. It can therefore be interpreted as the particular source's contribution to ambient levels. First, an overview of plumes is given.

## Plumes over South Africa

Plumes for distinct sources quickly dilute and merge with others. Airborne measurements capture the different stages of plumes. Most of the more than 1000 plumes penetrated during the experiment had relatively low concentrations (Table 3.1). Results are presented as a summary of all the objectively identified plumes. The unsupervised algorithm used the rate of change of particulate matter with an aerodynamic diameter smaller than  $3 \mu m$  ( $PM_3$ ),  $SO_2$ ,  $NO_x$  and  $CO_2$  to highlight possible plumes whereafter the start and end times were subjectively adjusted. The different response times, resolutions and the complex nature of the mixed atmosphere results in a significant uncertainty of the estimates in Table 3.1.

Table 3.1: In-plume dimensions and concentrations over South Africa.

|                  | $PM_3$<br>$m^{-3}$ | $SO_2$<br>ppb | $CO$<br>ppm | $CO_2$<br>ppm | $NO$<br>ppb | $NO_2$<br>ppb | $NO_x$<br>ppb | Dimension<br>m |
|------------------|--------------------|---------------|-------------|---------------|-------------|---------------|---------------|----------------|
| Number of plumes | 976                | 974           | 952         | 855           | 919         | 912           | 928           | 986            |
| Mean             | 2809               | 11.1          | 0.20        | 7             | 7.9         | 15.3          | 21.0          | 7134           |
| Standard dev     | 3651               | 24.7          | 0.21        | 12            | 23.1        | 29.9          | 45.6          | 5013           |
| Minimum          | 61                 | 0.1           | 0.00        | 0             | 0.1         | 0.0           | 0.1           | 189            |
| 25% percentile   | 922                | 1.2           | 0.07        | 1             | 0.5         | 0.9           | 1.0           | 2930           |
| Median           | 1725               | 2.7           | 0.14        | 3             | 1.1         | 3.4           | 3.9           | 5860           |
| 75% percentile   | 3455               | 8.7           | 0.24        | 7             | 4.3         | 13.7          | 16.9          | 10 492         |
| Maximum          | 40 033             | 270           | 2.20        | 119           | 200         | 205           | 392           | 19 950         |

Some flights specifically targeted plumes for sampling. These would bias the results towards large, visible plumes. An alternative strategy was employed; to fly surveillance patterns on preassigned routes. These flights were used to assess the typical spatial scales of plumes.

The  $PM_3$  measurements had the fastest response time and were therefore used to assess the spatial extent of plumes. Penetrations were either made perpendicular (lateral penetrations) or along the plume axis (axial penetrations). The typical (median) dimensions of plumes is around 7 km with large variability (a standard deviation twice as large as the median). The distribution is positively skewed. The physical dimensions of plumes can have important implications for satellite based remote sensing of aerosol and trace gases (Broccardo, 2014; Heue et al., 2008; Ross et al., 2007). Typical nadir ground-pixel sizes range from around 20 km for the Ozone Monitoring Instrument (OMI), 60 by 40 km for the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) to 80 by 40 km for the second Global Ozone Monitoring Experiment (GOME-2) (Wagner et al., 2008). These are well above the modal plume size for anthropogenic plumes over South Africa. The vertical distribution and amount of mixing have a significant impact on the extent that satellite based sensors are able to accurately quantify trace gases and aerosol (Hersey et al., 2015; Broccardo, 2014).

## **Emissions from major industrial sources**

Industrial sources were a major focus of measurements. Major industrial facilities with tall stacks were over represented during the airborne sampling. These sources are highly visible, always present and easy to sample. Measurements were possible very close to the release point where the plume is still undiluted and volatile species have not had time to transform.

It was possible to manually identify plume penetrations close to large industry by comparing the flight track and changes in measured pollutant concentrations with modelled wind vectors for that level in the atmosphere. Data from these penetrations are presented separately from the

semi-objective method where the identified plumes in Table 3.1 were matched to the closest industry at the time of maximum  $PM_3$  concentration.

## Emissions from coal-fired power stations

A total of 32 plumes were penetrated on 11 different days in proximity to power station stacks (Table 3.2). In undiluted plumes close to the stacks the  $SO_2$  and  $NO_x$  analysers were saturated.  $CO_2$  values peaked at 65 ppm and  $CO$  at 2.9 ppm. Maximum  $PM$  concentrations were relatively low at just under  $8000/cm^3$ . Time series plots of 12 subjectively selected penetrations are presented in Figure 3.3.

in situ measurements confirm that the power industry is the major emitter of  $NO_x$  and  $SO_2$ . The in-plume concentrations of  $NO_x$  exceeds 200 ppb and  $SO_2$  exceeds 500 ppb. Instrument sensors were saturated and maximum concentrations for most pollutants are under estimated (Figure 3.3). There is evidence of important secondary particulates as one moves downwind in the plume (labelled nucleation particles in Figure 3.3). As the aircraft moved out of the plume and turned to do a lateral penetration, the photo-chemical interaction of  $NO$ ,  $NO_2$  and  $O_3$  is evident. As you move to the edge of the plume,  $NO_x$  concentrations drop off rapidly and give way to  $O_3$ . Efficient combustion is clear from the low  $CO$  values. The  $CO$  values were barely detectable as the aircraft moved through the plume in Figure 3.3. Fairly low  $PM$  concentrations show efficient control technologies (Pretorius et al., 2015). Although some power stations have fabric filter plants, most use electrostatic precipitators. The current legislation require that all remaining power stations be retrofitted with fabric filter plants.

The subjective selection and objective plume detection algorithms compare well. The relative isolated nature of the power stations, tall stacks and high pollutant concentrations make them relatively easy to detect. The plumes were typically around 100 m higher than other prominent industrial plumes at 270 m (50 % between 220 magl and 320 magl). Power station stack heights are mostly between 200 magl and 300 magl (Pretorius, 2016).



Table 3.2: In-plume concentrations in excess of local background around coal-fired power stations in South Africa. The top rows show statistics of all plumes that were manually selected based on proximity and wind flow data from the closest pressure level of the ERA-Interim modelled fields. The bottom rows show all plumes in a 10 km radius from a major power station that was closer than any other major industrial source.

|                                            | <b>Units</b>      | <b>Mean</b> | <b>Std</b> | <b>Min</b> | <b>25%</b> | <b>Median</b> | <b>75%</b> | <b>Max</b> |
|--------------------------------------------|-------------------|-------------|------------|------------|------------|---------------|------------|------------|
| 12 subjectively selected samples on 6 days |                   |             |            |            |            |               |            |            |
| Dimension                                  | m                 | 24 827      | 15 184     | 7278       | 10 752     | 21 267        | 35 138     | 51 041     |
| Altitude                                   | magl              | 270         | 60         | 200        | 220        | 270           | 320        | 370        |
| <i>PM</i>                                  | 1/cm <sup>3</sup> | 1789        | 1502       | 200        | 358        | 1833          | 2639       | 4373       |
| <i>CO</i>                                  | ppm               | 0.2         | 0.2        | 0.1        | 0.1        | 0.2           | 0.3        | 0.7        |
| <i>CO</i> <sub>2</sub>                     | ppm               | 23.9        | 15.7       | 3.4        | 13.4       | 22.0          | 32         | 54         |
| <i>SO</i> <sub>2</sub>                     | ppb               | 85          | 51         | 1.0        | 53         | 83            | 124        | 172        |
| <i>H</i> <sub>2</sub> <i>S</i>             | ppb               | 130         | 149        | 35         | 64         | 94            | 117        | 569        |
| <i>NO</i>                                  | ppb               | 148         | 67         | 38         | 92         | 196           | 200        | 200        |
| <i>NO</i> <sub>2</sub>                     | ppb               | 127         | 57         | 28.4       | 81         | 144           | 169        | 205        |
| 32 objectively selected samples on 10 days |                   |             |            |            |            |               |            |            |
| Dimension                                  | m                 | 10 831      | 7920       | 473        | 4939       | 8932          | 16 588     | 27 505     |
| Altitude                                   | magl              | 286         | 102        | 105        | 199        | 297           | 351        | 598        |
| <i>PM</i>                                  | 1/cm <sup>3</sup> | 1902        | 1638       | 180        | 639        | 1790          | 2643       | 7973       |
| <i>CO</i>                                  | ppm               | 0.4         | 0.6        | 0.1        | 0.1        | 0.2           | 0.4        | 2.9        |
| <i>CO</i> <sub>2</sub>                     | ppm               | 18.0        | 15.3       | 1.3        | 7.5        | 15.2          | 26.0       | 65         |
| <i>SO</i> <sub>2</sub>                     | ppb               | 71          | 100        | 2.9        | 16.2       | 34            | 76         | 489        |
| <i>H</i> <sub>2</sub> <i>S</i>             | ppb               | 56          | 195        | 0.6        | 3.1        | 6.8           | 19.3       | 998        |
| <i>NO</i>                                  | ppb               | 42          | 74         | 0.5        | 1.8        | 2.7           | 27.0       | 200        |
| <i>NO</i> <sub>2</sub>                     | ppb               | 30          | 59         | 0.8        | 2.2        | 3.8           | 20.0       | 205        |

## Emissions from the petroleum industry

Plumes coming from petroleum industrial plants were sampled on 20 different days (Table 3.3). A total of 131 penetrations were made. The dimensions of these plumes were a little bit smaller (around 16 km) and at lower altitude (around 180 m) than those from power power stations. The highest particulate concentrations were measured in undiluted plumes from the petroleum

industry.  $PM$  values reached 37 000/cm<sup>3</sup>. A maximum of 95 ppm  $CO_2$  was measured. Relatively high  $NO_x$  (32 ppb  $NO$  and 70 ppb  $NO_2$ ) and  $SO_2$  (140 ppb) were observed close to stacks. Time series plots of 15 subjectively selected penetrations are presented in Figure 3.4.

Table 3.3: In-plume concentrations in excess of local background around major petrochemical plants in South Africa. The top rows show statistics of all plumes that were manually selected based on proximity and wind flow data from the closest pressure level of the ERA-Interim modelled fields. The bottom rows show all plumes in a 10 km radius from major plant that was closest than any other major industrial source.

|                                             | Units             | Mean   | Std  | Min    | 25%    | Median | 75%    | Max    |
|---------------------------------------------|-------------------|--------|------|--------|--------|--------|--------|--------|
| 15 subjectively selected samples on 7 days  |                   |        |      |        |        |        |        |        |
| Dimension                                   | m                 | 17 050 | 4720 | 10 400 | 13 330 | 16 070 | 21 270 | 24 760 |
| Altitude                                    | magl              | 197    | 74   | 108    | 163    | 180    | 196    | 397    |
| $PM$                                        | 1/cm <sup>3</sup> | 5716   | 9022 | 594    | 1736   | 2621   | 6050   | 37 129 |
| $CO$                                        | ppm               | 0.7    | 0.6  | 0.1    | 0.2    | 0.6    | 0.8    | 2.2    |
| $CO_2$                                      | ppm               | 19.7   | 10.1 | 4.1    | 11.3   | 21.1   | 26.9   | 37     |
| $SO_2$                                      | ppb               | 42     | 27.9 | 16.8   | 23.2   | 35     | 51     | 125    |
| $H_2S$                                      | ppb               | 31     | 17.9 | 8.3    | 14.2   | 34     | 45     | 62     |
| $NO$                                        | ppb               | 46     | 38   | 3.9    | 11.2   | 46     | 72     | 119    |
| $NO_2$                                      | ppb               | 91     | 57   | 24.1   | 43     | 81     | 119    | 189    |
| 131 objectively selected samples on 16 days |                   |        |      |        |        |        |        |        |
| Dimension                                   | m                 | 8904   | 8132 | 189    | 2410   | 6144   | 13 233 | 33 744 |
| Altitude                                    | magl              | 239    | 104  | 53     | 164    | 205    | 304    | 507    |
| $PM$                                        | 1/cm <sup>3</sup> | 4324   | 5775 | 22.0   | 1622   | 2661   | 5037   | 37 129 |
| $CO$                                        | ppm               | 0.5    | 0.4  | 0.0    | 0.2    | 0.3    | 0.5    | 2.5    |
| $CO_2$                                      | ppm               | 9.6    | 13.9 | 0.1    | 2.3    | 5.2    | 9.6    | 95     |
| $SO_2$                                      | ppb               | 18.0   | 21.8 | 0.1    | 5.5    | 11.6   | 20.5   | 143    |
| $H_2S$                                      | ppb               | 146    | 345  | 0.1    | 2.6    | 6.5    | 18.3   | 1055   |
| $NO$                                        | ppb               | 7.6    | 6.1  | 0.3    | 3.5    | 6.3    | 10.3   | 32     |
| $NO_2$                                      | ppb               | 19.6   | 15.5 | 0.9    | 7.7    | 16.5   | 25.7   | 70     |

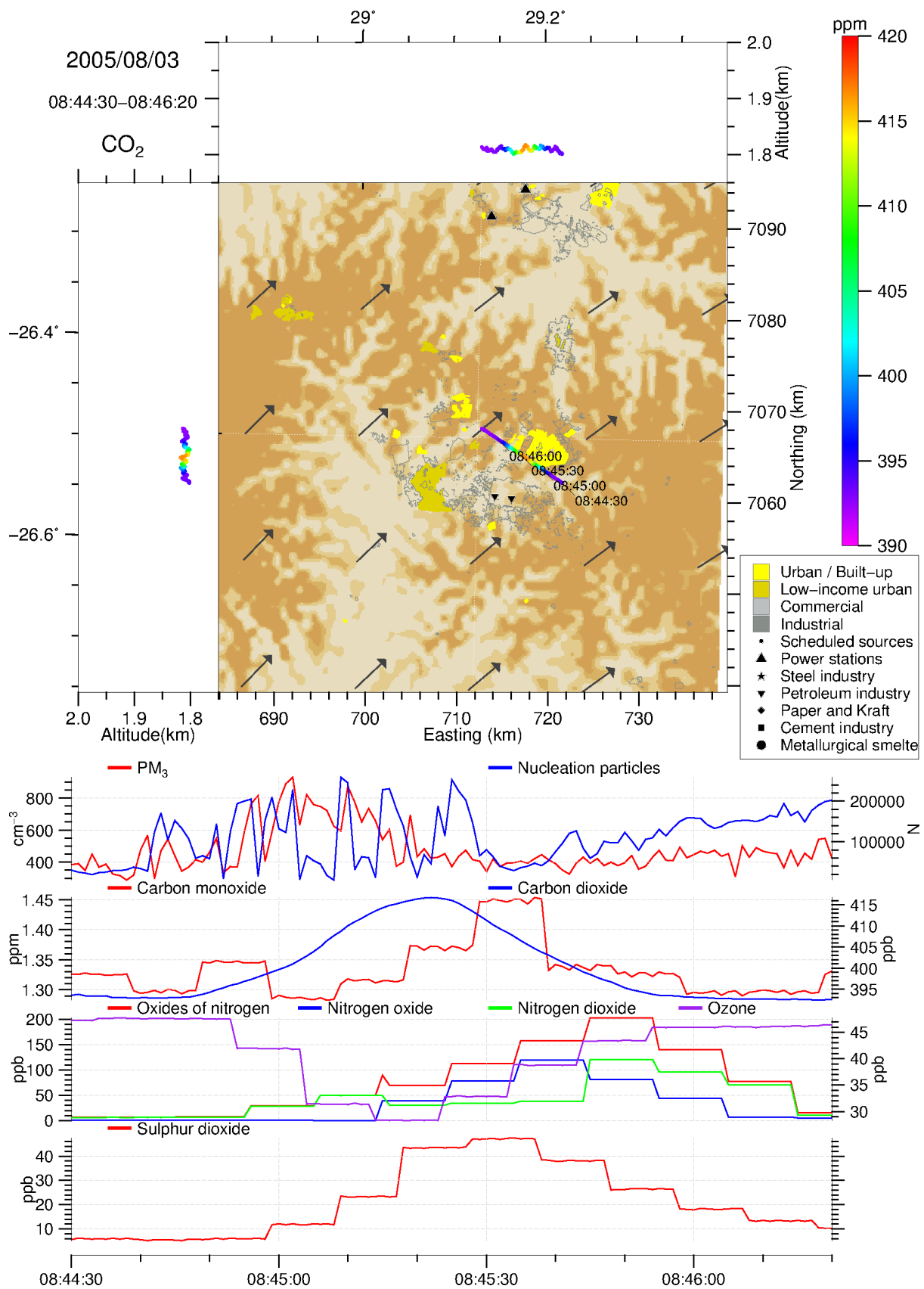


Figure 3.4: A composite plot of a lateral penetration of a petrochemical plume. The tracks are coloured according to measured  $CO_2$  concentration.

## Emissions from the steel industry

Emissions from the production of steel can result from various activities. A typical plant might be using interrelated processes producing coke, sinter, iron and steel. These might occur on different physical sites. Steel production can be done through an electric arc furnace using scrap metal. The major sources of emissions to the atmosphere from this industry are blast and electric arc furnaces.

Sixteen facilities situated in on the Highveld, Kwazulu-Natal (KZN) and the Western Cape were incorporated in this study. The KZN sites in particular were located close together with industries from other sectors and therefore difficult to isolate. A total of 41 different penetrations on 14 different days were made in plumes close to steel plants (Table 3.4). Time series plots of 12 subjectively selected penetrations are presented in Figure 3.5. Plumes have significant  $SO_2$  concentrations. It is however lower than that of the power and petroleum plumes (Table 3.4).

## Emissions from the paper and kraft industry

The pulp and kraft industry make use of recovery boilers, limestone kilns, dissolving tanks and auxiliary boilers. These result in emissions of  $PM$ ,  $CO$ ,  $CO_2$ ,  $NO_x$ ,  $SO_2$ ,  $H_2S$  and other  $VOCs$ , dioxins and furans (Bordado and Gomes, 1997). The  $PM$  emissions from this industry have been shown to be very hygroscopic and impacts on warm rain processes (Eagan et al., 1974). In fact, the Sappi Ngodwana Plant, located  $\pm 80$  km west of Nelspruit, played a key role in the development of the hygroscopic seeding technology in South Africa (Mather, 1991; Mather et al., 1996, 1997).

A total of 56 penetrations were made in close proximity to paper plants and 10 were subjectively selected. Observations show peaks in  $PM$ ,  $CO$ ,  $CO_2$ ,  $NO_x$  and less pronounced in  $H_2S$  (Figure 3.6). A summary of plume concentrations are shown in Table 3.5.

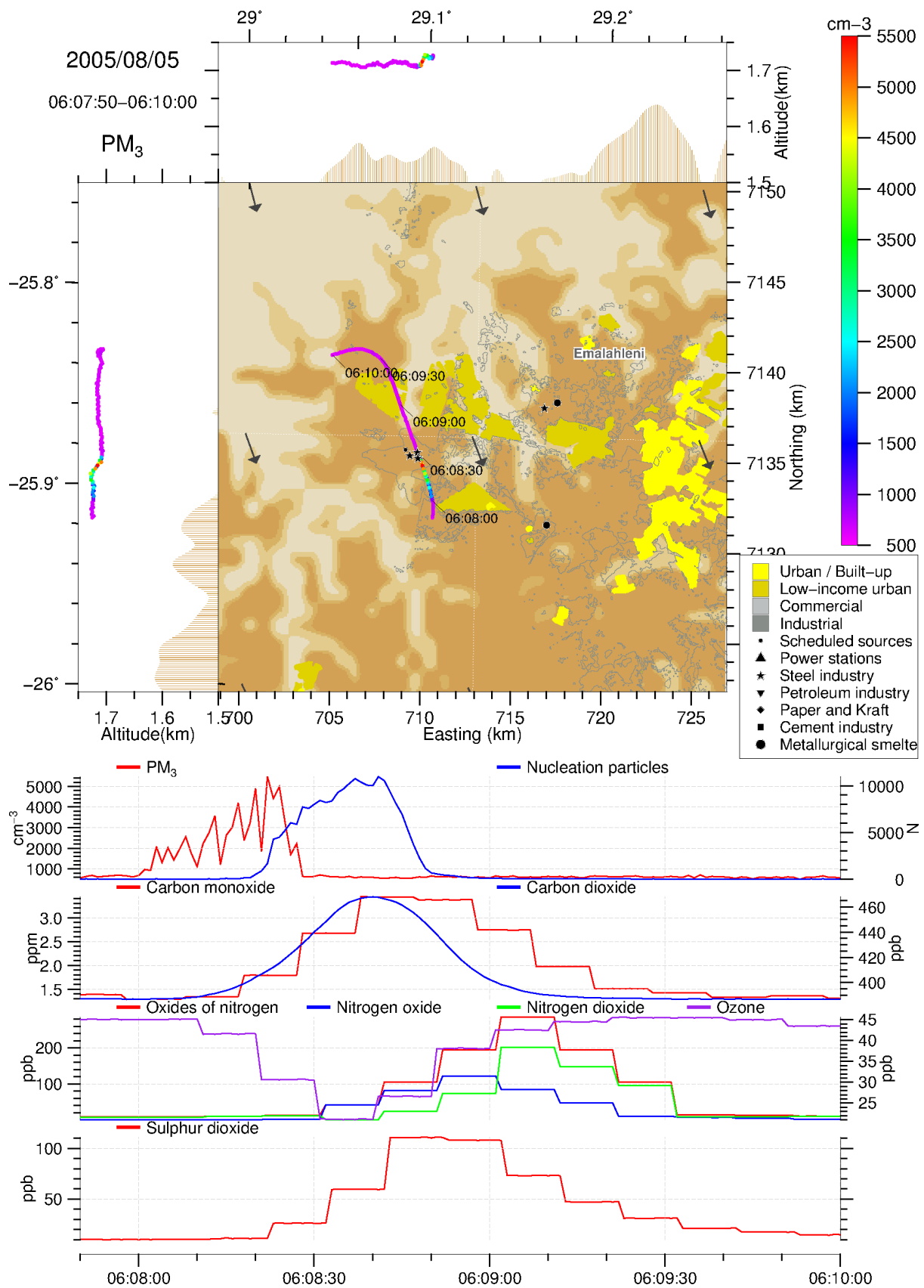


Figure 3.5: A composite plot of an axial penetration of a steel plant plume. The tracks are coloured according to measured  $PM_3$  concentration.

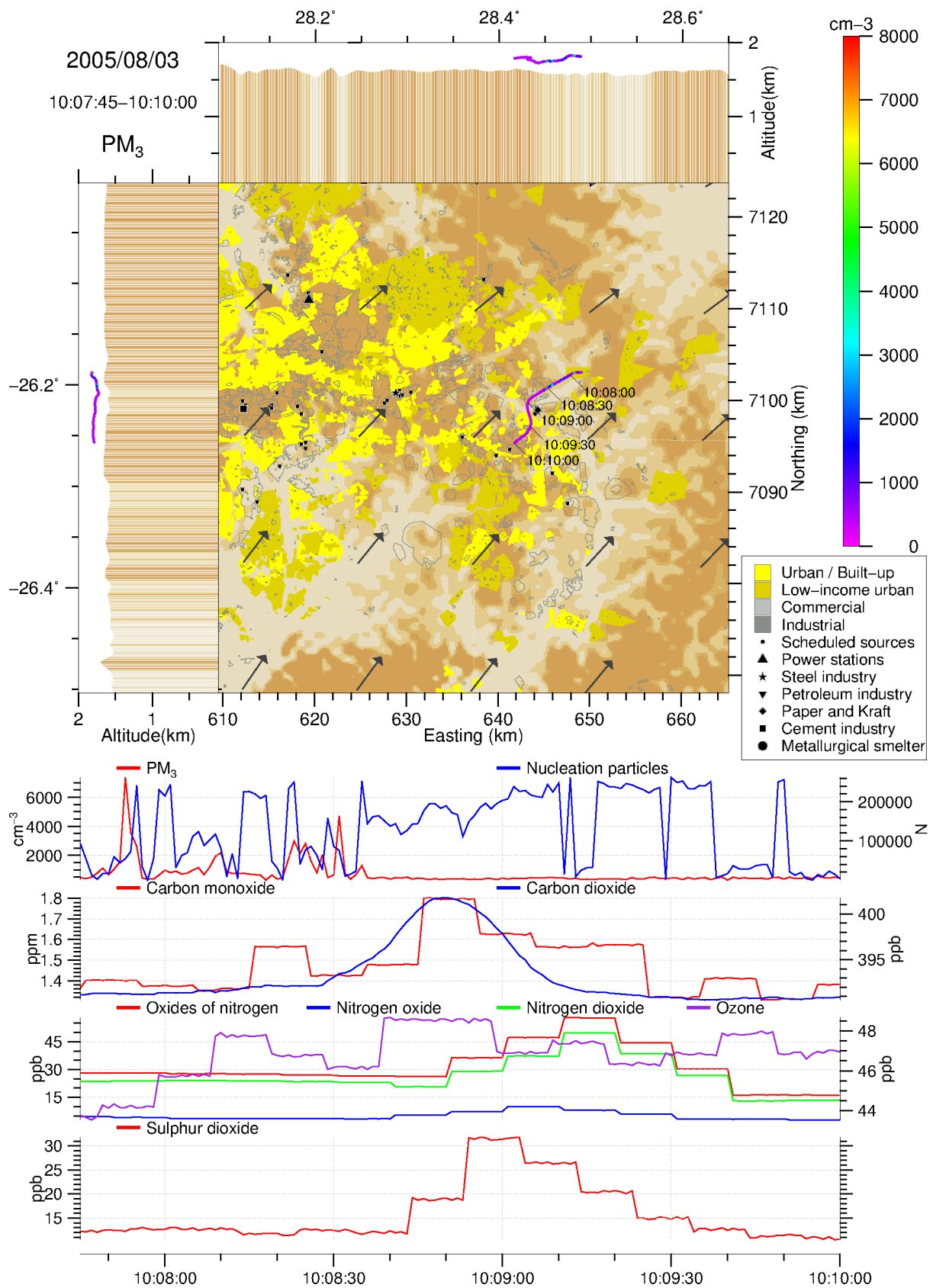


Figure 3.6: A composite plot of a lateral penetration of a paper plant plume. The tracks are coloured according to measured  $CO_2$  concentration.

Table 3.4: In-plume measurements in excess of local background from the steel industry. The top rows show statistics of all plumes that were manually selected based on proximity and wind flow data from the closest pressure level of the ERA-Interim modelled fields. The bottom rows show all plumes in a 10 km radius from major plant that was closest than any other major industrial source.

|                                            | <b>Units</b>      | <b>Mean</b> | <b>Std</b> | <b>Min</b> | <b>25%</b> | <b>Median</b> | <b>75%</b> | <b>Max</b> |
|--------------------------------------------|-------------------|-------------|------------|------------|------------|---------------|------------|------------|
| 12 subjectively selected samples on 5 days |                   |             |            |            |            |               |            |            |
| Dimension                                  | m                 | 13 894      | 5284       | 5104       | 12 169     | 12 855        | 14 462     | 26 655     |
| Altitude                                   | magl              | 234         | 122        | 127        | 168        | 178           | 296        | 546        |
| <i>PM</i>                                  | 1/cm <sup>3</sup> | 2389        | 1470       | 897        | 1404       | 2047          | 2820       | 5461       |
| <i>CO</i>                                  | ppm               | 0.2         | 0.1        | 0.0        | 0.1        | 0.1           | 0.2        | 0.5        |
| <i>CO</i> <sub>2</sub>                     | ppm               | 15.8        | 17.3       | 0.5        | 4.4        | 9.1           | 20.9       | 58         |
| <i>SO</i> <sub>2</sub>                     | ppb               | 19.3        | 18.9       | 0.5        | 4.5        | 14.7          | 32         | 56         |
| <i>H</i> <sub>2</sub> <i>S</i>             | ppb               | 14.7        | 14.6       | 0.9        | 3.5        | 8.7           | 22.9       | 42         |
| <i>NO</i>                                  | ppb               | 11.5        | 35         | 0.4        | 0.6        | 0.8           | 2.6        | 122        |
| <i>NO</i> <sub>2</sub>                     | ppb               | 18.3        | 57         | 0.5        | 0.9        | 1.8           | 2.7        | 201        |
| 41 objectively selected samples on 13 days |                   |             |            |            |            |               |            |            |
| Dimension                                  | m                 | 10 234      | 8557       | 1134       | 3308       | 8507          | 13 894     | 33 271     |
| Altitude                                   | magl              | 248         | 116        | 58         | 143        | 260           | 296        | 546        |
| <i>PM</i>                                  | 1/cm <sup>3</sup> | 2274        | 2173       | 243        | 993        | 1316          | 2762       | 9098       |
| <i>CO</i>                                  | ppm               | 0.3         | 0.2        | 0.1        | 0.1        | 0.3           | 0.4        | 1.0        |
| <i>CO</i> <sub>2</sub>                     | ppm               | 12.3        | 10.7       | 0.9        | 5.5        | 10.1          | 15.8       | 50         |
| <i>SO</i> <sub>2</sub>                     | ppb               | 34          | 47         | 1.9        | 8.5        | 26.5          | 38         | 259        |
| <i>H</i> <sub>2</sub> <i>S</i>             | ppb               | 8.3         | 8.5        | 0.5        | 2.0        | 4.5           | 13.4       | 33         |
| <i>NO</i>                                  | ppb               | 3.7         | 4.1        | 0.6        | 1.0        | 2.2           | 4.0        | 15.6       |
| <i>NO</i> <sub>2</sub>                     | ppb               | 8.3         | 16.7       | 0.8        | 1.9        | 3.5           | 5.8        | 77         |

## Emissions from metallurgical smelters

South Africa holds the world's biggest mineral resources reserves by value (Dworzanowski, 2013). This includes coal, which is the dominant source of emissions for the power and petrochemical industries, as well as iron ore, all discussed in the previous sections. Other metallurgical beneficiation includes gold, platinum, manganese, chromium, vanadium, copper, nickel, titanium and zirconium. Plumes from these industries are discussed in this section, which are predominantly as a result of pyrometallurgical processes.

Table 3.5: In-plume measurements in excess of local background from the paper and kraft industry. The top rows show statistics of all plumes that were manually selected based on proximity and wind flow data from the closest pressure level of the ERA-Interim modelled fields. The bottom rows show all plumes in a 10 km radius from major plant that was closest than any other major industrial source.

|                                            | <b>Units</b>      | <b>Mean</b> | <b>Std</b> | <b>Min</b> | <b>25%</b> | <b>Median</b> | <b>75%</b> | <b>Max</b> |
|--------------------------------------------|-------------------|-------------|------------|------------|------------|---------------|------------|------------|
| 10 subjectively selected samples on 5 days |                   |             |            |            |            |               |            |            |
| Dimension                                  | m                 | 5945        | 2837       | 1323       | 4608       | 5671          | 7089       | 11 342     |
| Altitude                                   | magl              | 195         | 76         | 63         | 177        | 184           | 191        | 329        |
| <i>PM</i>                                  | 1/cm <sup>3</sup> | 4329        | 3009       | 674        | 1583       | 4223          | 6668       | 8608       |
| <i>CO</i>                                  | ppm               | 0.1         | 0.1        | 0.0        | 0.0        | 0.1           | 0.2        | 0.3        |
| <i>CO</i> <sub>2</sub>                     | ppm               | 5.2         | 2.8        | 1.8        | 3.9        | 5.1           | 5.7        | 11.9       |
| <i>SO</i> <sub>2</sub>                     | ppb               | 9.5         | 12.2       | 0.7        | 1.8        | 5.4           | 7.6        | 34         |
| <i>H</i> <sub>2</sub> <i>S</i>             | ppb               | 7.6         | 5.7        | 1.1        | 4.0        | 6.1           | 9.0        | 21.1       |
| <i>NO</i>                                  | ppb               | 5.1         | 6.1        | 0.4        | 1.0        | 3.7           | 4.1        | 16.3       |
| <i>NO</i> <sub>2</sub>                     | ppb               | 36          | 63         | 1.3        | 2.2        | 6.3           | 23.1       | 188        |
| 56 objectively selected samples on 16 days |                   |             |            |            |            |               |            |            |
| Dimension                                  | m                 | 7487        | 6296       | 662        | 3096       | 5482          | 9925       | 30 435     |
| Altitude                                   | magl              | 222         | 105        | 0.1        | 169        | 192           | 269        | 571        |
| <i>PM</i>                                  | 1/cm <sup>3</sup> | 2886        | 4094       | 296        | 1093       | 1727          | 2960       | 25 427     |
| <i>CO</i>                                  | ppm               | 0.4         | 0.5        | 0.1        | 0.2        | 0.3           | 0.4        | 3.1        |
| <i>CO</i> <sub>2</sub>                     | ppm               | 12.3        | 20.1       | 0.8        | 5.1        | 7.1           | 11.0       | 111        |
| <i>SO</i> <sub>2</sub>                     | ppb               | 11.8        | 16.5       | 1.1        | 3.1        | 7.6           | 15.9       | 102        |
| <i>H</i> <sub>2</sub> <i>S</i>             | ppb               | 71          | 259        | 0.6        | 1.6        | 3.5           | 13.2       | 1283       |
| <i>NO</i>                                  | ppb               | 12.7        | 31         | 0.9        | 3.3        | 6.2           | 11.1       | 200        |
| <i>NO</i> <sub>2</sub>                     | ppb               | 18.5        | 29.7       | 0.1        | 6.5        | 11.6          | 23.7       | 198        |

A total of 27 industries were grouped into this sector. A large part of the mineral resources are found in the Bushveld Igneous Complex (Venter et al., 2012). The metallurgical smelters are concentrated in these areas, which includes Rustenburg, northern Gauteng, and Witbank in Figure 3.1. A total of 9 penetrations were made in-plumes in proximity to metallurgical smelters. Observations show relatively low concentrations of *PM*, *SO*<sub>2</sub> and negligible *NO*<sub>x</sub> (Figure 3.7 and Table 3.6). These facilities typically have much lower stack height and are not as well isolated from other industrial sources as the power stations.

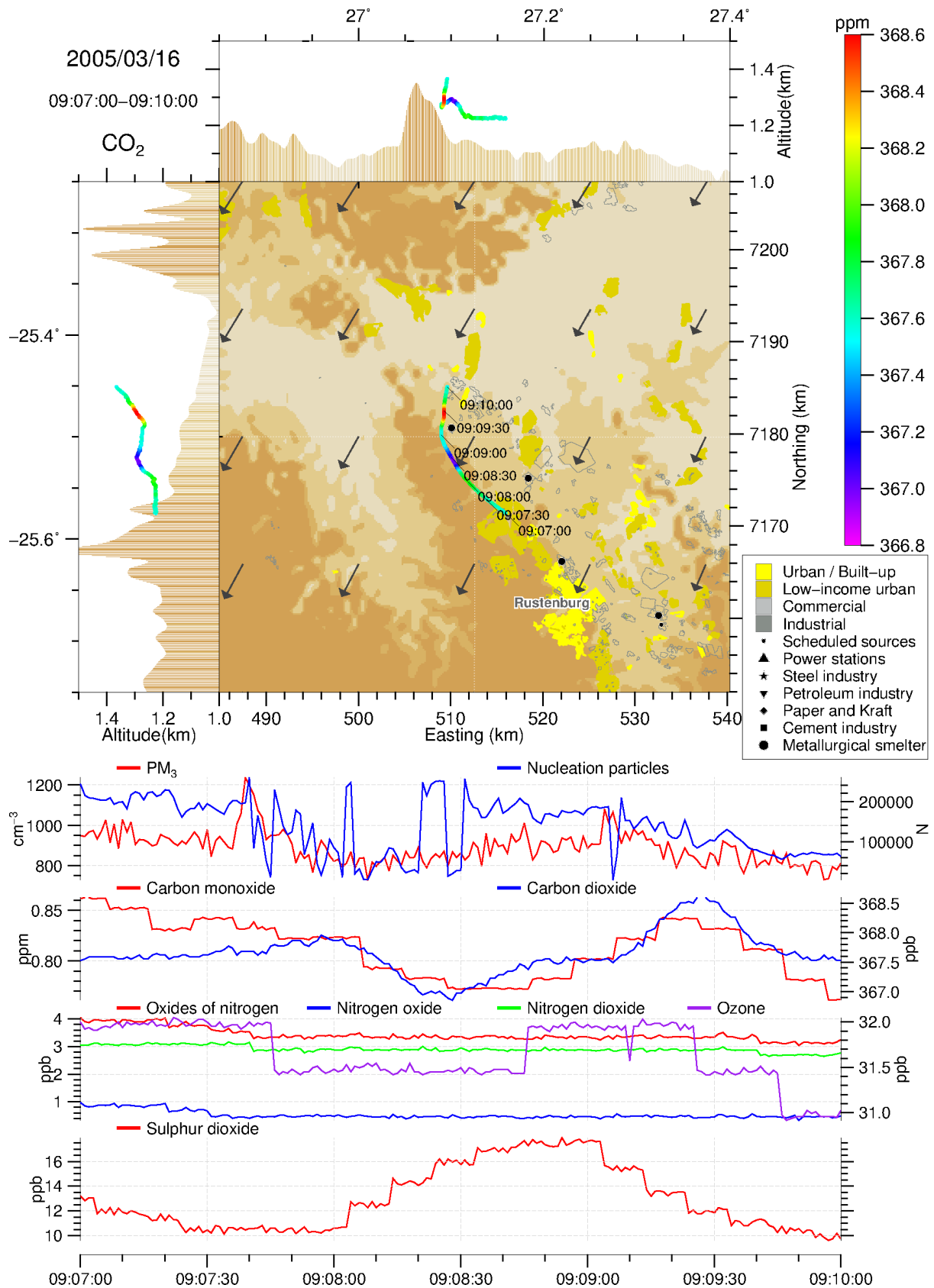


Figure 3.7: A composite plot of a lateral penetration of a metallurgical smelter plume. The tracks are coloured according to measured  $CO_2$  concentration.

Table 3.6: In-plume measurements in excess of local background from the metallurgical smelter industry. The top rows show statistics of all plumes that were manually selected based on proximity and wind flow data from the closest pressure level of the ERA-Interim modelled fields. The bottom rows show all plumes in a 10 km radius from major plant that was closest than any other major industrial source.

|                                           | <b>Units</b>      | <b>Mean</b> | <b>Std</b> | <b>Min</b> | <b>25%</b> | <b>Median</b> | <b>75%</b> | <b>Max</b> |
|-------------------------------------------|-------------------|-------------|------------|------------|------------|---------------|------------|------------|
| 9 subjectively selected samples on 4 days |                   |             |            |            |            |               |            |            |
| Dimension                                 | m                 | 16 615      | 10 596     | 5671       | 11 342     | 14 178        | 16 636     | 41 872     |
| Altitude                                  | magl              | 267         | 121        | 79         | 235        | 306           | 338        | 379        |
| $PM$                                      | 1/cm <sup>3</sup> | 2141        | 2119       | 508        | 896        | 1188          | 2488       | 7169       |
| $CO$                                      | ppm               | 0.1         | 0.1        | 0.0        | 0.1        | 0.1           | 0.1        | 0.3        |
| $CO_2$                                    | ppm               | 2.8         | 1.8        | 0.2        | 1.7        | 1.8           | 4.2        | 5.8        |
| $SO_2$                                    | ppb               | 28.1        | 60         | 0.2        | 3.6        | 7.8           | 9.6        | 187        |
| $H_2S$                                    | ppb               | 6.4         | 6.9        | 1.2        | 2.7        | 3.3           | 7.2        | 22.4       |
| $NO$                                      | ppb               | 3.2         | 7.6        | 0.3        | 0.5        | 0.6           | 0.6        | 23.3       |
| $NO_2$                                    | ppb               | 4.1         | 6.5        | 0.2        | 0.7        | 1.1           | 1.5        | 17.1       |
| 9 objectively selected samples on 2 days  |                   |             |            |            |            |               |            |            |
| Dimension                                 | m                 | 6732        | 4931       | 189        | 3214       | 6144          | 8129       | 15 218     |
| Altitude                                  | magl              | 302         | 111        | 138        | 219        | 309           | 370        | 487        |
| $PM$                                      | 1/cm <sup>3</sup> | 846         | 595        | 135        | 501        | 809           | 924        | 2205       |
| $CO$                                      | ppm               | 0.3         | 0.1        | 0.3        | 0.3        | 0.4           | 0.4        | 0.4        |
| $CO_2$                                    | ppm               | 2.8         | 1.6        | 1.0        | 1.3        | 3.1           | 3.8        | 5.4        |
| $SO_2$                                    | ppb               | 13.4        | 5.8        | 7.2        | 10.1       | 12.0          | 14.9       | 24.7       |
| $H_2S$                                    | ppb               | 6.3         | 3.7        | 2.2        | 3.9        | 6.0           | 7.6        | 13.1       |
| $NO$                                      | ppb               | 2.4         | 0.9        | 1.1        | 2.0        | 2.5           | 2.9        | 3.3        |
| $NO_2$                                    | ppb               | 5.8         | 3.0        | 2.9        | 3.5        | 5.4           | 7.3        | 10.7       |

## Emissions from the cement industry

The main sources of emissions from cement plants are the calcination of the raw materials and the coal firing of the kiln. The cement industry makes up about 3.5 % of the annual domestic coal consumption (Steyn and Minnitt, 2010). Cement manufacturing is a major source of  $CO_2$  emissions. The estimated average  $CO_2$  emissions from South African cement production, 690 kg  $CO_2$  per t, is larger than the global average of around 440 kg (Wright, 2011).

Table 3.7: In-plume measurements in excess of local background in from the cement industry. The top rows show statistics of all plumes that were manually selected based on proximity and wind flow data from the closest pressure level of the ERA-Interim modelled fields. The bottom rows show all plumes in a 10 km radius from major plant that was closest than any other major industrial source.

|                                           | Units             | Mean   | Std  | Min  | 25%  | Median | 75%    | Max    |
|-------------------------------------------|-------------------|--------|------|------|------|--------|--------|--------|
| 5 subjectively selected samples on 2 days |                   |        |      |      |      |        |        |        |
| Dimension                                 | m                 | 8356   | 4644 | 3308 | 3686 | 9452   | 12 099 | 13 233 |
| Altitude                                  | magl              | 221    | 149  | 55   | 130  | 186    | 299    | 434    |
| <i>PM</i>                                 | 1/cm <sup>3</sup> | 2299   | 743  | 1347 | 1946 | 2124   | 2873   | 3203   |
| <i>CO</i>                                 | ppm               | 0.2    | 0.1  | 0.1  | 0.1  | 0.1    | 0.3    | 0.4    |
| <i>CO</i> <sub>2</sub>                    | ppm               | 1.8    | 1.5  | 0.5  | 1.3  | 1.3    | 1.5    | 4.3    |
| <i>SO</i> <sub>2</sub>                    | ppb               | 4.0    | 2.1  | 1.7  | 2.6  | 3.6    | 5.0    | 7.1    |
| <i>H</i> <sub>2</sub> <i>S</i>            | ppb               | 5.2    | 3.7  | 1.7  | 2.3  | 3.7    | 9.1    | 9.2    |
| <i>NO</i>                                 | ppb               | 4.9    | 4.2  | 0.4  | 2.3  | 3.3    | 7.8    | 10.6   |
| <i>NO</i> <sub>2</sub>                    | ppb               | 7.5    | 4.9  | 1.4  | 3.1  | 10.5   | 10.7   | 11.9   |
| 36 objectively selected samples on 4 days |                   |        |      |      |      |        |        |        |
| Dimension                                 | m                 | 12 448 | 6985 | 2836 | 6900 | 11 201 | 16 636 | 32 704 |
| Altitude                                  | magl              | 232    | 86   | 91   | 171  | 206    | 295    | 434    |
| <i>PM</i>                                 | 1/cm <sup>3</sup> | 2533   | 1767 | 288  | 1236 | 2095   | 3339   | 5657   |
| <i>CO</i>                                 | ppm               | 0.5    | 0.2  | 0.2  | 0.3  | 0.4    | 0.6    | 1.2    |
| <i>CO</i> <sub>2</sub>                    | ppm               | 5.9    | 4.4  | 1.0  | 2.2  | 4.2    | 9.2    | 17.1   |
| <i>SO</i> <sub>2</sub>                    | ppb               | 12.7   | 9.2  | 1.6  | 6.4  | 10.1   | 17.2   | 35     |
| <i>H</i> <sub>2</sub> <i>S</i>            | ppb               | 43     | 185  | 1.7  | 4.2  | 7.6    | 10.6   | 1004   |
| <i>NO</i>                                 | ppb               | 9.5    | 9.0  | 1.3  | 4.9  | 6.9    | 9.7    | 46     |
| <i>NO</i> <sub>2</sub>                    | ppb               | 25.8   | 19.0 | 6.0  | 12.5 | 18.4   | 32     | 82     |

A total of 36 penetrations were made in the vicinity of cement industries, with 5 subjectively identified. As can be seen in the first case study (Figure 3.8) and the summary statistics (Table 3.7), *PM* is the most prominent pollutant in these plumes.

These sources are typically co-located with other pollutants and have relatively low stacks. It is therefore much more difficult to distinguish these using unsupervised approaches (Table 3.7).

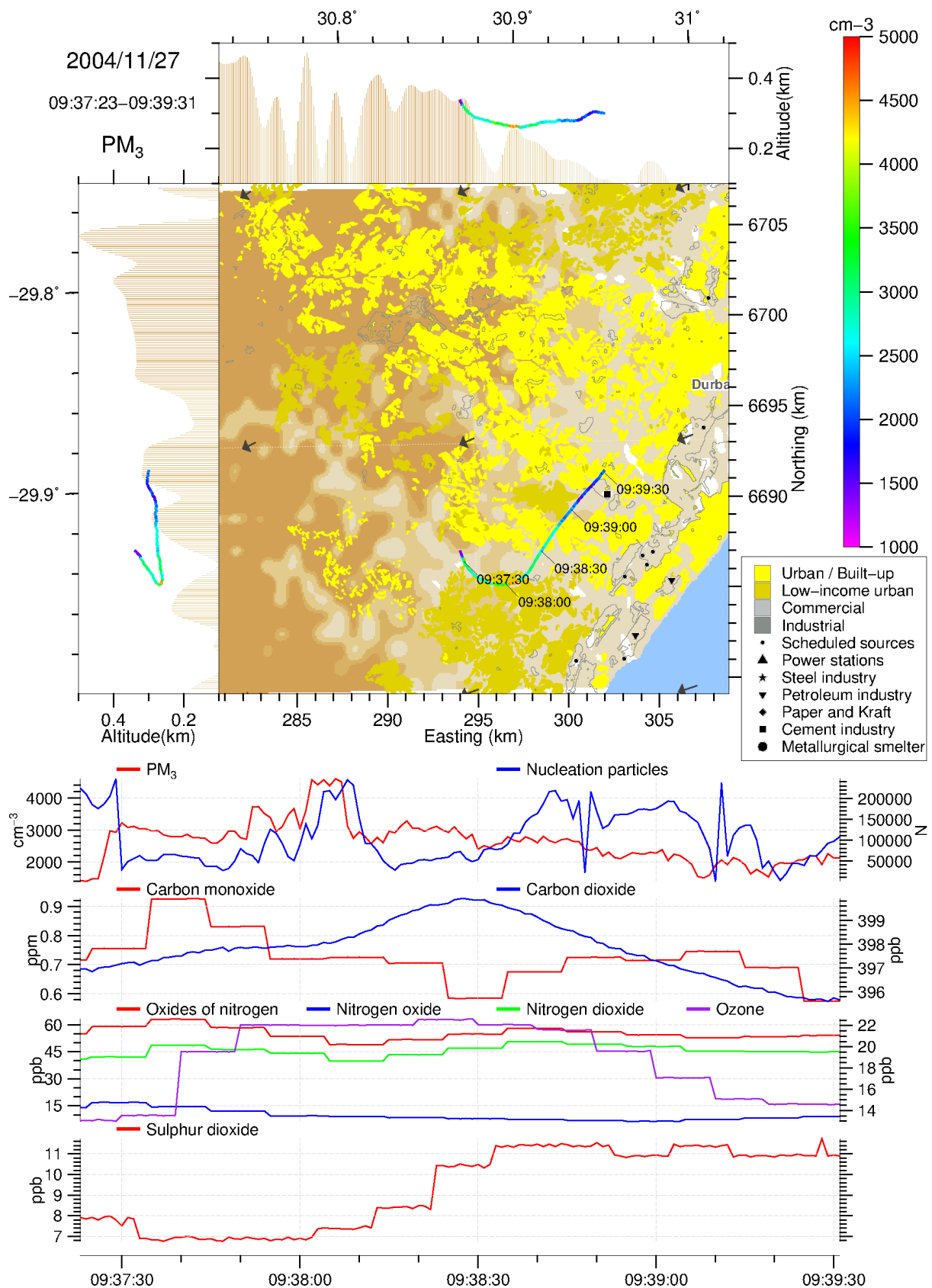


Figure 3.8: A composite plot of a lateral penetration of a cement industry plume. The tracks are coloured according to measured  $CO_2$  concentration.

## Emissions from road traffic

Petrol motor vehicles, petrol light delivery vehicles (LDV) and diesel trucks are the dominant vehicle types on South African roads (Table 3.8). Recent studies point to vehicle type being the biggest factor that determine emissions (Tongwane et al., 2015; Tongwane, 2013). It is therefore no surprise that reducing vehicle emissions should have the largest benefits in both air pollution and agents of climate change (Thambiran and Diab, 2011).

A typical diurnal cycle that correlates with traffic volumes is visible in most air pollutants (Figure 3.9). It should be noted that a similar cycle is present in residential solid fuel burning areas (see Figure 3.10) and even in the electricity supply sent out from major power stations (Pretorius, 2016). Nevertheless, these observations were made next to busy highways relatively far away from residential solid fuel burning areas and power stations. Pollutants have a typical log-normal distribution. The median levels are typically low, except for  $NO$  and  $NO_2$ . These have extremely high 1 min readings. Estimated plume (instantaneous minus background) concentrations of almost 1000 ppb for  $NO$  and 380 ppb for  $NO_2$  were observed (Table 3.8). Maximum  $VOC$  levels were high with 24 ppb benzene, 69 ppb toluene, 56 ppb ethylbenzene and 22 ppb xylene. The three sites, two in Johannesburg and one in Cape Town, showed similar characteristics.

Table 3.8: Details of vehicle number, average distance travelled, fuel type and fuel usage in South Africa for 2009 (Tongwane et al., 2015).

|             | Number of Vehicles | Distance Travelled | Fuel share (%) |        | Fuel economy (l/100km) |        |
|-------------|--------------------|--------------------|----------------|--------|------------------------|--------|
|             |                    |                    | Petrol         | Diesel | Petrol                 | Diesel |
| Busses      | 45 217             | 36 015             | 10             | 90     | 49                     | 45     |
| LDV         | 1 946 292          | 17 253             | 65             | 35     | 10                     | 8      |
| Minibuses   | 282 941            | 28 199             | 90             | 10     | 13                     | 12     |
| Motorcars   | 5 411 093          | 15 867             | 94             | 6      | 10                     | 8      |
| Motorcycles | 362 400            | 6041               | 100            | 0      | 4                      | 4      |
| Unknown     | 230 848            | 1409               | 8              | 92     | 9                      | 15     |
| Trucks      | 321 604            | 46 041             | 5              | 95     | 20                     | 36     |

Table 3.9: Plume concentrations measured next to major highways in South Africa. Plume concentrations were calculated as the difference between the maximum instantaneous measurement and the mean during off-peak traffic times. Only times when winds were blowing over the highway towards the monitoring site were considered.

|              | Units             | Events | Mean | Std Dev | 25%  | Median | 75%  | Max   |
|--------------|-------------------|--------|------|---------|------|--------|------|-------|
| CO           | ppm               | 75     | 4.5  | 2.8     | 2.2  | 3.7    | 6.7  | 10.7  |
| CO2          | ppm               | 73     | 23   | 132.7   | -8.8 | 0.1    | 13.9 | 899.8 |
| H2S          | ppb               | 75     | 5    | 6       | 1    | 3      | 9    | 25    |
| NH3          | ppb               | 75     | 43   | 52      | 9    | 19     | 61   | 220   |
| NO           | ppb               | 75     | 340  | 188     | 192  | 327    | 418  | 940   |
| NO2          | ppb               | 75     | 73   | 53      | 43   | 57     | 82   | 383   |
| PM10         | µg/m <sup>3</sup> | 7      | 28   | 33      | 2    | 11     | 44   | 85    |
| PM2.5        | µg/m <sup>3</sup> | 7      | 24   | 27      | 5    | 7      | 43   | 63    |
| SO2          | ppb               | 75     | 11   | 13      | 8    | 13     | 83   |       |
| Benzene      | ppb               | 38     | 4    | 6       | 1    | 2      | 4    | 24    |
| Toluene      | ppb               | 38     | 8    | 16      | 1    | 2      | 8    | 69    |
| Ethylbenzene | ppb               | 38     | 2    | 9       | 0    | 0      | 1    | 56    |
| mp-Xylene    | ppb               | 38     | 1    | 0       | 0    | 1      | 1    | 2     |
| o-Xylene     | ppb               | 38     | 1    | 4       | 0    | 0      | 1    | 22    |
| Xylene       | ppb               | 38     | 1    | 4       | 0    | 1      | 1    | 22    |

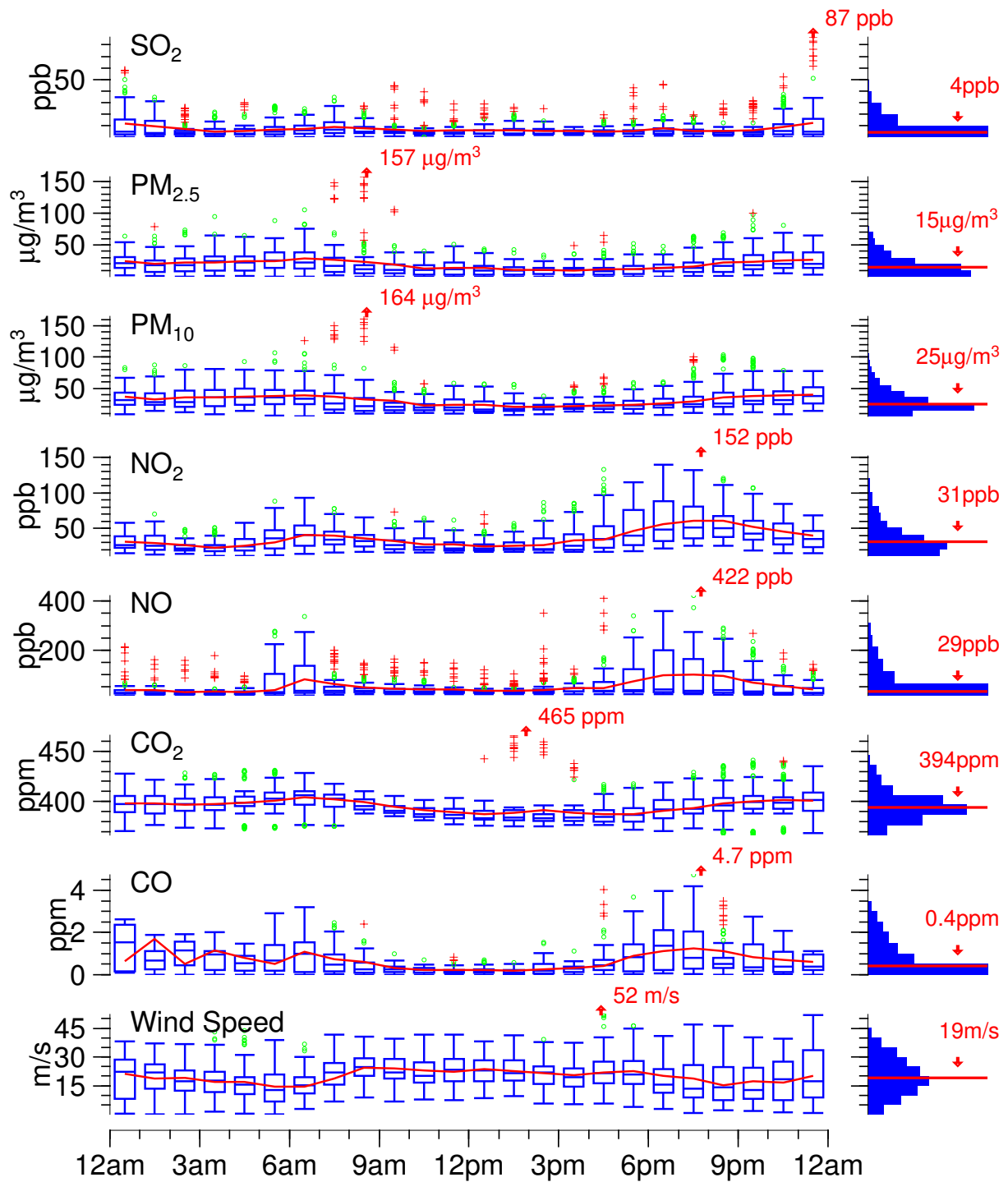


Figure 3.9: The diurnal distribution of aerosol and trace gases between 18 and 31 October 2007 next to the M1 Highway in Johannesburg. A frequency histogram with an annotated median is included for every variable. Data from two Johannesburg and one Cape Town campaigns were used.

## Domestic solid fuel burning emissions

South African households use electricity, coal, wood, paraffin, natural gas, candles and even animal dung as energy carriers (Balmer, 2007; Christopher, 2014; Kimemia and Annegarn, 2011). A small low-income settlement, Kwadela, on the South African Highveld was chosen to quantify typical ambient concentrations associated with residential solid fuel burning (Table 2.6). Although the Highveld is a region with many air pollution sources, no major anthropogenic emissions are located within 50 km of Kwadela. Availability and inexpensive price make coal the dominant energy carrier in this area, even for poor households.

Residential solid fuel burning emissions are driven by both cooking and heating needs. There is therefore a very pronounced seasonal, as well as diurnal cycle (Figure 3.10, Table 3.11 and Table 3.11). Median concentrations are low for all pollutants, except for *PM*. Most *PM* emissions associated with combustion are expected to be below  $1\ \mu\text{m}$ . Other significant sources in low-income areas include wind-blown dust (Annegarn et al., 1999). Even though emissions from residential solid fuel burning are relatively small compared to power and industrial sources, these emissions occur where people live, close to the ground and at times when the dispersion potential is at its minimum. Ambient concentrations were elevated by more than  $800\ \mu\text{g}/\text{m}^3$  for hourly  $PM_{10}$  and  $PM_{2.5}$  observations. Afternoon peaks are almost double morning peaks, and winter peaks almost double those of summer. Residential solid fuel burning is therefore an extremely important factor in air pollution impacts on human health. Despite the high *PM* concentrations, this source is difficult to quantify using satellite estimates, due to the limited vertical extent and the pronounced diurnal cycle high nocturnal concentrations have dispersed by the time of the overpass of polar satellites (between 10h00 and 14h00) (Hersey et al., 2015; Ichoku et al., 2003; Kneen et al., 2016) (Figure 3.10).

The importance of residential solid fuel burning emissions and their impacts on health have been studied in South Africa (Annegarn et al., 1999; Engelbrecht et al., 2000, 2001, 2002; Hersey et al., 2015; Rorich and Galpin, 1998; Worobiec et al., 2011). They have been shown to

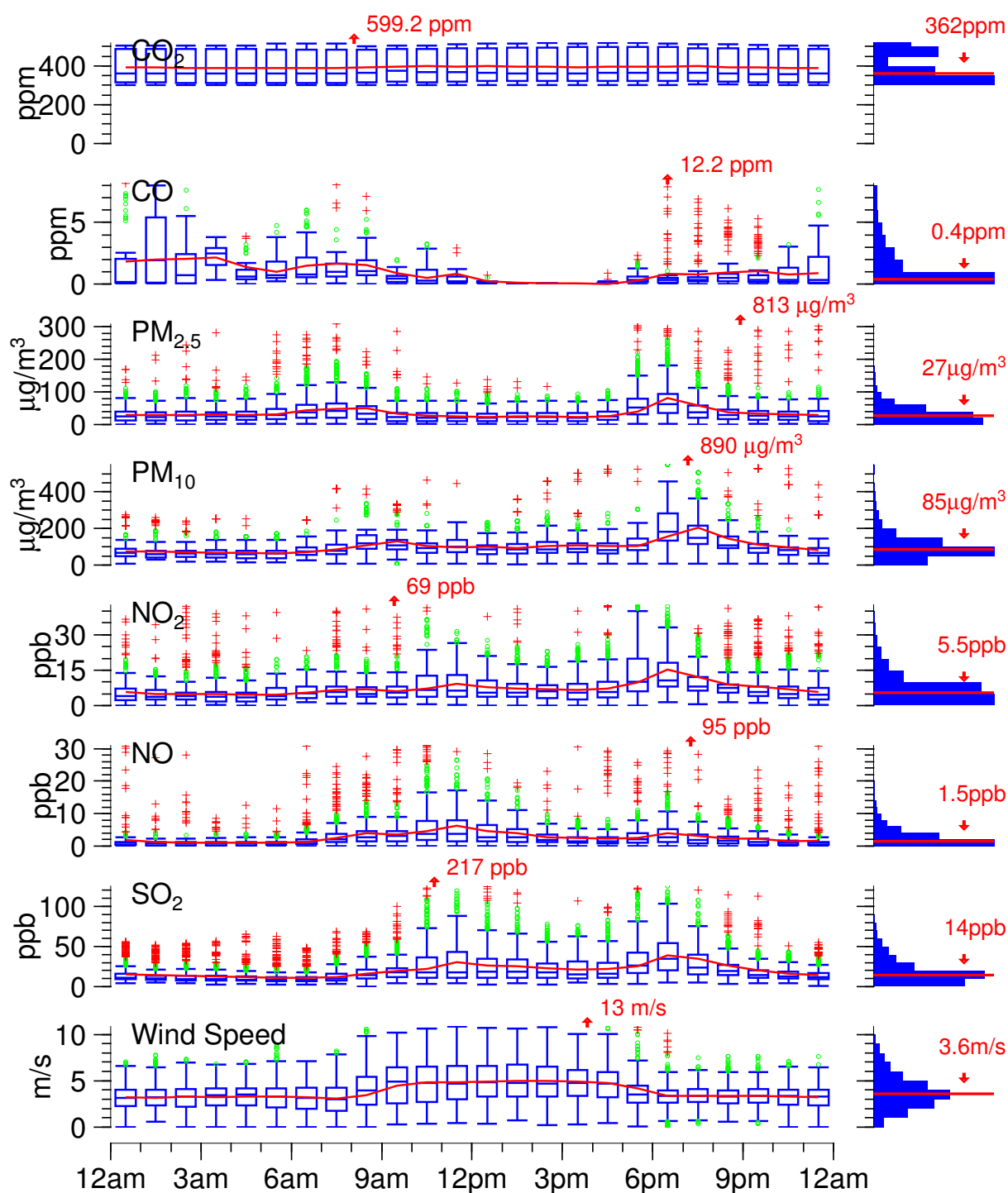


Figure 3.10: The diurnal distribution of aerosol and trace gases between 6 July and 9 September 2013 in Kwadela, an isolated, low-income settlement in the South African Highveld. A frequency histogram with an annotated median is included for every variable.

Table 3.10: Winter plume concentrations in an isolated low-income South African settlement. The difference between the maximum of instantaneous measurements every 5 minutes, and the average of all measurements between 13h00 and 14h00 are presented. The morning values correspond to the maximum measurement between 05h00 and 09h00 and the afternoon between 16h00 and 21h00. Measurements were made between 6 July and 9 September 2013.

|                                          | <b>Units</b>      | <b>Events</b> | <b>Mean</b> | <b>Std</b> | <b>25%</b> | <b>Median</b> | <b>75%</b> | <b>Max</b> |
|------------------------------------------|-------------------|---------------|-------------|------------|------------|---------------|------------|------------|
| Morning plumes between 05h00 and 09h00   |                   |               |             |            |            |               |            |            |
| $PM_{10}$                                | 1/cm <sup>3</sup> | 43            | 42          | 99         | -16        | 20.0          | 75         | 340        |
| $PM_{2.5}$                               | 1/cm <sup>3</sup> | 53            | 104         | 82         | 47         | 81            | 143        | 370        |
| $CO$                                     | ppm               | 11.0          | 2.9         | 4.3        | 0.0        | 1.6           | 2.8        | 12.6       |
| $CO_2$                                   | ppm               | 46            | -5.4        | 17.0       | -10.4      | -8.4          | -4.0       | 100        |
| $NO$                                     | ppb               | 43            | 13          | 20         | 2          | 5             | 12         | 73         |
| $NO_2$                                   | ppb               | 43            | 7           | 13         | 1          | 5             | 9          | 61         |
| $SO_2$                                   | ppb               | 59            | 1           | 23         | -13        | 1             | 14         | 62         |
| Benzene                                  | ppb               | 59            | 2           | 2          | 1          | 1             | 2          | 10         |
| Ethylbenzene                             | ppb               | 59            | 0           | 0          | 0          | 0             | 0          | 0          |
| Toluene                                  | ppb               | 59            | 1           | 2          | 0          | 0             | 1          | 10         |
| o-Xylene                                 | ppb               | 59            | 0           | 0          | 0          | 0             | 0          | 2          |
| p-Xylene                                 | ppb               | 59            | 0           | 0          | 0          | 0             | 0          | 1          |
| Afternoon plumes between 16h00 and 21h00 |                   |               |             |            |            |               |            |            |
| $PM_{10}$                                | 1/cm <sup>3</sup> | 48            | 162         | 171        | 36         | 126           | 255        | 810        |
| $PM_{2.5}$                               | 1/cm <sup>3</sup> | 58            | 163         | 141        | 71         | 107           | 190        | 800        |
| $CO$                                     | ppm               | 14.0          | 2.3         | 3.5        | 0.8        | 1.2           | 1.4        | 12.6       |
| $CO_2$                                   | ppm               | 54            | 4.5         | 3.1        | 2.7        | 3.9           | 5.8        | 14.9       |
| $NO$                                     | ppb               | 47            | 10          | 16         | 1          | 6             | 11         | 84         |
| $NO_2$                                   | ppb               | 47            | 17          | 10         | 10         | 16            | 23         | 39         |
| $SO_2$                                   | ppb               | 63            | 47          | 34         | 20         | 41            | 69         | 146        |
| Benzene                                  | ppb               | 62            | 2           | 2          | 0          | 1             | 2          | 13         |
| Ethylbenzene                             | ppb               | 62            | 1           | 7          | 0          | 0             | 1          | 57         |
| Toluene                                  | ppb               | 62            | 2           | 12         | 0          | 0             | 1          | 93         |
| o-Xylene                                 | ppb               | 62            | 0           | 2          | 0          | 0             | 0          | 11         |
| p-Xylene                                 | ppb               | 62            | 0           | 0          | 0          | 0             | 0          | 0          |

Table 3.11: Summer plume concentrations in an isolated low-income South African settlement. The difference between the maximum of instantaneous measurements every 5 minutes, and the average of all measurements between 13h00 and 14h00 are presented. The morning values correspond to the maximum measurement between 05h00 and 09h00 and the afternoon between 16h00 and 21h00. Measurements were made between 4 February and 5 April 2014.

|                                          | <b>Units</b>      | <b>Events</b> | <b>Mean</b> | <b>Std</b> | <b>25%</b> | <b>Median</b> | <b>75%</b> | <b>Max</b> |
|------------------------------------------|-------------------|---------------|-------------|------------|------------|---------------|------------|------------|
| Morning plumes between 05h00 and 09h00   |                   |               |             |            |            |               |            |            |
| $PM_{10}$                                | 1/cm <sup>3</sup> | 76            | 23.5        | 44         | -2.1       | 12.9          | 39         | 153        |
| $PM_{2.5}$                               | 1/cm <sup>3</sup> | 41            | 49          | 100        | 0.1        | 34            | 59         | 630        |
| $CO$                                     | ppm               | 77            | 0.4         | 1.0        | 0.0        | 0.1           | 0.4        | 3.9        |
| $CO_2$                                   | ppm               | 42            | -14.4       | 43         | -33.2      | -21.1         | -9.7       | 163        |
| $NO$                                     | ppb               | 77            | 9           | 12         | 2          | 7             | 11         | 72         |
| $NO_2$                                   | ppb               | 76            | 6           | 7          | 1          | 5             | 10         | 20         |
| $SO_2$                                   | ppb               | 76            | 13          | 44         | -4         | 2             | 13         | 216        |
| Benzene                                  | ppb               | 50            | 1           | 1          | 1          | 1             | 1          | 4          |
| Ethylbenzene                             | ppb               | 50            | 0           | 1          | 0          | 0             | 0          | 3          |
| Toluene                                  | ppb               | 50            | 1           | 1          | 0          | 1             | 1          | 5          |
| o-Xylene                                 | ppb               | 50            | 0           | 0          | 0          | 0             | 0          | 2          |
| p-Xylene                                 | ppb               | 50            | 0           | 1          | 0          | 0             | 0          | 3          |
| Afternoon plumes between 16h00 and 21h00 |                   |               |             |            |            |               |            |            |
| $PM_{10}$                                | 1/cm <sup>3</sup> | 74            | 51          | 60         | 18.4       | 37            | 74         | 310        |
| $PM_{2.5}$                               | 1/cm <sup>3</sup> | 42            | 99          | 157        | 19.0       | 40            | 84         | 580        |
| $CO$                                     | ppm               | 77            | 0.6         | 0.9        | 0.1        | 0.2           | 0.5        | 3.0        |
| $CO_2$                                   | ppm               | 45            | 21.4        | 48         | 2.6        | 10.2          | 22.2       | 294        |
| $NO$                                     | ppb               | 77            | 8           | 16         | 2          | 3             | 8          | 79         |
| $NO_2$                                   | ppb               | 75            | 12          | 8          | 5          | 11            | 16         | 34         |
| $SO_2$                                   | ppb               | 75            | 20          | 30         | 3          | 13            | 26         | 155        |
| Benzene                                  | ppb               | 51            | 1           | 1          | 0          | 1             | 2          | 6          |
| Ethylbenzene                             | ppb               | 51            | 1           | 2          | 0          | 0             | 2          | 11         |
| Toluene                                  | ppb               | 51            | 3           | 6          | 1          | 1             | 3          | 35         |
| o-Xylene                                 | ppb               | 51            | 1           | 2          | 0          | 0             | 1          | 9          |
| p-Xylene                                 | ppb               | 51            | 1           | 3          | 0          | 0             | 1          | 21         |

have the largest air pollution related impact on health in South Africa, with a total contribution close to 70 % (Scorgie et al., 2003, 2004; Scorgie, 2012). Nevertheless, they are still not a priority for management, their importance has been contested by senior government officials at the annual NACA conference and totally neglected by non-governmental pressure groups (O’Beirne, 2014). This study provides additional in situ evidence of the scale of the residential solid fuel burning problem. It underscores the importance of projects that explore local solutions to curb emissions in these areas (Kimemia et al., 2013; Makonese et al., 2015; Piketh et al., 2013, 2014; Wagner et al., 2005).

## Source character

The correlation between the in-plume concentrations of different species is an important indicator for air quality studies. This ratio is related to the character of the source responsible for the emission. It can therefore be used to identify the contributing sources, identify useful proxies for air quality in general, as well as explore the contribution of distinct emission sources to ambient air quality. The most frequently used ratios for anthropogenic sources sampled with the airborne laboratory are shown in Figure 3.11. The scale of the large industrial sources, such as power generation, petrochemical and steel plants is evident. Power stations have by far the highest in-plume concentrations of  $NO_x$  and  $SO_2$ . A  $NO_x$  proxy is therefore heavily biased towards these sources. Some steel and paper industries are large  $PM$  sources. The pollution control technologies employed in the metallurgical industry have meant lower stacks and an overall small footprint in these observations.

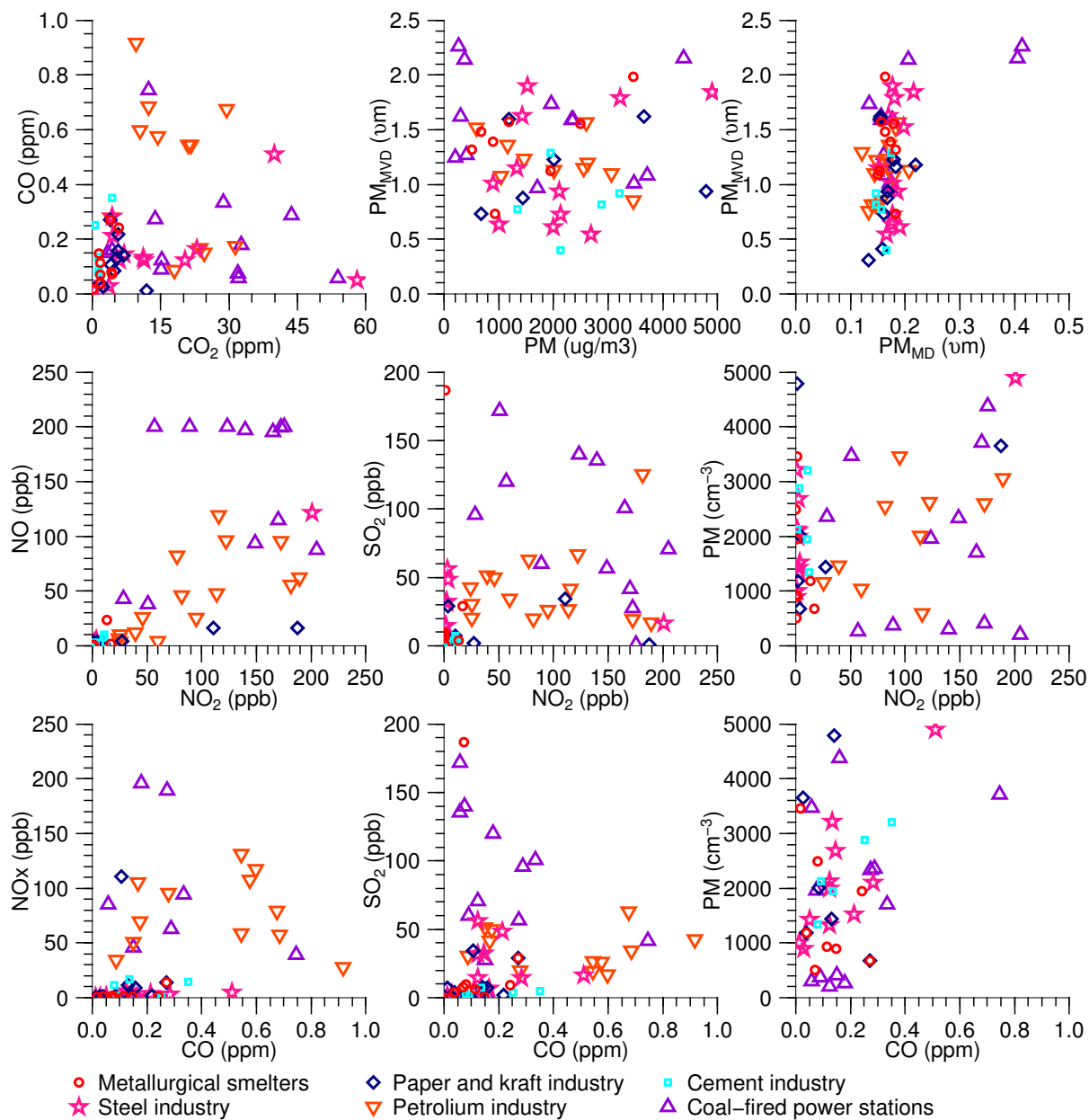


Figure 3.11: Correlation scatter diagrams of linear ratios from all anthropogenic sources. Each point represent an in-plume measurement derived from the difference between the maximum in-plume and the background. The mean volume diameter (MVD) and mean diameter (MD) of *PM* are also shown.

## Limitations of in situ plume characterisation

A method to characterise plume composition and pollutant concentrations is proposed. in situ measurements from plumes are presented. These provide a measure to compare against remotely sensed estimates, identify priority areas and could possibly be used for regulatory purposes. However, caveats with airborne sampling remain. Factors that impact on the quality of plume character estimates include: incorrect baseline caused by proximity of other sources; ascending or descending through haze layers might present as a plume; proximity of sources as well as the slow response of gas analysers dilute the estimates; lack of a clearly defined sampling methodology; small sources may present similar characteristics as aged plumes; sampling the same sources at different distances might lead to contradicting estimates; different meteorological conditions; and a sampling bias is present when larger sources are over represented. A major limitation is the lack of control for dilution of plumes.

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in situ observations confirm the important anthropogenic sources of aerosol and trace gases over South Africa. Large industry, especially power stations and petrochemical plants are prominent sources of  $NO_x$ ,  $SO_x$ ,  $CO_2$  and particulates. However, area sources such as vehicles and residential solid fuel burning have high concentrations of  $NO_x$ ,  $PM$  and  $CO$ . These sources are more difficult to quantify. Furthermore, they are likely underrepresented in satellite estimates due to their limited vertical extent.

## **Chapter 4**

# **The Spatial Distribution of Air Pollution in South Africa**

The spatial distribution of pollutants over South Africa is investigated using data from the airborne campaigns. The nature of the observations limits data to only a few hours per flight and only a few flights per area of interest. It makes up for the limited temporal scale by being mobile, as well as flexible in the design of the exact time and objective of each flight. Sampling in proximity, and manytimes inside plumes of important emitters still enable an assessment of the priority pollutants and areas with a large number of atmospheric emissions. Only data within the lowest 1 km above ground level was used to assess the spatial distribution and data was gridded to remove autocorrelation. Each criteria pollutant will be discussed in the following sections.

Emission sources are often clustered together spatially. This is especially the case for anthropogenic sources that either make use of a common mineral resource pool which are geographically limited, or existing infrastructure and labour forces. This chapter presents an overview of the aerosol and trace gas airborne measurements. The spatial distribution of each pollutant is discussed separately. Areas with a large number of atmospheric emissions of air pollution are therefore common. Management strategies naturally focus on specific geographic localities. In South Africa, this is the case for the coalfields on the Highveld (Wagner and Tlotleng, 2012), platinum group metals of the Bushveld Igneous Complex (Venter et al., 2012), petrochemical

and metallurgical industries in the Vaal triangle and other industrial areas sometimes in proximity to urban areas. Three air quality priority areas have been identified by the South African government: the Vaal triangle (Vereeniging in Figure 2.1), the Highveld (Witbank and Secunda in Figure 2.1) and the Waterberg (Rustenburg in Figure 2.1).

## Sulphur dioxide overview

The spatial distribution of maximum  $SO_2$  measurements (Figure 4.1) over Cape Town shows instantaneous peaks of almost 100 ppb close to the major industrial sources. An interesting peak of more than 50 ppb is observed south of the Khayelitsha and Michells Plain townships. These peaks are likely due to wood burning activities in the townships. Figure 4.1 shows that, on average, higher concentrations of  $SO_2$  are experienced over the township areas of the Cape Flats, but can be attributed to Consol Glass. Subsequent to these measurements been taken, the  $SO_2$  emissions from this industry have been reduced significantly through the implementation of  $SO_2$  control technologies. The deSOx was designed to reduce  $SO_2$  emissions by approximately 50 % (De Wind, Consol glass, personal communication, 2016). Concentrations drops to background as moving away the built-up areas of the Cape Metropolitan. This is indicative of the short atmospheric lifespan of  $SO_2$ , which oxidises to  $SO_4^{2-}$  particles.

Sulphur dioxide concentrations ranged between undetectable values and 136 ppb over Gauteng. The highest concentrations were measured from a single point source south of Daveyton, PG glass. On the whole, concentrations over Gauteng are relatively lower. From Figure 4.1 it becomes evident that there is some of the  $SO_2$  being emitted from residential solid fuel burning. The large gap of data that exists in the centre of this study area is due to the fact that the aircraft was not permitted to fly in OR Tambo International Airport controlled air space.

Maximum  $SO_2$  concentrations are detected over the Durban south industrial centre. In this region, a maximum concentrations were measured closest to the sources (300 ppb), the most significant of these being the oil refinery just south of the City of Durban. A maximum plume

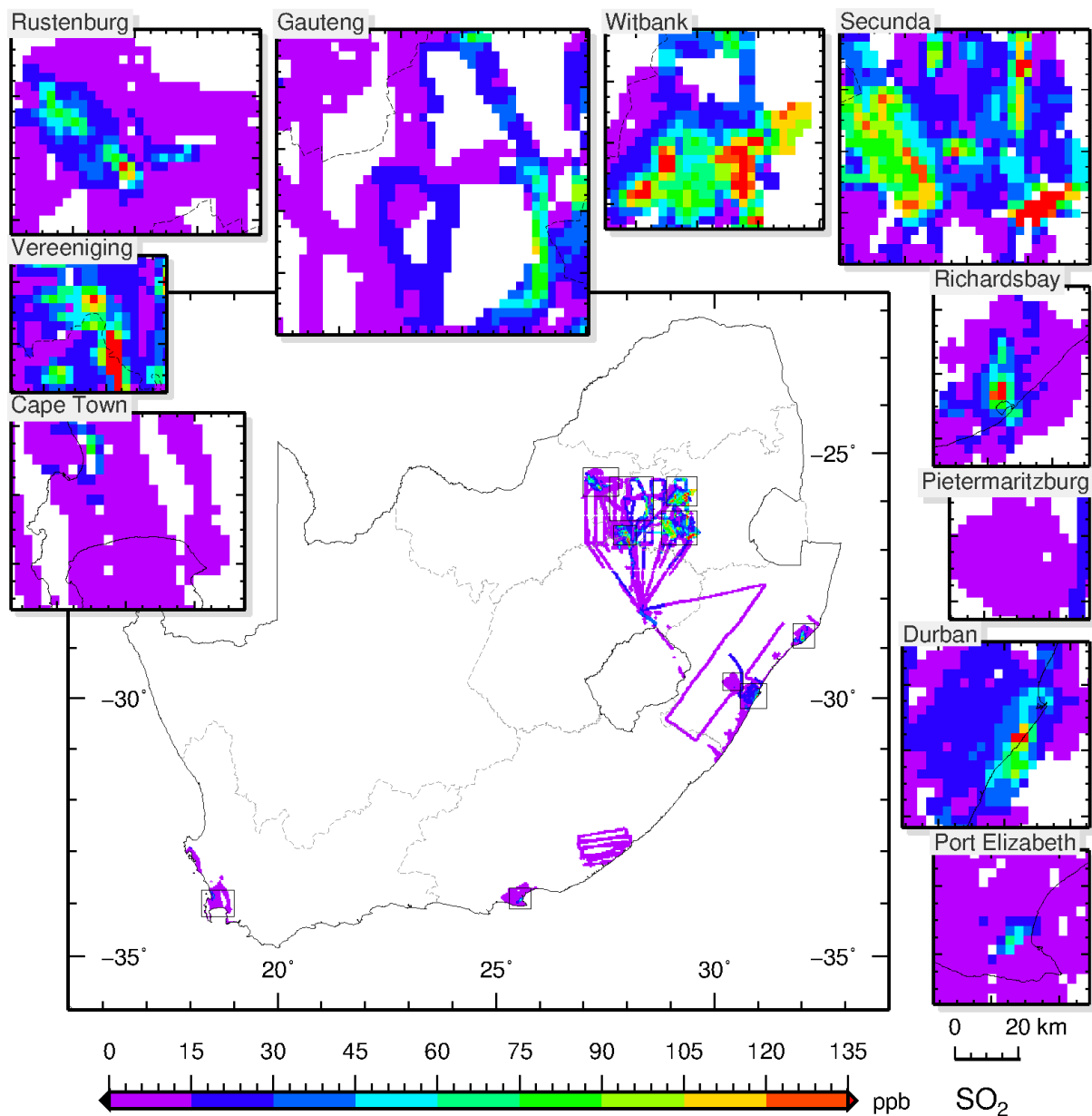


Figure 4.1: The spatial distribution of  $SO_2$  derived from all measurements below 1 km above ground level. The maximum concentration in each grid box is shown. A spatial resolution of 10 km was chosen to eliminate autocorrelation.

of  $SO_2$  extends off the coast from the industrial complex.  $SO_2$  was detected at the mouth of the Umkomazi river. These emissions are associated with a paper industry located approximately 4 km inland from the coast. Maximum concentrations of  $SO_2$  were approximately 60 ppb in this region. It is important to consider monitoring  $SO_2$  and other pollutants in the settlements surrounding this source. Although instantaneous concentrations measured on the airborne platform do not exceed the 10 min ambient standard, the aircraft likely underestimate the maximum concentrations at ground level.

The measured  $SO_2$  concentrations over Pietermaritzburg do not pose a significant threat from an air pollution point of view. Five point sources of  $SO_2$  were clearly identifiable over the region. A small area source of  $SO_2$  was detectable to the southeast of Thornville, most likely Hopewell.  $CO$  concentrations peaked in the same region. Two possible sources are present at this location. The Hopewell settlement and a high density of large scale chicken houses. The chicken industry utilise small scale boilers to control the temperatures inside the broiler houses. This source needs further investigation.

Richards Bay has a significant number of sources of  $SO_2$ . The aircraft measurements, however, did not pick up multiple sources of  $SO_2$  in Richards Bay which was expected. The proximity of the major sources of  $SO_2$  in Richards Bay include, Hillside Aluminium smelters, Bayside Aluminium smelter, Mondi paper and FOSKOR, made it impossible to distinguish these sources with the aircraft measurements. These plumes merge and due to uncertainties in wind speed and direction estimates measurements can not be reliably linked to a specific source. Only one point source was identified. The footprint of maximum  $SO_2$  concentrations in Richards Bay is fairly large with a large area with values over 120 ppb. The instantaneous measurements from the aircraft are best compared to the ten minute standard. It is possible that this ambient standard could be exceeded in Richards Bay given the  $SO_2$  concentrations measured over the entire industrial region.

Emissions of  $SO_2$  over Rustenburg are primarily from two industrial complexes. Concentrations as high as 200 ppb were detected over the smelting complex to the east of the Rustenburg

city. The  $SO_2$  fingerprint is fairly substantial over the region when Figure 4.1 is evaluated. Several townships have been identified around this region that utilise coal as a domestic source of energy. The largest domestic emissions occur in the Madibeng district municipality. The lower concentrations of  $SO_2$  over a wide spatial footprint are likely to be a combination of the industrial emissions and emissions from residential solid fuel burning. Concentrations from the industrial sites impact on residential areas in the region and are fairly close to the 10 min  $SO_2$  South African ambient standard.

Emissions of  $SO_2$  over the Highveld and Vaal priority areas are highest just south of Vereeniging. These emissions are associated with the industrial activities in that Sasolburg region, most notably SASOL and NATREF. Maximum concentration of  $SO_2$  exceeded 300 ppb with a substantial spatial footprint of  $SO_2$  exceeding 200 ppb. These measurements justify this region of South Africa being declared the first air pollution priority area. Figure 4.1 highlights additional areas which are clearly associated with residential solid fuel burning, including Shaprville, and Zamdela.

The major peaks of  $SO_2$  are associated with the various smelting and power generation industries in the Witbank region. Maximum sulphur dioxide concentration were recorded as 204 ppb. In addition to the industrial emissions of  $SO_2$  there are significant number of residential areas using coal as a primary source of domestic energy for cooking and heating. The maxima of  $SO_2$  over Middleburg in Figure 4.1 represents emissions from a stainless steel industry. A down turn in economic activity has seen the demise of a substantial source of pollution in the region, namely Highveld Steel.

As was the case in Witbank, Secunda is surrounded by major high temperature and tall stack industries. The concentrations of  $SO_2$  detected in this region represent the highest value of this species anywhere in the country. Maximum concentrations of  $SO_2$  were close to 500 ppb. No additional sources could be identified in Figure 4.1. This again indicates that the major emissions are from tall stacks. It is however important to note that a substantial  $SO_2$  source was detected south of Leandra stretching over tens of kilometres in a south easterly direction.

This  $SO_2$  is probably from both residential solid fuel burning emissions over Leandra and Embalenhle just south of Evander. Low income settlements are not a very significant source of  $SO_2$ , as shown in Chapter 3, but the size and extent of solid fuel use could possibly contribute to overall ambient  $SO_2$ .

Significant sources of  $SO_2$  were observed in the with instantaneous maximum values over 80 ppb (top of Figure 4.1). This did not contribute to background conditions and median values were less than 2 ppb for the whole area (bottom of Figure 4.1).

## Nitrogen oxides overview

The maximum  $NO$  concentrations over South Africa (Figure 4.2) show values in excess of 120 ppb in the region of major industries. Concentrations over Cape Town International airport show consistently elevated values of  $NO$  in the order of 5 ppb (bottom Figure 4.2). Typically 90 % of  $NO_x$  emissions is in the form of  $NO$ , which quickly oxidises in the atmosphere to  $NO_2$ .

The only real source of  $NO$  emissions in the Gauteng area where the aircraft could fly was identified over the Germiston-Brakpan-Springs industrial complexes, which include Consol Glas, Scan Metals and PGF glas. The nature and contribution of these sources needs to be identified.

$NO$  levels peak over the city of Durban directly. Concentrations over the city ranged from low levels to close to 200 ppb. A second source of  $NO$  was clearly visible over the Umkomaas river mouth. These  $NO$  levels are due to a paper industry located at this site.

Three major sources of  $NO$  are discernible from the spatial data, the power stations to the east and south west of Witbank and the stainless steel industry in Middleburg. The concentrations of  $NO$  recorded in the Witbank region represent the second highest values for the country

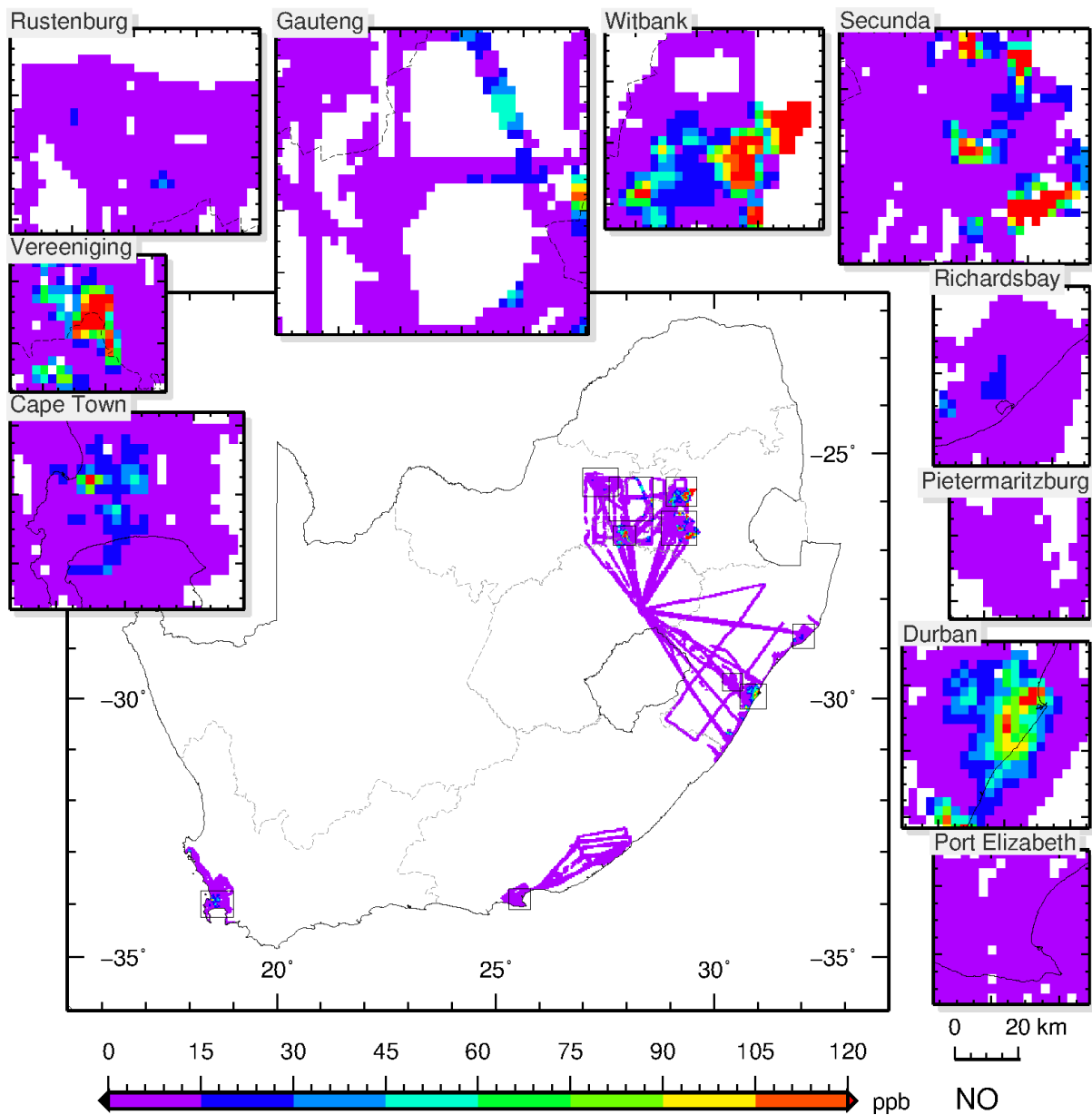


Figure 4.2: The spatial distribution of  $NO$  derived from all measurements below 1 km above ground level. The maximum concentration in each grid box is shown. A spatial resolution of 10 km was chosen to eliminate autocorrelation.

(194 ppb).  $NO_2$  concentrations are high in this region with maximum values of 198 ppb being detected. The lack of any major contributing source to Figure 4.2 is indicative of the fact that these are mostly high stack sources of nitrogen oxides.

The maximum  $NO_2$  concentrations show a much wider distribution than  $NO$  including all the major industrial areas as well as Cape Town city centre and the Cape Flats townships (top Figure 4.3). Maximum values of more than 160 ppb were measured. The larger sources such as traffic and the townships dominate the median values.

It is expected that over a major city complex such as Johannesburg and Ekurhuleni  $NO_2$  emissions would be high due to high motor vehicle emissions. Calculations by Tongwane et al. (2015) showed that approximately 33 % of all transport related emissions originate in Gauteng. The distribution of  $NO_2$  does not exactly conform to the location of the major cities and the expected regions of highest traffic volumes. The high levels of  $NO_x$  associated with busy highways were presented in Chapter 3 on page 86. Flight restrictions, as well as the low level or release prevented airborne estimates over city centres themselves.

In Durban, the  $NO_2$  levels are highest over the city and the industrial region in the South.  $NO_2$  concentrations reach as high as 240 ppb over Durban city. Associated with the  $NO_2$  levels are very high levels of  $O_3$  measured over the city (110 ppb). Ozone concentrations over 80 ppb constitute a significant hazard to humans. The ozone is generated as a result of the photochemical production during the daytime.

$NO_x$  are closely associated with the industrial emissions for most of the country. In Rustenburg, a source of  $NO$  or  $NO_2$  is visible to the south of Marikana. The concentrations are not extremely high and therefore currently do not pose a significant air pollution threat. These emissions are colocated with operations from Lonmin platinum industry. In particular a processing plant with a medium height stack is located close to Marikana. The metallurgical industry has implemented stricter  $SO_2$  control in recent years. The city of Rustenburg is an additional source of  $NO_2$  in this region. This is almost certainly associated with emissions from

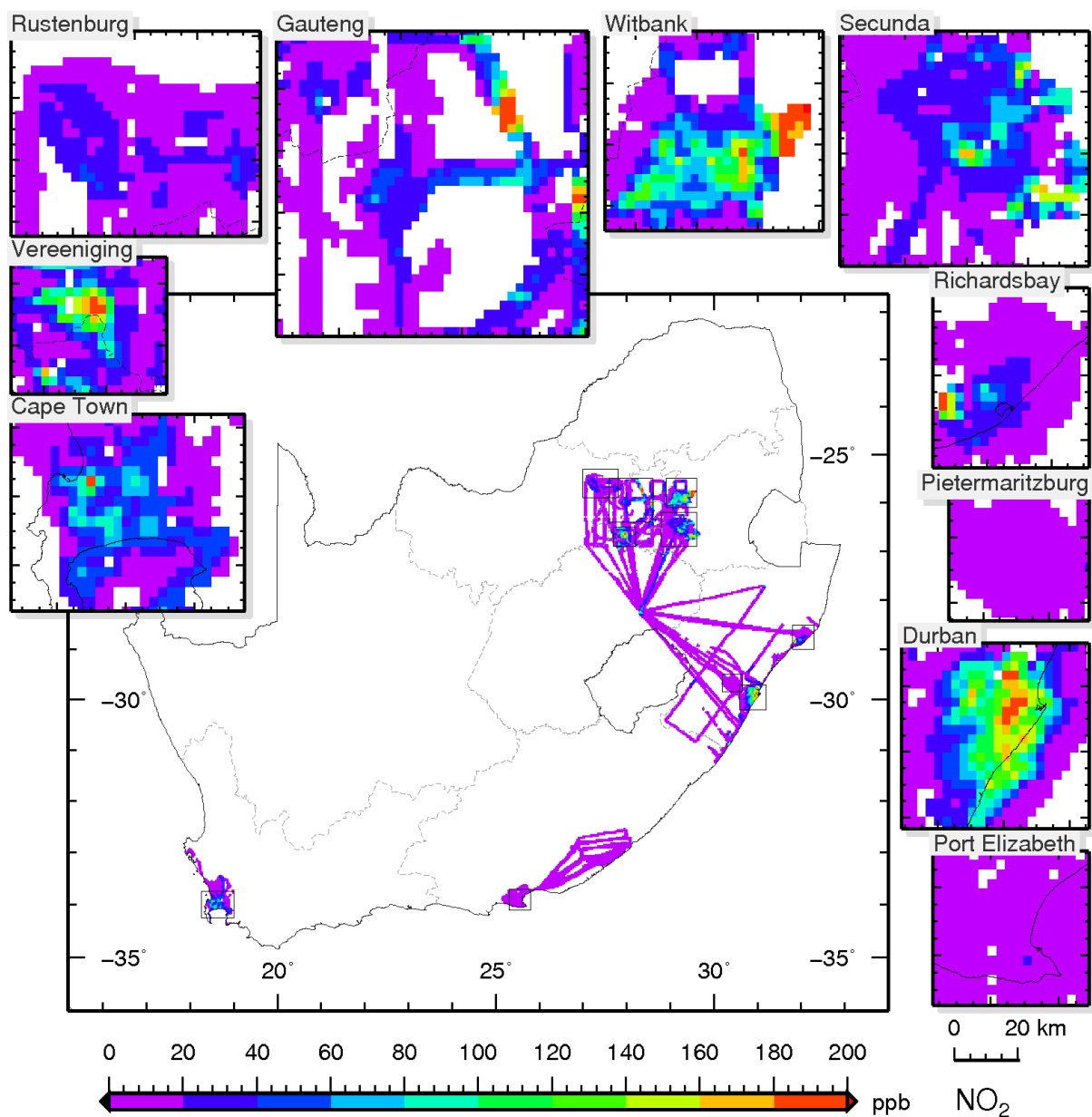


Figure 4.3: The spatial distribution of  $NO_2$  derived from all measurements below 1 km above ground level. The maximum concentration in each grid box is shown. A spatial resolution of 10 km was chosen to eliminate autocorrelation.

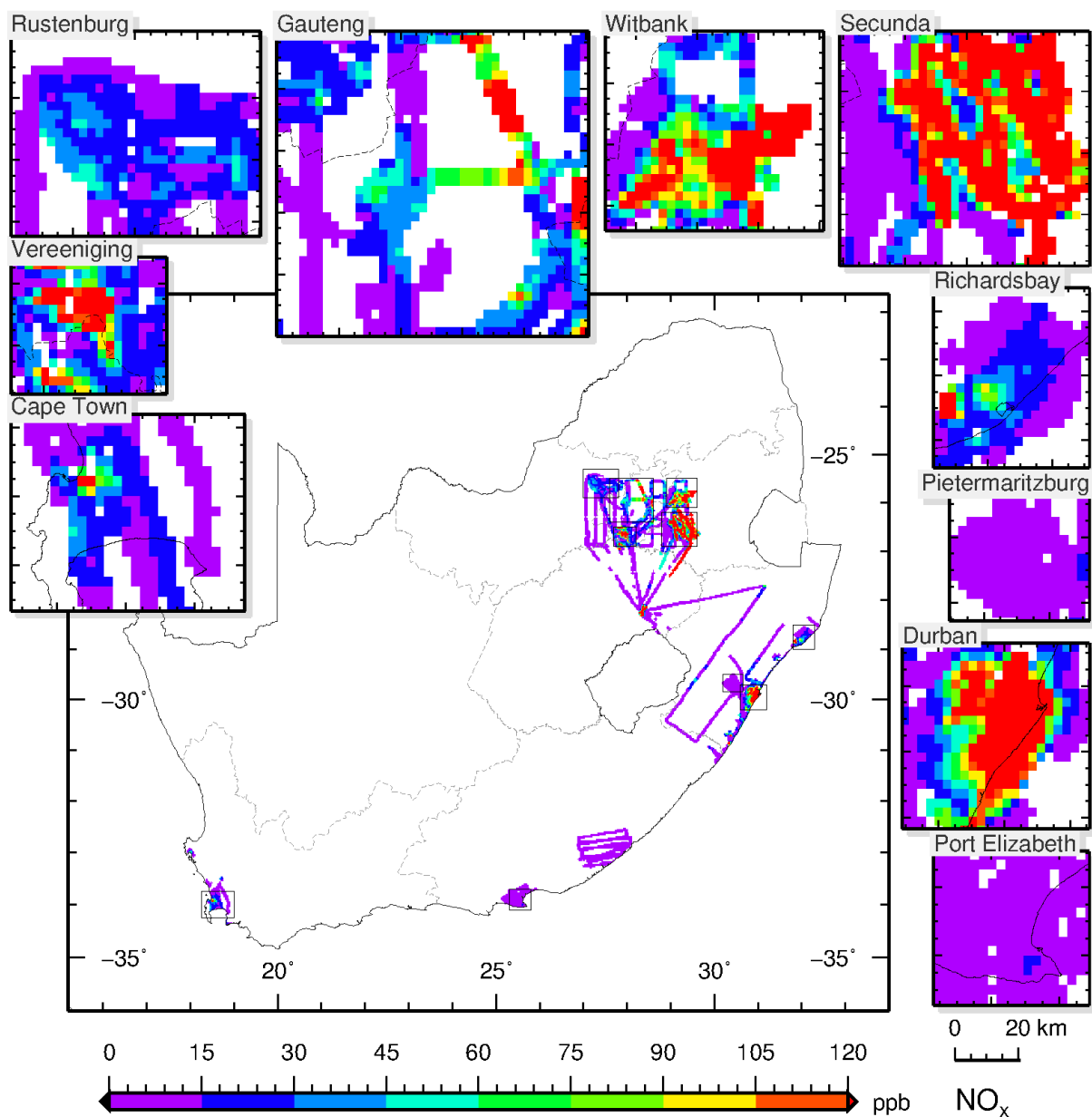


Figure 4.4: The spatial distribution of  $NO_x$  derived from all measurements below 1 km above ground level. The maximum concentration in each grid box is shown. A spatial resolution of 10 km was chosen to eliminate autocorrelation.

motor vehicles. Individual sources of  $NO_2$  are distinguishable to the north west of Rustenburg. These would represent industrial point sources. The townships of Phokeng contribute to the nitrogen dioxide loading in the Rustenburg area.

The  $NO$  emissions confirms the differences in source between the high temperature processes associated with the power utilities and petrochemical industry and the low temperature combustion associated with residential solid fuel burning. The  $NO$  and  $NO_2$  peaks detected in this region are the highest in the country with maximum values of 200 and 204 respectively. This is the only region in the country where the  $NO_2$  ambient standard is at risk of being exceeded according to the current data set.  $NO_2$  is primarily a secondary pollutant from these sources. It is evident from the fact that Figure 4.3 shows an extensive source region of  $NO_2$  in the down-wind direction. The major source of  $NO_2$  is centred over Vereeniging and Sasolburg, an area well known for its large industry.

The oxides of Nitrogen measured over Richards Bay both follow the spatial footprint detected for the  $SO_2$  levels. It is most likely that these species are associated with the extensive industrial activity discussed previously. Maximum  $NO$  concentrations were 30 ppb while  $NO_2$  levels reached 140 ppb. These values are fairly low when compared with concentrations measured in other cities of South Africa. Maximum  $O_3$  concentrations were high over Richards Bay. The  $O_3$  production in the day could have been associated with the  $NO$  and  $NO_2$  emissions in this region.

$NO$  was almost not detectable from the aircraft over Pietermaritzburg. The maximum recorded concentrations of  $NO$  was just slightly higher than 5 ppb.  $NO_2$  concentrations were fairly low over Pietermaritzburg. Maximum concentrations were detected in the same place as the slightly elevated  $SO_2$  concentrations. These emissions are almost certainly industrial. Ozone concentrations did reach extremely high levels over Pietermaritzburg. This is not consistent with the emissions of ozone precursors over the city. It is likely that the detected  $O_3$  has been transported to the region from other sources.

## Ozone overview

In the Cape Town region peak  $O_3$  values of over 80 ppb were measured over the Strand-Gordons area (top Figure 4.5). This is even more apparent in the median values (Figure 4.5). The shift of  $O_3$  over the Strand region of Cape Town is a function of the diurnal distribution of ozone production through the day. On most of the days on which aircraft measurements were taken the wind was blowing from the north west. Pollutants emitted during the morning (particularly  $NO_2$ ) were advected across False Bay. By midday these pollutants had transformed to  $O_3$  and were measured over Strand. This again illustrates the benefit of a mobile platform to detect downwind concentrations in areas not currently associated with large emission sources.

Maximum atmospheric  $O_3$  observations were higher than 40 ppb for most of the regions. Most of the campaigns focused on late winter and early spring. This coincides with the biomass burning peak and an associated rise in  $O_3$ . The relatively high levels do confirm modelling studies (van Tienhoven and Zunckel, 2004; Zunckel et al., 2006) that also estimate  $O_3$  concentrations to be above thresholds considered safe for the environment. The gradient of decreasing  $O_3$  with an increase in latitude of these modelling studies were observed.

## Carbon oxides overview

$CO$  is a tracer pollutant for human activity. Enhanced levels were observed over most urban and industrial areas. The highest concentrations over Cape Town reached values of 4.69 ppm. This is significantly elevated above typical background levels of between 200 and 300 ppb (Kirkman et al., 2000). The  $CO$  is emitted from a range of sources in Cape Town indicating incomplete combustion processes. No single source could be identified from the extensive flights over the region. Contributions to  $CO$  are probably being made by industry, domestic wood burning and motor vehicle emissions.

$CO$  levels measured from the airborne campaign over Gauteng show a band of elevated  $CO$  over the northern suburbs of Johannesburg and Ekurhuleni. The cause of these elevated concentrations of  $CO$  are not clear. The elevated concentrations of  $CO$  over the Germiston-Brakpan-Springs industrial complex is directly associated with the industrial activity.

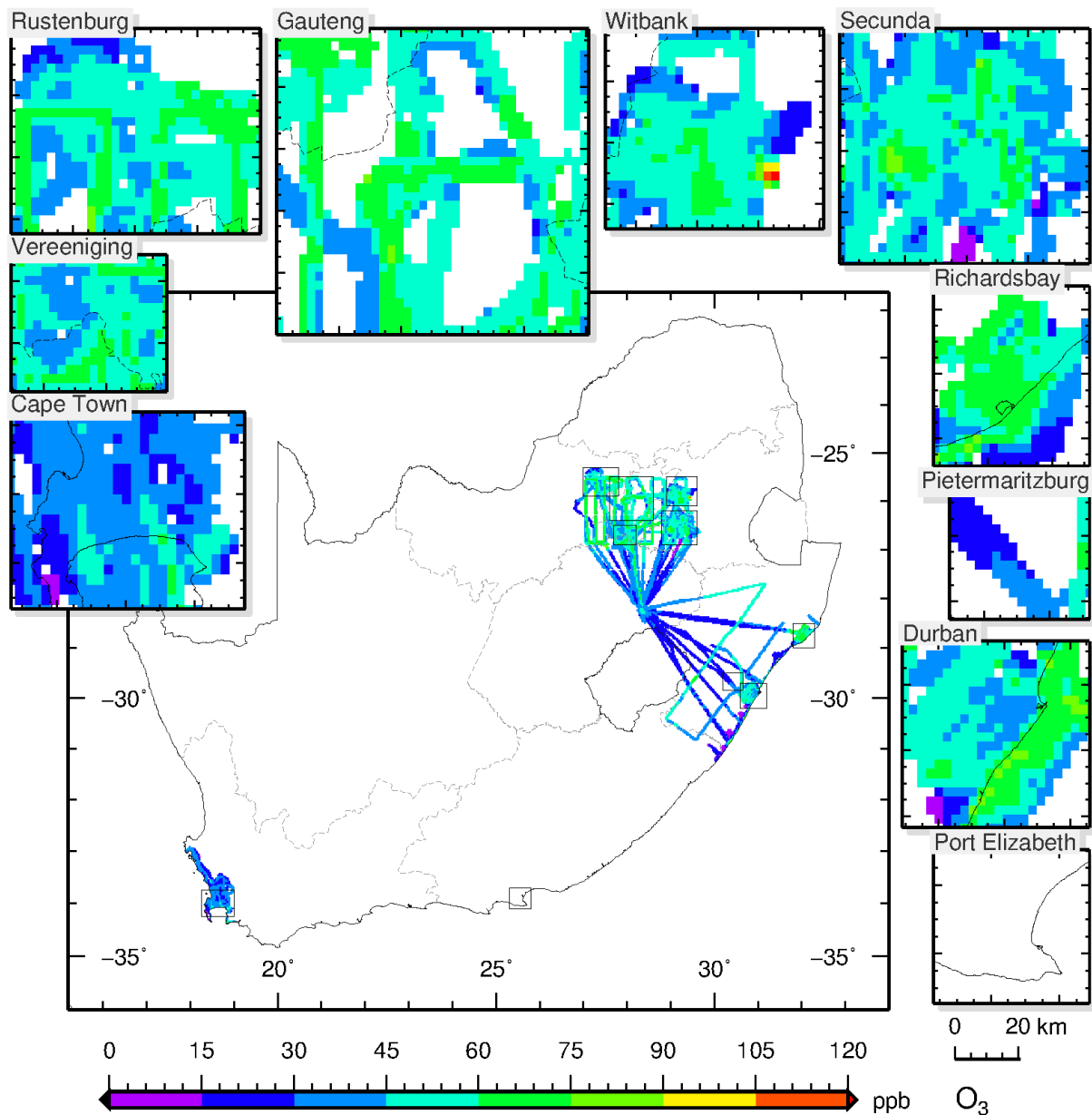


Figure 4.5: The spatial distribution of  $O_3$  derived from all measurements below 1 km above ground level. The maximum concentration in each grid box is shown. A spatial resolution of 10 km was chosen to eliminate autocorrelation.

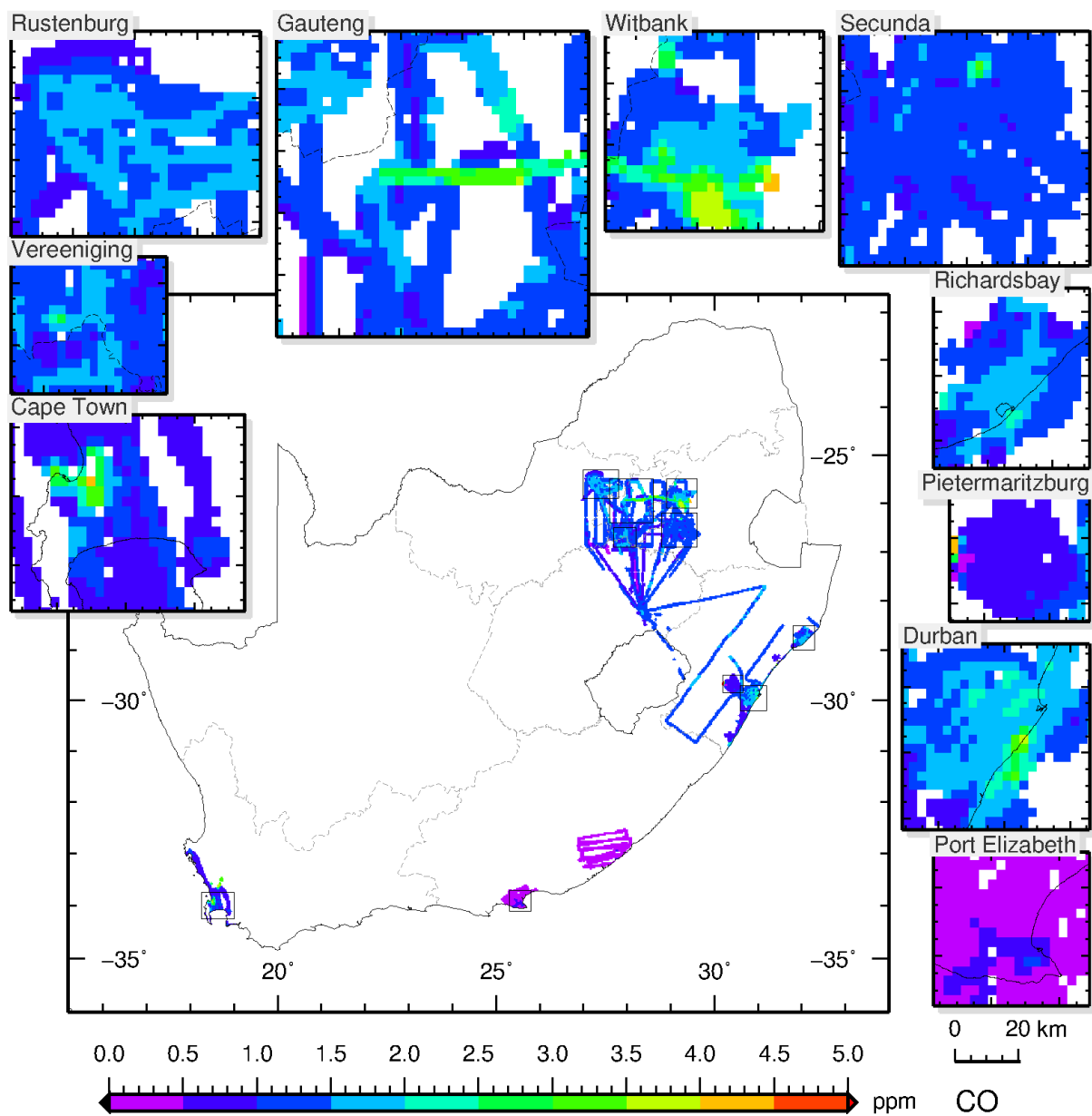


Figure 4.6: The spatial distribution of  $CO$  derived from all measurements below 1 km above ground level. The maximum concentration in each grid box is shown. A spatial resolution of 10 km was chosen to eliminate autocorrelation.

The levels of  $CO$  measured over Durban are only moderately elevated when compared to the of other cities. Concentrations of about 1 ppm represent a factor of 2 to 3 less  $CO$  than those measured over Cape Town and other areas with a large number of atmospheric emissions of air pollution. The majority of the  $CO$  seems to originate over the industrial region and possibly from motor vehicle emissions in the city.  $CO_2$  concentrations were elevated over the industrial region in Durban South and the city centre. Figure 4.7 shows little additional sources of  $CO_2$  in the Durban region with levels being close to the global average (400 ppm)

Carbon dioxide concentrations are surprisingly elevated over Johannesburg and some of the south western suburbs. Concentrations of the gas are elevated to approximately 480 ppm. This represents a significant enhancement over the global mean value.

$CO$  seem to be emitted from low income areas. This is probably due to the incomplete combustion of coal in low temperature fires. The smelter at Phoswan near Rustenburg is clearly burning fuel efficiently as the  $CO$  levels actually drop over the source. Maximum concentrations of  $CO$  stretch over the three major centres incorporated in the Vaal priority area, including Vereeniging, Vanderbijlpark and Sasolburg. Elevated carbon dioxide concentrations do not follow the  $CO$  distributions. Highest levels of  $CO_2$  were detected towards the north of Vereeniging. The  $CO_2$  is elevated to 500 ppm. These are the highest values recorded anywhere in South Africa. As indicated before, the major sources in this region are high temperature combustion sources. A significant enhancement of  $CO_2$  was detected over the central Highveld.  $CO$  concentrations are elevated but to a lesser extent. The complete combustion processes emits vast quantities of  $CO_2$ . The Highveld has a high concentration of power stations burning coal, as well as petrochemical facilities. The maximum concentrations of  $CO_2$  are 501 ppm. This is a substantial enhancement from regional background levels. The high emissions of  $CO_2$  make a contribution to the global accumulation of greenhouse gases in the atmosphere. The extent of the forcing caused by these emissions is difficult to quantify. Elevated  $CO$  (Figure 4.6) and  $CO_2$  (Figure 4.7) concentrations are visible over the city of Port Elizabeth as well as the industries to the north of the city.

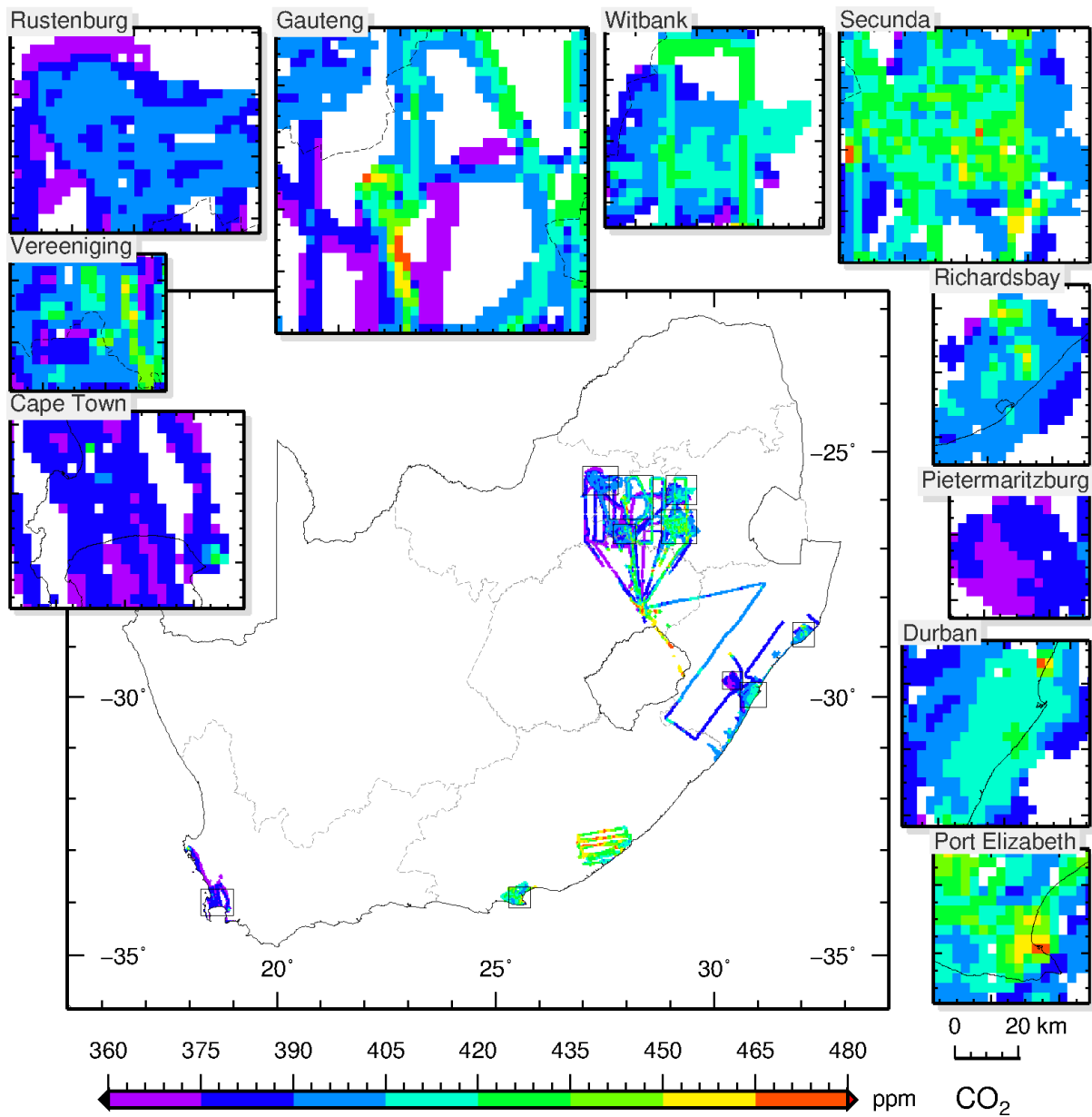


Figure 4.7: The spatial distribution of  $CO_2$  derived from all measurements below 1 km above ground level. The maximum concentration in each grid box is shown. A spatial resolution of 10 km was chosen to eliminate autocorrelation.

## Particulate matter overview

Fine particulate matter is responsible for many of the health impacts associated with atmospheric aerosol pollution as well as the majority of the brown haze observed in the atmosphere.  $PM_3$  levels over Cape Town reach extremely high levels. These particulate matter loadings are higher than any other area observed in this study. The highest concentration of  $PM_3$  was originating from the glass factory in Belville. Subsequent to these measurements been taken, Consol glass has instituted particulate matter mitigation measures which has significantly reduced the emissions of  $PM_3$  from their stacks. The median concentration map shows that much of the particulate matter is originating over the townships of Khayelitsha and Mitchells Plain. The most likely source of the particulate matter is domestic wood burning in the early morning and in the evening for cooking and space heating. The high concentrations over Strand are due to the movement of  $PM$  across False Bay during the day.

Over Gauteng, measured  $PM_3$  levels resemble the  $CO$  levels to a certain extent. A band of elevated concentrations was detected between Johannesburg and Pretoria. Unusually high levels of  $PM_3$  were detected over the Brits area. No obvious sources of particulates or  $CO$  have been identified in these regions. Contributions in northern Johannesburg could include motor vehicle emissions and possibly domestic coal combustion.

Over Durban and Pietermaritzburg, the highest concentrations of  $PM_3$  were clearly associated with industrial activities. A few additional sources could be identified between Durban and Umlhanga Rocks as well as close to Pinetown and Umbumbulu. Figure 4.8 highlights possible emissions from domestic sources to the west of Durban.

Fine particulate matter over Pietermaritzburg is mostly associated with the industrial sources identified from the  $SO_2$  emissions. An additional source of  $PM_3$  and  $NO_2$  is clearly detected between Pietermaritzburg and Cato Ridge. The most likely source is the Assmang manganese Cato Ridge works. The maximum concentrations in this region are significantly lower than those measured over the Highveld and Cape Town.

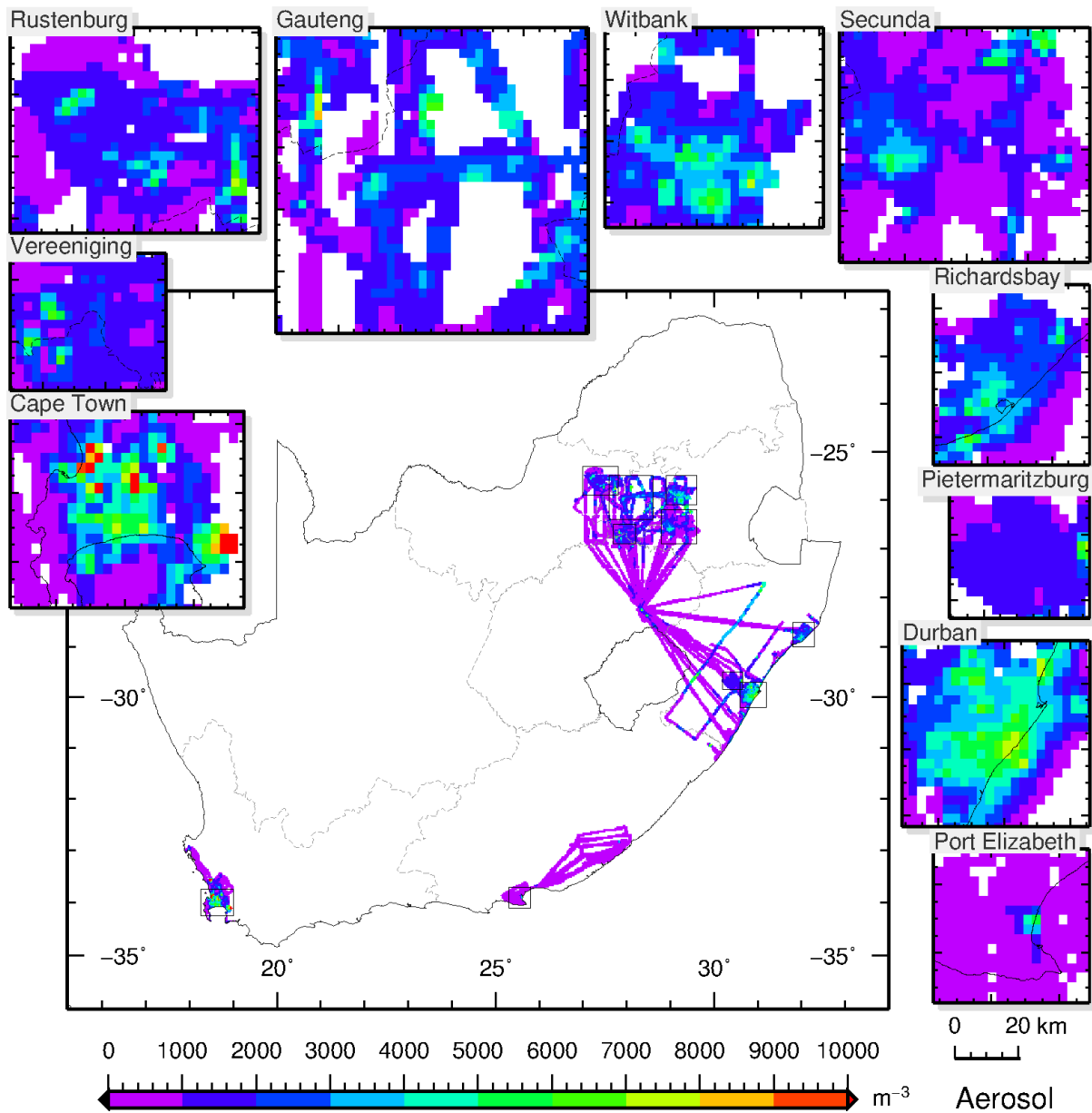


Figure 4.8: The spatial distribution of  $PM_{2.5}$  derived from all measurements below 1 km above ground level. The maximum concentration in each grid box is shown. A spatial resolution of 10 km was chosen to eliminate autocorrelation.

Over Richards Bay, the measurements of  $PM_3$  showed the same trend as the other pollutants measured. A general increase in the overall atmospheric concentrations could be detected over the entire industrial region. The concentrations of  $PM_3$  were significantly elevated over the industrial region. A secondary source of particulate matter as well as all other pollutants was detected to the north east of Richards Bay. The nature and identity of this source needs to be determined.

Over Rustenburg, the maximum concentrations of  $PM_3$  seem to emanate from the major industrial sources. The particulate matter leaves a fairly substantial spatial footprint over the region. The highest concentrations of particulate matter replicate the elevated concentrations of  $SO_2$  (100 ppb contour) detected around the industrial sources. A source of  $PM_3$  is clearly visible over the Brits area. The Particulate matter measured over Rustenburg is comparable to that measured over Cape Town.

In the Vaal priority area, the largest contribution to  $PM_3$  is made by industries in Sasolburg and Vanderbijlpark. These particulate matter values reach close to the concentrations recorded in Rustenburg and Richards Bay. An extensive number of lesser  $PM_3$  sources extends over the entire central to north eastern section of the defined study area. These aerosols are derived from domestic coal combustion.

In the Highveld priority area, the measured  $PM_3$  concentrations are high. The main sources of the aerosols are the major industrial sources. Due to the large quantities of  $SO_2$  being emitted in this region it is difficult to determine if the aerosols are primary or secondary pollutants.

The particulate matter concentrations detected in this region show that the industrial emissions are mitigating a major component of the particulate emission to the atmosphere. The exception on this case would be Kriel power station which seems to have been emitting higher than usual amounts of particulate matter. The major source of particulate matter other than the aforementioned industry is the combined particulate emissions from domestic coal burning from Leandra and Evander Township. The low level nature of the source is highlighted by the large plume

of  $PM_3$  in the Figure 4.8 originating from these two source regions. Maximum particulate concentrations were due to industry (Figure 4.8) and no significantly elevated concentrations were visible in the areas of townships.

## **Volatile organics overview**

Over Cape town, benzene levels between 2 and 20 ppb were detected. The highest concentration of benzene were detected over Cape Town International Airport. benzene and toluene levels around the large petrochemical plant in Table View were relatively low. Fewer measurement of *BTEX* were made over the Gauteng region. The highest concentrations of both benzene and toluene (500 and 550 ppb respectively) were recorded over Vorsterkroon south east of Gauteng. It is possible that these emissions were transported to this region from adjacent regions.

In Durban, typical concentrations of benzene were between 1 and 5 ppb. The Highest concentration of benzene was recorded close to Chatsworth (20 ppb). The highest concentration of toluene was measured close to Gologonde (20 ppb). The concentrations of *BTEX* measured over Durban probably do not pose a significant health threat. Annual average concentrations are unlikely to exceed the annual guideline.

In the Vaal priority area, high concentrations of both benzene (900 ppb) and toluene (1000 ppb) were detected north of Vanderbijlpark. Instantaneous concentrations as high as these represent an important health risk to the impacted populations. The source of these compounds should be identified and controlled. Measurements of *BTEX* will be made in the newly acquired monitoring stations for the priority area.

In the Highveld priority area, benzene and toluene concentrations detected around Witbank ranges between 5 and 250 and 300 ppb respectively. These concentrations constitute a high background value. It is difficult to know what the sources are that could be contributing to these

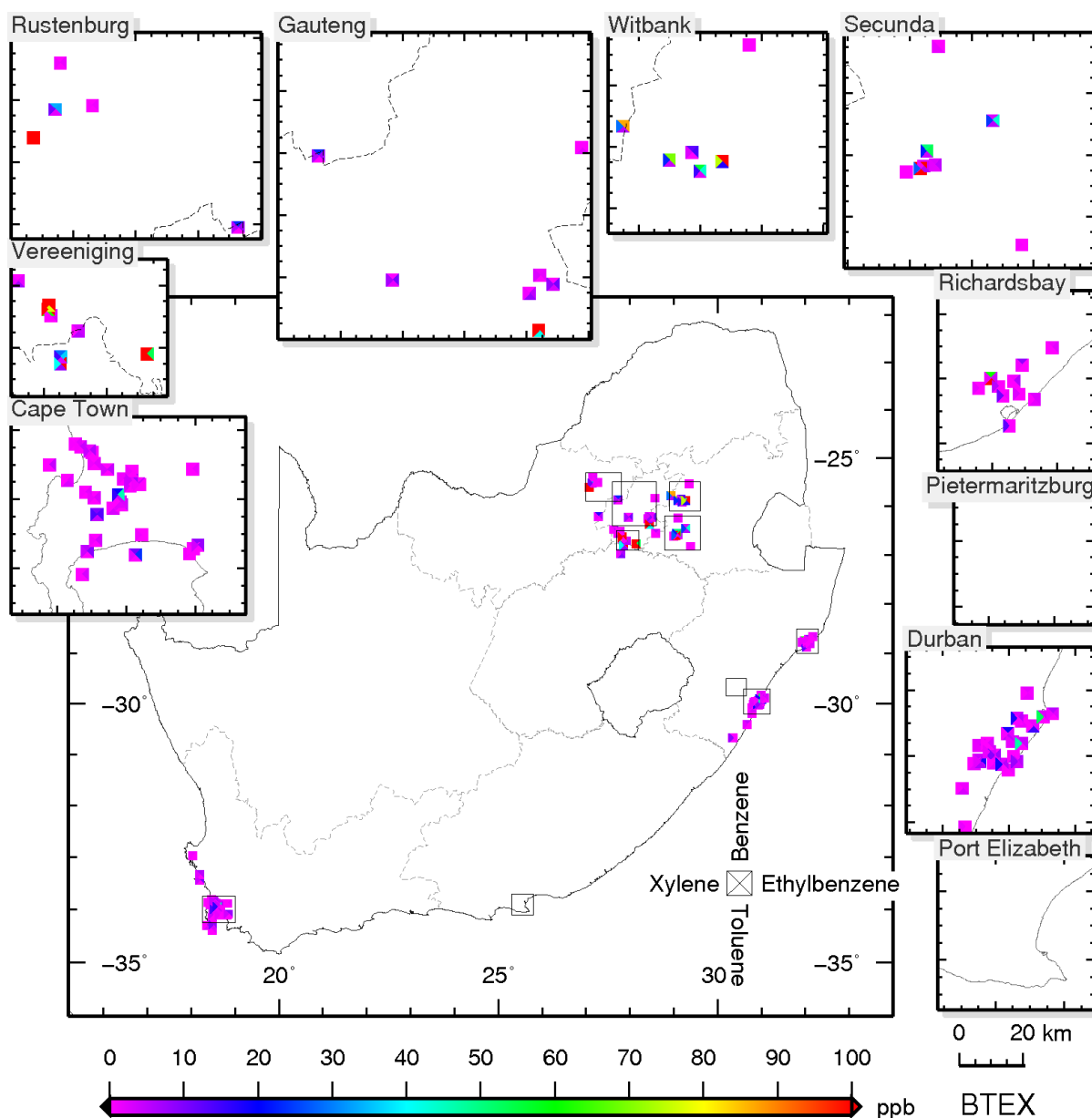
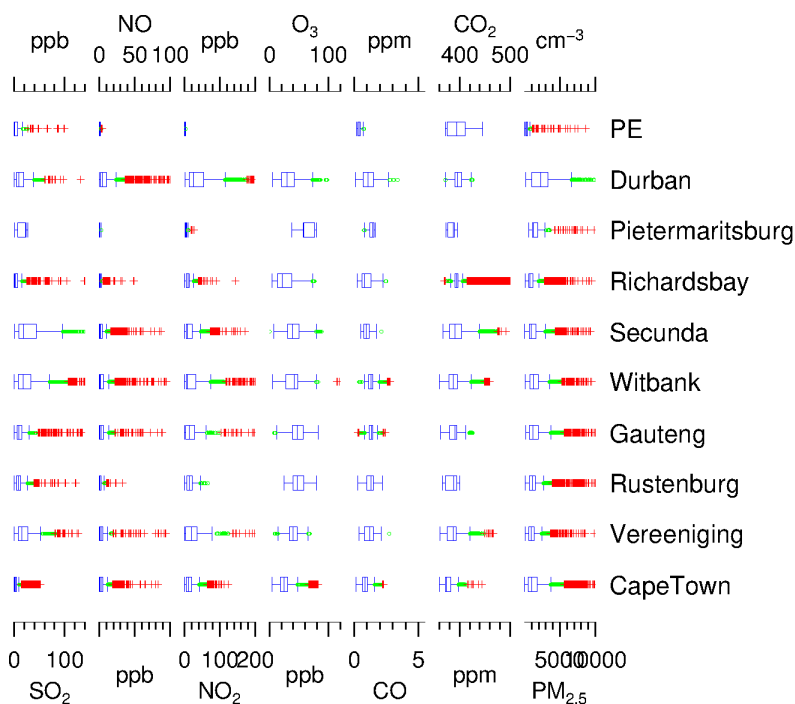


Figure 4.9: Distribution of *BTEX* from all in situ grab samples collected during the campaigning.

high levels of *BTEX*. Possible sources of the benzene and toluene are the many smouldering coal dumps and pits in the region. The concentrations of benzene and toluene over South Africa range between 2 ppb and 250 ppb. The concentrations are higher than would have been expected and need to be investigated. Summary statistics are presented in Figure 4.10.

a.



b.

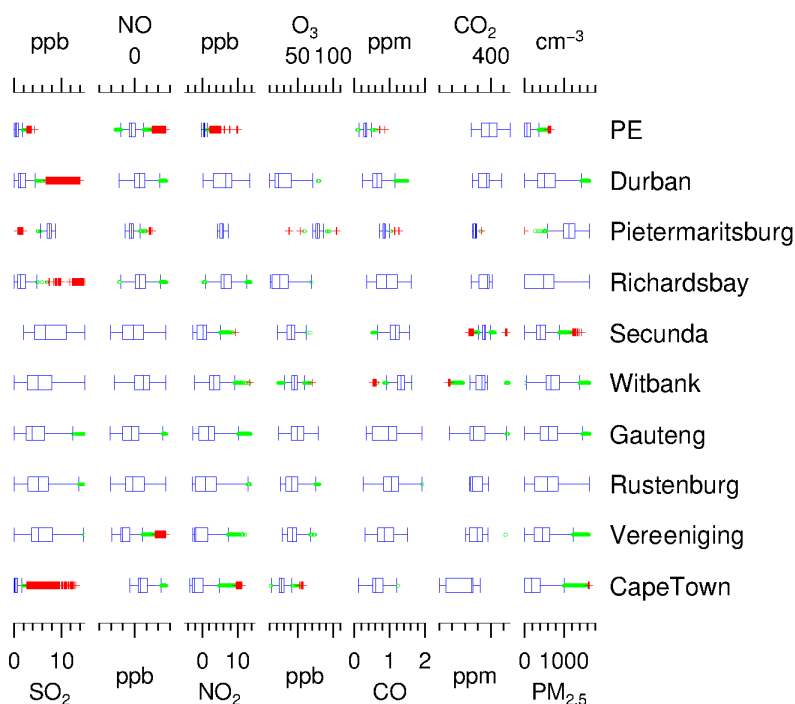


Figure 4.10: Ambient concentrations of pollutants in the lower tropospheric in 11 different regions around South Africa. a. includes all collected data and b. only times when no clearly identifiable plume was present and therefore serves as a proxy for background concentrations.

## Overview

The measured distribution of criteria pollutants over the different source areas is summarised in Figure 4.10a and background conditions not considering in-plume levels in Figure 4.10b confirms that the identified priority areas by the government are justified. The Highveld, Vaal and Bojanala priority areas have consistently high ambient concentrations for most pollutants (Figure 4.10a). Durban and Kwazulu Natal show high concentrations. The background levels show similar trends (Figure 4.10b).

These levels compare favourably with previous estimates of regional background (Kirkman et al., 2000), even though measured levels inside urban and industrial areas are slightly higher. Median  $CO$  concentrations are above 500 ppb, as opposed to below 200 ppb.  $O_3$  levels were slightly higher with median values just above 50 ppb, particularly over the Highveld areas. Aerosol concentrations were above  $500/\text{cm}^3$  for the Highveld and Durban, similar to those of Kirkman et al. (2000).

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Aerosol and trace gas distributions over South Africa were investigated using in situ measurements. Even though the study design suffered from a very limited sample in space and time, it captures the expected priorities. The Highveld and Vaal priority areas have high in-plume and background levels of most pollutants. Small problem areas, like the Durban South industrial area, shows similar levels. The mobile measurements can therefore further illuminate less prominent areas of concern. The areas with a high number of industrial facilities have high concentrations of most criteria pollutants, which indicates that proxies might be an effective way of identifying priorities.

## **Chapter 5**

# **The Vertical Stratification of Air Pollution in South Africa**

The vertical stratification of pollutants over South Africa are presented in this chapter. It is an useful proxy for the processes that distribute tracers through the troposphere and therefore influences the transport of trace gasses and aerosol away from sources. The vertical distribution of pollutants influences satellite based remote sensing estimates. The current conceptual model which uses stable layers in the atmosphere as a process and proxy to explain observed layering of pollution is challenged using an updated, higher resolution data set.

The vertical structure of the troposphere explains important mixing, transport and stability characteristic. The discontinuities in the troposphere have been described using radiosonde (Cosijn and Tyson, 1996; Garstang et al., 1996) and aircraft based in situ observations (Swap and Tyson, 1999). The troposphere is strongly stratified (Newell et al., 1999). Humidity and other tracers accumulate and are transported in distinct layers (Freiman and Tyson, 2000). Large-scale atmospheric systems that demonstrate the importance of the heterogeneous nature of the troposphere include Atmospheric Rivers (Zhu and Newell, 1994) and the southern African River of Smoke (Swap et al., 2003). The flux components of the transport are therefore very important and challenging to model. Processes responsible for moving tracers from the ABL into the free troposphere include the typical diurnal cycle (see Figure 1.9 on page 23), deep convection and lifting in front of cold fronts, sometimes called warm conveyor belts (WCB) (Carlson, 1980;

Dickerson et al., 2007). The latter would be more dominant over the South African interior during winter. Previous South African studies suggest that only a small portion of pollutants in the ABL (5 % reported by Swap and Tyson (1999)) penetrates the free troposphere.

The thermodynamic stability of the troposphere has been suggested to correlate with the observed layering of tracers (Cosijn and Tyson, 1996; Garstang et al., 1996; Swap and Tyson, 1999). Atmospheric stable layers (ASL) constrain vertical mixing and provide a proxy for the accumulation of tracers. This study provides an excellent opportunity to correlate stable discontinuities with increased concentrations of humidity and other tracers. Understanding the link between the thermodynamic stratification of the troposphere and discontinuities in the distribution of tracers such as humidity and aerosol will benefit chemical transport modelling, as well as inverse modelling application to remote sensing.

## **A critical evaluation of the current conceptual model**

The current accepted conceptual model of ASL was described on page 28 in Chapter 1. Persistent ASL are found to be an important feature of the southern African climate (Cosijn and Tyson, 1996). These studies made use of radiosonde ascents between the mid 1980s and mid 1990s. At the time of these studies, technology limited the number of reported levels to between around 50 (an average number of 49 for Pretoria and 51 for Cape Town). With only about 25 % soundings having more than 60 reported levels. Since the year 2000, the average number of reported levels for Pretoria went up to 75 and for Cape Town 81. The number of soundings with more than 60 reported levels went up to over 80 %. The vertical resolution of soundings has therefore increased significantly over the past 15 years.

Previously atmospheric stability was calculated between observed levels of more than 90 000 radiosonde soundings from all stations in southern Africa since the 1970s. The number of reported levels can have an impact on the observed ASL. The number of reported levels can differ between 5 to more than 100 (Figure 5.1). As the number of reported levels rise to 60,

the number of observed ASL increase to a median of 4 levels. A linear-response-with-plateau function suggests that when soundings have 60 or more reported levels, it does not significantly impact on the number of observed ASL. For this reason, only soundings with more than 60 reported levels should be included in the analysis, which amounted to 24 % of all soundings since the start of the record. A plateau is reached at 4.38 ASL. A frequency percent histogram of the number of ASL for soundings with more than 60 levels shows a mode of 4 ASLs. A total of 76 % of all 972 405 soundings had less than 60 vertical levels. The number of reported levels therefore had a serious impact on previous evaluations of atmospheric stability using radiosonde data.

It is further important to note that the standard sounding levels are reported regardless of their significance. For this reason, they represent a bias in the methodology. This becomes clear when the stability is visualised with (Figure 5.2) and without (Figure 5.3) the standard levels. The method for choosing *significant* levels have changed over time and is poorly defined. Including the standard levels therefore leads to an artificial persistent stability at around these levels. These levels were therefore excluded from the sample (as is the case in Figure 5.3).

Improvements in technology increased the number of reported sounding levels dramatically. The higher vertical resolution of the observations result in a much more detailed characterisation of the tropospheric structure (Figure 5.2). The number of observed ASL are still around 4, but the thickness has decreased significantly to less than 30 hPa. The pressure levels associated with relatively persistent ASL is close to the surface (below 900 hPa) and between 500 hPa and 600 hPa. Entainment at the top of the boundary layer results in prevalent ASL in the bottom 2 km. Another zone of prevalent ASL are found between 500 hPa and 600 hPa. However, at any time, numerous shallow ASL are prevalent. These considerations challenge the current conceptual model describing the vertical structure of the troposphere in the mid-latitudes.

These features are present in all 12 radiosonde sites that have data available till 2010. The 500 hPa to 600 hPa ASL are less persistent for sites at higher latitudes, such as Marion Island

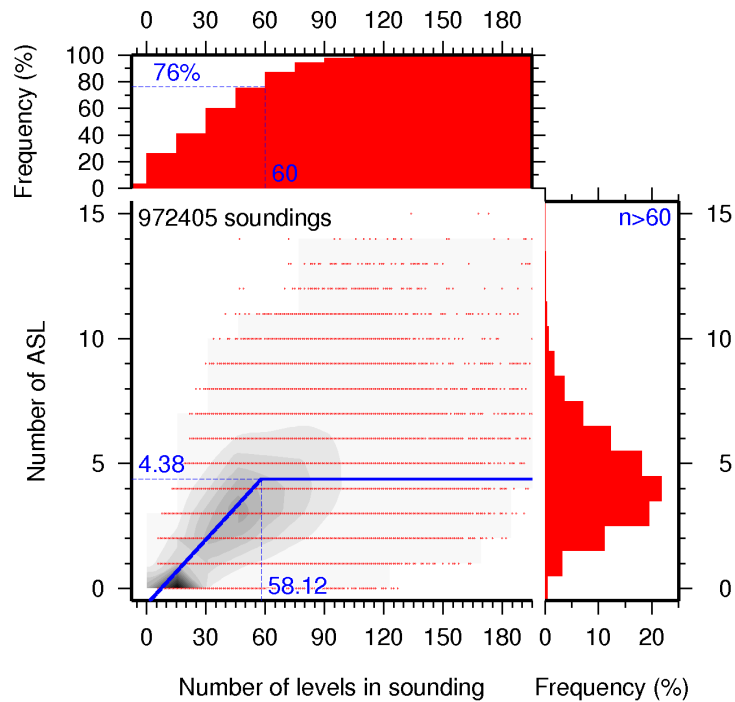


Figure 5.1: A composite graph showing the correlation of levels per sounding versus number of observed ASL. The main graph is a scatter plot of the total number of reported levels in a sounding (x-axis) versus the number of ASL. A density surface is shown in shades of grey (darker equals more data points) to illustrate areas with more data points. A linear-response-with-plateau function was fitted to the data and shown with the blue line. A threshold number of levels that corresponds to a plateau of number of ASL is 58.12. The plateau is reached at 4.38 ASL. A frequency percent histogram of number of ASL for soundings with more than 60 levels are shown on the right hand graph. A mode of 4 ASLs is observed. The top graph shows the cumulative frequency distribution of number of levels in a sounding. A total of 76 % of all 972 405 soundings had less than 60 vertical levels.

This is in contrast with lower latitude sites that have a very prominent 500 hPa to 600 hPa persistent ASL, for example at Upington. This could be ascribed to the lowering of the troposphere by the descending limbs of the Hadley circulation that could be partly responsible for this level.

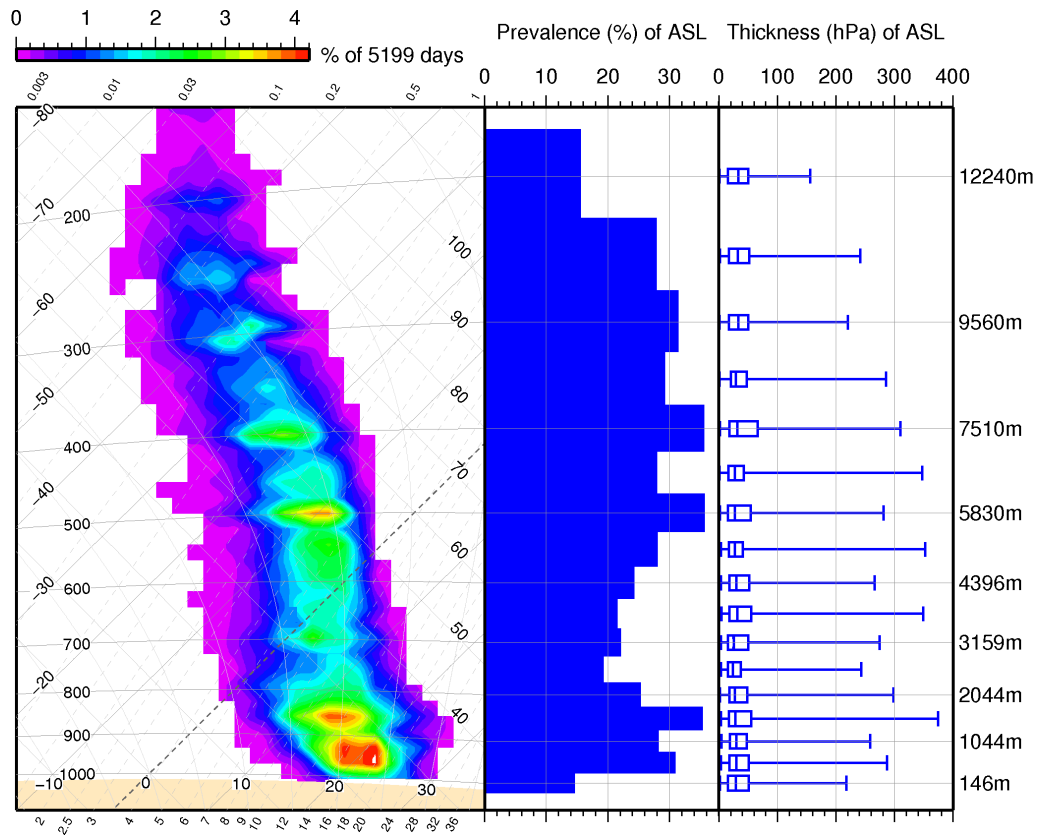


Figure 5.2: A composite graph showing the prevalence of ASL in the troposphere over Durban for midday soundings. The graph on the left shows a density surface of pressure and temperature data points of ASL bases plotted on a tephigramme. The graph in the middle shows a frequency percentage histogram of ASL in 50 hPa bins. The graph on the right shows a box-and-whisker plot of ASL thickness corresponding to bases at that level.

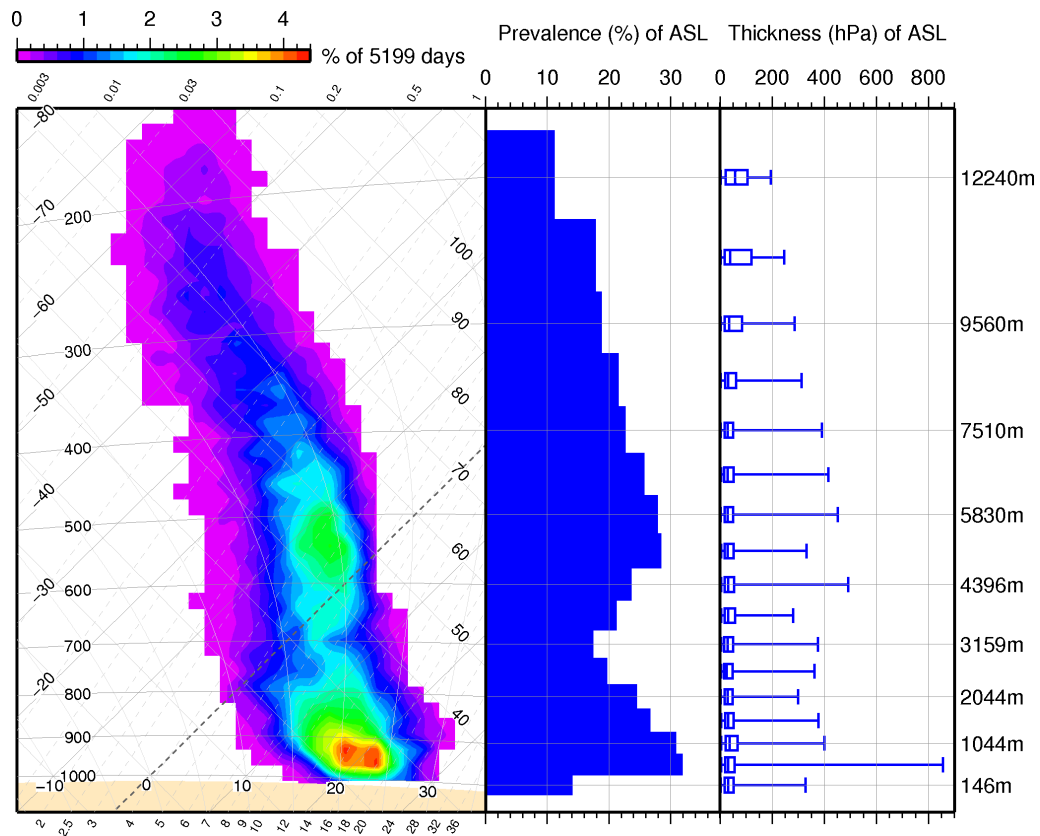


Figure 5.3: A composite graph showing the prevalence of ASL in the troposphere over Durban for midday soundings. The graph on the left shows a density surface of pressure and temperature data points of ASL bases plotted on a tephigramme. The graph in the middle shows a frequency percentage histogram of ASL in 50 hPa bins. The graph on the right shows a box-and-whisker plot of ASL thickness corresponding to bases at that level. This is the same graph as figure 5.2, except the standard reporting levels have been omitted from this analysis to remove a possible sampling bias.

## Mixing in the unstable boundary layer

Mixing in the ABL was frequently observed during the analysis period. Most pollutant concentrations are then relatively low, and drop sharply at a level that coincides with the top of the thermodynamic inversion associated with the layer of entrainment at the top of the mixing layer (for example Figure 5.4 and 5.4).

Two cases were observed on the same day (25 May 2005). The flights on this day started from Bethlehem, then proceeded to Vereeniging, where a vertical profile was undertaken (Figure 5.6), and repeated over eMalahleni (Figure 5.5) and a last one on the way back close to Bethlehem (Figure 5.4). The day was marked by a characteristic upper level subsidence due to a high pressure visible in the 500 hPa over the central and Eastern parts of South Africa (Figure 5.4). This caused a very pronounced capping inversion at around 700 hPa (3 km above sea level) clearly visible in the 10 UTC sounding at Pretoria (Figure 5.4). The winds in the ABL were light south-westerly. Figure 5.4 therefore represents a vertical profile upwind of any large emissions, Figure 5.5 one downwind of major sources, but still inside the source region and the profile depicted in Figure 5.6 is inside a source region. On the same day, within the same region, a well mixed ASL (Figure 5.4 and Figure 5.5), as well as a very stratified (Figure 5.6) ASL are observed.

A well mixed ABL conforms to the conceptual model and was observed frequently. However, stratification such as in Figure 5.6 is equally common. During this profile, several fresh plumes with high  $NO_x$ , low  $O_3$  and high  $PM$  can be observed in the ABL. The low  $O_3$ , smaller mean diameter of the  $PM$  and high  $NO$  (red line), are all good indicators of relatively fresh plumes. The concentrations still drop above the entrainment zone, but strong stratification is observed within the ABL. The upper air is dominated by a high pressure system at 500 hPa, however, the persistent 500 hPa to 600 hPa ASL is not yet visible. The aircraft only reached around 650 hPa (3.7 km above sea level), which captured the profile from the surface to above the ABL. The decrease is well correlated between the different pollutants. Right at the top of the ABL, around

2005/08/05 (13:09:00–13:23:50)

Absolutely stable layer

○ Sounding site

— Tracks

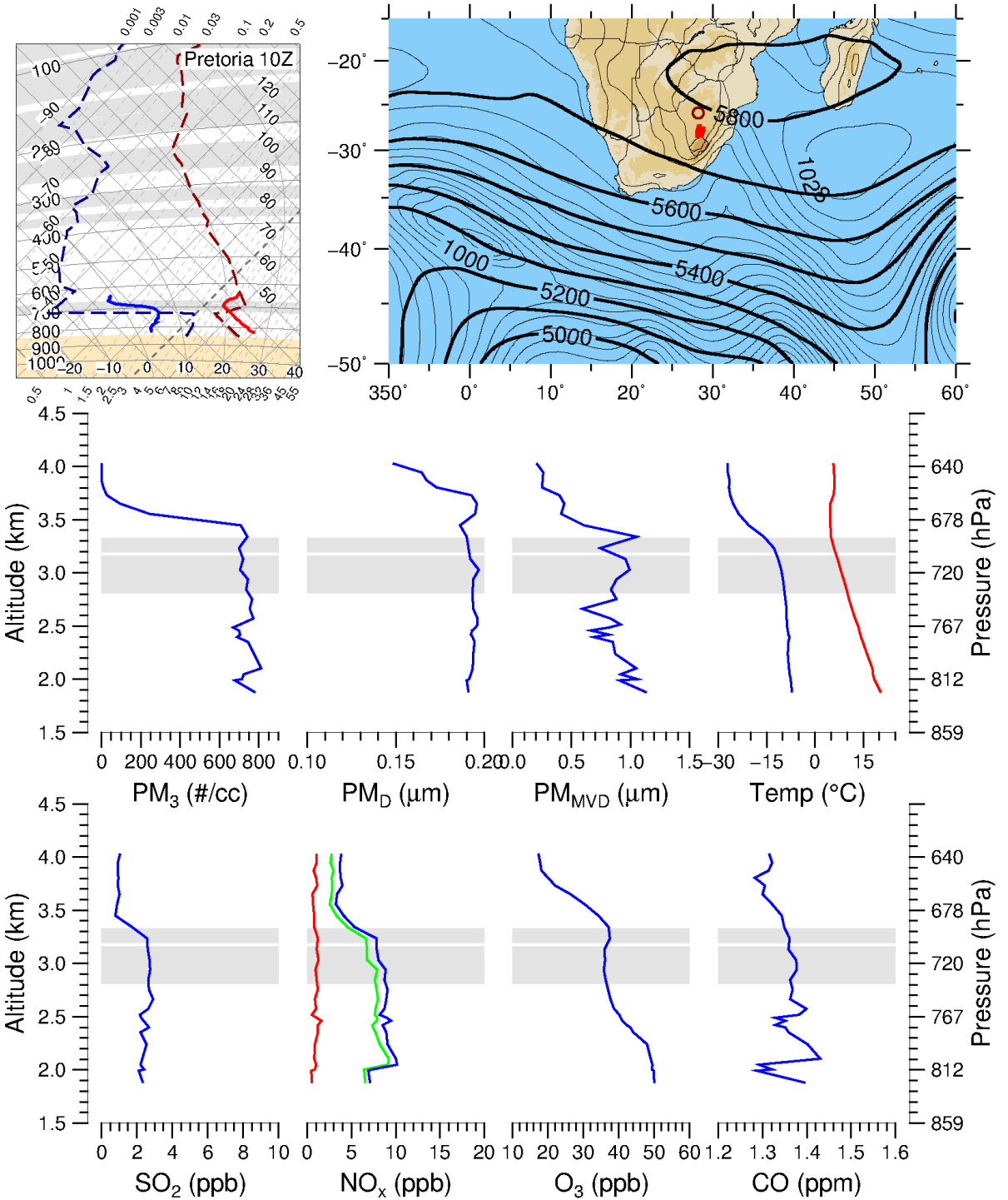


Figure 5.4: An example of a well mixed boundary layer is illustrated through a vertical profile over Cape Town early on 25 May 2005. The 10 UTC Cape Town sounding is shown on the tephigram. The mean sea level pressure and the 500 hPa geopotential heights were derived from the 6 UTC fields of the 0 UTC Era-interim reanalysis.

2005/08/05 (12:47:08–12:56:36)

Absolutely stable layer

○ Sounding site

— Tracks

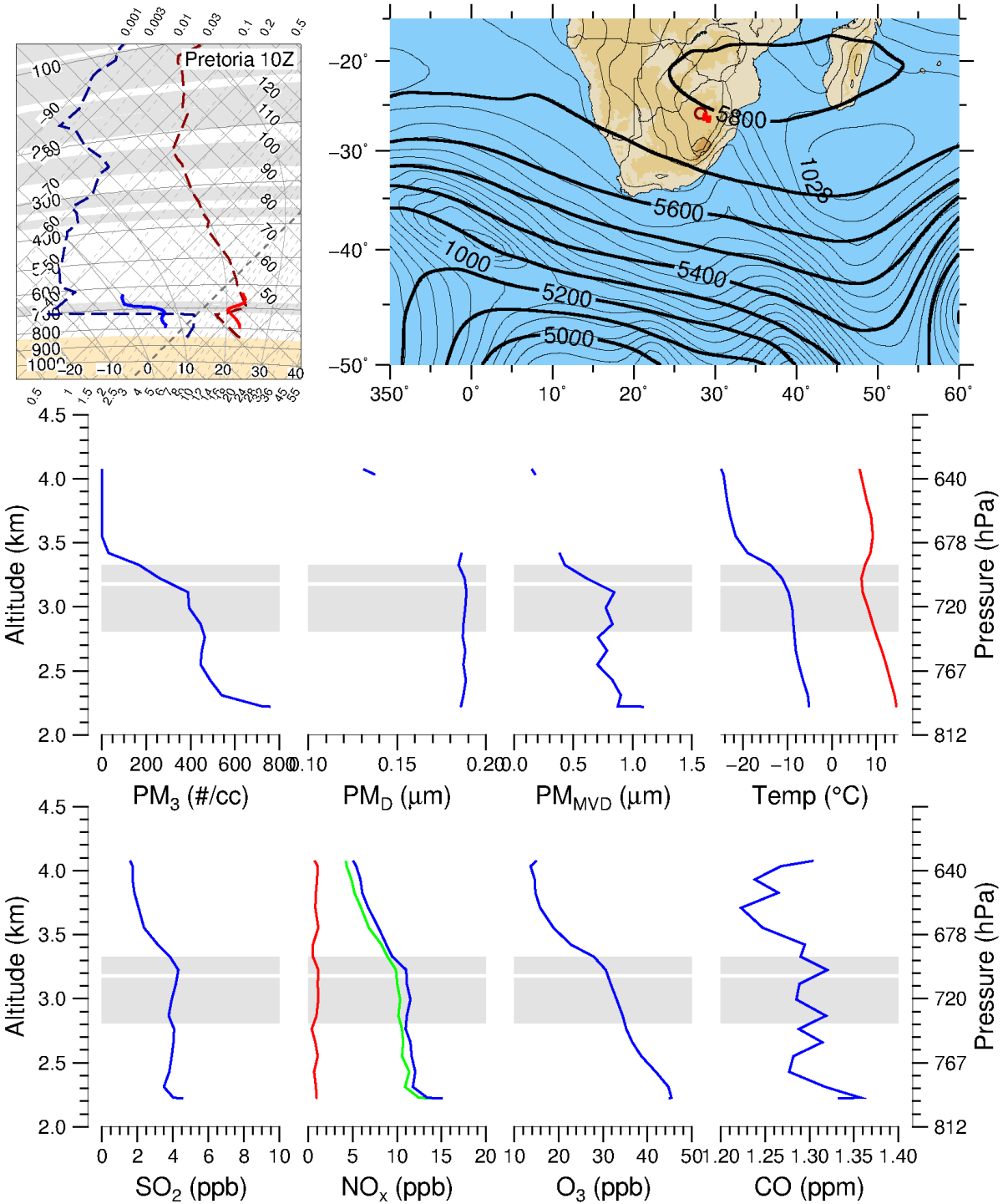


Figure 5.5: An example of a well mixed boundary layer is illustrated through a vertical profile over Cape Town early on 25 May 2005. The 10 UTC Cape Town sounding is shown on the tephigram. The mean sea level pressure and the 500 hPa geopotential heights were derived from the 6 UTC fields of the 0 UTC Era-interim reanalysis.

2005/08/05 (10:37:45–10:51:02)

Absolutely stable layer

○ Sounding site

— Tracks

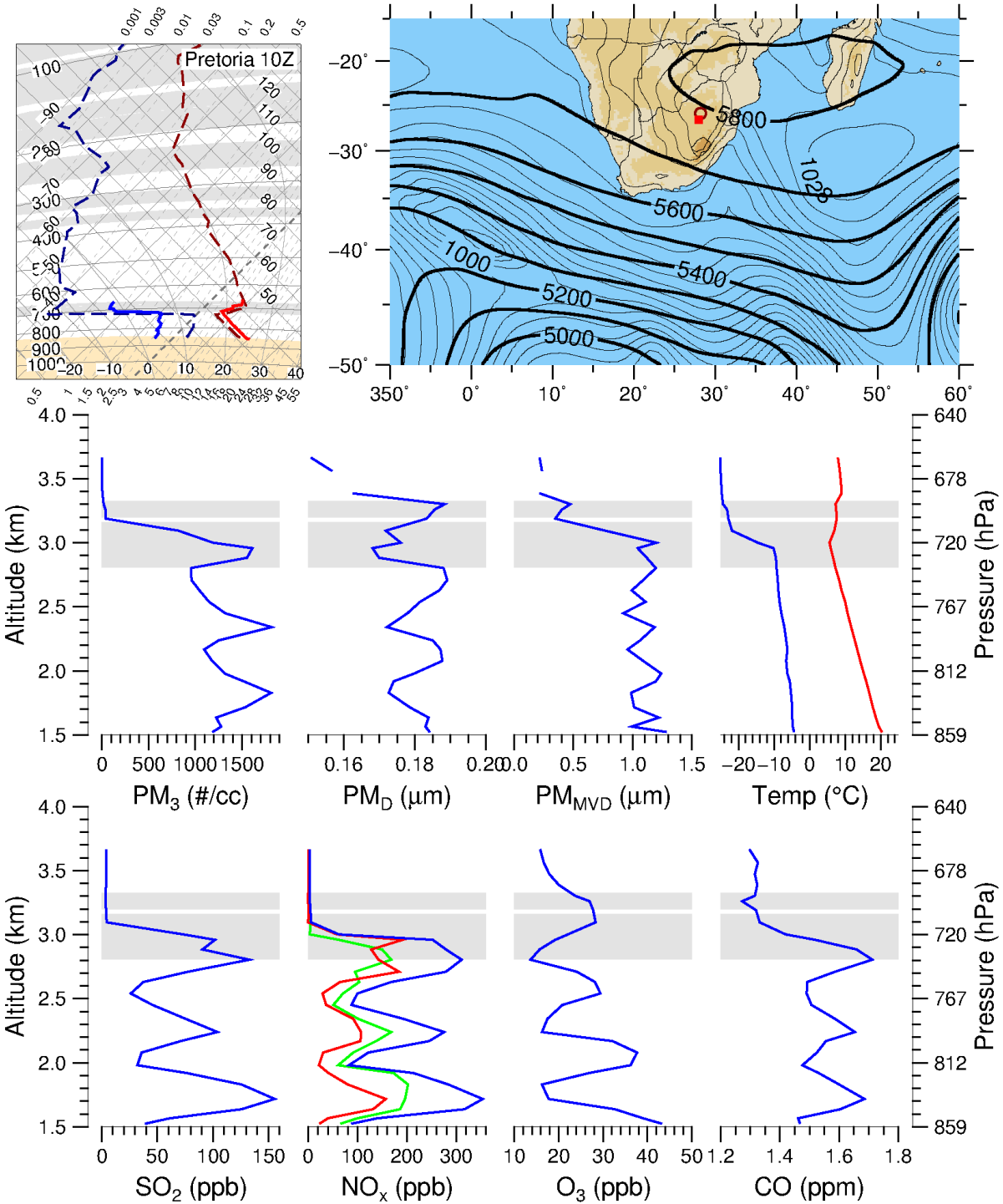


Figure 5.6: An example of strong stratification in the boundary layer is illustrated through a vertical profile over the Highveld on 5 August 2005. The 10 UTC Pretoria sounding is shown on the tephigram. The mean sea level pressure and the 500 hPa geopotential heights were derived from the 6 UTC fields of the 0 UTC Era-interim reanalysis.

700 hPa (3.3 km), another less pronounced layer can be seen in the  $O_3$  and  $PM$  size changes. This is likely an *aged* layer associated with more distant sources. Many more cases such as this type of stratification were encountered.

## **The impact of elevated stable layers on tracer transport**

The stability in the ABL moves through a diurnal cycle (see Figure 1.9 on page 23). Buoyant and mechanical forces create an environment where stratification is less likely. It make sense that some layering is present closer to the source region, as seen in the previous section. Although the extent of the observed layering in the mixing layer is surprising. Mixing processes are less common in the free troposphere. While the current conceptual model uses absolute stability, even a conditionally unstable lapse rate will not favour mixing in the free troposphere where moist processes are the exception.

The impact of elevated ASL has been postulated to coincide with stratified layers of aerosol and trace gases. The stability impedes vertical mixing and in time a layer of enhanced concentrations build up at or just below the ASL. This is frequently observed at the stable layer at the top of the ABL (Figure 5.7). This was observed on an earlier flight, the same day as Figure 5.4, 5.5 and 5.6. Before convective processes managed to mix pollutants, concentrations were significantly higher for  $SO_2$  and  $NO_x$  and confined to the level just below the entrainment inversion. These pollutants are associated with tall stack emissions from power stations (see page 72 in chapter 3) and petrochemical facilities (see page 74 in chapter 3).

Flights were confined to the lower troposphere for this study. Vertical profiles were rarely made above 3.5 km above sea level. Many cases were observed with elevated ASL and no real detectable stratification in the vertical distribution of aerosol and trace gases (for example Figure 5.8). During this day, a very shallow layer of enhanced concentrations exist in the early morning. Above the entrainment zone, concentrations drop to pristine levels typical of the westerly transport patterns. The developing ridging high is advecting colder air and causes a

2005/08/05 (06:39:11–06:51:47)

Absolutely stable layer

○ Sounding site

— Tracks

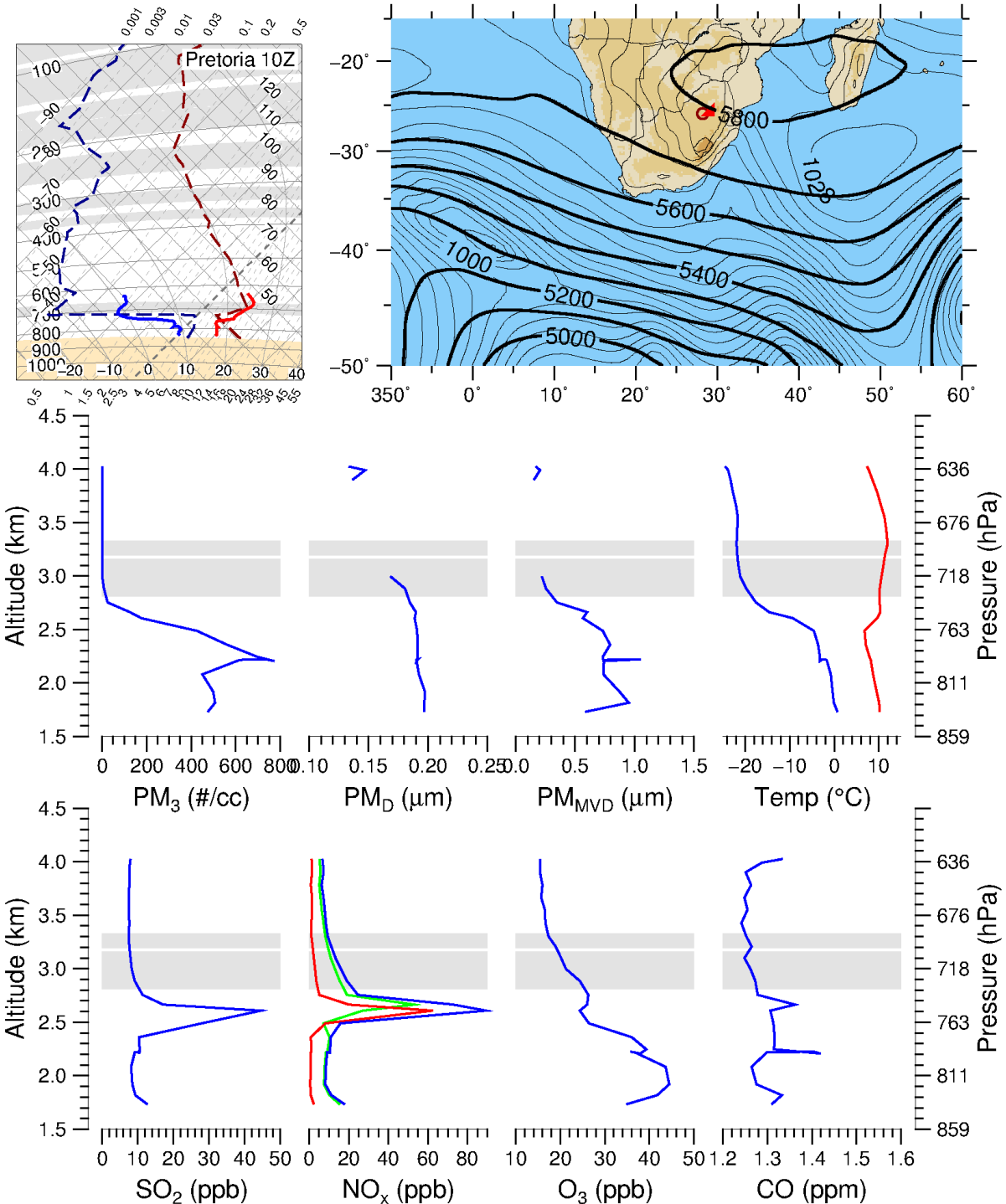


Figure 5.7: An example of a well defined layer at the top of the boundary layer is illustrated through a vertical profile over the Highveld on 5 August 2005. The 10 UTC Pretoria sounding is shown on the tephigram. The mean sea level pressure and the 500 hPa geopotential heights were derived from the 6 UTC fields of the 0 UTC Era-interim reanalysis.

surface inversion up to about 900 hPa. This has trapped pollutants close the ground level (in the lowest 500 m) and results in the observed vertical profile of pollutants. Two elevated ASL are observed, one at 1 km and another at 1.6 km. Neither of these show any stratification of aerosol or trace gasses associated with the ASL. It is not surprising, since the approaching westerly wave is likely advecting clean air from the free troposphere over the area.

Another scenario shows an associated stratification of a single pollutant,  $PM$  (Figure 5.9). An elevated stable layer is visible between 900 m and 1.5 km. A cold front is approaching the area and together with possible coastal low has resulted in a thermodynamically stratified troposphere. A surface inversion limits mixing and most pollutants are confined to the lowest 500 m.  $PM$  concentrations drop off above the surface inversion along with other pollutants ( $NO_x$ ), but then show a second peak associated with the ASL. The changing synoptic conditions could have played a major roll in the observed stratification. An existing boundary layer might have been broken up by the approaching front, or the WCB could have mixed  $PM$  through the surface inversion. This case presents the only observed coincidence of a ASL with a level of enhanced concentrations. Many other profiles showed no or little layering in the free troposphere. It is evident that ASL does not always coincide with enhanced concentrations of aerosol and trace gases.

It is worth noting that the current study focused on areas with different emission sources. However, it is precisely the location where potential application is sought. These are the areas for which better remote sensing estimates and modelling assessment are most needed. A single conceptual model that can be applied to a widely available dataset with a long archive has appeal. Nevertheless, the complex nature of the lower troposphere does not seem to be captured by radiosonde data alone.

2005/05/25 (09:39:07–09:50:49)

Absolutely stable layer

○ Sounding site

— Tracks

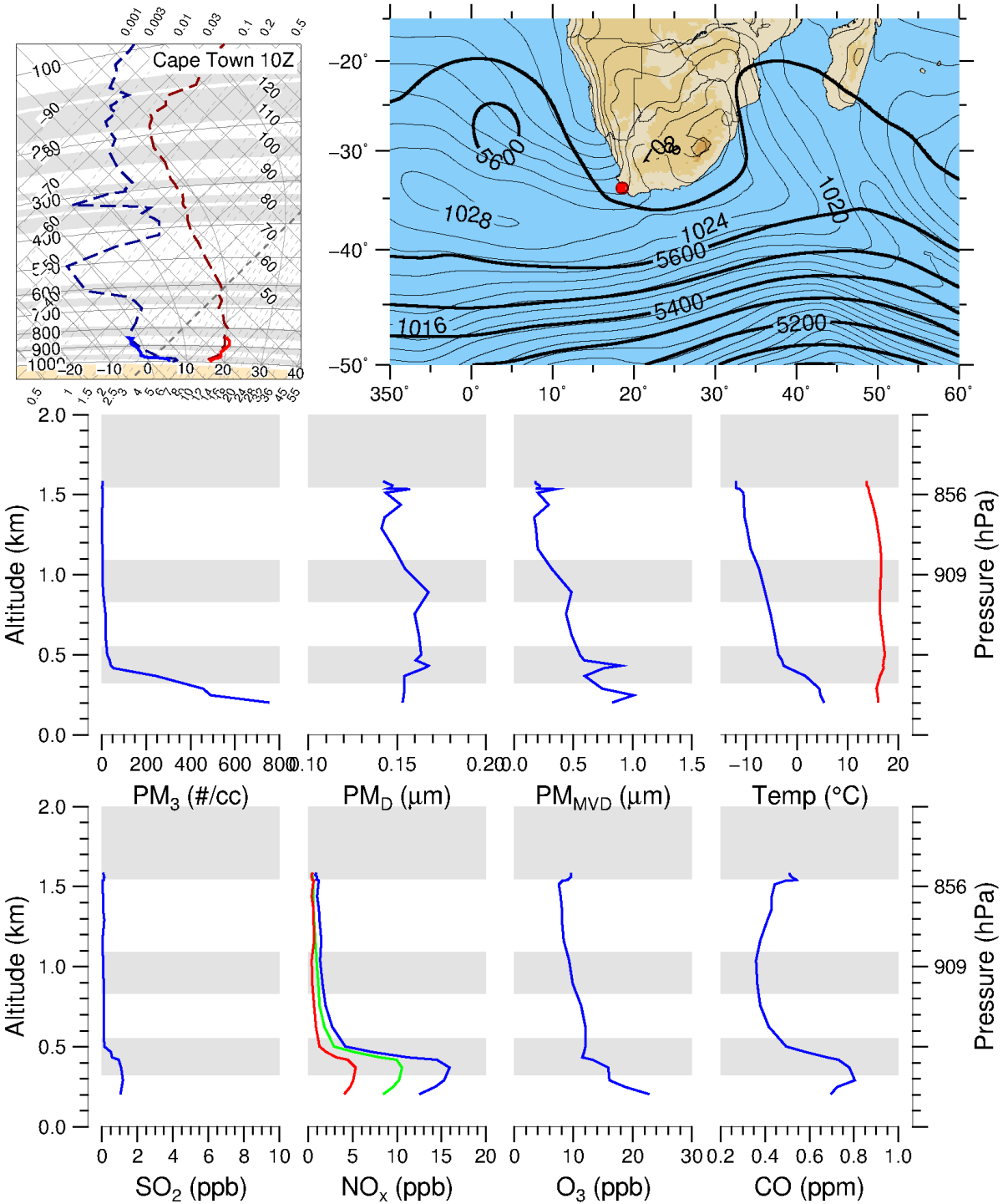


Figure 5.8: An example of an elevated ASL without strong stratification of pollutants is illustrated through a vertical profile over Cape Town early on 25 May 2005. The 10 UTC Cape Town sounding is shown on the tephigram. The mean sea level pressure and the 500 hPa geopotential heights were derived from the 6 UTC fields of the 0 UTC Era-interim reanalysis.

2006/02/14 (07:56:49–08:10:32)

Absolutely stable layer

○ Sounding site

— Tracks

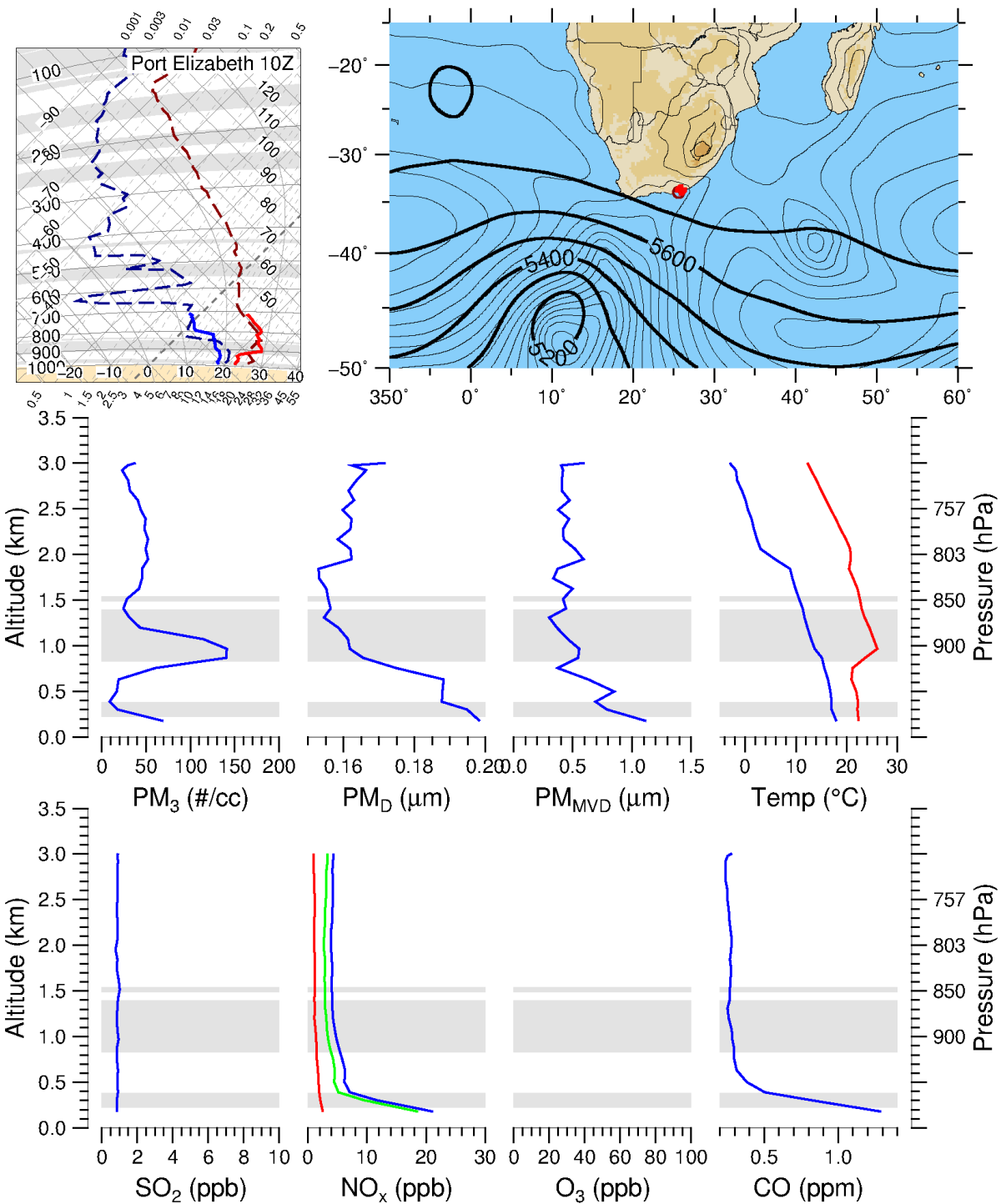


Figure 5.9: An example of stratification in association with an absolutely stable layer is illustrated through a vertical profile over Port Elizabeth early on 10 February 2006. The 10 UTC Port Elizabeth sounding is shown on the tephigram. The mean sea level pressure and the 500 hPa geopotential heights were derived from the 6 UTC fields of the 0 UTC Era-interim reanalysis.

## Vertical distribution of aerosol and trace gases

The current conceptual model of atmospheric stable layers was conceived at a time when data was scarce and a pragmatic philosophy was at the order of the day. The new paradigm of a complex world calls for change in how we explain vertical stratification. Simultaneous measurements of the thermodynamic profile, humidity and other tracers, such as particulates and trace gases, confirms the importance of stable discontinuities to vertical and horizontal transport. Only soundings with more than 60 reported levels should be used to describe the thermodynamic structure of the troposphere. Including the standard reporting levels biased the characterisation. These considerations challenge the current conceptual model describing the vertical structure of the troposphere in the mid-latitudes.

The dynamics of mixing in the troposphere are complex. The typical scenario of a well-mixed ABL with a drop in concentrations of aerosol and trace gases are observed, especially far from large sources. Closer to sources, individual plumes result in a total disconnect between the vertical thermodynamic structure of the troposphere and the distribution of aerosol and trace gases.

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The current model of ASL being the dominant factor in determining stratification in the atmosphere is overly simplistic. It is not only biased by limitations in the radiosonde dataset, but does not adequately describe the much more complex nature of the observed vertical structure of the troposphere. Aerosol and trace gases are mixed in the convective ABL. Close to sources, individual plumes are present in both the ABL and the free troposphere. The height of fresh plumes are determined by initial buoyancy, linked to combustion characteristics.

## **Chapter 6**

### **Summary and Conclusions**

This chapter reflects on the aims and objectives of the study. A critical evaluation of the meaningfulness of the findings are presented in a concise summary. The objectives of the study were first to characterise major natural and anthropogenic sources of air pollution over South Africa using in situ measurements. Secondly, to characterise the state of air quality over the major industrial and urbanised areas of South Africa using in situ measurements. The third objective was to investigate the vertical distribution of aerosol and trace gases over South Africa and the last was to prioritise the areas and sources of concern for effective air quality management in South Africa. These objectives are each discussed in a following section, but firstly the original research contributions are highlighted.

#### **Original contributions to the current body of knowledge**

Measurements of aerosol and trace gases were made in the lower troposphere over South Africa using a mobile laboratory. Uncertainties increase when mostly standard regulatory equipment are placed on a fast moving aircraft, even considering attempts to reduce errors. Even mobile ground based measurement campaigns lacks sufficient temporal scales to guarantee long-term representability. Notwithstanding all these caveats, this study has shown that a systematic approach to characterise sources and areas can prioritise air quality problem areas.

The main original contributions are summarised below:

- The spatial extent of prominent atmospheric plumes are much smaller than current remote sensing estimates;
- In situ measurements confirm that coal-fired power stations and petrochemical facilities have well defined plumes with high concentrations of criteria pollutants, most notably  $SO_2$  and  $NO_x$ ;
- in situ measurements confirm that residential solid fuel burning in low-income communities have a disproportionately large impact on the exposure to particulate matter (afternoon plumes exceeding  $800 \mu\text{g}/\text{m}^3$  of  $PM_{2.5}$  measured at 5 min intervals);
- in situ measurements confirm relatively high levels of  $NO_x$  (peak values exceeding 500 ppb  $NO$  and 300 ppb  $NO_2$  measured at 5 min intervals) close to busy highways, on the same order of magnitude as in-plume concentrations of large industrial facilities.
- Estimates of the background concentrations of criteria pollutants over the major urban and industrial areas;
- in situ confirmation of high levels of criteria air pollutants over the Vaal priority area, the Highveld priority area and to a lesser extent the Bojanala priority area, especially levels  $SO_2$  and  $NO_x$ . These areas with a large number of atmospheric emissions do however seem smaller than those estimated using satellite remote sensing.
- In situ confirmation of relatively high levels of  $NO_x$ ,  $SO_2$  and  $PM$  over Durban, which is not currently being managed as a priority area. This underscores the difficulty of accurately assessing environments with diverse, clustered sources and complex meteorology through modelling studies and satellite based remote sensing.
- The current conceptual model of absolute stable layers is biased because of limited data availability where a limited number of levels are reported. At least 60 levels should be reported in soundings to study ASLs.

- The current conceptual model of absolute stable layers are biased because of the inclusion of the standard reporting levels (850 hPa, 700 hPa, 500 hPa and 300 hPa). The persistent levels change in number when these are omitted from the analysis;
- The current conceptual model of absolute stable layers as a proxy for the vertical distribution of pollutants is over simplified, especially close to source regions where different pollutants are observed to peak at different elevations unrelated to absolutely stable layers. This suggests that the original buoyancy that is governed by the release temperature, exit velocity and height are important drivers for the stratification of pollutants.

## Major Sources of Air Pollution in South Africa

In situ characterisation of major anthropogenic sources of criteria pollutants and greenhouse gases were performed between 2003 and 2013.

1. Plumes with detectable concentration of criteria pollutants have spatial dimensions between between a couple of hundred meters (minimum of 190 m) to more than 20 km. This study sampled just less than 1000 plumes in the lower troposphere around South Africa. The median spatial extent was around 7 km, with a fair amount of variability (standard deviation of around 5 km).
2. Coal fire power stations plumes typically have very high levels of  $NO$  (greater than 200 ppb above background),  $NO_2$  (greater than 200 ppb above background),  $CO_2$  (greater than 50 ppm above background) and  $SO_2$  (greater than 500 ppb above background). These concentrations lead to high levels of secondary particulates.

# The Spatial Distribution of Air Pollution in South Africa

The state of air quality over the major industrial and urbanised areas of South Africa were evaluated using data from mobile air quality laboratories.

1. Areas with a large number of atmospheric emissions of  $SO_2$  (spot measurements between 50 magl and 1500 magl exceeding 120 ppb) are detected over Vereeniging, Rustenburg, Witbank (eMalahleni), Secunda, Richardsbay and Durban.
2. Areas with a large number of atmospheric emissions of  $NO_x$  (spot measurements between 50 magl and 1500 magl exceeding 120 ppb) are detected over Vereeniging, Witbank (eMalahleni), Secunda and Durban.
3.  $O_3$  levels decrease from north to south. Maximum levels in the lower troposphere are typically between 60 ppb and 90 ppb.
4. Areas with a large number of atmospheric emissions of  $NO_x$  (spot measurements between 50 magl and 1500 magl exceeding 120 ppb) are detected over Vereeniging, Rustenburg, Witbank (eMalahleni), Secunda, Richardsbay and Durban.
5. Areas with a large number of atmospheric emissions of  $CO$  with levels exceeding 1 ppm are present over all urban and industrial areas around South Africa.
6. Areas with a large number of atmospheric emissions of  $CO_2$  with levels exceeding 400 ppm are present over all urban and industrial areas around South Africa.
7. Enhanced levels of  $PM$  are detected over all urban and industrial areas, with significant extent over Cape Town and Durban.
8.  $BTEX$  levels reach very high concentrations, exceeding 100 ppb close to industrial areas near Vereeniging, Rustenburg, Witbank (eMalahleni) and Secunda.
9. Background  $SO_2$  concentrations over South Africa are below 10 ppb.
10. Background  $NO_x$  concentrations over South Africa are below 10 ppb.

# **The Vertical Stratification of Air Pollutant in South Africa**

The conceptual model of vertical distribution of aerosol were evaluated using in situ airborne measurements.

1. The current accepted conceptual model of atmospheric stability is sensitive to the number of reported sounding levels.
2. The number of detected ASL changes roughly linearly as the number of reported sounding levels increase from just the standard levels, to 60.
3. The number of detected ASL stabilise between 4 and 5 when the number of reported sounding levels are greater than 60.
4. More than 75 % of soundings have less than 60 levels.
5. The ever presence of the standard levels, at 850 hPa, 700 hPa, 500 hPa and 300 hPa, biases the position and nature of the detected ASL.
6. An unbiased climatology of ASL shows persistent layers at the top of the ABL and between 600 hPa and 500 hPa, likely the level of the subsidence related to the Hadley cell circulation.
7. Detected ASL are generally (more than 75 % of the time) less than 75 hPa thick.
8. The lower troposphere is highly stratified with respect to the distribution of criteria pollutants and trace gases.
9. The level of stratification changes moving away from clusters of atmospheric emission sources.

## **Conclusions and significance**

The overall conclusion is made that a small team with a set of regular instrumentation can prioritise pollutants and areas of concern on a national scale. This method could be valuable for countries with limited resources and infrastructures and can be used in combination with modelling and satellite based remote sensing to assess priorities. The ability to obtain in situ data of a large number of variables over vast areas in a short time may offset the caveats associated with mobile measurements and a limited sample volume.

These findings corroborate existing knowledge of air pollution sources over South Africa using a unique data set obtained with a mobile, in situ laboratory. Ground level concentration of particulate matter is the biggest concern for air quality related human health concerns.

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